

# Energies of Dipole-Bound Anionic States

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## ABSTRACT

Dipole-bound anionic states of  $\text{CH}_3\text{CN}$ ,  $\text{C}_3\text{H}_2$ , and  $(\text{HF})_2$  were studied using highly correlated electronic structure methods and extended one-electron basis sets. The electron detachment energies were calculated using the coupled cluster method with single, double, and noniterative triple excitations. Geometrical relaxation of the molecular framework upon electron attachment and the difference in the harmonic zero-point vibrational energies between the neutral and the dipole-bound anionic species were calculated at the MP2 level of theory. We demonstrate that the dispersion interaction between the loosely bound electron and the electrons of the neutral molecule is an important component of the electron binding energy, comparable in magnitude to the electrostatic electron-dipole stabilization. The geometrical relaxation upon electron attachment and the change in the zero-point vibrational energy is important for the weakly bound HF dimer. The predicted values of the vertical electron detachment energies for the dipole bound states of  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$  of  $112$  and  $188 \text{ cm}^{-1}$ , respectively, are in excellent agreement with the recent experimental results of  $93$  and  $171 \pm 50 \text{ cm}^{-1}$ , respectively. For  $(\text{HF})_2^-$ , the predicted value of adiabatic electron detachment energy is  $396 \text{ cm}^{-1}$ , whereas the experimental vertical detachment energy is  $508 \pm 24 \text{ cm}^{-1}$ . The possibility of formation of the neutral dimer in an excited vibrational state is considered. © 1997 John Wiley & Sons, Inc.

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## Introduction

The critical value of 1.625 D for a dipole to bind an electron was set forth in the seminal contribution by Fermi and Teller [1]. For dipole moments greater than this value, there is an infinity of bound states within the context of the Born–Oppenheimer (BO) approximation. It was subsequently shown that the same critical moment exists for finite dipoles, even in the presence of a short-range repulsive core potential [2–4]. Garrett demonstrated that the critical dipole moment increases by a few tenths of a Debye and becomes molecule dependent upon inclusion of non-BO effects [5–7]. However, non-BO effects are relatively unimportant for dipole-bound states with electron binding energies much larger than the molecular rotational constants.

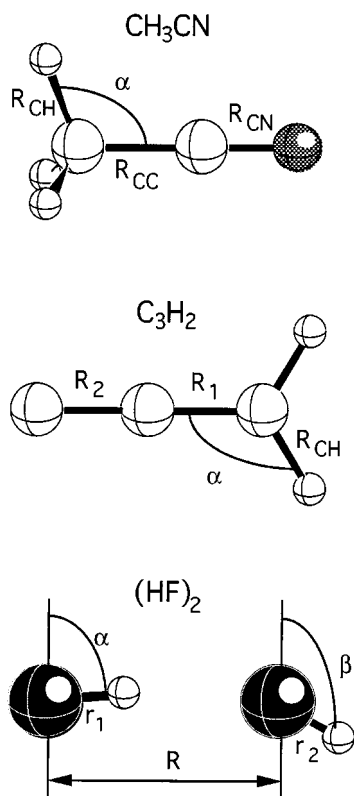
It was demonstrated about two decades ago that the loosely bound electron occupies a hybridized  $\sigma$  orbital localized on the positive side of the molecular dipole [8]. The average separation between the loosely bound electron and the neutral polar molecule is large (typically 10–100 Å). A variety of electronic structure methods have been used to calculate electron binding energies ( $E_{bind}$ ) in the context of the BO approximation. The electrostatic model of dipole-bound states and the large separation between the loosely bound electron and the neutral core led many researchers to adopt a Koopmans' theorem (KT) approach [9], in which the electron binding energy,  $E_{bind}^{KT}$ , is estimated from the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock self-consistent-field (SCF) calculation on the neutral molecule. This is a static approximation which neglects both electron correlation and orbital relaxation effects.

Orbital relaxation effects, which are included when the binding energy is obtained from the difference of the SCF energies of the neutral and anionic species, have proven to be quite small. On the other hand, the role of electron correlation effects is more controversial. Early studies of diatomics indicated that electron correlation effects are of secondary importance [10–16]. However, a significant destabilizing electron correlation effect was found in a coupled cluster study for the dipole-bound anion of nitromethane. This was interpreted as a consequence of a sizable overestima-

tion of the neutral molecule dipole moment at the SCF level of theory [17]. Recently, Gutsev and Adamowicz studied dipole-bound anions for a series of polar organic molecules [18]. They observed that the KT and SCF approaches provide rather similar values of  $E_{bind}$  and concluded that, in most of the cases considered, the second-order Møller–Plesset (MP2) electron correlation correction is small. Interestingly, the experimental values of  $E_{bind}$ , reported for the same series of molecules by Desfrancois et al. [19], are much larger than the values of  $E_{bind}^{KT}$  [18]. For example, for  $\text{CH}_3\text{CN}$ , the MP2 calculations of [18] gave an electron affinity of  $62 \text{ cm}^{-1}$ , significantly smaller than the experimental value of  $93 \text{ cm}^{-1}$  [19]. The Lineberger group has recently studied autodetaching resonances for the vibrationally excited dipole-bound state of  $\text{C}_3\text{H}_2$  and determined the electron binding energy of  $171 \pm 50 \text{ cm}^{-1}$  [20]. In contrast, the KT and SCF values of  $E_{bind}$  reported in [21] were only 52 and  $59 \text{ cm}^{-1}$ , respectively.

These conflicting results motivated us to take a closer look at electron binding energies of dipole-bound anionic states, focusing on  $\text{CH}_3\text{CN}^-$ ,  $\text{C}_3\text{H}_2^-$ , and  $(\text{HF})_2^-$ . In this article, we address two issues: (i) how significant are electron correlation and orbital relaxation effects in determining the energy of binding of electrons to polar molecules and (ii) how important are geometrical relaxation and the change of the zero-point vibrational energy upon electron attachment. Electron correlation was included by means of Møller–Plesset (MP) perturbation theory as well as by the coupled cluster for the single, double, and noniterative triple excitations [CCSD(T)] method [22]. In addition, the second-order dispersion interaction between the loosely bound electron and the neutral molecule was estimated from the MP2 binding energy. The minimum energy structures and harmonic vibrational frequencies of the neutral and anionic species were determined at the MP2 level of theory, and the dipole moments and polarizabilities of the neutral species were both calculated at the SCF and MP2 levels to aid in analyzing the factors important in determining the magnitude of  $E_{bind}$ .

The molecules studied here are  $\text{CH}_3\text{CN}$ ,  $\text{C}_3\text{H}_2$ , and the HF dimer (see Fig. 1). The existence of dipole-bound anions of  $\text{CH}_3\text{CN}$  and the HF dimer was originally suggested by Jordan and Wendoloski on the basis of KT calculations [23]. The dipole-bound anion of the HF dimer was first observed in the Bowen group [24]. The photoelectron spectrum displayed a signature of the dipole-



**FIGURE 1.** Internal coordinates of  $\text{CH}_3\text{CN}$ ,  $\text{C}_3\text{H}_2$ , and  $(\text{HF})_2$  used in the present work.

bound state with a vertical detachment energy (VDE) of  $508 \pm 24 \text{ cm}^{-1}$  [25]. For all three molecules, the relevant rotational energy level spacings are much smaller than are the calculated values of  $E_{bind}$ . Hence, non-BO effects are expected to be of secondary importance. In addition to a dipole-bound state,  $\text{C}_3\text{H}_2$  also has a bound valence anion state [26], which will not be considered here. Some of our theoretical results for  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$  were reported in a recent letter [27].

For the covalent  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$  molecules, it is expected that geometrical relaxations of the nuclear framework upon attachment of an electron will be very small as would be the vibrational zero-point energy corrections to the binding energies. In fact, the results of [18] indicate that these effects contribute less than  $3 \text{ cm}^{-1}$  to  $E_{bind}$  for  $\text{CH}_3\text{CN}$ . On the other hand, the HF dimer is bound by a weak hydrogen bond and its equilibrium  $\text{C}_s$  structure differs significantly from a linear structure which would maximize the dipole moment of

the complex. We anticipate therefore a sizable geometry change upon electron attachment and possibly also a difference between the adiabatic and vertical electron detachment energies.

## Computational Details

Dipole-bound anions pose a serious challenge to *ab initio* electronic structure techniques. The diffuse character of the outermost electron necessitates the use of very flexible basis sets containing functions with very low exponents. In our work, we used the aug-cc-pVDZ basis set [28] supplemented with diffuse *s*, *p*, and *d* symmetry functions centered on the carbon atom ( $\text{CH}_3\text{CN}$ ,  $\text{C}_3\text{H}_2$ ) or the hydrogen atom [ $(\text{HF})_2$ ], at the positive end of molecular dipole. For  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$ , we used a three-term *sp* set with exponents  $5.625(-3)$ ,  $1.125(-3)$ , and  $2.25(-4)$  au for geometry optimization and harmonic frequency calculations and an extended even-tempered seven-term *sp* and eight-term *d* set for highly correlated single-point calculations. For the latter set, the ratio between consecutive exponents is 3.2 and the smallest exponent is  $2.2(-5)$  au for each angular momentum. For  $(\text{HF})_2$ , we used an even-tempered five-term *sp* and five-term *d* basis set, with the lowest exponent equal to  $4.5(-5)$  au and the geometric progression ratio equal to 5.0 for each angular momentum. In this case, the diffuse *d* functions were omitted from the basis set when carrying out the geometry optimizations and the frequency calculations.

We tested that the MP2 values of  $E_{bind}$  are not affected by further extension of the *sp* and *d* diffuse sets or inclusion of diffuse *f* symmetry functions. In fact, the calculations with the *sp*-only diffuse sets recover more than 92% of  $E_{bind}$ , which justifies their use for geometry optimizations. For  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$ , we also tested that extension of the valence part of the basis set to aug-cc-pVTZ, keeping the diffuse *sp* set fixed, does not introduce significant changes in the MP2 values of  $E_{bind}$ .

The electron binding energies of the three molecules studied here are less than 0.07 eV. Beyond the KT level, they are obtained by subtracting the energies calculated for the anions from those of the neutrals. This procedure favors the use of size-extensive methods such as the MP perturbation theory and the coupled-cluster method with

single, double, and noniterative triple excitations [CCSD(T)] [22].

The MP2 contribution to the electron binding energy was separated into a dispersion-like interaction between the loosely bound electron and the electrons of the neutral molecule, denoted  $\Delta E_{bind}^{MP2-disp}$  and a nondispersion term  $\Delta E_{bind}^{MP2-no-disp}$ . The former is given by a sum over all pair contributions  $e_{lbe, i'}$  involving excitations of the form:  $\phi_{lbe} \phi_i \rightarrow \phi_v \phi_{v'}$ , where  $\phi_{lbe}$  corresponds

to the orbital occupied by the loosely bound electron,  $\phi_i$  is one of the other occupied orbitals of the molecule, and  $\phi_v$  and  $\phi_{v'}$  are unoccupied virtual orbitals.

The theoretical results reported here were obtained with the Gaussian 92 [29] and Gaussian 94 programs [30]. To avoid erroneous results from the default direct SCF calculations with the basis sets with the large *s*, *p*, and *d* sets of diffuse functions, the keyword SCF = NoVarAcc was used and the

**TABLE I**  
Geometries and harmonic vibrational frequencies for the neutral and dipole-bound anionic states of  $\text{CH}_3\text{CN}$ ,  $\text{C}_3\text{H}_2$ , and  $(\text{HF})_2$  molecules (frequencies in  $\text{cm}^{-1}$ , distances in Å, angles in degrees).<sup>a</sup>

System	Geometry	Frequencies
$\text{CH}_3\text{CN}$	$R_{\text{CN}} = 1.187$ $R_{\text{CC}} = 1.471$ $R_{\text{CH}} = 1.099$ $\alpha = 109.8$	$\omega(e) = 351$ $\omega(a_1) = 931$ $\omega(e) = 1048$ $\omega(a_1) = 1390$ $\omega(e) = 1466$ $\omega(a_1) = 2180$ $\omega(a_1) = 3089$ $\omega(e) = 3189$ $E_0^{vib} = 28.162$ kcal/mol
$\text{CH}_3\text{CN}^-$	$R_{\text{CN}} = 1.186$ $R_{\text{CC}} = 1.471$ $R_{\text{CH}} = 1.099$ $\alpha = 109.9$	$\omega(e) = 353$ $\omega(a_1) = 929$ $\omega(e) = 1047$ $\omega(a_1) = 1390$ $\omega(e) = 1465$ $\omega(a_1) = 2178$ $\omega(a_1) = 3088$ $\omega(e) = 3189$ $E_0^{vib} = 28.151$ kcal/mol $\Delta E_0^{vib} = 4.0$ $\text{cm}^{-1}$
$\text{C}_3\text{H}_2$	$R_{\text{CH}} = 1.097$ $R_1 = 1.350$ $R_2 = 1.306$ $\alpha = 121.3$	$\omega(b_1) = 124$ $\omega(b_2) = 205$ $\omega(b_2) = 1035$ $\omega(b_1) = 1047$ $\omega(a_1) = 1117$ $\omega(a_1) = 1480$ $\omega(a_1) = 2018$ $\omega(a_1) = 3144$ $\omega(b_2) = 3245$ $E_0^{vib} = 19.176$ kcal/mol
$\text{C}_3\text{H}_2^-$	$R_{\text{CH}} = 1.097$ $R_1 = 1.351$ $R_2 = 1.304$ $\alpha = 121.4$	$\omega(b_1) = 117$ $\omega(b_2) = 208$ $\omega(b_2) = 1032$ $\omega(b_1) = 1035$ $\omega(a_1) = 1117$ $\omega(a_1) = 1479$ $\omega(a_1) = 2006$ $\omega(a_1) = 3144$ $\omega(b_2) = 3246$ $E_0^{vib} = 19.133$ kcal/mol $\Delta E_0^{vib} = 15.0$ $\text{cm}^{-1}$
$(\text{HF})_2^b$	$R = 2.754$ $r_1 = 0.931$ $r_2 = 0.928$ $\alpha = 83.4$ $\beta = 160.0$	$\omega(a') = 157$ $\omega(a') = 213$ $\omega(a'') = 470$ $\omega(a') = 574$ $\omega(a') = 3940$ $\omega(a') = 4038$ $E_0^{vib} = 13.427$ kcal/mol
$(\text{HF})_2^{-b}$	$R = 2.726$ $r_1 = 0.934$ $r_2 = 0.932$ $\alpha = 92.2$ $\beta = 144.3$	$\omega(a') = 170$ $\omega(a') = 250$ $\omega(a'') = 507$ $\omega(a') = 570$ $\omega(a') = 3817$ $\omega(a') = 3926$ $E_0^{vib} = 13.210$ kcal/mol $\Delta E_0^{vib} = 76.0$ $\text{cm}^{-1}$

<sup>a</sup> MP2 results obtained with the aug-cc-pVDZ basis set supplemented with the diffuse *sp* functions.

<sup>b</sup> For the isolated HF molecule, the MP2/aug-cc-pVDZ harmonic frequency and  $R_e$  are  $4082$   $\text{cm}^{-1}$  and  $0.925$  Å, respectively.

two-electron integrals were evaluated (without prescreening) to a tolerance of  $10^{-20}$  au in the single-point calculations.

## Results and Discussion

### GEOMETRIES AND VIBRATIONAL FREQUENCIES

The geometrical parameters and harmonic vibrational frequencies for the neutral and anionic species are reported in Table I. For the anionic UHF wave functions, the value of  $S^2$  remains 0.75000, which indicates a lack of spin-contamination. For the neutral  $\text{CH}_3\text{CN}$ , we also tested that the UHF solution is identical to the RHF solution. Moreover, the equilibrium structure and harmonic vibrational frequencies are identical at the UMP2 and RMP2 levels. Henceforth, we believe that comparison of the properties of the open-shell anions and closed-shell neutrals, studied at the UMP2 and RMP2 levels, respectively, is meaningful.

For the neutral species, the discrepancies between our geometrical parameters and experimental ( $\text{CH}_3\text{CN}$  [31]) or highly accurate theoretical results ( $\text{C}_3\text{H}_2$  [21], and  $(\text{HF})_2$  [32]) do not exceed 0.03 Å for bond lengths and  $1^\circ$  for bond angles. Even for the weakly bound  $(\text{HF})_2$  dimer, which may pose extra problems due to the basis-set superposition error, there is good agreement with accurate results of Peterson and Dunning [32]. The geometrical relaxation upon electron attachment is negligible for  $\text{CH}_3\text{CN}$ , marginal for  $\text{C}_3\text{H}_2$ , and substantial for  $(\text{HF})_2$  (see Table I). For  $\text{C}_3\text{H}_2$ , the CC bond lengths are primarily affected but the changes do not exceed 0.002 Å. For  $(\text{HF})_2$ , the electron attachment leads to sizable changes in the mutual orientation of the two HF moieties. This is reflected by changes of  $9^\circ$  and  $16^\circ$  in  $\alpha$  and  $\beta$ , respectively. There is also an elongation of the HF bond lengths by 0.003 and 0.004 Å, for the proton donor and acceptor molecules, respectively. Due to distortion between the anion and neutral, the photoelectron spectrum of the dipole-bound anion of  $(\text{HF})_2$  is expected to display a vibrational structure.

The change of the harmonic zero-point vibrational energy upon electron attachment is 4, 15, and  $76\text{ cm}^{-1}$  for  $\text{CH}_3\text{CN}$ ,  $\text{C}_3\text{H}_2$ , and  $(\text{HF})_2$ , respectively (see Table I). For  $\text{CH}_3\text{CN}$ , the normal

modes of the anion agree to within  $2\text{ cm}^{-1}$  of those of the neutral molecule, whereas for  $\text{C}_3\text{H}_2$ , two modes experience a frequency decrease of  $12\text{ cm}^{-1}$  and a third a decrease of  $7\text{ cm}^{-1}$  due to the attachment of the electron. For  $(\text{HF})_2$ , the intramonomer vibrational frequencies are softened and the intermonomer frequencies are stiffened upon electron attachment. The largest shifts are for the two intramolecular HF stretching modes, which are reduced by 112 and  $123\text{ cm}^{-1}$  upon formation of the dipole bound anion.

### PROPERTIES OF NEUTRAL SPECIES

The SCF and MP2 values of dipole moments and polarizabilities for the neutral species are presented in Table II. For  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$ , these properties are reported for the MP2-optimized geometry of the neutral molecules, whereas for  $(\text{HF})_2$ , they are reported for both the optimized geometries of the neutral and the anion.

The SCF values of the dipole moments of both  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$  are 4.34 D. The inclusion of correlation via the MP2 procedure leads to a reduction of the dipole moment for  $\text{CH}_3\text{CN}$  by 0.42 D and to an increase of the dipole moment for  $\text{C}_3\text{H}_2$  by 0.15 D. The MP2 value of the dipole moment of  $\text{CH}_3\text{CN}$  is only 0.02 D larger than the experimental value of 3.92 D [33]. For  $\text{C}_3\text{H}_2$ , however, the SCF and the MP2 methods overestimate the experimental value of 4.14 D by 0.20 and 0.34 D, respectively [34].

The SCF value of the dipole moment of  $(\text{HF})_2$  at the geometry of the neutral molecule is 3.48 D. However, the geometrical relaxation upon electron attachment causes the dipole moment (of the neutral) to increase by 0.5 D. The inclusion of electron correlation effects by means of the MP2 procedure leads to a 0.2 D decrease in the dipole moment relative to its SCF value. The MP2 value of the dipole moment for the HF molecule is 1.82 D and it overestimates the experimental value by 0.02 D [35]. Our MP2 value of the dipole moment for the neutral  $(\text{HF})_2$  is 3.31 D. It overestimates the accurate theoretical result of Collins et al. by 0.02 D [36].

Due to its conjugated system of  $\pi$  bonds,  $\text{C}_3\text{H}_2$  is more polarizable along the  $z$  (long) axis than is  $\text{CH}_3\text{CN}$ , whereas the dipole polarizabilities perpendicular to the molecular axis are similar for these two molecules.  $(\text{HF})_2$  is much less polarizable than is  $\text{C}_3\text{H}_2$  or  $\text{CH}_3\text{CN}$ , and there is no

**TABLE II**  
Calculated properties of the neutral CH<sub>3</sub>CN, C<sub>3</sub>H<sub>2</sub>, and (HF)<sub>2</sub> molecules.<sup>a</sup>

Property	CH <sub>3</sub> CN <sup>b</sup>	C <sub>3</sub> H <sub>2</sub> <sup>b</sup>	(HF) <sub>2</sub> <sup>b</sup>	(HF) <sub>2</sub> <sup>c</sup>
$\mu^{SCF}$ (D)	4.34	4.34	3.48	3.98
$\mu^{MP2}$ (D)	3.94	4.48	3.31	3.78
$\alpha_{xx}^{SCF}$ ( $\perp$ ) (au)	23.8	26.8	7.6	7.5
$\alpha_{yy}^{SCF}$ ( $\perp$ ) (au)	23.8	27.7	8.8	8.3
$\alpha_{zz}^{SCF}$ ( $\parallel$ ) (au)	39.7	63.3	10.9	11.6
$\alpha_{xx}^{MP2}$ ( $\perp$ ) (au)	24.2	26.5	8.7	8.6
$\alpha_{yy}^{MP2}$ ( $\perp$ ) (au)	24.2	28.4	9.9	9.4
$\alpha_{zz}^{MP2}$ ( $\parallel$ ) (au)	39.9	60.3	12.5	13.2

<sup>a</sup> Results obtained with the aug-cc-pVDZ basis set supplemented with the diffuse *sp* functions.<sup>b</sup> Geometry of the neutral molecule from Table I.<sup>c</sup> Geometry of the anion molecule from Table I.

significant change in its polarizability tensor upon geometrical relaxation to the anionic structure. The values of the polarizabilities are not strongly affected by the inclusion of correlation effects.

### ELECTRON DETACHMENT ENERGIES

In Table III, we report the incremental contributions to the electron binding energies calculated at "successive" levels of theory [SCF, MP $n$  ( $n = 2, 3, 4$ ), and CCSD(T)] for all three molecules at the geometries of the neutrals. For the HF dimer, the results are also reported at the optimal geometry of the anion.

In the KT approximation, the electron binding energy results from the electrostatic interaction of the extra electron with the SCF charge distribution of the neutral molecule. The distribution is primarily characterized by the dipole moment, but interactions with higher permanent multipoles as well as occupied orbital exclusion and penetration effects are also important. The values of  $E_{bind}^{KT}$  are nearly the same for CH<sub>3</sub>CN and C<sub>3</sub>H<sub>2</sub>, consistent with the finding that the two molecules have nearly the same dipole moments in the SCF approximation. In contrast, (HF)<sub>2</sub> has a larger electron binding energy even though it has a smaller dipole moment than has CH<sub>3</sub>CN or C<sub>3</sub>H<sub>2</sub>. We speculate

**TABLE III**  
Incremental electron binding energies (in cm<sup>-1</sup>) for the dipole-bound anionic states of CH<sub>3</sub>CN, C<sub>3</sub>H<sub>2</sub>, and (HF)<sub>2</sub> molecules.<sup>a</sup>

Method	CH <sub>3</sub> CN <sup>b</sup>	C <sub>3</sub> H <sub>2</sub> <sup>b</sup>	(HF) <sub>2</sub> <sup>b</sup>	(HF) <sub>2</sub> <sup>c</sup>
$E_{bind}^{KT}$	53	55	72	165
$\Delta E_{bind}^{SCF}$	3	8	5	14
$\Delta E_{bind}^{MP2-disp}$	57	70	98	177
$\Delta E_{bind}^{MP2-no-disp}$	-38	5	-39	-73
$\Delta E_{bind}^{MP3}$	4	-38	-2	-3
$\Delta E_{bind}^{MP4}$	8	34	17	27
$\Delta E_{bind}^{CCSD(T)^d}$	21	39	71	81
Sum	108	173	224	387

<sup>a</sup> All results obtained with the aug-cc-pVDZ basis set augmented with the diffuse *sp* and *d* functions.<sup>b</sup> Geometry of the neutral molecule from Table I.<sup>c</sup> Geometry of the anion molecule from Table I.<sup>d</sup> The difference in the CCSD(T) and MP4 binding energies.

that occupied orbital exclusion effects are smaller in  $(\text{HF})_2^-$  than in  $\text{CH}_3\text{CN}^-$  and  $\text{C}_3\text{H}_2^-$ , thereby leading to the larger value of  $E_{bind}^{KT}$  in  $(\text{HF})_2^-$ .

For  $(\text{HF})_2^-$ ,  $E_{bind}^{KT}$  increases from  $72\text{ cm}^{-1}$  at the optimal geometry of the neutral to  $165\text{ cm}^{-1}$  at the optimal geometry of the anion, consistent with the sizable increase in the dipole moment accompanying the geometry changes. Clearly, it is the rapid increase of the binding energy with increasing dipole moment that drives the geometry change in going from the neutral to the anionic species.

The SCF binding energies include orbital relaxation and thus take into account both static polarization of the neutral molecule by the weakly bound electron and back-polarization. For all three systems, relaxation of the molecular charge distribution in the presence of the dipole-bound electron leads to relatively small ( $< 14\text{ cm}^{-1}$ ) increases in the binding energies. The values of  $\Delta E_{bind}^{SCF}$  do not correlate with the polarizability tensors of neutral molecules reported in Table II, which may reflect a different average separation between the loosely bound electron and the neutral core for different systems.

The total electron correlation contribution to  $E_{bind}$  encompasses two physically distinct effects: (1) dynamical correlation between the loosely bound electron and the electrons of the neutral molecule, and (2) the change in the binding energy due to improved description of the molecular dipole of the neutral "core." The former correlation effect, analogous to the dispersion interaction in van der Waals systems, first appears at the MP2 level and is denoted  $\Delta E_{bind}^{MP2-disp}$ . The remainder of the MP2 contribution to  $E_{bind}$ , denoted  $\Delta E_{bind}^{MP2-no-disp}$ , contains correlation corrections to the electrostatic, induction, and valence repulsion interactions between the loosely bound electron and the neutral molecule [37].

For all three molecules,  $\Delta E_{bind}^{MP2-disp}$  dominates the second-order correlation correction to the electron binding energy, and in each case, its value is larger in magnitude than  $E_{bind}^{KT}$ . This is an important finding since dispersion-type interactions have been neglected in various model potentials designed to describe electron binding to polar species [19,38]. The values of  $\Delta E_{bind}^{MP2-disp}$ , similarly as  $\Delta E_{bind}^{SCF}$ , do not correlate with the polarizability tensors of neutral molecules.

The trends in  $\Delta E_{bind}^{MP2-no-disp}$  are consistent with the changes of the dipole moment of the neutral species brought about by the inclusion of correla-

tion effects. For  $\text{CH}_3\text{CN}$  and  $(\text{HF})_2^-$ , correlation effects act so as to decrease the dipole moment and  $\Delta E_{bind}^{MP2-no-disp}$  is negative, whereas for  $\text{C}_3\text{H}_2^-$ , correlation effects lead to an enhanced value of the dipole moment and a positive value of  $\Delta E_{bind}^{MP2-no-disp}$ .

For  $(\text{HF})_2^-$ ,  $\Delta E_{bind}^{MP2}$  increases from  $59\text{ cm}^{-1}$  at the optimal geometry of the neutral to  $103\text{ cm}^{-1}$  at the optimal geometry of the anion. This increase is apparently due to enhancement of the dipole moment brought about by the geometrical distortion in going from the neutral to the  $(\text{HF})_2^-$  anion. This, in turn, causes a more localized dipole-bound electron and increased importance of  $\Delta E_{bind}^{MP2}$ . Due to the strong dependence of  $\Delta E_{bind}^{MP2}$  on the structure of the molecular framework, geometry optimizations of nonrigid dipole-bound anions should be performed using MP2 or other correlated methods.

For  $\text{CH}_3\text{CN}^-$ , both the third- and fourth-order MP contributions to  $E_{bind}$  are relatively small and act so as to increase the electron binding energy. In contrast, for  $\text{C}_3\text{H}_2^-$  and  $(\text{HF})_2^-$ , the third- and fourth-order corrections to  $E_{bind}$  enter with opposite signs. For  $\text{C}_3\text{H}_2^-$ , they are sizable in magnitude but essentially cancel each other, whereas for  $(\text{HF})_2^-$ , only the fourth-order correction is significant. For all three molecules, the fourth-order correction acts so as to increase the electron binding energy. Moreover, for all three molecules, correlation beyond fourth order, approximated here by  $\Delta E_{bind}^{CCSD(T)}$  [the difference in the CCSD(T) and MP4 binding energies], is responsible for ca. 20% of the net electron binding energies and acts so as to increase the electron binding energy.

The difference in electronic energy of  $(\text{HF})_2$  and  $(\text{HF})_2^-$  at their respective minimum geometries is  $320\text{ cm}^{-1}$  at the CCSD(T) level of theory. Correcting this value by the difference in the zero-point vibrational energy ( $76\text{ cm}^{-1}$ ) gives the adiabatic detachment energy of  $(\text{HF})_2^-$ , or, equivalently, the adiabatic electron affinity of  $(\text{HF})_2^-$ , of  $396\text{ cm}^{-1}$ . If the dominant peak of the photoelectron spectrum of  $(\text{HF})_2^-$  corresponds to the 0–0 transition, then our prediction of VDE would be the same. The experimental value of VDE is  $508 \pm 24\text{ cm}^{-1}$  [25]. If this is due to the 0–0 transition, then our calculation underestimates the electron binding energy by ca. 20%. However, there remains a possibility that the observed maximum in the photoelectron spectrum is due to formation of the neutral dimer with excitation by one quantum of the low-frequency bending mode. To resolve this issue, the

calculation of the corresponding Franck–Condon factors is in progress [39].

For  $\text{CH}_3\text{CN}^-$  and  $\text{C}_3\text{H}_2^-$ , our final VDEs are based on the electronic energy differences from Table III and the MP2 zero-point vibrational energy differences from Table I and amount to 112 and  $188\text{ cm}^{-1}$ , respectively. Formally, the CCSD(T) energy of the anion should be recalculated at the anion equilibrium geometry, but we tested that for these molecules the differences between the MP2 energy of the anion as calculated at the anion and the neutral geometries are much smaller than are the values of  $\Delta E_0^{vib}$  reported in Table I. For these two anions, the calculated VDEs are in very good agreement with the experimental values of  $93\text{ cm}^{-1}$  for  $\text{CH}_3\text{CN}^-$  [19] and  $171 \pm 50\text{ cm}^{-1}$  for  $\text{C}_3\text{H}_2^-$  [20].

## Summary

Highly correlated electronic structure methods offer new insight into the nature of dipole-bound anionic states. Our results for  $\text{CH}_3\text{CN}^-$ ,  $\text{C}_3\text{H}_2^-$ , and  $(\text{HF})_2^-$  demonstrate that the traditional model of dipole-bound states, which includes only the electrostatic interaction between an electron and the rigid dipole, is far from complete. In particular, the dispersion interaction between the loosely bound electron and the electrons of the neutral molecule is an important component of the electron binding energy for all three systems considered. It is of comparable magnitude to the electrostatic electron–dipole stabilization. In addition, it is found that electron correlation effects beyond the MP2 level contribute substantially to the electron binding energy.

The geometrical relaxation of the molecular framework upon electron attachment and the difference in zero-point vibrational energy between the neutral and the dipole-bound anion are found to be unimportant for  $\text{CH}_3\text{CN}$  and  $\text{C}_3\text{H}_2$ . In contrast, for the HF dimer, electron attachment leads to a sizable geometrical distortion, primarily in intermonomer degrees of freedom, which is accompanied by an enhancement of the dipole moment of the neutral and a larger electron binding energy. In fact, the electronic energy difference between the neutral and the anion increases from  $224\text{ cm}^{-1}$  for the structure of the neutral to  $387\text{ cm}^{-1}$  for the structure of the anion. The geometrical distortion is accompanied by a change in the

zero-point vibration energy of  $76\text{ cm}^{-1}$ . Large geometry changes upon electron attachment are expected to be general for clusters of polar molecules.

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