

Contribution of electron correlation to the stability of dipole-bound anionic states

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It has long been assumed that electron correlation effects are relatively unimportant for describing dipole-bound anionic states. It is shown here that this assumption is incorrect: high-level electronic structure calculations on the dipole-bound anion states of CH_3CN , C_3H_2 , and C_5H_2 reveal that for these species a large fraction of the electron binding energy derives from the dispersion-type interaction between the loosely bound electron and the neutral molecule. The predicted values of the electron affinities of the dipole bound states of CH_3CN and C_3H_2 , 108 and 173 cm^{-1} , respectively, are in excellent agreement with the recent experimental results, 93 cm^{-1} and $171 \pm 50 \text{ cm}^{-1}$, respectively. The predicted value for C_5H_2 is 614 cm^{-1} . [S1050-2947(96)09208-6]

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The problem of the binding of electrons by polar molecules has a long and fascinating history, starting with the demonstration by Fermi and Teller in 1947 that an electron can be bound in the field of a point dipole, if the value of the dipole exceeds 1.625 D [1]. For dipole moments greater than this value, there is an infinity of bound states within the context of the Born-Oppenheimer 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]. Upon inclusion of corrections to the Born-Oppenheimer approximation, the critical moment for electron binding increases by several tenths of a Debye and becomes molecule dependent [5–7].

For highly polar nonionic molecules the average separation between the loosely bound electron and the neutral molecule is large (typically 10–100 Å) and it has been generally assumed that, as a result, dynamical electron correlation between the loosely bound electron and the neutral molecule is relatively unimportant. This has motivated researchers to adopt a Koopmans theorem (KT) approach [13] for calculating the binding energies of electrons to polar molecules [8–12]. In this approximation, the binding energy, E_{bind} , is given as minus the energy of the relevant unfilled orbital obtained from a Hartree-Fock self-consistent-field (SCF) calculation of the neutral molecule. This is a static approximation that neglects both electron correlation and relaxation effects.

However, recent experimental results for C_3H_2^- and CH_3CN^- indicate that the errors due to the KT model for electron binding to polar molecules can be quite large. Specifically, Yokoyama *et al.* have determined an electron binding energy of $171 \pm 50 \text{ cm}^{-1}$ for the dipole-bound anion of C_3H_2 [14] and Desfrancois *et al.* have measured an electron binding energy of 93 cm^{-1} for CH_3CN^- [15]. In contrast, recent KT values of E_{bind} are 55 and 46 cm^{-1} for C_3H_2^- [16] and CH_3CN^- [17,18], respectively. Since the relevant rotational energy-level spacings for CH_3CN and C_3H_2 are

much smaller than the reported electron binding energies, electron correlation and relaxation corrections to the KT approximation, rather than non-Born-Oppenheimer effects, are expected to be responsible for these sizable discrepancies. However, it has been found in numerous studies of dipole-bound anions that relaxation and correlation corrections to the KT binding energies are relatively small [17–27].

These conflicting results have motivated us to take a closer look at the role of electron correlation in determining the energy of binding of electrons to polar molecules. The molecules studied are CH_3CN , C_3H_2 , and C_5H_2 , depicted in Fig. 1. All three of these molecules have dipole-bound anion states. C_3H_2 and C_5H_2 also have bound valence anion states, which will not be considered here. As noted above, the dipole-bound anions of CH_3CN and C_3H_2 have been studied experimentally.

In this study, electron correlation was included by means of Møller-Plesset (MP) perturbation theory as well as by the coupled-cluster for single, double, and noniterative triple [CCSD(T)] excitations method [28]. In addition, the second-order correlation contribution to E_{bind} was decomposed into dispersion-type and non-dispersion components. The theoretical results reported here were obtained with the GAUSSIAN 92 program [29]. The binding energies at the SCF, MPn ($n=2,3$, and 4) and CCSD(T) levels of theory were obtained by subtracting the energies calculated for the anions from those of the neutrals. All calculations on both the anionic and neutral species were carried out using the MP2 optimized geometries of the neutral molecules [30]. Thus, geometry relaxation of the molecular frameworks upon electron attachment was neglected as were differences in zero-point vibrational energies between the dipole-bound anion and the neutral molecule. Recent calculations indicate that in the case of CH_3CN^- these effects contribute less than 3 cm^{-1} to E_{bind} [17,18]. Larger effects due to geometry relaxation and vibrational zero-point energy corrections are expected for molecules, such as C_5H_2^- , in which the “extra” electron is close to the nuclear framework.

The diffuse character of the outermost electron of dipole-bound anions necessitates the use of very flexible basis sets

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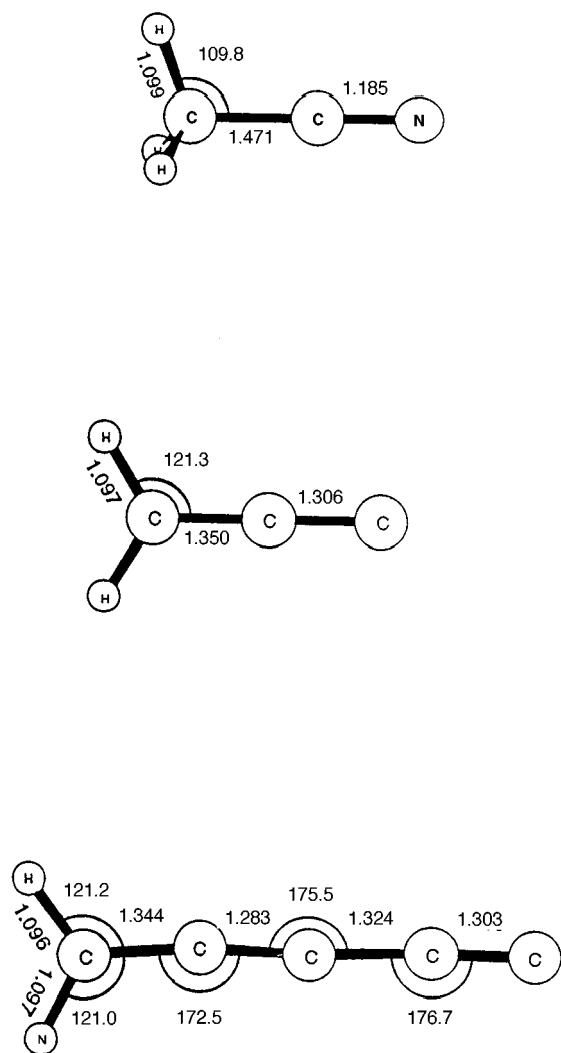


FIG. 1. MP2 optimized geometries of neutral CH_3CN , C_3H_2 , and C_5H_2 with bond lengths and angstroms and angles in degrees.

containing functions with low exponents [8–10]. In this work, we employ the augmented, correlation-consistent, polarized, valence double-zeta (aug-cc-pVDZ) Gaussian-orbital basis set [30], supplemented with a large set of diffuse primitive Gaussian functions centered on the carbon atom at the positive end of the molecular dipole. The exponents of the supplemental seven sp and eight d functions form an even-tempered sequence, with the ratio between consecutive exponents being 3.2 and the smallest exponent being $2.2 \times 10^{-5} a_0^{-2}$ for each angular momentum. In order to minimize errors due to the use of such diffuse functions, the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} a.u. 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.

The dipole moments and polarizabilities of the neutral molecules are reported in Table I, and the calculated electron binding energies are summarized in Table II. The SCF values of the dipole moments of both CH_3CN and C_3H_2 are 4.34 D, and that of C_5H_2 is 6.28 D. For CH_3CN , inclusion of correlation via the MP2 procedure leads to a 0.42 D reduction of the dipole moment, giving a value of 3.94 D, which is in excellent agreement with the experimental value

TABLE I. Calculated properties of the neutral CH_3CN , C_3H_2 , and C_5H_2 molecules. Results obtained with the aug-cc-pVDZ basis set and using MP2 aug-cc-pVDZ optimized geometries.

Property	CH_3CN	C_3H_2	C_5H_2
μ^{SCF} (D)	4.34	4.34	6.28
μ^{MP2} (D)	3.94	4.48	6.40
$\alpha_{xx}^{\text{SCF}}(\perp)$ (a.u.)	24	27	38
$\alpha_{yy}^{\text{SCF}}(\perp)$ (a.u.)	24	28	39
$\alpha_{zz}^{\text{SCF}}(\parallel)$ (a.u.)	40	63	170
$\alpha_{xx}^{\text{MP2}}(\perp)$ (a.u.)	24	26	38
$\alpha_{yy}^{\text{MP2}}(\perp)$ (a.u.)	24	28	40
$\alpha_{zz}^{\text{MP2}}(\perp)$ (a.u.)	40	60	155

of 3.92 D [32]. For C_3H_2 and C_5H_2 , inclusion of second-order electron correlation effects leads to increases in the dipole moments by 0.15 and 0.12 D, respectively. CH_3CN and C_3H_2 have similar dipole polarizabilities, whereas C_5H_2 is much more polarizable, particularly along the z (long) axis. The values of the polarizabilities are not strongly affected by the inclusion of correlation effects.

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 a dipole moment, but interactions with higher permanent multipoles as well as penetration and occupied orbital exclusion effects are also taken into account. Consistent with the trends in the dipole moments, the KT values of E_{bind} for CH_3CN^- and C_3H_2^- are similar, while that for C_5H_2^- is approximately four times larger.

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 CH_3CN^- and C_3H_2^- , relaxation of the molecular charge distribution in the presence of the dipole-bound electron leads to relatively small ($< 8 \text{ cm}^{-1}$) increases in the binding energies, but for C_5H_2^- , it leads to a 73 cm^{-1} increase of E_{bind} relative to its KT value. This can be understood in terms of the smaller separation of the “extra” electron from the neutral molecule and the larger polarizability of C_5H_2 (as compared to CH_3CN and C_3H_2).

TABLE II. Incremental electron binding energies (in cm^{-1}) for the dipole-bound anionic states of CH_3CN , C_3H_2 , and C_5H_2 . All results obtained with the aug-cc-pVDZ basis set augmented with seven diffuse sp and eight diffuse d functions.

Method	CH_3CN	C_3H_2	C_5H_2
$E_{\text{bind}}^{\text{KT}}$	53	55	216
$\Delta E_{\text{bind}}^{\text{SCF}}$	3	8	73
$\Delta E_{\text{bind}}^{\text{MP2-disp}}$	57	70	288
$\Delta E_{\text{bind}}^{\text{MP2-no-disp}}$	-38	5	-32
$\Delta E_{\text{bind}}^{\text{MP3}}$	4	-38	-144
$\Delta E_{\text{bind}}^{\text{MP4}}$	8	34	148
$\Delta E_{\text{bind}}^{\text{CCSD(T)}}$	21	39	65
Sum	108	173	614
Experiment	93 ^a	171 ± 50 ^b	

^aReference [15].

^bReference [14].

The total electron correlation contribution to E_{bind} encompasses two physically distinct effects: (1) the change in the binding energy due to improved description of the molecular dipole of the neutral "core," and (2) dynamical correlation between the loosely bound electron and the electrons of the neutral molecule. The latter correlation effect, analogous to the dispersion interaction in van der Waals systems, first appears at the MP2 level and is denoted $\Delta E_{\text{bind}}^{\text{MP2-disp}}$. It can be approximated as a sum over all pair contributions $\epsilon_{lbe,i}$, involving excitations of the form $\phi_{lbe}\phi_i \rightarrow \phi_v\phi_{v'}$, where ϕ_{lbe} corresponds to the orbital occupied by the loosely bound electron, ϕ_i is one of the other occupied orbitals of the molecule, and ϕ_v and $\phi_{v'}$ are unoccupied virtual orbitals. The remainder of the MP2 contribution to E_{bind} , denoted $\Delta E_{\text{bind}}^{\text{MP2-no-disp}}$ contains correlation corrections of the electrostatic, induction, and valence repulsion interactions between the loosely bound electron and the neutral molecule [31].

For all three molecules, the dispersion contribution $\Delta E_{\text{bind}}^{\text{MP2-disp}}$ dominates the second-order correlation correction to the electron binding energy and, in each case, its value is larger in magnitude than $E_{\text{bind}}^{\text{KT}}$. This is an important finding since dispersion-type interactions have been neglected in various model potentials designed to describe electron binding to polar species [15,33]. The importance of the dispersion interaction is, however, understandable in view of the significant polarizabilities of the neutral molecules and the loosely bound electron. The $\Delta E_{\text{bind}}^{\text{MP2-no-disp}}$ term is relatively unimportant for C_3H_2^- and C_5H_2^- . However, for CH_3CN^- , it results in a 51 % decrease of the electron binding energy (compared to the net MP2 value). This is on account of the sizable reduction of the dipole moment of the neutral CH_3CN brought about by the inclusion of correlation effects.

For CH_3CN^- , 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 C_3H_2^-

and C_5H_2^- , the third- and fourth-order corrections to E_{bind} are sizable in magnitude, but they enter with opposite signs and essentially cancel each other. Correlation beyond fourth order, approximated here by $\Delta E_{\text{bind}}^{\text{CCSD(T)}}$ [the difference in the CCSD(T) and MP4 binding energies], leads to sizable increases in the magnitude of E_{bind} for all three molecules. For CH_3CN^- and C_3H_2^- , the $\Delta E_{\text{bind}}^{\text{CCSD(T)}}$ correction is responsible for almost 20% of the net electron binding energies; for C_5H_2^- it is responsible for about 10% of the binding energy.

Our final values of E_{bind} calculated at the CCSD(T) excitation level for CH_3CN^- and C_3H_2^- are 108 and 173 cm^{-1} , respectively, which are in excellent agreement with the corresponding experimental values of 93 cm^{-1} [15] and $171 \pm 50 \text{ cm}^{-1}$ [14]. For C_5H_2^- , the CCSD(T) value of E_{bind} is 614 cm^{-1} . Hence, the dipole-bound anion possesses several vibrationally excited levels which are stable with respect to electron detachment.

The present study shows that electron correlation can contribute significantly to electron binding energies of dipole-bound anionic states of polar molecules. For each of the three systems studied, over half of the binding energy is due to electron correlation effects. A significant fraction of the correlation contribution to the binding energy is due to the dispersion-type interaction between the loosely bound electron and the neutral molecule. Although electron correlation effects play a major role in determining the magnitudes of the electron binding energies, the anion states can still be viewed as "dipole bound" since their existence stems from the large dipole moments of the neutral molecules.

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