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Electronic Structure of Dipole-Bound Anions

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Dipole-bound anionic states of HCN, $(HF)_2$, CH_3CN, C_3H_2, C_4H_2, C_5H_2, and stretched CH_3F are studied using extended one-electron basis sets at the coupled cluster level of theory with single, double, and noniterative triple excitations (CCSD(T)). Orbital relaxation and electron correlation corrections to the Koopmans' theorem prediction of electron binding energy are analyzed, and a physical interpretation of low-order corrections is proposed. It is demonstrated that the second-order dispersion interaction between the loosely bound electron and the electrons of the neutral host should be included into physical models of dipole-bound anions. Higher-order electron correlation corrections are also found to be important, and a slow convergence of the Møller−Plesset series for electron binding energies is documented. Modifications of the potential energy surfaces of the above polar molecules upon electron attachment are studied at the second-order Møller−Plesset level, and Franck−Condon factors for the anion/neutral pairs are calculated. It is predicted that photoelectron spectra of the dipole-bound anions of C_4H_2 and C_5H_2 should display vibrational structure.

1. Introduction

It has long been assumed that the stability of dipole-bound anions is determined primarily by the static Coulomb interaction of the loosely bound electron *(*lbe*)* with the charge distribution of the neutral molecular host. In these species the interaction of the "extra" electron with the dipole moment of the neutral molecular host leads to a bound anionic state and localization of the lbe on the positive side of the molecular dipole.[1,2] The existence of a 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.[3−5] 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.[6−8] However, non-BO effects are relatively unimportant for dipole-bound states with electron binding energies (E_{bind}) much larger than the molecular rotational constants.

The simplest theoretical approach to estimate E_{bind} of a dipole-bound anion is based on Koopmans' theorem (KT).[9] The KT binding energy ($E_{\mathrm{bind}}^{\mathrm{KT}}$) is given by 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 that includes the electrostatic electron−dipole stabilization but that neglects both electron correlation and orbital relaxation effects. Orbital relaxation effects have been found to be quite small for a variety of dipole-bound anionic states.[10−18] On the other hand, the role of electron correlation effects has proven to be more controversial. Early studies of polar diatomics[19,20] and simple polar organic molecules[11] indicated that electron correlation effects played only a small role in electron binding to these species. In contrast, we have found that inclusion of electron correlation effects leads to a sizable stabilization of the dipole-bound anions of C_3H_2, CH_3CN, C_5H_2, $(HF)_n$ ($n = 2, 3$), $H_2O\cdots NH_3$, $(H_2O)_2$, $(HCN)_2$, and uracil systems.[12−18] An early theoretical study of the dipole-bound anion of nitromethane concluded that inclusion of correlation effects destabilizes the anion,[21] but a more recent theoretical study reached the opposite conclusion.[22] Our recent studies[12−18] and that of Gutsev and Bartlett[22] have shown that the stabilizing dynamical electron correlation between the lbe and core electrons is always significant relative to the $E_{\mathrm{bind}}^{\mathrm{KT}}$ value and that it is necessary to employ flexible basis sets and to include high-order correlation effects in order to adequately describe the dynamical correlation contribution. Electron correlation also becomes important by modifying the dipole moment of the neutral core. This may either decrease or increase the dipole moment, with decreased dipole moments being more common.[12−18]

Experimental results for dipole-bound anions, obtained from photoelectron spectroscopy (PES),[23] Rydberg electron-transfer experiments,[24,25] and autodetachment spectroscopy studies,[13,26]

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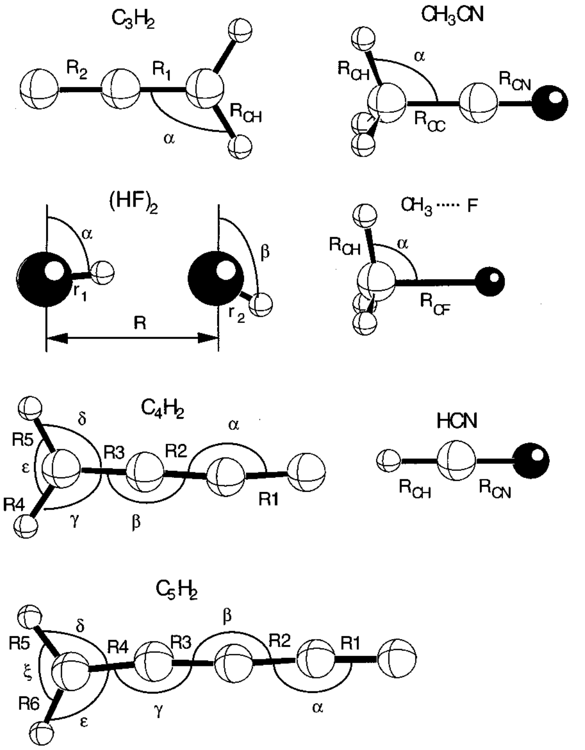

Figure 1. Internal coordinates for molecular systems studied in the present work. For stretched $CH_3{\cdots}F/CH_3{\cdots}F^-$ the coordinates are R_{CF} = 1.8 Å, R_{CH} = 1.079 Å, α = 100°. For coordinates of $(HF)_2^-$ see Gutowski and Skurski.[14]

present a serious challenge to theorists. In addition to the fact that experimental electron binding energies are much larger than theoretical predictions based on the electrostatic/KT model,[12−18] the PES spectra of dipole-bound anions frequently display vibrational structure.[23] For many years the prevailing view of dipole-bound anions was that the excess electron is so far from the molecular core that the neutral system and its anion should have essentially the same equilibrium geometries and force constants.[10,11,23,27] If this picture were correct, vibrational structure would not be expected to appear in the PES spectra of the anions based on consideration of the Franck−Condon (FC) factors. This has led researchers to invoke resonant or vibronic effects to explain details of the PES spectra of dipole-bound anions when such structure appears.[28] While such effects may be important in some cases, we have recently demonstrated that significant modifications of potential energy surfaces may occur upon attachment of an electron to hydrogen-bonded clusters.[14−18] For $(HF)_2^-$, the differences in anionic and neutral potential energy surfaces led to sizable nonzero FC factors to excited vibrational levels of the neutral, and the theoretical PES spectrum of $(HF)_2^-$, calculated using the FC factors, was found to be in excellent agreement with the experimental spectrum.[14,29] The question of whether dipole-bound states of polar chemically bonded systems, with small (<0.1 eV) electron binding energies, will also display a vibrational structure due to differences in anionic and neutral potential energy surfaces is addressed in this contribution.

In this report we present the results of ab initio calculations on the dipole-bound anions of HCN, CH_3CN, C_3H_2, C_4H_2, C_5H_2, $(HF)_2$, and a stretched CH_3F molecule; see Figure 1. These systems cover a wide range of dipole moments from 3.0 D for HCN to 6.4 D for C_5H_2. They also represent a variety of molecular electronic structures: organic molecules which are well (HCN, CH_3CN) and poorly (C_3H_2, C_4H_2, C_5H_2) described within the Hartree−Fock approximation, a hydrogen-bonded complex $(HF)_2$, and a system with artificially magnified electron correlation correction to the dipole moment (stretched CH_3F). Partial results for some of these systems were reported in previous communications.[12−15] The electronic structure methods used to study E_{bind} in dipole-bound anions are discussed in section 2, and requirements for the one-electron basis sets are summarized in section 3.1. In section 3.2 a large contribution to E_{bind} from electron correlation effects is demonstrated, an analysis of higher-than-second-order electron correlation effects is reported, and the role of different electronic excitations is discussed. In section 3.3 we consider modifications of the potential energy surfaces upon attachment of an electron, and vibrational structure in PES spectra is predicted for $C_4H_2^-$ and $C_5H_2^-$.

2. Methods to Calculate E_{bind}

The calculated values of E_{bind} were obtained by subtracting the energies of the anion from those of the neutral. This approach favors the use of size-extensive methods, and we have employed the Møller−Plesset (MP) perturbation theory up to the fourth order and the coupled cluster method with single and double excitations (CCSD) supplemented with a perturbational treatment of triple excitations (CCSD(T)).[30,31] In addition, E_{bind} was analyzed within a perturbation framework designed for dipole-bound anions and solvated electrons.[16]

In the perturbation scheme,[16] we consider a neutral molecule (N) and the lbe as weakly interacting species, and we follow the analogy with the theory of intermolecular interactions[32,33] to analyze E_{bind} in terms of physically meaningful components. The total electronic Hamiltonian for the anion is partitioned into H^0, which corresponds to the Hartree−Fock level of theory for N and the KT level of theory for the lbe, and two perturbations, W^N and V^{lbe}:

$$H = H^0 + \lambda W^N + \eta V^{lbe} \tag{1}$$

where the expansion parameters λ and η are introduced to define the perturbation theory orders and are set to 1 in evaluating the contributions. The zeroth-order Hamiltonian

$$H^0 = F^N + F^{lbe} \tag{2}$$

is the sum of Fock operators for all electrons in the anion, and every Fock operator is determined by the occupied orbitals of N. The fluctuation operator for the neutral molecule, W^N, results from Møller−Plesset partitioning of the electronic Hamiltonian of N, and the fluctuation−interaction operator V^{lbe} has the form

$$V^{lbe} = \sum_{i \in N} \frac{1}{r_{lbe,i}} - (J_N(lbe) - K_N(lbe)) \tag{3}$$

where $r_{lbe,i}$ is the distance between the ith electron of N and the lbe, and J_N and K_N are respectively the Coulomb and exchange operators for N.

By use of double-perturbation theory,[32] the anion energy may be expressed as

$$E = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \epsilon^{(kl)} \tag{4}$$

where $\epsilon^{(kl)}$ is of kth order in W^N and lth order in V^{lbe}. The sum of the three lowest-order terms reproduces the SCF energy of N and $E_{\mathrm{bind}}^{\mathrm{KT}}$:

$$\epsilon^{(00)} + \epsilon^{(10)} + \epsilon^{(01)} = E_{\mathrm{N}}^{\mathrm{SCF}} - E_{\mathrm{bind}}^{\mathrm{KT}} \tag{5}$$

$E_{\mathrm{bind}}^{\mathrm{KT}}$ takes into account the Coulomb and exchange interaction between the lbe and the SCF charge distribution of N. This is a static approximation that neglects both orbital relaxation and electron correlation effects.

The non-KT contributions to E_{bind} are given by other $\epsilon^{(kl)}$ terms with l ≥ 1. The term $\epsilon^{(02)}$ separates into the induction and dispersion contributions,[32,33]

$$\epsilon^{(02)} = \epsilon_{\mathrm{ind}}^{(02)} + \epsilon_{\mathrm{disp}}^{(02)} \tag{6}$$

The term $\epsilon_{\mathrm{ind}}^{(02)}$ describes polarization of N by the lbe and, as an orbital relaxation effect, is reproduced when E_{bind} is obtained from the difference in the SCF energies of the neutral and anionic species:

$$\Delta E_{\mathrm{bind}}^{\mathrm{SCF-ind}} = E_{\mathrm{bind}}^{\mathrm{SCF}} - E_{\mathrm{bind}}^{\mathrm{KT}} \approx -\epsilon_{\mathrm{ind}}^{(02)} \tag{7}$$

where

$$E_{\mathrm{bind}}^{\mathrm{SCF}} = E_{N}^{\mathrm{SCF}} - E_{\mathrm{A}}^{\mathrm{SCF}} \tag{8}$$

and $E_{\mathrm{A}}^{\mathrm{SCF}}$ is the SCF energy of the anion. In fact, the term $\Delta E_{\mathrm{bind}}^{\mathrm{SCF-ind}}$ includes not only the static polarization of N by the lbe but also the secondary effect of back-polarization. The magnitude of $\Delta E_{\mathrm{bind}}^{\mathrm{SCF-ind}}$ is expected to grow with increasing polarizability of N and with decreasing average separation between the lbe and N.

The term $\epsilon_{\mathrm{disp}}^{(02)}$ describes dynamical correlation between the lbe and the electrons of N. This stabilizing effect, brought by quantum mechanical charge fluctuations, may be very important for weakly bound anions in view of a significant polarizability of the lbe. The term $\epsilon_{\mathrm{disp}}^{(02)}$ is approximated here by $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}}$, which takes into account proper permutational symmetry for all electrons in the anion

$$\epsilon_{\mathrm{disp}}^{(02)} \approx -\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}} = \sum_{a\in N}\sum_{r<s} \frac{|\langle \phi_a \phi_{\mathrm{lbe}} || \phi_r \phi_s \rangle|^2}{e_a + e_{\mathrm{lbe}} - e_{\mathrm{r}} - e_{\mathrm{s}}} \tag{9}$$

where ϕ_a and ϕ_{lbe} are spin orbitals occupied in the zeroth-order wave function, ϕ_r and ϕ_s are unoccupied orbitals, and e's are the corresponding orbital energies. Similar values of $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}}$ are obtained using the SCF orbitals of N or those of the dipole-bound anion, and the results reported in this work are obtained using the orbitals of the anion.

Higher-order corrections to E_{bind} cannot be neglected. There are two sources of such corrections: those due to V^{lbe} only, given by the $\epsilon^{(0l)}$ ($l > 2$) terms, and those from $\epsilon^{(kl)}$ for $k, l \neq 0$ which contribute to E_{bind} not only through V^{lbe} but also through W^{N}. It is well established that electron correlation affects the static charge distribution of N and leads, for instance, to a discrepancy between the SCF and correlated dipole moments of polar molecules. Therefore, the static Coulomb interaction between the lbe and the SCF charge density of N, which is contained in $E_{\mathrm{bind}}^{\mathrm{KT}}$, has to be corrected for this charge density change. The lowest-order correction of this type is contained in the MP2 electron binding energy.

The MP2 contribution to E_{bind} defined as

$$\Delta E_{\mathrm{bind}}^{\mathrm{MP2}} = E_{\mathrm{bind}}^{\mathrm{MP2}} - E_{\mathrm{bind}}^{\mathrm{SCF}} \tag{10}$$

is naturally split into the dispersion and nondispersion terms:

$$\Delta E_{\mathrm{bind}}^{\mathrm{MP2}} = E_{\mathrm{bind}}^{\mathrm{MP2-disp}} + \Delta E_{\mathrm{bind}}^{\mathrm{MP2-no-disp}} \tag{11}$$

with the latter being dominated by $\epsilon^{(21)}$.[33] The higher-order MP contributions to E_{bind} are defined as

$$\Delta E_{\mathrm{bind}}^{\mathrm{MP}n} = E_{\mathrm{bind}}^{\mathrm{MP}n} - E_{\mathrm{bind}}^{\mathrm{MP}(n-1)}, \quad n = 3,4 \tag{12}$$

Finally, the contributions beyond the fourth-order are estimated by subtracting the MP4 results from those obtained at the coupled cluster level.

$$\Delta E_{\mathrm{bind}}^{\mathrm{CC}} = E_{\mathrm{bind}}^{\mathrm{CC}} - E_{\mathrm{bind}}^{\mathrm{MP4}} \tag{13}$$

In particular, the DQ, SDQ, and SDTQ MP4 energies are subtracted from the D, SD, and SD(T) coupled cluster binding energies, respectively. Our final adiabatic electron affinities are based on the CCSD(T) electronic energy differences and the MP2 zero-point vibrational energy differences.

We made attempts to relate the components of E_{bind} to the dipole moment and dipole polarizability of the neutral molecular host. Both SCF and MP2 values of these quantities are reported; the latter were obtained with the generalized density corresponding to the second-order energy.[34]

The 1s orbitals of first-row atoms were excluded from the electron correlation treatments. All electronic structure results reported in this study were obtained with the Gaussian 92 and 94 programs.[35,36]

3. Results

For the molecules considered here, with the exception of HCN, the relevant rotational energy level spacings are much smaller than the calculated values of $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$. Hence, non-BO coupling between the electronic and rotational degrees of freedom is expected to be of secondary importance for these dipole-bound anions and is not considered in this study. Even for HCN our best estimate of E_{bind} is 5 times larger than the rotational constant.

3.1. Basis Set Dependence of E_{bind}. The diffuse character of the lbe (see Figure 2) necessitates the use of basis sets containing extra diffuse functions with very low exponents.[2] In addition, the initial basis set chosen-to describe the neutral molecular host should be flexible enough to (i) accurately describe the static charge distribution of the neutral, and (ii) allow for polarization of the neutral upon electron attachment and for the dispersion stabilization between the neutral and the lbe. The majority of our calculations were performed with the aug-cc-pVDZ basis set[37] supplemented with diffuse s and p functions and in some cases also diffuse d and f functions. The extra diffuse s and p functions always share the exponent values.

First, the dependence of E_{bind} on the choice of the extra diffuse functions was explored. These tests were performed with the aug-cc-pVDZ core basis set, with only the extra diffuse functions being varied. These functions were centered on the carbon atom (CH_3CN, C_3H_2, C_4H_2, C_5H_2, stretched CH_3F molecule) or the hydrogen atom (HCN, $(HF)_2$), at the positive end of molecular dipole. To describe the molecular orbital (MO) occupied by the lbe, it is essential that both diffuse s and p functions are contained in the supplemental set. The MO occupied by the

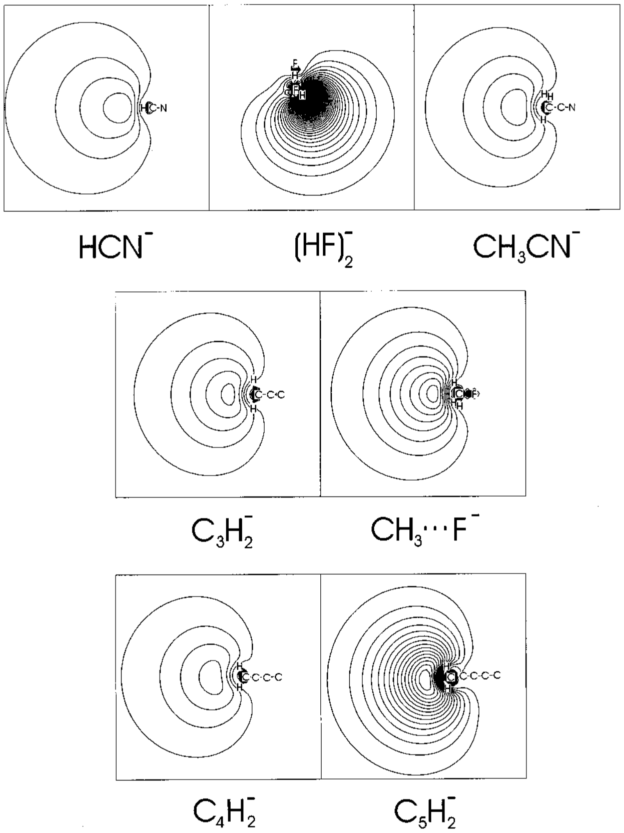

Figure 2. Contour plots of the density of the loosely bound electron in dipole-bound anionic states. The separation between contour lines is 0.000 002 e/Å^3 for HCN^- and 0.000 005 e/Å^3 for other systems.

lbe is then described as a hybrid orbital formed from the diffuse s and p basis functions; see Figure 2.

The dependence of selected contributions to E_{bind} on the diffuse basis set is documented in Table 1, which reports the KT, SCF, MP2, and higher-order contributions to E_{bind}. The last of these, $\Delta E_{\text{bind}}^{\text{HO}}$, is defined as the difference between $E_{\text{bind}}^{\text{CCSD(T)}}$ and $E_{\text{bind}}^{\text{MP2}}$. Even-tempered sequences of diffuse s, p, d, and f functions with the nth exponent α_n given by

$$\alpha_n = \alpha_1 q^{n-1}, \quad n = 1,... \tag{14}$$

are used. The value of the lowest exponent α_1 is dictated by the dipole moment of the neutral host. The lower the dipole moment, the smaller the exponent needed to describe the spatial extent of the lbe. The simplest approach to determine an adequate diffuse set is to calculate SCF orbitals for the neutral molecule with the diffuse set present and to monitor the LCAO coefficients of the virtual orbital, occupied by the lbe in the anion. In particular, the LCAO coefficients of the most diffuse s and p functions should not be dominant for this molecular orbital. Of the systems considered here, HCN with the smallest dipole moment ($\mu_{\text{SCF}} = 3.3$ D) requires the lowest exponent of 4.0(−5) au, whereas for C_5H_2, with μ_{SCF} of 6.3 D, a value of 7.0(−4) au for the smallest exponent is sufficient. In addition, it is found that the spacing between the exponents can be greater for systems with small dipole moments than for those with large dipole moments. For example, for neutral molecular hosts with dipole moments in the 3.0-4.5 D range, the geometrical progression parameter q in eq 14 may be as large as 5.0, whereas for molecules with dipole moments around 6 D a value of 3.2 is satisfactory. The largest exponent in the supplemental diffuse set is chosen to be smaller by at least a factor of 2 than the most diffuse exponent in the initial basis set used for describing the neutral molecular host. For our most extended diffuse sp sets (9sp for HCN and 7sp for other systems) the values of $E_{\text{bind}}^{\text{KT}}$ and $E_{\text{bind}}^{\text{SCF}}$ do not depend on which nucleus the set is centered, confirming that the saturation of the sp set has been accomplished.

TABLE 1: Dependence of E_{bind} on the Quality of the Diffuse Set. All Results Obtained with the aug-cc-pVDZ Set Supplemented with Diffuse Functions. Energies in cm^{-1}

system	basis	$E_{\text{bind}}^{\text{KT}}$	$\Delta E_{\text{bind}}^{\text{SCF-ind}}$	$\Delta E_{\text{bind}}^{\text{MP2}}$	$\Delta E_{\text{bind}}^{\text{HO}}$
HCN	4(sp)[a]	11.3	0.5	−1.2	−3.2
	9(sp)[b]	12.0	0.5	−1.0	
	9(sp)8d[b]	13.8	0.6	−1.5	−3.7
CH_3CN	3(sp)[c]	46	3	20	31
	7(sp)[d]	48	3	20	
	7(sp)8d[d]	53	3	19	34
	7(sp)8d8f[d]	53	3	19	
C_3H_2	3(sp)[c]	46	7	71	34
	7(sp)[d]	51	5	71	
	7(sp)8d[d]	55	7	75	35
	7(sp)8d8f[d]	55	8	75	
C_5H_2	4(sp)[e]	209	70	255	69
	4(sp)[c]	206	68	255	
	7(sp)[d]	209	70	257	
	7(sp)8d[d]	216	73	256	69
$(HF)_2$	5(sp)[a]	156	13	102	103
	5(sp)5d[a]	165	14	103	103
	5(sp)5d5f[a]	165	15	104	
	7(sp)8d[d]	167	14	105	

[a] $\alpha_1^{spdf} = 4.5(-5)$, $q = 5.0$. [b] $\alpha_1 = 2.062(-6)$, $\alpha_1^{d} = 2.1574(-5)$, $q = 3\ 2341$.[50] [c] $\alpha_1^{spdf} = 2.25(-4)$, $q = 5.0$. [d] $\alpha_1^{spdf} = 2.1574(-5)$, $q = 3.2341$.[50] [e] $\alpha_1^{sp} = 2.2564(-4)$, $q = 3.2341$.[50]

The role of diffuse higher angular momentum functions on the binding of the extra electron proves to be relatively unimportant. For the systems considered here, E_{bind} increased by less than 10% when diffuse d functions were added to the basis set. The low-order contributions, such as $E_{\text{bind}}^{\text{KT}}$, $\Delta E_{\text{bind}}^{\text{SCF-ind}}$, and $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ are primarily affected, whereas $\Delta E_{\text{bind}}^{\text{HO}}$ is relatively unchanged by the inclusion of diffuse d functions. Diffuse f functions proved unimportant for every system studied, as may be seen from Table 1. The diffuse d and f functions were omitted from the basis set when carrying out the MP2 geometry optimizations and the frequency calculations.

Finally, we tested the extent to which our extended sp sets can be trimmed. The results are very encouraging. We found that four- and even three-term sp sets are sufficient to reproduce more than 90% of E_{bind} at the CCSD(T) level of theory. The possibility of using small sp diffuse sets to describe dipole-bound anions is advantageous from the point of view of numerical stability of iterative algorithms such as SCF or CCSD. In basis sets containing several sets of diffuse s, p, and d functions, convergence difficulties are often a problem.[38]

The dependence of E_{bind} on the standard basis set chosen to describe the neutral core is documented in Table 2. These tests were performed with fixed supplemental diffuse sets, with only the standard core basis set being varied. The electron binding energies obtained using the aug-cc-pVTZ sets are only slightly larger than those obtained with the aug-cc-pVDZ sets, and as a result, we have decided to use the aug-cc-pVDZ set in further applications. The results obtained with Sadlej's medium-size polarized (MSP) basis sets, which were carefully designed for calculations of molecular dipole moments and polarizabilities,[39] are consistent with those obtained with the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

TABLE 2: Dependence of E_{bind} on the Quality of the Initial Basis Set Designed to Describe a Neutral Molecular Host. Energies in cm^{-1}. See Text for Description of Basis Sets

system	basis	E_{bind}^{KT}	$\Delta E_{bind}^{SCF-ind}$	ΔE_{bind}^{MP2}
CH_3CN[a]	aug-cc-pVDZ	46	3	20
	aug-cc-pVTZ	46	3	24
	MSP	46	3	21
C_3H_2[a]	aug-cc-pVDZ	46	7	71
	aug-cc pVTZ	46	5	73
	MSP	46	5	70
$(HF)_2$[b]	aug-cc-pVDZ	165	14	103
	aug-cc-pVTZ	160	15	114
	MSP	162	14	110

[a] 3sp diffuse set. [b] 5spd diffuse set.

3.2. Electron Binding Energies. In Table 3 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)). The molecules are ordered according to the value of the SCF dipole moment; see Table 4. For HCN, CH_3CN, C_3H_2, C_4H_2, and C_5H_2 the MP2 geometries of the neutrals are used. For $(HF)_2$ we have found a significant geometrical relaxation upon electron attachment,[14,15] and the results reported in Tables 3 and 4 correspond to the MP2 geometry of the anion. CH_3CN and C_3HC_2 have similar dipole moments in the SCF approximation. However, inclusion of second-order electron correlation effects leads to a decrease of the dipole moment of the former and an increase in that of the latter; see Table 4. The CH_3F molecule is of special interest for our analysis of E_{bind} of dipole-bound anions. For CH_3F the R_{CF} distance was stretched by ca. 0.4 Å to give an SCF dipole moment of 4.34 D, equal to the SCF values of the dipole moments of CH_3CN and C_3H_2. The main purpose of this distortion is to create a model system with large electron correlation correction to the SCF dipole moment. Indeed, the dipole moment of stretched CH_3F decreases from 4.34 D in the SCF approximation to 3.50 D in the MP2 approximation.

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 dependence of E_{bind}^{KT} on the SCF dipole moment of neutrals, displayed in Figure 3, is not monotonic. For example, $(HF)_2$ has a much larger E_{bind}^{KT} value than CH_3CN, C_3H_2, stretched CH_3F, and C_4H_2 even though $(HF)_2$ has a much smaller SCF dipole moment. Even for the triad CH_3CN, C_3H_2, and stretched CH_3F, which share the same value of the SCF dipole moment, the values of E_{bind}^{KT} span the range of 26 cm^{-1}. As has been recognized for some time,[3,4,5,40] the charge

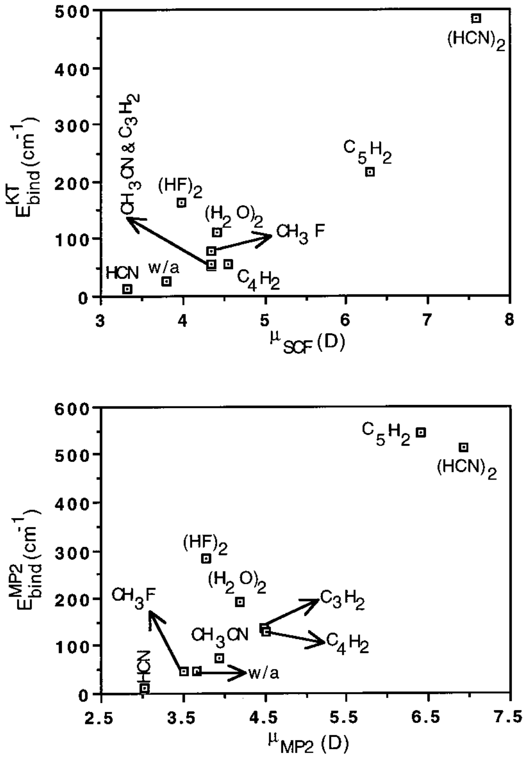

Figure 3. Dependence of E_{bind}^{KT} (E_{bind}^{MP2}) on the SCF (MP2) dipole moments of the neutral species. In addition to the systems discussed in this study, we have also included our results for $H_2O\cdots NH_3$ (w/a),[17] $(H_2O)_2$, and $(HCN)_2$.[18]

TABLE 3: Incremental Electron Binding Energies (in cm^{-1}) for the Dipole-Bound Anionic States of HCN, $(HF)_2$, CH_3CN, C_3H_2, Stretched CH_3F, C_4H_2, and C_5H_2. All Results are Obtained with the aug-cc-pVDZ Basis Supplemented with Diffuse Functions

component	HCN[a]	$(HF)_2$[b]	CH_3CN[c]	C_3H_2	CH_3F[c]	C_4H_2	C_5H_2[c]
E_{bind}^{KT}	13.8	165	53	55	79	54[c]	216
$\Delta E_{bind}^{SCF-ind}$	0.6	14	3	7	5	9[c]	73
$\Delta E_{bind}^{MP2-disp}$	13.8	177	57	70	79	79[c]	288
$\Delta E_{bind}^{MP2-no-disp}$	−15.3	−73	−38	5	−116	−14[c]	−32
ΔE_{bind}^{MP3}	−0.3	−3	4	−38	10	−17[d]	−143
ΔE_{bind}^{MP4}	1.8	27	8	34	1	26[d]	148
$\Delta E_{bind}^{CCSD(T)}$	−5.2	81	22	39	−8	76[d]	64
sum	9.1	387	108	173	49	213	614

[a] 9sp8d diffuse set. [b] 5sp5d diffuse set. [c] 7sp8d diffuse set. [d] 3sp diffuse set.

TABLE 4: Calculated Dipole Moments (D) and Polarizabilities (au) of the Neutral HCN, $(HF)_2$, CH_3CN, C_3H_2, Stretched CH_3F, C_4H_2, and C_5H_2. See Text for Molecular Geometries. All Results are Obtained with the aug-cc-pVDZ Basis Set

system	μ_{SCF}	μ_{MP2}	α_{xx}^{SCF}	α_{yy}^{SCF}	α_{zz}^{SCF}	α_{xx}^{MP2}	α_{yy}^{MP2}	α_{zz}^{MP2}
HCN	3.33	3.03	13.8	13.8	23.5	13.9	13.9	22.8
$(HF)_2$	3.98	3.78	7.5	8.3	11.6	8.6	9.4	13.2
CH_3CN	4.34	3.94	23.8	23.8	39.7	24.2	24.2	39.9
C_3H_2	4.34	4.48	26.8	27.7	63.3	26.5	28.4	60.3
CH_3F	4.34	3.50	15.2	15.2	25.3	16.5	16.5	28.0
C_4H_2	4.56	4.52	32.6	33.4	105.3	33.2	33.7	98.6
C_5H_2	6.28	6.40	38.1	39.4	170.2	37.8	40.3	154.7

TABLE 5: Values of E_{bind} (cm^{-1}) Obtained with Different Electronic Structure Methods. For Each Method the Value of ΔE_{bind} (cm^{-1}) Is Given in Parentheses

method	HCN[a]	$(HF)_2$[b]	CH_3CN[c]	C_3H_2[c]	CH_3F[c]	C_4H_2[d]	C_5H_2[e]
MP3(D)	12.5 (−0.3)	268 (−3)	79 (4)	100 (−38)	56 (10)	103 (17)	394 (−140)
MP4(DQ)	12.6 (0 .1)	266 (−2)	73 (−6)	91 (−9)	57 (1)	98 (−5)	364 (−30)
MP4(SDQ)	14.1 (1.6)	282 (14)	82 (4)	109 (9)	62 (6)	118 (15)	439 (46)
MP4(SDTQ)	14.3 (1.8)	294 (26)	87 (8)	134 (34)	57 (1)	129 (26)	539 (146)
CCD	11.8 (−0.9)	264 (−2)	71 (−2)	84 (−7)	56 (−1)	93 (−5)	343 (−20)
CCSD	13.0 (−1.1)	348 (66)	114 (31)	147 (39)	72 (10)	181 (63)	528 (89)
CCSD(T)	9.1 (−5.2)	374 (80)	108 (22)	173 (39)	49 (−8)	205 (76)	603 (63)
T4(CCSD)	(1.4)	(38)	(23)	(50)	(3)	(59)	(146)
T5(CCSD)	(−5.3)	(−12)	(−29)	(−25)	(−26)	(−35)	(−72)

[a] 9sp8d diffuse set. [b] 5sp diffuse set. [c] 7sp8d diffuse set. [d] 3sp diffuse set. [e] 4sp diffuse set.

distribution of the lbe depends on the chemical nature of the neutral host, not just on the dipole moment. The charge distribution of the lbe becomes less compact along the series CH_3F^-, $C_3H_2^-$, and CH_3CN^- (see Figure 2), and the values of $E_{\mathrm{bind}}^{\mathrm{KT}}$ decrease in the same order. The charge distribution of the lbe in $C_4H_2^-$ is very similar to that in CH_3CN^-, and the $E_{\mathrm{bind}}^{\mathrm{KT}}$ values are similar for these two species despite the difference of 0.22 D in the SCF dipole moments. The charge distribution of the lbe in $(HF)_2^-$ is very compact, consistent with a large value of $E_{\mathrm{bind}}^{\mathrm{KT}}$. An important conclusion from this analysis is that the value of $E_{\mathrm{bind}}^{\mathrm{KT}}$ may serve as an approximate measure of extendedness of the lbe.

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. With the exception of C_5H_2, relaxation of the molecualar charge distribution in the presence of the dipole-bound electron leads to relatively small (<17%) increases in the binding energies relative to the $E_{\mathrm{bind}}^{\mathrm{KT}}$ values. For C_5H_2 the increase is about 34%. The importance of the polarization contribution, $\Delta E_{\mathrm{bind}}^{\mathrm{SCF-ind}}$, depends on the polarizability of the neutral along the molecular axis (α_z) as well as on the average separation of the lbe from the molecular framework. As discussed above, the latter also correlates with $E_{\mathrm{bind}}^{\mathrm{KT}}$. $\Delta E_{\mathrm{bind}}^{\mathrm{SCF-ind}}$ is found to scale roughly as $c\alpha_z(E_{\mathrm{bind}}^{\mathrm{KT}})^n$, and the least-squares fit leads to $n = 1.2987$ and $c = 6.445(-4)$, for $\Delta E_{\mathrm{bind}}^{\mathrm{SCF-ind}}$and $E_{\mathrm{bind}}^{\mathrm{KT}}$ in cm^{-1}; r^2 is 0.857 for this fit.

The term $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}}$ results from dynamical correlation between the lbe and the electrons of the neutral molecule. This stabilizing effect is comparable to or larger than $E_{\mathrm{bind}}^{\mathrm{KT}}$ for all systems considered; see Table 3. This finding has important implications for model potentials designed to describe dipole-bound anions and solvated electrons.[41,42] The values of $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}}$ correlate roughly with the $E_{\mathrm{bind}}^{\mathrm{KT}}$ values.

In addition to the dispersion interaction, electron correlation modifies the electrostatic, induction, and valence repulsion interactions between the lbe and the neutral molecule. The correlation correction to the electrostatic interaction first appears at the MP2 level and is contained in $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-no-disp}}$. The trends in $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-no-disp}}$ are consistent with the changes of the dipole moment of the neutral species brought about by the inclusion of correlation effects. For typical closed-shell polar systems, such as HCN, CH_3CN, and $(HF)_2$, correlation effects act so as to decrease the dipole moment by a small amount and $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-no-disp}}$ is negative. Usually $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}}$ is greater in absolute value than $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-no-disp}}$, with the net $\Delta E_{\mathrm{bind}}^{\mathrm{MP2}}$ contribution being stabilizing. However, the resulting partial cancellation between $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-disp}}$ and $\Delta E_{\mathrm{bind}}^{\mathrm{MP2-no-disp}}$ may obscure the importance of the dispersion stabilization. The stretched CH_3F experiences a large (0.8 D) decrease in the dipole moment upon inclusion of second-order correlation effects, causing $\Delta E_{\mathrm{bind}}^{\mathrm{MP2}}$ to be destabilizing. The values of $\Delta E_{\mathrm{bind}}^{\mathrm{MP2}}$ do not correlate well with the MP2 values of dipole moments of the neutral species; see Figure 3.

The single-configuration approximation is particularly poor for C_3H_2, C_4H_2, and C_5H_2. For example, for C_3H_2 the CCSD(T) value of the dipole moment (4.14 D) is 0.34 D smaller than the MP2 value,[43] and the convergence of E_{bind} in a perturbative treatment of electron correlation is expected to be very slow for these systems.

The third-order contribution $\Delta E_{\mathrm{bind}}^{\mathrm{MP3}}$ is usually destabilizing and contributes more than 22% to $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ for C_3H_2 and C_5H_2. It contributes a similar fraction of $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ for the stretched CH_3F, but is stabilizing in this case. For the other systems considered, this contribution does not exceed 8% of $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$. The fourth-order term $\Delta E_{\mathrm{bind}}^{\mathrm{MP4}}$ is stabilizing for every system and exceeds 20% of $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ for HCN, C_3H_2; and C_5H_2. For the two latter systems and for C_4H_2, there is a near cancellation between the $\Delta E_{\mathrm{bind}}^{\mathrm{MP3}}$ and $\Delta E_{\mathrm{bind}}^{\mathrm{MP4}}$ contributions. Finally, correlation beyond fourth order, approximated here by $\Delta E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ (the difference between $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ and $E_{\mathrm{bind}}^{\mathrm{MP4}}$), always exceeds 10% of $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ in magnitude.

Different contributions to $\Delta E_{\mathrm{bind}}^{\mathrm{MP4}}$ and $\Delta E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ are summarized in Table 5. The MP4 contribution from double and quadruple excitations, $\Delta E_{\mathrm{bind}}^{\mathrm{MP4(DQ)}}$, is small and usually destabilizing. The contribution from single excitations, given by the difference between $\Delta E_{\mathrm{bind}}^{\mathrm{MP4(SDQ)}}$ and $\Delta E_{\mathrm{bind}}^{\mathrm{MP4(DQ)}}$, is always stabilizing and usually a few times larger than $\Delta E_{\mathrm{bind}}^{\mathrm{MP4(DQ)}}$. Finally, the contribution from triple excitations, given by the difference between $\Delta E_{\mathrm{bind}}^{\mathrm{MP4(SDTQ)}}$ and $\Delta E_{\mathrm{bind}}^{\mathrm{MP4(SDQ)}}$, is stabilizing for all systems except for the stretched CH_3F and is generally as important as the contribution from single excitations.

The contributions from single and triple excitations are magnified in coupled cluster calculations. The contribution from single excitations, calculated as the difference between $E_{\mathrm{bind}}^{\mathrm{CCSD}}$ and $E_{\mathrm{bind}}^{\mathrm{CCD}}$, is stabilizing, as it was at the MP4 level, but now represents a larger fraction of $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$, for example being 43, 40, and 36% for C_4H_2, CH_3CN, and C_3H_2, respectively. The coupled cluster contribution from triple excitations, calculated as the difference between $E_{\mathrm{bind}}^{\mathrm{CCSD(T)}}$ and $E_{\mathrm{bind}}^{\mathrm{CCSD}}$, contains the fourth-order contribution with the CCSD amplitudes and a fifth-order term,[30,31] which are labeled T4(CCSD) and T5(CCSD), respectively, in Table 5. The former contribution is usually larger than at the MP4 level and is always stabilizing. The latter, however, is always destabilizing and is of the same order of magnitude as the former. The resulting total contribution from triple excitations is stabilizing for $(HF)_2$, C_3H_2, C_4H_2, and C_5H_2 and destabilizing for HCN, CH_3CN, and stretched CH_3F.

TABLE 6: Geometries and Harmonic Vibrational Frequencies for the Neutral and Dipole-Bound Anionic States of HCN, CH_3CN, C_3H_2, C_4H_2, and C_5H_2 Molecules. Frequencies in cm^{-1}, Distances in Å, Angles in Degrees[51]

system	geometry	frequencies
HCN	$R_{CH} = 1.078$ $R_{CN} = 1.183$	$\omega(\pi) = 701$, $\omega(\sigma) = 1990$, $\omega(\sigma) = 3456$ $E_0^{vib} = 9.789$ kcal/mol
HCN^-	$R_{CH} = 1.078$ $R_{CN} = 1.183$	$\omega(\pi) = 703$ $\omega(\sigma) = 1993$, $\omega(\sigma) = 3453$ $E_0^{vib} = 9.795$ kcal/mol $\Delta E_0^{vib} = 2.1$ cm^{-1}
CH_3CN	$R_{CN} = 1.185$ $R_{CC} = 1\ 471$ $R_{CH} = 1.099$ $\alpha = 109.8$	$\omega(e) = 351$, $\omega(a_1) = 931$, $\omega(e) = 1048$ $\omega(a_1) = 1390$, $\omega(e) = 1466$, $\omega(a_1) = 2180$ $\omega(a_1) = 3089$, $\omega(e) = 3189$ $E_0^{vib} = 28.162$ kcal/mol
CH_3CN^-	$R_{CN} = 1.186$ $R_{CC} = 1.471$ $R_{CH} = 1\ 099$ $\alpha = 109.9$	$\omega(e) = 353$, $\omega(a_1) = 929$, $\omega(e) = 1047$ $\omega(a_1) = 1390$, $\omega(e) = 1465$, $\omega(a_1) = 2178$ $\omega(a_1) = 3088$, $\omega(e) = 3189$ $E_0^{vib} = 28.151$ kcal/mol $\Delta E_0^{vib} = 4.0$ cm^{-1}
C_3H_2	$R_{CH} = 1.097$ $R_1 = 1.350$ $R_2 = 1.306$ $\alpha = 121.3$	$\omega(b_1) = 124$, $\omega(b_2) = 205$, $\omega(b_2) = 1035$ $\omega(b_1) = 1047$, $\omega(b_1) = 1117$, $\omega(a_1) = 1480$ $\omega(a_1) = 2018$, $\omega(a_1) = 3144$, $\omega(b_2) = 3245$ $E_0^{vib} = 19.176$ kcal/mol
$C_3H_2^-$	$R_{CH} = 1.097$ $R_1 = 1.351$ $R_2 = 1.304$ $\alpha = 121.4$	$\omega(b_1) = 117$, $\omega(b_2) = 208$, $\omega(b_2) = 1032$ $\omega(b_1) = 1035$, $\omega(a_1) = 1117$, $\omega(a_1) = 1479$ $\omega(a_1) = 2006$, $\omega(a_1) = 3144$, $\omega(b_2) = 3246$ $E_0^{vib} = 19.133$ kcal/mol $\Delta E_0^{vib} = 15.0$ cm^{-1}
C_4H_2	$R_1 = 1.304$, $R_2 = 1.313$ $R_3 = 1.325$, $R_4 = 1.093$ $R_5 = 1.093$, $\alpha = 173.3$ $\beta = 179.1$, $\gamma = 119.9$ $\delta = 120.2$, $\epsilon = 120.0$	$\omega(a') = 126$, $\omega(a'') = 128$, $\omega(a') = 366$ $\omega(a'') = 376$, $\omega(a'') = 745$, $\omega(a') = 901$ $\omega(a'') = 918$, $\omega(a') = 1368$, $\omega(a') = 1708$ $\omega(a') = 2144$, $\omega(a') = 3175$, $\omega(a') = 3283$ $E_0^{vib} = 21.784$ kcal/mol
C_4H_2	$R_1 = 1.302$, $R_2 = 1.315$ $R_3 = 1.324$, $R_4 = 1.095$ $R_5 = 1.093$, $\alpha = 173.6$ $\beta = 178.5$, $\gamma = 119.7$ $\delta = 120.5$, $\epsilon = 119.8$	$\omega(a') = 127$, $\omega(a'') = 137$, $\omega(a') = 300$ $\omega(a'') = 375$, $\omega(a'') = 755$, $\omega(a') = 898$ $\omega(a') = 909$, $\omega(a') = 1363$, $\omega(a') = 1711$ $\omega(a') = 2117$, $\omega(a') = 3154$, $\omega(a') = 3206$ $E_0^{vib} = 21.517$ kcal/mol $\Delta E_0^{vib} = 93.1$ cm^{-1}
C_5H_2	$R_1 = 1.303$, $R_2 = 1.324$ $R_3 = 1.283$, $R_4 = 1.344$ $R_5 = 1.096$, $R_6 = 1.097$ $\alpha = 176.7$, $\beta = 175.5$ $\gamma = 172.6$, $\delta = 121.2$ $\epsilon = 121.0$, $\zeta = 117.8$	$\omega(a'') = 44$, $\omega(a') = 123$, $\omega(a'') = 187$ $\omega(a') = 228$, $\omega(a'') = 394$, $\omega(a') = 507$ $\omega(a') = 750$, $\omega(a'') = 967$, $\omega(a') = 1027$ $\omega(a') = 1348$, $\omega(a') = 1496$, $\omega(a') = 1951$ $\omega(a') = 2187$, $\omega(a') = 3142$, $\omega(a') = 3245$ $E_0^{vib} = 25.155$ kcal/mol
$C_5H_2^-$	$R_1 = 1.299$, $R_2 = 1.329$ $R_3 = 1.280$, $R_4 = 1.347$ $R_5 = 1.096$, $R_6 = 1.097$ $\alpha = 176.9$, $\beta = 175.4$ $\gamma = 172.8$, $\delta = 121.4$ $\epsilon = 121.1$, $\zeta = 117.6$	$\omega(a'') = 61$, $\omega(a') = 127$, $\omega(a'') = 189$ $\omega(a') = 230$, $\omega(a'') = 390$, $\omega(a') = 507$ $\omega(a') = 748$, $\omega(a'') = 989$, $\omega(a') = 1021$ $\omega(a') = 1343$, $\omega(a') = 1493$, $\omega(a') = 1960$ $\omega(a') = 2169$, $\omega(a') = 3136$, $\omega(a') = 3240$ $E_0^{vib} = 25.165$ kcal/mol $\Delta E_0^{vib} = -3.5$ cm^{-1}

Higher-than-fourth-order electron correlation contributions to E_{bind} may also be extracted from the data collected in Table 5. The difference between E_{bind}^{CCD} and $E_{bind}^{MP4(DQ)}$ is usually very small and destabilizing. However, when single excitations are included, the situation is quite different; indeed, the difference between E_{bind}^{CCSD} and $E_{bind}^{MP4(SDQ)}$ represents 31, 30, and 22% of $E_{bind}^{CCSD(T)}$ for C_4H_2, CH_3CN, and C_3H_2, respectively. Finally, the contribution $\Delta E_{bind}^{CCSD(T)}$ is usually stabilizing and reaches 36 and 23% of $\Delta E_{bind}^{CCSD(T)}$ for C_4H_2 and C_3H_2. However, it exerts a sizable destabilizing effect for HCN and for stretched CH_3F.

The results discussed above indicate that a fourth-order treatment of electron correlation effects is in general not sufficient for dipole-bound anions. The role of single excitations is extremely important and may be related to the fact that the charge distribution of the lbe is significantly modified when the neutral molecular core is modified by correlation effects. This is indicated by the fact that in the anionic CCSD calculations the largest amplitudes correspond to single excitations from the orbital occupied by the lbe. It may well be that the physical interpretation of E_{bind} calculated in the coupled cluster framework would benefit if Brueckner orbitals[30,31] were used to construct the single determinantal wave functions for the anion and the neutral. Since the differences between the CCSD and QCISD methods involve single-excitation operators,[30,31] it is not surprising that the CCSD and QCISD values of electron binding energies differ by 26 and 31% for $C_3H_2^-$ and CH_3CN^-, respectively. Inclusion of noniterative triple excitations does not remove these discrepancies. As a consequence, we do not recommend using the QCISD(T) method for dipole-bound anions.

The contribution from triple excitations proved to be very sensitive to the form of amplitudes of the single and double excitations. In some dipole-bound anions it may be necessary to adopt methods such as CCSDT-1 and CCSDT, which treat high-order correlation effects more accurately than does the CCSD(T) method.[30,31] On the other hand, we believe that physical models of dipole-bound anions may be restricted to

TABLE 7: Theoretical Values of Franck−Condon Factors and Transition Energies (cm^{-1}) in the Photoelectron Spectra of Dipole-Bound Anions of C_3H_2, C_4H_2, and C_5H_2

system	transition	position	FC factor
$C_3H_2^-$	0_0^0	188	1.000
	7_0^1	2206	0.001
$C_4H_2^-$	0_0^0	301	1.000
	1_0^1	427	0.002
	$1_0^1 3_0^1$	794	0.003
	$1_0^1\,10_0^1$	2571	0.001
	2_0^2	557	0.001
	3_0^1	667	0.002
	3_0^2	1034	0.006
	$3_0^1 12_0^1$	3950	0.001
	10_0^1	2445	0.001
$C_5H_2^-$	0_0^0	630	1.000
	1_0^2	720	0.017
	2_0^1	753	0.001
	10_0^1	1979	0.001
	13_0^1	2818	0.006

the first-order Coulomb and exchange and the second-order induction and dispersion terms if based on accurate rather than SCF properties of neutral molecular hosts.

3.3. Modifications of Potential Energy Surfaces upon Electron Attachment. The MP2 level equilibrium geometries and harmonic frequencies of the neutral and anionic species are collected in Table 6. These equilibrium geometries and geometrical Hessians were used to calculate polyatomic FC factors using Doktorov and co-workers' recursion relations[44] as implemented in the code of Roy.[45] Only ground vibrational states of the anions were considered because we assumed the temperature of 10 K, which is typical in PES experiments.[29] The intensity for the 0−0 transition was normalized to 1, and all other intensities were scaled accordingly. Due to limitations resulting from the finite signal-to-noise ratio in PES experiments[46] and numerical inaccuracies of ab initio geometry optimizations and frequency calculations,[47] we report in Table 7 only these FC factors that exceed 0.001. The notation n_k^l means that for the nth mode there is an excitation from k to l quanta, and 0_0^0 stands for the 0−0 transition. For $C_4H_2^-$ and $C_5H_2^-$ the calculated FC factors were convoluted with Gaussian line shapes (fwhm = 218 cm^{-1}),[29] and the resulting PES spectra are presented in Figures 4 and 5, respectively.

The bond lengths of HCN are affected by less than 0.0002 Å upon electron attachment, and vibrational frequencies of the neutral and anionic species agree to within 3 cm^{-1}. The dipole moments of the neutral HCN calculated at the equilibrium geometries of the neutral and the anion differ by less than 0.0001 D, and the FC factors for the non-0−0 transitions are less than 2.0(−6). Our calculated adiabatic electron affinity of HCN is 7 cm^{-1}. This value is only a factor of 5 greater than the rotational constant and thus could be modified upon inclusion of corrections to the BO approximation. An experimental determination of the electron binding energy of HCN and exploration of vibrational structure in the PES spectrum of HCN$^-$ would be especially valuable.

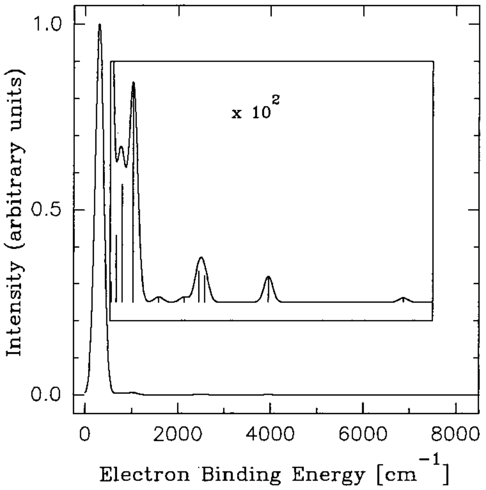

Figure 4. Theoretical photoelectron spectrum of $C_4H_2^-$ based on calculated Franck−Condon factors.

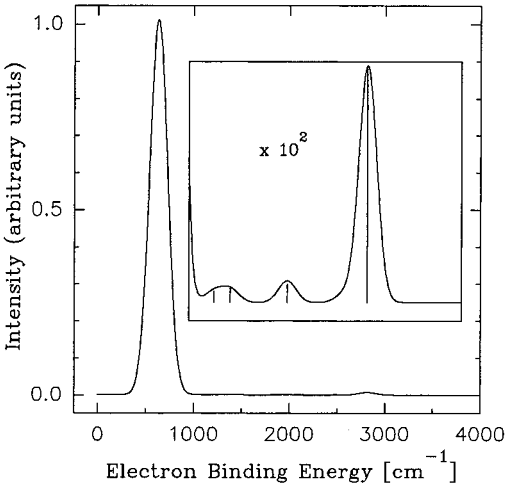

Figure 5. Theoretical photoelectron spectrum of $C_5H_2^-$ based on calculated Franck−Condon factors.

Our calculated adiabatic electron affinity of CH_3CN is 112 cm^{-1}, which is within the experimental range of 11.5−18 meV ≈ 93-145 cm^{-1} obtained from the Rydberg electron-transfer experiments.[24,41] For CH_3CN^- produced by photodissociation of the $I^-\cdots CH_3CN$ complex, the electron binding energy estimated from a field detachment experiment was 11 meV ≈ 89 cm^{-1},[48] while in a PES experiment the 0−0 transition was determined at 3 ± 5 meV ≈ 24 ± 40 cm^{-1}.[28]

We find that the bond lengths of CH_3CN are affected by less than 0.0003 Å and the α angle by less than 0.02° upon electron attachment and that the vibrational frequencies of the neutral and anionic species differ by not more than 3 cm^{-1}. A very small geometrical relaxation in this system was also reported by Gutsev et al.[10] The dipole moments of the neutral calculated at the equilibrium geometry of the neutral and the anion differ by less than 0.0003 D. Our FC factors for the non-0−0 transitions are less than 4.0(−5), and thus they cannot account for vibrational structure in the PES spectrum of CH_3CN^- observed by Bailey et al.[28] These authors suggested that resonant and vibronic effects are operative for the dipole-bound anion of CH_3CN and are responsible for the vibrational structure. While our results exclude FC factors as the main source of vibrational structure and therefore support the conclusion of Bailey et al.,[28] a further experimental confirmation of the vibrational structure in the PES spectrum of CH_3CN^- is highly desirable in view of a discrepancy between the calculated position of the 0−0 transition at 112 cm^{-1} and the measured position in the PES spectrum at 24 ± 40 cm^{-1}.[28] The latter result is also inconsistent with electron binding energies obtained in the field detachment experiments.[24,41,48]

Our adiabatic electron detachment energy for the dipole-bound anion of C_3H_2 is 188 cm^{-1} and is within the experimental range of 171 ± 50 cm^{-1} obtained in a recent autodetachment spectroscopy study.[26] We find that the length of the terminal, hydrogen-free, CC bond decreases by 0.002 Å upon electron attachment and that the angles are changed by less than 0.06°. The *A* rotational constant is found experimentally to be larger for the dipole-bound anion than for the neutral by ca. 0.19%,[26,49] whereas our calculations give an increase by 0.12%. The vibrational frequencies of the neutral and anionic C_3H_2 differ by 7, 12, and 12 cm^{-1} for the first, fourth, and seventh mode, respectively. The largest FC factors are predicted to be for the 7^1_0, 1^2_0, and $1^1_0\,4^1_0$ transitions, with the values of 0.0005, 0.0004, and 0.0002, respectively. The geometrical relaxation to the anionic structure is accompanied by an increase of the dipole moment of the neutral by 0.01 D.

To the best of our knowledge, there is no experimental information about dipole-bound anions of C_4H_2 and C_5H_2. C_5H_2 possesses a valence anionic state in addition to the dipole-bound state and therefore is suitable for autodetachment spectroscopy studies. Both molecules have C_s equilibrium structures. The C_{2v} stationary points are only slightly higher in energy and display larger dipole moments. Therefore, a distortion along soft bending modes may increase the dipole moment of the neutral and the electron binding energy in the anion. Our adiabatic electron detachment energy for the dipole-bound anion of C_4H_2 is calculated to be 301 cm^{-1}, and the predicted PES spectrum displays a weak vibrational structure due to nonzero FC factors; see Table 7 and Figure 4. The CC bond lengths are predicted to decrease by up to 0.002 Å upon electron attachment, whereas the angles change by up to 0.6°. The vibrational frequencies of the neutral and anionic C_4H_2 differ by 77, 66, 27, and 21 cm^{-1} for the 12th, 3rd, 10th, and 11th modes, respectively, and the largest non-0−0 FC factor corresponds to the 3^2_0 transition and amounts to 0.006. The geometrical relaxation to the anionic structure is accompanied by an 0.03 D increase of the dipole moment of the neutral and by an 0.92% increase of the *A* rotational constant.

Our calculated adiabatic electron detachment energy for the dipole-bound anion of C_5H_2 is 630 cm^{-1}, and we predict that the PES spectrum of $C_5H_2^-$ will display a weak vibrational structure due to nonzero FC factors; see Table 7 and Figure 5. Electron attachment is found to enhance alternation of the CC bond lengths, with the largest changes being 0.005 Å. Also some of the angles change by up to 0.2°. The vibrational frequencies of the neutral and anionic C_5H_2 differ by 18 and −17 cm^{-1} for the 13th and 1st mode, respectively, and the largest non-0−0 FC factors of 0.017 and 0.006 correspond to the 1^2_0 and 13^1_0 transitions, respectively. The geometrical relaxation to the anionic structure is accompanied by a 0.09 D increase of the dipole moment of the neutral and by a 0.65% increase of the A rotational constant.

4. Summary

We have studied the contributions of electron correlation and orbital relaxation to the electron binding energies for a variety of dipole-bound anions, and we presented a physical interpretation of the electron binding energy. Orbital relaxation effects are found to be significant only for the relatively strongly bound $C_5H_2^-$ species. In contrast, electron correlation effects proved to be important for each species studied. The electron correlation contribution may be split into two physically different components. The first is the stabilizing dispersion interaction between the loosely bound electron and the electrons of the neutral molecule. Interestingly, it is of the same order of magnitude as the electrostatic stabilization reproduced at the Koopmans' theorem level. It depends on the polarizability of the neutral molecule and on the average separation of the loosely bound electron from the neutral molecular core. The second type of correlation contribution to electron binding energy involves a modification of the static stabilization of the loosely bound electron by the electrostatic potential of the neutral. Depending on whether inclusion of correlation effects decreases or increases the dipole moment (relative to the SCF value), the correction to the electron binding energy will be, respectively, destabilizing or stabilizing. Inclusion of electron correlation effects higher than second order proved to be necessary to obtain qualitatively correct electron binding energies, with coupled cluster results differing significantly from fourth-order Møller−Plesset results.

Ab intio calculations for dipole-bound anions require extended basis sets to describe the diffuse charge density of the loosely bound electron. Our studies show that the extra diffuse set may be limited to a few sp functions, that the contribution of d diffuse functions may be estimated at the second-order Møller−Plesset level, and that the contribution of f diffuse functions is negligible. Extensions of the "core" basis set beyond the aug-cc-pVDZ level does not lead to significant changes in electron binding energies.

We also examined modifications of potential energy surfaces induced by electron attachment. For each system studied, the relaxation from the neutral to anionic equilibrium structure is accompanied by an increase of the dipole moment of the neutral. This is consistent with the dipole-bound nature of these anions. This behavior has also been observed for polar hydrogen-bonded clusters.[14−18] For $C_4H_2^-$ and $C_5H_2^-$ we found that modifications of anionic potential energy surfaces are sufficient to generate sizable Franck−Condon factors between the ground vibrational state of the anion and excited vibrational states of the neutral. The calculated values of Frank−Condon factors for CH_3CN^-/CH_3CN are not large enough to explain vibrational structure in the photoelectron spectrum recorded by Bailey et al.[28]

We predicted an adiabatic electron affinity of 112 cm^{-1} for CH_3CN, which is in good agreement with experimental findings: 93−145,[24,41] 89,[48] and 24 ± 40 cm^{-1}.[28] For the dipole-bound anion of C_3H_2 our adiabatic electron detachment energy of 188 cm^{-1} is within the experimental range of 171 ± 50 cm^{-1} obtained in the recent autodetachment spectroscopy study.[26] Our adiabatic electron detachment energies for dipole-bound anions of HCN, C_4H_2, and C_5H_2 are 7, 301, and 630 cm^{-1}. Experimental results do not yet exist for these species.

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