Solvated Electrons in Very Small Clusters of Polar Molecules: $(HF)_3{}^-$

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Photoelectron spectra of $(HF)_3{}^-$ reveal coexistence of two anionic isomers with vertical electron detachment energies (VDE) of 0.24 and 0.43 eV. The results of electronic-structure calculations, performed at the coupled cluster level of theory with single, double, and noniterative triple excitations, suggest that the two isomers observed experimentally are an open, zigzag, dipole-bound anion and an asymmetric solvated electron, in which the dipole-bound anion of $(HF)_2$ is solvated by one HF monomer at the side of the excess electron. The theoretical VDE of 0.21 and 0.44 eV, respectively, are in excellent agreement with the experimental data.

A cluster of polar molecules can host an excess electron in at least two ways. First, the excess electron can be tethered to the cluster by its interaction with the cluster's dipole moment [1,2]. Second, the electron can localize inside the cluster, bulk analogs being the hydrated and ammoniated electrons [3–5]. While the structural reorganization of the cluster, due to attachment of an excess electron, is typically small for dipole-bound electrons (dbe), it is usually quite significant for "solvated electrons" (se), since the solvation occurs at the expense of breaking of preexisting hydrogen bonds. The se structures, however, provide more contact interactions between the polar molecules and the excess electron [6]. For these reasons, it is often assumed that dbe dominate for small polar clusters, whereas large clusters form se. Here we show that dbe and se coexist in as small a cluster as $(HF)_3{}^-$. The stability of these anions with respect to the neutral cluster results not only from the excess electron binding energy but also from favorable entropic effects, which reflect the greater "floppiness" of the anionic structures.

Low energy electrons are of paramount importance in radiation-induced chemical processes [7–9], and negatively charged clusters of polar molecules have been extensively studied, both experimentally [10–17] and theoretically [18–23]. The isolated ten-electron molecules, HF, H_2O, and NH_3, are closed-shell species, which are not known to form stable associations with an excess electron, i.e., stable anions. However, their hydrogen-bonded assemblies, even as small as dimers, are known to trap excess electrons and to form stable anions in the gas phase [10]. Early studies of small anionic clusters composed of intact polar molecules concentrated on dbe [19] also known as surface electron states [24], in which the cluster's dipole moment is fortified by coalignment of the dipoles of the monomers forming the cluster. On the other hand, solvated electrons (sometimes referred to

as internal electron states) were considered inherent to large clusters of polar molecules [25]. In 1997, however, theoretical studies showed that a fully symmetric D_{3h} se structure is a local minimum on the potential energy structure of $(HF)_3{}^-$, and that it is only a few kcal/mol higher than the global minimum corresponding to an open zigzag dbe structure of C_s symmetry (see Fig. 1 for both) [26]. In addition, the vertical electron detachment
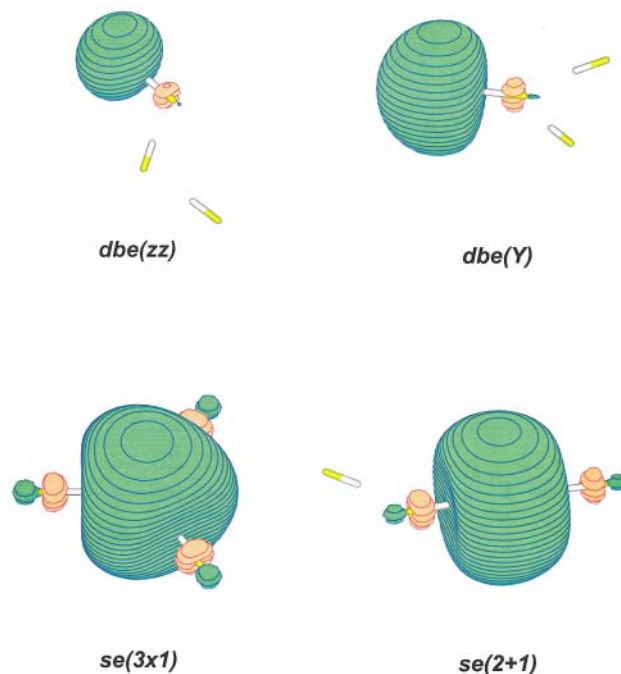

FIG. 1 (color).   The minimum energy structures and orbitals occupied by the excess electron for different isomers of $(HF)_3{}^-$. The white-yellow bars represent HF monomers. Singly occupied orbitals (green and orange for different signs) of $(HF)_3{}^-$ are plotted with a contour spacing of 0.0275 bohr$^{-3/2}$.

energy was predicted to be 3 times larger for the se than for the dbe. These theoretical findings prompted us to look for new isomers of small anionic clusters of polar molecules. In particular, we searched for hybrid states that display features of both solvated electrons and dipole-bound anions. Here we report a discovery of the isomerism of $(HF)_3{}^-$ based on photoelectron spectroscopy measurements and quantum mechanical calculations.

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency laser beam and energy analyzing the resultant photodetached electrons [27]. It is governed by the energy-conserving relationship: $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Thus EBE is an independent variable, analogous to the wavelength or frequency in optical spectroscopy, which is defined by two experimentally measurable quantities: the photon energy $h\nu$ and EKE. In the apparatus used to conduct these studies, we used an argon ion laser operated intracavity at 488 nm (2.540 eV photons), and a hemispherical electron energy analyzer with a resolution of ~ 25 meV. A supersonic expansion nozzle-ion source was used, through which a gas mixture of 5% HF in argon was expanded into high vacuum. Because of the corrosive nature of HF gas, this ion source was a challenge to operate, showing extreme sensitivity to source conditions, which in turn made precise day-to-day recipes elusive.

Three photoelectron spectra of $(HF)_3{}^-$ are shown in Fig. 2. On most days, we observed the spectrum shown in Fig. 2a. It is dominated by a strong, narrow peak at low EBE, with a much weaker peak to its high EBE side. The strong peak is assigned as the origin-containing peak, and its vertical electron detachment energy (VDE) is 0.24 eV. VDE is a value of EBE that corresponds to the most intense Franck-Condon feature in the electron detachment spectrum. The additional weak peak is separated from the center of the strong peak by 0.45 eV, and it is assigned as an excitation of a HF molecular stretching vibration. This pattern is characteristic of photoelectron spectra of dipole bound anions and other highly diffuse excess electron systems. On other days, however, we observed the spectrum shown in Fig. 2b. It looks much like the spectrum in Fig. 2a, except that it is located at a different electron binding energy. Its main peak is also assigned as its origin-containing peak, and its VDE is 0.43 eV. The spacing between its strong and its weak peaks is also close to the energy of a HF vibration. Lastly, on a single occasion, we observed the spectrum shown in Fig. 2c, where the spectral features of both Figs. 2a and 2b appear in the same spectrum. While the prospect was very unlikely that the spectrum in Fig. 2b had been due to an instrumentally induced shift of the spectrum in Fig. 2, their simultaneous observation eliminates this possibility and authenticates the legitimacy of both. Thus, we have observed two different forms of $(HF)_3{}^-$, with one normally being favored over
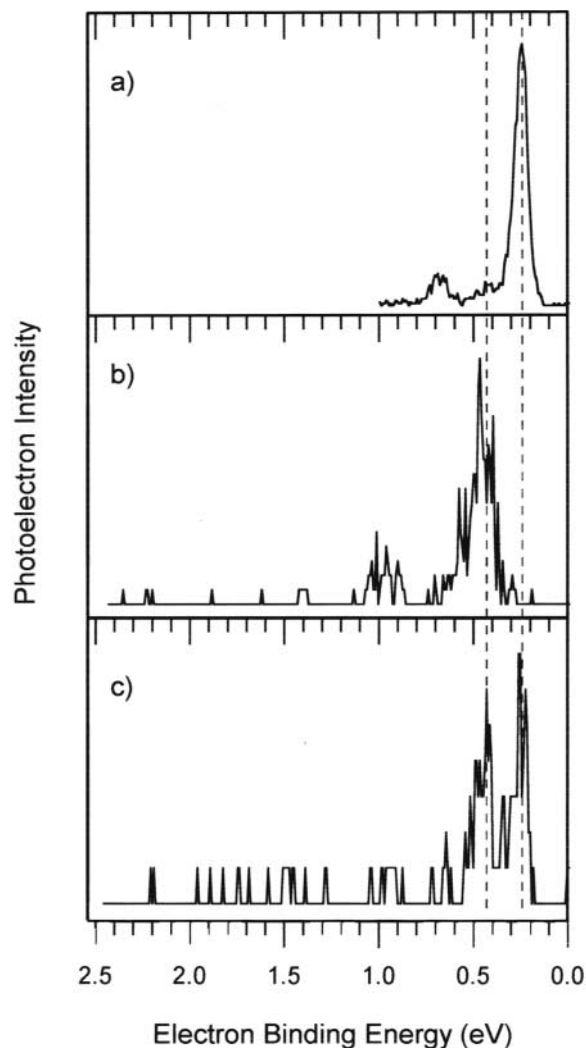

FIG. 2. Three photoelectron spectra of $(HF)_3{}^-$, each measured under slightly different source conditions.

the other under most source conditions but with their co-existence also a rare possibility.

An extensive computational analysis of the configuration topology of $(HF)_3{}^-$ has been performed to assist in the interpretation of experimental results. The minima on the potential energy surfaces of the neutral and the anion and harmonic vibrational frequencies were determined at the second-order Møller-Plesset (MP2) level, and the values of VDE were determined at the coupled cluster level of theory with iterative single, double, and noniterative triple excitations [CCSD(T)] [28]. The one-electron basis set was of augmented correlation consistent valence double-zeta quality [29] and was supplemented with additional sets of s, p, and d diffuse functions required to accommodate an excess electron. The calculations were performed with the MOLPRO [30] and GAUSSIAN98 [31] programs, and the 3D plots of molecular orbitals were generated with the MOLDEN program [32].

The lowest energy structure of the neutral trimer is planar and cyclic (C_{3h}) [33], and it does not support a

bound anionic state. The anionic structures, identified as minima on the potential energy surface of $(HF)_3^-$, are presented in Fig. 1. The orbitals occupied by the excess electron, also provided in Fig 1, display a variety of electron trapping possibilities. First, the excess electron can form a dipole-bound state supported by a large dipole moment ($\mu = 6.3$ D) of an open, zigzag structure [dbe(zz)]. Second, a high-dipole structure can be a Y-branched structure ($\mu = 4.9$ D) rather than a zigzag structure, and the resulting dipole-bound state is labeled dbe(Y). Next, the excess electron can be symmetrically solvated by three HF molecules forming a trigonal solvated electron [se(3 × 1)]. Finally, the excess electron can be asymmetrically solvated by the dimer and the monomer and the resulting structure is labeled se(2 + 1). The isomers dbe(zz), dbe(Y), and se(2 + 1) can be viewed as a dipole-bound anion of $(HF)_2$ additionally solvated by one HF monomer, with the solvation site being the F terminus of the dimer, in middle F of the dimer, and the excess electron, respectively. The question we will attempt to answer is which two of the four structures correspond to the two peaks observed experimentally.

The energy of the anion, determined with respect to the lowest energy isomer of the neutral cluster, is given by a sum of the reorganization energy of the neutral, E_{reorg}^N, the negative of VDE, and the difference in the zero-point vibration energy of the anion and the neutral, ΔE_{vib}^0,

$$E^A = E^N(G_A) - E^N(G_N) - VDE + E_{vib,A}^0 - E_{vib,N}^0$$
$$= E_{reorg}^N - VDE + \Delta E_{vib}^0,$$

where $E^N(G_X)$ denotes the electronic energy of the neutral at the equilibrium geometry of X. The values of E_{reorg}^N were determined at the CCSD(T) level with augmented correlation consistent valence quadruple-zeta basis sets [29] to suppress the effect of basis set superposition error. E^A is a measure of the relative stability of the anion with respect to the neutral at 0 K, whereas the relative stability at finite temperatures is given by the difference of Gibbs free energies of the anion and the neutral plus a free electron. This difference is denoted G^A below. The terms (ΔE_{vib}^0) and $G^A - E^A$ were determined in the harmonic oscillator-rigid rotor approximation using the MP2 geometries and frequencies.

Because of significant structural dissimilarities between the different anion species, the different contributions to the stabilization energy have considerably different magnitudes as displayed in Fig. 3. The destabilizing term E_{reorg}^N, determined with respect to the most stable, cyclic, neutral cluster, is the largest for the fully symmetric solvated electron se(3 × 1), in which all hydrogen bonds have been broken, and the smallest for the open zigzag dipole-bound anion dbe(zz), in which only one hydrogen bond has been broken and a strain has been relieved from the cyclic structure. The opposite holds for the stabilizing electron binding energy, VDE, which is the largest for the se(3 × 1), as
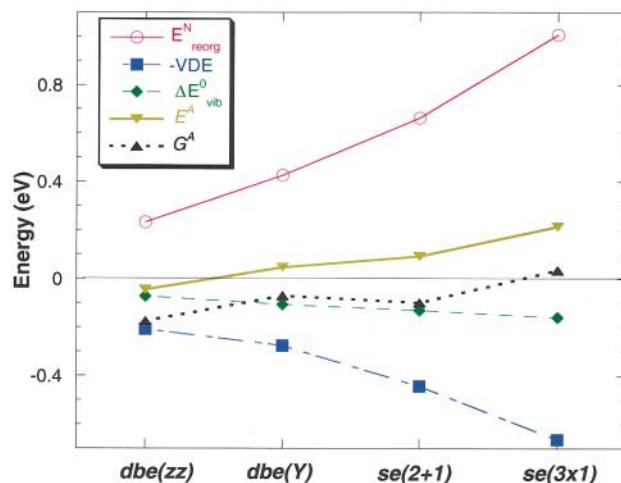

FIG. 3 (color). The interplay between the reorganization energy of the neutral (E_{reorg}^N), the electron binding energy (VDE), and the difference in zero-point vibrational energy (ΔE_{vib}^0), which determine the energy of the anion (E^A) with respect to the energy of the cyclic neutral cluster. The values of Gibbs free energies for anions (G^A) (with respect to the cyclic neutrals) are also displayed.

se(3 × 1) provides the largest number of direct electron-molecule contacts, and the smallest for the dbe(zz), with only one electron-molecule contact. The small but always stabilizing ΔE_{vib}^0 term plays a pivotal role in the stability of the anionic species due to a cancellation between the opposing E_{reorg}^N and VDE terms. The stabilization provided by ΔE_{vib}^0 is greater the floppier the anionic structure is; i.e., the largest stabilization is reported for the hydrogen-bond-free se(3 × 1).

The stability of all of the anionic species with respect to the neutral cyclic clusters is greatly enhanced at finite temperatures as shown in Fig. 3, where the values of E^A and G^A are displayed. The Gibbs free energy values, G^A, were obtained for $T = 298$ K and $p = 1$ atm. The larger stability of the anions in terms of G^A rather than E^A results from the vibrational contribution to entropy, which favors less rigid anionic species over the more rigid, hydrogen-bonded, cyclic neutral cluster. All anions, but the se(3 × 1), are stable with respect to the neutral at $T = 298$ K, whereas at $T = 0$ K only the dbe(zz) is stable. The results indicate that both dipole-bound anions *and* solvated electrons may be stable with respect to the neutral clusters at elevated temperatures. Moreover, the small differences in the harmonic Gibbs free energies for anionic isomers suggest the possibility that some of them can *coexist* in the gas phase. We should mention, however, that while our predictions are based on very reliable values of the E_{reorg}^N and VDE terms, the thermal contributions to thermodynamic functions were determined only in the rigid rotor-harmonic oscillator approximation. Statistical analysis using a global anharmonic potential energy surface for the anion would be required to better understand the equilibrium population of the species. Unfortunately, such a

surface is not readily available [34]. Fortunately, a comparison of the calculated and measured values of VDE provides a straightforward verification of our predictions as to the coexistence of different anionic isomers.

The experimental values for VDE of 0.24 and 0.43 eV are in good agreement with the calculated values of 021 and 0.44 eV for the dbe(zz) and se(2×1), respectively. These are also the most stable anionic isomers at $T = 298$ K; see Fig. 3. Thus, strong evidence has been obtained that dipole-bound and solvated-electron anions of small HF clusters coexist in the gas phase at finite temperatures.

A detectable population of asymmetric solvated electrons in the anionic beam of $(HF)_3^-$ prompts us to conclude that the preference by small polar clusters to form dipole-bound anionic states rather than solvated electrons is much smaller than assumed heretofore. The asymmetric solvated electrons are viable species to be searched for in future experimental and theoretical studies. They are characterized by a well-balanced combination of the destabilizing reorganization energy of the neutral cluster, stabilizing electron binding energy, and stabilizing vibrational contribution to the Gibbs free energy. In fact, our recent results indicate that there is a rich variety of anionic species formed by small polar clusters, which are neither open zigzag, dipole-bound anions nor fully symmetric solvated electrons. Fully symmetric solvated electron, such as trigonal $(HF)_3^-$ [se(3×1)] and tetragonal $(HF)_4^-$ [se(4×1)], are less stable than asymmetric solvated electrons se($n + m$) that can be viewed as dipole-bound precursors, $(HF)_n^-$, solvated by $(HF)_m$ at the side of the excess electron.

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