Negative ion photoelectron spectroscopy of the ground state, dipole-bound dimeric anion, $(HF)_2^-$

Jay H. Hendricks,[a)] Helen L. de Clercq, Svetlana A. Lyapustina, and Kit H. Bowen, Jr.[b)]

Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

We present the mass spectral and photoelectron spectroscopic results of our study of $(HF)_2^-$. Our main findings are as follows. The $(HF)_2^-$ anion was observed experimentally for the first time, confirming the 20 year old prediction of Jordan and Wendoloski. The photoelectron spectrum of $(HF)_2^-$ exhibits a distinctive spectral signature, which we have come to recognize as being characteristic of dipole bound anions. The vertical detachment energy (VDE) of $(HF)_2^-$ has been determined to be 63 ± 3 meV, and the adiabatic electron affinity (EA_a) of $(HF)_2$ was judged to be close to this value as well. Relatively weak spectral features, characteristic of intramolecular vibrations in the final (neutral dimer) state, were also observed. We have interpreted these results in terms of slight distortions of the dimer anion's geometric structure which lead to an enhanced dipole moment. This interpretation is supported to a considerable extent by theoretical calculations reported in the companion paper by Gutowski and Skurski. © *1997 American Institute of Physics.* [S0021-9606(97)00432-7]

I. INTRODUCTION

For 25 years now, hydrogen fluoride dimers, $(HF)_2$, have served as important prototypes for studying hydrogen bonding and weak binding interactions between polar molecules.[1–10] Neutral dimers of hydrogen fluoride form readily and occur both in expansions of hydrogen fluoride gas and in its static vapors. The parent positive and negative ions, i.e., $(HF)_2^+$ and $(HF)_2^-$, on the other hand, have been elusive, raising questions about their stabilities.

The focus of the present work is on the ground state, negatively charged dimer of hydrogen fluoride, $(HF)_2^-$. In the late 1960's and mid-1970's, experimental evidence implicating the existence of the related species, $(HCl)_2^-$, as a reaction intermediate was inferred from radiation chemistry.[11–14] Then, in 1977, calculations by Jordan and Wendoloski predicted that $(HF)_2^-$ should be stable.[15] The existence of $(HF)_2^-$ might have been confirmed only a few years later in 1983, when collisional charge transfer experiments designed to search for intact hydrogen halide cluster anions were conducted, but these did not find it.[16] For several years more, $(HF)_2^-$ would remain a predicted, but unobserved species.

Jordan and Wendoloski[15] conceived of $(HF)_2^-$ as a dipole bound anion, in which the binding of the excess electron is due to the dipolar field of its corresponding neutral, $(HF)_2$. Their work on $(HF)_2^-$, however, was but one important milestone in the sequence of theoretical developments occurring both before and after it. The concept of dipole bound anions has its roots in a 1947 paper by Fermi and Teller.[17] Subsequent theoretical work[18–40] by other pioneers in this field refined the topic considerably; eventually to the point that the main expected properties of dipole bound anions could be stated as follows. (1) There is a critical dipole moment, μ_c, which is necessary for dipole binding of an excess electron. (2) The excess electron cloud is spatially diffuse, reminiscent of that of a Rydberg electron. (3) The electron binding energies in such systems are rather small, increasing with the magnitude of the dipole moment beyond μ_c. (4) The molecular structure of an anion having a dipole bound electron is essentially the same as that of its corresponding neutral.

Early on, the critical dipole moment was computed to be 1.625 D in the Born–Oppenheimer approximation, but after more work (both theoretical[21] and experimental[41]), the critical dipole moment was established to be about 2.5 D for a real system. In regard to the requirement for a minimum dipole moment, HF and $(HF)_2$ are both interesting cases.[42] The dipole moment of HF is ~ 1.8 D. Not only does the HF molecule not have a large enough dipole moment to form a dipole bound anion, it does not form a stable, conventional (valence) anion either. When, however, two HF molecules join together to form the complex, $(HF)_2$, the composite dipole moment of the resultant neutral dimer is ~ 3.2 D,[43] meeting an important condition for the formation of dipole bound anions. Since the weakly bound hydrogen fluoride dimer is formed from molecular components which themselves form neither conventional[44] nor dipole bound anions, one can be reasonably assured that it is the dipolar field of the dimer that is essentially responsible for the excess electron's binding in $(HF)_2^-$, as was originally proposed by Jordan and Wendoloski.[15] Certainly, $(HF)_2^-$ is not a valence anion in the conventional sense.

In this paper, we present the mass spectral and photoelectron spectroscopic results of our study of $(HF)_2^-$. While the specifics will be presented below, our main findings can be summarized as follows. (a) The $(HF)_2^-$ anion has been observed experimentally for the first time, confirming the 20 year old prediction of Jordan and Wendoloski.[15] (b) The pho-

[a)]Present address: N.I.S.T., Process Measurements Division, 221/B312, Gaithersburg, Maryland 20899.
[b)]Author to whom correspondence should be addressed.

toelectron spectrum of $(HF)_2^-$ exhibits a distinctive photo-electron spectral signature, which we have come to recognize as being characteristic of and unique to dipole bound anions. (c) The vertical detachment energy (VDE) of $(HF)_2^-$ has been determined to be 63 ± 3 meV, and the adiabatic electron affinity (EA_a) of $(HF)_2$ was judged to be close to this value as well. (d) Relatively weak spectral features, characteristic of component molecular (intramolecular) vibrations in the final (neutral dimer) state, were observed.

Some of these results are at odds with expectations gleaned from the calculations available through early 1996. Consider, for example, the ground state, dipole bound dimer anion, $(H_2O)_2^-$. This species is analogous to $(HF)_2^-$ in many ways, and it is the most heavily theoretically studied example of a dipole bound dimer anion system. Starting in 1979, the $(H_2O)_2^-$ problem was addressed by several theoretical groups, some using rather different computational approaches.[34–39] Collectively, these benchmark studies tended to find the electron affinity of water dimer to be very small (ranging between ~ 0.2 and 6 meV) and the global minimum structure of $(H_2O)_2^-$ to be the same as the equilibrium structure of the neutral, $(H_2O)_2$. Together with other calculations on dipole bound molecular anions,[45,46] these studies provided a basis for expecting dipole bound anions to have ultrasmall, excess electron binding energies and equilibrium structures which are the same as those of their corresponding neutrals.

Our measured electron affinity for $(HF)_2$, while small, is nevertheless easily an order of magnitude greater than that expected on the basis of the above mentioned calculations.[47] Also, the unexpected appearance of vibrational features in the photoelectron spectrum raised the question as to whether there might be some degree of structural dissimilarity between $(HF)_2^-$ and $(HF)_2$. Thus, when experimental results, (c) and (d), were first obtained for $(HF)_2^-$, both were unexpected, one quantitatively and the other qualitatively, in light of then available theoretical expectations. Of course, these two results may well be related, in that a stronger-than-expected electron-dipole coupling interaction goes hand-in-hand with the possibility of anion/neutral structural dissimilarity. We have also studied a variety of other dipole bound dimer anions by photoelectron spectroscopy,[48–54] including $(H_2O)_2^-$, $[(CH_3CN)(H_2O)]^-$, $[C_2H_2(OH)_2]_2^-$, $[(HCl)(H_2O)]^-$, and $[(HCN)(H_2O)]^-$. These all exhibit higher electron affinities than expected and weak vibrational spectral features, characteristic of their molecular components. The measured VDE's for these dimeric systems range from ~ 40–100 meV. That for $(H_2O)_2^-$ for example, is 45 meV. Confusion as to the origin(s) of these discrepancies between theory and experiment persisted until this past year (see below).

By 1987, we were interpreting our photoelectron spectrum of $(H_2O)_2^-$ in terms of the structural distortion of at least one of its water components.[48] Gradually, however, this picture was refined, and we came to view our $(H_2O)_2^-$ results in terms of an overall distortion of the dimer anion's geometric structure, so as to increase the dipole moment of its neu-

tral core. This was consistent with our observations in that it accounted for both an enhancement in the electron binding energy and the appearance of vibrational features (through Franck–Condon overlap) in the photoelectron spectrum. This model, which is as applicable to $(HF)_2^-$ as it was to $(H_2O)_2^-$, is intuitively attractive in that a relatively slight (and low energy cost) modification of the dimer anion's intermolecular structure (relative to the equilibrium structure of its corresponding neutral dimer) could cause a considerable increase in its dipole moment, leading to further excess electron stabilization and counterbalancing 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. This is consistent with our observations. More difficult to reconcile are the intramolecular vibrations that were observed (and readily resolved) in the spectra. According to this model, the appearance of intramolecular vibrational spectral features would seem to imply that the structures of component molecules within the dimer anion had also been modified, at least slightly, due to their interaction with the excess electron.

The above interpretation treats the appearance of molecular vibrational features in the photoelectron spectra of dipole bound dimer anions in terms of anion/neutral structural dissimilarities, i.e., via Franck–Condon overlap. In the case of the dipole bound molecular anion, CH_3CN^-, however, other mechanisms have also been proposed. While examining the photoelectron spectrum of CH_3CN^-, Johnson and co-workers[55] found that the relative intensities of the low signal, molecular vibrational features that they observed depended on photon energy. If anion/neutral structural dissimilarity had been the only cause of these vibrational features, this should not have happened. They interpreted their results in terms of photon access to an excited state of CH_3CN^- (a resonant state) lying above CH_3CN in energy and/or a coupling of the excess electron to the oscillating dipole moment of the molecule. While this interpretation was convincing for the case of CH_3CN^-, its generality to other systems was unclear, especially in regard to floppy dimeric species, in which intermolecular structural reorganization can occur relatively easily.

Over the past year, Gutowski, Skurski, Boldyrev, Simons, and Jordan[56,57] have made dramatic progress in banishing discrepancies between theory and experiments regarding several dipole bound anions. Before this work was done, it was characteristic of calculations on dipole bound anions to seriously underestimate their electron affinities. The key ingredient in their theoretical methodology involved accounting for the dispersion interaction between the excess electron and the neutral. In a companion paper, Gutowski and Skurski[58] use these advances to compute the electron binding energy of $(HF)_2^-$, its geometrical structure, and its modeled photoelectron spectrum. As discussed further below, their calculated electron affinity (49 meV) is close to our experimental value; their global minimum structure of $(HF)_2^-$ is distorted relative to the equilibrium structure of

$(HF)_2$, enhancing the dipole moment by ~ 0.5 D; and their modeled photoelectron spectrum is strikingly similar to our experimentally-determined one, including the intramolecular vibrational features and their observed relative intensities. Furthermore, the structural differences they found between $(HF)_2^-$ and $(HF)_2$ were indicative of $(HF)_2^-$ structural distortions at both the inter- and intramolecular levels, and the vibrational features seen in their modelled photoelectron spectrum were entirely attributable to dissimilarities between the potential energy surfaces of $(HF)_2^-$ and $(HF)_2$, i.e., to Franck–Condon overlap.

In essence, these calculations support most of the tenets of our model for dipole bound dimer anions. There is a structural dissimilarity between $(HF)_2$ and $(HF)_2^-$, with the neutral core of $(HF)_2^-$ exhibiting an enhanced dipole moment, and the vibrational features observed in the photoelectron spectrum of $(HF)_2^-$ are Franck–Condon in character. In addition, however, these calculations have also shown where our model falls short. In particular, our model focuses on electrostatic electron-dipole stabilization and dipole moment enhancement due to structural changes associated with electron attachment, but it is blind to the important role played by the dispersion interaction between the excess electron and the neutral. Indeed, it is the dispersion interaction ingredient that is primarily responsible, in the above-mentioned calculations, for closing the considerable gap between calculated and measured electron binding energies for many dipole bound anions.

II. EXPERIMENT

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy analyzing the resultant photodetached electrons. This is a direct approach for determining 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. Our apparatus has been described in detail previously.[59] The spectra reported here were calibrated against the well-known photoelectron spectra of O^- and NO^-, and the resolution of our electron energy analyzer was 27 meV. Photodetachment was most often accomplished using ~ 220 circulating watts of 2.540 eV photons, but when, on occasion, it was also done with 2.409 eV and 2.707 eV photons, the photoelectron spectrum (electron counts vs EBE) did not change.

Hydrogen fluoride dimer anions were generated in a supersonic expansion ion source. In this device, relatively low energy electrons are injected directly into the high density portion of an expanding gas jet in the presence of weak axial magnetic fields, and negative ions are extracted from the resulting microplasma. Typical source conditions during these experiments were as follows. The nozzle's stagnation chamber pressure was 5–7 atm of a 2%–5% HF/Ar gas mixture, and its temperature was near 0 °C. The nozzle diameter was 20 μm, the beam energy was 500 V, the thoriated-iridium filament bias voltage was -20 to -30 V, and its emission current was 1.5–3 mA. Typical ion currents of
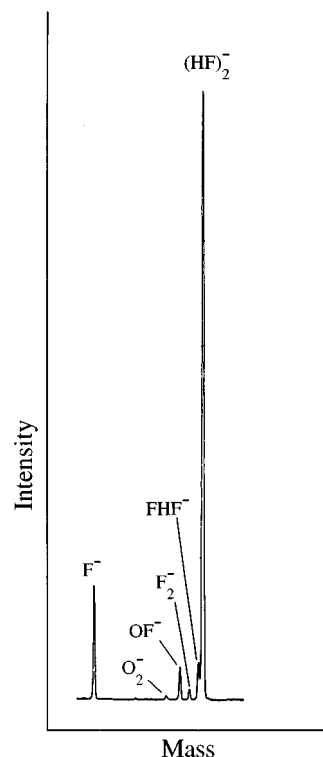

FIG. 1. Typical mass spectrum obtained under the source conditions used in this experiment. The mechanism for anion formation is not known, but the region in which they are formed provides large numbers of very low energy, secondary electrons in a many-collision environment.

$(HF)_2^-$ just beyond the ion–laser interaction region were ~ 50 pA. Based on source conditions and the fragility of $(HF)_2^-$, its ion temperature was presumed to be on the order of 10 K. A typical mass spectrum taken under these conditions is dominated by $(HF)_2^-$ as shown in Fig. 1.

By changing source conditions, it was possible to obtain mass spectra dominated by other anions, i.e., either by F^-, FHF^-, and $F^-(HF)_n/(FHF)^-(HF)_{n-1}$ or by a combination of homogeneous hydrogen fluoride cluster anions and heterogeneous argon/hydrogen fluoride cluster anions. While none of the former group photodetached in our photon range, those in the latter group did. Particularly intriguing is $(HF)_3^-$, which cannot have a mass coincidence with $Ar_n(HF)_2^-$. Its photoelectron spectrum will be the subject of a future report.

III. RESULTS AND INTERPRETATION

The photoelectron spectrum of $(HF)_2^-$ is presented in Fig. 2. This spectrum consists of an intense, narrow peak (labeled as A) at low electron binding energy and two considerably weaker intensity peaks (labeled as B and C) at higher electron binding energies. Peak A provides both energetic information and a basis for maintaining that $(HF)_2$ and $(HF)_2^-$ are, for the most part, structurally similar, while the mere visibility of peaks B and C provides a basis for moderating this interpretation and invoking the view that
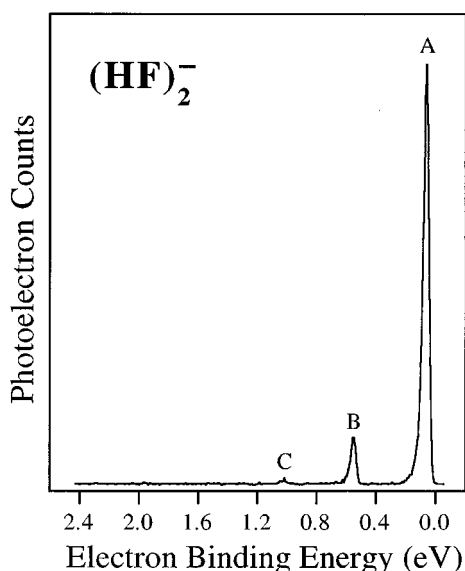
FIG. 2. Photoelectron spectrum of $(HF)_2^-$ recorded with 2.540 eV photons.

$(HF)_2$ and $(HF)_2^-$ are, in fact, very slightly dissimilar structurally. Table I summarizes our results and assignments.

Peaks B and C are separated from peak A by energies equivalent to the HF molecule's stretching frequency and its first overtone frequency, respectively. We assign these peaks as being due primarily to intramolecular vibrational excitations in neutral $(HF)_2$, with peak B arising from the transition between cold $(HF)_2^-$ and $(HF)_2$ with one quanta of neutral monomer vibrational excitation and with peak C arising from the transition between cold $(HF)_2^-$ and $(HF)_2$ with two quanta of neutral monomer vibrational excitation. As noted above, we interpret peaks B and C as arising due to Franck–Condon overlap and thus as evidence for some degree of structural dissimilarity between $(HF)_2^-$ and $(HF)_2$. Negative ion photoelectron spectroscopy is so sensitive to anion/neutral structural differences and the intensities of peaks B and C are so weak, that the structural dissimilarity between $(HF)_2^-$ and $(HF)_2$ is probably only slight. The appearance of HF molecular vibrations in this spectrum also confirms that $(HF)_2^-$ is composed of intact HF molecules, and that $(HF)_2^-$

is not $[H^+\cdots(FHF)^-]^-$ internally. As for transitions involving intermolecular (hydrogen bonding) modes, they are also most probably present but are unresolved at the resolution of our spectrum.

Peak A is the dominant feature in the photoelectron spectrum of $(HF)_2^-$. The vertical detachment energy (VDE) is the electron binding energy at the maximum intensity of this peak, and it is 63 ± 3 meV. The fact that peak A is the highest intensity and the lowest EBE feature in the spectrum suggests that the origin transition lies (unresolved) within it, while its narrowness indicates that the origin transition probably lies very near the VDE.[60] The adiabatic electron affinity (EA_a) corresponds to the electron binding energy of the origin transition. Thus, the EA_a of $(HF)_2$ is either equal in value to the VDE of $(HF)_2^-$, or perhaps a few meV less. Structural implications also emerge from a consideration of peak A's spectral properties. Because peak A is an unusually narrow, origin-containing spectral feature with a high proportion of the Franck–Condon overlap, this implies that $(HF)_2^-$ and $(HF)_2$ share major structural similarities, even though other features in the spectrum suggest the presence of slight structural dissimilarities. Thus, our picture of the structure of $(HF)_2^-$ is that it is mostly like that of $(HF)_2$, but with some slight differences.

The features seen here are typical of the distinctive spectral signature that we have observed in the photoelectron spectra of every dipole bound anion we have studied, these including not only dimeric,[48–54] but also molecular[61] dipole bound anions. This spectral fingerprint consists of an intense, narrow peak at unusually low electron binding energy plus much weaker vibrational features, characteristic of the constituent molecules, at higher electron binding energies. This signature is unlike that of any known conventional anionic species.

IV. DISCUSSION

In the accompanying paper, Gutowski and Skurski[58] calculate the EA_a of $(HF)_2$, the geometries of $(HF)_2^-$ and $(HF)_2$, and the modeled photoelectron spectrum of $(HF)_2^-$. They found the EA_a of $(HF)_2$ to be 49 meV and the VDE of $(HF)_2^-$ to be 50 meV, in reasonably good agreement with our values; they found slight structural differences between the geometries of $(HF)_2^-$ and $(HF)_2$ at both the inter- and the intramolecular levels (see their Table I); and they found excellent agreement, in most respects, between their modeled photoelectron spectrum and our measured one.

Figure 3 compares their modeled photoelectron spectrum of $(HF)_2^-$ to our experimentally obtained spectrum of $(HF)_2^-$. Gutowski and Skurski generated this spectrum by broadening their calculated line spectrum to an instrumental resolution of 27 meV. Notice that the relative intensities match very well. The A–B and A–C peak spacings in their modeled spectrum, however, are slightly larger than the ones actually measured. They attribute this to the fact that their calculation was conducted in a harmonic approximation for

TABLE I. Summary of results obtained from the photoelectron spectrum of $(HF)_2^-$.

Peak	Electron binding energy[a] in eV (in cm⁻¹)	Energy relative to peak A in eV (in cm⁻¹)	Assignment
A	0.063 (508)	⋯	Vertical detachment energy (VDE)[b]
B	0.553 (4460)	0.490 (3950)	One quantum of H–F stretch vibration[c]
C	1.018 (8210)	0.955 (7700)	Two quanta of H–F stretch vibration

[a]A typical error bar is ±0.003 eV in determining peak position.
[b]The adiabatic electron affinity (EA_a) is very close to the value of VDE.
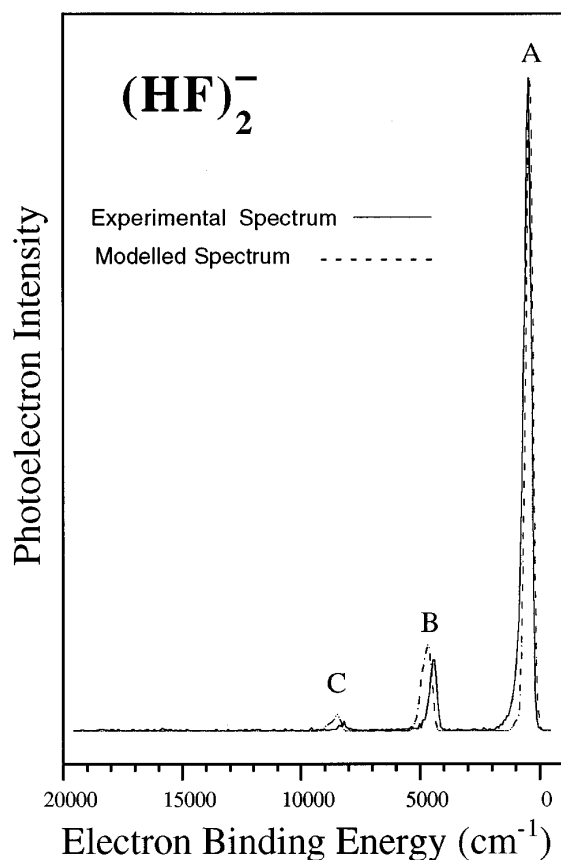[c]Literature value is 3931 cm⁻¹ (Ref. 63).

FIG. 3. Comparison between the modeled photoelectron spectrum of $(HF)_2^-$ (Gutowski and Skurski) and its experimental spectrum (present work). The modeled intensity of peak A was normalized to that of peak A in the experimental spectrum.

all of the modes in this problem. Nevertheless, this is the first time that theory has so successfully modeled the photoelectron spectrum of a dipole bound anion.

The work of Gutowski and Skurski has shown that the potential surfaces for $(HF)_2$ and $(HF)_2^-$ are slightly different from each other, both in terms of their displacement relative to one another (structural differences) and their curvatures (force constants). All of the peaks appearing in the modeled photoelectron spectrum are the result of differences between these potential surfaces, and they are Franck–Condon in character. It is also likely that both displacement and curvature factors contribute to peak intensities. Thus, these calculations are supportive of the contention that the visibility of peaks B and C in the experimental spectrum is indicative of structural differences between $(HF)_2$ and $(HF)_2^-$.

Structural distortions in dipole bound dimer anions have also been explored theoretically for the case of $(H_2O)_2^-$. Several years ago, using quantum simulation techniques and *ab initio* electronic structure calculations, Landman and co-workers[39] found that "...while the minimum energy of $(H_2O)_2^-$ corresponds to a nuclear configuration similar to that found for the neutral $(H_2O)_2$ cluster, other nuclear configurations are also exhibited at finite temperature, characterized by a higher total molecular cluster dipole moment and a

larger magnitude of the excess electron binding energy." Just a few months ago, Bouteiller and co-workers[62] used density functional calculations to study water dimer and its anion. They found "...that a significant modification of the neutral parent geometry is introduced by the electron attachment process...," and that their "theoretical values of the very weak electron affinities and vertical detachment energies show good agreement with available experimental data." This constitutes still another example of recent calculations coming to grips with past discrepancies between theory and experiment regarding dipole bound anions.

Among the more important lessons to emerge from both the theoretical and the experimental study of $(HF)_2^-$ is that the interaction of an excess electron with $(HF)_2$ is capable of changing its potential energy surface. Given that even intramolecular structure is affected, this interaction can be viewed as a form of weak electrostriction. Apparently, this lesson can also be applied to $(H_2O)_2^-$, and we anticipate that small anion/neutral geometry changes will occur in other dipole bound dimer anion systems as well. In treating electron–polar molecule interactions theoretically, it is probably important to utilize methods which allow the molecules to distort slightly under the influence of their interaction with an excess electron.

ACKNOWLEDGMENTS

[1] T. R. Dyke, B. J. Howard, and W. Klemperer, J. Chem. Phys. **56**, 2442 (1972).
[2] A. S. Pine and W. J. Lafferty, J. Chem. Phys. **78**, 2154 (1983).
[3] D. W. Michael, C. E. Dykstra, and J. M. Lisy, J. Chem. Phys. **81**, 5998 (1984).
[4] B. J. Howard, T. R. Dyke, and W. Klemperer, J. Chem. Phys. **81**, 5417 (1984).
[5] Z. S. Huang, K. W. Jucks, and R. E. Miller, J. Chem. Phys. **85**, 3338 (1986).
[6] K. von Puttkamer and M. Quack, Mol. Phys. **62**, 1047 (1987).
[7] G. T. Fraser, J. Chem. Phys. **90**, 2097 (1989).
[8] D. G. Truhlar, in *Proceedings of the NATO Workshop on the Dynamics of Polyatomic van der Waals Complexes*, NATO Series B (Plenum, New York, 1989), Vol. 227, p. 159, and references therein.
[9] M. D. Schuder, C. M. Lovejoy, R. Lascola, and D. J. Nesbitt, J. Chem. Phys. **99**, 4346 (1993).
[10] H.-C. Chang and W. Klemperer, J. Chem. Phys. **104**, 7830 (1996).
[11] L. G. Christophorou, R. N. Compton, and H. W. Dickson, J. Chem. Phys. **48**, 1949 (1968).
[12] D. A. Armstrong and S. S. Nagra, J. Phys. Chem. **79**, 2875 (1975); S. S. Nagra and D. A. Armstrong, Can. J. Chem. **54**, 3580 (1976).
[13] D. E. Wilson and D. A. Armstrong, Radiat. Res. Rev. **2**, 297 (1970).
[14] G. R. A. Johnson and J. L. Redpath, Trans. Faraday Soc. **66**, 861 (1970).
[15] K. D. Jordan and J. J. Wendoloski, Chem. Phys. **21**, 145 (1977).
[16] E. L. Quitevis, K. H. Bowen, G. W. Liesegang, and D. R. Herschbach, J. Phys. Chem. **87**, 2076 (1983).
[17] E. Fermi and E. Teller, Phys. Rev. **72**, 406 (1947).

[18] O. H. Crawford, Proc. Phys. Soc. London **91**, 279 (1967).

[19] W. R. Garrett, J. E. Turner, and V. E. Anderson, Phys. Rev. **199**, 513 (1969).

[20] W. R. Garrett, Chem. Phys. Lett. **5**, 393 (1970); Phys. Rev. A **3**, 961 (1971).

[21] O. H. Crawford, Mol. Phys. **20**, 585 (1971).

[22] O. H. Crawford and W. R. Garrett, J. Chem. Phys. **66**, 4964 (1977).

[23] K. D. Jordan and W. Luken, J. Chem. Phys. **64**, 2760 (1976).

[24] K. D. Jordan, K. M. Griffing, J. Kenney, E. L. Anderson, and J. Simons, J. Chem. Phys. **64**, 4730 (1976).

[25] W. R. Garrett, J. Chem. Phys. **71**, 651 (1979).

[26] W. R. Garrett, J. Chem. Phys. **73**, 5721 (1980).

[27] L. Adamowicz and E. A. McCullough, Jr., J. Phys. Chem. **88**, 2045 (1984).

[28] J. Simons and K. D. Jordan, Chem. Rev. **87**, 535 (1987).

[29] D. C. Clary, J. Phys. Chem. **92**, 3173 (1988).

[30] D. C. Clary, Phys. Rev. A **40**, 4392 (1989).

[31] J. Simons, J. Chem. Phys. **91**, 6858 (1989).

[32] N. A. Oyler and Adamowicz, J. Phys. Chem. **97**, 11122 (1993).

[33] J. E. Turner, Am. J. Phys. **45**, 758 (1977).

[34] D. M. Chipman, J. Phys. Chem. **83**, 1657 (1979).

[35] A. Wallqvist, D. Thirumalai, and B. J. Berne, J. Chem. Phys. **85**, 1583 (1986).

[36] U. Landman, R. N. Barnett, C. L. Cleveland, D. Schaff, and J. Jortner, J. Phys. Chem. **91**, 4890 (1987).

[37] R. N. Barnett, U. Landman, and A. Nitzan, Phys. Rev. A **38**, 2178 (1988).

[38] R. N. Barnett, U. Landman, and A. Nitzan, J. Chem. Phys. **89**, 2242 (1988).

[39] R. N. Barnett, U. Landman, S. Dhar, N. R. Kestner, J. Jortner, and A. Nitzan, J. Chem. Phys. **91**, 7797 (1989).

[40] S. B. Hill, M. T. Frey, F. B. Dunning, and I. I. Fabrikant, Phys. Rev. A **53**, 3348 (1996).

[41] C. Desfrancois, H. Abdoul-Carime, and J. P. Schermann, Int. J. Mod. Phys. B **10**, 1339 (1996).

[42] An analogous case is described in C. Desfrancois, B. Baillon, J. P. Schermann, S. T. Arnold, J. H. Hendricks, and K. H. Bowen, Phys. Rev. Lett. **72**, 48 (1994).

[43] The total dipole moment was calculated from experimental data in Refs. 1 and 4.

[44] Nor does HF have a low-lying temporary anion state.

[45] D. C. Clary, Phys. Rev. A **40**, 4392 (1989).

[46] G. L. Gutsev and L. Adamowicz, Chem. Phys. Lett. **246**, 245 (1995).

[47] While the EA_a for $(HF)_2$, originally calculated by Jordan and Wendoloski, was ~ 90 meV, this early (Koopman's theory level) study substantially overestimated the dipole moment and utilized a relatively small basis set. For these reasons, the specific value of their calculated EA_a would not be expected to be highly reliable; K. D. Jordan (private communication).

[48] K. H. Bowen and J. G. Eaton, in *The Structure of Small Molecules and Ions*, in *Proceedings of the International Workshop on The Structure of Small Molecules and Ions*, Neve Ilan, Israel, 1987, edited by R. Naaman and Z. Vager (Plenum, New York, 1988), pp. 165–168.

[49] S. T. Arnold, J. G. Eaton, D. Patel-Misra, H. W. Sarkas, and K. H. Bowen, in *Ion and Cluster Ion Spectrosopy and Structure*, edited by J. P. Maier (Elsevier, Amsterdam, 1989), pp. 444–450.

[50] S. T. Arnold, J. V. Coe, J. G. Eaton, C. B. Freidhoff, L. H. Kidder, G. H. Lee, M. R. Manaa, K. M. McHugh, D. Patel-Misra, H. W. Sarkas, J. T. Snodgrass, and K. H. Bowen, in *The Chemical Physics of Atomic and Molecular Clusters*, edited by G. Scoles (North–Holland, Amsterdam, 1990), pp. 485–488.

[51] J. V. Coe, G. H. Lee, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewigt, H. Haberland, and D. Worsnop, J. Chem. Phys. **92**, 3980 (1990).

[52] G. H. Lee, S. T. Arnold, J. G. Eaton, H. W. Sarkas, K. H. Bowen, C. Ludewigt, and H. Haberland, Z. Phys. D **20**, 9 (1991).

[53] C. Desfrancois, N. Khelifa, A. Lisfi, J. P. Schermann, J. G. Eaton, and K. H. Bowen, J. Chem. Phys. **95**, 7760 (1991).

[54] J. H. Hendricks, H. L. de Clercq, S. A. Lyapustina, C. A. Fancher, T. P. Lippa, J. M. Collins, S. T. Arnold, G. H. Lee, and K. H. Bowen, in *Structures and Dynamics of Clusters*, in *Proceedings of the XLIII Yamada Conference*, edited by T. Kondow, K. Kaya, and A. Terasaki (Universal Academy, Tokyo, 1995), pp. 321–328.

[55] C. G. Bailey, C. E. H. Dessent, M. A. Johnson, and K. H. Bowen, J. Chem. Phys. **104**, 6976 (1996).

[56] M. Gutowski, P. Skurski, A. I. Boldyrev, J. Simons, and K. D. Jordan, Phys. Rev. A **54**, 1906 (1996).

[57] M. Gutowski, P. Skurski, J. Simons, and K. D. Jordan, in *Proceedings from the Second International Congress on Theoretical Chemical Physics*, New Orleans, April 9–13, 1996 (in press).

[58] M. Gutowski and P. Skurski, J. Chem. Phys. **107**, 2968 (1997), following paper.

[59] J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, J. Chem. Phys. **84**, 618 (1986).

[60] Additional peak A parameters; the FWHM of peak A is 43 meV. Also, on the low EBE side of peak A, the intensity of electron counts goes to base line before EBE=0. At the resolution employed in this experiment, this threshold is ~ 17 meV.

[61] J. H. Hendricks, S. A. Lyapustina, H. L. de Clercq, J. T. Snodgrass, and K. H. Bowen, J. Chem. Phys. **104**, 7788 (1996).

[62] Y. Bouteiller, C. Desfrancois, H. Abdoul-Carime, and J. P. Schermann, J. Chem. Phys. **105**, 6420 (1996).

[63] A. S. Pine, W. J. Lafferty, and B. J. Howard, J. Chem. Phys. **81**, 2939 (1984).