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EXCESS ELECTRON CLUSTERS COMPOSED OF POLAR, HYDROGEN BOND-FORMING MOLECULES: NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC STUDIES

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INTRODUCTION

Here, we discuss the photoelectron spectra of several gas-phase cluster anions composed of hydrogen-bond forming molecules. Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon (laser) beam and energy analyzing the resultant photodetached electrons (see Figure 1). This is a straightforward approach to the determination of excess electron binding energies (EBE), relying as it does on the relationship, $h\nu = \text{EBE} + \text{EKE}$, in which $h\nu$ is the photon energy and EKE is the measured electron kinetic energy. In this work, cluster anions were generated in a supersonic expansion ion source. In this type of source, relatively low energy electrons are injected directly into the high density portion of an expanding jet in the presence of weak axial magnetic fields. Negative ions are extracted from the resulting microplasma. The negative ion formation environment most probably involves the attachment of even lower energy secondary electrons to target species in the presence of many cooling collisions. This source and our apparatus have been described in detail previously.¹

In the past, we have used this technique to study a wide variety of solvated cluster anions as well as solvated electron, metal oxide, alkali metal halide, and alkali metal cluster anions. Here, we focus on small cluster anions composed of polar, hydrogen bond-forming molecules. The smallest of these are dimer anions, such as $(\text{HF})_2^-$, $(\text{H}_2\text{O})_2^-$, $(\text{CH}_3\text{CN})(\text{H}_2\text{O})^-$, $(\text{HCl})(\text{H}_2\text{O})^-$, and $(\text{EG})(\text{H}_2\text{O})^-$, where EG = ethylene glycol. Slightly larger cluster anions include trimers, such as $(\text{HF})_3^-$, $(\text{H}_2\text{O})_3^-$, $(\text{HCl})(\text{H}_2\text{O})_2^-$, $(\text{HCN})(\text{H}_2\text{O})_2^-$, and $(\text{EG})_3^-$, and tetramers, such as $(\text{H}_2\text{S})_4^-$. Below, we summarize representative findings from our laboratory in regard to these species.

DIMER ANIONS

The dimer ion species, $(\text{HF})_2^-$, $(\text{H}_2\text{O})_2^-$, $(\text{CH}_3\text{CN})(\text{H}_2\text{O})^-$, $(\text{HCl})(\text{H}_2\text{O})^-$, $(\text{HCN})(\text{H}_2\text{O})^-$, and $(\text{EG})_2^-$ all exhibit qualitatively similar photoelectron spectra, characteristic of dipole bound anions. In their purest form, dipole bound anions exhibit the following properties. Their excess electron clouds are extremely diffuse (spread over tens

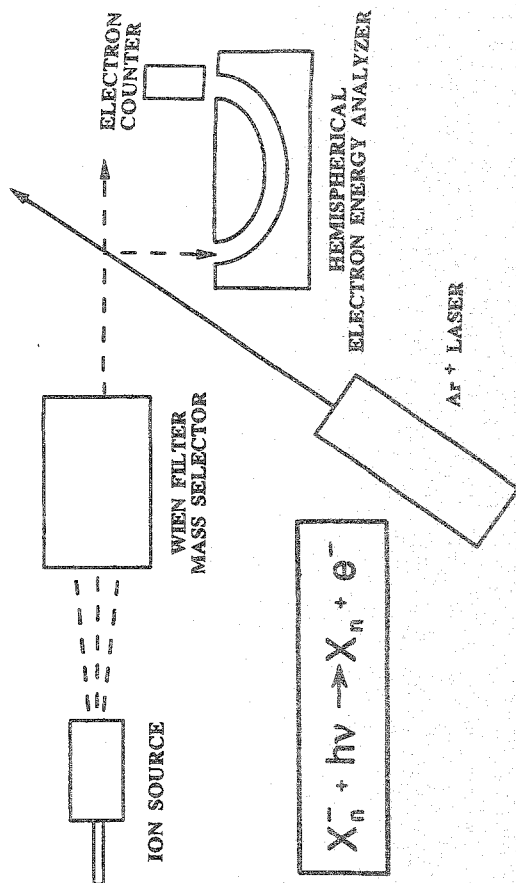


Figure 1. Schematic diagram of a negative ion photoelectron spectrometer.

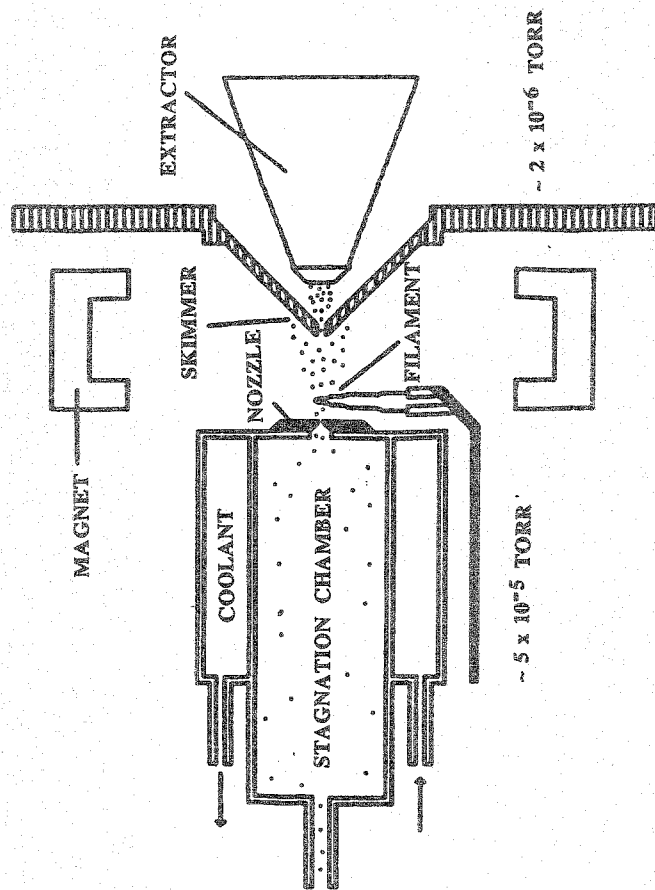


Figure 2. Schematic representation of a supersonic expansion nozzle ion source.

of Angstroms outside their molecular frameworks) and anisotropic (tethered to the positive end of their dipoles); their excess electron binding energies are very small; and their structures are the same as or very similar to those of their corresponding neutrals.

Dipole bound anions exhibit a distinctive photoelectron spectral signature. It is characterized by a single, strong, narrow spectral feature at very low electron binding energy and by several much lower intensity features at slightly higher electron binding energies. These spectra are unique, i.e., they are unlike those of any other anionic species we have encountered. The photoelectron spectra of dipole bound dimer anions are exemplified by those of $(H_2O)_2^-$ and $(HF)_2^-$ [see Figures 3 and 4]. The dominant peak in each of these spectra arises due to the transition between the ground state of the dimer anion and that of its corresponding neutral. The fact that the electron binding energy is so small indicates that the excess electron is bound very weakly, while the relative strength and unusual narrowness of this peak imply that the structure of the anion and its parent neutral are similar. The much weaker intensity features lying at slightly higher electron binding energies are respectively assigned to the vibrations of molecular water (the bend and the stretch) and molecular hydrogen fluoride (one and two quanta of the HF molecule's stretch, respectively). The vertical detachment energy (VDE) is the electron binding energy corresponding to the maximum of the dominant peak in these spectra. The VDE's of $(H_2O)_2^-$ and $(HF)_2^-$ were measured to be 45 ± 6 and 63 ± 3 meV, respectively.

The concept of dipole bound anions has its roots in a 1947 paper by Fermi and Teller.² Early theory found the electron binding energies for dipole bound anions to be extremely small and the most stable structures of such anions to be the same as the equilibrium structures of their corresponding neutrals. Our measured electron binding energies for dipole bound dimer anions, while small, were still an order of magnitude larger than predicted. Also, the unexpected appearance of vibrational features in these photoelectron spectra raised the question as to whether there might actually be some degree of structural dissimilarity between these dimer anions and their corresponding neutral dimers.

We interpreted these spectra in terms of the structural distortion of particular molecular components and an overall distortion of the dimer anion's geometric structure, both of which would increase the dipole moment of the neutral core. This is consistent with our observations and accounts for an enhancement in the electron binding energy and the appearance of vibrational features (through Franck-Condon overlap) in these photoelectron spectra. This model is intuitively attractive in that a relatively slight and low energy cost modification of the dimer anion's intermolecular structure could cause a considerable increase in the dipole moment of its neutral core, leading to further excess electron stabilization and counter-balancing the energy cost of the structural perturbation. Excitation of intermolecular modes in the neutral dimer would not be resolved in our spectra, but would instead appear as spectral broadening (tailing) to the high electron binding energy side of observed spectral features.

Recently, dramatic theoretical progress has been made in dealing with dipole bound anions.³ Building on these developments, Gutowski and Skurski⁴ very recently conducted calculations on $(HF)_2^-$ in which they found an electron binding energy that is quite close to our measured value, a structural dissimilarity between $(HF)_2^-$ and $(HF)_2$ with the neutral core of $(HF)_2^-$ exhibiting an enhanced dipole moment, and molecular vibrational features in their modeled photoelectron spectrum of $(HF)_2^-$ which are Franck-Condon in character.

TRIMER ANIONS

The trimer anions, $(HF)_3^-$, $(H_2O)_3^-$, $(HCl)(H_2O)_2^-$, $(HCN)(H_2O)_2^-$, and $(EG)_3^-$ all exhibit photoelectron spectra which are similar to those of the dimer anions presented above. However, the dominant peak in each is broader and occurs at significantly higher electron binding energy than in dimer anion photoelectron spectra. It appears to be the dipole moments of these systems that are primarily responsible for binding the electron, and in that sense, these species are also dipole bound anions. The major distinction between the dimer anions that we have discussed above and these trimer anions is probably the degree of structural distortion of the anion relative to its neutral. While in dipole bound

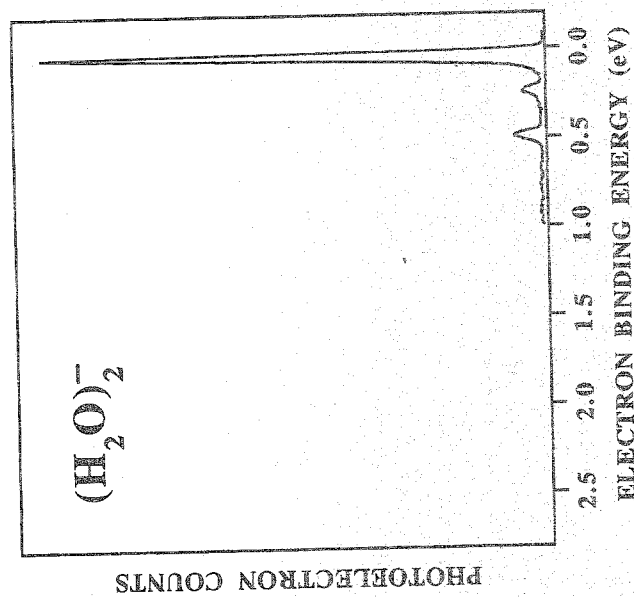


Figure 3. Photoelectron spectrum of $(\text{H}_2\text{O})_2^-$ recorded with 2.540 eV photons.

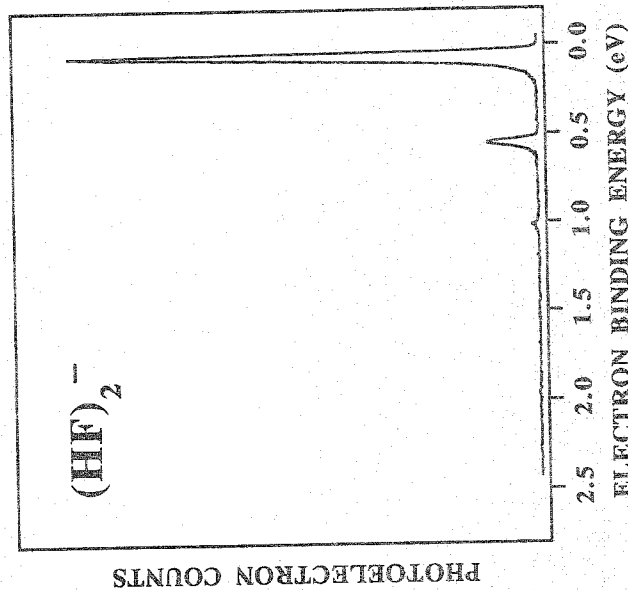


Figure 4. Photoelectron spectrum of $(\text{HF})_2^-$ recorded with 2.540 eV photons.

dimer anions the structural difference is slight in relation to its corresponding neutral, in trimer anions the structural difference must be much larger. This is due to the fact that equilibrium structures of hydrogen bonded neutral trimers are generally cyclic and therefore have no permanent dipole moment. For the neutral core of a trimer anion to have a large enough dipole moment to bind an electron, there must be a substantial structural change. The most likely structure for dipole bound trimer anions is an open, chain-like structure, although others have been proposed.

TETRAMER ANIONS

The tetramer anion, $(\text{H}_2\text{S})_4^-$, also has a dipole bound-like photoelectron spectrum, but in this case the situation is more intriguing. We were unable to observe any other size cluster anions composed of intact hydrogen sulfide molecules. Hydrogen sulfide has a somewhat lower dipole moment than water and is a much poorer hydrogen bonding species than water. It makes sense that we could not make $(\text{H}_2\text{S})_2^-$, since the sum of its molecular dipole moments is still less than the critical dipole moment value of 2.5 D. The trimer anion is a borderline case, having enough dipole moment only if one assumes specific structures or enough induced dipole moment. The tetramer, on the other hand, is the first cluster in this system that clearly has enough dipole moment available, and so in this sense, it is not surprising that it forms. Still, it is an odd species, especially when one considers that larger cluster anions of hydrogen sulfide did not appear in our experiment. We speculate that $(\text{H}_2\text{S})_4^-$ has a rather open structure of substantial dipole moment in its neutral core. Its poor hydrogen bonding facilitates this structure, since unlike water it is relatively unconstrained in the structures that it can form.

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