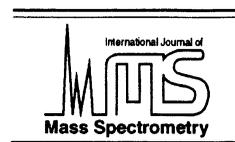




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Bi-dipole-bound anions

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Abstract

The possibility of electron binding by a molecule with two polar ends, each of which is capable of electron binding, is studied using electronic structure methods. The destabilizing effects of each dipole on the ability of the other dipole to bind an electron as well as the through-bond splitting between the *g* and *u* anion states are examined. In addition, the ability of the two polar ends to bind two electrons, one to each end, is investigated. Numerical results are presented for the anions of $(\text{HCN})_n \cdots \text{HCCH} \cdots (\text{NCH})_n$ ($n = 2-4$) and for the corresponding $n = 2$ dianion. (Int J Mass Spectrom 201 (2000) 245–252) © 2000 Elsevier Science B.V.

Keywords: Anions, dipole

1. Introduction

The binding of an excess electron by valence-saturated polar molecules has been studied extensively, both experimentally [1–7] and theoretically [8–17]. Such bound excess electrons may be localized primarily outside the molecular frame and form a surface anionic state (e.g. as in small water clusters) or it may be localized inside the cluster and form an internal state (i.e. a “solvated electron” as in large clusters of ammonia) [18]. In the former case, it is natural to analyze the binding of the extra electron in terms of its interaction with various electrostatic and induced moments of the neutral’s charge distribution because the “extra” electron is localized primarily outside this charge distribution. This has given rise to

many studies of anions whose states have been called dipole- or quadrupole-bound, depending on the nature of the lowest nonvanishing multipole moment of the neutral system. The recent theoretical and experimental studies on dipole-bound anions are reviewed in [17] and those on quadrupole-bound anions in [7,14].

In this contribution, we report on electron binding to linear molecules having two polar ends and we term the resulting anions bi-dipole bound (bdb). Our primary goals are (1) to monitor the splitting between the *g* and *u* anion states as the distance between the polar groups varies (this splitting is caused by “through bond” coupling), (2) to monitor the destabilizing effect of one dipole on the other as the distance between the dipoles varies, and (3) to determine under what conditions the double anion is stable.

For an anion bound due to the static interaction of the extra electron with the charge distribution of the

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neutral molecule N , the one-particle Schrödinger equation

$$\left(-\frac{1}{2}\Delta + V_{elst}^{exact} + V_{ooe-exch}^{exact}\right)\phi = \epsilon\phi \quad (1)$$

possesses a bound solution [14]. Here, V_{elst}^{exact} represents the classical electrostatic potential from the exact charge distribution ρ_N^{exact} of N

$$V_{elst}^{exact}\phi(1) = \int \frac{\rho_N^{exact}(2)}{r_{1,2}} d\tau_2\phi(1) \quad (2)$$

and the occupied orbitals exclusion effects (ooe) and the exchange interaction between the excess electron and the electrons of N are included in the $V_{ooe-exch}^{exact}$ potential. In practical calculations, the V_{elst}^{exact} and $V_{ooe-exch}^{exact}$ operators are not available. There is, however, a well known approximation to Eq. (1) at the Hartree-Fock (HF) self-consistent field (SCF) level of theory. With ρ_N^{exact} in V_{elst}^{exact} replaced by the SCF density ρ_N^{HF} and $V_{ooe-exch}^{exact}$ replaced by the SCF exchange operators K [19], Eq. (1) becomes equivalent to the Koopmans' theorem (KT) description of the excess electron binding, with ϵ being equal to the energy of the virtual orbital ϕ obtained in the SCF calculation for N [19]. The vertical electron attachment energy at the KT level of theory is given by the negative of ϵ and is labeled VAE^{KT} .

The V_{elst} operator for a neutral $D_{\infty h}$ molecule with two polar ends separated by a distance $2L$ may be approximated (especially at distances exterior to the charge density of N) by a sum of two dipole potentials having opposite orientations. With $V_{ooe-exch}$ neglected and V_{elst} so approximated, Eq. (1) reduces to

$$\left[-\frac{1}{2}\Delta + V_1(+\mu, +L) + V_2(-\mu, -L)\right]\phi^{bdb} = \epsilon^{bdb}\phi^{bdb} \quad (3)$$

where V_1 and V_2 describe the electron–dipole interactions. The solutions of Eq. (3) for large L 's are expected, by symmetry, to be of the form

$$\phi_{\pm}^{bdb} \approx \frac{1}{\sqrt{2}}(\chi_1 \pm \chi_2) \quad (4)$$

$$\epsilon_{\pm}^{bdb} \approx e \pm H_{12} \quad (5)$$

where χ and e are the eigenfunctions and energies of the one-particle Schrödinger equation for the dipole-bound anion

$$\left(-\frac{1}{2}\Delta - \frac{\mu \cos \theta}{r^2}\right)\chi = e\chi \quad (6)$$

with χ_1 centered at L and χ_2 at $-L$. The + and – solutions of Eq. (4) describe σ_g and σ_u orbitals, respectively. The term $H_{12} = \langle \chi_1 | -1/2\Delta + V_1(+\mu, +L) + V_2(-\mu, -L) | \chi_2 \rangle$, which relates to the through-bond coupling of the two dipole-bound orbitals, approaches zero as $L \rightarrow \infty$, but produces a nonvanishing $\epsilon_+^{bdb} - \epsilon_-^{bdb}$ energy splitting for finite L 's. On the basis of the ab initio calculations whose results are reported here, we attempt to learn, in a more quantitative sense, about the strength of these couplings as well as about the stability of the state having one electron in χ_1 and a second electron in χ_2 .

$$V_2(-\mu_1 - L) | \chi_2 \rangle$$

2. Molecules, geometries, and basis sets

The linear $(\text{HCN})_n \cdots \text{HCCH} \cdots (\text{NCH})_n$ species, for which we introduce the short-hand notation $\mathcal{H}_n S \mathcal{H}_n$, are bi-dipolar because they contain pairs of oppositely oriented polar $(\text{HCN})_n$ oligomers (denoted \mathcal{H}_n) separated by the acetylene spacer molecule (S). We chose to use the \mathcal{H}_n oligomers because we have experience studying electron binding to these species [15].

The \mathcal{H}_n clusters are known to have a propensity for linear equilibrium structures, and the dimer and trimer have been experimentally characterized as linear [20]. Also solid \mathcal{H} is known to contain “infinite” linear \mathcal{H} chains [21]. The dipole-bound anionic states of the linear \mathcal{H}_n clusters have recently been theoretically studied [12,15] and the vertical electron attachment energies calculated at the KT (VAE^{KT}), SCF (VAE^{SCF}), and the second-order Møller-Plesset (MP2) levels (VAE^{MP2}) are collected in Table 1 for $n = 1-4$.

Table 1

Vertical electron attachment energies (in cm^{-1}) calculated at the KT, SCF, and MP2 levels, the linear clusters $(\text{HCN})_n$ and $(\text{HCN})_n \dots \text{HCCH} \dots (\text{NCH})_n$ are denoted by \mathcal{H}_n and $\mathcal{H}_n S \mathcal{H}_n$, respectively

System	Anionic state	$V AE^{KT}$	$V AE^{SCF}$	$V AE^{MP2}$
\mathcal{H}^a	${}^2\Sigma$	14	14	13
\mathcal{H}_2^b	${}^2\Sigma$	465	511	494
\mathcal{H}_3^b	${}^2\Sigma$	1007	1094	1044
\mathcal{H}_4^b	${}^2\Sigma$	1400	1503	1430
$\mathcal{H}_2 S \mathcal{H}_2$	${}^2\Sigma_g^+$	158	165	206
$\mathcal{H}_2 S \mathcal{H}_2$	${}^2\Sigma_u^+$	151	159	197
$\mathcal{H}_3 S \mathcal{H}_3$	${}^2\Sigma_g^+$	557	581	638
$\mathcal{H}_3 S \mathcal{H}_3$	${}^2\Sigma_u^+$	560	582	637
$\mathcal{H}_4 S \mathcal{H}_4$	${}^2\Sigma_g^+$	895	925	982
$\mathcal{H}_4 S \mathcal{H}_4$	${}^2\Sigma_u^+$	895	925	982

^a see [23]

^b see [24]

Our ab initio calculations of electron binding energies for the $D_{\infty h} \mathcal{H}_n S \mathcal{H}_n$ ($n = 1-4$) species have been performed at the MP2 level of theory with the aug-cc-pVDZ basis sets [22] supplemented with six extra sets of s and p functions centered on the terminal hydrogen atoms. The exponents of the extra even-tempered diffuse sets span the range from 2.4684×10^{-2} to 6.9771×10^{-5} au. Our strategy for constructing the diffuse basis set employed here is detailed in [15] where such bases have been shown to be flexible enough to describe the $(\text{HCN})_n$ groups in species such as we consider here. Moreover, our earlier studies [15,17], which include species containing $(\text{HCN})_n$ groups, showed that electron correlation corrections beyond MP2 are relatively unimportant. For example, for reproducing the electron binding energies of $(\text{HCN})_2^-$ and $(\text{HCN})_3^-$, corrections beyond MP2 were as small as 3% of the total values of electron binding energies. Therefore, we believe that the electron correlation corrections calculated at the third order MP (MP3), fourth order MP (MP4), coupled cluster single double (CCSD), and CCSD triple [CCSD(T)] levels are not likely to be significant for the species that we describe here.

The structures of the neutral $\mathcal{H}_n S \mathcal{H}_n$ ($n = 1-4$) species, optimized at the SCF level of theory, have all positive curvatures (i.e. the hessian matrix eigenval-

ues). For $n = 2$ we also performed SCF geometry optimization and frequency calculations for the ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ anionic states and found the geometry relaxation upon electron attachment to be very small for both states. The largest distortion of 0.02 Å occurs for the hydrogen bonds between the \mathcal{H} moieties. The anions in the g and u states are found to have nearly identical structures with valence bonds differing by less than 0.0001 Å and hydrogen bonds by less than 0.0007 Å. Both g and u anionic structures are found to have all positive curvatures at the SCF level of theory.

We also performed additional calculations for the anion and dianion of $\mathcal{H}_2 S \mathcal{H}_2$ with (1) the geometry of \mathcal{H}_2 set to the optimal geometry of the dipole-bound anion \mathcal{H}_2^- , (2) the geometry of the spacer S set to the optimal geometry of the neutral acetylene, and we then varied only one internal geometry parameter L (the distance between the terminal hydrogen atom and the center of symmetry). These model calculations were carried out to allow us to monitor how the dipole-dipole repulsion and through-bond couplings vary with distance.

3. ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ mono-anionic states

3.1. g/u splitting and through-bond coupling

Bound anionic states of ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ symmetry were found in the $\mathcal{H}_n S \mathcal{H}_n$ systems for $n \geq 2$ but not for $n = 1$. The vertical electron attachment energies, displayed with those of the corresponding \mathcal{H}_n oligomers in Table 1, show a near degeneracy in the g and u states (e.g. the MP2 values of the VAE for the g and u states differ by less than 9.3, 0.6, and 0.04 cm^{-1} for $n = 2, 3$, and 4, respectively), even for the $n = 2$ cluster where through-bond coupling should be largest. This means that the through-bond coupling [see Eq. (5)] is 5 cm^{-1} for $n = 2$ and even smaller for $n \geq 3$.

The charge distributions of the excess electron in the ${}^2\Sigma_g^+$ (${}^2\Sigma_u^+$) state of $\mathcal{H}_n S \mathcal{H}_n^-$ ($n = 2-4$) are described by symmetric (antisymmetric) combinations of the sp hybrid type orbitals localized on the terminal H atoms (see Fig. 1 for the g and u

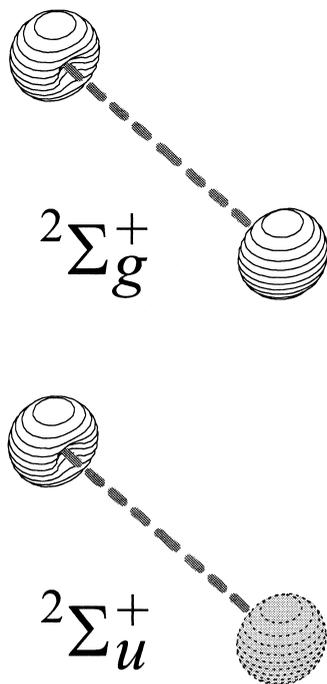


Fig. 1. Singly occupied molecular orbital of $\mathcal{H}_4S\mathcal{H}_4^-$ in the lowest ${}^2\Sigma_g^+$ (top) and ${}^2\Sigma_u^+$ (bottom) electronic state (plotted with a 0.005 contour spacing).

distributions for $n = 4$). The hybrid orbitals become more spatially compact as n increases, consistent with the increase of the electron binding energy (see Table 1) and with the increasing polarity of the \mathcal{H}_n moieties as reflected in their increasing dipole moments. For each n , the spatial extent is very similar for the g and u states and the fraction of the excess electron density localized in the interatomic region of the molecular frame is very small, which explains the negligible geometry differences and energy splittings between the anionic g and u states.

As noted above, the excess electron remains unbound at the KT level of theory for $n = 1$. This was not a surprise to us because (1) the \mathcal{H} monomer binds an electron by only 11 cm^{-1} at the KT level [23], (2) its polarity is less in the $\mathcal{H}S\mathcal{H}$ environment than in \mathcal{H} , and (3) in $\mathcal{H}S\mathcal{H}$ one has the repulsion between the dipoles of the oppositely oriented \mathcal{H} units. These effects are probably responsible for the electronic instability of $\mathcal{H}S\mathcal{H}^-$. Likewise, for $n \geq 2$, the

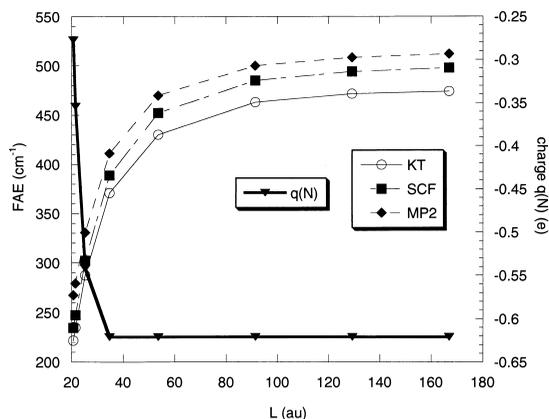


Fig. 2. The FAE energy for $\mathcal{H}_2S\mathcal{H}_2^-$ as a function of the distance L between the terminal hydrogen atom and the center of symmetry. $q(N)$ denotes the Mulliken charge of the nitrogen atom closest to the acetylen molecule.

electron binding energies are smaller in the $\mathcal{H}_nS\mathcal{H}_n^-$ than in the \mathcal{H}_n^- species (see Table 1) for similar (i.e. smaller polarity and dipole–dipole repulsion) reasons.

3.2. Dipole–dipole repulsion effect

In Fig. 2 we display the dependence of the energy associated with attaching the first electron (FAE) to form either the g or u state (note that we already established that these two energies differ very little) on the distance L in $\mathcal{H}_2S\mathcal{H}_2^-$. The Mulliken charges from the SCF calculations on the neutral $\mathcal{H}_2S\mathcal{H}_2$ are also reported in Fig. 2 for the nitrogen atom which is closest to the acetylene molecule. Of course, as $L \rightarrow \infty$ the value of the FAE is the same as the vertical electron detachment energy for the isolated \mathcal{H}_2^- , and these limiting values of the FAE are 481, 529, and 512 cm^{-1} for the KT, SCF, and MP2 methods, respectively [15]. The values of the FAE decrease as L decreases (see Fig. 2). For L larger than 35 a.u., the polarity of the \mathcal{H}_2 groups is the same in $\mathcal{H}_2S\mathcal{H}_2^-$ as in the isolated \mathcal{H}_2 , as indicated by the values of the Mulliken charge on the N atom. In this region, the dependence of the FAE on L relates only to the fact that the excess electron localized on one side of the cluster is destabilized by the repulsive potential of the dipole on the opposite side of the cluster. For $L < 36$

a.u., the polarity of the \mathcal{H}_2 groups in $\mathcal{H}_2S\mathcal{H}_2$ rapidly decreases, as indicated by the values of the Mulliken charge on the nitrogen. For such values of L , the values of the FAE further decrease due both to the decrease in polarity and to changes in dipole–dipole repulsion.

3.3. Effects of orbital relaxation and correlation

The electron binding energies in the $\mathcal{H}_nS\mathcal{H}_n^-$ systems are dominated by the KT contribution which takes into account the coulomb and exchange interaction between the excess electron and the SCF charge distribution of N . The effect of orbital relaxation, which is given by the difference between VAE^{SCF} and VAE^{KT} and which describes polarization of N by the excess electron and the effect of backpolarization, is small and does not exceed 5% of VAE^{KT} . The MP2 electron correlation contribution to the electron binding energy, given by the difference between VAE^{MP2} and VAE^{SCF} , describes (1) the dispersion interaction between the excess electron and the electrons of N and (2) the correlation correction to the static coulomb interaction between the extra electron and the charge distribution of N [24]. The stabilizing former term represents a significant fraction of VAE^{KT} (50% for $n = 3$) but it is largely canceled by the latter. In consequence, the total MP2 contribution does not exceed 30% of VAE^{KT} .

4. Doubly charged anion

We have also studied the electronic stability of the dianion $\mathcal{H}_2S\mathcal{H}_2^{2-}$ as a function of the spacing parameter L . The $^1\Sigma_g^+$ and $^3\Sigma_u^+$ di-anionic states become quasidegenerate for large values of L . A single-reference $\sigma_g^1\sigma_u^1$ wave function is appropriate for the triplet state, but the singlet state requires two strongly mixed electronic configurations (σ_g^2 and σ_u^2) or one configuration based on localized orbitals ($\chi_1^1\chi_2^1$). For these reasons, we studied only the $^3\Sigma_u^+$ state but the results for the $^1\Sigma_g^+$ state are expected to be very similar especially in the regime of large L .

The second electron attachment energy (SAE),

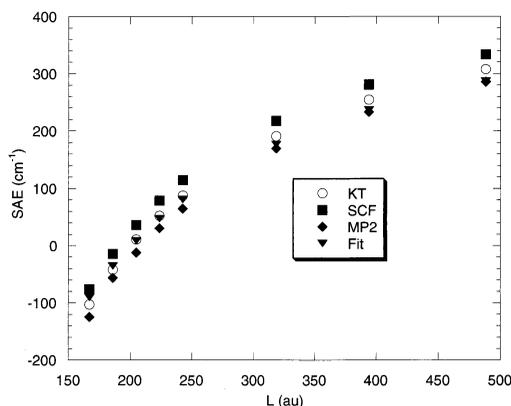


Fig. 3. The SAE energy for $\mathcal{H}_2S\mathcal{H}_2$ as a function of the distance L between the terminal hydrogen atom and the center of symmetry. The approximate values of SAE^{KT} resulting from the fit [Eq. (7)] are also reported.

defined as the difference between the energies of the di-anion and of the mono-anion, is plotted in Fig. 3 for the $^3\Sigma_u^+$ state as a function of L for the KT, SCF, and MP2 methods. The KT SAE is given as the negative of the energy of the lowest unoccupied molecular orbital obtained from an unrestricted Hartree-Fock (UHF) SCF calculation on the monoanion.

As $L \rightarrow \infty$, the asymptotic value of the SAE is the same as the FAE, as expected for two noninteracting \mathcal{H}_2 species. For every method, the electronic stability of the dianion decreases as L decreases (see Fig. 3), and the di-anion becomes unstable (i.e. the SAE becomes negative) for $L \approx 210$ a.u. A simple electrostatic argument suggests that the di-anion should remain electronically bound as long as the coulomb repulsion between the two excess electrons localized at opposite ends of the molecule is smaller than the FAE. For example, the KT values of the SAE, with all quantities expressed in atomic units, should fit the following equation:

$$SAE^{KT}(L) \approx FAE^{SCF}(L) - \frac{1}{2L + C} \quad (7)$$

where $2L$ is the distance between the terminal hydrogen atoms and C takes into account the spatial extent of the orbitals $\chi_{1,2}$ holding the two excess electrons. The value of C was determined by least squares fitting

the SAE and FAE energies and a value of $C = 39.4$ a.u. was achieved. As shown in Fig. 3, the model of Eq. (7) performs well for $\mathcal{H}_2S\mathcal{H}_2^-$ and allows us to relate the SAE to the FAE and the length L of a bi-dipolar molecule. Clearly, the small \mathcal{H}_n clusters, considered in this article, have too small FAEs to form bound dianions for realistic values of L . However, this is not the case when more polar building blocks such as LiCN are used to build clusters [25].

5. Polarizability and electron localization in mono-anions

The electric dipole transition moment connecting the ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ anion states, denoted $\langle g|\mu_z|u\rangle$, was found to be 33 and 36 a.u. for $n = 2$ and 3, respectively, at the configuration interaction level of theory with single excitations (CIS). These significant values of the electric dipole-transition moment and the quasidegeneracy of the ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states (especially for larger n) suggest a large value of the longitudinal polarizability of the anion, α_{\parallel} , if calculated using the second-order perturbation theory expression for a non-degenerate state [26]. This perturbation theory is, however, not applicable when the matrix element $\langle g|\mu_z|u\rangle$ is large in comparison with the energy difference between the unperturbed ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states [27]. The response of the molecule in a quasidegenerate state to an external electric field requires a multiconfigurational approach similar to that used in analysis of the “sudden polarization” effect [28]. In fact, for large n 's, one expects to observe a linear Stark effect rather than the quadratic dependence of the energy on electric field, that is characteristic of polarizability.

Even for large n , however, the precise degeneracy of the g and u states in $\mathcal{H}_nS\mathcal{H}_n^-$ is almost certainly unattainable due to vibronic coupling between the ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ states. This coupling is expected to lead to negative curvature along an antisymmetric stretching mode of σ_u symmetry. The strength of the factor that produces negative σ_u -mode curvature on the lower, e.g. ${}^2\Sigma_g^+$, surface is governed by matrix elements of the form [29]

$$\frac{|\langle {}^2\Sigma_g^+|\partial H/\partial Q_{\sigma_u}|{}^2\Sigma_u^+\rangle|^2}{E({}^2\Sigma_g^+) - E({}^2\Sigma_u^+)} \quad (8)$$

where $\partial H/\partial Q_{\sigma_u}$ represents the derivative of the electronic Hamiltonian with respect to distortion along the σ_u mode. The closer the ${}^2\Sigma_u^+$ state approaches the underlying ${}^2\Sigma_g^+$ state, the larger is the magnitude of the ${}^2\Sigma_g^+$ -state negative curvature factor. Once negative σ_u -mode curvature occurs, the molecular framework distorts from $D_{\infty h}$ to $C_{\infty v}$ symmetry, the two molecular polar ends become nonequivalent, and the near-degeneracy of the two bound anionic states is removed.

Moreover, the experimental conditions used to form such anions can give rise to distortion and hence to electron localization. If the excess electron is initially attached to one end of $\mathcal{H}_nS\mathcal{H}_n^-$, the preparation has formed a nonstationary solution given by the localized orbital χ_1 of Eq. (4). The probability that the excess electron will be found at the opposite end of the molecule at a time t later is approximately given by $\sin^2(H_{12}t/\hbar)$ [30], where $2H_{12}$ is the $E({}^2\Sigma_g^+) - E({}^2\Sigma_u^+)$ energy splitting, which becomes unity for $t \approx 10^{-10}$ s for $n = 4$. The significant residence time ($\approx 10^{-10}$ s) for the excess electron at one molecular end is sufficient to polarize the molecular framework and thus to stabilize the localized-electron state.

With these reservations in mind, we decided to calculate the SCF polarizability of $\mathcal{H}_nS\mathcal{H}_n^-$ using a single-determinantal wave function with the excess electron localized on one side of the molecule, and our results are reported in Table 2. We also report there the SCF values of polarizabilities for the neutral and anionic \mathcal{H}_n oligomers.

The polarizabilities of the neutral \mathcal{H}_n clusters display the standard pattern: α_{\parallel} is larger than the transverse polarizability α_{\perp} and both increase as n increases. The opposite trend holds for the dipole-bound anions \mathcal{H}_n^- : α_{\parallel} is smaller than α_{\perp} and both decrease as n increases. Finally for the bdb anions $\mathcal{H}_nS\mathcal{H}_n^-$, the values of both polarizabilities are larger than for the corresponding dipole-bound anions \mathcal{H}_n^- and they decrease as n increases. Moreover, α_{\parallel} is smaller than α_{\perp} for $n = 3$ and 4.

The polarizabilities of dipole-bound anions \mathcal{H}_n^- are

Table 2.

Longitudinal and transverse polarizabilities in au; the linear clusters $(\text{HCN})_n$ and $(\text{HCN})_n \dots \text{HCCH} \dots (\text{NCH})_n$ are denoted by \mathcal{H}_n and $\mathcal{H}_n\mathcal{S}\mathcal{H}_n$, respectively

System	α_{\parallel}	α_{\perp}
\mathcal{H}_2	48	26
\mathcal{H}_3	75	38
\mathcal{H}_4	102	50
\mathcal{H}_2^-	3.2×10^4	5.5×10^4
\mathcal{H}_3^-	1.1×10^4	2.0×10^4
\mathcal{H}_4^-	9.0×10^3	1.6×10^4
$\mathcal{H}_2\mathcal{S}\mathcal{H}_2^-$	1.4×10^5	1.0×10^5
$\mathcal{H}_3\mathcal{S}\mathcal{H}_3^-$	1.9×10^4	2.4×10^4
$\mathcal{H}_4\mathcal{S}\mathcal{H}_4^-$	1.1×10^4	1.8×10^4

dominated by the contribution from the loosely bound excess electron. As n increases, the electron binding energy increases, the orbitals become more compact, and therefore both α_{\parallel} and α_{\perp} decrease. The larger value of α_{\perp} than of α_{\parallel} reflects the nature of the $\mu \cos \theta/r^2$ potential, which has a strong $1/r^2$ decay relevant to the longitudinal electron polarization, but a softer $\cos \theta$ decay relevant to the transverse electron polarization. For the bi-dipole-bound anions, the dependence of the α 's on n is qualitatively the same as for dipole-bound anions but the values are larger due to the smaller electron binding energies in $\mathcal{H}_n\mathcal{S}\mathcal{H}_n^-$ than in \mathcal{H}_n^- . The finite values of α_{\parallel} for $\mathcal{H}_n\mathcal{S}\mathcal{H}_n^-$ in low electric fields are related to the longitudinal polarization of the localized excess electron. For a sufficiently large value of the electric field a non-linear polarization of the anion is anticipated related to the excess electron transfer from one molecular end to another.

6. Summary

Linear molecules with two polar ends, such as $(\text{HCN})_n \dots \text{HCCH} \dots (\text{NCH})_n$ support two anionic states of ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$ symmetry. These two states are nearly degenerate (i.e. the coupling H_{12} is less than 5 cm^{-1}) even for the shortest ($n = 2$) stable anion, thus suggesting that the through-bond coupling of the two dipole-bound orbitals is very small.

The electron binding energy depends both on the polarity of the \mathcal{H}_n group and the spacing (L) between

the groups, which relates to the dipole–dipole repulsion.

The electron binding energies for the $\mathcal{H}_n\mathcal{S}\mathcal{H}_n^-$ anions are well reproduced at the Koopmans' theorem level due to small orbital relaxation effects and partial cancelation of physically different electron correlation contributions.

The doubly charged anion can be stable if the spacing L is large enough to overcome the coulomb repulsion between the two excess electrons.

We expect localization of the excess electron on one side of the bi-dipolar anion $\mathcal{H}_n\mathcal{S}\mathcal{H}_n^-$ for sufficiently large n .

The transverse polarizability of dipole-bound anions may be larger than the longitudinal polarizability, which is related to the character of the electron-dipole potential $\mu \cos \theta/r^2$.

The polarizabilities of bi-dipole-bound anions are larger than those of the corresponding dipole-bound anions, which is related to the smaller electron binding energies in the former species. The longitudinal polarizabilities of bi-dipole-bound anions are expected to be large but finite due to localization of the excess electron on one side of the molecule and nonlinearity is anticipated in response to the electric field due to electron transfer from one molecular end to another.

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