Photoelectron Spectroscopy of Small Cluster Anions: Dipole Bound, Ground State Systems

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Abstract

Here, we report on our photoelectron spectroscopic studies of small, ground state cluster anions in which the excess electron is bound primarily by the dipole moment of the system. To insure that the excess electron's binding is due largely to its interaction with the dipolar field of the system, the cluster species under study have typically been constructed from molecular components which do not themselves form conventional (valence) anions. When the composite dipole moment of the resultant dimer or other small cluster is large enough (the critical dipole moment is thought to be about 2.5 D), dipole binding of the excess electron may occur. Two examples of dipole bound dimer anions will be discussed to illustrate our work in this area.

1. Introduction

As we all know, the overwhelming majority of atomic and molecular systems are governed by electron binding to monopoles, i.e., to positively charged nuclei. Still, one might wonder if the next term in the multipole expansion, i.e., the dipole, can also bind an electron, albeit more weakly. Starting with a polar neutral, so that pure monopolar interactions are not an issue, the binding of an additional electron by its dipolar field would result in a negative ion. Theory, starting with the work of Fermi and Teller[1] in 1947, says that such species can exist. Subsequent work[2-26] has refined this topic, and some of the milestones in the development of dipole bound electron theory are indicated on the right side of Figure 1. The cumulative fruits of these studies can be roughly summarized with several statements. In particular, there is a critical dipole moment, now thought to be around 2.5 D, which is necessary for dipole binding of an electron. The electron binding energies in such systems are small (typically in the meV range as opposed to the eV range often found for conventional anions), and they depend on the magnitude of the dipole moment. The excess electron cloud is extremely diffuse, reminiscent of Rydberg electrons. The molecular structure of an anion having a dipole bound electron is expected to be the same as that of its corresponding neutral.

Figure 1.

SOME MILESTONES IN THE STUDY OF DIPOLE-BOUND SPECIES

EXPERIMENT		THEORY
	1947	**Fermi & Teller** - e⁻ binding to a proton-muon pair
Sugiura & Arakawa - observed CH_3CN^-		**Crawford** - electron binding to a rotating dipole
Tsuda & Yokohata - observed CH_3CN^-	**1970**	**Garrett** - electron binding to a rotating dipole
Compton - observed CH_3CN^- & interpreted it as being DB		**Jordan & Simons**-DB anions of ionic molecules
Brauman - tunable photodetachment (PD) of DB excited states of enolate anions		**Jordan** - DB anions of $(HF)_2^-$ CH_3CN^-, HCN^-, ...
	1980	**Chipman** - $(H_2O)_2^-$
Haberland - observed & field-detached $(H_2O)_2^-$, observed $(EG)_{2,3}^-$		
Lineberger - high resolution tunable PD of DB excited states of enolate anions and of CH_2CN^-		
Lineberger & Brauman - DB excited states of enolate anions		**Berne** - $(H_2O)_2^-$
Bowen - photoelectron spectroscopy of $(H_2O)_{2,3}^-$, $(EG)_{2,3}^-$		**Clary** - enolate anions & CH_2CN^-
	1990	**Landman** - $(H_2O)_2^-$
Schermann & Bowen - Rydberg CT e⁻ attachment to form $(H_2O)_2^-$; predicted & observed $(H_2O)(NH_3)^-$		**Muguet** - $(H_2O)_2^-$
Schermann-e⁻ attachment via Rydberg atom CT coll. to form molecular & small cluster DB anions		**Adamowicz**-DB DNA/RNA base anions
Bowen-photoelectron spectroscopy of DB ground state molecular & small cluster anions		
Johnson-DB excited states of anion-molecule complexes formed via photoexcitation		

Furthermore, there is a relatively weak rotational dependence to excess electron binding in anions having a dipole bound electron. As a matter of terminology, these anions are often loosely referred to as dipole bound anions, where we understand that it is the excess electron that is actually dipole bound.

Some of the milestones in experimental work[27-55] on dipole bound anions are indicated on the left side of Figure 1. Even though gas-phase acetonitrile anions had been observed in the late 1960's, they had not been interpreted as being dipole bound anions until 1978, when Compton[30], who himself had seen them previously[29], proposed that the excess electron in these species is dipole bound. There followed over the next fifteen or so years a variety of experiments dealing with both dipole bound excited states and with dipole bound ground states of anions, with both dipole bound monomer anions and with dipole bound dimer and trimer anions, and with techniques such as field detachment, tunable photodetachment, photoelectron spectroscopy, and Rydberg atom charge transfer.

Our own work in this field has focused on photoelectron spectroscopic studies of small, ground state dipole bound cluster anions. Starting with the photoelectron spectrum[41-45] of water dimer anion, $(H_2O)_2^-$ in 1986, we have gone on to take the photoelectron spectra of a variety of small dipole bound cluster anions. To an extent, our work has been motivated by the following observations. The water monomer does not form a stable conventional anion, nor does it possess enough dipole moment (1.85 D) to hold an excess electron through dipole binding. But when two water molecules are allowed to interact and form water dimer (neutral), the composite dipole moment[56] of the resultant dimer goes up to 2.6 D, and $(H_2O)_2^-$ can be formed. As a counter case, when two ammonia molecules interact to form ammonia dimer (neutral), the composite dipole moment[57] is only ~ 0.75 D, and despite extensive efforts to make it, ammonia dimer anion has never been observed. Thus, it appears that one may be able to use dimer (and perhaps other small cluster) formation to construct species having tailored dipole moments, such that when they are bigger than the threshold dipole moment needed for dipole electron binding, dipole bound cluster anions can exist. By starting with molecular components which are known not to form conventional (valence) anions, one essentially insures that any observed dimer anion formation is due largely to dipole binding and not to some other electron binding mechanism. These thoughts led us to propose the mixed water/ammonia dimer as a test case. Neither water nor ammonia molecules form conventional anions, and neither has enough dipole moment on its own to evoke dipole binding, but together as a mixed dimer, the composite dipole moment[58] is 2.9 D. The search for this previously unseen species was carried out collaboratively between Schermann, Desfrancois and ourselves[50] using their Rydberg atom charge transfer collision apparatus, which provided an extraordinarily gentle method for forming these fragile species. This search was successful, and the observation of $(H_2O)(NH_3)^-$ mixed dimer anion added impetus to the hunt for other systems using the rough rationale outlined above.

At this point in time, we have measured the photoelectron spectra of the following dipole bound and related anions; $(H_2O)_{2,3}^-$, $(D_2O)_2^-$, $(EG)_{2,3}^-$, (where EG = ethylene glycol), $(HF)_{2,3}^-$, $(CH_3CN)(H_2O)^-$, $(CD_3CN)(D_2O)^-$, $(HCl)(H_2O)_{n=1-7}^-$, $(HCN)(H_2O)_{n=1-13}^-$, $(HCN)_2(H_2O)_{n=1-11}^-$, (uracil)$^-$, (thymine)$^-$, $(H_2S)_4^-$, $Ar_{n=1-3}(H_2O)_2^-$, $Ar_{n=1-4}(EG)_2^-$, $Ar_{n=1-3}(EG)_3^-$, $Kr_{n=1-4}(EG)_{2,3}^-$, and

Ar(HF)$_2^-$. Below, we briefly illustrate some of our work in this area with two examples of dipole bound dimer anions.

2. Experimental

These experiments were conducted by crossing a mass selected beam of negative ions with a fixed frequency (visible) laser beam and energy analyzing the resultant photodetached electrons. The anions being discussed here were generated using a magnetically confined, supersonic expansion nozzle ion source. This source provides a great many low energy electrons in the microplasma formed just outside the nozzle. To form dipole bound anions this source had to be operated under extremely cold expansion and very gentle ion formation conditions, i.e., strong expansions of the seed gas greatly diluted by argon plus low electron energies and small electron emission currents.

3. Results and Discussion

The photoelectron spectra of all of the dipole bound anions we have studied so far are characterized by a distinctive spectral signature, consisting of an intense, narrow peak at unusually low electron binding energy plus much weaker molecular vibrational features at higher electron binding energies. This spectral fingerprint is essentially unlike that of any other anionic species we have encountered to date.
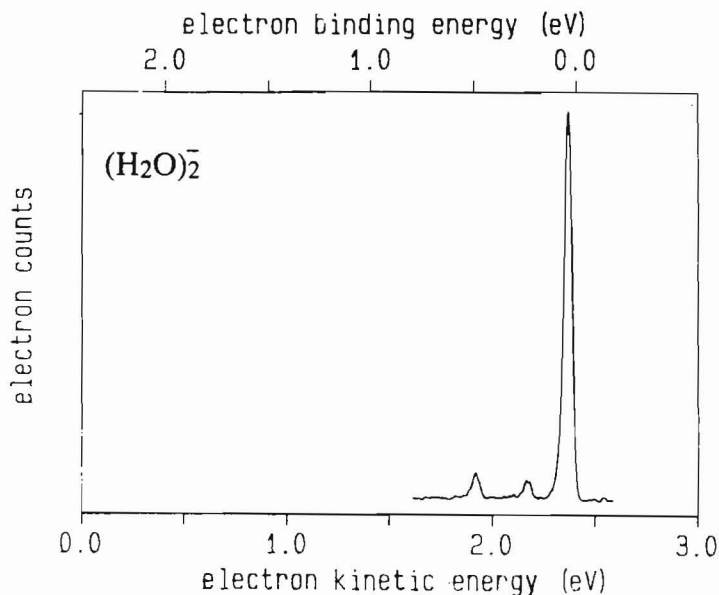
Fig. 2. The photoelectron spectrum of water dimer anion.

To illustrate our work, we present two examples of dipole bound dimer anions, $(H_2O)_2^-$, the spectrum of which is shown in Figure 2 and $(CH_3CN)(H_2O)^-$, whose spectrum is seen in Figure 3. Water dimer anion is not only a homogeneous system, but it is, as mentioned above, a dimer made up of molecules which themselves do not form intact anions of any kind, neither conventional nor dipole bound ones. Water-acetonitrile dimer anion, on the other hand, is a heterogeneous system, in which the acetonitrile molecular component, while not forming a stable conventional anion, does have a big enough dipole moment to form a dipole bound molecular anion.
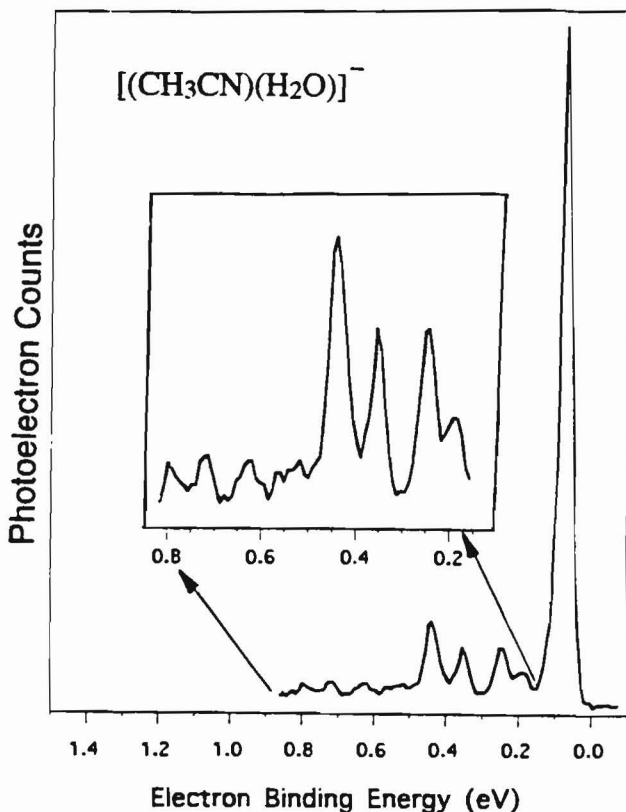

Fig. 3. The photoelectron spectrum of acetonitile-water anion

The narrowness of the dominant peak in these spectra imply, at least to first order, that the structure of the anion and its corresponding neutral are similar. Even more important information, however, comes from the values of the vertical

detachment energy (VDE) and the adiabatic electron affinity (EA_a). The former quantity is the electron binding energy at the maximum of the main peak, and the latter is the electron binding energy at the threshold for electron counts on the low electron binding energy side of the main peak. For $(H_2O)_2^-$, VDE = 45 meV and EA_a = 8 meV, while for $(CH_3CN)(H_2O)^-$, VDE = 78 meV and EA_a = 35 meV. Given that the dipole moment of neutral water dimer is 2.6 D, and the dipole moment of neutral acetonitrile-water dimer is about 5.5 D, we are observing an increase in electron binding energy with increasing dipole moment as expected from theory. Generally, in the other dipole bound dimer anion systems we have studied, there is also a substantial correlation between dimer structure (through the dipole moment of the dimer) and excess electron binding energies. What is unexpected are the magnitudes of electron binding energies. They are somewhat larger than expected from theory.

The relatively weak vibrations that appear in most of these spectra are a particularly interesting aspect of these studies. The ones that we resolve are clearly the vibrations of component molecules. In water dimer anion, the two vibrational peaks are due to molecular water bending and stretching motions. In acetonitrile-water dimer anion, where vibrational peaks are both intense and numerous, we have assigned all of them to known vibrations of either water or acetonitrile. Deuteration of both dimer anions supports these asignments. The deeper meaning of these vibrations is still an open question. The anomalously low velocity of the excess electron in these systems might lead to some unusual effects. If, however, Franck-Condon analysis is still applicable, as it usually is in negative ion photoelectron spectroscopy, then the appearance of these vibrations imply slight structural distortions of the molecular components, and by inference, of the dimer's intermolecular structure as well, due to the presence of and interaction with the dipole bound excess electron. Slight structural distortions (possibly to achieve a higher dipole moment configuration) would not be inconsistent with the narrowness of the main peak described above.

Acknowledgements

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