High-Resolution Photoelectron Imaging of Cryogenically-Cooled Anions

By

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Publications

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3. **G. Z. Zhu**, Y. Liu, Y. Hashikawa, Q. F. Zhang, Y. Murata, and L. S. Wang. Probing the Interaction between the Encapsulated Water Molecule and the Fullerene Cages in $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$. *Chem. Sci.* **9**, 5666−5671 (2018).
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10. D. L. Huang, **G. Z. Zhu**, and L. S. Wang. Communication: Observation of Dipole-Bound State and High-Resolution Photoelectron Imaging of Cold Acetate Anions. *J. Chem. Phys.* **142**, 091103 (2015).

Contributed Presentations

1. *256ᵗʰ ACS National Meeting*. Aug. 19-23, 2018. Boston, MA. (Poster)
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To my mom

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Table of Contents

List of Tables

List of Figures

Abstract of

High-Resolution Photoelectron Imaging of Cryogenically-Cooled Anions

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Photoelectron spectroscopy (PES) is a powerful technique to investigate the electronic structure and chemical bonding of gaseous anions and the corresponding neutrals upon electron detachment. The Wang lab first introduced electrospray ionization (ESI) to spectroscopy by developing a magnetic-bottle PES apparatus with an ESI ion source to study multiply-charged anions. The development of the third-generation ESI-PES apparatus at Brown by coupling a cryogenically-controlled Paul trap with high-resolution PE imaging has enabled accurate vibrational and electronic information to be obtained for singly charged anions produced by ESI and the neutral radicals. Here, the thesis work has focused on both non-resonant and resonant PES of cryogenically-cooled anions.

PES is usually done non-resonantly at the fixed laser wavelength. The first research project is to accurately measure the electron affinity (EA) of tetracyanoquinodimethane (TCNQ), an important organic electron acceptor, to be 3.383 ± 0.001 eV, which was erroneously reported in the literatures. High-resolution PES studies on fullerene-related anions, including $C_{59}N^-$, $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$, have yielded accurate EAs and vibrational structures for the corresponding neutral fullerenes. The

weak intramolecular interactions between the encapsulated water molecule and the cage anions in $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ have also been probed.

Anions with dipolar neutral cores can have dipole-bound excited states (DBSs) just below the electron detachment threshold. Optical excitations to vibrational levels of DBS will induce vibrational autodetachment. DBSs of cryogenically-cooled phenoxide and thiophenoxide anions have been observed below the detachment thresholds. Vibrational autodetachments from the DBS levels in the resonant PES result in highly non-Franck-Condon photoelectron spectra, which have shown to be an effective method to obtain vibrational information of dipolar neutral radicals. In addition, DBSs of tautomeric deprotonated cytosine anions have been investigated, yielding tautomer-specific information in the resonant PES.

Molecule with vanishing dipole moment but large quadrupole moment can weakly bind an electron to form the quadrupole-bound anion. The first observation of excited quadrupole-bound state in the 4-cyanophenoxide anion, which shows similar autodetachment properties as DBS, will be discussed.

Chapter 1 Introduction

Negative ions, or anions, are atoms, molecules or clusters possessing net negative charges. The attention on gaseous anions was first draw by Wildt in 1939 when he proposed the absorption of H^- to be the main source of solar opacity in the region of red and infrared wavelengths.[1] Since then, anions have been found to play important roles in a wide range of fields, such as ionic liquids,[2] anion-π interactions in supramolecular system,[3] radiation damage of DNA in biological environments,[4] formation of atmospheric aerosols,[5] the interstellar medium in astronomical environment[6] and Titan's upper atmosphere as well as other planetary surroundings.[6]

One of the most powerful tools to study gaseous anions is photoelectron spectroscopy (PES), as schematically shown in Fig. 1.1. Briefly, a beam of mass-selected anions (M^-) is intersected with a laser beam. When the laser photon energy (hv) exceeds the binding energy (BE) of the electron in the anion, photoelectrons (e^-) can be ejected with various kinetic energies (KEs) depending on the resulting final neutral states (M). Since the energy applied to the system must be conserved, BE of the electrons can be readily determined as:

$$BE = hv - KE,$$

where the photon energy hv is known and the photoelectron KE is measured experimentally. The electron BE is usually used to plot the photoelectron spectrum as BE is independent on the laser photon energy used in the experiment. The intensities of the peaks in the spectrum follow the Franck-Condon principle,[9] which means that the intensity of a vibronic transition is proportional to the square of the overlap integral

between the respective vibrational wavefunctions of the two electronic states involved in the transition.

$$M^- + h\nu \rightarrow M + e^-$$
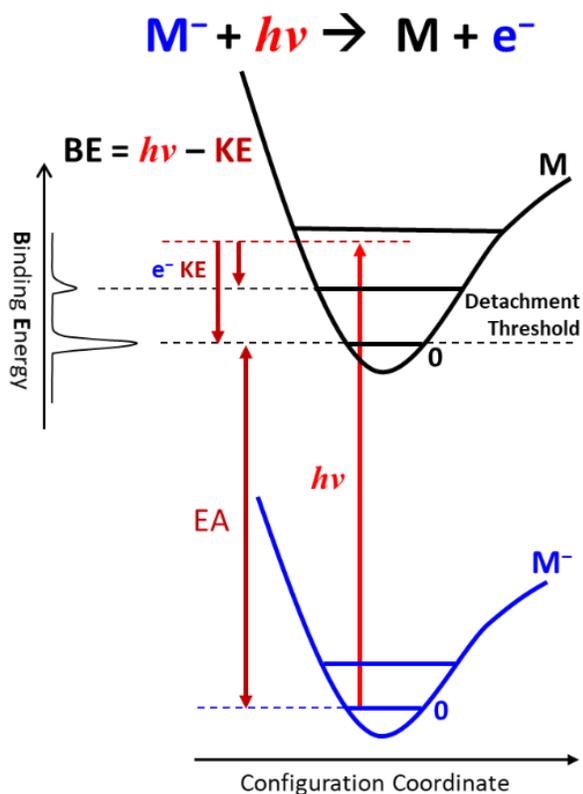
Figure 1.1. Schematic diagram describing the principle of anion PES.

PES can yield rich information about the anions and the corresponding neutrals. Directly, we can readily determine the electron affinity (EA) of the underlying neutral,[9] i.e., detachment threshold of the anion, from the lowest-binding-energy peak in the spectrum, which represents the 0-0 detachment transition from the ground vibrational state of the anion to the ground vibrational state of the neutral (Fig. 1.1). Under high energy resolution, both vibrational and electronic information of the neutral can be obtained. Anion PES has been extensively utilized to probe the electronic structure of inorganic complexes,[10] chemical bonding and structures of clusters,[11,12] stepwise

solvation of anions to bulk limits,[13] transition-state dynamics of bimolecular reactions[12,14] and so on.

For my thesis work, anion PES, which was developed to the high-resolution photoelectron imaging apparatus[15] in the Wang group (Chapter 2), has been applied to accurately determine the EA and vibrational structures of tetracyanoquinodimethane (Chapter 3), which is an important organic electron acceptor, and fullerene-related molecules, including $C_{59}N$ (Chapter 4), $H_2O@C_{60}$ and $H_2O@C_{59}N$ (Chapter 5). The intramolecular interactions between water molecules and the fullerene cage anions have been probed. In addition, I have studied the exotic excited states of various anions, such as the dipole-bound states of $C_6H_5O^-$ and $C_6H_5S^-$ (Chapter 6), deprotonated cytosine anions (Chapter 7) and quadrupole-bound states of $NC(C_6H_4)O^-$ (Chapter 8). It is found that dipole-bound states of deprotonated cytosine anions can be used to obtain the tautomer-specific information (Chapter 7).

The first chapter is organized as follows. In Section 1.1, a brief history of anion PES, which has spanned more than half a century, will be introduced. Section 1.2 will describe the instrumental developments in the Wang group, involving the combination of PES with electrospray ionization, cryogenic Paul trap and high-resolution photoelectron imaging. The historical studies of multipole-bound states, including dipole-bound state and quadrupole-bound state, will be discussed in Section 1.3. Lastly, Section 1.4 will discuss two experimental methods, photodetachment spectroscopy and resonant PES via vibrational autodetachment that we have developed to study multipole-bound states.

1.1 A brief history of anion photoelectron spectroscopy

PES is built on the photoelectric effect, which was first observed by Hertz in 1887[16] and understood by Einstein in 1905.[17] Fifty years later, Siegbahn and coworkers[18] first developed the X-ray PES (XPS), which used X-ray photons to eject core electrons from atoms for chemical analyses of solids. In the early 1960s, Vilesov et al.[19] and Turner et al.[20] independently utilized vacuum ultraviolet radiations, possessing much lower photon energies than X-ray, to study gaseous neutral molecules, which is well known as UPS. Several years later, Hall and coworkers reported the first anion PES experiment on He^- and measured the EA of an excited helium atom.[21] In their experiment, continuous-wave (cw) argon ion monochromatic laser was used to photodetach He^- produced by a continuous ion source, while the resulting photoelectrons were detected by a hemispherical electron analyzer. And the technique of anion PES was quickly extended to study diatomic anions,[22,23] alkali-metal anions,[24] small molecular anions,[25] negative cluster ions,[26] and transient species[27] by the groups of Hall, Lineberger, Ellison, Bowen, etc.

With the development of pulsed ion sources in the 1980s,[28,29] the Johnson group reported the first pulsed PES experiment on anions of O^-, O_2^- and O_4^- in 1986.[30] The mass-selected anions prepared by electron impact ionization of a pulsed supersonic jet was photodetached by a pulsed Nd:YAG laser with the photoelectrons analyzed by a field-free time-of-flight (TOF) electron energy analyzer. Soon after, Smalley et al.[31,32] and Gantefőr et al.[33,34] studied the metal and semiconductor cluster anions prepared from a pulsed supersonic beam coupled to a laser vaporization set-up. An excimer laser (6.4 eV) was used in photodetachment for the first time,[31,32] allowing the investigations of the

valence states of metallic and semiconductor clusters possessing high BEs. A magnetic bottle TOF system[34,35] was developed to detect the photoelectron with high efficiency. The Smalley's set-up[35] has been further developed by the Wang group[36] to study the chemical bonding and structures of metallic,[36,37] oxides,[38,39] carbides[40,41] and boron-related clusters.[11,42] The pulsed experiments have allowed the investigation of a variety of anionic species prepared by pulsed ion sources and enabled the utilization of pulsed laser with shorter wavelength for photodetachment. For example, the ninth harmonic of a Nd:YAG laser at 118.2 nm (10.488 eV) was reported recently by the Wang group[43] to study the superhalogen anions, which have detachment thresholds about 7 eV.

One of the major concerns of anion PES is the energy resolution of the photoelectron KE. The early cw experiments used the hemispherical electron analyzer could achieve a KE resolution of 5-8 meV for molecular anions.[27] The field-free and magnetic bottle TOF analyzer were mainly used in the pulsed experiments. The resolution that the field-free TOF could achieve was 5-8 meV with a lower collection efficiency.[44] The magnetic bottle system showed a good collection efficiency but suffered from severe Doppler broadening effect, yielding a KE resolution as good as 6 meV.[45]

A more recently developed technique to improve the photoelectron energy resolution is velocity-map imaging (VMI). The technique was based on the ion imaging method originally used in the photodissociation experiment by Chandler and Houston in 1987.[46] The low resolution and distortion of the imaging was highly improved when Eppink and Parker developed the VMI in 1997.[47] It was introduced to photoelectron imaging of anions by Bordas et al.[48] and Sanov et al.[49] in the early 2000s. It was found that VMI was suitable for the detection of slow and fast photoelectrons simultaneously.[50]

Impressive experimental accuracy of 0.06 meV (0.5 cm^{-1}) has been achieved very recently for the EA measurement of the Nb atom by the Ning group.[51]

Besides the instrumental development to achieve better performances of anion PES, a different spectroscopy, anion zero electron kinetic energy (ZEKE),[52] was also developed to improve the resolution. ZEKE experiments were originally built to study neutral molecules by Müller-Dethlefs and Schlag.[53,54] In ZEKE, a tunable pulsed laser is scanned across the detachment threshold, and the photoelectrons with nearly zero kinetic energies are selectively detected, yielding a very high energy resolution. The Neumark group adapted ZEKE to study anions and achieved an energy resolution as high as 1 cm^{-1} for atomic anions and 8-10 cm^{-1} for molecular anions due to the rotational broadening.[52,55,56] However, due to the experimental difficulties[52] that near-zero energy photoelectrons are quite sensitive to stray electric and magnetic fields and requirement of s-wave detachment based on Wigner threshold law,[57] the high-resolution anion ZEKE were limited to a small fractions of anions, such as the anionic clusters[58] and anion-neutral complexes.[59]

To overcome the issues of anion ZEKE, the VMI and anion ZEKE techniques were combined as slow photoelectron velocity-map imaging (SEVI) by the Neumark group.[12,52] Simply, a tunable laser at several fixed wavelengths is used to photodetach the anion near the threshold of each detachment transition. The resulting slow photoelectrons are analyzed by VMI at low extraction voltages to achieve high resolutions. A series of high-resolution images obtained at various wavelengths are combined to yield the photoelectron spectrum with sub-meV energy resolution. Based on various VMI systems, the Neumark group achieved a resolution of 1.5 cm^{-1} for photodetachment of Cl^{-},[52] while

the high-resolution imaging system in the Wang group (Section 1.2.3) recently obtained a

1.2 cm^{-1} resolution for near threshold electrons detached from Bi$^-$.[60] The best resolution

was reported by the Ning group to be just 1 cm^{-1} for Nb$^-$.[51] The developments of SEVI

and high-resolution imaging techniques have achieved very impressive energy

resolutions for atomic anions. However, the energy resolutions of molecular anions or

anionic clusters are not as good as those in atomic anions due to the substantial internal

energy of the anions even at room temperature, which can cause vibrational hot bands

and rotational broadening for the spectrum. Therefore, it would be critical to cool down

the anions to achieve a better resolution for molecular or cluster anions.

In 2005, the Wang group reported the first anion PES experiment for cold

anions,[61] which were cooled down via collisions with a buffer gas in a cryogenic Paul

trap (Section 1.2.2).[62] Vibrational hot bands were completely eliminated in the spectrum

of C_{60}^-.[63] Very recently, the Neumark incorporated a cryogenic octupole ion trap into

SEVI to develop cryo-SEVI[64] and achieved a resolution of 2-3 cm^{-1} for deprotonated

anthracene anions.[65] A similar combination of cryogenic ion trap with high-resolution

imaging system has been developed in several groups, including the von Issendorff,[66]

Ning[67] and Garand.[68]

After more than fifty years of development of anion PES since 1967, the

combination of high-resolution imaging system in detecting slow electrons based on

SEVI and cryogenic ion trap to cool down the anions has been proven to be a huge

success for excellent performance and extensive applicability. With the high-resolution

photoelectron detection and preparation of cold anions, the anion PES has been widely

applied to study weakly bound excited states of anions,[15] structures of large polycyclic

aromatic hydrocarbons,[12,69] anionic clusters[12,66,67] and transient species in bimolecular reactions.[12]

1.2 The development of electrospray photoelectron spectroscopy in the Wang group

The Wang group have pioneered the study of solution anions in the gas phase by electrospray ionization and PES since 1998. The first-generation ESI-PES allowed the first spectroscopic studies of multiply-charged anions from solution samples (Section 1.2.1). Later, they introduced the cryogenic Paul trap to cool down anions using a closed cycle helium refrigerator for the first time (Section 1.2.2). The vibrational hot band was completely eliminated, and the spectra were much better resolved. Very recently, a multi-lens high-resolution photoelectron imaging system has been developed in the third-generation apparatus, showing an energy resolution as good as 1.2 cm^{-1} (Section 1.2.3). The coupling of the cryogenic Paul trap and high-resolution imaging has allowed the study of exotic excited states of anions, including dipole-bound states and quadrupole-bound states, which have very low electron binding energies as small as 20 cm^{-1}. More details are described as follow.

1.2.1 Coupling electrospray ionization with photoelectron spectroscopy

Electrospray ionization (ESI) is a soft ionization method, allowing ions prepared in the solution phase to be isolated into the gas phase.[70] As schematically shown in Fig. 1.2, the sample solution is loaded into the syringe of which the capillary tip is applied with a high voltage (several kV). The large charged droplets sprayed out in the electrospray process then enter into the heated desolvation capillary. With the removal of solvent molecules, the Coulomb repulsions between the ions in the droplets cause the

large droplets breaking up into small droplets, eventually forming isolated ions or solvated ionic clusters in the gas phase.
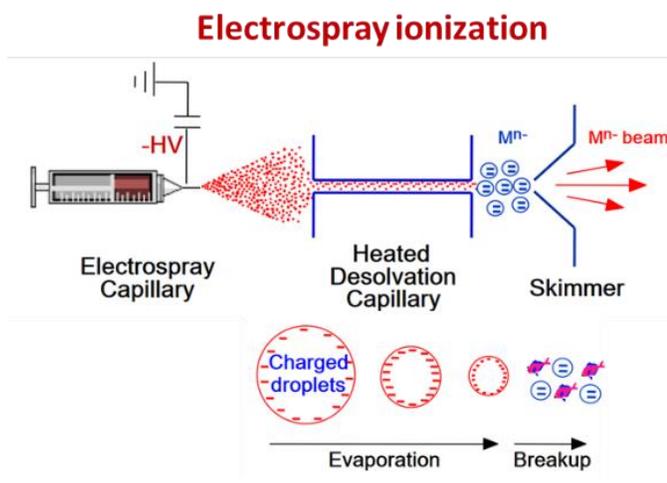
Figure 1.2. Schematic description of the electrospray ionization process.

The original idea of the method could date back to 1968 when Dole et al. tried to electrospray a solution of polystyrene molecules to generate a beam of macromolecules or macroions.[71] Fifteen years later, Fenn fully developed ESI into a soft ionization method for biological molecules, that eventually won him a Nobel Prize in 2002.[72,73] They even suggested that ESI might be useful to produce ions for various spectroscopic studies in the original report.[72]

The application of ESI as ion source for spectroscopic studies was first developed by the Wang group in 1998.[74,75] They successfully coupled the ESI with anion PES in their first-generation ESI-PES apparatus,[76] as presented in Fig. 1.3. Basically, the anions produced from the ESI were guided into a room-temperature Paul trap. After accumulation of 0.1 s, the ions were pulsed out into the extraction zone of a TOF mass spectrometer at a repetition rate of 10 Hz. The mass-selected anions were intersected by a

pulse laser for photodetachment. The magnetic-bottle electron analyzer was used to collect the photoelectrons with an energy resolution of about 2% (ΔKE/KE).
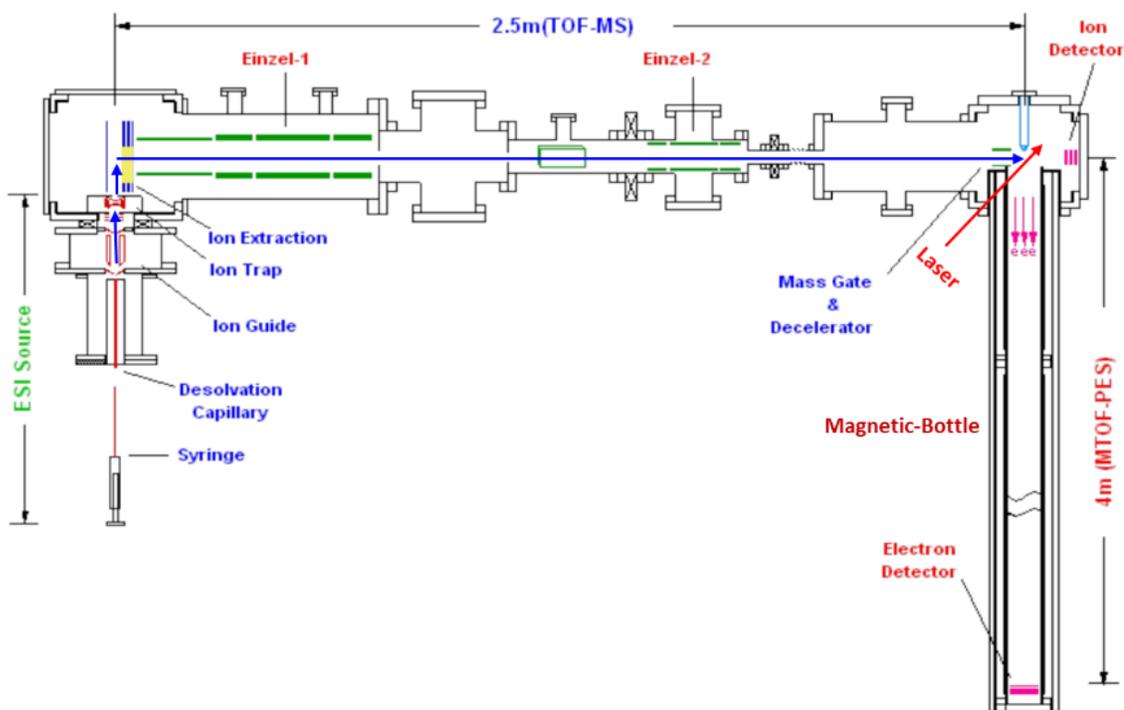
Figure 1.3. Schematic view of the first-generation ESI-PES apparatus. The blue arrows indicate the trajectory of the ion beam produced by ESI. Reproduced from [L. S. Wang, C. F. Ding, X. B. Wang, and S. E. Barlow, Photodetachment photoelectron spectroscopy of multiply charged anions using electrospray ionization. *Rev. Sci. Instrum.* **70**, 1957 (1999).], with the permission of AIP Publishing.

The combination enabled the spectroscopic study of multiply charged anions (MCAs) and the first direct observation of the repulsive Coulomb barrier,[74,75] which is due to the short-range attraction by the nuclei and long-range repulsion from the negatively charged residual ion when an electron is detached from MCAs. MCAs with negative electron binding energies were even observed.[77] In addition, the stepwise solvations of various inorganic anions and the electronic structures of a number of inorganic clusters and coordination complexes were studied by anion PES with the

convenient preparation of the corresponding anions in the gas phase.[10,78] The introduction

of ESI to anion PES has been proven to be a general and powerful technique to study the

solution phase species and chemistry in the gas phase.

Besides, ESI has been used to produce deprotonated protein chromophores for

time-resolved PES studies by the Fielding group.[79] It has also been used to prepare

protonated peptides or larger biomolecules for studies of various vibrational

spectroscopies by the groups of Rizzo,[80] Johnson[81] and Garand.[82]

1.2.2 Incorporating the cryogenic ion trap into ESI-PES

Most of the species studied by the first-generation ESI-PES were MCAs, large

molecular anions, anionic complexes and clusters, which could carry considerable

internal energies at room temperature. As a result, rotational broadening and vibrational

hot bands, which are due to photodetachment from rotationally and vibrationally excited

anions, can cause the congestion of the spectra, limiting the spectral resolution and

accuracy. Also, the temperature-dependent information from different conformations of

molecules or isomers of weakly bound complexes and clusters may be easily averaged

out when the ions are hot. Therefore, it is critical to cool down and control the

temperatures of ions in order to improve the power of anion PES.

A number of methods, such as supersonic expansion,[83] helium nanodroplet[84,85]

and argon tagging,[86,87] have been used to prepare cold molecules and ions. However,

none of the methods could control the temperature precisely and be compatible with PES.

A suitable cooling method with temperature tuning capability would be cryogenic ion

cooling in a trap, which was first demonstrated by Gerlich and coworkers using a 22-pole

trap.[88,89] They successfully cooled down molecular ions to cryogenic temperature via

collisions with helium buffer gas in a radio-frenquency (rf) 22-pole ion trap, which was attached to a helium refrigerator. The thermalized collision processes, which removed the thermal energy of the ions confined in the trap, could be well controlled by tuning the temperature of the attached cold head and the pressure of the loading buffer gas. Due to the flat trapping potential of the 22-pole trap minimizing the rf heating, it showed an excellent cooling capability for ions, which was subsequently applied to numerous studies in ion-molecule reactions and molecular ions pectroscopy.[80,90-92] However, the flatness of the potential also caused deficient axial confinement of the ions, making it unsuitable for the ESI-PES experiments running at a low-repetition rate of 10 Hz.[62]

In the late 2004, the Wang group first developed the temperature-controlled (10 – 350 K) 3D Paul trap for the second-generation ESI-PES apparatus.[62] The Paul trap, with good axial and radial confinements of ions, was demonstrated to be quite suitable to extract ions for subsequent TOF mass analyses. And the anions were cooled by collision with buffer gas of 0.1 – 1 mTorr He/H_2 (4/1) for temperatures below 70 K or N_2 for temperatures above 70 K. The cooling effect on the ions was substantial. When the temperature decreased from 300 K to 70 K, the photoelectron spectra of both small anion ClO_2^- and large anion C_{60}^- showed better resolved peaks and complete elimination of vibrational hot bands, which usually cause the spectral congestions and inaccurate measurement of EA. Additionally, the temperature-dependent experiments of monocarboxylate anions $CH_3CH_3NCO_2^-$ (n = 0-8) observed the week C-H … O hydrogen bonding for alkanes and conformational changes from linear to cyclic geometries.[61]

While the original set-up of cryogenic Paul trap built at Pacific Northwest National Laboratory has continued to show interesting observations,[83,94] the Wang group has developed a new cold ion trap equipped with pulsed buffer gas and a more powerful cold head in the third-generation apparatus when moved to Brown University.[15] When running experiment around 4.5 K, the ion temperature in the new trap has been determined to be 30 – 35 K from simulations of rotational profiles in the photodetachment spectra of several anions.[95-97]

Furthermore, a similar 3D quadrupole ion trap has recently been developed in the Garand group for anion SEVI experiment of polycyclic aromatic hydrocarbons.[68,69] The powerfulness of cryogenic Paul trap has also been adapted by several groups to study cold ions and ionic clusters by vibrational or UV-UV spectroscopy.[81,82,98-101]

1.2.3 High-resolution photoelectron imaging system

As the anions were cooled down to low temperature without hot bands, the performance of the second-generation ESI-PES was mainly limited by the low resolution of the photoelectron KE analyzer. The magnetic-bottle electron analyzer was used in the second-generation apparatus. It had an electron energy resolution of 2% ($\Delta KE/KE$),[62] which severely limited the benefits from cold anions. Very recently, the Wang group incorporated the high-resolution imaging system in the third-generation equipment.[15]

The particle imaging technique[102] was initially inspired from Solomon et al.[103] who attempted to visualize the photodissociation products in 1969 and from Yates et al.[104] who imaged the ion desorptions from electron stimulations on surfaces in 1974. In 1987, Chandler and Houston[46] first developed the ion imaging technique and obtained a two-dimensional image for the photodissociation products of CH_3I, showing both spatial

and angular distributions. The imaging technique was soon applied to study more photodissociations[105,106] and bimolecular reactions.[107] However, the images suffered considerable distortions and low resolution. The big improvement came in 1997 when Eppink and Parker[47] developed velocity-map imaging (VMI) by using a simple three-plate electrostatic design (Fig. 1.4) with open electrodes instead of conventional grid electrodes. Due to the curved electric fields in VMI, particles with same initial velocity vectors but different initial spatial positions can be mapped onto the same point on the detector (Fig. 1. 4), greatly enhancing the energy resolution. Since then, it has been widely used in various experiments, such as photodissociation[108,109] and reaction dynamics.[110,111] In the early 2000s, Bordas et al.[48] and Sanov et al.[49] introduced VMI to PES experiments of cluster anions and yielded nice photoelectron images, which were previously obtained by Helm et al.[112] for multiphoton ionization of xenon atom with regular imaging technique. Both KE and angular distributions of photoelectrons could be obtained.[113] And it was found that both slow and fast photoelectrons could be observed.[50] The ability to detect low-energy electrons and angular distributions makes VMI a popular method for high-resolution PES of anions. And SEVI developed by the Neumark group[12,52] has achieved a high resolution of 1.5 cm^{-1}.
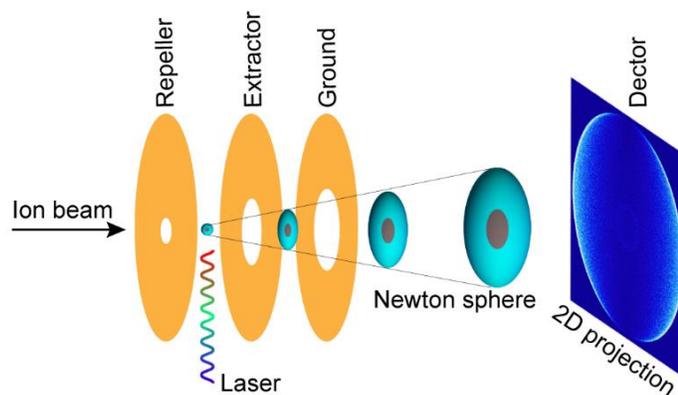
Figure 1.4. Schematic view of velocity-map imaging.

The initial VMI system in the Wang group was constructed based on the three-plate VMI from Eppink and Parker.[47]And it was used to image the intramolecular Coulomb repulsions of various MCAs produced by ESI, showing strong anisotropies in the photoelectron angular distributions.[114,115] To study the anionic clusters with higher resolution, a multi-lens high-resolution VMI system was built in 2013.[60] The new VMI system could achieve energy resolution of 1.2 cm^{-1} for slow electrons while maintaining good resolution (ΔKE/KE ~ 0.53 %) for high KE electrons. The high-resolution photoelectron imaging system was then combined with the ESI-PES in the third-generation apparatus.[15]

The third-generation ESI-PES apparatus, equipped with the cryogenic Paul trap and high-resolution photoelectron imaging, was able to yield the most accurate EA of C_{60} measured to date as 2.6835 (6) eV.[116] It has allowed the study of weakly bound states of anions, including both dipole-bound[12,95,117-122] and quadrupole-bound excited states.[97]

1.3 Multipole-bound states of anions

Electrons in neutrals and cations can experience net Coulomb attractions as $-ne^2/r$ (n = 1 for a neutral and 2 for a singly charged cation.) at large r distance, which gives rise to a series of bound electronic states.[123] In contrast, the excess electron in anion (singly-charged) has no net Coulomb attraction in the asymptotic regions. Instead, the electron experiences a long-range attractive potential with the neutral core expressed as:

$$V(r) = -\mu e \cos\theta/r^2 - eQ \bullet\bullet (3\mathbf{rr} - r^2\mathbf{1})/3r^5 - \alpha \bullet\bullet \mathbf{rr}\ e^2/2r^6,$$

where r is the distance between the electron and the molecule, θ is the angle between the molecule's dipole vector and the electron's position vector $\mathbf{r}$, μ is the electric dipole

moment. Q is the quadrupole tensor of the molecule and **1** is the unit tensor. α is the polarizability tensor of the molecule.[123] When the charge-dipole potential is dominating, the anion can be viewed as a dipole-bound anion, which can support dipole-bound state. Similarly, quadrupole-bound state and polarization (or correlation)-bound state can exist for anions of which the corresponding interactions are dominant.[123-125]

1.3.1 Dipole-bound state

When a neutral molecule possesses a large dipole moment (μ > ≈ 2.5 D), it can bind an excess electron by the long-range charge-dipole attraction scaled as $1/r^2$ with a BE on the order of a few to few hundreds meV.[114-116] The resulting anion can support a dipole-bound state (DBS) with a diffuse orbital, which is analogous to Rydberg state in a neutral atom or molecule. This makes it an excellent many-body system to study quantum halo states[126] and electron-molecule interactions, such as vibronic coupling[127] and low-energy electron rescattering.[121] DBS has also been proposed as the "doorway" to the formation of stable valence-bound anions,[128-130] especially for those formed in the reductive DNA damage process by low-energy electrons attachment[131] and those in the interstellar medium under astronomical environments.[6,132,133]

In 1947, Fermi and Teller[134] first predicted a minimum dipole moment of 1.625 D (or 0.639 ea_0, where e is the charge of the electron and a_0 is the Bohr radius) for a point dipole to bind an electron when studying the capture of negative mesotrons in matter. Interestingly, only one sentence, "*In the special case of mesotron capture by the hydrogen atom, it is found that when the mesotron approaches the nucleus to a distance of 0.639 Bohr radii, the binding energy of the electron becomes zero.*", was described in the whole paper about the critical value without any derivation or interpretation. In 1950,

Wightman[135] obtained the same value by solving the Schrödinger equation describing the motion of a single electron in the presence of a charge-dipole potential. In the 1966-1967, several theoretical groups[136-139] derived a similar value of minimum dipole moment for point or finite dipole to bind an electron, seemingly unaware of the earlier work. Later in 1976, Turner[140] wrote an interesting article detailing the history of earlier theoretical studies about the minimum dipole moment for electron binding and the numerical solution found in Fermi's notebook.

In the early 1970s, Crawford and Garrett[141-144] extended the calculations to include the effects of rotation, moment of inertia and dipole length on the minimum dipole moment to bind an electron and increased the value up to 2.0 D. A more practical estimate of 2.5 D was later suggested from extensive experimental observations.[124,145,146] Later on, several groups,[147-159] mainly including Adamowicz, Gutowski, Jordan, Simon, Skurski and Sommerfeld, used or developed various theoretical methods to study the electron binding energies in the dipole-bound anions of molecules and clusters, and to investigate the electronic structure as well as dispersion contributions in the electron-molecule interactions in DBS.

In addition, molecules with even larger dipole moments may possess more than one bound DBS. Early studies of a fixed dipolar system concluded that 9.64 D is required for the second DBS.[160,161] Considering the rotational effects, Garrett predicted a critical dipole moment of 4.5 D for the second DBS.[162,163] Very recently, the Wang group[164] attempted to search for a second DBS for deprotonated 2-hydroxypyrimidine anion, which has a calculated dipolar neutral core of 6.2 D. Although a large binding energy of

598 cm^{-1} was observed for ground DBS, no evidence of a second DBS was indicated below the detachment threshold. So far, higher DBS has not been observed yet.

Experimentally, the dipole-bound electron was first suggested by Wong and Schulz in 1974.[165] In their low-energy electron scattering experiment, the sharp structure near the threshold of excited state of CO (1.38 D) was attributed to dipole-dominated resonances. However, the small dipole moment was not able to bind the electron from theoretical perspectives. The direct evidence for DBS came from photodetachment experiments by Brauman and coworkers,[166,167] who attributed the observed sharp resonances in the photodetachment cross section of enolate anions to dipole-supported excited states. Subsequently, Lineberger and coworkers carried out high-resolution photodetachment spectroscopy for a series of anions and observed rotational autodetachments via short-lived DBSs.[168-172]

Besides the studies of excited DBS, the other major experimental studies are about ground state dipole-bound anions (DBAs).[146] which were formed by Rydberg electron transfer (RET)[173,174] or electron attachment to dipolar molecules or clusters. RET has been widely used by groups of Compton,[124,129,175,176] Schermann,[129,145,146,177] Bowen[178-180] and Dunning[181,182] to produce a variety of DBAs, which could be detached by electric field. Several DBAs of solvated clusters were prepared by free-electron attachment[183-185] and studied by PES.[178-180,183-185] In addition, Johnson et al.[186] reported the preparation for CH_3CN^- DBA by photodissociation of $I^-•CH_3CN$ ion-molecule complex. Neumark et al. conducted time-resolved PES for anionic complexes of $I^-•CH_3NO_2$[187] and $I^-•$adenine.[188] They found the DBAs of CH_3NO_2 and adenine were

produced by electron transfer from I^- and showed the transition from DBAs to valence-bound anions.

Very recently, the Wang group first reported the resonant PES via vibrational autodetachment from DBS of $C_6H_5O^-$.[117] The ground DBS of $C_6H_5O^-$ was found to be 97 cm^{-1} below the detachment threshold. The small binding energy of the DBS confirmed the weakly-bound nature and its fragility, which was able to be probed because of the preparation of cold $C_6H_5O^-$ anions in the cryogenic Paul trap and high-resolution photoelectron imaging analyzer equipped in the third-generation ESI-PES.[15] More interestingly, mode-specific autodetachment from eight vibrational levels of the DBS was observed, yielding highly non-Franck-Condon resonant photoelectron spectra, due to the $\Delta v = -1$ vibrational propensity rule.[189,190] Subsequently, more anions were found to support excited DBS below the anion photodetachment threshold[95, 118-122,164] and the resonant PES obtained from vibrational autodetachment via DBS has resolved abundant vibrational features, especially for the low-frequency and Franck-Condon-inactive vibrational modes as well as conformation-selective information. In addition, the groups of Mabbs[191] and Heaven[192,193] have reported vibrational autodetachments from DBS resonances of diatomic anions.

1.3.2 Quadrupole-bound state

With vanishing dipole moments, but strong quadrupole moments, neutral molecules can form quadrupole-bound anions, in which the long-range charge-quadrupole attractive potential ($\sim 1/r^3$) dominates.[123,124,194,195] Jordan and Liebman first suggested the rhombic $(BeO)_2^-$ cluster as a quadrupole-bound anion.[196] This cluster and the similar $(MgO)_2^-$ cluster studied by PES[197] have relatively high electron binding

energies and should probably be considered as valence-bound anions.[123] In addition, the rhombic alkali-halide dimers, such as $(KCl)_2^-$ and $(NaCl)_2^-$, and a series of complex organic molecules with vanishing dipole moments but large quadrupole moments have also been proposed to form quadrupole-bound anions.[198-200] Experimental studies of electron binding to quadrupolar molecules have been scarce. The CS_2^- anion was first observed via RET and was suggested to be a possible quadrupole-bound anion.[201,202] The formamide dimer and the *para*-dinitrobenzene anions formed via RET were also suggested to be quadrupole-bound anions.[203,204] A more conclusive example of a quadrupole-bound anion was from RET to the *trans*-succinonitrile.[205,206] A valence-bound anion with a non-polar core may possess excited quadrupole-bound state (QBS) just below the electron detachment threshold, if the neutral core possesses a large quadrupole moment. However, such an excited QBS was not observed until 2017 when we reported the first observation of excited QBS,[97] which will be presented in Chapter 8.

1.4 Experimental approaches to study multipole-bound states

A significant part of this thesis concerns the studies of DBS and QBS of anions (Chapter 6-8). We have used two experimental approaches, photodetachment spectroscopy and resonant PES via vibrational autodetachment of DBS or QBS, which will be briefly described here.

1.4.1 Photodetachment spectrosopy

Photodetachment spectroscopy (PDS) is a method to study the photon energy dependences of photodetachment cross sections of anions. Photodetachment experiment was first done by Branscomb and coworkers[207,208] for H^- and D^- using conventional

tungsten lamp as the light source. With the development of tunable dye laser in the late 1960s,[209,210] Lineberger and Woodward[211] applied it to photodetachment of the sulfur anion and obtained a very accurate EA for the sulfur atom. Later, the photodetachment experiment on the dipolar enolate anion done by Brauman and coworkers led to the first observation of resonances due to an excited DBS.[166,167] Recently, PDS has been largely used to search for DBS or QBS resonances[95,117-122,164,191-193] and accurately measure detachment thresholds of anions.[212,213]

In our experiments, we have used PDS to search for DBS and QBS resonances, as schematically shown in Fig.1.5. If the anion (M^-) has a dipolar neutral core ($\mu > \approx 2.5$ D), it can support a DBS (M^{-*}_{DBS}) below the detachment threshold with a small binding energy of 1-100 meV. A tunable dye laser is used to scan across the detachment threshold of M^- while monitoring the photoelectron yield. When the laser wavelengths match with the DBS resonances, the corresponding electron yield is spiked as a sharp peak in the photodetachment spectrum. While the peak below the threshold is the ground vibrational level of the DBS due to resonant two-photon detachment, the peaks above the detachment threshold are excited vibrational levels of the DBS, which undergo vibrational autodetachment. The gradually increasing cross section of the baseline above the threshold is from regular non-resonant detachment process.

Photodetachment spectroscopy

Figure 1.5. Schematic view for the principle of photodetachment spectroscopy.

1.4.2 Resonant photoelectron spectroscopy via vibrational autodetachment of DBS

Resonant PES, in which the laser wavelengths are fixed at the resonances, can be viewed as a new way to do PES, different from the regular non-resonant PES. Here the resonant PES has been carried out to assign DBS resonances and obtain more fruitful vibrational information for the dipolar neutral molecules. It is based on the vibrational autodetachments from DBS resonances above the threshold, which means that the excess electron in the DBS can autodetach upon excitation to vibrational level of DBS when the binding energy of DBS electron is less than the energies of some of the vibrational modes.

Autodetachment is the process in which the excess electron is emitted from a metastable state of an anion. In 1974, Lineberger et al. first observed autodetaching

resonances in the photodetachment experiments of alkali atomic anions,[214] followed with sodium halide negative ions[215] and C_2^-.[216] The rotational autodetachments were also observed for a series of dipole-bound anions by high-resolution PDS.[168-172] No spectroscopic study of vibrational autodetachment was reported until 1985 when Lineberger and coworkers reported the infrared spectrum of NH^-.[217] The extra electron was ejected via autodetachment after excitation to ro-vibrational levels of NH^-. Later, vibrational autodetachment was applied to study the DBS of the enolate anion by PDS.[218] In 1996, Johnson et al.[186] reported the photon energy-dependent photoelectron spectra of CH_3CN^-, which showed non-Franck-Condon features due to a broad shape resonance. The resonant PES at the photon energy near the vibrationally-resolved shape resonances of O_2^- also resulted in the spectrum with non-Franck-Condon distribution, different from the non-resonant spectrum.[219] In addition, in the resonant PES of the p-benzoquinone anion[220] and Au_2^-,[221] significant non-Franck-Condon behaviors were observed due to autodetachments from shape and Feshbach resonances.

The pure vibrational autodetachment from DBS was first done for $C_6H_5O^-$ in 2013 by the Wang group using resonant PES.[117] The vibrational autodetachments from DBS, involving a vibronic coupling with the breakdown of the Born-Oppenheimer approximation, are governed by the $\Delta v = -1$ propensity rule under harmonic approximation developed by Simon et al.,[190,222] which was laid on Berry's theory[189] for autoionization in neutral molecules. More examples[118-122,164] showed that the resulting resonant photoelectron spectra were highly non-Franck-Condon, giving rise to vibrational features involving low-frequency and Franck-Condon-inactive vibrational modes. The

resonant PES via vibrational autodetachment of DBS has been demonstrated as a very powerful tool to obtain vibrational information for dipolar neutrals.

The principle of resonant PES via vibrational autodetachment of DBS is schematically described in Fig. 1.6. It involves two processes. The first is resonant excitation, which has a high cross section, from the anion ground state to the DBS vibrational levels in the detachment continuum. Then autodetachment occurs from the DBS level to the neutral level. Briefly, when the photon energy is fixed at one of the DBS resonances above threshold found by PDS, vibronic coupling of the DBS electron and the vibrational modes can induce vibrational autodetachment. The autodetachment follows the $\Delta v = -1$ propensity rule under harmonic approximation,[189,190,222] indicating that one quantum of vibrational energy is transferred to the DBS electron. The resulting neutral peak shows a higher intensity in comparison to the peak in the non-resonant spectrum due to the large cross section of the resonant excitation process. The resonant spectrum is also highly non-Franck-Condon with specific peaks enhanced from autodetachment. By comparing the relative peak intensities in the non-resonant and resonant spectra, we can deduce which peak is enhanced. Based on the $\Delta v = -1$ rule and excitation energies, the DBS vibrational levels of the anions can be assigned. Because the diffuse dipole-bound electron has little effect on the structure of neutral core, the geometries of the DBS and the corresponding neutral state are almost identical,[95,117-122,164] which also means that the vibrational frequencies of DBS are the same as those in the neutral states. Therefore, the vibrational frequencies of neutral molecules can be obtained from the assignments of DBS vibrational levels.
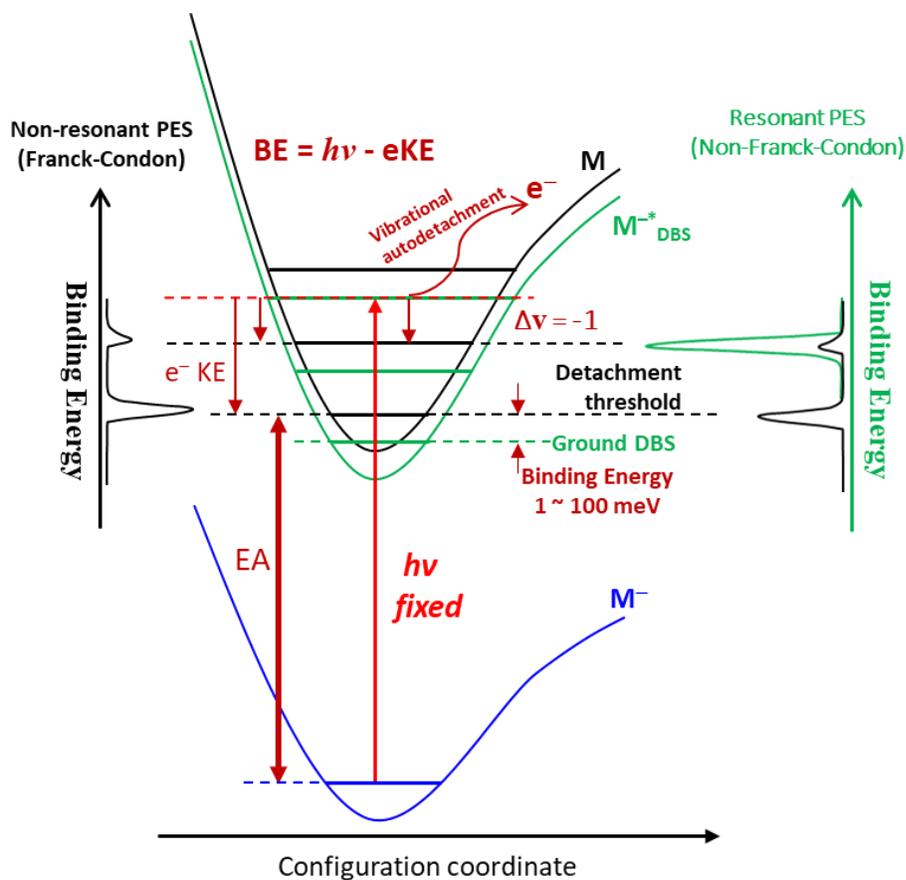
Figure 1.6. Principle of resonant PES via vibrational autodetachment of DBS of anion.

Chapter 2 Experimental methods

All experiments were carried out using the third-generation ESI-PES apparatus,[15] as schematically shown in Fig. 2.1. It mainly consists of four parts, including an ESI source, a cryogenic Paul trap, a TOF mass spectrometer and a high-resolution photoelectron imaging analyzer, which has been partially or fully described previously in the Ph. D. dissertations of Dr. Phuong Diem Dau (January 2014)[223] and Dr. Daoling Huang (May 2016).[224] This chapter will discuss each component for experimental processes, from anion preparations (Section 2.1), ion cooling (Section 2.2) and mass analyzing (Section 2.3) to the photoelectron image taking (Section 2.4) and data processing (Section 2.5) as well as timing sequences (Section 2.6). The overall operation procedure is described here.
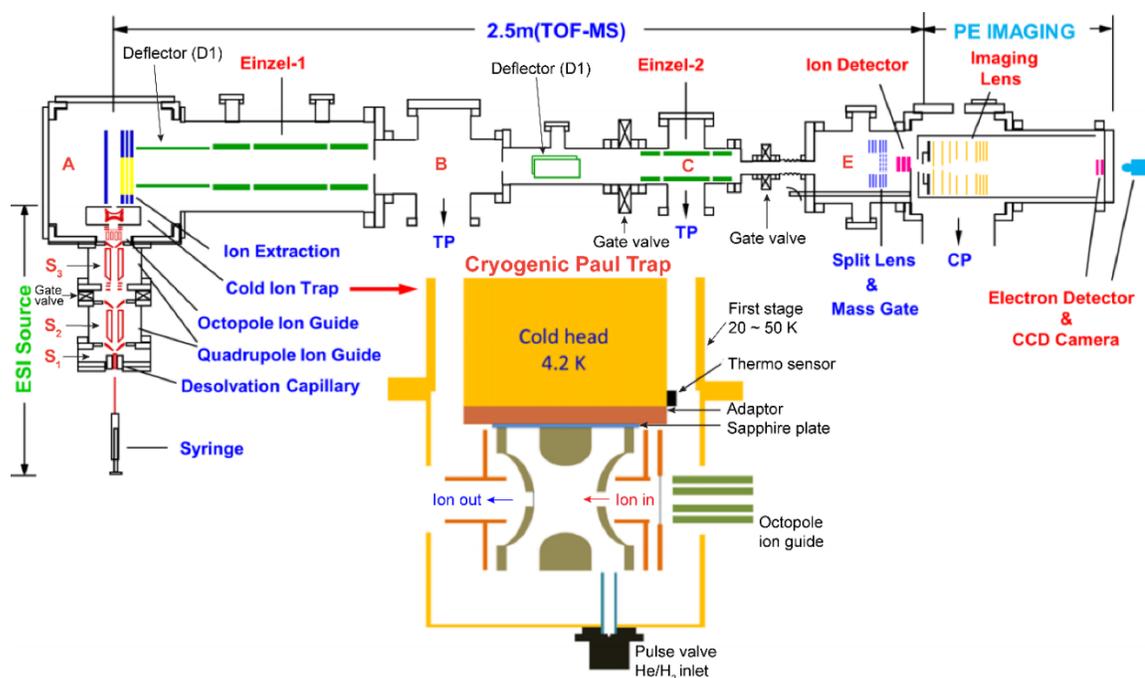
Figure 2.1. Schematics of the third-generation ESI-PES apparatus. TP, turbomolecular pump; CP, cryopump. Reproduced from [L. S. Wang, Perspective: Electrospray photoelectron spectroscopy: From multiply-charged anions to ultracold anions. *J. Chem. Phys.* **143**, 040901 (2015).], with the permission of AIP Publishing.

Briefly, anions were produced by electrospray of ~1 mM sample solutions. Two radio-frequency quadrupole and one octopole ion guides directed anions from the ESI source into a cryogenically-cooled Paul trap operated at 4.5 K. After being accumulated for 0.1 s and thermally cooled via collisions with 1 mTorr He/H$_2$ (4/1 in volume) buffer gas, anions were pulsed out at a 10 Hz repetition rate into the extraction zone of a TOF mass spectrometer. The desired anions were selected by a mass gate and photodetached in the interaction zone of the imaging lens by a Nd:YAG laser or a tunable dye laser. Photoelectrons were focused by a set of imaging lenses and projected onto a pair of 75-mm diameter micro-channel plates (MCPs) coupled to a phosphor screen, which were finally captured by a charge-coupled device (CCD) camera. The images were inverse-Abel transformed and reconstructed using the BASEX[225] and pBasex[226] programs, which were found to give similar results. The photoelectron spectra were based on BASEX, whereas the images are based on pBasex because it gives higher quality images. The photoelectron spectra were calibrated with the known spectra of Au$^-$ at different photon energies. The electron kinetic energy (KE) resolution achieved was 3.8 cm^{-1} for electrons with 55 cm^{-1} KE and about 1.5% (ΔKE/KE) for KE above 1 eV.

2.1 ESI source – Preparation of anions

The details of ESI source chamber is schematically presented in Fig. 2.2. It consists of three differentially pumped vacuum regions, S$_1$, S$_2$ and S$_3$. S$_1$ is pumped down to 470 mTorr by a mechanical pump (Edwards, E2M275). S$_2$ has a base pressure of around 30 mTorr, which is pumped by a blower pump (Stokes Vacuum 310.401) with the mechanical pump (Edwards, E2M80) as a backing pump. A turbomolecular pump

(Edwards, nEXT 300D), backed by a scroll pump (Edwards, XDS 35i), is used for vacuum region S_3 yielding a pressure of around 1.0×10^{-6} torr.
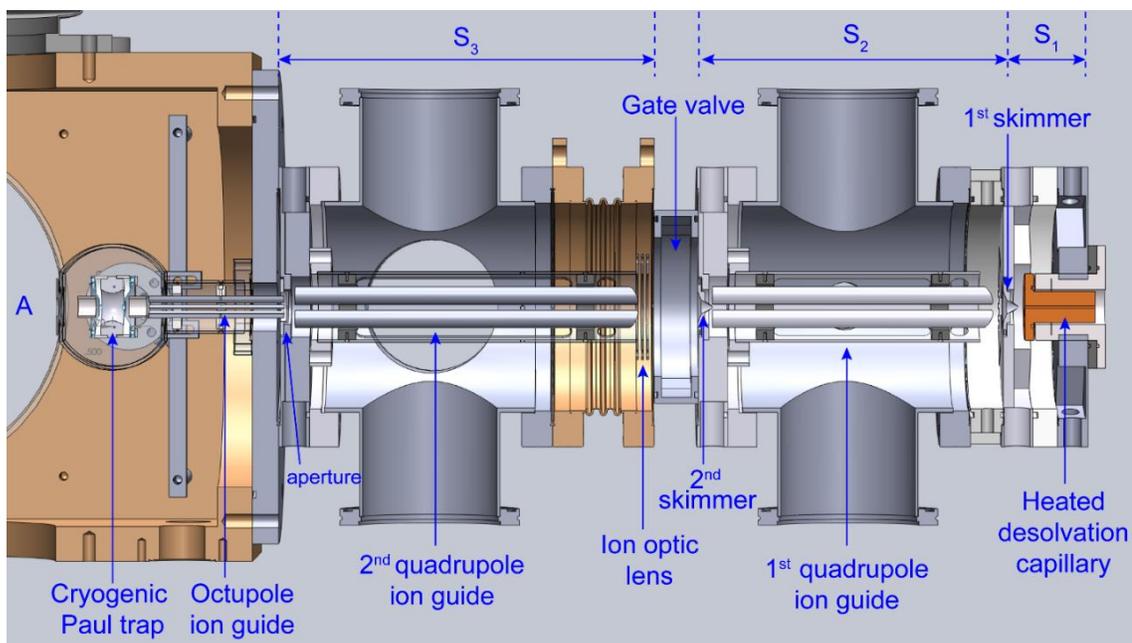
Figure 2.2. Schematics of the ESI source chamber. $S_1 – S_3$ are three vacuum regions.

All the anions studied in Chapters 3-8 were produced by electrospray (Section 1.2.1 in Chapter 1) of ~ 1 mM various solutions, which were made by dissolving the corresponding compounds into solvents with additive compounds, as listed in Table 2.1. Fullerene-related Compounds [$(C_{59}N)_2$, $H_2O@C_{60}$ and $(H_2O@C_{59}N)_2$][227] and tetrakis(dimethylamino)ethylene (TDAE)[228,229] were synthesized, other compounds were commercially purchased. The additives of NaI and TDAE were added as reducing agents, while NaOH was used for deprotonation.

The prepared solutions are loaded into 2.5 mL syringe (Hamilton 1002LTN Syringe), which was placed on a microprocessor-controlled syringe pump (World Precision Instrument SP100i) for solution delivery. A fused silica needle with an outer diameter (O.D.) of 0.2 mm is connected to the end of the stainless-steel needle as spray

capillary. A biased negative voltage of 1.6 kV ~ 5.0 kV is applied to the capillary to generate the negatively charged droplets, which entered into a heated desolvation capillary (Fig. 2.2) acting as the interface between atmosphere and vacuum region.

Table 2.1. Preparations of solutions for ESI.

Chapter	Anions	Compounds	Solvents	Additive compounds
3	$TCNQ^-$	$TCNQ^b$	CH_3CN	NaI
4,5	$C_{59}N^-$, $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$	$(C_{59}N)_2$, $H_2O@C_{60}$ and $(H_2O@C_{59}N)_2$	$ODCB^c/CH_3CN$ (1/3 in volume)	$TDAE^d$
6	$C_6H_5O^-$, $C_6H_5S^-$	Phenol,thiophenol	CH_3OH/H_2O (9/1 in volume)	NaOH
7	$[Cy-H]^{-a}$	cytosine	CH_3OH/H_2O (9/1 in volume)	NaOH
8	$NC(C_6H_4)O^-$	$NC(C_6H_4)OH$	CH_3OH/H_2O (9/1 in volume)	NaOH

[a][Cy-H]$^-$ indicates the deprotonated cytosine anion. [b]TCNQ is tetracyanoquinodimethane. [c]ODCB is o-dichlorobenzene. [d]TDAE is tetrakis(dimethylamino)ethylene.

The desolvation capillary is a stainless-steel tube, with an interior diameter of 0.8 cm, tightly inserted into a copper block (3.7 cm long and 3.4 cm O.D.), which is heated by a heater inserted through a drilled hole (3.1 cm long, 0.7 cm diameter) and mounted to the flange with insulation. The temperature of the capillary is measured by a thermal couple and tuned around 60 °C by the voltage output from a transformer. With the removal of solvents by the heated desolation capillary, the charged droplets break up and form the isolated anions in the gas phase.

After the capillary, the first skimmer with a negative voltage of 5 – 20 V applied is mounted on the flange to separate the vacuum regions S_1 and S_2. In vacuum region S_2, a rf-only quadrupole ion guide (QID) is used to transmit ions with a transmission rate as high as 90% at low vacuum. The QID consists of four stainless steel electrodes (10 cm long, 2.5 cm diameter) of which the entrance end is cut by 45° to adjust to the skimmer. The power supply is centered at 1.0 MHz for ions with m/z around 70 – 2500.

A second skimmer with biased negative voltages of 0 – 5 V and a gate valve are placed to define the vacuum region S_3. A set of three-plate ion optic lens is followed to guide ions exiting from the first QID into the second QID due to the large thickness (around 3 cm) of the gate valve. The middle plate of the ion optic lens is applied with a + 70 V biased voltage and the other two plates are grounded. To guide the ions through, a second QID (23 cm long, 2.5 cm diameter), of which the power supply is constructed based on previous designs. [230,231]

After the second QID, ions enter through an aperture (3 mm diameter) into the octopole ion guide (8 cm long, 0.3 cm diameter) with 1.0 MHz rf frequency applied, which guides the ions into the cryogenic Paul trap more effectively with a flatter potential than QID.

2.2 Cryogenic Paul trap – Accumulation and cooling of anions

The cryogenic Paul trap is placed in vacuum region A, which is mainly pumped by the big magnetically levitated turbomolecular pump (Edwards, STP-A2203C) to a base pressure of ~1.0 x 10^{-7} torr and running pressure of ~ 1.0 x10^{-6} torr.

As shown in the inset of Fig. 2.1, the ion trap consists of a hyperbolic ring electrode and two end cap electrodes for ion entrance and exit. During the operation, voltages of two end caps are kept at ground potential and only the ring electrode is applied with a rf potential to trap ions. The rf frequency is fixed at 1.0 MHz and the rf voltage is optimized for specific mass range. The rf voltage is off for a period of about 100 µs for loading ions from the octopole ion guide. One grid electrode with varied

voltages (+ 30 V to + 70 V) and a tube lens (+ 10 V to + 60 V) are added in front of entrance end cap to assist ion loading.

With a repetition rate of 10 Hz running experiment, the loaded ions are accumulated in the trap for 0.1 s. Then, the entrance end cap is pulsed to around – 70 V with the exit end cap simultaneously pulsed by + 30 V to extract ions out. A tube lens after the exit end cap is applied with a voltage about + 1 V to aid ions unloading and focusing into the extraction area of mass analyzer.

The Paul trap is cooled by a two-stage closed cycle helium coldhead (Sumitomo, RDK-415D2B) accompanied with a compressor (Sumitomo, F-70 L). The first stage can achieve a temperature of 20 – 50 K. The temperature of the second stage is achieved around 4.2 K. The Paul trap is attached to the second stage of the cold head via an extension and an adapter made of oxygen-free high purity copper. A 1 mm thick sapphire plate is inserted between the ion trap and the adapter for electrical insulation. To achieve better thermal conductivity, a 0.1 mm thick indium foil is placed between these junctions. In addition, the trap is enclosed in a gold-coated copper cylinder attached to the first stage of the coldhead to achieve better thermal shielding. A silicon diode thermal sensor is wrapped around the adapter to measure the temperature of the coldhead and send feedback to a temperature controller (LakeShore, 336 temperature controller). The temperature can be tuned at the range of 4.6 – 350 K. All the experiments were done at the lowest temperature around 4.6 K. The buffer gas is a mixture of 1 mbar He/H_2 (4:1 volume ratio), which is inlet into the trap by a pulsed valve (Parker Instrumentation, 060-0001-900).

2.3 TOF-MS – Mass analyzing and selecting of anions

TOF-MS is a method to determine ions mass-to-charge (m/z) ratio by measuring the different times of flights for ions possessing the same kinetic energy. As shown in Fig. 2.1, our set-up is a 2.5 m long flight tube, spanning over four differentially pumped vacuum regions A, B. C and E, which consists of an ion extraction zone, two deflectors, two sets of Einzel lens, a split lens, a mass gate and a MCP detector. The pumping configurations and pressures are listed in Table 2.2.

Table 2.2. Pump configurations and pressures for TOF-MS vacuum chambers. The unit of pressure is torr.

Region	A	B	C	E
Pump	Edwards, STP-A2203C	Edwards, nEXT 300 D or 400 T	Pfeiffer, TPU 180H	CTI-cryogenics, Cryo-torr 8 cryopump with 8200 compressor
Backing pump	Edwards, XDS 35i		Pfeiffer, MVP 070-3 diaphragm pump	
Base pressure	~ 1.0×10^{-7}	~ 1.5×10^{-8}	~ 1.0×10^{-8}	~ 7.0×10^{-9}
Running pressure	~ 1.0×10^{-6}	~ 8.0×10^{-7}	~ 4.0×10^{-7}	~ 1.5×10^{-8}

After thermal cooling and accumulation, ions are extracted and focused by a tube lens into the extraction zone of TOF-MS. As presented in Fig. 2.3, the ion extraction zone consists of a stack of electrode plates. Entering in the zone through the region of plate 3, ions are accelerated with the same kinetic energies by a pulsed voltage of – 1.25 kV distributed over the whole stack. As the length of the flight tube is constant, ions with different m/z ratios can have different time of flights (t). The relation can be expressed as m/z = c * t^2, where c is a constant related with the length of the flight tube and the voltage supply. It can be easily determined by the known m/z ratio and time of flights of atomic anions of I^- and Au^-.
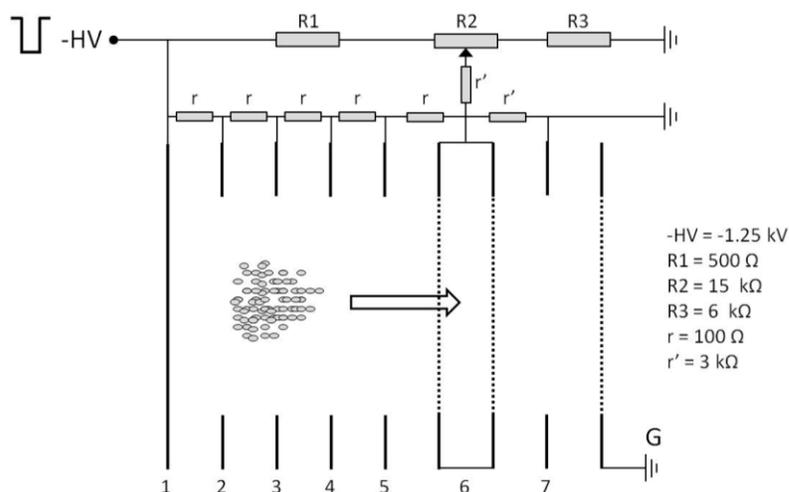
Figure 2.3. The assembly of the ion extraction electrodes.

After the extraction zone, the ion trajectory is aligned by a horizontal deflector (D1) and a vertical deflector (D2). The voltages are usually optimized between – 10 V and + 10 V to correct the trajectory to detector and achieve optimal ion signal. Two sets of Einzel lens made by three isolated copper cylinders are used to refocus the ion beam onto the detector. The middle electrodes of EL1 and EL2 are set at – 511 V and – 360 V, respectively, while two end electrodes are at ground potential.

The ion beam is refocused by a split lens (0.3 – 0.5 kV) into a mass gate, which can filter out undesired anions. The mass gate contains three grid electrodes (Fig. 2.4). The two end grid electrodes are grounded, while the middle one is applied by a pulsed voltage of – 1.3 kV. When the desired anion arrives at the first grid, the second grid will be pulsed to ground for a short time (0.5 – 1.2 µs) for the selected anion to pass through. The high voltage of – 1.3 kV is then applied back to the second grid to block the rest of unwanted anions. The timing and the width of the pulse is based on the time of flight and the width of the mass signal of the desired anion. Anions are detected by a pair of MCP at the voltage of – 2.5 kV.
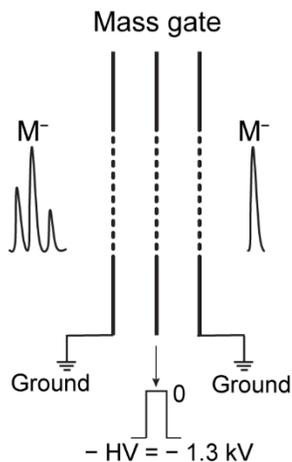
Figure 2.4. Schematics of mass gate assembly.

2.4 High-resolution photoelectron imaging system

The desired anions are intersected with the pulsed Nd:YAG (Continuum, SLII-20) or tunable nanosecond pulsed dye laser ($\Delta\lambda \sim 0.0015$ nm, Cobra-Stretch, Sirah CSTR-G-30) for photodetachment in the interaction zone of the image lens (Fig. 2.5). The photoelectron imaging system contains multiple electrodes based on the three-plate VMI system.[47] L_R represents the repeller electrode. L_1 and L_2 are the extractor electrodes, while L_3 is the ground electrode. Extra plates L_{12} and L_{23} are added as guarding electrodes between $L_1 - L_2$ and $L_2 - L_3$, respectively, to prevent fringe field penetration due to the relative large distances. After L_3, three more shielding plates are added at ground potential to achieve optimal focusing. All the electrodes, made of oxygen-free copper with gold coated, have a thickness of 0.8 mm and outer diameter of 106 mm.

In experiments, voltage on L_R, named V_R, was set at low extraction voltage of – 300 V to detect slow electrons with high resolution. V_R was also applied with a voltage of – 1000 V or – 1100 V to capture the fast photoelectrons, such as the electron detached

from vibrational ground DBS. The voltages of V_1 (~ 480 V) and V_2 (~ 160 V) were optimized to achieve an optimal focusing and resolution.
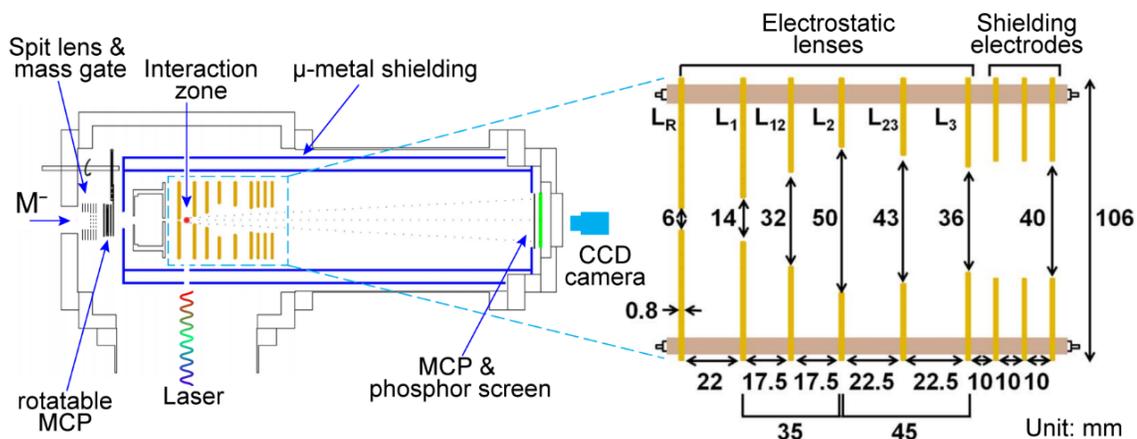
Figure 2.5. Schematics of the high-resolution photoelectron imaging system. Reproduced from [Iker León, Zheng Yang, Hong-Tao Liu, and L. S. Wang, The design and construction of a high-resolution velocity-map imaging apparatus for photoelectron spectroscopy studies of size-selected clusters *Rev. Sci. Instrum.* **85**, 083106 (2014).], with the permission of AIP Publishing.

After photodetachment, photoelectrons travel through the image system and impinge on the position-sensitive detector, which consists of a set of 75 mm diameter MCP detector coupled to a phosphor screen (Photonis USA, Inc.). The images are captured by a CCD camera (Uniq Vision Inc., Model UP930CL, 1024 × 1024 pixels). The imaging detector is about 1 m away from the interaction zone. The image lens and the entire electron flight path are enclosed by two concentric cylinders of µ-metal shielding with a thickness of 0.51 mm and diameters of 14.1 cm and 17.7 cm, respectively. Two holes are drilled on the µ-metal shielding below and above the interaction zone to allow detachment lasers travel through.

2.5 Data processing

The photoelectron image is two-dimensional (2D) projection of the three-dimensional (3D) photoelectron Newton sphere (Fig. 1.4), containing both the energy and angular information of photoelectrons, which has a cylindrical symmetry with the axis defined by the laser polarization direction. To reconstruct the initial distribution, an inverse-Abel transformation was carried out by both BASEX[228] and pBasex[229] programs, which yielded similar results. Due to a 2% distortion of our image, all the raw photoelectron images were circularized with a factor of 0.981 before the transformation. Assuming the interaction zone is a point source, the photoelectron KE is proportional to the radius (r) of the photoelectron image, which can be expressed as KE = $a*r^2$. In experiments, the interaction zone is not a perfect point, an additional term [$b*r$] was added in the expression as KE = $a*r^2 + b*r$ for extra effects. Constants a and b, depending on the geometry of the imaging system and the repeller voltage V_R, were determined by the known spectra of Au$^-$ or I$^-$ at different photon energies.

2.6 Timing sequences

The high-resolution photoelectron imaging experiments are operated at a repetition rate of 10 Hz, following the timing sequences as shown in Fig. 2.6. The timing is generated by four digital delay generators (Stanford Research Systems, DG 535).

Briefly, T_0 is the starting pulse of a whole experimental cycle. The anions produced by ESI are continuously loaded into the cryogenic Paul trap with a trapping time of 100 ms (T_1). After a short delay of 2 μs (T_2) for the damping of the rf voltage applied to the trap, two end caps of the trap are applied with pulsed voltages (10 μs of

pulse width) to unload anions. A delaying period (T_3), which indicates the time of flight

of anions to the extraction region of TOF-MS, is carefully tuned before the high negative

voltage pulse (– 1.25 kV, 20 μs) is applied to the extraction stacks. T_4 is the time of flight

of desired anions from extraction region to the mass gate. It can be monitored on the

oscilloscope (Tektronix, TDS 3032C). The pulse width of the mass gate is optimized

between 0.5 to 1.2 μs. The time of firing the laser is reference to repeller with a delaying

period T_5, which is the time of flight of the selected anion from the repeller to the

photodetachment zone in the image lens. The width of Q-switch is 10 μs. A pulsed

voltage with width of 0.8 μs (T_7) is applied to the MCP detecting photoelectrons about

0.5 μs (T_6) prior the laser Q-switch. The CCD camera is started 100 μs (T_8) after the

starting pulse with a width of 50 μs (T_9).
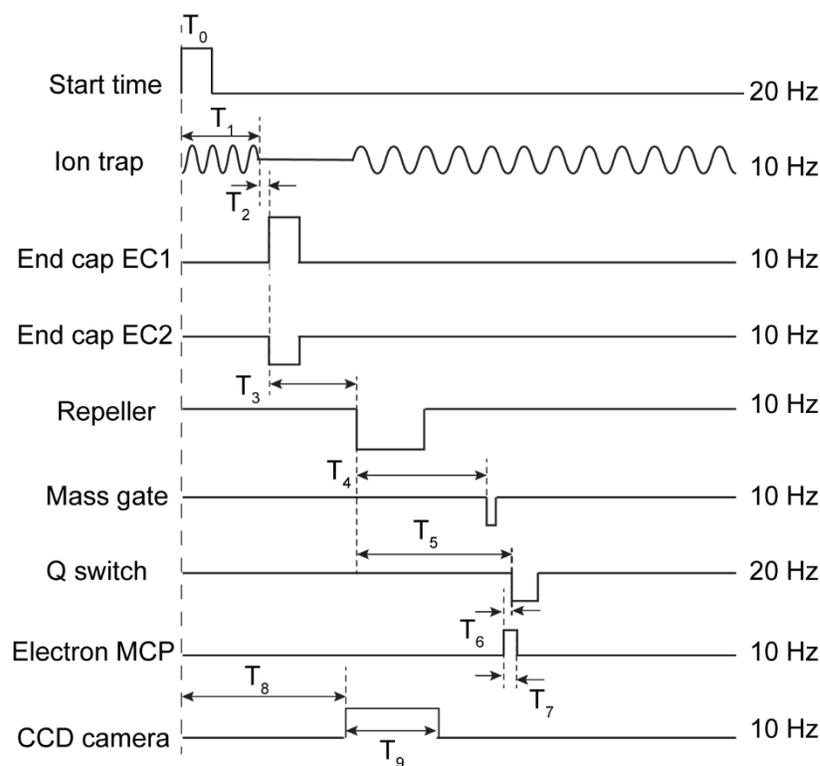
Figure 2.6. Timing sequences for the high-resolution photoelectron imaging experiments.

Chapter 3 Accurate determination of the electron affinity of

TCNQ[*]

This chapter[232] will discuss the first experiment I did independently for my thesis work. It was to measure the electron affinity (EA) of tetracyanoquinodimethane (TCNQ), which was erroneously reported in the literatures.

TCNQ is widely used as an electron acceptor to form highly conducting organic charge-transfer solids. Surprisingly, the electron affinity of TCNQ is not well known and has never been directly measured. Here we report vibrationally-resolved PES of the TCNQ⁻ anion produced using electrospray and cooled in a cryogenic ion trap. Photoelectron spectrum taken at 354.7 nm represents the detachment transition from the ground vibrational state of TCNQ⁻ to that of neutral TCNQ with a short vibrational progression. The EA of TCNQ is measured accurately to be 3.383 ± 0.001 eV ($27,289 \pm 8$ cm^{-1}), compared to the 2.8 ± 0.1 eV value known in the literature and measured previously using collisional ionization technique. In addition, six vibrational peaks are observed in the photoelectron spectrum, yielding vibrational frequencies for three totally symmetric modes of TCNQ. Two-photon PES via a bound electronic excited state of TCNQ⁻ at 3.100 eV yields a broad low kinetic energy peak due to fast internal conversion to vibrationally excited levels of the anion ground electronic state. The high EA measured for TCNQ underlies its ability as a good electron acceptor.

3.1 Introduction
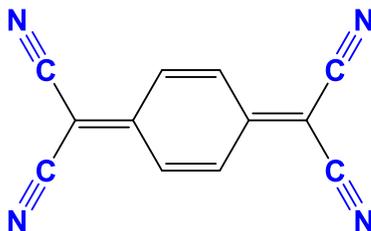
Figure 3.1. The molecular structure of TCNQ.

TCNQ (Fig. 3.1) is one of the best electron acceptors to form charge-transfer conducting organic solids.[233-236] The electronic and structural properties of TCNQ and its anion (TCNQ⁻) have been studied quite extensively both experimentally and theoretically.[237-251] TCNQ possesses a high EA due to the presence of the highly electron-withdrawing CN groups (Fig. 3.1). The EA of TCNQ was first measured as 2.8 ± 0.1 eV by Compton and co-workers using collisional ionization between Cs and TCNQ to form Cs^+ + TCNQ⁻.[237] A later study by Compton and Cooper refined the EA of TCNQ to be 2.8 +0.05/-0.3 eV,[238] but the EA value has been usually cited in the literature as 2.8 ± 0.1 eV for TCNQ. Brauman and co-workers measured the photodetachment spectrum of TCNQ⁻ in an ion cyclotron resonance mass spectrometer in the wavelength range of 350−1060 nm.[239] They observed two resonant bands: a low-energy broad resonance between 600 and 1000 nm (2.1 to 1.2 eV) and another resonance between 360 and 470 nm (3.4 to 2.6 eV). These two resonances, corresponding to transitions to two electronic excited states of TCNQ⁻, were found to be very similar to electronic absorption spectrum of TCNQ⁻ in solution.[240] However, no EA was measured from the photodetachment spectrum. More recently, Verlet and co-workers examined the ultrafast relaxation dynamics of the first excited state of gaseous TCNQ⁻ and also reported the photoelectron spectrum of TCNQ⁻ at a photon energy of 3.1 eV.[242] Two bands were observed in their

photoelectron spectrum, a narrower band centered at a photoelectron kinetic energy of 0.2 eV and a broad band centered at a kinetic energy of 2 eV. The narrower band was interpreted to be due to a one-photon detachment (resonant absorption followed by autodetachment to the ground state of neutral TCNQ), yielding an EA of 2.9 eV, which was considered to be in good agreement with the previous value of 2.8 ± 0.1 eV.

The EA of TCNQ has been calculated in several theoretical studies. Ortiz and co-workers obtained an EA of 2.74 eV using an electron propagator method.[245] Skurski and Gutowski gave a range of EA between 2.76 and 2.95 eV at the configuration interaction (CI/PM3) level.[247] These computed EAs were considered to be in good agreement with the available experimental EA of 2.8 ± 0.1 eV. More recently, Milian et al.[250] computed the EA of TCNQ using the higher-level couple-cluster method [CCSD(T)] and obtained an EA of 3.22 eV, which was overestimated by 0.4 eV relative to the 2.8 eV experimental value. However, the authors showed that the same theoretical method tended to underestimate the EAs by 0.1 to 0.2 eV for similar compounds. This discrepancy made the authors skeptical about the previously measured EA for TCNQ and prompted them to call for additional measurement. Very recently, Nakashima et al. computed an EA of 3.31 eV for TCNQ using the symmetry adapted cluster configuration interaction method.[251]

Here, we report vibrationally-resolved PES of TCNQ⁻ using photoelectron imaging at 354.7 nm. The 354.7 nm photoelectron spectrum represented detachment transition from the ground state of TCNQ⁻ to that of neutral TCNQ with a short vibrational progression consisting of seven resolved vibrational peaks. The EA of TCNQ was measured directly and accurately to be 3.383 ± 0.001 eV from the 0-0 vibrational transition. In addition, vibrational frequencies for three totally symmetric vibrational

modes were obtained for TCNQ, ν_1 (114 cm⁻¹), ν_2 (331 cm⁻¹), and ν_4 (709 cm⁻¹). A photoelectron spectrum was also obtained at 3.100 eV, in resonance with the second excited state of TCNQ⁻, as a result of two-photon detachment, following fast internal conversion.

3.2 Experimental methods

The experiment was done using our third-generation ESI-PES apparatus.[15] The TCNQ⁻ anions were produced by electrospray of a 1 mM solution of TCNQ dissolved in acetonitrile and spiked with a small amount of NaI. More experimental details are provided in Chapter 2.

3.3 Results and discussion
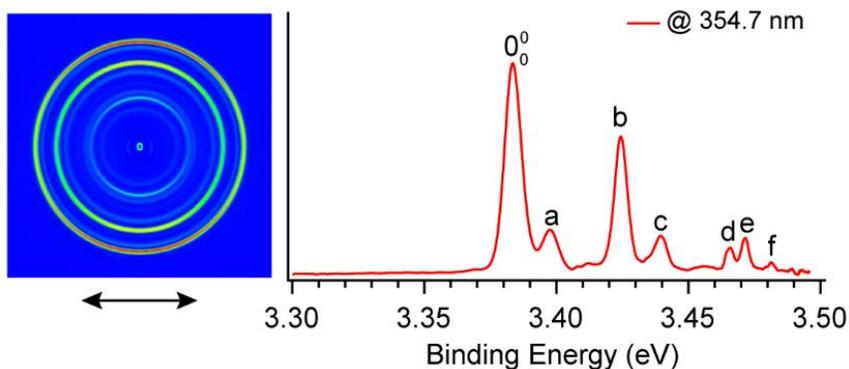
Figure 3.2. The photoelectron image and spectrum of TCNQ⁻ at 354.7 nm. The arrow below the image indicates the polarization direction of the laser.

Figure 3.2 shows a photoelectron image and spectrum of TCNQ⁻ at 354.7 nm. The spectrum was obtained by summing up several images to enhance the signal-to-noise ratios. This spectrum represents detachment transitions from the ground electronic and vibrational state of TCNQ⁻ to the ground electronic state of neutral TCNQ. The binding

energies of the seven observed peaks are given in Table 3.1, along with their assignments. The peaks correspond to the vibrational levels of neutral TCNQ. The short vibrational progression suggests that there is little geometry change between the anion and neutral TCNQ. The first and most intense peak at 27,289 cm^{-1} (3.383 eV) corresponds to the 0-0 transition and defines accurately the EA of TCNQ. We note that the most recently computed EAs for TCNQ, 3.22 eV by Milian et al.[250] and 3.31 eV by Nakashima et al.,[251] are in good agreement with the current measurement.

Table 3.1. Assignments of the observed vibrational peaks in the photoelectron spectrum of TCNQ⁻. The measured binding energies (BEs), shifts relative to the neutral vibrational ground state (0-0) are compared with the computed vibrational frequencies (ν_{theo}) of TCNQ.

Observed peaks	BE (cm^{-1})^a	Shift (cm^{-1})	ν_{theo} (cm^{-1})^b	Assignment
0-0	27,289(8)	0		
a	27,403(8)	114	118 (ν_1)	ν_1
b	27,620(8)	331	334 (ν_2)	ν_2
c	27,739(8)	450		$\nu_2 + \nu_1$
d	27,952(9)	663		$2\nu_2$
e	27,998(9)	709	725 (ν_4)	ν_4
f	28,079(10)	790		$2\nu_2 + \nu_1$

^{a}The number in the parenthesis represents the uncertainty in the last digits.
^{b}See the Table 3.2 in Section 3.5 for the full list of the computed vibrational frequencies and Fig. 3.3 for the normal modes of the observed frequencies.

To help assign the vibrational peaks, we computed the vibrational frequencies of TCNQ using density functional theory at the B3LYP/6-31+G(d,p) level using the Gaussian 09 package.[252] Since both TCNQ and its anion are planar with D$_{2h}$ symmetry, only totally symmetric modes are allowed. Peak *a* represents a vibrational spacing of 114 cm^{-1} (Table 3.1) which is in good agreement with the calculated frequency of vibrational mode ν_1 (118 cm^{-1}) involving the in-plane bending of four –CN groups (Fig. 3.3). Peak *b* represents the mode with the strongest Franck-Condon factors and the vibrational spacing of 331 cm^{-1} (Table 3.1) agrees well with the calculated frequency of the in-plane

stretching mode v_2 (334 cm⁻¹, Fig. 3.3). As shown in Table 3.1, peak d represents the first

overtone of the v_2 mode, whereas peaks c and f are combination modes of v_2 and v_1. Peak

e with a spacing of 709 cm⁻¹ from the vibrational ground state is in good agreement with

the computed frequency of the v_4 mode (725 cm⁻¹), which involves the ring breathing

vibration. The normal modes of the three observed vibrational frequencies are shown in

Fig. 3.3.

$v_1 = 118$ cm⁻¹ $\qquad$ $v_2 = 334$ cm⁻¹ $\qquad$ $v_4 = 725$ cm⁻¹
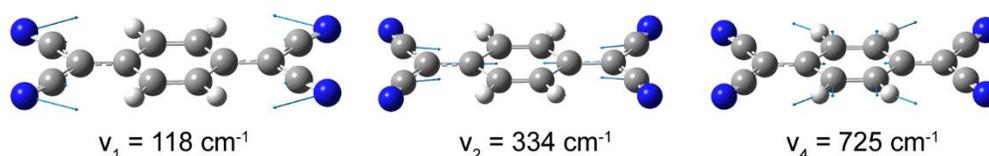
Figure 3.3. Displacements for the three observed vibrational modes of TCNQ. All the modes have symmetry of A_g (Table 3.2). The computed harmonic frequencies are also shown.

The highest occupied molecular orbital (HOMO) of TCNQ is a π orbital of b_{3u}

symmetry. The lowest unoccupied molecular orbital (LUMO), where the extra electron

resides in TCNQ⁻, is an antibonding π^* orbital of b_{2g} symmetry. The LUMO+1 orbital is

also of b_{3u} symmetry. The ground state of TCNQ⁻ is $^2B_{2g}$ with an electron configuration

of $3b_{3u}^2 3b_{2g}^1 4b_{3u}^0$. The photoelectron image shown in Fig. 3.2 exhibited a perpendicular

distribution indicating an $s + d$ character, in agreement with detachment of a π electron

from the π^* $3b_{2g}$ orbital. The first electronic excited state (1^2B_{3u}) of TCNQ⁻, observed

between 600 to 1000 nm (2.1 to 1.2 eV),[239] corresponds to excitation of an electron from

the HOMO to the LUMO with an electron configuration of $3b_{3u}^1 3b_{2g}^2 4b_{3u}^0$, whereas the

second excited state (2^2B_{3u}), observed between 360 and 470 nm (3.4 to 2.6 eV),

corresponds to excitation of the electron in the LUMO to LUMO+1 with an electron

configuration of $3b_{3u}^2 3b_{2g}^0 4b_{3u}^1$. Our measured EA of TCNQ indicates that the two

excited states of TCNQ⁻ are both bound states, as schematically shown in Fig. 3.4. Thus, a single photon absorption to the second excited state (2^2B_{3u}) of TCNQ⁻ would be impossible to induce electron detachment, as reported by Verlet and co-workers at a photon energy of 3.1 eV.[242]
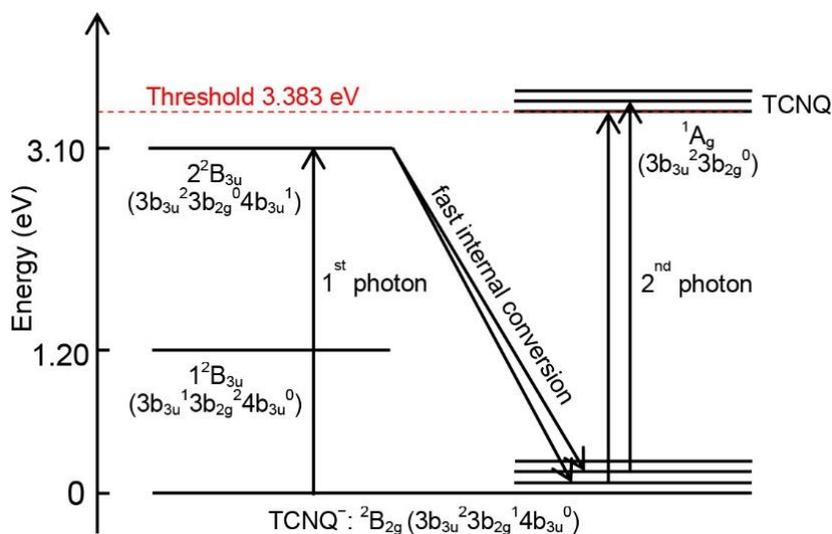
Figure 3.4. Schematic energy levels for TCNQ⁻ and TCNQ. It shows the resonant excitation using a 400.0 nm (3.100 eV) photon to the 2^2B_{3u} excited state of TCNQ⁻, followed by fast internal conversion to the vibrational levels of the TCNQ⁻ ground electronic state, as well as the detachment by a second photon off the vibrationally excited TCNQ⁻ to yield the spectrum in Fig. 3.5.

We have recently observed a bound excited state for AuS⁻ and observed vibrational level-dependent photoelectron spectra via resonant two-photon detachment.[253] We tried to carry out a similar experiment using a photon energy of 3.100 eV (400.0 nm), which is in resonance with the 2^2B_{3u} excited state of TCNQ⁻. Resonant two-photon detachment should yield a photoelectron spectrum similar to Fig. 3.2, but at a much higher electron kinetic energy (~2.8 eV). However, we observed a spectrum with a very low electron kinetic energy centered at around 0.2 eV, as shown in Fig. 3.5. This observation suggests that the 2^2B_{3u} excited state of TCNQ⁻ must have a very short lifetime and undergoes fast internal conversion to the ground electronic state of TCNQ⁻,

producing highly vibrationally excited states. The second photon then detaches an electron from the highly vibrationally excited TCNQ⁻ in its ground electronic state, giving rise to the broad low kinetic energy band shown in Fig. 3.5. Since our detachment laser pulse had a pulse length of a few nanoseconds, the lifetime of the 2^2B_{3u} excited state must be much shorter than a few nanoseconds. We note that the spectrum in Fig. 3.5 is similar to the 0.2 eV KE band observed by Verlet and co-workers.[242] The broad band centered at a KE of 2 eV observed in their spectrum was likely due to resonant two-photon detachment, because of the short laser pulse used in their experiment.
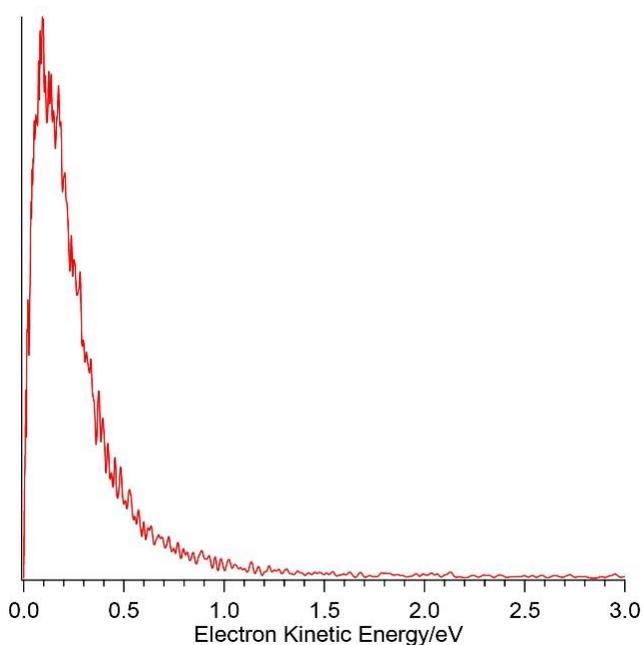
Figure 3.5. Two-photon photoelectron spectrum of TCNQ⁻ at 400.0 nm (3.100 eV). See Fig. 3.4 for the excitation processes.

3.4 Conclusions

In conclusion, we have obtained the first vibrationally-resolved photoelectron spectrum of TCNQ⁻ at 354.7 nm that allowed us to accurately measure the electron affinity of TCNQ to be 3.383 ± 0.001 eV. Additionally, three totally symmetric

vibrational modes were observed with frequencies of 114, 331, and 709 cm^{-1} for the ν_1, ν_2, and ν_4 modes, respectively. The current EA value indicates that the isolated TCNQ⁻ anion possesses two bound electronic excited states (Fig. 3.4). Resonant excitation to the second excited state suggested a very short lifetime and fast internal conversion to the vibrational levels of the ground electronic state of TCNQ⁻. The current measurement uncovered an extremely high EA for TCNQ, which is comparable to that of the F atom (3.401 eV),[254] and underlies its capacity as an excellent electron acceptor.

3.5 Supporting information

Table 3.2. Theoretical vibrational frequencies of neutral TCNQ. The harmonic frequencies were calculated using the B3LYP/6-31+G(d,p) method. The observed frequencies for the modes ν_1, ν_2, and ν_4 are given for comparison.

Symmetry	Mode	Theoretical (cm^{-1})	Experimental (cm^{-1})	Peak	Symmetry	Mode	Theoretical (cm^{-1})
A_g	ν_1	118	114	a	A_u	ν_{28}	50
	ν_2	334	331	b		ν_{29}	400
	ν_3	607				ν_{30}	470
	ν_4	725	709	e		ν_{31}	1014
	ν_5	973			B_{1u}	ν_{32}	140
	ν_6	1233				ν_{33}	558
	ν_7	1493				ν_{34}	608
	ν_8	1673				ν_{35}	987
	ν_9	2327				ν_{36}	1005
	ν_{10}	3223				ν_{37}	1430
B_{1g}	ν_{11}	116				ν_{38}	1583
	ν_{12}	446				ν_{39}	2329
	ν_{13}	814				ν_{40}	3209
B_{2g}	ν_{14}	147			B_{2u}	ν_{41}	84
	ν_{15}	305				ν_{42}	287
	ν_{16}	633				ν_{43}	508
	ν_{17}	764				ν_{44}	1137
	ν_{18}	1013				ν_{45}	1230
B_{3g}	ν_{19}	134				ν_{46}	1379
	ν_{20}	374				ν_{47}	1594
	ν_{21}	528				ν_{48}	2313
	ν_{22}	622				ν_{49}	3222
	ν_{23}	1206			B_{3u}	ν_{50}	47
	ν_{24}	1341				ν_{51}	221
	ν_{25}	1482				ν_{52}	482
	ν_{26}	2313				ν_{53}	668
	ν_{27}	3210				ν_{54}	872

Chapter 4 High-resolution photoelectron imaging of C$_{59}$N$^{-\dagger}$

This chapter[255] will discuss photoelectron imaging study of cryogenically-cooled C$_{59}$N$^-$produced from electrospray ionization. High-resolution photoelectron spectra are obtained for C$_{59}$N$^-$ for the first time, allowing seven vibrational frequencies of the C$_{59}$N azafullerene to be measured. The electron affinity of C$_{59}$N is determined accurately to be 3.0150 ± 0.0007 eV. The observed vibrational features are understood based on the calculated frequencies and compared with those of C$_{60}$ and C$_{59}$HN. The photoelectron image of (C$_{59}$N)$_2{}^{2-}$, which has the same mass/charge ratio as C$_{59}$N$^-$, is also observed, allowing the second electron affinity of the (C$_{59}$N)$_2$ azafullerene dimer to be measured as 1.20 ± 0.05 eV. The intramolecular Coulomb repulsion of the (C$_{59}$N)$_2{}^{2-}$ dianion is estimated to be 1.96 eV and is investigated theoretically using the electron density difference between (C$_{59}$N)$_2{}^{2-}$ and (C$_{59}$N)$_2$.

4.1 Introduction

Azafullerene (C$_{59}$N), with one carbon atom in C$_{60}$ substituted by a nitrogen atom, has received particular attention due to its unique electronic and chemical properties.[256,257] The N-substitution results in a *n*-type doping, adding one electron to the close-shell π system of C$_{60}$.[259,260] The extra unpaired electron is mainly localized on the C atom that is closest to the N atom in the [6,6] closed structure and exhibits *sp^3* character.[260-265] Hence, C$_{59}$N is a reactive radical and can easily dimerize.[256,257,262-265] The C$_{59}$N$^+$ cation is isoelectronic to C$_{60}$ and was first observed as a gaseous species.[266] The

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first macroscopic synthesis of $C_{59}N$ was in its dimer form, $(C_{59}N)_2$,[267] allowing its physical and chemical properties to be characterized by a variety of techniques.[268-282] Most interestingly, the azafullerene has promising applications in molecular electronics as the basis for single-molecule rectifiers,[283-285] field-effect transistors,[286,287] and electron donor-acceptor systems.[288-290] However, the electron affinity (EA) of $C_{59}N$, one of its most fundamental electronic and thermodynamic properties, is still not known experimentally. Theoretical calculations suggested an EA for $C_{59}N$ to be around 2.70 eV,[260,262] which is comparable to the EA of C_{60} accurately known to be 2.6835 eV.[116] In a C_{60}-$C_{59}N$ dyad,[288] a higher reduction potential was observed for $C_{59}N$ than C_{60}, indicating a higher EA for $C_{59}N$ than C_{60}.

In the current study, we present a high-resolution photoelectron imaging study of cryogenically-cooled $C_{59}N^-$ anions produced from an electrospray ionization source. Vibrationally-resolved photoelectron spectra at various photon energies have been obtained, allowing us to measure the EA of $C_{59}N$ accurately for the first time to be 3.0150 eV, which is 0.3315 eV higher than that of C_{60}. Seven vibrational frequencies are also obtained for $C_{59}N$, five of which are found to be similar to those observed in the high-resolution photoelectron spectra of C_{60}^-.[116] Additionally, we have also obtained the photoelectron spectrum for the parent $(C_{59}N)_2^{2-}$ dimer dianion, which has the same mass/charge ratio as $C_{59}N^-$, yielding the second EA of $(C_{59}N)_2$ to be 1.20 eV. The intramolecular Coulomb repulsion in the dimer dianion is estimated to be 1.96 eV. The extra charges in the dianion are shown to be more localized at the two ends of the dimer due to the electron-electron repulsion.

4.2 Experimental methods

The experiment was carried out on our third-generation ESI-PES apparatus. The details were described in Chapter 2.

4.3 Results and discussion
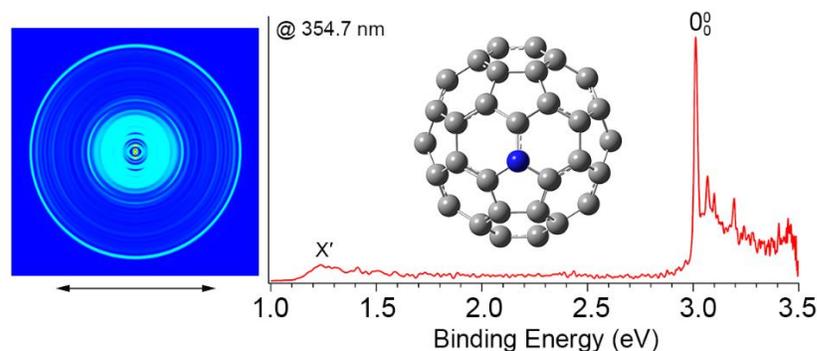
Figure 4.1. The photoelectron image and spectrum of $C_{59}N^-$ and $(C_{59}N)_2^{2-}$ at 354.7 nm. The inset shows the structure of $C_{59}N^-$. The weak peak X' represents detachment from $(C_{59}N)_2^{2-}$, while peak 0_0^0 denotes the detachment threshold of $C_{59}N^-$. The double arrow below the image indicates the direction of the laser polarization. Note the image corresponding to peak X' is cut off.

Figure 4.1 displays the photoelectron image and spectrum of the anion at m/z = 722 at a photon energy of 354.7 nm. The spectrum reveals two detachment regions, a weak and broad peak (X') at around 1.2 eV and a group of more intense peaks above 3 eV. This spectral pattern immediately suggests that the m/z = 722 mass signals contained both $C_{59}N^-$ and $(C_{59}N)_2^{2-}$. The 1.2 eV peak should come from the dianion, which is expected to have low binding energies due to the strong intramolecular Coulomb repulsion.[291] This low binding energy is comparable to that for a similar dianion, $[C_{60}OC_{60}]^{2-}$, which has an electron binding energy of 1.02 eV.[292] The strong peaks above 3.0 eV, which display some resemblances to the 354.7 nm spectrum of C_{60}^-,[116] should come from $C_{59}N^-$, representing transitions from the ground vibrational level of the anion

to vibrational levels of the electronic ground state of neutral $C_{59}N$. The first intense peak labeled 0_0^0 defines the EA of $C_{59}N$, which is more accurately measured to be 3.0150 ± 0.0007 eV in Fig. 4.2a to be discussed below. It should be noted that because of the existence of the repulsive Coulomb barrier no low-energy electrons are allowed for detachment from the $(C_{59}N)_2^{2-}$ dianion,[291] i.e., the spectral region for $C_{59}N^-$ above 3 eV should contain no contributions from higher binding energy detachment transitions from the dianion.

To better resolve the vibrational peaks for $C_{59}N$, we took high-resolution photoelectron images at six different wavelengths near the detachment threshold, as shown in Fig. 4.2. Photoelectron imaging allows low-energy electrons to be detected, significantly improving the spectral resolution for near-threshold detachment transitions.[52,60] At 409.80 nm in Fig. 4.2a, peak 0_0^0 corresponds to an electron kinetic energy of 84 cm^{-1} and a line width (FWHM) of 12 cm^{-1}, yielding the most accurate value for the EA of $C_{59}N$ as 3.0150 ± 0.0007 eV. As reported previously,[96-97] anions in our cryogenic Paul trap have a rotational temperature of ~30 K. Thus, the near-threshold peak width should mainly come from rotational broadening. Because of the p-wave detachment character, the cross section for the near-threshold detachment was quite low, as can be seen from the relatively poor signal/noise ratios in Fig. 4.2a. The EA of $C_{59}N$ is 0.3315 eV higher than that of C_{60} at 2.6835 eV.[166]

By tuning the photon energies above threshold systematically, we were able to resolve seven additional vibrational peaks, labeled from A to G, up to a binding energy of 3.15 eV, as shown in Fig. 4.2b-f. The observed peaks, their binding energies, the shifts from peak 0_0^0 (i.e. the measured fundamental vibrational frequencies of $C_{59}N$) are

summarized in Table 4.1 and compared with our computed frequencies for C$_{59}$N (see Table 4.2 in Section 4.5 for all the 174 calculated frequencies), as well as those of C$_{60}$ and C$_{59}$HN.
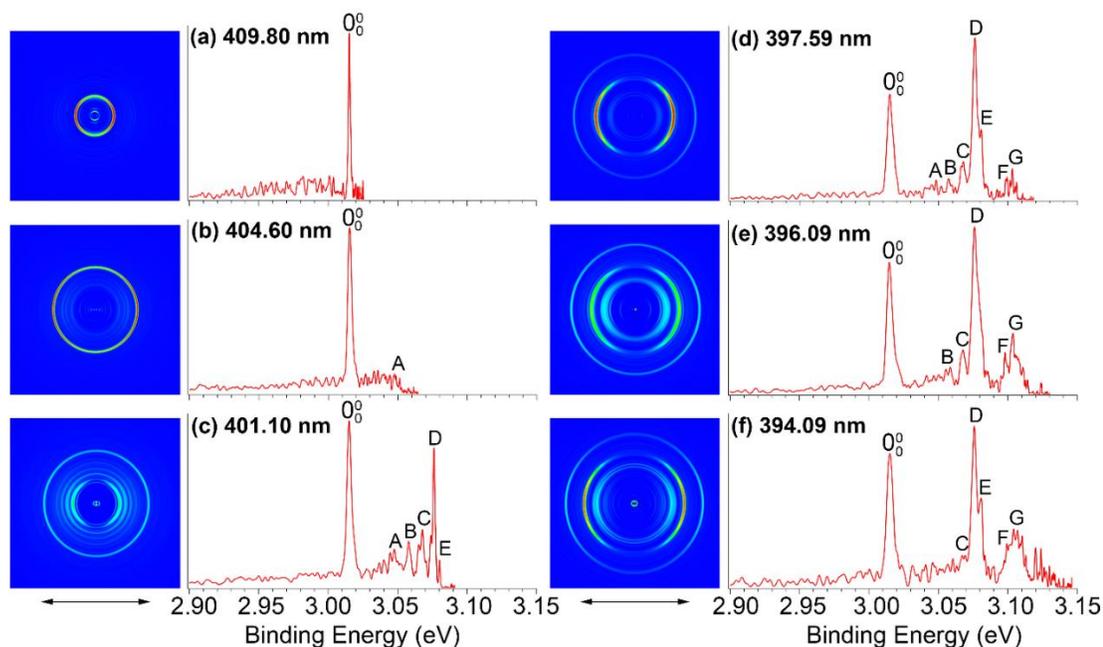
Figure 4.2. Photoelectron images and spectra of C$_{59}$N$^-$ at six different wavelengths. The double arrow below the images indicates the directions of the laser polarization.

Because of the structural similarities between C$_{59}$N and C$_{60}$ or C$_{59}$HN, we expect that they should share similar vibrational properties. Indeed, peaks A, B, and E-G, with shifts of 260, 341, 528, 674, and 713 cm^{-1}, are in good agreements with the vibrational frequencies of C$_{60}$ obtained from our previous study of the cold C$_{60}^-$ anion,[116] as well as those from inelastic neutron scattering of solid C$_{60}$.[293] The significant vibrational activities observed in the high-resolution photoelectron imaging of cold C$_{60}^-$ were due to the Jahn-Teller effect in C$_{60}^-$ (^{2}T$_{1u}$), which does not have the I$_h$ symmetry of neutral C$_{60}$. On the other hand, the substitution of a C by a N atom in C$_{60}$ lowers the symmetry of C$_{59}$N to *C$_s$*.[263] Since neutral C$_{59}$N and C$_{59}$N$^-$ both have *C$_s$* symmetry, all vibrational

Table 4.1. Assignments of observed vibrational peaks from the photoelectron spectra of C$_{59}$N$^-$. Their binding energies (BE) are given.[a]

Peak	BE (eV)	Shift (cm^{-1})	Vibrational frequencies (cm^{-1})			
			C$_{60}^{-}$ [b]	Solid C$_{60}$ [c]	C$_{59}$HN [d]	Theo. C$_{59}$N [e]
0$_0^0$	3.0150(7)	0				
A	3.0473(12)	260	262	262, H$_g$(1)	261.5	ν_1 (258)
				268, H$_g$(1)	271	ν_2 (262)
						ν_3 (268)
B	3.0573(10)	341	348	340, T$_{2u}$(1)		ν_4 (337)
				353, G$_u$(1)		ν_5 (342)
						ν_6 (350)
C	3.0673(10)	421		431, H$_g$(2)	424	ν_{10} (418)
					427	
D	3.0760(7)	492		494, A$_g$(1)	492	ν_{15} (498)
E	3.0805(10)	528	531	526, T$_{1u}$(1)	523	ν_{17} (524)
				534, H$_u$(2)	529	ν_{18} (532)
					531	ν_{19} (535)
F	3.0986(7)	674	670	668, H$_u$(3)		ν_{26} (675)
						ν_{27} (678)
G	3.1035(7)	713	717	709, H$_g$(3)		ν_{30} (718)
				713, T$_{2u}$(2)		ν_{31} (720)

[a]Their relative shifts to peak 0$_0^0$ are compared with the vibrational frequencies of C$_{60}$ and C$_{59}$HN, as well as our calculated frequencies for C$_{59}$N.
[b]Ref. 116: 16 vibrational frequencies of C$_{60}$ were measured by high-resolution PE imaging of cold C$_{60}^{-}$.
[c]Ref. 293: Vibrational frequencies of C$_{60}$ were measured by inelastic neutron scattering of solid C$_{60}$.
[d]Ref. 294, Vibrational frequencies of C$_{59}$HN were measured by IR and Raman spectroscopy.
[e]The vibrational frequencies of C$_{59}$N were calculated with at the B3LYP/Def2SVP level (see Table 4.2).

modes with A' symmetry are allowed in the photodetachment. We computed the vibrational frequencies of neutral C$_{59}$N at the B3LYP/Def2SVP level and found 89 A' and 85 A" modes, as given in Table 4.2 in Section 4.5. Because there is no vibrational degeneracy for the C_s C$_{59}$N, many vibrational modes have close frequencies, making unique assignments of the observed vibrational features for C$_{59}$N challenging.

Comparing the experimental frequencies with the computed frequencies, we found that peaks A, B, and E can each be assigned to three possible A' modes with close frequencies, while peaks F and G can each be assigned to two possible A' modes, as shown in Table 4.1. Only peaks C and D, with shifts of 421 and 492 cm^{-1}, can be possibly

assigned uniquely to vibrational mode ν_{10} (418 cm^{-1}) and mode ν_{15} (498 cm^{-1}), respectively. The ν_{10} mode involves strong stretching of the N atom, while the mode ν_{15} is a totally symmetric breathing mode, as shown in Fig. 4.4. Note that peak D is the most intense vibrational feature in Figs. 4.2d-f. Similarly, one vibrational peak with frequency of 531 cm^{-1} in the photoelectron spectra of C_{60}^- was observed to be dominant at lower photon energies. This non-Franck-Condon and photon-energy-dependent vibrational intensities were interpreted previously as being due to a strong Hertzberg-Teller coupling in C_{60}^-.[166] The dominant intensity of peak D in Fig. 4.2 may be due to similar vibronic coupling effects in $C_{59}N^-$. The vibrational frequencies of $C_{59}HN$ have been measured by IR and Raman spectroscopy in the form of thin solid films.[294] A number of the vibrational frequencies of $C_{59}N$ obtained in the current study are similar to those measured for $C_{59}HN$, as shown in Table 4.1.

The photoelectron images in Fig. 4.2 all exhibit distinct *p*-wave character with the photoelectron angular distributions parallel to the direction of the laser polarization, indicating that photodetachment of $C_{59}N^-$ is from an *s*-type orbital. This observation is consistent with the partial localization of the HOMO on the N atom and the nearby C atom, which shows sp^3 character (Fig. 4.5).[260-265]

Even though the closed-shell $(C_{59}N)_2$ dimer was the parent azafullerene used to prepare the ESI solution and it was known to be stable in solution,[256,257] the weak intensity of peak X' compared to peak 0_0^0 in Fig. 4.1 suggested that the majority of the $(C_{59}N)_2$ dimer was dissociated to the monomer either during the reduction by TDAE or in the ESI source. Assuming that $(C_{59}N)_2^{2-}$ and $C_{59}N^-$ have similar detachment cross sections at 354.7 nm, we estimated that the $(C_{59}N)_2^{2-}$ intensity was only ~5% of that for

C$_{59}$N$^-$ in the m/z = 722 mass peak. The low binding energy peak X' in Fig. 4.1 represents the detachment transition from (C$_{59}$N)$_2$$^{2-}$ to (C$_{59}$N)$_2$$^-$, yielding the second EA of (C$_{59}$N)$_2$ to be 1.20(5) eV. The first EA of (C$_{59}$N)$_2$ was calculated to be 2.85 eV, 0.15 eV higher than the calculated EA of C$_{59}$N (2.70 eV).[262] If we assume the same error in the calculated EAs for the monomer and the dimer, we estimated the first EA of (C$_{59}$N)$_2$ to be ~3.16 eV. The difference between the first and second EA of (C$_{59}$N)$_2$ can be viewed as the intramolecular Coulomb repulsion between the two extra charges in (C$_{59}$N)$_2$$^{2-}$, which is estimated as 1.96 eV. In fact, the difference between the electron binding energies of C$_{59}$N$^-$ and (C$_{59}$N)$_2$$^{2-}$ (1.82 eV) gives a similar intramolecular Coulomb repulsion. The intramolecular electron-electron repulsion in the fullerene dianions, C$_n$$^{2-}$ (n = 70, 76, 78, 84) were estimated to be in the range of 2.745 – 2.37 eV, with smaller values for the larger fullerenes.[295,296] The even smaller value of 1.96 eV in (C$_{59}$N)$_2$$^{2-}$ is consistent with its larger molecular size. The C$-$C bond between the two C$_{59}$N units in the azafullerene dimer is known to be quite weak, estimated to be only 7 kcal/mol (0.3 eV) by a thermal homolysis study.[278] The Coulomb repulsion between the two extra charges in the dianion is much larger than the C$-$C bond energy, indicating the (C$_{59}$N)$_2$$^{2-}$ dianion is metastable relative to the bond cleavage to form two C$_{59}$N$^-$ monoanions. This result is consistent with the weak intensity of the dianion in the mass spectrum.

(a) $\rho[(C_{59}N)_2{}^{2-} - (C_{59}N)_2]$

(b) $\rho[C_{59}N^- - C_{59}N]$

(c) $\rho[C_{60}{}^- - C_{60}]$
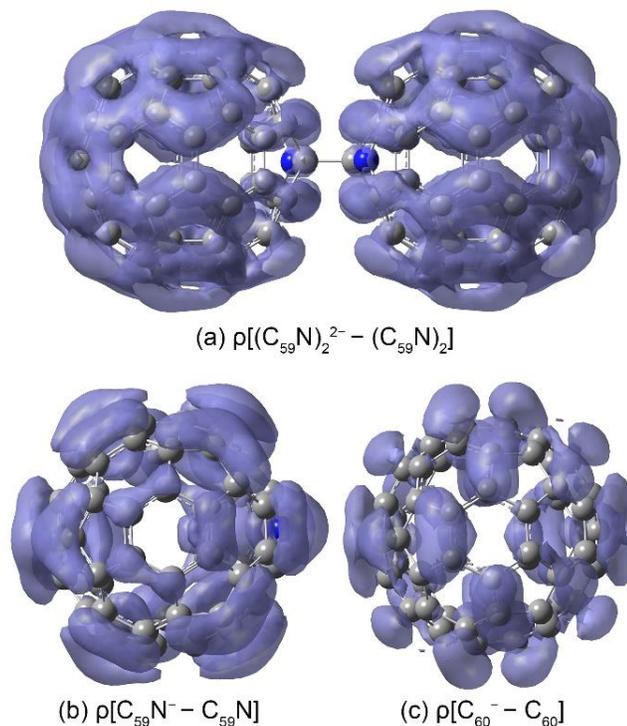
Figure 4.3. Differences of the total electron density ($\Delta\rho$) between anions and neutrals. (a) $(C_{59}N)_2{}^{2-}$ and $(C_{59}N)_2$, (b) $C_{59}N^-$ and $C_{59}N$, and (c) $C_{60}{}^-$ and C_{60}. The calculations were done at the level of B3LYP/6-311++G(d,p).

To further understand the intramolecular Coulomb repulsion in $(C_{59}N)_2{}^{2-}$, we calculated the difference of the total electron density ($\Delta\rho$) between $(C_{59}N)_2{}^{2-}$ and $(C_{59}N)_2$ at the B3LYP/6-311++G(d,p) level using the Gaussian 09 package,[252] as shown in Fig. 4.3a. We used the optimized geometries under the same level of theory and basis sets for both the dianion and neutral. For comparison, we also computed the $\Delta\rho$ between $C_{59}N^-$ and $C_{59}N$ (Fig. 4.3b), as well as that between $C_{60}{}^-$ and C_{60} (Fig. 4.3c). As shown in Fig. 4.3a, the extra electrons are delocalized over the surface of the azafullerene dimer with less densities near the N atoms but higher densities on the two ends. The uneven charge distribution is consistent with the expected Coulomb repulsion between the two extra electrons, and it is quite different from the localization of the HOMO on the N atoms in

neutral $(C_{59}N)_2$.[260-262,268,269] In comparison, the extra electron in $C_{59}N^-$ is delocalized over the azafullerene surface with slightly more charge localized on the N atom (Fig. 4.3b), while the extra charge in C_{60}^- is evenly distributed over the fullerene surface (Fig. 4.3c).

4.4 Conclusion

In conclusion, we report the first high-resolution photoelectron imaging study of $C_{59}N^-$ and the first observation of the azafullerene dimer dianion $(C_{59}N)_2^{2-}$. The EA of $C_{59}N$ is measured accurately to be 3.0150(7) eV. Seven vibrational frequencies are also obtained for $C_{59}N$ and are assigned by comparing with calculated frequencies and those of C_{60} and $C_{59}HN$. Similar vibrational frequencies are observed for the three species, suggesting relatively small geometry changes upon substitution of one C by one N atom on the C_{60} cage. The photoelectron spectrum of the $(C_{59}N)_2^{2-}$ dimer dianion yielded a second EA for $(C_{59}N)_2$ to be 1.20(5) eV. The intramolecular Coulomb repulsion between the two extra charges in the dimer dianion was estimated to be 1.96 eV, much higher than the C−C bond linking the dimer, suggesting $(C_{59}N)_2^{2-}$ is metastable relative to dissociation to two $C_{59}N^-$, i.e., the $(C_{59}N)_2^{2-}$ → $2C_{59}N^-$ reaction is exothermic. The intramolecular electron repulsion is investigated by the difference of the total electron density between $(C_{59}N)_2^{2-}$ and $(C_{59}N)_2$, revealing that the extra charges are pushed away from each other toward the two ends of the azafullerene dimer.

4.5 Supporting information
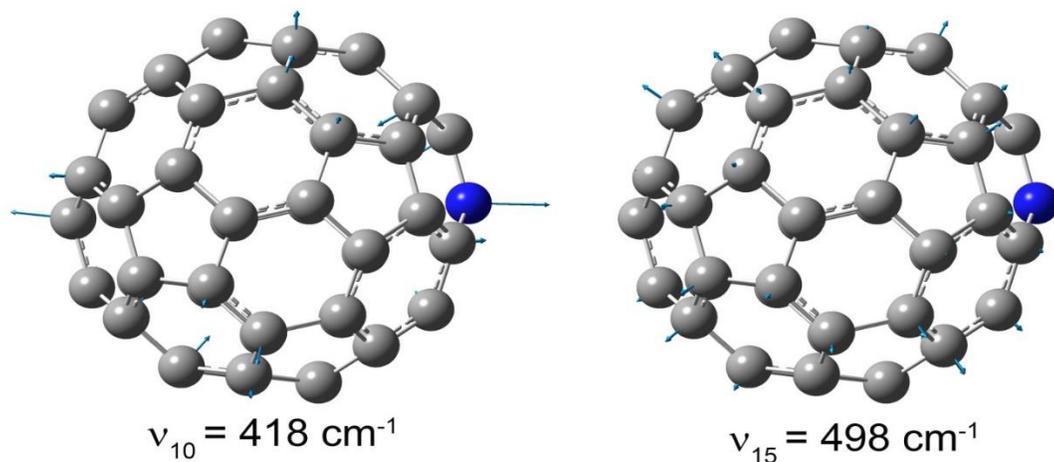
Figure 4.4. The ν_{10} and ν_{15} vibrational modes of C$_{59}$N.
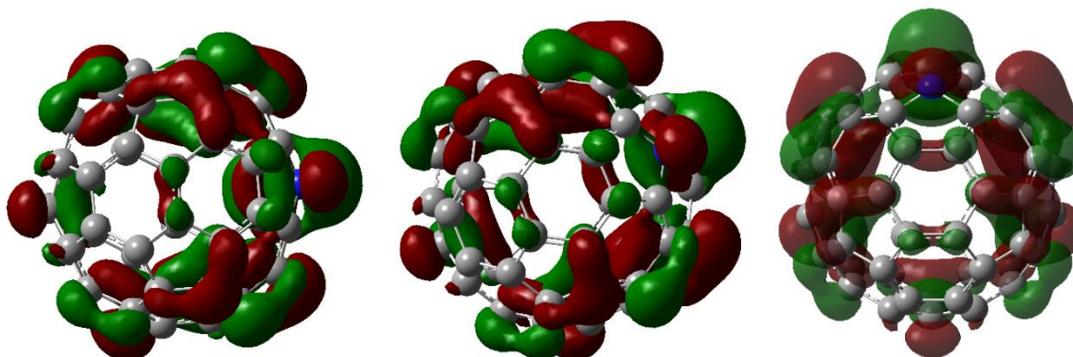
Figure 4.5. Three different views of the HOMO of C$_{59}$N$^-$. It shows the extra electron densities near the N atom.

Table 4.2. Calculated harmonic frequencies for $C_{59}N$. The calculations were done at the B3LYP/Def2SVP level of theory. The unit of frequency is cm^{-1}.

Mode	Freq.	Mode	Freq.		Mode	Freq.	Mode	Freq.
	A′ symmetry					A″ symmetry		
ν_1	258	ν_{46}	840		ν_{90}	261	ν_{135}	845
ν_2	262	ν_{47}	981		ν_{91}	265	ν_{136}	967
ν_3	268	ν_{48}	985		ν_{92}	346	ν_{137}	982
ν_4	337	ν_{49}	989		ν_{93}	352	ν_{138}	983
ν_5	342	ν_{50}	996		ν_{94}	355	ν_{139}	997
ν_6	350	ν_{51}	1107		ν_{95}	398	ν_{140}	1108
ν_7	356	ν_{52}	1115		ν_{96}	404	ν_{141}	1117
ν_8	406	ν_{53}	1122		ν_{97}	408	ν_{142}	1130
ν_9	407	ν_{54}	1132		ν_{98}	419	ν_{143}	1136
ν_{10}	418	ν_{55}	1140		ν_{99}	438	ν_{144}	1196
ν_{11}	431	ν_{56}	1207		ν_{100}	480	ν_{145}	1220
ν_{12}	435	ν_{57}	1216		ν_{101}	483	ν_{146}	1233
ν_{13}	477	ν_{58}	1223		ν_{102}	526	ν_{147}	1248
ν_{14}	482	ν_{59}	1231		ν_{103}	526	ν_{148}	1251
ν_{15}	498	ν_{60}	1239		ν_{104}	533	ν_{149}	1274
ν_{16}	506	ν_{61}	1257		ν_{105}	538	ν_{150}	1289
ν_{17}	524	ν_{62}	1281		ν_{106}	564	ν_{151}	1310
ν_{18}	532	ν_{63}	1291		ν_{107}	568	ν_{122}	1320
ν_{19}	535	ν_{64}	1295		ν_{108}	569	ν_{153}	1338
ν_{20}	563	ν_{65}	1315		ν_{109}	577	ν_{154}	1343
ν_{21}	567	ν_{66}	1341		ν_{110}	579	ν_{155}	1347
ν_{22}	576	ν_{67}	1343		ν_{111}	582	ν_{156}	1350
ν_{23}	579	ν_{68}	1350		ν_{112}	590	ν_{157}	1364
ν_{24}	587	ν_{69}	1355		ν_{113}	675	ν_{158}	1381
ν_{25}	592	ν_{70}	1378		ν_{114}	679	ν_{159}	1383
ν_{26}	675	ν_{71}	1384		ν_{115}	683	ν_{160}	1389
ν_{27}	678	ν_{72}	1397		ν_{116}	690	ν_{161}	1393
ν_{28}	684	ν_{73}	1415		ν_{117}	712	ν_{162}	1417
ν_{29}	699	ν_{74}	1430		ν_{118}	713	ν_{163}	1451
ν_{30}	718	ν_{75}	1456		ν_{119}	721	ν_{164}	1461
ν_{31}	720	ν_{76}	1463		ν_{120}	727	ν_{165}	1473
ν_{32}	724	ν_{77}	1472		ν_{121}	728	ν_{166}	1476
ν_{33}	724	ν_{78}	1473		ν_{122}	732	ν_{167}	1542
ν_{34}	729	ν_{79}	1478		ν_{123}	734	ν_{168}	1553
ν_{35}	735	ν_{80}	1505		ν_{124}	741	ν_{169}	1569
ν_{36}	743	ν_{81}	1531		ν_{125}	742	ν_{170}	1588
ν_{37}	748	ν_{82}	1543		ν_{126}	752	ν_{171}	1599
ν_{38}	751	ν_{83}	1558		ν_{127}	755	ν_{172}	1603
ν_{39}	751	ν_{84}	1571		ν_{128}	763	ν_{173}	1614
ν_{40}	764	ν_{85}	1585		ν_{129}	767	ν_{174}	1617
ν_{41}	768	ν_{86}	1606		ν_{130}	785		
ν_{42}	786	ν_{87}	1612		ν_{131}	792		
ν_{43}	789	ν_{88}	1616		ν_{132}	805		
ν_{44}	791	ν_{89}	1623		ν_{133}	807		
ν_{45}	810				ν_{134}	841		

Chapter 5 Probing the intramolecular interactions in

$H_2O@C_{60}^-$ and $H_2O@C_{59}N^{-\ddagger}$

This chapter[297] will report a high-resolution photoelectron imaging study of cryogenically-cooled $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ endohedral fullerene anions. The electron affinity (EA) of $H_2O@C_{60}$ is measured to be 2.6923 ± 0.0008 eV, which is 0.0088 eV higher than the EA of C_{60}, while the EA of $H_2O@C_{59}N$ is measured to be 3.0058 eV ± 0.0007 eV, which is 0.0092 eV *lower* than the EA of $C_{59}N$. The opposite shifts are found to be due to the different electrostatic interactions between the encapsulated water molecule and the fullerene cages in the two systems. There is a net Coulombic attraction between the guest and host in $H_2O@C_{60}^-$, but a repulsive interaction in $H_2O@C_{59}N^-$. We have also observed low-frequency features in the photoelectron spectra tentatively attributed to the hindered rotational excitations of the encapsulated H_2O molecule, providing further insights into the gust-host interactions in $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$.

5.1 Introduction

Endohedral fullerenes with encapsulated atoms, molecules or clusters have attracted wide interest due to their unique electronic, magnetic, and optical properties.[298-300] Since the first observation of the endohedral fullerene $La@C_{60}$ in a mass spectrum in 1985,[301] a variety of such novel guest-host complexes containing noble gas atoms,[302,303] the N atom and the N_2 moleucle,[304,305] metal atoms and metal clusters,[300,306,307] have been

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synthesized using the arc discharge or ion bombardment methods. These harsh production conditions were unable to make endofullerenes containing light molecules.[308] A more rational synthetic approach, called molecular surgery on the fullerene surfaces,[309,310] was successfully applied to the macroscopic synthesis of $H_2@C_{60}$,[311] followed by the syntheses of $H_2O@C_{60}$,[312,313] $H_2O@C_{59}N$,[227] $HF@C_{60}$,[314] $(H_2O)_2@C_{70}$,[315] and very recently even $(H_2O \cdot HF)@C_{70}$.[316] The $H_2O@C_{60}$ and $H_2O@C_{59}N$ species are of special interest because the water molecule is isolated without hydrogen bonds. Many experimental and theoretical studies have been carried out to elucidate the novel properties of $H_2O@C_{60}$, such as its polarity,[317-323] quantum dynamics,[324-329] magnetic,[227,330] mechanical,[331] thermal[332] and electric properties[322,323,333,334] as well as its chemical reactivity.[321,335,336]

One of the most interesting questions about $H_2O@C_{60}$ concerned the nature of the guest-host interactions of the water molecule trapped in the C_{60} cage. No detectable difference was observed between the UV-Vis absorption spectra of the empty C_{60} and $H_2O@C_{60}$, suggesting that the water molecule has very weak interactions with the cage.[312] This observation was further confirmed by studies of nuclear spin relaxation[330] and electric conductance.[334] However, theoretical calculations found strong dispersion interactions[319,320,337-339] between the free rotating water molecule and C_{60}.[312,320,324,339,340] The quantized rotational levels and the nuclear spin-isomerism of *ortho-* and *para-*water in $H_2O@C_{60}$ were studied by inelastic neutron scattering, far-infrared spectroscopy, and nuclear magnetic resonance.[324-326] These studies revealed a splitting of the ground rotational state of *ortho-*H_2O and a symmetry-breaking of the C_{60} cage, indicating a quadrupolar interaction between H_2O and C_{60}.[327-329] In addition, the dipole moment of

$H_2O@C_{60}$ was measured to be around 0.5 D,[322,323] in good agreement with theoretical calculations.[317-321] The significant reduction of the dipole moment of the encapsulated H_2O is a result of the strong shielding effect by the nonpolar C_{60} cage. A recent study reported that the rotation of the encapsulated water can be electrostatically perturbed by introducing polarized $C(C_{60})$-X (X: heteroatom) bonds.[341]

Unlike the extensive studies on $H_2O@C_{60}$, the $H_2O@C_{59}N$ endohedral azafullerene was only synthesized very recently in the dimer form, $(H_2O@C_{59}N)_2$.[227] The presence of the N atom breaks the symmetry of the fullerene and introduces a polar center. Theoretical calculations suggested an attractive electrostatic interaction between the O atom of H_2O and the N atom of $C_{59}N$.[227,342,343] Comparison of the different guest-host interactions in $H_2O@C_{60}$ and $H_2O@C_{59}N$ would be very interesting. In particular, the electron affinity (EA) of the endohedral fullerenes can be a good probe of these guest-host interactions, because the extra electron in the C_{60}^- and $C_{59}N^-$ anions is expected to be sensitive to the encapsulated H_2O molecule.

Here, we present a high-resolution photoelectron imaging study of the $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ anions cooled in a cryogenic ion trap. The EA of $H_2O@C_{60}$ is accurately measured to be 2.6923 ± 0.0008 eV, which is 0.0088 eV higher than the EA of C_{60},[116] while the EA of $H_2O@C_{59}N$ is measured to be 3.0058 eV $\pm$ 0.0007 eV, which is 0.0092 eV *lower* than the EA of $C_{59}N$.[255] The opposite shifts suggest different guest-host interactions between the encapsulated water molecule and the fullerene cages, which are understood by an electrostatic model. A net Coulombic attraction between the water molecule and the HOMO electron in $H_2O@C_{60}^-$ is found to stabilize the anion and enhance the EA of $H_2O@C_{60}$ compared to C_{60}, while a repulsive interaction in

$H_2O@C_{59}N^-$ destabilizes the anion and decreases the EA of $H_2O@C_{59}N$ relative to $C_{59}N$. In addition, low-frequency features in the photoelectron spectra are observed and tentatively attributed to the hindered rotational excitations[327-329] of the encapsulated H_2O molecule, providing further insights into the gust-host interactions in $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$.

5.2 Experimental methods

The experiments were done using our ESI-PES apparatus. The experimental details were provided in Chapter 2.

5.3 Results and discussion

5.3.1 The photoelectron images and spectra at 354.7 nm

Figure 5.1 shows the photoelectron images and spectra of $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ at 354.7 nm. The first intense peak in each spectrum, labeled as 0_0^0, represents the 0-0 transition from the anion to the neutral and defines the EAs for $H_2O@C_{60}$ and $H_2O@C_{59}N$, which are measured more accurately in the low photon energy spectra (*vide infra*). The peaks at higher binding energies represent transitions from the ground vibrational state of the anion to the excited vibrational levels of the neutral ground electronic state. They are better resolved in the high-resolution photoelectron images at lower photon energies near the detachment threshold to be discussed below. Fig. 5.1b also shows a weak peak (X′) at ~1.2 eV, which is derived from the parent dimer dianion, $(H_2O@C_{59}N)_2^{2-}$ with the same m/z as the monoanion. A similar dimer dianion was also observed in the 354.7 nm PE spectrum of $C_{59}N^-$

recently.[255] The low binding energy for the dianion was due to the strong intramolecular Coulomb repulsion.[15,75,291]
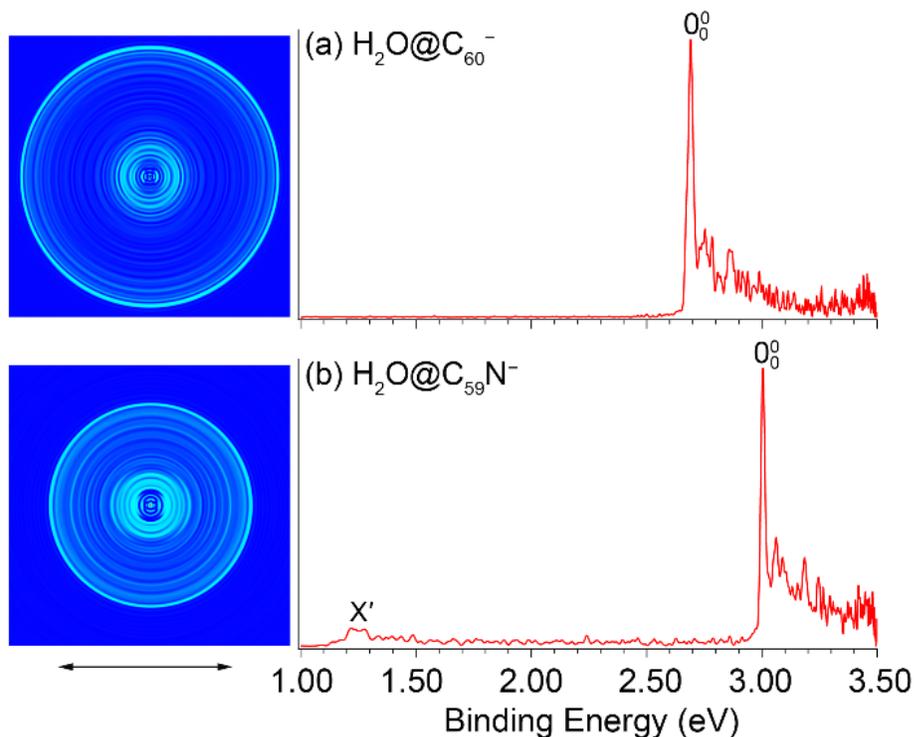
Figure 5.1. Photoelectron images and spectra of fullerene anions at 354.7 nm. (a) H$_2$O@C$_{60}^-$ and (b) H$_2$O@C$_{59}$N$^-$. The double arrow below the images indicates the direction of the laser polarization. Note the image corresponding to peak X' in (b) is cut off.

The 354.7 nm spectra of the endohedral fullerenes appear to be nearly identical to those of their corresponding parent fullerenes,[116,255] as directly compared in Fig. 5.2. This observation suggests that indeed the encapsulated water molecule has little effect on the electronic and geometrical structures of the fullerene hosts. However, upon closer examination, a small spectral shift was revealed in each case, as shown in the expanded threshold region given in the respective inset of Fig. 5.2. Surprisingly, the two endohedral fullerenes exhibit opposite shifts. The electron binding energy of H$_2$O@C$_{60}^-$ was observed to be shifted slightly higher relative to that of C$_{60}^-$ (Fig. 5.2a), whereas the

electron binding energy of $H_2O@C_{59}N^-$ was shifted slightly lower relative to that of $C_{59}N^-$. The opposite spectral shifts suggest subtle differences in the guest-host interactions of the encapsulated water molecule with the fullerene or azafullerene cages.
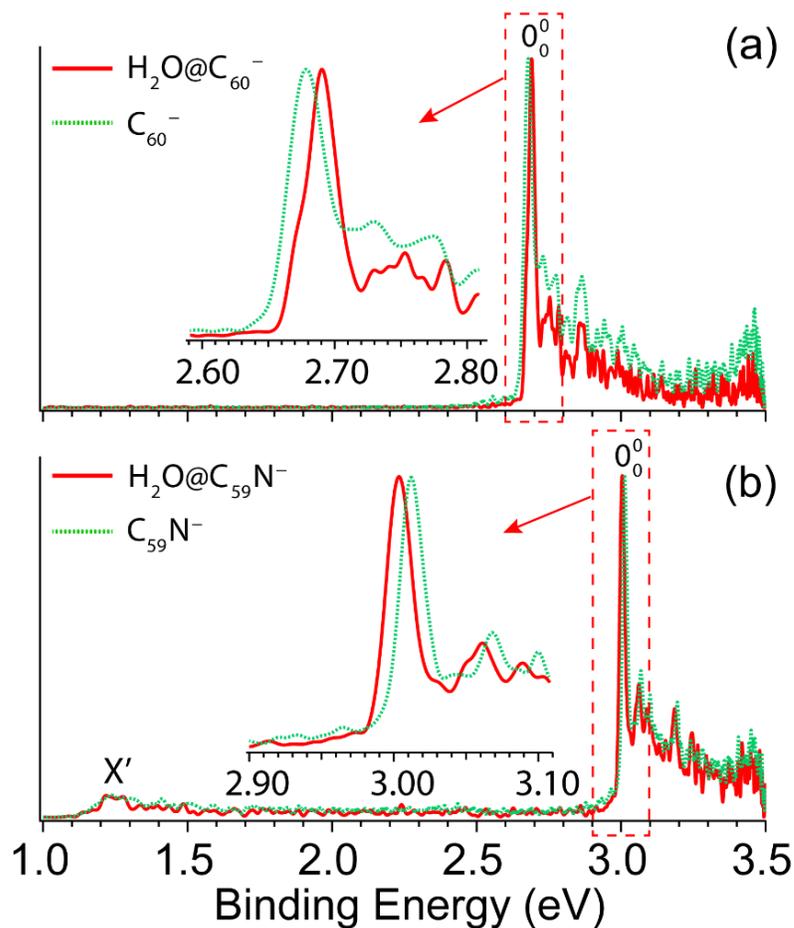
Figure 5.2. Comparisons of the photoelectron spectra of fullerene anions. (a) C_{60}^- and $H_2O@C_{60}^-$, (b) $C_{59}N^-$ and $H_2O@C_{59}N^-$ at 354.7 nm.

5.2.2 The photoelectron images and spectra near detachment thresholds

To measure the EAs more accurately and to resolve low-frequency vibrations, we measured PE images for $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ at lower photon energies near the detachment thresholds, as shown in Fig. 5.3. We found that the detachment cross sections for the endohedral fullerenes were weaker than those of the corresponding empty fullerenes,[116,255] in particular near the detachment thresholds. The spectra shown in Fig.

5.3 were averaged from 300,000 to 500,000 laser shots. At 456.60 nm (Fig. 5.3a), the 0_0^0

peak with a linewidth of 38 cm^{-1} at an electron kinetic energy of 186 cm^{-1} defines the

most accurate value for the EA of $H_2O@C_{60}$ as 2.6923 ± 0.0008 eV, which is 0.0088 eV

higher than the EA of C_{60}.[116] The detachment cross section at this wavelength for

$H_2O@C_{60}^-$ was particularly poor. The features below the 0_0^0 peak in Fig. 5.3a were partly

due to background noise and partly due to hot band transitions, which were amplified

relative to the 0_0^0 transition. At 411.12 nm (Fig. 5.3d), the 0_0^0 peak with an electron

kinetic energy of 80 cm^{-1} and linewidth of 15 cm^{-1} yields the most accurate EA for

$H_2O@C_{59}N$ to be 3.0058 eV ± 0.0007 eV, which is 0.0092 eV lower than the EA of

$C_{59}N$.[255]
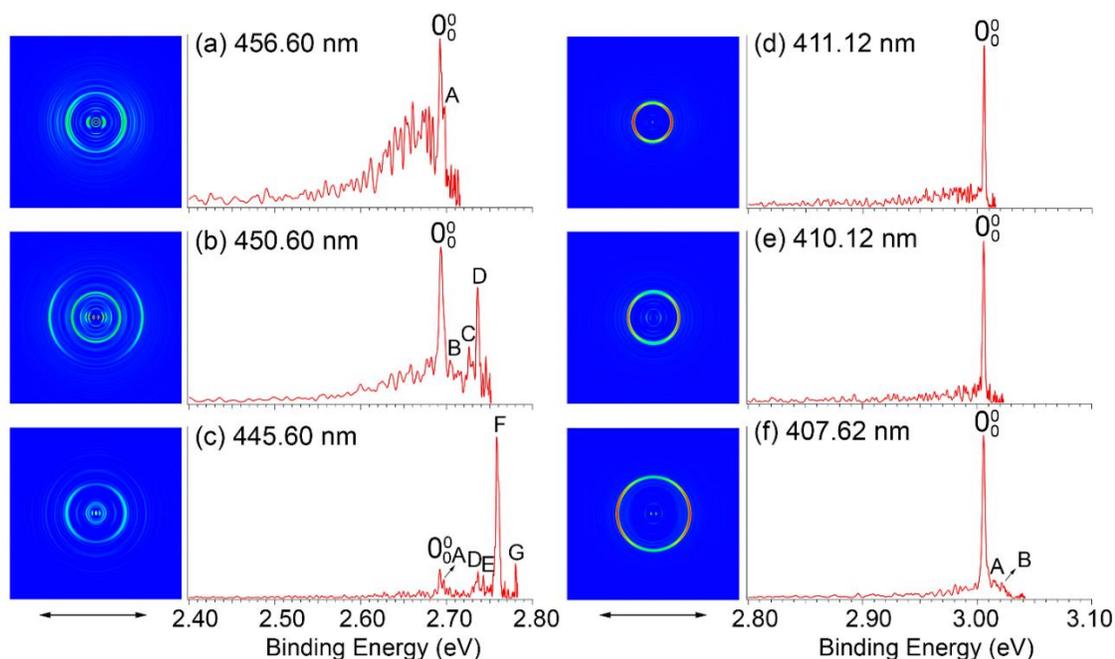
Figure 5.3. Photoelectron images and spectra of $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$. at various photon energies. $H_2O@C_{60}^-$: (a) 456.60 nm, (b) 450.60 nm and (c) 445.60 nm. $H_2O@C_{59}N^-$: (d) 411.12 nm, (e) 410.12 nm and (f) 407.62 nm. The double arrows below the images indicate the direction of the laser polarization.

In addition to the near-threshold spectra, two more spectra were taken to resolve low-frequency vibrational features for H$_2$O@C$_{60}$ and H$_2$O@C$_{59}$N, as shown in Figs. 5.3b-c and Figs. 5.3e-f, respectively. There are two types of vibrations for the endohedral fullerenes, one involving the fullerene cage and the other involving the encapsulated water molecules including the hindered rotations. The latter should be particularly sensitive to the guest-host interactions in the endohedral fullerenes. Figs. 5.3a-c resolve seven vibrational peaks, labeled as A-G for H$_2$O@C$_{60}$, while Fig. 5.3f resolve two peaks, A and B for H$_2$O@C$_{59}$N. The relative intensities of the low frequency peaks (A, B) are quite weak for both species, but they seem to be reproducible. The binding energies and shifts to the 0_0^0 peak for all the vibrational features are summarized in Table 5.1.

Table 5.1. Observed vibrational peaks for H$_2$O@C$_{60}^-$ and H$_2$O@C$_{59}$N$^-$. Their binding energies (BE) measured from the photoelectron spectra in Fig. 5.3. Their shifts to peak 0_0^0 are compared with the vibrational frequencies of C$_{60}$. The numbers in parentheses indicate the experimental uncertainties.

Anions	Peaks	BE (eV)	Shifts (cm^{-1})	Vib. Freq. (cm^{-1})[a]
C$_{60}^-$		2.6835(6)[a]		
H$_2$O@C$_{60}^-$	0_0^0	2.6923(8)	0	
	A	2.6967(7)	35	
	B	2.7041(10)	95	
	C	2.7259(10)	271	262
	D	2.7361(7)	353	348
	E	2.7427(10)	406	
	F	2.7582(7)	531	531
	G	2.7803(10)	710	717
C$_{59}$N$^-$		3.0150(7)[b]		
H$_2$O@C$_{59}$N$^-$	0_0^0	3.0058(7)	0	
	A	3.0151(12)	74	
	B	3.0217(12)	128	

[a]Ref. 116; [b]Ref. 255.

Peaks C, D, F, G with shifts of 271, 353, 531, and 710 cm^{-1}, are similar to those observed in the photoelectron spectra of C60$^-$ and they should correspond to vibrational modes involving the C$_{60}$ cage.[116] The strong and highly non-Franck-Condon peak F

observed in the 445.60 nm spectrum (Fig. 5.3c) is also observed for $C60^-$, which was attributed to strong Hertzberg-Teller coupling.[116] The weak peak E with a shift of 406 cm^{-1} corresponds to a $H_u(1)$ vibrational mode of C_{60} also observed by inelastic neutron scattering.[293] These observations suggest that the H_2O molecule has little effect on the geometrical and electronic structure of the C_{60} host. Additionally, two weak peaks A and B with small shifts of 35 and 95 cm^{-1}, corresponding to very low-frequency transitions, are also tentatively identified. The lowest vibrational frequency of C_{60} is 260 cm^{-1}.[116,255] Hence, these features should correspond to the hindered rotational excitations of the encapsulated water molecule, as revealed by the rigorous full-dimensional quantum calculations of the coupled translation-rotation excitations of the encapsulated water molecule. The observation of hindered rotational transitions indicates weak interactions between the encapsulated water molecule and the fullerene cages. The relatively high frequencies observed for the hindered rotational transitions in $H_2O@C_{59}N$ suggest stronger guest-host interactions in this system.

The photoelectron images of $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ in Fig. 5.3 all exhibit distinct *p*-wave character with the photoelectron angular distributions parallel to the direction of the laser polarization, similar to those for C_{60}^- and $C_{59}N^-$.[116,255] These observations indicate that the encapsulated water molecule does not affect the *s*-like HOMO of the fullerene cages. The *p*-wave nature of the outgoing electron is partly responsible for the low detachment cross sections near threshold according to the Wigner threshold law.[57]

5.2.3 The opposite shifts of the EAs: An electrostatic model

The opposite shifts of the EAs of H$_2$O@C$_{60}$ and H$_2$O@C$_{59}$N relative to their corresponding empty cages are consistent with previous theoretical calculations.[321,342] The different effects of the encapsulated water on the EAs can be glimpsed from the electrostatic potential maps of the HOMO of the fullerene anions, as presented in Fig. 5.4. The extra charge in the half-filled HOMO of C$_{60}-$ is evenly distributed on the surface (Fig. 5.4a). Even though the encapsulated water molecule was known to have no preferred directions,[312,320,324,339,340] it breaks the symmetry and dynamically induces a slightly higher charge density on the cage surface, where the H atoms point to (Fig. 5.4b).
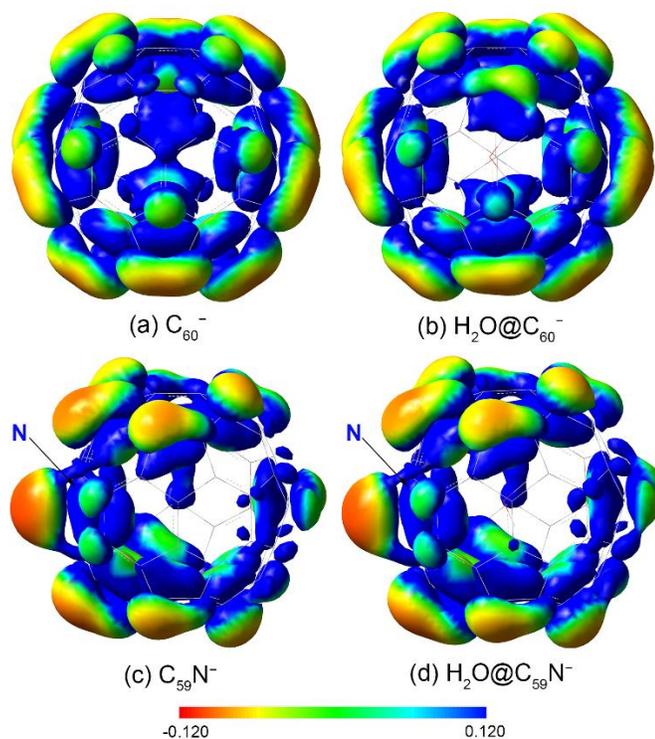
Figure 5.4. The electrostatic potential maps for the HOMO of fullerene anions. (a) C$_{60}^-$, (b) H$_2$O@C$_{60}^-$, (c) C$_{59}$N$^-$, (d) H$_2$O@C$_{59}$N$^-$. The calculation were done at B3LYP/6-311++G(d,p) level using the Gaussian 09 package.[252]

On the contrary, the HOMO of C$_{59}$N$^-$ is partially localized on the N atom and the C atoms around the N atom (Fig. 5.4c).[255] The water molecule in H$_2$O@C$_{59}$N$^-$ has been

shown to adopt a global minimal structure with the O atom pointing to the N atom of the cage due to a weak N…O attractive interaction.[342,343] Despite its orientation preference, the water encapsulation has relatively little effect on the HOMO of $C_{59}N^-$ (Fig. 5.4d). However, this orientation of the water molecule brings the electronegative O atom closer to the extra charge, inducing a repulsive interaction.

A simple electrostatic model is used to understand the interactions between the water molecule and the extra charge in the HOMO of the fullerene cages and to obtain insights about the observed different EA shifts in the two systems. In the model, partial charges on the water molecule are represented by point charges with –2q located on the oxygen atom and +q on each H atom, where q is obtained from a Mulliken population analysis of the total wavefunction of the water molecule. The Coulomb interaction can be expressed as:

$$V_{Coulomb} = -\sum_{i=1}^{3} q_i \int d\vec{r} \frac{|\varphi_{HOMO}(\vec{r})|^2}{|\vec{r} - \vec{r_i}|}$$

where q_i and r_i represent the charge and position of each atom in the water molecule, $\varphi_{HOMO}(r)$ is the Kohn-Sham wavefunction of the HOMO of $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$ extracted from DFT calculations.[344] The numerical integration is done with a fine grid converging to 1 meV accuracy. All the geometry optimization and electronic structure calculations were done using DFT at B3LYP/6-311++G(d,p) level of theory with the Gaussian 09 package.[252]

The Coulomb interaction in $H_2O@C_{60}^-$ was calculated to be -23 meV, indicating an attractive interaction between the encapsulated water molecule and the HOMO electron in $H_2O@C_{60}^-$. This weak attraction, which is in good agreement with previous

calculations,[319,337-339] stabilizes the $H_2O@C_{60}^-$ anion and increases the EA of $H_2O@C_{60}$ relative to C_{60}. On the other hand, the simple electrostatic calculation on the $H_2O@C_{59}N^-$ anion yields a repulsive interaction of 64 meV. Hence, the water encapsulation destabilized the HOMO of the $C_{59}N^-$ anion, reducing the EA of $H_2O@C_{59}N$ relative to $C_{59}N$. This repulsive interaction is expected from the orientation of the H_2O molecule in $C_{59}N^-$ and its asymmetric electron density distribution (Fig. 5.4d). Even though the electrostatic model is rather crude, it correctly predicts the directions of the EA shifts in the two endohedral fullerenes. The interactions between the encapsulated water molecule and the fullerene cages are so weak that they were not detectable in the UV-Vis absorption spectra[312] or the electrical conductance experiment.[334]

5.4 Conclusions

In conclusion, we report a high-resolution photoelectron imaging study of two endohedral fullerene anions, $H_2O@C_{60}^-$ and $H_2O@C_{59}N^-$. Accurate electron affinities are obtained for $H_2O@C_{60}$ (2.6923 ± 0.0008 eV) and $H_2O@C_{59}N$ (3.0058 ± 0.0007 eV) for the first time. The EA of $H_2O@C_{60}$ is found to be higher than that of C_{60} by 0.0088 eV, whereas the EA of $H_2O@C_{59}N$ is found to be lower than that of $C_{59}N$ by 0.0092 eV. These small EA shifts reflect the weak guest-host interactions in the endohedral fullerenes and the opposite shifts are understood using a simple electrostatic model between the encapsulated H_2O molecule and the HOMO of the fullerene anions. Low-frequency features due to the hindered rotational transitions of the encapsulated water molecule are also tentatively identified, providing further insight into the weak guest-host interactions in the two endohedral fullerenes.

Chapter 6 Dipole-bound excited states and resonant photoelectron imaging of $C_6H_5O^-$ and $C_6H_5S^{-\S}$

This chapter[122] reports a photodetachment and resonant photoelectron-imaging studies of cryogenically cooled phenoxide ($C_6H_5O^-$) and thiophenoxide ($C_6H_5S^-$) anions. In a previous study[117] a dipole-bound excited state was observed for $C_6H_5O^-$ at 97 cm^{-1} below the detachment threshold. Eight resonant photoelectron spectra were obtained via excitations to eight vibrational levels of the dipole-bound state (DBS) followed by autodetachment. Here we present a complete photodetachment spectrum of $C_6H_5O^-$ covering a spectral range 2,600 cm^{-1} above the detachment threshold and revealing nine additional vibrational resonances of the DBS. We also report the first observation of a dipole-bound excited state for $C_6H_5S^-$, 39 cm^{-1} below its detachment threshold of 18,982 cm^{-1}. Photodetachment spectroscopy covering a spectral range 1,500 cm^{-1} above threshold reveals twelve vibrational resonances for the DBS of $C_6H_5S^-$. By tuning the detachment laser to the vibrational resonances in the DBS of $C_6H_5O^-$ and $C_6H_5S^-$, we obtain highly non-Franck-Condon resonant photoelectron spectra, as a result of mode-selectivity and the $\Delta v = -1$ propensity rule for vibrational autodetachment. Five new fundamental vibrational frequencies are obtained for the ground state of the C_6H_5O (X^2B_1) radical. Intramolecular inelastic scattering is observed in some of the resonant photoelectron spectra, leading to the excitation of the Franck-Condon-inactive lowest-frequency bending mode (v_{20}) of C_6H_5O. The first excited state of C_6H_5O (A^2B_2) is observed to be 0.953 eV above the ground state. Twelve resonant photoelectron spectra

are obtained for $C_6H_5S^-$, allowing the measurements of seven fundamental vibrational frequencies of the C_6H_5S radical, whereas the non-resonant photoelectron spectrum only exhibits a single Franck-Condon active mode. The current study again demonstrates that the combination of photodetachment spectroscopy and resonant photoelectron spectroscopy is a powerful technique to obtain vibrational information about polar radical species.

6.1 Introduction

Due to the important role as the chromophore in aromatic amino acid tyrosine, which acts as the key catalysis in biological enzymes like photosystem II and the water oxidizing enzyme,[345] the photochemistry of phenol has received considerable attentions.[346-348] Extensive studies on the photodissociation of phenol, i.e., fission of the O-H bond to form H atom and the phenoxy radical (C_6H_5O), have shown the significance of the nonradiative decay pathway via the optically dark $^1\pi\sigma^*$ state for the protection from photochemical damage following UV absorptions.[346,349-356] The photodissociation of thiophenol, the sulfur analogue of phenol, has also been widely investigated, revealing a similar $^1\pi\sigma^*$-mediated pathway yielding the thiophenoxy radical (C_6H_5S).[357-361] As photodissociation products, C_6H_5O and C_6H_5S are also of great interest in many systems. For example, C_6H_5O is a crucial transient intermediate in the combustion and atmospheric chemistry of small aromatic molecules.[362-365] As a part of the phenolic compounds, like vitamin E and resveratrol, C_6H_5O is also involved in the antioxidant and radical scavenging processes.[366] Moreover, both C_6H_5O and C_6H_5S have been considered as the potential candidate molecules for the diffuse interstellar bands in astrophysics.[367,368]

The electronic and vibrational properties of C_6H_5O and C_6H_5S have been extensively investigated both experimentally and theoretically.[117,369-385] The electron affinities (EAs) of the C_6H_5O and C_6H_5S radicals were first estimated by photodetachment spectroscopy of the corresponding anions $C_6H_5O^-$ and $C_6H_5S^-$.[369] An improved value for C_6H_5O was later measured by anion photoelectron spectroscopy (PES),[370] which also yielded the excited state of C_6H_5O. Later, high-resolution PE spectra of $C_6H_5O^-$ and $C_6H_5S^-$ were obtained by slow electron velocity-map imaging (SEVI), which accurately determined the EAs of C_6H_5O and C_6H_5S to be 2.2538(8) eV and 2.3542(6) eV, respectively.[371] The electronically excited state of C_6H_5O was studied[372-375] and the lowest electronic transition ($X^2B_2 \leftarrow A^2B_1$) was determined to be 0.9523(1) eV by cavity ringdown spectroscopy.[375] The lowest excited state of C_6H_5S was also calculated[376] and experimentally measured to be 0.3719(9) eV above the ground state.[371] In addition, the ground-state vibrational frequencies of C_6H_5O and C_6H_5S have been computed in several theoretical works[376-380] and examined by various spectroscopies,[370,371,381-385] such as anion PES,[370,371] resonance Raman spectroscopy,[381-383] IR spectroscopy,[384] and laser-induced fluorescence.[385] Recently, we measured the vibrational frequencies of C_6H_5O by high-resolution resonant photoelectron imaging of cold $C_6H_5O^-$ from vibrational autodetachment via dipole-bound states (DBSs).[117]

In the current study, we report the complete photodetachment spectra of $C_6H_5O^-$ and $C_6H_5S^-$ and resonant photoelectron imaging. A DBS is observed for the first time for $C_6H_5S^-$, 39 cm^{-1} below its detachment threshold. In addition to the eight DBS vibrational resonances reported previously,[117] nine new resonances are observed for $C_6H_5O^-$, whereas twelve vibrational resonances are observed for $C_6H_5S^-$. By setting the

detachment laser wavelengths to the DBS resonances for $C_6H_5O^-$ and $C_6H_5S^-$, we obtain resonant photoelectron images and spectra, which are highly non-Franck-Condon due to mode-selectivity[117] and the $\Delta v = -1$ vibrational propensity rule.[189,190] In total, five new fundamental vibrational frequencies are obtained for C_6H_5O and seven for C_6H_5S. Interestingly, intramolecular inelastic rescattering is observed in some resonant PE spectra of $C_6H_5O^-$, allowing the excitation of the Franck-Condon-inactive lowest-frequency bending mode v_{20} of C_6H_5O to be observed. It is further shown that the photodetachment spectra for both $C_6H_5O^-$ and $C_6H_5S^-$ are in perfect agreement with the non-resonant PE spectra, vividly demonstrating the similar geometries between the neutral radicals and the dipole-bound anions, i.e. the weakly dipole-bound electron has little effect on the structure of the neutral core. Hence, the combination of photodetachment spectroscopy and resonant PES can be used to yield vibrational information for neutral polar radicals, rivaling IR spectroscopy.

6.2 Experimental methods

The experiments were done using our third-generation ESI-PES apparatus. The details were provided in Chapter 2.

6.3 Results

6.3.1 Non-resonant photoelectron spectra of $C_6H_5O^-$

Figure 6.1 shows the non-resonant photoelectron spectra of $C_6H_5O^-$ at 480.60 nm and 354.7 nm. At 480.60 nm, the first intense peak 0_0^0 represents the 0-0 transition from the anion to the neutral ($X^2B_1 \leftarrow X^1A_1$), giving an accurate EA of 18,173 cm^{-1}.[117,371] Peaks A$-$D define a single vibrational progression of mode v_{11}, as also observed previously.[117,371] At the higher photon energy of 354.7 nm, transitions to the neutral
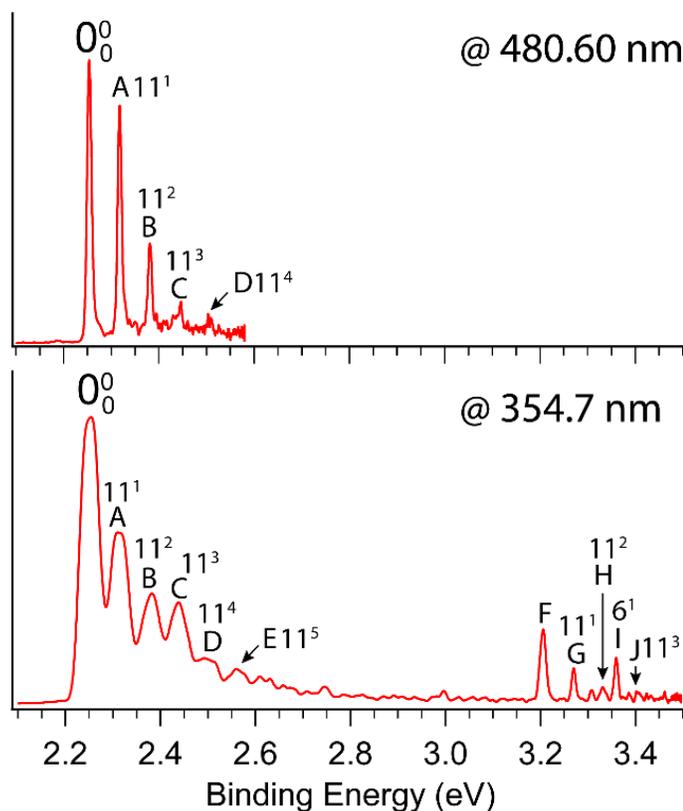
Figure 6.1. Non-resonant photoelectron spectra of $C_6H_5O^-$ at 480.60 nm and 354.7 nm.

excited state (A^2B_2) are also observed. The origin transition represented by peak F is measured to be 3.2056 ± 0.0020 eV, which lies 0.9524(20) eV above the ground state, consistent with the value determined by cavity ringdown spectroscopy.[375] Peaks G−J represent vibrational excitations of the excited state. The electron binding energies of all the observed peaks A−J for the ground and excited states of C_6H_5O, their shifts from the origin of each state and assignments are summarized in Table 6.1, where other vibrational features from the resonant photoelectron spectra are also given (*vide infra*).

6.3.2 Photodetachment spectrum of $C_6H_5O^-$

The photodetachment spectrum of $C_6H_5O^-$ was measured by monitoring the total electron yield while scanning the dye laser wavelength at 0.1 nm/step across the

Table 6.1. Summary of the observed vibrational peaks from the photoelectron spectra of $C_6H_5O^-$. Their binding energies (BE), shifts from the 0-0 transitions of the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2B_2$ states, assignments are given. The calculated frequencies at the B3LYP/6-311++G(d,p) level of theory are also given for the fundamental vibrational modes (see Table 6.6 in Section 6.6 for all modes).

Peak[a]	BE (eV)[b]	Shift (cm^{-1})	Assignment	Theor. Freq. (cm^{-1})
0_0^0	2.2532(4)	0	$\tilde{X}^2B_1$	
A	2.3175(6)	519	11^1	531
B	2.3815(6)	1035	11^2	
C	2.4460(6)	1555	11^3	
D	2.5097(6)	2069	11^4	
E	2.5740(20)	2587	11^5	
a	2.2750(10)	176	20^1	184
b	2.2984(10)	365	14^1	375
c	2.3116(10)	471	19^1	474
d	2.3315(6)	632	18^1	642
e	2.3511(6)	790	10^1	804
f	2.3737(6)	972	9^1	983
g	2.3956(6)	1149	$11^1 18^1$	
h	2.4044(6)	1220	$11^2 20^1$	
i	2.4152(6)	1307	$10^1 11^1$	
j	2.4298(10)	1425	$10^1 18^1$	
k	2.4374(6)	1486	$9^1 11^1$	
l	2.4602(6)	1670	$11^2 18^1$	
m	2.4680(6)	1733	$11^3 20^1$	
n	2.4928(6)	1933	$10^1 11^1 18^1$	
o	2.5008(6)	1997	$9^1 11^2$	
F	3.2056(20)	0	$\tilde{A}^2B_2$	
G	3.2699(20)	519	11^1	524
H	3.3328(20)	1026	11^2	
I	3.3594(20)	1240	6^1	1319
J	3.4029(20)	1591	11^3	

[a]Peaks in bold were reported previously in ref. 117. The peaks designated by lower case letters were observed in the resonant photoelectron spectra.
[b]Numbers in parentheses indicate the experimental uncertainties in the last digit.

detachment threshold, as presented in Fig. 6.2. A smaller step size of 0.01 nm/step was used in separate scans near each observed resonance to determine a more accurate peak position. In the previous study,[117] photodetachment spectra were only measured for the

v_{11} progression without continuously scanning the dye laser. The arrow in Fig. 6.2 denotes the detachment threshold at 18,173 cm^{-1}. Below threshold, the weak peak labeled as 0 represents the ground vibrational level of the DBS of $C_6H_5O^-$, which is due to resonant two-photon detachment.[117] The binding energy of the DBS, defined as the energy difference between the neutral ground state and the ground state of the DBS, was determined to be 97 ± 5 cm^{-1} previously.[117] Above threshold, the continuous baseline indicates the cross section of the non-resonant detachment signal. The seventeen peaks,
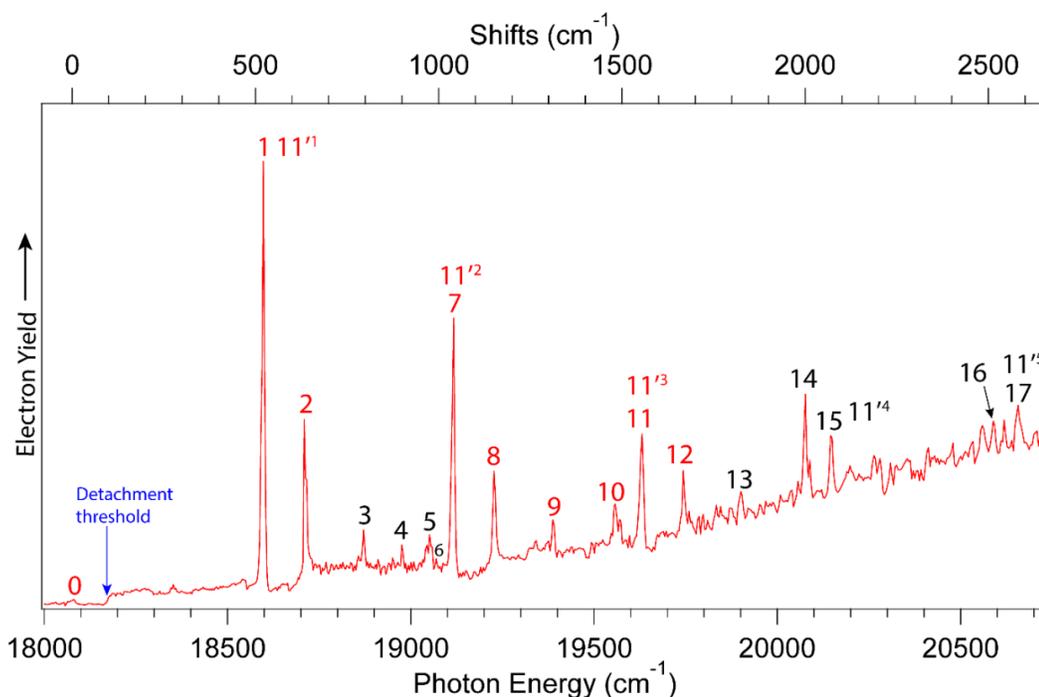
Figure 6.2. The photodetachment spectrum of $C_6H_5O^-$. It was done by measuring the total electron yield as a function of photon energy across the detachment threshold. The arrow at 18,173 cm^{-1} marks the detachment threshold. The peak 0 below threshold represents the vibrational ground state of the dipole-bound excited of $C_6H_5O^-$ and it is from resonant two-photon detachment, while peaks **1−17** are due to autodetachment from the DBS vibrational levels. The peaks labeled in red color were reported previously,[117] and the peaks in black color are newly resolved. The assignments of peaks **1**, **7**, **11**, **15**, and **17** to the vibrational progression of mode v_{11}' are also given.

labeled as **1−17**, represent optical excitations to the vibrational levels of the DBS of $C_6H_5O^-$, followed by autodetachment. The peak numbers in red were reported

previously.[117] The peaks labeled in black numbers are newly observed, because of the continuous scan of the detachment wave length and the broader spectral range covered in the current study (up to ~2,600 cm^{-1} above threshold). The vibrational progression of mode v_{11}' up to the fifth quantum (peak **17**) is observed in the current spectrum.

The photon energies, shifts from the ground vibrational level of the DBS, and the assignments of the observed vibrational resonances are given in Table 6.2. The assignments are all based on the resonant photoelectron spectra in Figs. 6.3 and 6.4 and the calculated vibrational frequencies presented in Table 6.6 in Section 6.6.

Table 6.2. Assignments of the observed resonances in the photodetachment spectrum of $C_6H_5O^-$.

Peak[a]	Wavelength (nm)	Photon Energy (cm^{-1})[b]	Shift (cm^{-1})	Assignment
0	553.22	18076(5)		Ground state
1	537.78	18595(5)	519	$11'^1$
2	534.53	18708(5)	632	$18'^1$
3	529.93	18870(5)	794	$10'^1$
4	527.00	18975(5)	899	$16'^1$
5	524.86	19053(5)	977	$9'^1$
6	524.42	19069(5)	993	$8'^1$
7	523.22	19112(5)	1036	$11'^2$
8	520.17	19224(5)	1148	$11'^118'^1$
9	515.90	19384(5)	1308	$10'^111'^1$
10	511.05	19568(5)	1492	$9'^111'^1$
11	509.36	19632(5)	1556	$11'^3$
12	506.50	19743(5)	1667	$11'^218'^1$
13	502.47	19902(5)	1826	$10'^111'^2$
14	498.04	20079(5)	2003	$9'^111'^2/10'^111'^220'^1$
15	496.33	20148(5)	2072	$11'^4$
16	485.67	20590(5)	2514	$9'^111'^3/10'^111'^320'^1$
17	483.90	20665(5)	2589	$11'^5$

[a]Peaks in bold were reported in ref. 117.
[b]Numbers in parentheses indicate the experimental uncertainties in the last digit.

6.3.3 Resonant photoelectron spectra of $C_6H_5O^-$

By tuning the detachment laser to the newly observed peaks in Fig. 6.2, we obtain nine resonant PE spectra of $C_6H_5O^-$, as shown in Figs. 6.3 and 6.4. Resonant PE spectra corresponding to the peaks numbered in red were reported before.[117] As discussed previously,[97,117-121,164,386] two detachment pathways contributed to the resonant PE spectra: the non-resonant detachment process represented by the continuous signals in Fig. 6.2 and the resonantly-enhanced vibrational autodetachment via the DBS. Due to the mode selectivity[97,117-121,164,386] and the $\Delta v = -1$ propensity rule[189,190] in the autodetachment process, the resonantly-enhanced spectra in Figs. 6.3 and 6.4 are highly non-Franck-Condon in comparison to the non-resonant spectra in Fig. 6.1: one or more vibrational peaks are enhanced in the resonant photoelectron spectra.
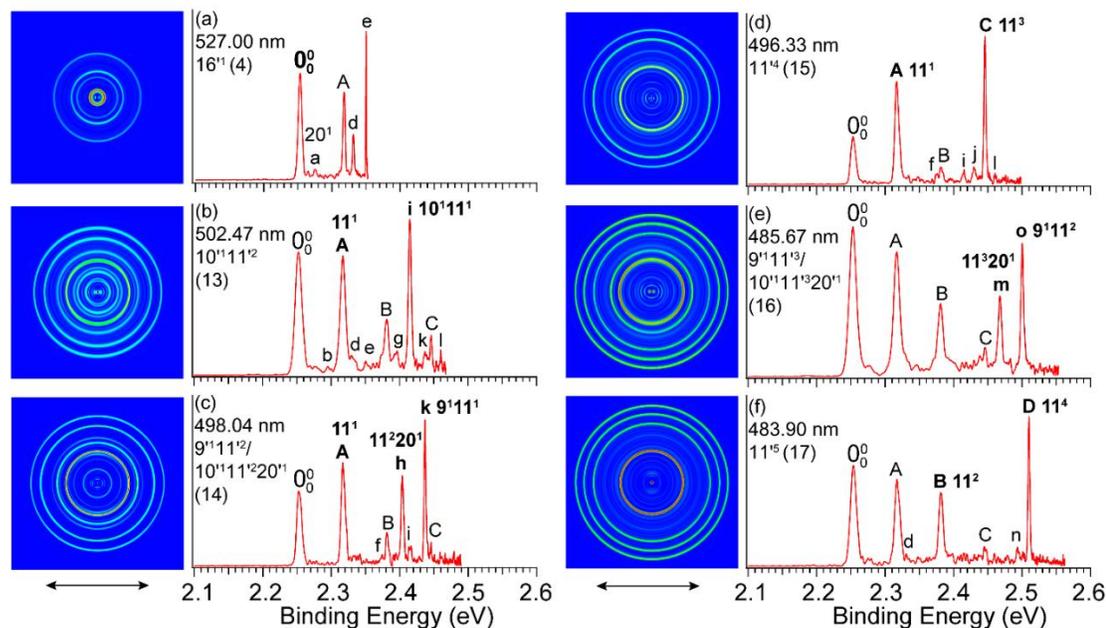
Figure 6.3. Resonant photoelectron images and spectra of $C_6H_5O^-$. The laser wavelengths are corresponding to the six resonances (in parentheses) in Fig. 6.2. The autodetachment-enhanced peaks are labeled in bold face. And the assigned vibrational levels of DBS are given. The double arrows below the images indicate the direction of the laser polarization.
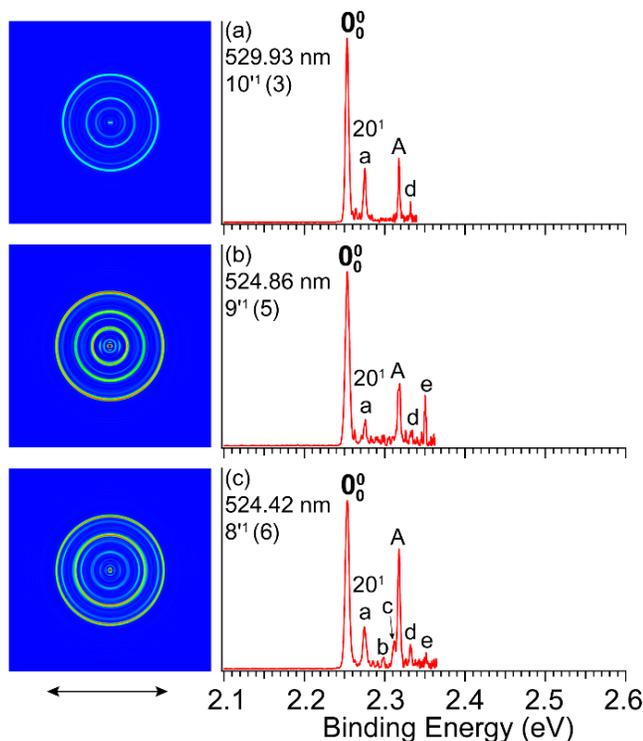
Figure 6.4. Resonant photoelectron images and spectra of $C_6H_5O^-$ at three different wavelengths. They are corresponding to peaks **3**, **5**, and **6** in Fig. 6.2. The first peak 0_0^0 labeled in bold face is enhanced due to autodetachments from fundamental vibrational levels of the DBS. The peak *a* assigned to the out-of-plane bending mode v_{20} of C_6H_5O is observed to be due to the intramolecular inelastic rescattering effect.[119,121,164] The double arrow below the images indicates the direction of the laser polarization.

Figures 6.3b, 6.3c, and 6.3e contain autodetachment from combinational and overlapping vibrational levels of the DBS of $C_6H_5O^-$, while Figs. 6.3a, 6.3d, 6.3f and Fig. 6.4 are due to autodetachment from a single vibrational level of the DBS. The assignments of the enhanced vibrational peaks are given in bold face in Figs. 6.3 and 6.4. All the additionally observed peaks (*a-o*), their binding energies, shifts relative to the 0_0^0 transition and the assignments are also given in Table 6.1.

6.3.4 Dipole-bound excited state and photodetachment spectrum of $C_6H_5S^-$

High-resolution photoelectron spectra of $C_6H_5S^-$ using SEVI were reported previously and the EA of C_6H_5S was measured to be 18,982(5) cm^{-1}.[371] For the ground

state transition, a single vibrational progression in the ν_{11} mode was observed with a frequency of 427 cm^{-1} without observable Franck-Condon activities in any other vibrational modes. We measured additional non-resonant PE spectra at several different laser wavelengths (Fig. 6.10 in Section 6.6). These spectra agree with the previous SEVI spectra. The near threshold spectrum (Fig. 6.10a) has a peak width of 1.5 meV mainly due to rotational broadening, yielding an EA of 2.3535(6) eV (18,982 ± 5 cm^{-1}).

To search for the DBS, we measured the photodetachment spectrum of $C_6H_5S^-$ from below the detachment threshold up to ~1,500 cm^{-1} above threshold, as shown in Fig. 6.5. We indeed found a DBS for $C_6H_5S^-$, as revealed by the resonant peaks on top of the
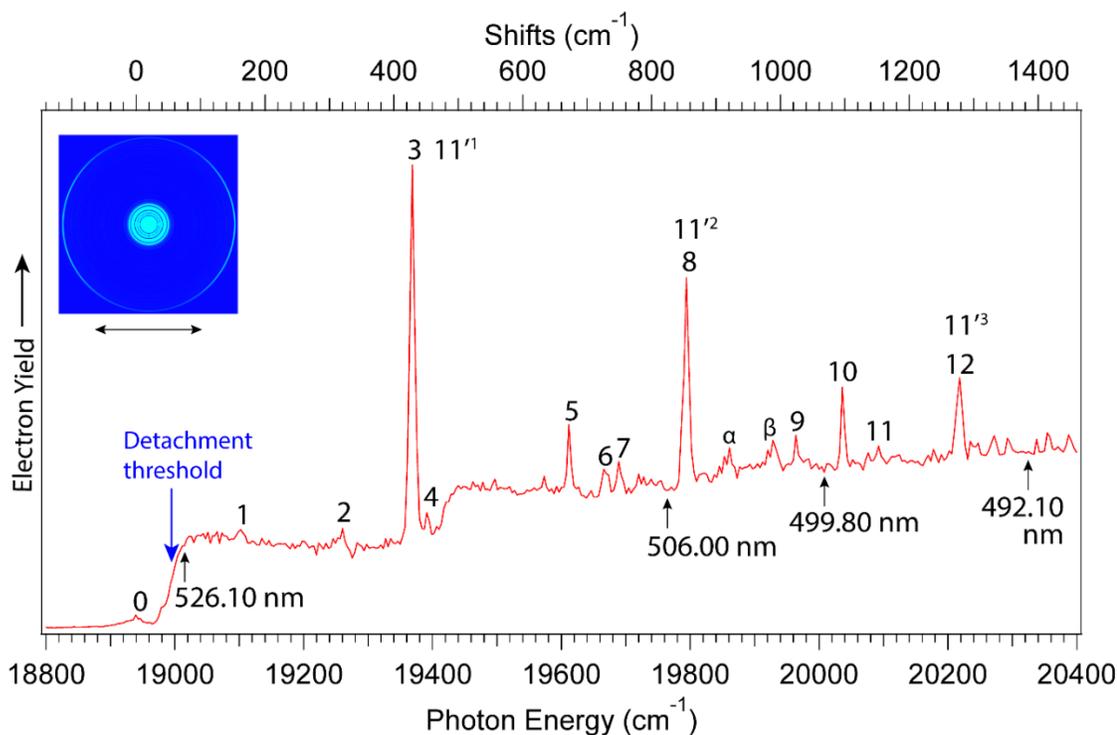
Figure 6.5. Photodetachment spectrum of $C_6H_5S^-$. It was done by measuring the total electron yield as a function of photon energy across the detachment threshold. The down-pointing arrow at 18,982 cm^{-1} marks the detachment threshold. The four up-pointing arrows pointing at the baseline indicate the detachment photon energies used in the non-resonant spectra presented in Fig. 6.10a−d. The peak 0 below threshold represents the vibrational ground state of the DBS of $C_6H_5S^-$. It is due to resonant two-photon detachment, corresponding to the outmost ring in the inset. The double arrow below the inset image indicates the direction of the laser polarization. The assignments of peaks **3**, **8**, and **12** to the vibrational progression of mode ν_{11}' are given.

continuous detachment signals (**1−12**). The down-pointing arrow indicates the detachment threshold at 18,982 cm^{-1}. It is interesting to note that the non-resonant detachment cross section of $C_6H_5S^-$ seems to be significantly higher than that of $C_6H_5O^-$ (Fig. 6.2). The four up-pointing arrows indicate the wavelengths used to take the non-resonant photoelectron spectra in Fig. 6.10. The twelve peaks, labeled as **1−12**, correspond to resonant excitations to vibrational levels of the DBS of $C_6H_5S^-$ followed by autodetachment, while peaks α and β exhibit a strong threshold enhancement (see below).[57] The weak below-threshold peak **0** at an excitation energy of 18,943 cm^{-1} came from resonant two-photon detachment, as revealed by the PE image in the inset of Fig. 6.5. This peak is 39 cm^{-1} below the detachment threshold, defining the binding energy of the DBS. This value is smaller than the 97 cm^{-1} binding energy of the DBS in $C_6H_5O^-$, as expected from the smaller dipole moment of C_6H_5S (3.2 D, see Section 6.4.2 below) than that of C_6H_5O (4.1 D). The outmost ring in the inset of Fig. 6.5 is the resonant two-photon detachment signal from the DBS ground state and the *p*-wave character of the image is consistent with the *s*-like orbital of the DBS, as also observed in $C_6H_5O^-$ and other anions.[117-120,164,386]

The photon energies, shifts from the ground vibrational level of the DBS and assignments of the vibrational resonances observed in Fig. 6.5 are given in Table 6.3. The assignments are all based on the resonant photoelectron spectra in Figs. 6.6 and the calculated vibrational frequencies presented in Table 6.6 in Section 6.6.

Table 6.3. Assignments of the observed resonances in the photodetachment spectrum of $C_6H_5S^-$.

Peak	Wavelength (nm)	Photon Energy $(cm^{-1})^a$	Shift (cm^{-1})	Assignment
0	527.90	18943(5)		Ground state
1	523.53	19101(5)	158	$20'^1$
2	519.22	19260(5)	317	$20'^2$
3	516.33	19367(5)	424	$11'^1$
4	515.68	19392(5)	449	$19'^1$
5	509.91	19611(5)	668	$18'^1$
6	508.51	19665(5)	722	$10'^1$
7	507.92	19688(5)	745	$11'^1 20'^2$
8	505.25	19792(5)	849	$11'^2$
9	500.91	19964(5)	1021	$8'^1$
10	499.10	20036(5)	1093	$11'^1 18'^1$
11	497.72	20092(5)	1149	$10'^1 11'^1$
12	494.64	20217(5)	1274	$11'^3$
α	503.55	19859(5)	916	Threshold enhancement
β	501.84	19927(5)	984	Threshold enhancement

^{a}Numbers in parentheses indicate the experimental uncertainties in the last digit.

6.3.5 Resonant photoelectron images and spectra of $C_6H_5S^-$

The resonant photoelectron images and spectra of $C_6H_5S^-$ are presented in Fig. 6.6. Similar to $C_6H_5O^-$, the resonant spectra, comprising of non-resonant detachment signals and resonant autodetachment signals, are highly non-Franck-Condon compared with the non-resonant spectra in Fig. 6.10 in Section 6.6 due to the mode selectivity and the $\Delta v = -1$ propensity rule. Except for the spectra in Figs. 6.6g, j and k, which involve autodetachment from combinational vibrational levels of the DBS, most of the resonant photoelectron spectra are from vibrational levels of single modes. The assignments of the enhanced vibrational peaks are given in bold face. As can be seen in Fig. 6.5, the non-resonant detachment cross sections of $C_6H_5S^-$ are relatively high. Hence, some of the resonant enhancement in the resonant spectra of $C_6H_5S^-$ are not as dramatic as those in $C_6H_5O^-$. The resonant spectra corresponding to peaks α and β in Fig. 6.5 are displayed in

Fig. 6.7 and there seem to be a strong threshold effect. All the observed peaks in the photoelectron spectra, their binding energies, shifts from the 0_0^0 transition and assignments are summarized in Table 6.4.
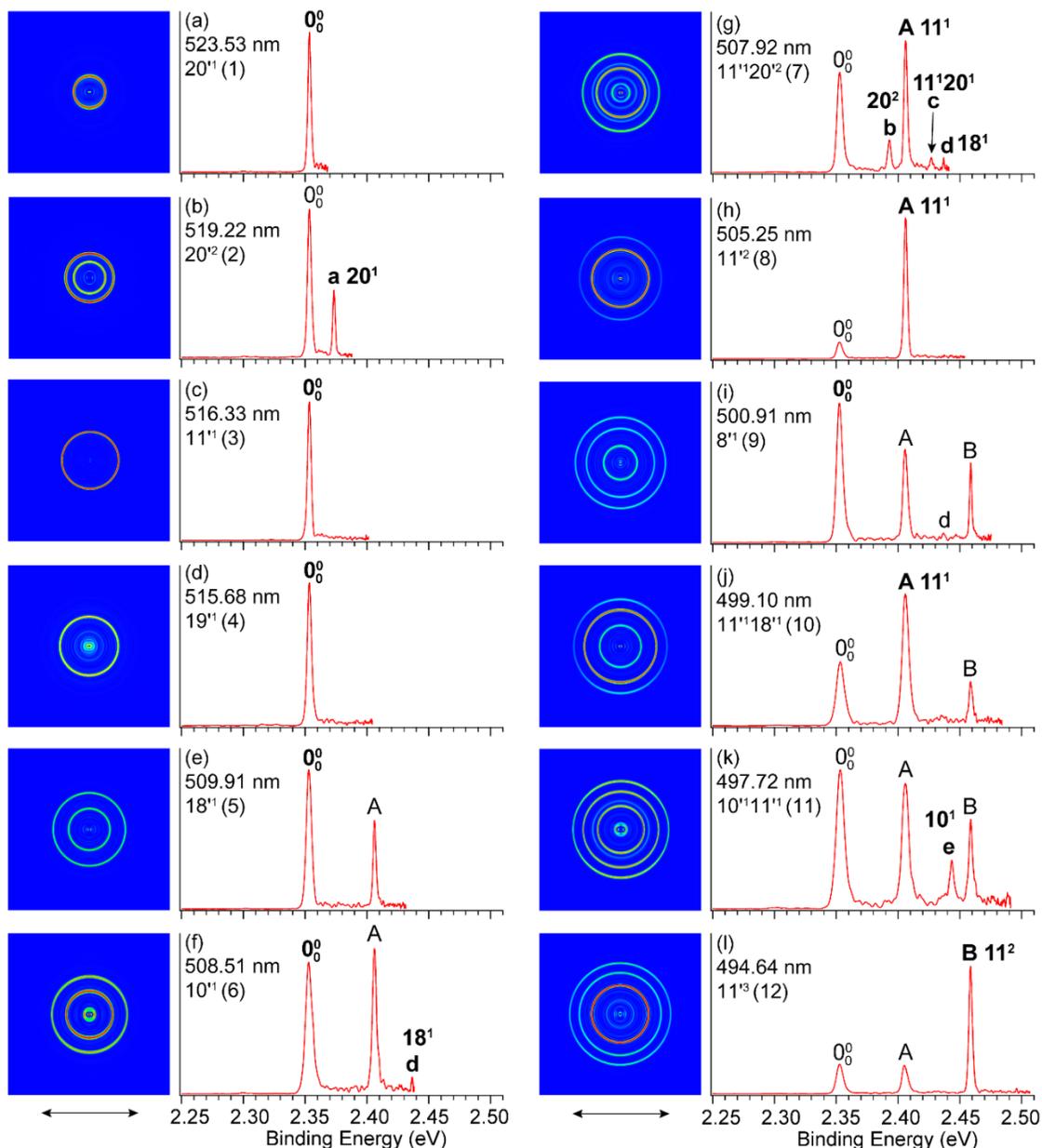
Figure 6.6. Resonant photoelectron images and spectra of $C_6H_5S^-$ at twelve wavelengths. They correspond to peaks **1-12** (in parentheses) in Fig. 6.5. The autodetachment-enhanced peaks are labeled in bold face. And the assigned vibrational levels of DBS are also given. The double arrows below the images indicate the direction of the laser polarization.
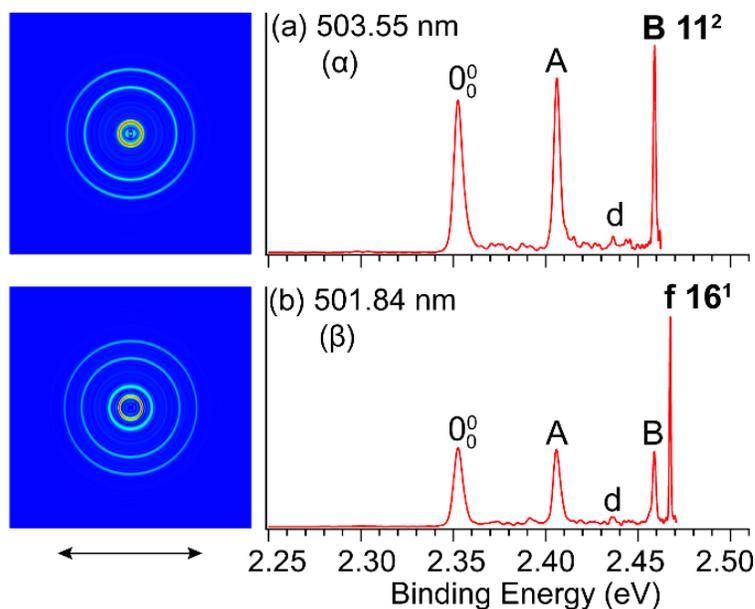
Figure 6.7. Photoelectron images and spectra of $C_6H_5S^-$ at 503.55 nm and 501.84 nm. They correspond to the peaks α and β in Fig. 6.5. The enhanced peaks B (11^2) and f (16^1) are due to threshold enhancement,[57] rather than the autodetachment enhancement via DBS. The double arrow below the images indicates the directions of the laser polarization.

Table 6.4. Summary of the observed vibrational peaks in the photoelectron spectra of $C_6H_5S^-$. Their binding energies (BE), shifts from the 0-0 transition, and assignments are given. The theoretical frequencies of the fundamental vibrational modes of C_6H_5S radical at the B3LYP/6-311++G(d,p) level of theory are also given (see Table 6.6 in Section 6.6 for a full list).

Peak	BE (eV)[a]	Shift (cm^{-1})	Assignment	Theo. freq. (cm^{-1})
0_0^0	2.3535(6)	0	Neutral ground state	
A	2.4058(6)	422	11^1	427
B	2.4587(6)	848	11^2	
C	2.5109(6)	1269	11^3	
a	2.3733(8)	160	20^1	161
b	2.3929(8)	318	20^2	
c	2.4274(10)	596	$11^1 20^1$	
d	2.4362(10)	667	18^1	683
e	2.4435(10)	726	10^1	730
f	2.4678(6)	922	16^1	937

[a]Numbers in parentheses indicate the experimental uncertainties in the last digit.

6.4 Discussion

6.4.1 Non-resonant photoelectron spectra of $C_6H_5O^-$

The vibrational peaks shown in the non-resonant photoelectron spectra in Fig. 6.1 are governed by the Franck-Condon principle, i.e., only symmetry-allowed modes with significant Franck-Condon activities can be observed. To assist the spectral assignments of the numerous non-Franck-Condon vibrational modes observed in the resonant PE spectra, we calculated the harmonic frequencies of the ground electronic state of C_6H_5O (X^2B_1) and C_6H_5S (X^2B_1) at the B3LYP/6-311++G(d,p) level of theory with the Gaussian 09 package.[252] The frequencies of the excited state for C_6H_5O (A^2B_2) were calculated using the time-dependent density function theory at the same level. These computed frequencies are given in Table 6.6 in Section 6.6.

As reported previously,[117,370,371] peaks A-E in Fig. 6.1 represent the vibrational progression of the most Franck-Condon-active mode v_{11} with a measured frequency of 519 cm^{-1}, which involves an in-plane ring stretching (Table 6.7 in Section 6.6). At 354.7 nm, peaks F-J at higher binding energies represent the excited state of C_6H_5O (A^2B_2), which was observed in a previous low resolution photoelectron spectrum at 1.06(5) eV above the ground state.[370] Peak F at 3.2056 eV is the 0_0^0 transition to the excited state, defining a more accurate excitation energy of 0.9524(20) eV above the ground state, in agreement with the value measured previously in the cavity ringdown experiment.[375] Peaks F, G, H, and J represent the vibrational progression of the ring-stretching v_{11} mode with a spacing of 519 cm^{-1}, the same as that of the ground state. Peak I is from a different vibrational mode with a frequency of 1,240 cm^{-1}. Our calculation shows two A_1 modes v_6 (1319 cm^{-1}) and v_7 (1199 cm^{-1}) close to the 1240 cm^{-1} experimental frequency. Previous

high-level calculations reported scaled frequencies of 1201-1252 cm^{-1} for v_6 and 1143-1154 cm^{-1} for v_7.[374] Hence, we tentatively assign peak I to the fundamental mode v_6 of the excited state of C_6H_5O (A^2B_2). This mode involves the C-O stretching, as shown in Table 6.7 in Section 6.6.

6.4.2 Photodetachment spectra of $C_6H_5O^-$ and $C_6H_5S^-$

The vibrational resonances in $C_6H_5O^-$ were first observed serendipitously using our room temperature ion trap.[15] With the cryogenically-controlled ion trap, we examined these resonances more carefully and observed the mode-selectivity in the first resonant PE spectra via vibrational autodetachment.[117] Eight DBS resonances including the progression of mode v_{11}' up to the third quantum were probed then. The binding energy of the DBS was found to be 97 cm^{-1}, but the photodetachment spectrum was not continuously scanned. In the current work, the full photodetachment spectrum of $C_6H_5O^-$ is obtained up to ~2,600 cm^{-1} above the detachment threshold, as shown in Fig. 6.2. Apart from the previously reported DBS resonances labeled in red color, nine more vibrational resonances are observed and labeled in black color in the new photodetachment spectrum (Fig. 6.2). As shown previously,[95,118-121,164,386] all the resonances display the asymmetric Fano line shapes as expected,[387] due to the interference between the non-resonant direct detachment and the resonant autodetachment. The vibrational progression of mode v_{11}' is observed up to the fifth quantum in Fig. 6.2. We found previously that the vibrational frequencies of the v_{11}' mode in the DBS of $C_6H_5O^-$ was the same as the v_{11} mode in neutral C_6H_5O within our experimental accuracy (the ' was used to designate the DBS vibrational modes), consistent with the fact that the highly diffuse dipole-bound electron has no effect on the structure of the molecular core. This is further verified by the perfect

match of the frequencies and relative intensities of almost all the vibrational peaks between the non-resonant photoelectron spectrum and the photodetachment spectrum (see Fig. 6.11 in Section 6.6).

We estimated the dipole moment of C_6H_5S to be 3.2 D at the B3LYP/6-311++G(d, p) level of theory. Hence, the $C_6H_5S^-$ anion should also be able to support a DBS, which is indicated by the vibrational resonances in the photodetachment spectrum in Fig. 6.5. With a smaller dipole moment compared to that of C_6H_5O (4.1 D),[117] the binding energy for the DBS of $C_6H_5S^-$ is also expected to be smaller, as indicated by the peak 0 in Fig. 6.5, which is measured to be 39 cm^{-1} below the detachment threshold. This peak represents the ground vibrational level of the DBS, which is confirmed by the resonant two-photon detachment image (inset in Fig. 6.5). This is further verified by the similarity of the non-resonant photoelectron spectrum at 492.10 nm and the photodetachment spectrum of $C_6H_5S^-$, as shown in Fig. 6.12 in Section 6.6.

In addition, more vibrational peaks, which are absent in the non-resonant PE spectra, are observed in the photodetachment spectra (see Figs. 6.11 and 6.12 in Section 6.6). The relative intensities of the v_{11} progression between the photodetachment spectra and the photoelectron spectra obey the Franck-Condon principle for both systems. However, the resonant excitations to the DBS allow some vibrational levels with low or negligible Franck-Condon factors in the photoelectron spectra to be observed in the photodetachment spectra. Therefore, richer and more accurate vibrational information for the C_6H_5O and C_6H_5S radicals can be obtained from the photodetachment spectra in Figs. 6.2 and 6.5, as well as the resonant photoelectron spectra. The assignments of the observed vibrational resonances given in Tables 6.2 and 6.3 are all based on the resonant

photoelectron spectra presented in Figs. 6.3, 6.4, 6.6, and 6.7 along with the calculated vibrational frequencies given in Table 6.6 in Section 6.6. The schematic energy level diagrams showing autodetachment from the vibrational levels of the DBS to the neutral states are presented in Figs. 6.8 and 6.9 for $C_6H_5O^-$ and $C_6H_5S^-$, respectively.
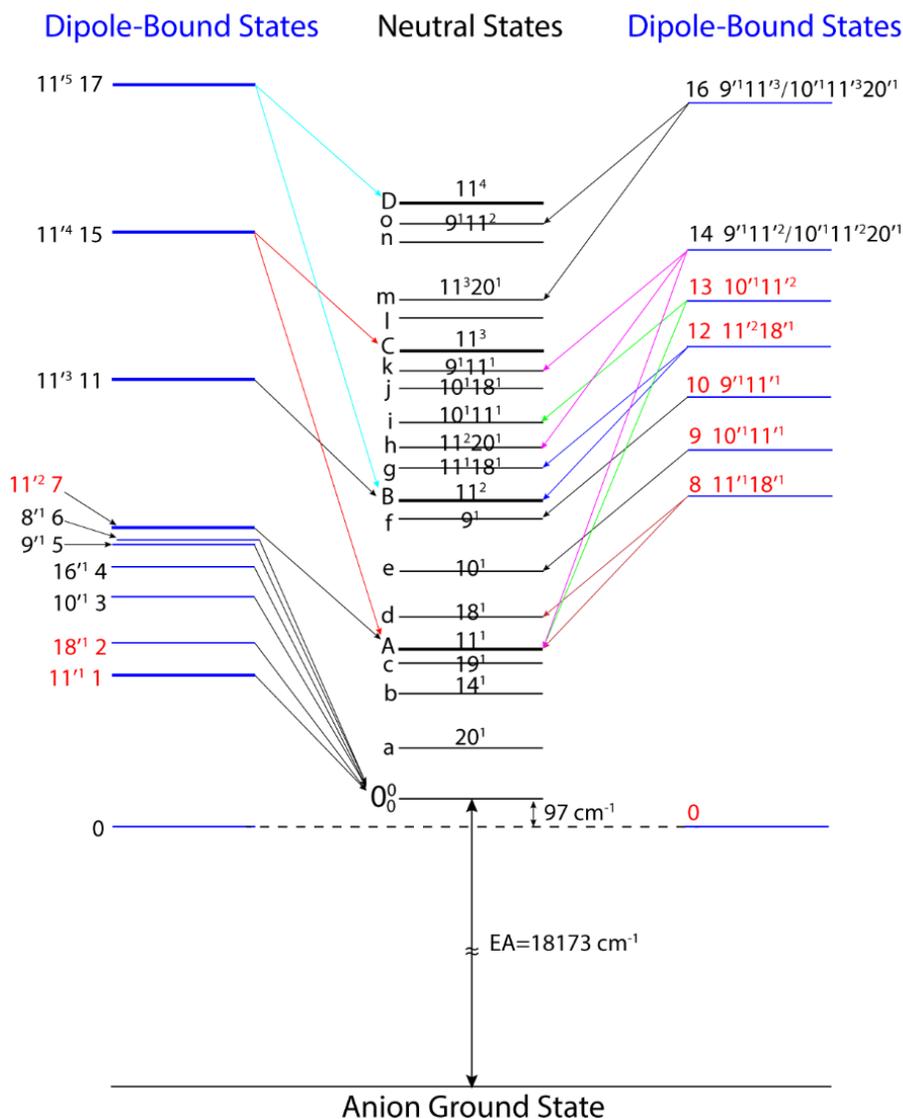
Figure 6.8. Schematic energy level diagram for autodetachment from the DBS vibrational levels of $C_6H_5O^-$ to the neutral final states of C_6H_5O. The single-mode vibrational levels of the DBS are given on the left with arrows indicating the autodetachment. The combinational and overlapping vibrational levels of the DBS are given on the right. The vibrational progressions of mode v_{11} in the DBS and neutral states are highlighted in bold face. The detachment threshold (18,173 cm^{-1}) and the DBS binding energy (97 cm^{-1}) of $C_6H_5O^-$ are also given. The peaks and assignments in red color were reported previously.[117] The assignments of the final neutral states and the DBS levels are given in Tables 6.1 and 6.2, respectively.
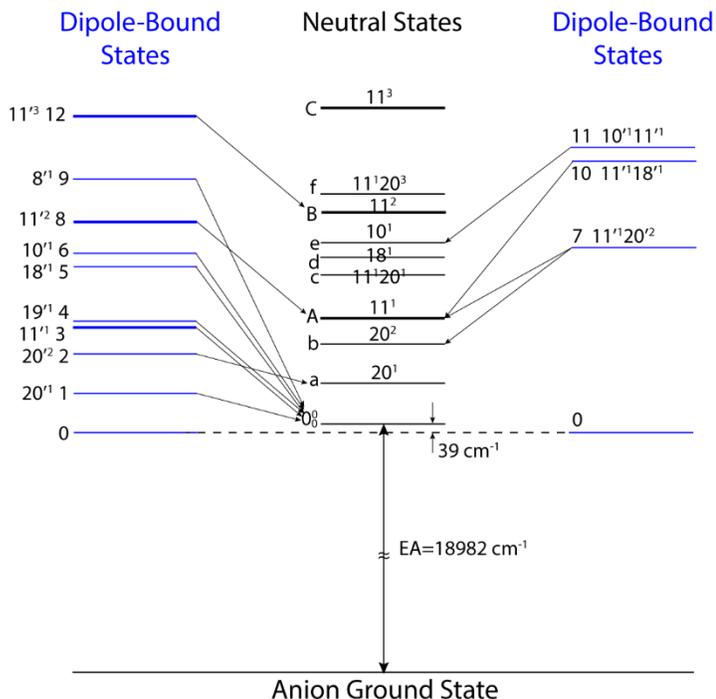
Figure 6.9. Schematic energy level diagram for autodetachment from the DBS vibrational levels of $C_6H_5S^-$ to the neutral final states of C_6H_5S. The single-mode vibrational levels of the DBS are given on the left with arrows indicating the autodetachment. The combinational vibrational levels of the DBS are given on the right. The vibrational progressions of mode v_{11} in the DBS and neutral states are highlighted in bold face. The detachment threshold (18,982 cm^{-1}) and the DBS binding energy (39 cm^{-1}) of $C_6H_5S^-$ are also given. The assignments of the DBS levels and the final neutral states are given in Tables 6.3 and 6.4, respectively.

6.4.3 Resonant PES of $C_6H_5O^-$ via vibrational autodetachment from the DBS

As shown previously,[117-121,164,386] autodetachment from the vibrational levels of the DBS to final neutral states exhibits mode selectivity and obeys the $\Delta v = -1$ propensity rule under the harmonic approximation.[189,190] For autodetachment involving vibrational levels of a single mode (v'_x), the nth vibrational level of this mode (v'^n_x) in the DBS autodetaches to the $(n-1)$th level of the same mode in the neutral (v^{n-1}_x), in which one quantum of vibrational energy is coupled to the dipole-bound electron. For autodetachment from a combinational vibrational level ($v'^m_x v'^n_y \ldots$) of the DBS, the final neutral level can be either $v^{m-1}_x v^n_y \ldots$ or $v^m_x v^{n-1}_y \ldots$ (mode selectivity), provided the

vibrational frequencies are all larger than the binding energy of the DBS. Hence, relative peak intensities of these final neutral vibrational levels will be enhanced in comparison to those in non-resonant photoelectron spectra, giving rise to highly non-Franck-Condon resonant photoelectron spectra. It has also been shown that certain modes in the combinational levels have stronger couplings with the dipole-bound electron.[117]

Tuning the detachment laser to the seventeen resonances in Fig. 6.2 will result in seventeen resonant photoelectron spectra for $C_6H_5O^-$. The resonant spectra obtained for peaks **1**, **2** and **7−12** were reported previously.[117] As can be seen in Fig. 6.2, these resonances are relatively strong, which was why they were found previously without systematic wave length scans.[15,117] The nine new resonant photoelectron spectra presented in Figs. 6.3 and 6.4 are discussed in detail here.

Figure 6.3a at 527.00 nm is from the weak resonant peak **4** (Fig. 6.2). As shown previously,[117] peaks d and e are due to the 18^1 and 10^1 final vibrational states, which have negligible Franck-Condon factors (Fig. 6.1), but they are very intense in Fig. 6.3a mainly due to threshold enhancement,[57] in particular for peak e. The photon energy used in Fig. 6.3a agrees with the excitation to the $16'^1$ DBS level (Table 6.2), which should show an enhancement of the 0_0^0 transition relative to peak A (11^1). However, this enhancement is not very obvious, probably due to the fact that peak A also displays some threshold enhancement. Figs. 6.3d and f correspond to resonant excitations to $11'^4$ and $11'^5$ of the DBS, respectively, resulting in strong enhancement of 11^3 (C) and 11^4 (D), following the $\Delta v = -1$ propensity rule. However, peak A (11^1) is also significantly enhanced in Fig. 6.3d, as well as peak B (11^2) in Fig. 6.3f. These enhancements are surprising, which indicate $\Delta v = -3$ for the autodetachment, i.e., coupling of three quanta of the v_{11}' mode to

the dipole-bound electron to induce autodetachment. These deviations from the $\Delta v = -1$ propensity rule are due to anharmonic effects at higher vibrational levels, which have been observed previously.[118,121,164,386] It is interesting to note that $\Delta v = -2$ does not seem to occur for this mode. This vibrational level dependence of the anharmonic effects is not well understood and deserves further theoretical attention.

In Fig. 6.3b, peak A (11^1) is slightly enhanced and peak i ($10^1 11^1$) is greatly enhanced, suggesting that the resonant peak **13** corresponds to a combinational DBS level of $10'^1 11'^2$. However, it is surprising that the 11^2 final state, involving coupling of one quantum of the v_{10}' mode, is not enhanced, whereas the slight enhancement of the 11^1 final state would require the coupling of one quantum of the v_{11}' mode and one quantum of the v_{10}' mode. We also observed previously that the v_{10}' mode does not seem to couple to the dipole-bound electron in the resonant excitation to the $10'^1 11'^1$ DBS level.[117] In Fig. 6.3c, the enhancements of three peaks, A (11^1), h ($11^2 20^1$) and k ($9^1 11^1$), are due to autodetachment from two degenerate combinational DBS levels, $9'^1 11'^2$ and $10'^1 11'^2 20'^1$. The same case is observed in Fig. 6.3e, where the excitations to combinational vibrational levels of $9'^1 11'^3$ and $10'^1 11'^3 20'^1$ give the enhancement of peak o ($9^1 11^2$) and peak m ($11'^3 20^1$), respectively. Only one peak getting enhanced in each combinational level indicates the selectivity of vibrational mode in the vibronic coupling induced autodetachment, meaning that mode v_{11}' in $9'^1 11'^3$ and mode v_{10}' in $10'^1 11'^3 20'^1$ are favored to couple with the dipole-bound electron, which cause the enhancement of peaks o and m, respectively.

In addition, numerous weak peaks a, b, d, f, g, j, l and n are also observed in Fig. 6.3. The assignments of peaks a, b and j are based on the comparison to the calculated

frequencies in Table 6.6 in Section 6.6. Peak *a* will be discussed below. The weak peak *b* with a shift of 365 cm^{-1} is assigned to the mode v_{14} (calculated frequency 375 cm^{-1}), which is an out-of-plane bending mode as shown in Table 6.7 in Section 6.6. Peak *j* shifted by 1,425 cm^{-1} from peak 0_0^0 is assigned to a combinational vibrational level of $10^1 18^1$ with the frequencies measured to be 790 cm^{-1} for v_{10} and 632 cm^{-1} for v_{18}.[117] The other peaks were reported preiously.[117] All the observed peaks, their binding energies, shifts and the assignments are summarized in Table 6.1. The observed vibrational resonances of the DBS and their autodetachment channels for $C_6H_5O^-$ are given schematically in Fig. 6.8.

6.4.4 Intramolecular inelastic rescattering in autodetachment from DBS of $C_6H_5O^-$

Figure 6.4 shows three resonant photoelectron spectra due to autodetachment from three fundamental vibrational levels, $10'^1$, $9'^1$, and $8'^1$ of the DBS of $C_6H_5O^-$. The 0_0^0 peak in all spectra is enhanced, as expected from the $\Delta v = -1$ propensity rule. Interestingly, peak *a* is also observed in these spectra with significant intensities. With a shift of 176 cm^{-1} from the 0_0^0 peak, peak *a* is assigned to the lowest-frequency bending mode v_{20} of C_6H_5O (184 cm^{-1} calculated frequency, Table 6.7 in Section 6.6), which is Franck-Condon-forbidden and absent in the non-resonant photoelectron spectra.[117,371] Excitation of this vibrational state in these resonant photoelectron spectra is attributed to intramolecular inelastic rescattering, which has been observed previously and usually results in excitations of low-frequency and Franck-Condon-forbidden vibrational modes.[119,121,164] The idea is that the outgoing autodetached electron from the DBS can interact with the neutral core to cause excitations of the low-frequency vibrations. The rescattering process is similar to electron energy loss spectroscopy,[388,389] in which

electrons with fixed kinetic energies cause vibrational excitations of surface adsorbates or gaseous molecules via electronic to vibrational energy transfers. In the current cases, autodetachment from vibrational levels $10'^1$ (794 cm^{-1}), $9'^1$ (977 cm^{-1}) and $8'^1$ (993 cm^{-1}) results in the outgoing photoelectrons with kinetic energies of 697 cm^{-1}, 880 cm^{-1}, and 896 cm^{-1}, respectively. Some of the outgoing electrons are rescattered inelastically by the neutral core and excite the v_{20} vibrational mode. In fact, the photoelectron kinetic energies in these three cases are all higher than the calculated frequencies of several other bending modes, i.e., v_{14} (375 cm^{-1}), v_{30} (446 cm^{-1}), v_{19} (474 cm^{-1}), v_{29} (597 cm^{-1}) and v_{18} (642 cm^{-1}). Some of these modes are indeed excited, such as peak d due to the v_{18} mode or peak b (v_{14}) and c (v_{19}) in Fig. 6.4c (Table 6.1), but mode v_{20} exhibits the strongest rescattering effect.

Vibronic coupling or Herzberg-Teller coupling has been invoked previously to explain observations of Franck-Condon-inactive vibrational modes or anomalous vibrational intensities in PES.[116,390] While we cannot rule out the effects of vibronic coupling in the observation of the v_{20} mode, the strong intensity observed in the resonant photoelectron spectra shown in Fig. 6.4 seems to be similar to the inelastic rescattering we observed previously,[119,121,164] as well as that observed in electron-impact induced autodetachment[391] and that in rotationally-resolved photoelectron spectra of NH_3.[392] It appears that the relative intensity of the rescattering depends on the outgoing electron kinetic energies and the relative contribution of the autodetached electrons. For example, no significant v_{20} excitation was observed in any of the resonant spectra from autodetachment of the v_{11}' (519 cm^{-1}) levels of the DBS (Figs. 6.3d and f and in ref. 117), resulting in an outgoing electron with a much smaller kinetic energy of 422 cm^{-1}.

Autodetachment from the $16'^1$ (899 cm^{-1}) level would yield an outgoing electron with a kinetic energy similar to those from $10'^1$, $9'^1$ or $8'^1$. However, the autodetachment contribution to the 0_0^0 transition is very small (Fig. 6.3a), consistent with the very weak v_{20} excitation according to the rescattering model.

6.4.5 Resonant PES of $C_6H_5S^-$

Similar to the resonant photoelectron spectra of $C_6H_5O^-$, twelve resonant spectra are obtained for $C_6H_5S^-$ (Fig. 6.6), by tuning the detachment laser to the twelve resonances in Fig. 6.5. The non-resonant photoelectron spectra of $C_6H_5S^-$ are very simple, showing a progression of the v_{11} mode only (Fig. 6.10 in Section 6.6).[371] The resonant spectra of $C_6H_5S^-$ are also quite simple, and some of the expected enhancements are not very prominent. Figs. 6.6a, c and d, corresponding to resonances **1**, **3** and **4** in Fig. 6.5, only show the single 0_0^0 peak, suggesting excitations to fundamental vibrational levels of $20'^1$, $11'^1$, and $19'^1$ of the DBS, respectively, following the $\Delta v = -1$ vibrational autodetachment propensity rule. Figs. 6.6e, f and i correspond to excitations to the $18'^1$, $10'^1$ and $8'^1$ DBS levels, respectively, according to the computed frequencies (Table 6.6 in Section 6.6). However, the enhancement of peak 0_0^0 relative to peak A in these resonant photoelectron spectra is not so obvious, probably because there may also be a slight near-threshold enhancement of peak A. In Figs. 6.6b, h and l, peaks a (20^1), A (11^1) and B (11^2) are greatly enhanced, respectively. These spectra correspond to excitations to the $20'^2$, $11'^2$, and $11'^3$ DBS levels, respectively, following straightforwardly the $\Delta v = -1$ propensity rule. The peak a in Fig. 6.6b with a shift of 160 cm^{-1} from the 0_0^0 peak is due to the lowest-frequency bending mode v_{20} of C_6H_5S, which has a calculated frequency of 161 cm^{-1} (Tables 6.6 and 6.7 in Section 6.6).

The remaining resonant photoelectron spectra in Figs. 6.6g, j and k all involve autodetachment from combinational vibrational levels of the DBS of $C_6H_5S^-$. The enhancement of peak A (11^1) in Fig. 6.6j and peak e (10^1) in Fig. 6.6k are due to autodetachment from combinational levels of $11'^118'^1$ and $10'^111'^1$, respectively. Clearly, one vibrational mode is more favored to couple with the dipole-bound electron during autodetachment, i.e., mode v_{18}' in $11'^118'^1$ and mode v_{11}' in $10'^111'^1$, resulting in the significantly enhanced peak A (11^1) and peak e (10^1). Such mode-selectivity in the autodetachment processes involving combinational vibrational levels is observed previoouly,[117-119,121,164,386] as well as above for $C_6H_5O^-$. Finally, Fig. 6.6g shows three enhanced peaks, b (20^2), A (11^1), and c (11^120^1), implying autodetachment from a combinational level of $11'^120'^2$. The autodetachment to peak b and c follows the $\Delta v = -1$ rule, but autodetachment to peak A (11^1) would involve $\Delta v = -2$ in the bending mode v_{20}'. A weak peak d is also observed in Fig. 6.6g with a shift of 667 cm^{-1} from the 0_0^0 peak, consistent with the excitation of v_{18} (computed frequency of 683 cm^{-1}, Table 6.6 in Section 6.6). Peak d is likely due to a threshold effect, which is in fact also observed near the threshold in Fig. 6.6f.

All the observed vibrational resonances of the DBS and their autodetachment channels for $C_6H_5S^-$ are schematically shown in Fig. 6.9.

6.4.6 Near-threshold resonances of $C_6H_5S^-$

Figure 6.7 shows the photoelectron spectra of $C_6H_5S^-$ taken at the photon energies corresponding to the weak resonant peaks α and β in Fig. 6.5. Peak B in Fig. 6.7a is the 11^2 vibrational level of C_6H_5S. The photon energy of peak α is 916 cm^{-1} above the ground state of the DBS, but 916 cm^{-1} does not correspond to any combinational levels of $v_{11}'^2$.

Hence, the enhanced 11^2 peak seems to be a near-threshold effect. Similarly, peak f in Fig. 6.7b also seems to be due to a near-threshold enhancement. Peak f is at 922 cm^{-1} relative to the 0_0^0 peak and corresponds to 16^1 (computed frequency of v_{16} is 937 cm^{-1}, Table 6.6 in Section 6.6), which is not present in the non-resonant photoelectron spectra (Fig. 6.10 in Section 6.6). The photon energy of peak β is 984 cm^{-1} above the DBS ground state of $C_6H_5S^-$, but 984 cm^{-1} does not correspond to any combination level of $v_{16}'^1$. According to the Wigner threshold law,[57] s-wave detachment channels from p-type orbitals should have significant intensities near the detachment threshold. As shown in Fig. 6.13 in Section 6.6, the HOMO of $C_6H_5S^-$ is a p-type delocalized π orbital. And the detachment from the HOMO results in an $s + d$ angular distribution,[371] as also shown in the current non-resonant photoelectron spectra.

However, in the vicinity of the 11^1 detachment channel near 19,420 cm^{-1} (Fig. 6.5), a step was observed, also consistent with the expected threshold behavior for s-wave detachment, rather than a peak as observed in the case of peak α for the 11^2 detachment channel. Hence, the α peak was most likely due to vibronic coupling.[116,390] The v_{16} mode is an out-of-plane bending mode (Table 6.7 in Section 6.6) and should be Franck-Condon-inactive. Hence, the strong enhancement of the 16^1 peak corresponding to peak β is also most likely due to vibronic coupling.

6.4.7 Photoelectron angular distributions

For one-photon detachment with linearly polarized light, the photoelectron angular distribution (PAD) depends on the symmetry of the orbital where the electron is detached, and is governed by an anisotropy parameter β which varies between −1 and 2.[113,393] The π type HOMOs of $C_6H_5O^-$ and $C_6H_5S^-$ (Fig. 6.13 in Section 6.6) are similar

and are expected to give rise to PADs of $s + d$ characters, in agreement with the observed

β values of $-0.6 \sim -0.3$ in the non-resonant photoelectron spectra.[117,371] The resonant

two-photon detachment from the ground vibrational level of a DBS always gives a

distinct p-wave character,[117-121,164,386] as presented in the inset of Fig. 6.5 for $C_6H_5S^-$,

which indicates an s-type orbital for the DBS. However, autodetachment from the above-

threshold resonances results in isotropic distributions.[117] With contributions from both

direct detachment and vibrational autodetachment via DBS, the enhanced peaks in the

resonant photoelectron spectra can have various PADs depending on the relative ratio of

the two detachment channels. For example, the weakly enhanced peak 0_0^0 in Figs. 6.3a

and 6.4 from autodetachment of resonances **3−6** in Fig. 6.2 has a β value of $-0.5 \sim -0.2$,

close to the value from direct detachment. On the other hand, peak 0_0^0 in Fig. 6.6c, peak

A (11^1) in Fig. 6.6h, and peak B (11^2) in Fig. 6.6l, corresponding to strong resonances of

3, **8**, and **12** in Fig. 6.5, respectively, possess β values of around 0.15 The images are

almost isotropic due to the large contribution from the autodetachment channel.

However, the images of the enhanced peaks i ($10^1 11^1$), m ($11^3 20^1$), and o ($9^1 11^2$)

in Fig. 6.3 for $C_6H_5O^-$ show clear p-wave distributions with β values of $0.5 \sim 0.8$.

Similarly, the images of peaks a (20^1) and d (18^1) in Figs. 6.3a and 6.4 for $C_6H_5O^-$ also

exhibit distinct p-wave distributions. Similar PADs are observed for peaks a (20^1), c

($11^1 20^1$) and d (18^1) with β values of $0.1 \sim 0.3$ in Fig. 6.6 for $C_6H_5S^-$. It turns out that

these peaks all represent out-of-plane bending excitations of C_6H_5O and C_6H_5S (Table

6.7 in Section 6.6). It is understandable that the low-frequency bending modes play

important roles in the PADs for electron ejections. Further studies of these PADs may

gain interesting insights into the vibronic coupling leading to autodetachment from the DBS.

6.4.8 Fundamental vibrational information resolved for C_6H_5O and C_6H_5S

The resemblances between the non-resonant photoelectron spectra and the photodetachment spectra (Figs. 6.11 and 6.12 in Section 6.6) suggest similar geometries of the neutral radicals and the dipole-bound anions, because the weakly dipole-bound electron has little effect on the structure of the neutral core. Since photodetachment spectroscopy has higher spectral resolution, it could be a powerful tool to resolve vibrational information for the neutral radicals with large dipole moment.[95,117-121,164,386] Furthermore, the vibrational features with negligible Franck-Condon factors can be resolved in resonant photoelectron spectra via vibrational autodetachment from DBS. As summarized in Table 6.5, the combination of photodetachment spectroscopy and resonant photoelectron spectra yields five new fundamental vibrational modes for the ground state of the C_6H_5O radical and seven fundamental vibrational modes for the ground state of C_6H_5S. Two vibrational modes, v_{11} and v_6, are also obtained for the excited state (A^2B_2) of C_6H_5O from the non-resonant spectrum at 354.7 nm (Fig. 6.1). The experimental frequencies for the ground states of the two radicals agree well with the theoretical frequencies calculated at both the B3LYP/6-311++G(d,p) level and the B3LYP/aug-cc-pVTZ (scaled by 0.9687 in ref. 371) level of theory. It is interesting to note that the frequencies calculated by the B3LYP/6-311++G(d,p) level have not been scaled. The good agreement with the experimental values suggest the suitability of using B3LYP/6-311++G(d,p) to calculate vibrational frequencies, in particular, the low frequencies of small organic molecules.

Table 6.5. Summary for all the observed fundamental vibrational frequencies of C_6H_5O and C_6H_5S. They are corresponding to the peaks observed from the photodetachment and photoelectron spectroscopy.

	State	Mode[a]	Observed freq. (cm^{-1})[b]	Observed peaks[c]	B3LYP/ 6-311++G(d,p)	B3LYP/aug-cc-pVTZ (scaled by 0.9687)[d]
	$\tilde{X}^2B_1$	v_{20}	176(8)	a	184	182
		v_{14}	365(8)	b	375	369
		v_{19}	471(8)	c	474	466
		v_{11}	519(6)/519(5)	A/1	531	515
		v_{18}	632(6)/632(5)	d/2	642	635
C_6H_5O		**v_{10}**	790(6)/794(5)	e/3	804	782
		v_{16}	899(5)	4	919	906
		v_9	977(5)	5	983	959
		v_8	993(5)	6	1008	979
	$\tilde{A}^2B_2$	v_{11}	519(15)	G	524	501-508[e]
		v_6	1240(15)	I	1319	1201-1252[e]
	$\tilde{X}^2B_1$	v_{20}	160(6)/158(5)	a/1	161	156
		v_{11}	422(6)/424(5)	A/3	427	414
		v_{19}	449(5)	4	463	450
C_6H_5S		v_{18}	667(8)/668(5)	d/5	683	667
		v_{10}	726(8)/722(5)	e/6	730	709
		v_{16}	922(5)	f	937	923
		v_8	1021(5)	9	1038	1009

[a]The modes in bold were reported in a previous study.[117]
[b]Numbers in parentheses indicate the experimental uncertainties in the last digit.
[c]Peaks in letter are observed in the photoelectron spectra and peaks in number are observed in the photodetachment spectra.
[d]The reported fundamental frequencies and the calculated frequencies are from ref. 371.
[e]The calculated frequencies for the C_6H_5O ($\tilde{A}^2B_2$) at various high level of theories are from ref. 374.

6.5 Conclusions

In conclusion, we report an investigation of the photodetachment spectroscopy and resonant photoelectron imaging of cryogenically-cooled $C_6H_5O^-$ and $C_6H_5S^-$ anions via vibrational levels of the dipole-bound states. Nine new DBS vibrational resonances are observed for $C_6H_5O^-$. The dipole-bound excited state is observed for the first time for $C_6H_5S^-$ with a binding energy of only 39 cm^{-1}. Twelve above-threshold vibrational resonances are observed for $C_6H_5S^-$. Resonant photoelectron images and spectra are obtained by tuning the detachment laser to the vibrational levels of the DBS. The observed vibrational features in both the photodetachment spectra and the resonant photoelectron spectra are assigned using the calculated frequencies and the $\Delta v = -1$ propensity rule for vibrational autodetachment from DBS. Five extra fundamental vibrational modes, including three low-frequency modes, are resolved for the ground state of C_6H_5O (X^2B_1). And two fundamental vibrational modes are also resolved for its excited state (A^2B_2). Intramolecular inelastic rescattering has been observed in the autodetachment process leading to the excitation of the lowest-frequency bending mode (v_{20}) of C_6H_5O. Seven fundamental vibrational modes, including several low-frequency modes, are resolved for the ground state of C_6H_5S (X^2B_1), compared to the single v_{11} vibrational progression observed in the non-resonant photoelectron spectra. The combination of photodetachment spectroscopy and resonant photoelectron imaging for cold anions is shown again to be a powerful method to obtain vibrational information of dipolar neutral radicals.

6.6 Supporting information

Table 6.6. Theoretical harmonic frequencies of C_6H_5O (X^2B_1) and C_6H_5S (X^2B_1). The calculations were done with density functional theory at the B3LYP/6-311++G(d,p) level. The harmonic frequencies of C_6H_5O (A^2B_2) are calculated with time-dependent density-functional theory at the same level.

Mode	Symmetry	C_6H_5O (cm^{-1})		C_6H_5S (cm^{-1})
		X^2B_1	A^2B_2	X^2B_1
ν_1	A_1	3199	3208	3202
ν_2		3188	3199	3190
ν_3		3167	3168	3169
ν_4		1585	1624	1595
ν_5		1481	1461	1480
ν_6		1417	1319	1199
ν_7		1166	1199	1077
ν_8		1008	1045	1038
ν_9		983	989	1004
ν_{10}		804	834	730
ν_{11}		531	524	427
ν_{12}	A_2	978	953	990
ν_{13}		797	807	844
ν_{14}		375	434	384
ν_{15}	B_1	977	946	1007
ν_{16}		919	868	937
ν_{17}		787	731	764
ν_{18}		642	654	683
ν_{19}		474	512	463
ν_{20}		184	223	161
ν_{21}	B_2	3196	3207	3199
ν_{22}		3174	3173	3178
ν_{23}		1544	1574	1576
ν_{24}		1442	1458	1458
ν_{25}		1338	1351	1341
ν_{26}		1275	1266	1302
ν_{27}		1165	1182	1179
ν_{28}		1089	1095	1095
ν_{29}		597	623	621
ν_{30}		446	378	299

Table 6.7. The vibrational displacements and frequencies for selected fundamental modes of C_6H_5O (X^2B_1 and A^2B_2) and C_6H_5S (X^2B_1). They were calculated at the B3LYP/6-311++G(d,p) level of theory.

C_6H_5O (X^2B_1)			
v_{20} (B$_1$) = 184 cm^{-1}	v_{19} (B$_1$) = 474 cm^{-1}	v_{18} (B$_1$) = 642 cm^{-1}	v_{16} (B$_1$) = 919 cm^{-1}
v_{14} (A$_2$) = 375 cm^{-1}	v_{11} (A$_1$) = 531 cm^{-1}	v_{10} (A$_1$) = 804 cm^{-1}	v_9 (A$_1$) = 983 cm^{-1}
v_8 (A$_1$) = 1008 cm^{-1}			

C_6H_5O (A^2B_2)			
v_{11} (A$_1$) = 524 cm^{-1}	v_6 (A$_1$) = 1319 cm^{-1}		

C_6H_5S (X^2B_1)			
v_{20} (B$_1$) = 161 cm^{-1}	v_{19} (B$_1$) = 161 cm^{-1}	v_{18} (B$_1$) = 683 cm^{-1}	v_{16} (B$_1$) = 937 cm^{-1}
v_{11} (A$_1$) = 427 cm^{-1}	v_{10} (A$_1$) = 730 cm^{-1}	v_8 (A$_1$) = 1038 cm^{-1}	

Figure 6.10. Non-resonant images and spectra of $C_6H_5S^-$ at five different wavelengths. The double arrow below the images indicates the direction of the laser polarization.
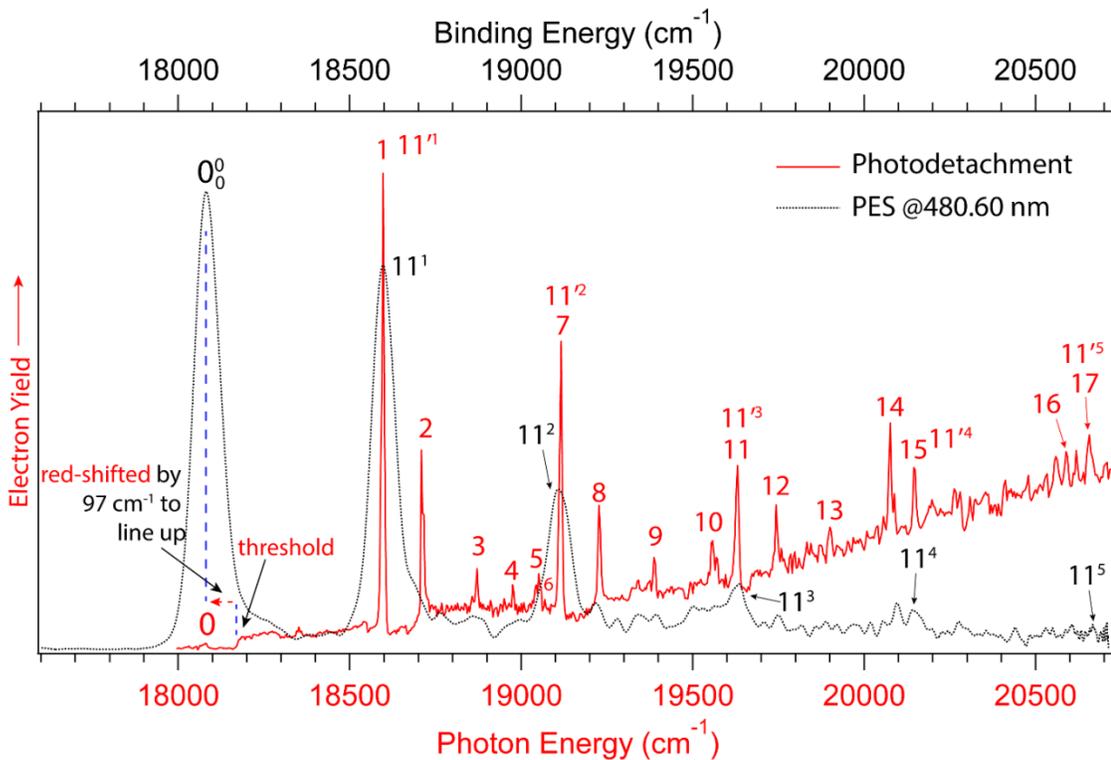
Figure 6.11. Comparison of the non-resonant photoelectron spectrum at 480.60 nm (Fig. 6.1) with the photodetachment spectrum (Fig. 6.2) for $C_6H_5O^-$. The photoelectron spectrum is red-shifted by 97 cm^{-1} to line up the peak 0_0^0 with peak 0 (the ground vibrational level of the neutral C_6H_5O and the DBS of $C_6H_5O^-$). The vibrational progression of mode ν_{11} agrees well with each other, indicating that the weakly bound electron in the DBS of $C_6H_5O^-$ has little effect on the neutral core C_6H_5O.
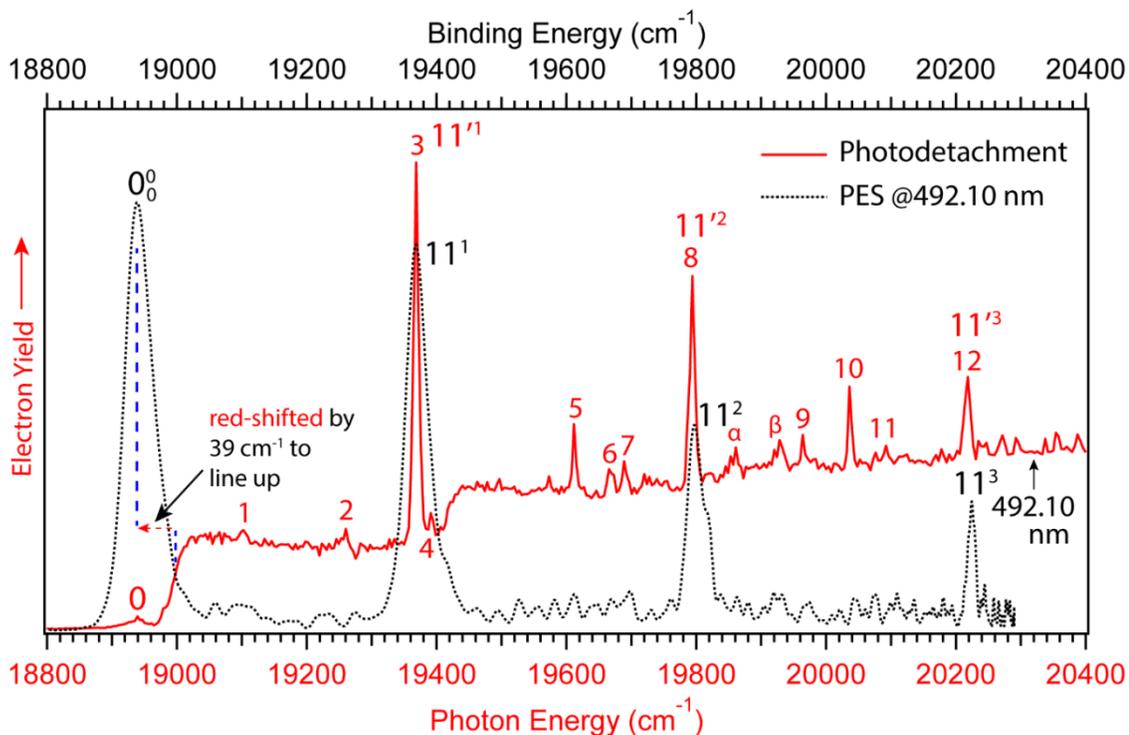
Figure 6.12. Comparison of the non-resonant photoelectron spectrum at 492.10 nm (Fig. 6.10) with the photodetachment spectrum (Fig. 6.5) for $C_6H_5S^-$. The photoelectron spectrum is red-shifted by 39 cm^{-1} to line up the peak 0_0^0 and peak 0 (the ground vibrational level of neutral C_6H_5S and the DBS of $C_6H_5S^-$). The vibrational progression of mode v_{11} agrees well with each other, indicating the weakly bound nature of the DBS electron, which has little effect on the neutral C_6H_5S core.
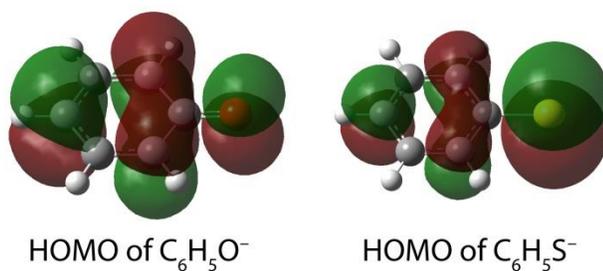
Figure 6.13. The HOMO orbitals of $C_6H_5O^-$ and $C_6H_5S^-$. The calculations were done at the B3LYP/6-311++G(d, p) level of theory.

Chapter 7 Tautomer-specific resonant photoelectron imaging of deprotonated cytosine anions**

This chapter[394] will discuss one of applications of DBS, which is to obtain the tautomer-specific information for deprotonated cytosine anions.

Tautomers of the nucleobases play fundamental roles in spontaneous mutations of DNA. Tautomers of neutral cytosine have been studied in the gas phase, but much less are known about charged species. Here we report the observation and characterization of three tautomers of deprotonated cytosine anions, [trans-keto-amino-N3H-H8b] (**tKAN3H8b⁻**), [cis-keto-amino-N3H–8a] (**cKAN3H8a⁻**) and [keto-amino–H] (**KAN1⁻**), produced by electrospray ionization. Excited dipole-bound states (DBSs) are uncovered for the three anions by photodetachment spectroscopy. Excitations to selected DBS vibrational levels of **cKAN3H8a⁻** and **tKAN3H8b⁻** yield tautomer-specific resonant photoelectron spectra. The current study provides further insight into tautomerism of cytosine and suggests a new method to study the tautomers of nucleobases using electrospray ionization and anion spectroscopy.

7.1 Introduction

As fundamental building blocks of DNA and RNA, nucleic acid bases are involved in the transmission and encoding of genetic information. Tautomerism is crucial to the structure and proper function of DNA because the formation of rare tautomers can cause mismatches in base pairing, resulting in spontaneous mutagenesis.[395,396] The

tautomers of cytosine, one of the pyrimidine bases, have been studied in different environments. Theoretical calculations have shown that the isolated neutral cytosine molecule can adopt six tautomers, as shown in Fig. 7.5 in Supporting Section 7.5, where their relative stabilities in aqueous solution[397] and gas phase[398] are also given. The canonical tautomer of keto-amino-N1H (**KAN1H**) predominantly exists under the physiological condition, and it is the tautomer that forms the Watson-Crick pair with guanine via hydrogen-bonding.[395] The other rare tautomers have been observed by various spectroscopic techniques.[399-405] The effect of water molecules on the structural dynamics and tautomerism of cytosine have also been investigated,[406,407] showing that water can facilitate tautomerization from the canonical form to the rare tautomers by lowering the activation barriers of the prototropic process. The high stability of the keto-amino tautomers in solution derives from their large dipole moment.[397,408] Early thermodynamic and kinetic studies showed that the major **KAN1H** and minor **KAN3H** forms (Fig. 7.5a in Supporting Section 7.5) are in equilibrium in aqueous solution.[409] In addition, various tautomeric forms have also been studied for the radical anion and cation of cytosine, and the protonated cytosine.[410--414]

However, relatively little is known for the deprotonated cytosine anion ([Cy-H]$^-$),[415-417] despite their potential roles in DNA damage. The ionization of DNA bases by low-energy electrons is a crucial process for DNA damage after radiation.[418] Dissociative electron attachment experiment has shown that [Cy-H]$^-$ is the most abundant anion fragment,[419] which can pair with guanine to form anionic complexes.[420] The cytosine tautomers can be deprotonated at different sites to produce a plethora of negative ions (Fig. 7.6 in Supporting Section 7.5). Luo et al.[415] calculated the structures of five

different [Cy-H]⁻ anions deprotonated from the canonical **KAN1H** tautomer and computed the electron affinities (EAs) for the corresponding neutral [Cy-H] radicals. Considering the deprotonation from other rare tautomers and searching for 95 initial structures, Vázquez et al.[416] found that the six most stable [Cy-H]⁻ anions were, in the order of stability, **tKAN3H8b⁻** > **cKAN3H8a⁻** > **KAN1⁻** > **cEAOH8a⁻** > **cKAN1H8a⁻** > **tEAOH8a⁻** (Table 7.1 in Supporting Section 7.5).

For the current study, we recalculated the structures and relative energies of these six anions, as well as a seventh anion **tKAN1H8b⁻** (Fig. 7.1) from deprotonation of **KAN1H**. The computed EAs and dipole moments of their corresponding radicals are presented in Table 7.1. The three most stable [Cy-H]⁻ anions are similar to those by Vázquez et al..[416] It is interesting to note that the most stable anion **tKAN3H8b⁻** is not deprotonated from the canonical **KAN1H** cytosine (Fig. 7.6 in Supporting Section 7.5). Parsons et al.[417] reported a low-resolution photoelectron imaging study on the [Cy-H]⁻ anion produced by a pulsed discharge method. A congested broad band was observed and the spectrum was assigned to be from the **KAN1⁻** anion with a measured EA for the **KAN1** neutral radical as 3.037(15) eV, compared with the theoretical values of 3.00 eV by Lou et al.[415] and 3.37 eV by Vázquez et al.[416] However, no other tautomeric forms of the [Cy-H]⁻ anion have been disclosed.
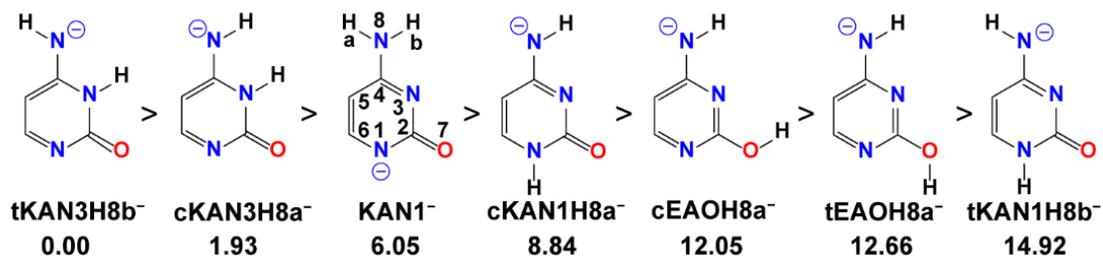
Figure 7.1. The seven most stable tautomers of deprotonated cytosine anions in the gas phase. The values below the structures show the calculated relative stabilities in kcal/mol.

Here we report a high-resolution photoelectron imaging and photodetachment spectroscopy study of [Cy-H]$^-$. Three tautomeric deprotonated cytosine anions, **tKAN3H8b$^-$**, **cKAN3H8a$^-$** and **KAN1$^-$**, have been observed. The photodetachment spectrum shows strong DBS resonances, due to autodetachment from vibrational levels of the excited DBSs of the **tKAN3H8b$^-$** and **cKAN3H8a$^-$** anions. Several weak resonant peaks are tentatively assigned to a third deprotonated anion **KAN1$^-$**, which is expected to have weak ion abundance due to its low stability.

7.2 Experimental methods

The experiments were done using the third-generation ESI-PES apparatus. The details were described in the Chapter 2.

7.3 Results and discussion
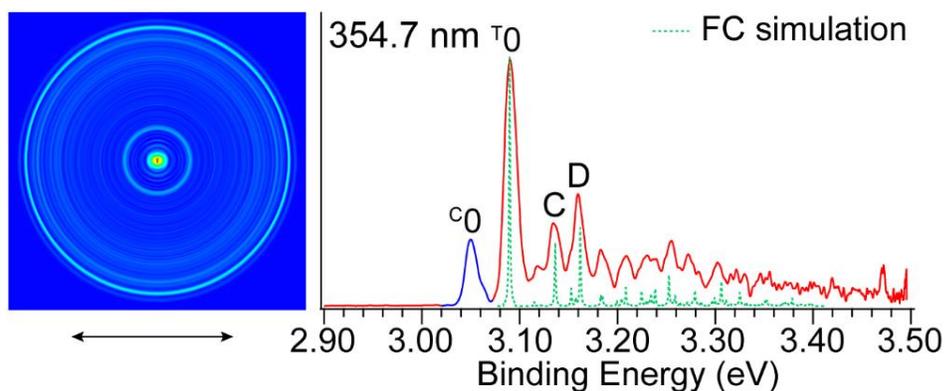
Figure 7.2. Non-resonant photoelectron image and spectrum of [Cy-H]$^-$ at 354.7nm. The peak (^{C}0) is due to detachment from **cKAN3H8a$^-$**, while the peaks above ^{T}0 are from **tKAN3H8b$^-$**. The Franck-Condon (FC) simulation of **tKAN3H8b$^-$** is presented as dot. The double arrow below the image shows the direction of the laser polarization.

Figure 7.2 shows the non-resonant photoelectron image and spectra of [Cy-H]$^-$ at 354.7 nm. The complexity of the vibrational structures suggests possible presence of

different tautomeric anions. To assist the spectral assignments, we have done Franck-Condon simulations for all the seven low-lying anions using the FC-LabII program[421] and compared them with the spectrum. Figure 7.2 shows that the simulated spectrum of **tKAN3H8b**$^-$ is in good agreement with the spectral features at higher binding energies (above the peak ^{T}0), while the simulated spectra of the other anions are not (Fig. 7.7 in Supporting Section 7.5). This means that the peaks at higher binding energies are due to photodetachment from **tKAN3H8b**$^-$, which is the most stable tautomeric anion according to our calculations (Table 7.1 in Supporting Section 7.5) and previous study by Vázquez et al.[416] The peak labeled ^{T}0 defines the EA of the neutral **tKAN3H8b** radical, which is more accurately measured to be 3.0870(5) eV in the near-threshold resonant photoelectron spectra (*vide infra*). The measured EA is in perfect agreement with our computed value for **tKAN3H8b**, which also represents the largest EA among the first seven tautomers (Table 7.1 in Supporting Section 7.5). Peaks C and D, with shifts of 373 cm^{-1} and 575 cm^{-1} from peak ^{T}0, represent the most Franck-Condon-active vibrational modes $^T\nu_{21}$ (376 cm^{-1}) and $^T\nu_{18}$ (583 cm^{-1}) of **tKAN3H8b** (Table 7.2 in Supporting Section 7.5), respectively. Both modes involve in- plane H-atom vibrations (Fig. 7.8b in Supporting Section 7.5). The peak labeled ^{C}0 at the lower binding energy should come from another tautomer, most likely the second most stable **cKAN3H8a**$^-$ species (*vide infra*). The EA of the **cKAN3H8a** radical defined by peak ^{C}0 is measured to be 3.0471(5) eV, which agrees well with our computed value (Table 7.1 in Supporting Section 7.5).

The **cKAN3H8a** and **tKAN3H8b** radicals are calculated to have dipole moments of 3.35 D and 5.55 D (Table 7.1 in Supporting Section 7.5), respectively, which are large enough to support excited DBSs for the corresponding anions. We conducted

photodetachment spectroscopy by monitoring the total electron yield while scanning the laser wavelength across the detachment thresholds, as shown in Fig. 7.3. The arrow (^{C}EA) at 24577 cm^{-1} and the arrow (^{T}EA) at 24898 cm^{-1} indicate the detachment thresholds of **cKAN3H8a**⁻ and **tKAN3H8b**⁻, respectively, which are consistent with the measured EAs from the photoelectron spectra (Fig. 7.2 and 7.4). Around 24300 cm^{-1}, the peaks labeled ^{C}0' and ^{T}0' represent the ground vibrational levels of the DBSs of **cKAN3H8a**⁻ and **tKAN3H8b**⁻, respectively. These peaks are below the respective detachment thresholds by 325 cm^{-1} (^{C}0' below ^{C}EA) and 577 cm^{-1} (^{T}0' below ^{T}EA), representing the binding energies of the DBSs of the two anions. The larger DBS binding energy for **tKAN3H8b**⁻ is consistent with the larger dipole moment of the corresponding neutral **tKAN3H8b** radical. The below-threshold peaks ^{C}0' and ^{T}0' are due to resonant two-photon detachment. The resonant two-photon photoelectron image corresponding to peak ^{T}0' is shown in the inset of Fig. 7.3. The *p*-wave angular distribution of the two-photon signals is consistent with detachment from an *s*-type dipole-bound orbital of **tKAN3H8b**⁻, as observed previously.[117-122] Above ^{C}EA, the peaks ^{C}1 to ^{C}3 correspond to vibrational levels of the DBS of **cKAN3H8a**⁻, as a result of vibrational autodetachment. The peaks ^{T}1 to ^{T}7 represent the DBS vibrational levels of **tKAN3H8b**⁻. The weaker peaks ^{T}1 and ^{T}2 below ^{T}EA are due to resonant two-photon detachment, while the strong peaks ^{T}3 to ^{T}7 are due to autodetachments from vibrational levels of the DBS of **tKAN3H8b**⁻.
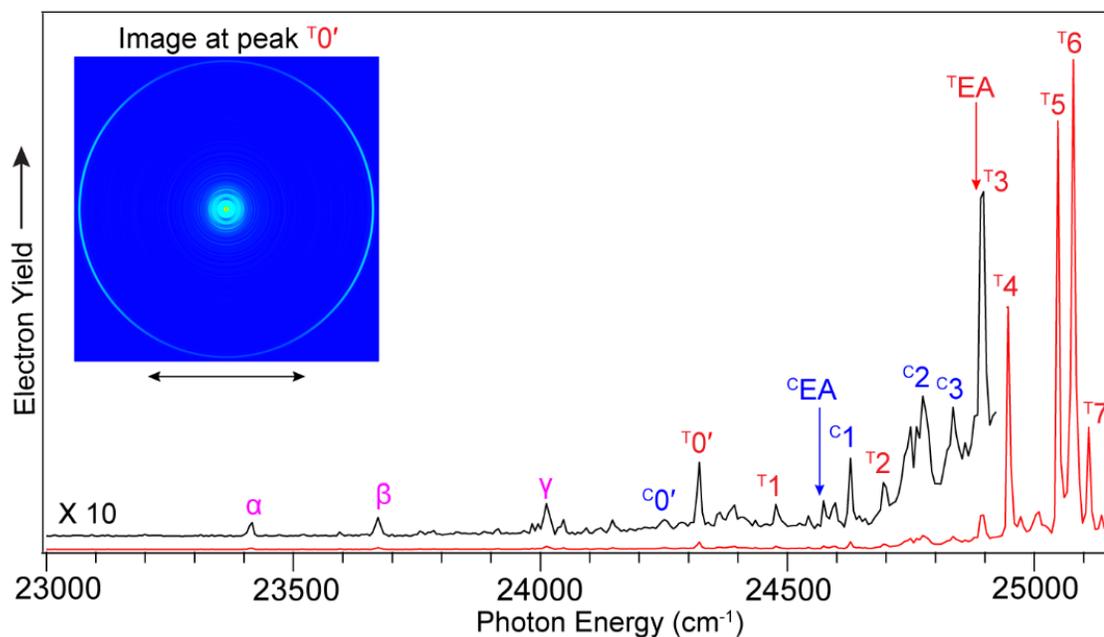
Figure 7.3. The photodetachment spectrum of [Cy-H]⁻. The spectrum was obtained by measuring the total electron yield as a function of photon energy across the detachment thresholds of **cKAN3H8a⁻** and **tKAN3H8b⁻**, indicated by the arrows below ^{C}EA and ^{T}EA, respectively. The curve below 24900 cm⁻¹ is expanded by 10 times. Peaks $^C0'$ and $^T0'$ represent the ground DBS vibrational levels of **cKAN3H8a⁻** and **tKAN3H8b⁻**, respectively. Peaks $^C1$-$^C3$ are due to autodetachment from vibrational levels of the DBS of **cKAN3H8a⁻**, while peaks $^T1$-$^T7$ are from **tKAN3H8b⁻**. Peaks α, β and γ at lower photon energies are assigned to DBS levels of **KAN1⁻**. The outmost ring in the inset shows the photoelectron image obtained with a photon energy corresponding to peak $^T0'$, due to resonant two-photon detachment. The double arrow below the image indicates the direction of the laser polarization.

At even lower photon energies in Fig. 7.3, three weak peaks, labeled as α, β and γ, are also observed, which are not from **cKAN3H8a⁻** or **tKAN3H8b⁻**. They could be from the DBS of the **KAN1⁻** anion, whose neutral core has a very large dipole moment of 7.79 D (Table 7.1 in Supporting Section 7.5). The energy shifts of peaks β and γ relative to peak α are 255 cm⁻¹ and 594 cm⁻¹, respectively. We also calculated the vibrational frequencies of all the other neutral radicals with dipole moments larger than 2.5 D (Table 7.2 in Supporting Section 7.5). The shifts of 255 cm⁻¹ and 594 cm⁻¹ are found to agree well with the fundamental vibrational modes $^{KA}\nu_{28}$ (231 cm⁻¹) and $^{KA}\nu_{22}$ (593 cm⁻¹) of **KAN1**, respectively (Fig. 7.8c in Supporting Section 7.5). This indicates the presence of

a third tautomer in the ion beam (Fig. 7.1). The intensity of the **KAN1⁻** anion is very weak, because of its relatively high energy, so that no clear spectral features are observed for this tautomer in the photoelectron spectra.

The photon-energy shifts from the respective ground vibrational levels of the DBS and assignments of the observed resonances are given in Table 7.3 in Supporting Section 7.5. The assignments of all the resonances are based on the calculated vibrational frequencies (Table 7.2 in Supporting Section 7.5) and vibrational autodetachments in the resonant photoelectron spectra (Figs. 7.4a-h), which yield tautomer-specific information. We have shown previously that vibrational frequencies in the DBS are the same as those in the neutral states,[117-122] i.e., the diffuse dipole-bound electron has little effect on the neutral cores.

By tuning the detachment laser wavelengths to the above-threshold peaks ($^C1$-$^C3$ and $^T3$-$^T7$), we have obtained eight high-resolution resonantly-enhanced photoelectron images and spectra (Figs. 7.4a-h). As discussed previously,[117-122] two detachment channels contribute to the resonant photoelectron spectra: the non-resonant detachment represented by the baseline in Fig. 7.3 and the resonantly-enhanced vibrational autodetachment via the DBS resonances. Autodetachment from DBS vibrational levels generally follows the mode selectivity[117] and $\Delta v = -1$ propensity rule,[189,190] which result in highly non-Franck-Condon photoelectron spectra.

The resonant photoelectron spectra involving autodetachment from vibrational levels of the DBSs of **cKAN3H8a⁻** or **tKAN3H8b⁻** are essentially tautomer-specific because resonant excitations to the DBSs have much higher cross sections than the non-resonant photodetachment processes, which are not tautomer-specific. In comparison
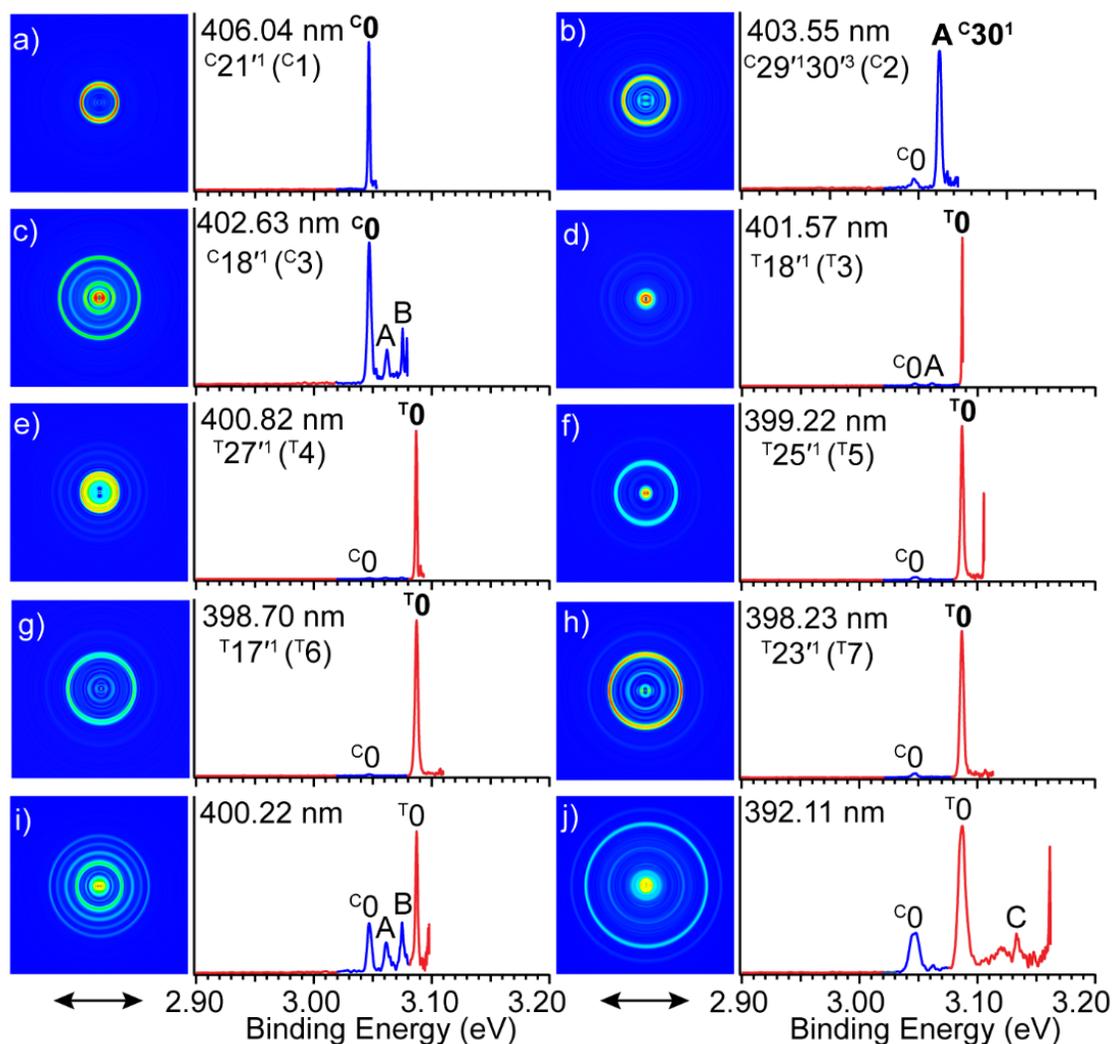
Figure 7.4. Photoelectron images and spectra of deprotonated cytosine anions. Tautomer-specific resonant spectra were taken at a) 406.04 nm, b) 403.55 nm, c) 402.63 nm, d) 401.57 nm, e) 400.82 nm, f) 399.22 nm, g) 398.70 nm and h) 398.23 nm and the non-resonant images/spectra were taken at i) 400.22 nm and j) 392.11 nm. a)-c) correspond to autodetachment from fundamental vibrational levels of the DBS of **cKAN3H8a⁻**, while d)−h) are from the DBS of **tKAN3H8b⁻**. The peak numbers in the parentheses correspond to the DBS resonances in Figure 7.3 and the assignments are also given. Peaks labeled in bold face indicate the enhanced final neutral vibrational levels due to vibrational autodetachment from the DBS. The double arrows below the images show the directions of the laser polarization.

with non-resonant spectra in Figs. 7.4i and 7.4j, resonant spectra in Figs. 7.4a and 7.4c showing spectral features from the **cKAN3H8a⁻** tautomer displays enhancement of peak $^C0$, which should be due to autodetachment from fundamental vibrational levels of the DBS of **cKAN3H8a⁻**, according to the $\Delta v = -1$ propensity rule. The photon energies used

in Figs. 7.4a and 7.4c, corresponding to the DBS resonances of $^C1$ and $^C3$ in Fig. 7.3, are 375 cm^{-1} and 585 cm^{-1} above the DBS ground vibrational level ($^C0'$) of **cKAN3H8a**⁻, in good agreement with the calculated frequencies of the fundamental vibrational modes of $^C\nu_{21}$ (375 cm^{-1}) and $^C\nu_{18}$ (581 cm^{-1}) of **cKAN3H8a**, respectively (Table 7.2 and Fig. 7.8a in Supporting Section 7.5). Hence, the DBS resonances of $^C1$ and $^C3$ should be assigned to the $^C21'^1$ and $^C18'^1$ DBS vibrational levels of **cKAN3H8a**⁻. The good agreement of the frequencies of the neutral radical and the dipole-bound anions is consistent with the weakly-bound nature of the extra electron in the DBS, as shown previously.[117-122] The greatly enhanced peak A ($^c30^1$) in Fig. 7.4b is due to excitation to the combinational DBS vibrational level of $^C29'^130'^3$ of **cKAN3H8a**⁻ followed by the $\Delta v = -3$ vibrational autodetachment, indicating a breakdown of the $\Delta v = -1$ propensity rule due to anharmonic effects involving the low-frequency bending mode. Similarly, Figs. 7.4d-h all display strongly enhanced peak $^T0$, due to resonant excitations to the DBS vibrational levels of $^T18'^1$, $^T27'^1$, $^T25'^1$, $^T17'^1$ and $^T23'^1$ of **tKAN3H8b**⁻, followed by $\Delta v = -1$ vibrational autodetachment. The tautomer-specificity of the resonant spectra is vividly revealed in these spectra, as can be seen by the almost negligible intensity of the $^C0$ peak due to the **cKAN3H8a**⁻ tautomer. A schematic energy level diagram showing the autodetachment processes for the eight resonant photoelectron spectra is displayed in Fig. 7.9 in Supporting Section 7.5.

The photon energies and assignments of all the observed DBS resonances of the [Cy-H]⁻ anions are summarized in Table 7.3 in Supporting Section 7.5. The measured vibrational frequencies for neutral **cKAN3H8a** and **tKAN3H8b** radicals are compared with the calculated frequencies in Table 7.4 in Supporting Section 7.5.

The observed ion abundance suggests the order of stabilities for the three anions as **tKAN3H8b⁻** > **cKAN3H8a⁻** > **KAN1⁻**, consistent with the theoretical predictions for the deprotonated cytosine anions both from the current study (Table 7.1 in Supporting Section 7.5) and the previous calculation by Vázquez et al.[416] It is interesting to note that the three observed anions could all come from direct deprotonation from the **KAN3H** tautomer (Fig. 7.6 in Supporting Section 7.5), which is the second most stable tautomer in solution. The **tKAN3H8b⁻** and **cKAN3H8a⁻** anions can also come from direct deprotonation from the rare *trans*- and *cis*-keto-imino tautomers, respectively. Only the **KAN1⁻** anion can come from direct deprotonation of the most stable **KAN1H** canonical cytosine in solution. Direct deprotonation from the **KAN1H** canonical cytosine would also produce the **cKAN1H8a⁻** and **tKAN1H8b⁻** anions, which are higher energy species.

7.4 Conclusions

In summary, two tautomeric deprotonated cytosine anions, **tKAN3H8b⁻** and **cKAN3H8a⁻**, have been identified by high-resolution PEI, photodetachment spectroscopy, and resonant PEI. The EAs of **tKAN3H8b** and **cKAN3H8a** are measured accurately to be 3.0870(5) eV and 3.0471(5) eV, respectively. Excited dipole-bound states are observed for **tKAN3H8b⁻** and **cKAN3H8a⁻** and their vibrational ground states are found to be bound by 577 cm⁻¹ and 325 cm⁻¹ below the respective detachment thresholds. Tautomer-specific photoelectron spectra are obtained for **tKAN3H8b⁻** and **cKAN3H8a⁻** using resonant PEI via vibrational autodetachment from specific vibrational resonances of the DBSs. Photodetachment spectroscopy also revealed weak DBS resonances assigned to a third tautomer, **KAN1⁻**, which is relatively high in energy. The

ion abundances revealed in the relative intensities in the PEI and photodetachment spectra indicate the order of stabilities for the three anions as **tKAN3H8b⁻** > **cKAN3H8a⁻** > **KAN1⁻**. The current study suggests that photodetachment spectroscopy and resonant PEI, coupled with cryogenic ion cooling, are powerful techniques to investigate the structures and stabilities of the nucleic acid base anions and to obtain tautomer-specific spectroscopic information.

7.5. Supporting information
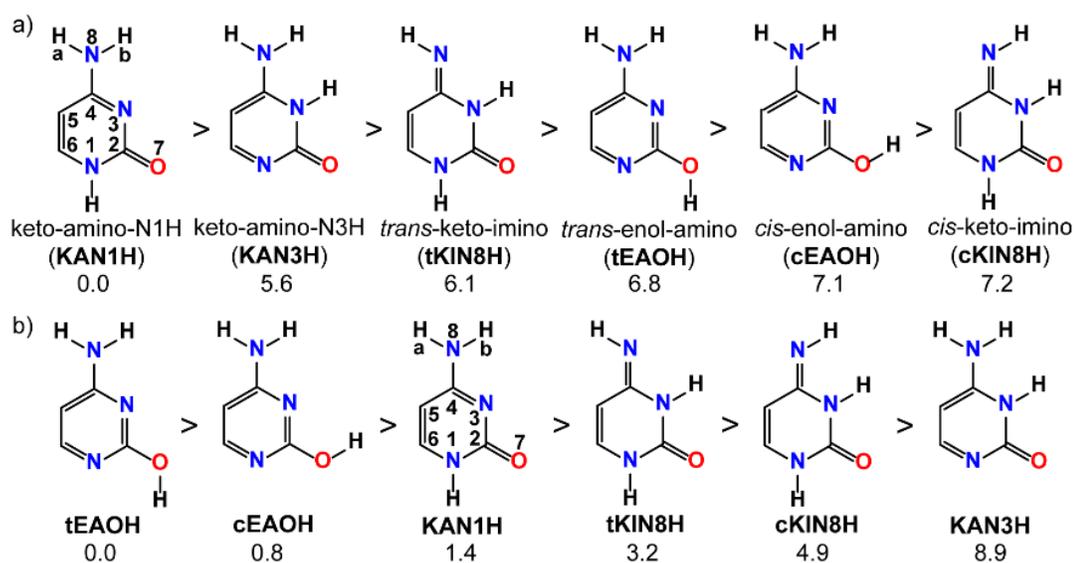
Figure 7.5. The top six tautomers of neutral cytosine in different conditions. (a) aqueous solution[397] and (b) gas phase.[398] The numbers below the structure shows the relative stabilities in kcal/mol.
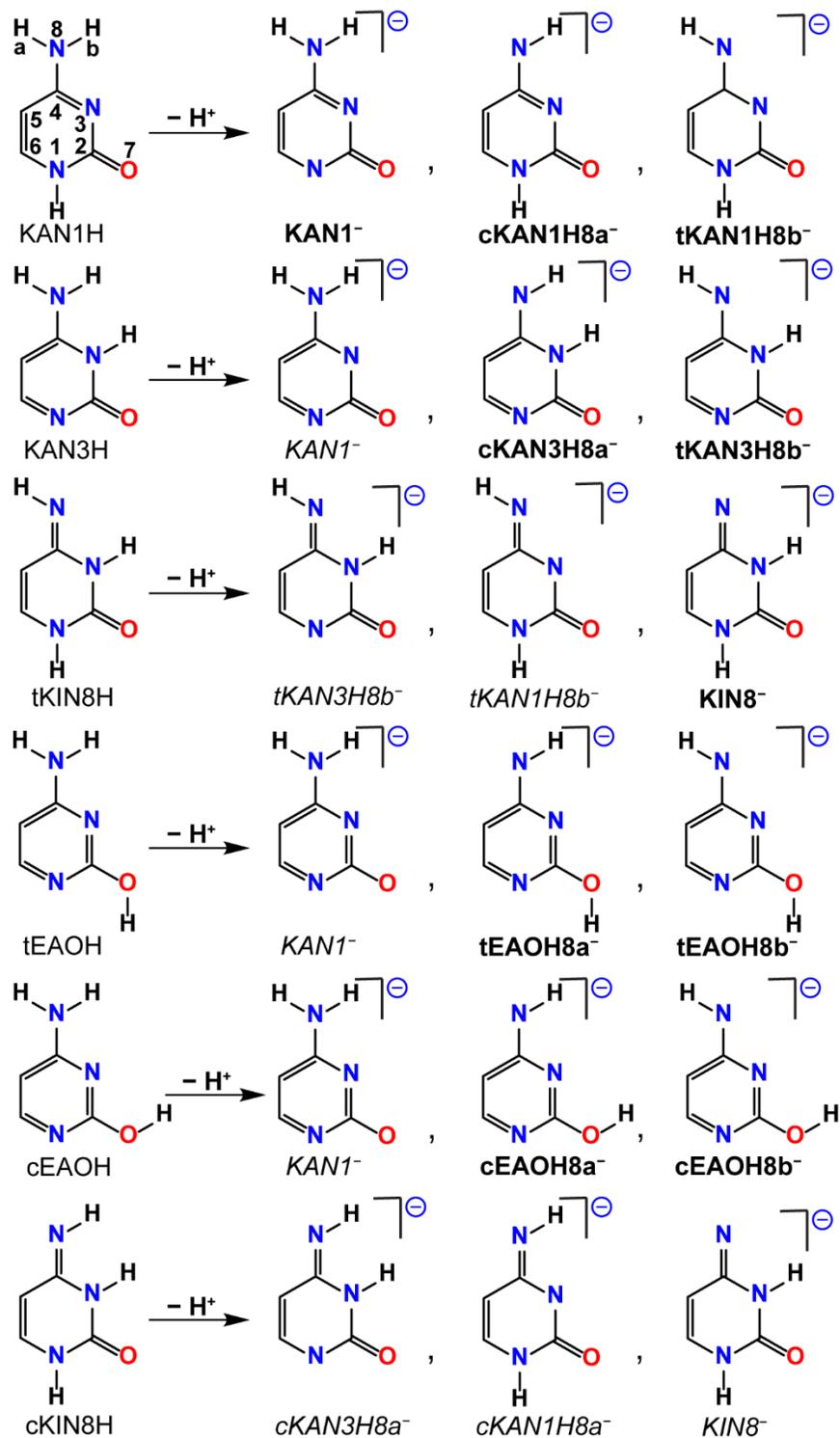
Figure 7.6. Possible deprotonation from the nitrogen sites of the six most stable neutral cytosines in aqueous solution. A total of ten unique anions can be obtained and named in **bold** face. Deprotonation from different tautomers can lead to the same anions and the repetitive anions are named in *Italic* face.
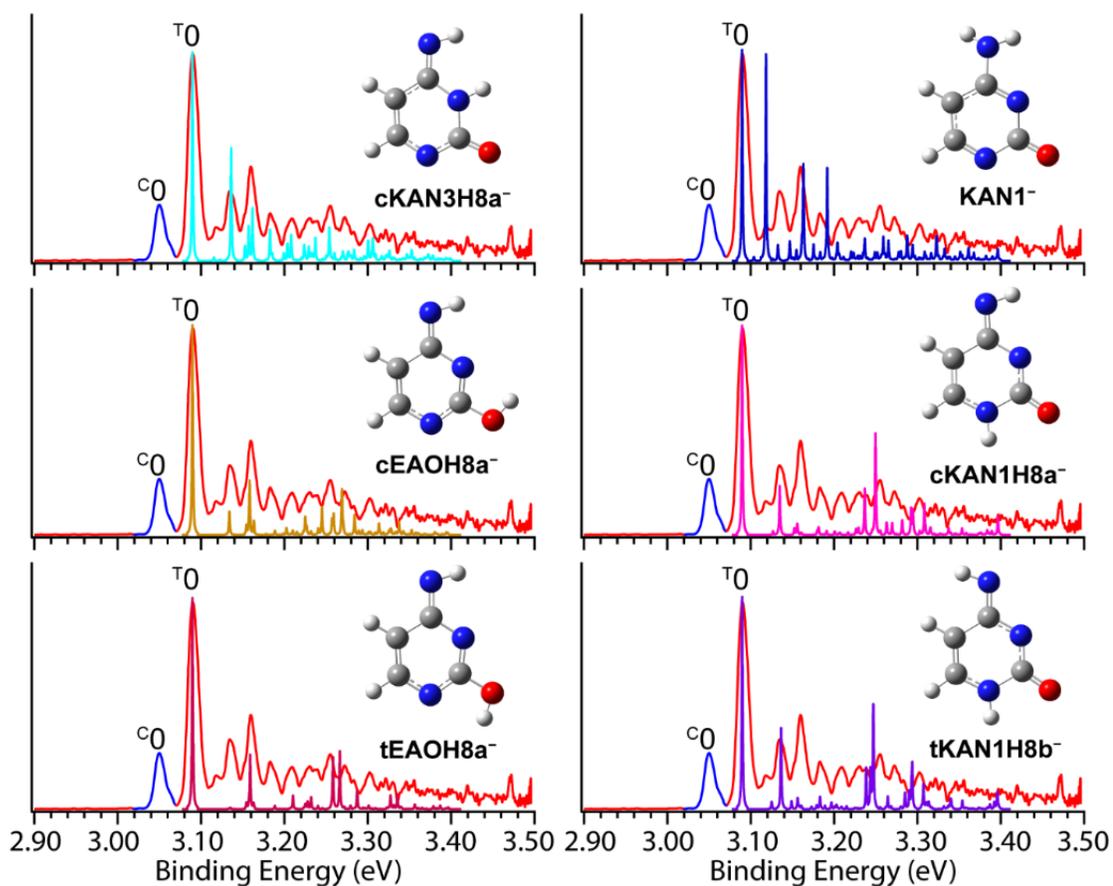
Figure 7.7. Comparisons of the major vibrational progression in photoelectron spectrum at 354.7 nm to the Franck-Condon simulations of six higher energy tautomeric [Cy-H]⁻ anions. The structures for the neutrals and anions of **cKAN1H8a⁻** and **tKAN1H8b⁻** were optimized at the B3LYP/6-31+G(d,p) level of theory, while those of other tautomeric forms were done at the B3LYP/6-311++G(d,p) level using the Gaussian 09package.[252]

a) **cKAN3H8a**

v_{30} (A″) = 104 cm⁻¹ v_{21} (A′) = 375 cm⁻¹ v_{18} (A′) = 581 cm⁻¹

b) **tKAN3H8b**

v_{29} (A″) = 156 cm⁻¹ v_{27} (A″) = 633 cm⁻¹ v_{25} (A″) = 725 cm⁻¹ v_{23} (A″) = 783 cm⁻¹

v_{21} (A′) = 376 cm⁻¹ v_{18} (A′) = 583 cm⁻¹ v_{17} (A′) = 767 cm⁻¹

c) **KAN1**

v_{28} (A) = 231 cm⁻¹ v_{22} (A) = 593 cm⁻¹
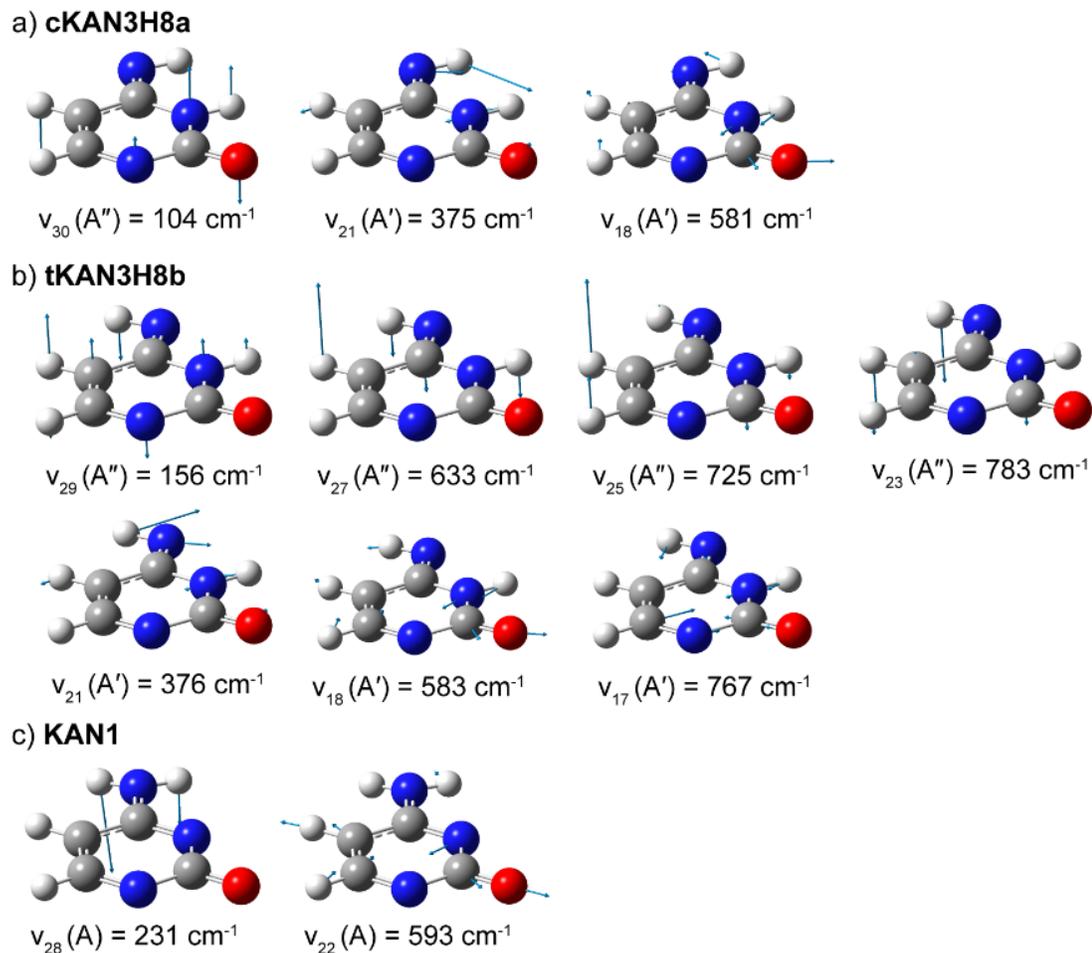
Figure 7.8. Vibrational displacements and frequencies for the observed fundamental modes of the three deprotonated cytosine radicals. a) **cKAN3H8a**, b) **tKAN3H8b** and c) **KAN1**, calculated at the B3LYP/6-311++G(d,p) level of theory. **cKAN3H8a** and **tKAN3H8b** have C$_s$ symmetry, while **KAN1** has C$_1$ symmetry.
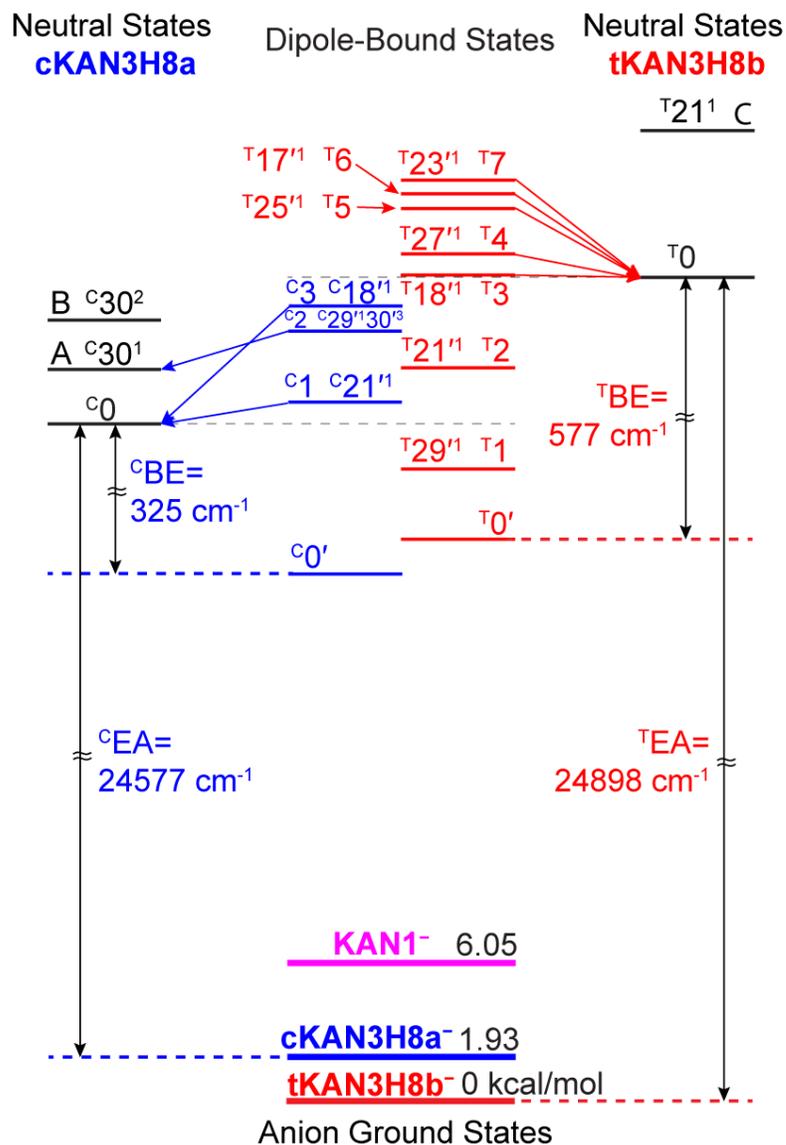
Figure 7.9. A schematic energy level diagram of deprotonated cytosine anions. The arrows represent autodetachments from the DBS vibrational levels of **cKAN3H8a⁻** an **tKAN3H8b⁻** to the respective neutral levels, corresponding to the eight resonant photoelectron spectra in Figures 3a-3h. The autodetachments from the DBS of **cKAN3H8a⁻** are given on the left, while those of **tKAN3H8b⁻** are presented on the right. The relative energies calculated for the three anions are presented in kcal/mol. The detachment thresholds of the **cKAN3H8a⁻** and **tKAN3H8b⁻** anions and the binding energies (BE) of the corresponding DBS are also given.

Table 7.1. The optimized structures and relative energies of seven deprotonated cytosine anions. Our calculations were done at the B3LYP/6-311++G(d,p) level of theory. The energies (ΔE) are relative to the most stable anion **tKAN3H8b⁻**. The electron affinity (EA) and dipole moment (µ) of the corresponding neutral radicals are calculated at the same level. The theoretical values of ΔE and EA from Luo et al.[415] and Vázquez et al.[416] are also compared. Luo et al.[415] used the B3LYP/DZP++ method for both ΔE and EA. Vázquez et al.[416] calculated the ΔE at the MP2/6-3111+G(2d,p) level of theory. The electron detachment energies of the anions were done at the P3//6-3111++G(2df,2p) level from MP2/6-3111+G(2d,p) optimized geometries.

		tKAN3H8b⁻	cKAN3H8a⁻	KAN1⁻	cKAN1H8a⁻
ΔE (kcal/mol)	Current work	0	1.93	6.05	8.84
	Luo et al.[415]			0.00	3.15
	Vázquez et al.[416]	0	1.9	3.0	8.0
EA (eV)	Current work	3.087	3.031	3.029	3.016
	Luo et al.[415]			3.00	2.96
	Vázquez et al.[416]	3.45	3.43	3.37	3.57
µ (D)	Current work	5.55	3.35	7.79	5.04

		cEAOH8a⁻	tEAOH8a⁻	tKAN1H8b⁻
ΔE (kcal/mol)	Current work	12.05	12.66	14.92
	Luo et al.[415]			8.78
	Vázquez et al.[416]	7.8	8.5	
EA (eV)	Current work	2.732	2.707	2.993
	Luo et al.[415]			2.94
	Vázquez et al.[416]	3.10	3.10	
µ (D)	Current work	5.55	3.35	7.79

Table 7.2. The harmonic frequencies of six deprotonated cytosine radicals. The calculations were done at the B3LYP/6-311++G(d,p) level of theory. The **KAN1** species has C_1 symmetry, while the other neutral radicals have C_s symmetry. The unit of frequency is cm^{-1}.

Modes	KAN1	Modes	cKAN3H8a	tKAN3H8b	cKAN1H8a	tKAN1H8b	tEAOH8a
ν_1 (A)	3725	ν_1 (A')	3589	3589	3601	3603	3792
ν_2 (A)	3595	ν_2 (A')	3454	3499	3420	3419	3429
ν_3 (A)	3189	ν_3 (A')	3231	3210	3246	3222	3227
ν_4 (A)	3139	ν_4 (A')	3142	3137	3203	3198	3167
ν_5 (A)	1650	ν_5 (A')	1745	1748	1758	1751	1593
ν_6 (A)	1600	ν_6 (A')	1532	1528	1627	1631	1533
ν_7 (A)	1536	ν_7 (A')	1510	1515	1543	1530	1469
ν_8 (A)	1440	ν_8 (A')	1443	1434	1452	1438	1426
ν_9 (A)	1378	ν_9 (A')	1404	1404	1394	1407	1360
ν_{10} (A)	1366	ν_{10} (A')	1374	1366	1281	1259	1344
ν_{11} (A)	1282	ν_{11} (A')	1324	1314	1238	1235	1255
ν_{12} (A)	1246	ν_{12} (A')	1190	1202	1180	1197	1214
ν_{13} (A)	1109	ν_{13} (A')	1147	1159	1117	1129	1148
ν_{14} (A)	1078	ν_{14} (A')	1080	1087	1101	1093	1093
ν_{15} (A)	982	ν_{15} (A')	994	999	962	966	1014
ν_{16} (A)	977	ν_{16} (A')	927	925	933	916	972
ν_{17} (A)	910	ν_{17} (A')	773	767	769	764	796
ν_{18} (A)	820	ν_{18} (A')	581	583	572	571	591
ν_{19} (A)	750	ν_{19} (A')	545	545	546	553	557
ν_{20} (A)	747	ν_{20} (A')	509	508	533	535	523
ν_{21} (A)	645	ν_{21} (A')	375	376	365	377	356
ν_{22} (A)	593	ν_{22} (A")	986	977	969	959	990
ν_{23} (A)	558	ν_{23} (A")	794	783	794	769	839
ν_{24} (A)	526	ν_{24} (A")	789	741	775	759	775
ν_{25} (A)	494	ν_{25} (A")	737	725	702	702	690
ν_{26} (A)	369	ν_{26} (A")	641	649	625	620	647
ν_{27} (A)	347	ν_{27} (A")	576	633	539	464	535
ν_{28} (A)	231	ν_{28} (A")	382	376	392	374	430
ν_{29} (A)	181	ν_{29} (A")	162	156	183	185	201
ν_{30} (A)	114	ν_{30} (A")	104	102	102	85	167

Table 7.3. The summary of the observed peaks in the photodetachment spectrum. Their corresponding wavelengths, photon energies (hν), shifts from the ground DBS vibrational levels of **cKAN3H8a⁻**, **tKAN3H8b⁻** and **KAN1⁻** are given. Theoretical frequencies are from Table 7.2.

Peak	Wavelength (nm)	hν (cm⁻¹)	Shift (cm⁻¹)	Assignment	Theo. Freq. (cm⁻¹)
$^C0'$	**412.34**	**24252 (7)**	**(C)0**	**Ground DBS of cKAN3H8a⁻**	
$^C1$	406.06	24627(5)	(C)375	$^C21'^1$	375
$^C2$	403.55	24780(5)	(C)528	$^C29'^130'^3$	
$^C3$	402.63	24837(5)	(C)585	$^C18'^1$	581
$^T0'$	**411.16**	**24321(5)**	**(T)0**	**Ground DBS of tKAN3H8b⁻**	
$^T1$	408.56	24476(5)	(T)155	$^T29'^1$	156
$^T2$	404.88	24699(5)	(T)378	$^T21'^1$	376
$^T3$	401.57	24902(5)	(T)581	$^T18'^1$	583
$^T4$	400.82	24949(5)	(T)628	$^T27'^1$	633
$^T5$	399.22	25049(5)	(T)728	$^T25'^1$	725
$^T6$	398.70	25082(5)	(T)761	$^T17'^1$	767
$^T7$	398.23	25111(5)	(T)790	$^T23'^1$	783
			DBS resonances of KAN1⁻		
α	**427.04**	**23417 (7)**	**(KA)0**	**Ground DBS of KAN1⁻**	
β	422.42	23672 (5)	(KA)255	$^{KA}28'^1$	231
γ	416.47	24011(5)	(KA)594	$^{KA}22'^1$	593

Table 7.4. Assignments of the observed vibrational peaks from the photoelectron spectra of [Cy-H]⁻. Their binding energies (BE), energy shifts from the vibrational origins of deprotonated neutral radicals, **cKAN3H8a** and **tKAN3H8b**, are given. Theoretical frequencies are from Table 7.2.

Peaks	BE (eV)	Shift to $^C0$ (cm⁻¹)	Shift to $^T0$ (cm⁻¹)	Assignment	Theo. Freq. (cm⁻¹)
$^C0$	3.0471 (5)	0		Neutral ground state (**cKAN3H8a**)	
$^T0$	3.0870 (5)		0	Neutral ground state (**tKAN3H8b**)	
A	3.0619 (7)	119		$^C30^1$	104
B	3.0752 (5)	227		$^C30^2$	
C	3.1332 (5)		373	$^T21^1$	376
D	3.1583 (6)		575	$^T18^1$	583

Chapter 8 Observation of excited quadrupole-bound states in NC(C$_6$H$_4$)O$^{-\dagger\dagger}$

This chapter[97] will discuss the first observation of an excited quadrupole-bound state (QBS) in an anion. High-resolution photoelectron imaging of cryogenically-cooled 4-cyanophenoxide anions (4CP$^-$) yields an electron detachment threshold of 24927 cm^{-1}. Photodetachment spectrum reveals a resonant transition 20 cm^{-1} below the detachment threshold, which is attributed to an excited QBS of 4CP$^-$ because neutral 4CP has a large quadrupole moment with a negligible dipole moment. The QBS is confirmed by observation of seventeen above-threshold resonances due to autodetachment from vibrational levels of the QBS.

8.1 Introduction

A dipolar molecule can bind an electron in a diffuse orbital, which is dominated by the long-range charge-dipole attractive potential scaled as $1/r^2$.[123-125] Such dipole-bound states (DBSs) play important roles in electron-molecule interactions and considered to be the "doorway" to the formation of valence-bound anions. When a molecule has vanishing dipole moment, but large quadrupole moments, it can bind an extra electron by the long-range charge-quadrupole attractive potential ($\sim 1/r^3$), forming the quadrupole-bound anion (QBA).[146] The QBA at ground state has been observed by Rydberg electron transfer. However, excited quadrupole-bound state (QBS) of anion, which is optically excited from valence-bound state of anion, has not been observed.

More detailed introduction was described in the Chapter 1. Here we report the first observation of an excited QBS in the 4-cyanophenoxide anion (4CP$^-$) cryogenically-cooled in an ion trap. The neutral 4CP radical (see inset of Fig. 8.1) has a very small dipole moment of 0.3 D, which is insufficient to form a DBS. Its large quadrupole moment (traceless quadrupole moment: Q_{xx} = 5.4, Q_{yy} = 15.1, Q_{zz} = –20.5 D•Å) suggests that it may be a good candidate to search for excited QBS.

8.2 Experimental methods

The experiments were done using our third-generation ESI-PES apparatus. The detailed descriptions were provided in the Chapter 2.

8.3 Results and discussion

Figure 8.1 shows the non-resonant PE images and spectra of 4CP$^-$ at three photon energies. The first intense peak, labeled as 0_0^0, denotes the detachment transition from the vibrational ground state of 4CP$^-$ to that of neutral 4CP, representing the electron affinity of 4CP or the electron detachment threshold of 4CP$^-$. The spectrum in Fig. 8.1a, with a photon energy slightly above the detachment threshold, gives the best resolved 0_0^0 peak with a width of 11 cm^{-1} mainly due to rotational broadening, yielding an accurate electron affinity for 4CP as 24927 ± 5 cm^{-1}. At higher photon energies, numerous vibrational peaks, labeled as A−J, are resolved for the ground electronic state of 4CP. The strongest vibrational peak B corresponds to the most Franck-Condon-active mode. To better resolve peak B, we tuned the detachment laser to be just above the binding energy of peak B at 393.57 nm, resolving an additional peak C. The intensity of peak B is

significantly enhanced due to the threshold effect. The electron binding energies of all the observed vibrational peaks, their shifts from peak 0_0^0, and their assignments are summarized in Table 8.1 in Supporting Section 8.5.
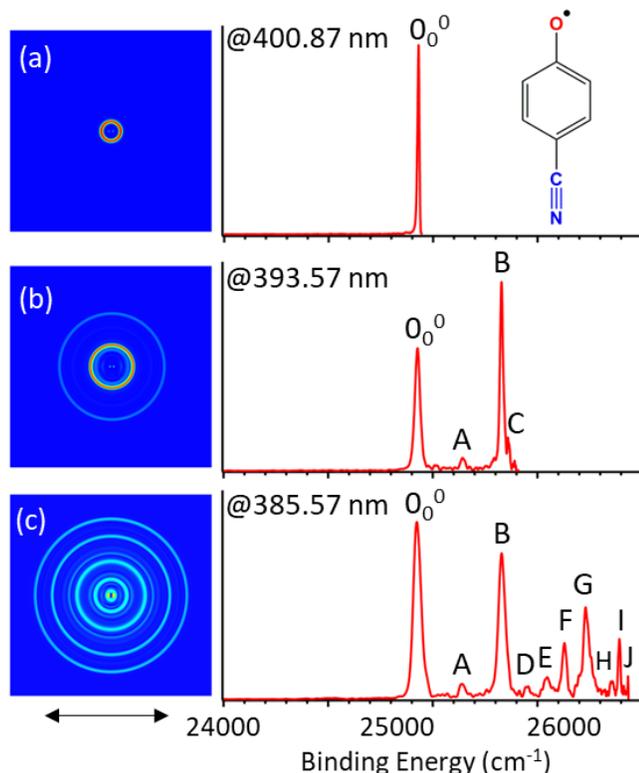
Figure 8.1. Non-resonant photoelectron images and spectra of 4CP$^-$ at different laser wavelengths. (a) 400.87 nm, (b) 393.57 nm, and (c) 385.57 nm. The double arrow below the images indicates the direction of the laser polarization. The structure of neutral 4CP is shown in the inset of (a).

To search for possible QBSs, we measured the photodetachment spectrum of 4CP$^-$ by monitoring the total electron yield while scanning the dye laser across the detachment threshold (Fig. 8.2). The arrow at 24927 cm^{-1} indicates the detachment threshold, consistent with the photoelectron spectra in Fig. 8.1. The three underneath-baseline arrows indicate the detachment wavelengths used in the non-resonant photoelectron images in Fig. 8.1.
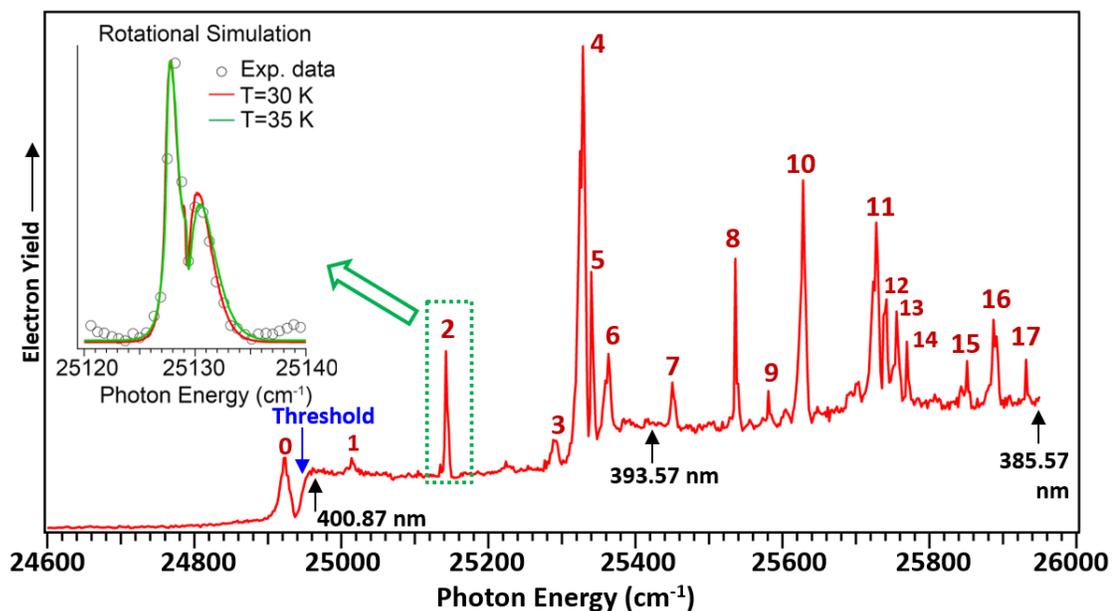
Figure 8.2. Photodetachment spectrum of 4CP$^-$. It was done by measuring the total electron yield as a function of photon energy across the detachment threshold. The blue arrow at 24927 cm^{-1} indicates the detachment threshold of 4CP$^-$. The three black arrows indicate the detachment photon energies used for the non-resonant photoelectron spectra in Fig. 8.1. The peaks 1−17 are due to autodetachment from QBS vibrational levels of 4CP$^-$; while peak 0 below threshold represents the vibrational ground state of the QBS and is from resonant two-photon processes. The inset shows a high-resolution scan of peak 2, revealing the rotational profile, along with rotational simulations at two temperatures.

Below threshold, one broad peak, labeled as 0, is observed due to two-photon processes. Because 4CP$^-$ cannot support DBSs, this below-threshold peak should be due to the vibrational ground state of the putative QBS, because no other peaks were observed below peak 0. This peak is 20 cm^{-1} below the detachment threshold, suggesting the weakly-bound nature of the electron in the QBS relative to the detachment continuum. The continuous signals above threshold represent non-resonant photodetachment signals. Seventeen above-threshold peaks are observed, due to autodetachment from excited vibrational levels of the QBS. The inset shows the simulation of the rotational profile for peak 2 at a high-resolution scan, yielding a rotational temperature of 30-35 K, consistent with previous estimates.[95,96] See the Supporting Section 8.5 for details of the rotational

simulation. The top scale is relative to the vibrational ground state of the QBS. The corresponding photon energies, shifts from peak 0, and assignments of the QBS resonances in photodetachment spectrum are given in Table 8.2 in Supporting Section 8.5.

The local dipoles of the two polar centers (–CN and C-O) in the neutral planar 4CP radical have opposite directions, resulting in a vanishing dipole moment of 0.3 D but a large quadrupole moment. Hence, the dominating potential that binds the electron in the excited state of 4CP$^-$ should be between the quadrupole moment and the electron. This interaction is scaled as $1/r^3$, much weaker than the electron and dipole interaction in DBSs. The peak 0 observed in Fig. 8.2 gives rise to a small binding energy of 20 cm^{-1} for the QBS of 4CP$^-$. Thus, any vibrational excitation of the QBS would be above the detachment threshold and can lead to vibrationally-induced autodetachment via vibrational to electronic energy transfer or vibronic coupling. The electron in the excited QBS is expected to be in a highly diffuse orbital with little effect on the structure of the neutral core. This is confirmed by the similarity of the observed vibrational peaks in the photodetachment spectrum in Fig. 8.2 and those in the non-resonant photoelectron spectrum in Fig. 8.1c. A direct comparison is presented in Fig. 8.6 in Supporting Section 8.5, where the 385.57 nm photoelectron spectrum is overlaid onto the photodetachment spectrum in the same energy scale by lining up the peak 0_0^0 in the photoelectron spectrum and the peak 0 of the photodetachment spectrum. All the major vibrational peaks and their relative intensities agree with each other in the two spectra, except that the photodetachment spectrum has higher resolution. This resemblance provides strong evidence for the weakly bound nature of the excess electron in the QBS, which has little effect to the neutral core, just as that observed for DBSs.[117-120] Hence, the

photodetachment spectrum of the QBS can be used to yield more accurate vibrational information for the neutral radical.

By tuning the dye laser wavelength to the above-threshold peaks, we have obtained seventeen high-resolution resonantly-enhanced photoelectron images and spectra, as shown in Figs. 8.3 and 8.4. These resonant photoelectron spectra consist of contributions from two different detachment processes: i) non-resonant detachment represented by the baseline in Fig. 8.2 (such as the spectra in Fig. 8.1), and ii) the much stronger resonant autodetachment signal represented by the above-threshold peaks. The
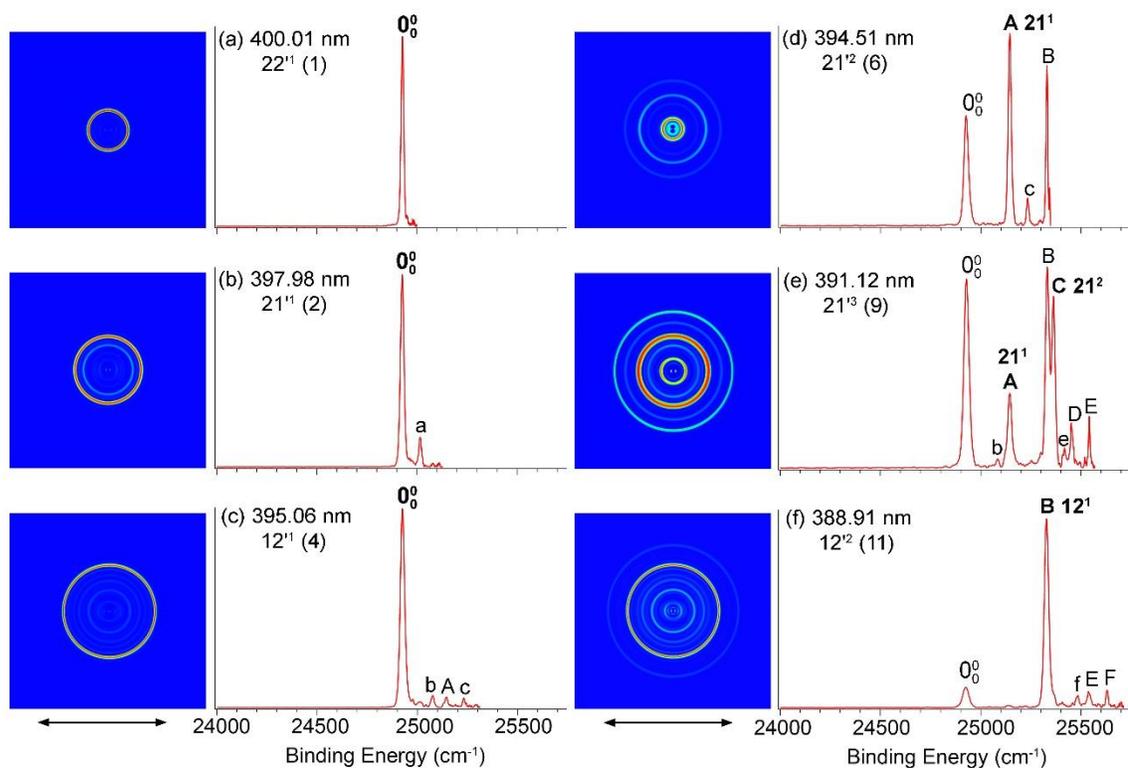
Figure 8.3. Resonant photoelectron images and spectra of 4CP$^-$ at six different detachment wavelengths. They are corresponding to excitations to vibrational levels involving single vibrational modes of the QBS followed by autodetachment via vibronic coupling. The QBS vibrational levels and the peak number (in parentheses) used in Fig. 8.2 are given. The peaks labeled in bold face indicate the autodetachment-enhanced final neutral vibrational levels. The double arrows below the images represent the direction of the laser polarization.
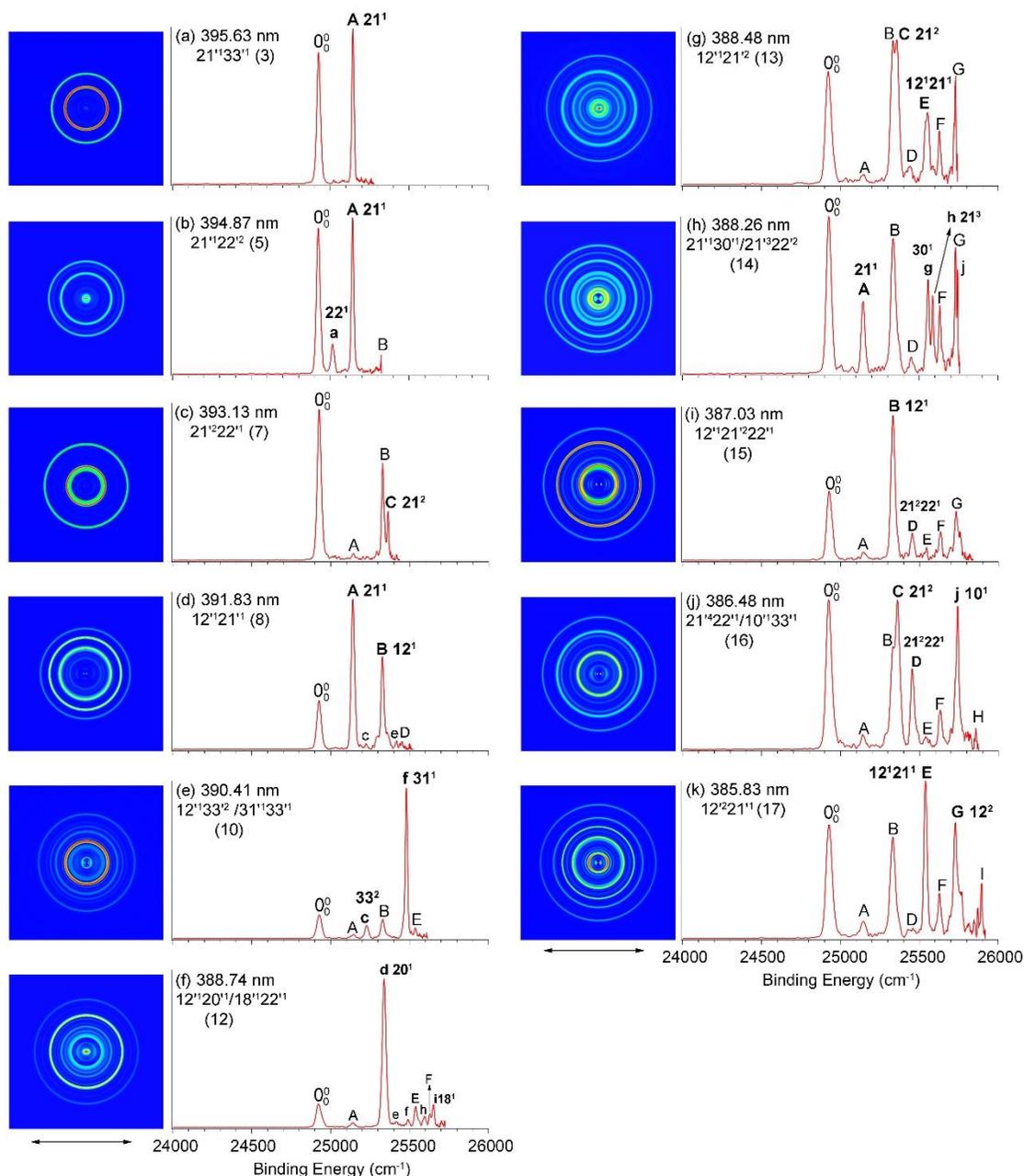
Figure 8.4. Resonant photoelectron images and spectra of 4CP$^-$ at eleven different detachment wavelengths. They are involving autodetachment from combinational and overlapping vibrational levels of the quadrupole-bound state. The QBS vibrational levels and the peak number (in parentheses) used in Fig. 8.2. are given. The labels in bold face indicate the autodetachment-enhanced final neutral vibrational levels. The double arrows below the images indicate the direction of the laser polarization.

latter involves two steps, i.e., resonant excitation to a vibrational level of the QBS,

followed by transfer of vibrational energies to the weakly-bound electron to induce

detachment. The vibrationally-induced autodetachment from DBSs generally obeys the

$\Delta v = -1$ propensity rule under the harmonic-oscillator approximation[189,190] and yields

highly non-Franck-Condon PE spectra.[117-120] This propensity rule is expected to hold true

for vibrational autodetachment from the QBS due to the even more weakly-bound nature

of the QBS electron. The six spectra in Fig. 8.3 show autodetachment involving single

vibrational modes of the QBS; while the eleven spectra in Fig. 8.4 represent excitations to

combinational and overlapping vibrational levels of the QBS. The enhanced vibrational

levels (in bold face), the detachment laser wavelengths, the assigned vibrational levels of

the QBS, and the corresponding peak number (in parentheses) used in Fig. 8.2 are given

in each spectrum. Ten new vibrational peaks, labeled as a–j, are observed in the resonant

spectra and are also listed in Table 8.1 in Supporting Section 8.5.

To understand the vibrational peaks in Figs. 8.1 and 8.2, we calculated the

vibrational frequencies of neutral 4CP at the B3LYP/6-311++G(d,p) level using the

Gaussian 09 package.[252] The thirty-three normal modes are shown in Fig. 8.7 in

Supporting Section 8.5. The calculated frequencies are unscaled and agree well with the

observed frequencies for most vibrational modes. Because both 4CP$^-$ and 4CP have C$_{2v}$

symmetry, only modes with A$_1$ symmetry are allowed in principle. Peaks B and G form a

vibrational progression for the most Franck-Condon-active mode v_{12} (A$_1$), which is an in-

plane N…O stretching mode (Fig. 8.7 in Section 8.5). The very weak peaks A and C

correspond to a vibrational progression of the v_{21} (B$_1$) mode, which is an out-of-plane

bending mode (Fig. 8.7 in Section 8.5). The assignments of all the observed peaks are

given in Table 8.1 (Section 8.5) by using the calculated vibrational frequencies and the

resonant photoelectron spectra.

According to the $\Delta v = -1$ propensity rule for vibrationally-induced autodetachment, excitation to the nth vibrational level of a given mode (v'^n_x) of the QBS autodetaches to the (n-1)th level of the same neutral mode (v^{n-1}_x) with one vibrational quantum transferred to the QBS electron. The corresponding v^{n-1}_x vibrational peak will be enhanced significantly in comparison to that in the non-resonant photoelectron spectrum, giving rise to highly non-Franck-Condon resonant photoelectron spectra. Figures 8.3a-c show significant enhancement of peak 0^0_0, indicating autodetachments from the fundamental vibrational level of different modes (v'^1_x) of the QBS. The photon energies used for the spectra in Figs. 8.3a-c correspond to excitations to vibrational levels $22'^1$, $21'^1$ and $12'^1$ of the QBS, respectively. In Figs. 8.3d and 8.3f, peaks A and B, corresponding to vibrational level 21^1 and 12^1 of 4CP, respectively, are greatly enhanced in comparison to the intensity of peak 0^0_0 in the non-resonant photoelectron spectra. These are due to excitations to the QBS vibrational levels of $21'^2$ and $12'^2$, followed by $\Delta v = -1$ autodetachment. Both peaks A (21^1) and C (21^2) in Fig. 8.3e are enhanced. The photon energy used for the spectrum in Fig. 8.3e corresponds to excitation to the $21'^3$ vibrational level of the QBS. Hence, the enhancement of peak A is a result of transferring two vibrational quanta to the QBS electron (i.e. $\Delta v = -2$), which suggests a large anharmonicity in the v'_{21} (B$_1$) mode.[189] In addition, numerous weak peaks a-c, e, and f are also observed in Fig. 8.3. As given in Table 8.1 (Section 8.5), the shifts of peak a and b relative to peak 0^0_0 are 89 cm^{-1} and 155 cm^{-1}, respectively, which correspond to the two lowest frequency modes v_{22} (B$_1$, 93 cm^{-1}) and v_{33} (B$_2$, 157 cm^{-1}) of neutral 4CP (Table 8.2 in Section 8.5). Their appearances in the resonant photoelectron spectra are most likely

due to intramolecular electron rescattering, as observed previously.[121] The assignments of peaks c (33^2), e ($12^1 22^1$), and f (31^1) are based on the calculated frequencies.

The remaining eleven resonant photoelectron spectra in Fig. 8.4 all involve excitations to combinational or overlapping vibrational levels of the QBS with more complicated autodetachment processes. For excitation to a combinational level, $\nu'^m_x \nu'^n_y \ldots$, of the QBS, the final neutral level can be either $\nu^{m-1}_x \nu^n_y \ldots$ or $\nu^m_x \nu^{n-1}_y \ldots$, based on the $\Delta\nu = -1$ propensity rule under harmonic approximation[189,190] and mode-selectivity.[117] For example, the wavelength used in Fig. 8.4a probes the combinational level of $21'^1 33'^1$ of the QBS. The great enhancement of peak A (21^1) indicates the mode-selectivity during autodetachment, i.e., the in-plane scissoring mode ν_{33}' (B$_2$) couples more strongly with the QBS electron than the ν_{21}' (B$_1$) mode does. The enhancement of peak A (21^1) and B (12^1) in Fig. 8.4d suggest excitation to the combinational level of $12'^1 21'^1$ of the QBS. The higher intensity of peak A is due to the stronger coupling of the QBS electron with the in-plane stretching mode ν_{12}' (A$_1$).

Figures 8.4b, c, g, and k all display cases involving transitions to combinational vibrational levels of the QBS, in which one vibrational mode is combined with an overtone of another mode. The spectra in Figs. 8.4c, g, and k all show autodetachment following the $\Delta\nu = -1$ rule. The enhancement of peak C (21^2) in Fig. 8.4c is due to autodetachment from combinational level of $21'^2 22'^1$ of the QBS with one quantum of mode ν_{22}' coupled to the outgoing electron; while the enhancement of peak E ($12^1 21^1$) and G (12^2) in Fig. 8.4k are from autodetachment from the $12'^2 21'^1$ QBS level, involving the coupling of the QBS electron with one quantum of mode ν_{12}' (A$_1$) and ν_{21}' (B$_1$), respectively. The breakdown of the $\Delta\nu = -1$ propensity rule is observed in Fig. 8.4b.,

where peaks a (22^1) and A (21^1) are enhanced due to autodetachment from the $21'^1 22'^2$ of QBS level. To reach the 21^1 final state, two quanta of mode ν_{22}' (B$_1$) must be coupled to the outgoing electron during the autodetachment. The spectrum in Fig. 8.4i involves autodetachment from a combinational level of three vibrational modes of the QBS, $12'^1 21'^2 22'^1$. The enhancement of peak B (12^1) indicates breakdown of the $\Delta\nu = -1$ rule, while the enhancement of peak D ($21^2 22^1$) follows the $\Delta\nu = -1$ rule.

Even more complicated cases are those involving resonant excitations to overlapping vibrational levels of the QBS, as shown in Figs. 8.4e, f, h and j. In Fig. 8.4e, a new peak f (31^1) is observed, suggesting excitation to the $31'^1 33'^1$ QBS vibrational level with strong vibronic coupling involving the ν_{33}' (B$_2$) mode in the autodetachment. A weaker peak c (33^2), which is also enhanced, is due to autodetachment from the combinational level of $12'^1 33'^2$. Fig. 8.4f also shows two new enhanced peaks d (20^1) and i (18^1), implying two overlapping combinational levels, $12'^1 20'^1$ and $18'^1 22'^1$, respectively, with only one mode in each case strongly coupled with the outgoing electron. In Fig. 8.4h, the enhancement of peak A (21^1) and g (30^1) is due to autodetachment from the combinational level of $21'^1 30'^1$; while the new peak h (21^3) is due to autodetachment from the $21'^3 22'^2$ level in violation of the $\Delta\nu = -1$ rule. The enhancements of peak G and j are attributed to the threshold effect. Finally, the enhanced peak j (10^1) in Fig. 8.4j suggests excitation to the $10'^1 33'^1$ combinational level with the ν_{33}' (B$_2$) mode coupled to the QBS electron. The other two enhanced peaks C (21^2) and D ($21^2 22^1$) are due to autodetachment from the $21'^4 22'^1$ combinational level, with violation of the $\Delta\nu = -1$ rule in both autodetachment channels. It seems that there is a higher probability for the

breakdown of the $\Delta v = -1$ rule involving the v_{21}' (B$_1$) and v_{22}' (B$_2$) modes, suggesting strong anharmonicity in these modes.

Figure 8.5 shows schematically the seventeen vibrational levels of the QBS and their autodetachment channels to the neutral final states of 4CP. All the assignments for the observed vibrational resonances of the QBS are summarized in Table 8.2 in Section 8.5. The experimental vibrational frequencies for 4CP are compared with the calculated frequencies in Table 8.3 (Section 8.5).

8.4 Conclusions

In summary, we report the first observation of an excited quadrupole-bound state for cryogenically-cooled cyanophenoxide anions, whose neutral core possesses a vanishing dipole moment but a large quadruple moment. The quadrupole-bound state is found to have a binding energy of 20 cm^{-1} relative to the detachment threshold. Seventeen excited vibrational levels of the QBS are observed as resonances in the photodetachment spectrum. The weakly-bound nature of the electron in the QBS is confirmed by the observation of the similarity of the non-resonant photoelectron spectra and the photodetachment spectrum and the $\Delta v = -1$ vibrational autodetachment propensity rule in the resonant photoelectron spectra.

Quadrupole-Bound States   Neutral States   Quadrupole-Bound States
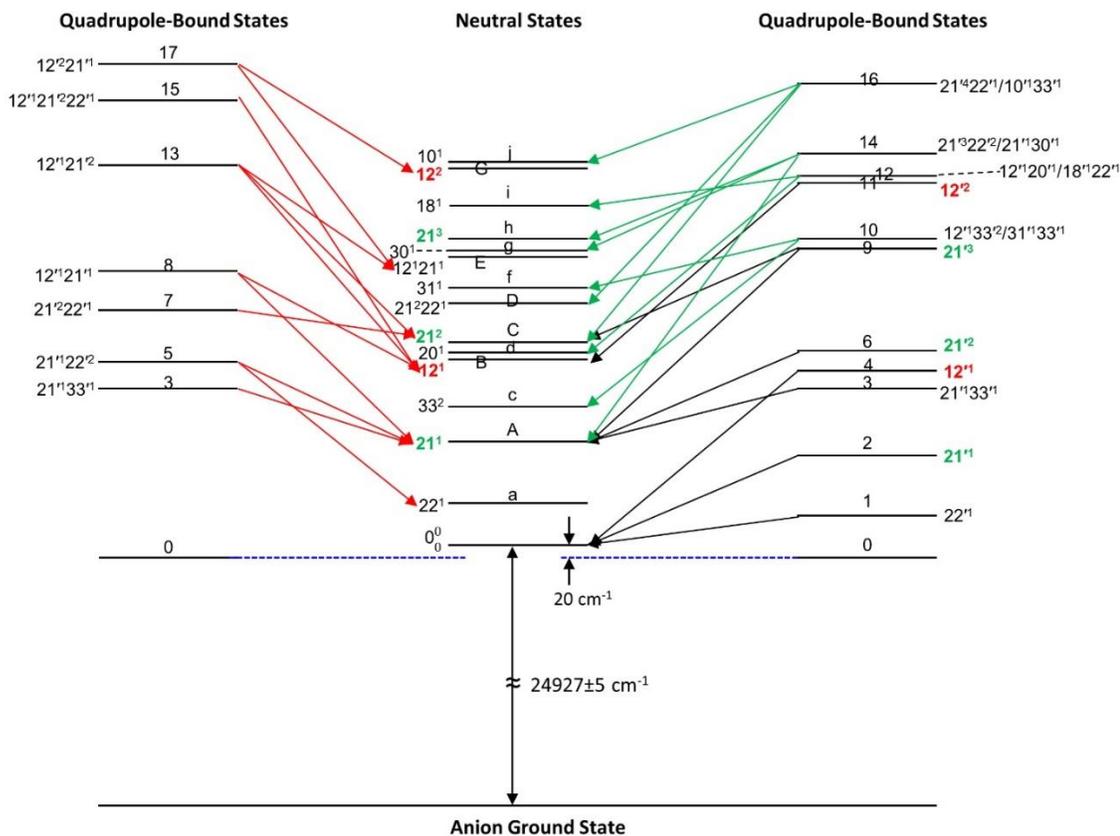
Figure 8.5. A schematic energy level diagram for autodetachment from the QBS vibrational levels of 4CP$^-$ to the neutral final states of 4CP. The combinational vibrational levels of the QBS are given on the left with the red arrows denoting the autodetachment. Single-mode and overlapping vibrational levels of the QBS are given on the right with the black arrows indicating autodetachment from single-mode levels and the green arrows for autodetachment from the overlapping levels. The vibrational progressions for mode ν_{12} and ν_{21} are highlighted both in the neutral levels and the QBS levels (red and green, respectively). The detachment threshold (24927 cm^{-1}) and the QBS binding energy (20 cm^{-1}) of 4CP$^-$ are also given. The QBS peak labels (numbers) and the peak labels from the photoelectron spectra (letters) are given. The assignments of the final neutral states and the QBS levels are given in Tables 8.1 and 8.2 in Supporting Section 8.5, respectively.

8.5 Supporting information

The high-resolution spectrum of peak 2, shown in inset of Fig. 8.2, resolves its rotational profile, which is simulated using the Pgopher program[422] with the calculated rotational constants for 4CP$^-$ ($a = 5637.36$ MHz, $b = 1006.73$ MHz, $c = 854.19$ MHz) and 4CP ($a = 5470.65$ MHz, $b = 1030.83$ MHz, $c = 867.39$ MHz). The simulation yields J$_{max}$

= 70 and T$_{rot}$ = 30-35 K with a line width of 0.15 cm^{-1}. The obtained rotational temperature of 30−35 K for the cryogenically cooled anion in the Paul trap is consistent with the values estimated previously for the uracil anion[95] and the acetate anion.[96]

Table 8.1. Assignments of the observed vibrational peaks from the photoelectron spectra of 4CP$^-$. The binding energies (BE) and energy shifts from the vibrational origins of 4CP are given. Peaks A-J correspond to those observed in the non-resonant photoelectron spectra in Fig. 8.1, while peaks a-j are observed from the resonant photoelectron spectra in Figs. 8.3 and 8.4. The binding energies of peaks 0$_0^0$, and A−J are measured more accurately from the resonant photoelectron spectra. Numbers in parentheses indicate the experimental uncertainties in the last digit.

Peak	BE (cm^{-1})	Shift (cm^{-1})	Assignment
0_0^0	24927(5)	0	Neutral Ground State
A	25145(5)	218	21^1
B	25331(5)	404	12^1
C	25362(5)	435	21^2
D	25451(5)	525	$21^2 22^1$
E	25541(5)	614	$12^1 21^1$
F	25630(5)	703	$11^1/12^1 33^2/31^1 33^1$
G	25731(5)	804	12^2
H	25853(5)	926	$12^1 21^2 22^1$
I	25891(5)	964	$10^1 33^1/21^4 22^1$
J	25933(5)	1006	$12^2 21^1$
a	25016(5)	89	22^1
b	25082(5)	155	33^1
c	25231(5)	304	33^2
d	25339(5)	412	20^1
e	25418(5)	491	$12^1 22^1$
f	25480(5)	553	31^1
g	25557(5)	630	30^1
h	25586(5)	659	21^3
i	25652(5)	725	18^1
j	25742(5)	815	10^1

Table 8.2. Assignments of observed QBS resonances in photodetachment spectrum of 4CP$^-$. Numbers in parentheses indicate the experimental uncertainties in the last digit.

Peak	Photon energy (cm^{-1})	Shift (cm^{-1})	Assignment
0	24907(5)	0	Ground state
1	24999(5)	92	22$'^1$
2	25127(5)	220	21$'^1$
3	25276(5)	369	21$'^1$33$'^1$
4	25313(5)	406	12$'^1$
5	25325(5)	418	21$'^1$22$'^2$
6	25348(5)	441	21$'^2$
7	25437(5)	530	21$'^2$22$'^1$
8	25521(5)	614	12$'^1$21$'^1$
9	25568(5)	661	21$'^3$
10	25614(5)	707	12$'^1$33$'^2$/31$'^1$33$'^1$
11	25713(5)	806	12$'^2$
12	25724(5)	817	12$'^1$20$'^1$/18$'^1$22$'^1$
13	25741(5)	834	12$'^1$21$'^2$
14	25756(5)	849	21$'^3$22$'^2$/21$'^1$30$'^1$
15	25838(5)	931	12$'^1$21$'^2$22$'^1$
16	25875(5)	968	21$'^4$22$'^1$/10$'^1$33$'^1$
17	25918(5)	1011	12$'^2$21$'^1$

Table 8.3. Experimental vibrational frequencies of 4CP, in comparison to theoretical harmonic frequencies. The calculations were done at the B3LYP/6-311++G(d,p) level of theory. The peaks from which the experimental vibrational frequencies are obtained are also given. The peaks 1−4, 10, 12, 14, 16, refer to the labels used in Fig. 8.2 and Table 8.2. The peaks labeled with letters refer to those used in the photoelectron spectra (Figs. 8.1, 8.3, and 8.4) and in Table 8.1.

Mode	Symmetry	Theoretical (cm^{-1})	Experimental (cm^{-1})	Peak
ν_1	A$_1$	3205		
ν_2		3187		
ν_3		2291		
ν_4		1590		
ν_5		1492		
ν_6		1429		
ν_7		1222		
ν_8		1156		
ν_9		988		
ν_{10}		803	819/815	16/j
ν_{11}		711	703	F
ν_{12}		413	406/404	4/B
ν_{13}	A$_2$	986		
ν_{14}		795		
ν_{15}		374		
ν_{16}	B$_1$	980		
ν_{17}		863		
ν_{18}		733	725/725	12/i
ν_{19}		553		
ν_{20}		435	412/412	12/d
ν_{21}		226	220/218	2/A
ν_{22}		93	92/89	1/a
ν_{23}	B$_2$	3203		
ν_{24}		3187		
ν_{25}		1491		
ν_{26}		1435		
ν_{27}		1293		
ν_{28}		1277		
ν_{29}		1114		
ν_{30}		638	629/630	14/g
ν_{31}		556	558/553	10/f
ν_{32}		441		
ν_{33}		157	149/155	3/b

Figure 8.6. Comparison of the non-resonant photoelectron spectrum at 385.57 nm with the photodetachment spectrum. The photodetachment spectrum is blue-shifted by 20 cm^{-1} to line up the peak 0_0^0 and peak 0 (the ground vibrational level of the neutral and the QBS). All the peaks in the non-resonant photoelectron spectrum can be found in the corresponding photodetachment spectrum, suggesting the weakly bound nature of the excited QBS electron, which has little effect on neutral 4CP core.

ν_1=3205 cm^{-1}

ν_2=3187 cm^{-1}

ν_3=3187 cm^{-1}

ν_4=1590 cm^{-1}

ν_5=1492 cm^{-1}

ν_6=1429 cm^{-1}

ν_7=1222 cm^{-1}

ν_8=1156 cm^{-1}

ν_9=988 cm^{-1}

ν_{10}=803 cm^{-1}

ν_{11}=711 cm^{-1}

ν_{12}=413 cm^{-1}

ν_{13}=986 cm^{-1}

ν_{14}=795 cm^{-1}

ν_{15}=374 cm^{-1}

ν_{16}=980 cm^{-1}

ν_{17}=863 cm^{-1}

ν_{18}=733 cm^{-1}

ν_{19}=553 cm

ν_{20}=435 cm^{-1}

ν_{21}=226 cm^{-1}

ν_{22}=93 cm^{-1}

ν_{23}=3203 cm^{-1}

ν_{24}=3187 cm^{-1}

ν_{25}=1491 cm^{-1}

ν_{26}=1435 cm^{-1}

ν_{27}=1293 cm^{-1}

ν_{28}=1277 cm^{-1}

ν_{29}=1114 cm^{-1}

ν_{30}=638 cm^{-1}

ν_{31}=556 cm^{-1}

ν_{32}=441 cm^{-1}

ν_{33}=157 cm^{-1}

Figure 8.7. The calculated vibrational normal modes for neutral 4CP and their frequencies. The arrows indicate the displacement vectors.

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Abbreviations

BE	Binding energy
CCD	Charge-copuled device
cw	Continuous-wave
[Cy-H]$^-$	Deprotonated cytosine anion
DBA	Dipole-bound anion
DBS	Dipole-bound state
DFT	Density functional theory
DNA	Deoxyribonucleic acid
EA	Electron affinity
ESI	Electrospray ionization
FC	Franck-Condon
FWHM	Full-width at half-maximum
HOMO	Highest occupied molecular orbital
KE	Kinetic energy
LUMO	Lowest unoccupied molecular orbital
MCA	Multiply-charged anion
MCP	Micro-channel plates
MP2	Møller-Plesset second-order perturbation theory
MS	Mass spectrometry
O.D.	Outer diameter
ODCB	o-dichlorobenzene
PAD	Photoelectron angular distribution
PDS	Photodetachment spectroscopy
PES	Photoelectron spectroscopy
QBA	Quadrupole-bound anion
QBS	Quadrupole-bound state
QID	Quadrupole ion guide
RET	Rydberg electron transfer
rf	Radio-frequency
SEVI	Slow photoelectron velocity-map imaging
TCNQ	Tetracyanoquinodimethane
TDAE	Tetrakis(dimethylamino)ethylene
TOF	Time-of-flight
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
VMI	Velocity-map imaging
XPS	X-ray photoelectron spectroscopy
ZEKE	Zero-electron kinetic energy