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Dispersion Stabilization of Solvated Electrons and Dipole-Bound Anions

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It has long been assumed that stability of "solvated electrons" and dipole-bound anions results primarily from the static Coulomb interaction of an excess electron with charge distribution of the neutral molecular host. Our results indicate, however, that the dispersion interaction between the loosely bound electron and the neutral molecular host is as important as the static Coulomb stabilization. A perturbation scheme is designed to analyze physically meaningful components of electron binding energy, and highly correlated electronic structure results are presented for dipole-bound anions and solvated electrons in the $(HF)_n$ clusters ($n = 2, 3$). The vertical electron detachment energy for $(HF)_3^-$ was found to be 0.63 and 0.21 eV for the solvated electron and dipole-bound anion, respectively. The equilibrium zigzag geometrical structure of the dipole-bound anion differs drastically from the cyclic C_{3h} structure of the neutral trimer.

1. Introduction

The dispersion interaction is commonly associated with an attractive component of van der Waals interactions that displays asymptotic R^{-6} behavior, where R is the distance between interacting species.[1] As recognized by London, the dispersion effect results from correlated fluctuations of electron charge densities of interacting atomic or molecular species.[2] In this contribution we discuss the role of dispersion interaction in a different molecular context. We consider a loosely bound electron (lbe) as a chemical species, and we discuss its interaction with the neutral molecular host as if we were dealing with a weakly bound molecular dimer. Our theoretical framework applies to dipole-bound states (dbs) of molecular anions and to "solvated electrons" (se) because these anions share a feature that the excess electron is bound by physical rather than chemical interactions with its neutral molecular host.[3] The results presented here extend our earlier observations about the role of dynamic electron correlation in dipole-bound anions,[4−6] in particular in systems with hydrogen bonds such as $(HF)_2^-$ [7] and $(H_2O\cdots NH_3)^-$.[8]

It has long been assumed that stabilization of dipole-bound anions and solvated electrons is dominated by the static Coulomb interaction of the lbe with the charge distribution of the neutral molecular host. For dipole-bound anions, it is the interaction of the excess electron with the total dipole moment of the neutral host that leads to a bound anionic state and localization of the lbe on the positive side of the molecular dipole.[9,10] On the other hand, a solvated electron is localized primarily inside the cluster of polar molecules. There is no requirement for a significant net dipole moment of the neutral molecular host to solvate an electron and an extensive, if not complete, cancellation of dipole moments of individual solvent molecules is anticipated in the cluster.[3]

In this contribution we demonstrate that the static Coulomb interaction is only a part of the total electron stabilization in dipole-bound anions and solvated electrons and the second-order dispersion interaction between the lbe and electrons of the neutral molecular host has to be taken into account to alleviate a serious discrepancy between experimental and theoretical electron binding energies (E_{bind}).[4−8] The role of higher-order electron correlation contributions to E_{bind} is also documented.

2. Results and Discussion

We present electronic structure results for a weakly bound electron in the $(HF)_2^-$ and $(HF)_3^-$ clusters. Our second-order Møller−Plesset (MP2) analysis of the anionic potential energy surfaces indicates that for both systems there are minima that may be associated with a solvated electron and a dipole-bound anion; see Figure 1. Here, we discuss primarily the issue of electron binding energy, whereas the relative stability of dipole-bound anions and solvated electrons will be discussed in detail elsewhere.[11] The electron binding energies were obtained by subtracting the energies calculated for the anion from those of the neutral. This procedure requires the use of size extensive methods, and we have performed coupled-cluster calculations with single, double, and noniterative triple excitations (CCSD-(T)).[12] The Gaussian 94 package was used throughout this study.[13]

The charge distribution of an excess electron in physically bound anions cannot be approximated by a linear combination of valence orbitals of atoms that form a neutral molecular host; see Figure 1. These charge distributions necessitate the use of very flexible basis sets containing functions with very low exponents. Our calculations were performed with the aug-cc-pVDZ basis set[14] supplemented with diffuse s, p, and d functions. For dipole-bound anions, which require more diffuse functions, we have used five- and four-term spd sets with the lowest exponent equal to 4.5(−5) and 2.25(−4) au for the dimer and trimer, respectively. We have recently studied basis set effects in calculations of electron binding energies in dipole-bound anions,[15] and we expect that the results reported here differ by less than 15% from the CCSD(T) complete basis set limits.

The simplest approach to determine E_{bind} of a physically bound electron is based on Koopmans' theorem (KT).[16] E_{bind}^{KT} is estimated from the negative of the energy of the
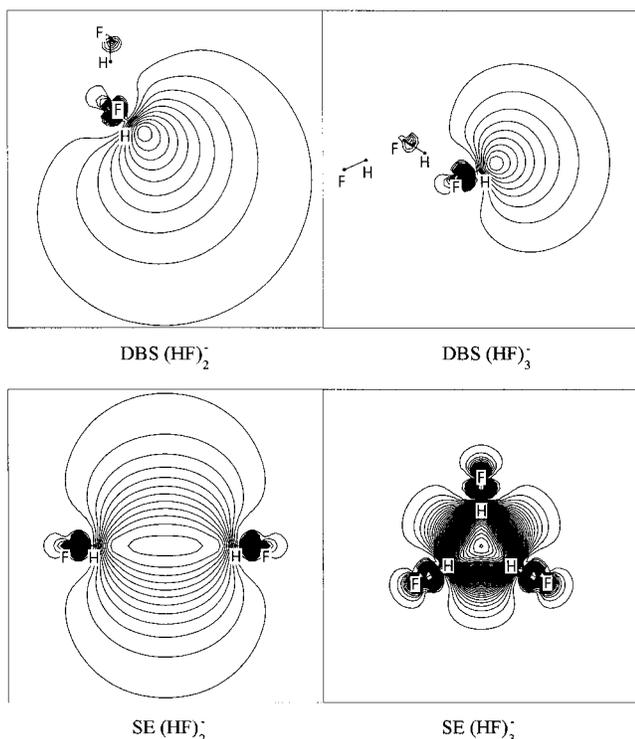
Figure 1. Contour plots of charge densities resulting from singly occupied molecular orbitals in anions of $(HF)_2$ and $(HF)_3$. Both dipole-bound states (DBS) and solvated electrons (SE) are illustrated. The separation between contour lines is 0.000 03 and 0.000 15 $e/\text{Å}^3$ for dimers and trimers, respectively.

TABLE 1: Decomposition of the Vertical Electron Detachment Energy $E_{\text{bind}}^{\text{total}}$ into Physically Meaningful Components for Solvated Electrons (se) and Dipole-Bound Anionic States (dbs) in the $(HF)_n$, $n = 2, 3$, Clusters[a]

system	$E_{\text{bind}}^{\text{KT}}$ ($E_{\text{IP}}^{\text{KT}}$)	$\Delta E_{\text{bind}}^{\text{SCF-ind}}$	$\Delta E_{\text{bind}}^{\text{MP2-disp}}$	$\Delta E_{\text{bind}}^{\text{HO}}$	$E_{\text{bind}}^{\text{total}}$
$(HF)_2^-$ se	99 (160)	28	339	35	431
$(HF)_3^-$ se	1966 (4815)	1282	3445	−1588	5105
$(HF)_2^-$ dbs	165 (195)	14	177	31	387[b]
$(HF)_3^-$ dbs	950 (1174)	104	625	−14	1666

[a] All energies in cm^{-1}. [b] The experimental electron binding energy is $508 \pm 24 \text{ cm}^{-1}$.[17]

relevant unfilled orbital obtained from a Hartree−Fock self-consistent-field (SCF) calculation on the neutral molecular host. The results presented in Table 1 demonstrate that $E_{\text{bind}}^{\text{KT}}$ is only a part of the total electron binding energy. The value of $E_{\text{bind}}^{\text{KT}}$ for the dbs of $(HF)_2^-$ seriously underestimates the experimental electron binding energy of $508 \pm 24 \text{ cm}^{-1}$,[17] and similar discrepancies were observed for other systems.[4,5]

In Table 1 we also presented the KT predictions of ionization potentials for the anionic species, which are labeled $E_{\text{IP}}^{\text{KT}}$. It is well-known that ionization potentials are usually better reproduced at the KT level than electron affinities due to a partial cancellation of orbital relaxation and electron correlation corrections.[18] This is also true for weakly bound species studied here, as the values of $E_{\text{IP}}^{\text{KT}}$ are systematically closer to our most accurate results than the $E_{\text{bind}}^{\text{KT}}$ values. Formally, $E_{\text{IP}}^{\text{KT}}$ and $E_{\text{bind}}^{\text{KT}}$ limit the SCF electron binding energy from the top and the bottom, respectively, and differences between the KT predictions and the SCF result are defined as orbital relaxation effects. The discrepancies between $E_{\text{bind}}^{\text{KT}}$ and $E_{\text{IP}}^{\text{KT}}$ are larger for solvated electrons than for dipole bound anions because the former display larger orbital relaxation effects, vide infra. We prefer to start our analysis of electron binding energies in weakly

bound anions from $E_{\text{bind}}^{\text{KT}}$ rather than from $E_{\text{IP}}^{\text{KT}}$ because the former takes into account the Coulomb and exchange interaction between the lbe and the SCF charge distribution of the unperturbed neutral host. This is consistent with a scheme developed below in which we analyze interactions between a neutral molecular host and an excess electron in a perturbative manner and $E_{\text{bind}}^{\text{KT}}$ is reproduced at the lowest level of theory.

We consider a neutral molecular host (N) and a loosely bound electron (lbe) as weakly interacting species, and we exploit this analogy with the theory of intermolecular interactions[19,20] to design a perturbation scheme for analysis of 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}

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

where the formal expansion parameters λ and η have physical values equal to unity and are introduced to define the perturbation theory orders. The zeroth-order Hamiltonian

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

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

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

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

On applying double-perturbation theory[19] to the Hamiltonian (1) one obtains the perturbation expansion for the anion energy

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

where $\epsilon^{(kl)}$ is of the 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 $E_{\text{bind}}^{\text{KT}}$:

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

The non-KT contributions to E_{bind} are given by other $\epsilon^{(kl)}$ terms with $l \geq 1$. The term $\epsilon^{(02)}$ separates into the induction and dispersion components[19,20]

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

The term $\epsilon_{\text{ind}}^{(02)}$ 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

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

where

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

and $E_{\text{A}}^{\text{SCF}}$ stands for the SCF energy of the anion. In fact, the

term $\Delta E_{\text{bind}}^{\text{SCF-ind}}$ includes not only the static polarization of N by the lbe but also the secondary effect of back-polarization. The values of $\Delta E_{\text{bind}}^{\text{SCF-ind}}$, presented in Table 1, are more important for solvated electrons than for dipole-bound anions, which is probably related to smaller average separations between the excess electron and the HF molecules in the se clusters; see Figure 1.

The term $\epsilon_{\text{disp}}^{(02)}$ results from a 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 $\epsilon_{\text{disp}}^{(02)}$ is approximated here by $\Delta E_{\text{bind}}^{\text{MP2-disp}}$, which takes into account proper permutational symmetry for all electrons in the anion

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

where ϕ_a and ϕ_{lbe} are occupied spin orbitals in the zeroth-order wavefunction, ϕ_r and ϕ_s are unoccupied orbitals, and e's are the corresponding orbital energies. This expression for $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ has also been used in our earlier studies on dipole-bound anions.[4,6,7] The values of $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ are very similar when calculated with the SCF orbitals of N and A, and the results reported in Table 1 were obtained with the latter to be consistent with the supermolecular electron binding energy. It is remarkable that in many cases the values of $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ exceed the values of $E_{\text{bind}}^{\text{KT}}$. This is an important finding since the dispersion interaction has been neglected in many studies of electron binding to polar species.[21,22]

We define the higher-order contribution to E_{bind}, denoted $\Delta E_{\text{bind}}^{\text{HO}}$ in Table 1, as the difference between the electron binding energy obtained at the CCSD(T) level of theory and the sum of $E_{\text{bind}}^{\text{KT}}$, $\Delta E_{\text{bind}}^{\text{SCF-ind}}$, and $\Delta E_{\text{bind}}^{\text{MP2-disp}}$. The term $\Delta E_{\text{bind}}^{\text{HO}}$ takes into account two kinds of $\epsilon^{(kl)}$ corrections. First, there are higher order corrections in V^{lbe} given by the $\epsilon^{(0l)}$ ($l > 2$) terms. Second, there are corrections $\epsilon^{(kl)}$, 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 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 $E_{\text{bind}}^{\text{KT}}$, has to be rectified, and the first corection of this type is given by the $\epsilon^{(21)}$ term.

The values of $\Delta E_{\text{bind}}^{\text{HO}}$ are significant and cannot be omitted in high-quality electronic structure modeling of weakly bound electrons. Moreover, we have found evidence that relatively small values of the $\Delta E_{\text{bind}}^{\text{HO}}$ terms, reported in Table 1, result from a fortuitous cancellation of different $\epsilon^{(kl)}$ terms. One may hope, however, that quantum mechanical molecular dynamics simulations may be restricted to the Coulomb, exchange, induction, and dispersion effects if based on accurate rather than SCF properties of neutral molecular hosts.

Our theoretical vertical electron detachment energy (VDE) for the dbs form of $(\text{HF})_2^-$ is 387 cm^{-1}, when calculated from the difference in the CCSD(T) energies of the anion and the neutral at the anionic geometry, and 396 cm^{-1} when the neutral and the anion are calculated at their MP2 equilibrium geometries and the zero-point vibrational correction is estimated from the harmonic MP2 frequencies.[7] These results are in good agreement with the experimental finding of 508 ± 24 cm^{-1} from Bowen's group[17] and confirm the 20-year old prediction of the existence of $(\text{HF})_2^-$ by Jordan and Wendoloski.[23] These form of $(\text{HF})_2^-$, though a minimum on the anionic potential energy surface, is thermodynamically unstable with respect to both the neutral dimer and the dbs anion, due to significant reorganization energy of the neutral cluster required to form the $D_{\infty\text{h}}$ structure.[11]

The neutral trimer has a cyclic $C_{3\text{h}}$ equilibrium structure with zero dipole moment,[24] and therefore the relative stability of the C_{s} zigzag dbs and the $D_{3\text{h}}$ se cannot be a priori predicted. Our preliminary results indicate that the dbs form of $(\text{HF})_3^-$ is in fact ca. 6 kcal/mol lower in energy than the se form.[11] In addition, the zigzag dbs anion is thermodynamically stable with respect to the cyclic neutral cluster. This is an important finding since for many years a dipole-bound anion was regarded as being an *unperturbed*[25] or *slightly perturbed*[7,17] neutral molecule with the excess distant electron tethered to the dipole, and a distinctive spectral feature has been assigned to dipole-bound anions.[3,17] 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 energy. Our results for $(\text{HF})_3^-$ demonstrate that the equilibrium structure of the dbs anion may differ drastically from the equilibrium structure of the neutral and therefore the narrowness of the dominant peak should not be taken for granted.

On the experimental side, $(\text{HF})_3^-$ has recently been observed in Bowen's group.[17] Their preliminary photoelectron spectrum displays two features at about 0.4−0.5 and 0.2−0.3 eV,[26] to be compared with our theoretical VDE's of 0.63 and 0.21 eV for the solvated electron and dipole-bound anion, respectively. The $D_{3\text{h}}$ isomer of $(\text{HF})_3^-$ may be the smallest solvated electron that has thus far been characterized theoretically and observed experimentally.

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