

Electrons weakly bound to molecules by dipolar, quadrupolar or polarization forces

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Abstract. Within the framework of a simple electrostatic model we here discuss the stability of very weakly bound molecular negative ions. In contrast with the case of conventional valence anions, the excess electron is then located in a very diffuse orbital and is mainly bound by electrostatic dipolar, quadrupolar and polarization forces at large distances from the neutral molecular core. By fitting a single repulsion parameter of the model to the available experimental data, it is possible to make quantitative predictions of the excess electron binding energies in these species. Critical values of dipole moment, quadrupole moment or polarizability required for the observation of stable dipole-bound, quadrupole-bound or polarization-bound negative ions are predicted.

PACS. 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.) – 36.90.+f Other special atoms, molecules, ions, and clusters

1 Introduction

Neutral molecules or even more valence negative ions are the result of many different interactions between all the bound electrons at short distances which can be accurately treated only with high level *ab initio* calculations. However, an electron excited far outside the ionic or neutral molecular core is mainly submitted to electrostatic (Coulombic, dipolar, quadrupolar, polarization...) forces. Simple models can then be expected to be accurate enough to give a qualitative and quantitative picture of the physical processes at large distances. This is true for the Rydberg levels of a neutral molecule, for which the main interactions are Coulombic. We wish to show in this paper that this is also true for the weakly bound states of an electron in a molecular negative ion for which the main interactions are the dipolar quadrupolar or polarization forces.

Since the first short theoretical note of Fermi and Teller [1], fifty years ago, many theoretical [2–6] and experimental [7,8] studies have been devoted to dipole-bound (DB) anions of polar molecules. In these species, the extra electron is located in a very diffuse orbital and is very weakly bound mainly by the dipolar forces. In contrast to the case of valence anions, the neutral molecular core can thus be nearly unaffected by the electron attachment, leading to a non-perturbative and reversible type of ionization process [9]. The minimum dipole moment required for the formation of stable DB anions of common closed-shell molecules has been experimentally determined to be about

2–2.5 D [8]. However, it has also been stressed that the quadrupolar and polarization forces can bring a non negligible contribution to the electron binding energy [7]. Even a non polar molecule, with a large enough quadrupole moment or a large enough polarizability, could then sustain a quadrupole-bound (QB) or a polarization-bound (PB) anion state. Three previous studies have indeed been devoted to possible QB anions of carbon disulfide molecules [10] and PB anions of fullerene molecules [11,12]. However, the lack of energetic data and of pertinent parameters for the model simulations did not allow for definitive conclusions. Very recently an experimental evidence for the existence of stable QB anions of succinonitrile molecules has been reported [13], in which the excess electron binding energy has been measured.

In the next section we first present a semi-empirical electrostatic model for the description of such loosely bound negative ions in the case of symmetric top molecules, which depends on a single empirical parameter. Section 3 is devoted to DB anions and the comparison with experimental data allows us to derive an empirical law for the determination of this fitted parameter. This law is used in Section 4 for the prediction of the electron binding energies either for DB or for pure QB or PB anions.

2 Electrostatic model for weakly bound anions

As in our previous work on DB anions [4,7,8], we follow the Clary's rotationally adiabatic theory [3] which

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provides a theoretical framework for the description of weakly bound anions with simple electrostatic pseudopotentials and which takes into account the possible non-Born-Oppenheimer effects. For the sake of simplicity we restrict this study to symmetric top molecules for which the dipole moment μ and the quadrupole moment Q are both held by the symmetry axis [14]. The mean molecular polarizability α can then be split into a component parallel to the symmetry axis $\alpha_{//}$ and two equal perpendicular components α_{\perp} . The pseudopotential between the excess electron and the molecule is expressed as $V(r, \theta) = V_{\mu}(r, \theta) + V_Q(r, \theta) + V_{\alpha}(r, \theta)$, where r and θ are the electron cylindrical coordinates with respect to the molecular symmetry axis. The respective dipolar, quadrupolar and polarization potential terms are taken as (in atomic units):

$$\begin{aligned} V_{\mu}(r, \theta) &= \frac{-\mu \cos(\theta)}{r^2} \left[1 - \exp(-(2r/\mu)^3) \right] \\ &= f_1(r) \cos(\theta) \\ V_Q &= \frac{-Q(3 \cos^2(\theta) - 1)}{4r^3} \left[1 - \exp\left(-\left(2r/\sqrt{|Q|}\right)^5\right) \right] \\ &= f_2^Q(r) (3 \cos^2(\theta) - 1) \\ V_{\alpha}(r, \theta) &= \frac{\alpha_{//} \cos^2(\theta)}{2r_{//}^4} \left[\left(\frac{r_{//}}{r}\right)^8 - \left(\frac{r_{//}}{r}\right)^4 \right] \\ &\quad + \frac{\alpha_{\perp} (1 - \cos^2(\theta))}{2r_{\perp}^4} \left[\left(\frac{r_{\perp}}{r}\right)^8 - \left(\frac{r_{\perp}}{r}\right)^4 \right] \\ &= f_0(r) + f_2^{\alpha}(r) (3 \cos^2(\theta) - 1). \end{aligned}$$

The first two terms V_{μ} and V_Q possess damping functions in order to avoid unphysical divergency close to the origin but they only depend on the molecular parameters μ and Q . The third polarization term depends on the molecular polarizabilities, $\alpha_{//}$ and α_{\perp} , but also contains a repulsive part [12] which scales as $1/r^8$. This term physically represents the Pauli exclusion of the attached electron from the closed-shell neutral valence orbitals and also avoids the divergency of the polarization potential at short distances. As shown in our previous works [4, 7], the two repulsion distances $r_{//}$ and r_{\perp} can be naturally linked to the respective polarizabilities by taking $r_{//} = C\alpha_{//}^{1/3}$ and $r_{\perp} = C\alpha_{\perp}^{1/3}$, so that we now deal with only one empirical parameter C .

Following Clary's theory, we then calculate the lowest rotationally adiabatic potential $V_{ad}(r)$ as the lowest eigenvalue of the total Hamiltonian $H = H_{rot} + \mathbf{l}^2/2r^2 + V(r, \theta)$, for each value of the electron-molecule distance r . H_{rot} is the rotational Hamiltonian of the neutral molecule and \mathbf{l} is the relative orbital angular momentum operator of the electron about the molecule. As shown by Clary [3], an excellent approximation to $V_{ad}(r)$ is obtained as the sum of the lowest eigenvalue $\varepsilon_{ad}(r)$ of the reduced Hamiltonian $H' = (B + 1/2r^2)\mathbf{l}^2 + V(r, \theta)$, using the basis set of

the spherical harmonics in the rotating molecular frame in which the z axis coincides with the molecular symmetry axis $\{Y_m^l\}$, and the anion rotational energy E_{rot} obtained by replacing the rotational angular momentum quantum number j of the molecule by the total angular quantum number J of the anion. The total anion energies are then given by $E = -E_b + E_{rot}$ where the electron binding energy E_b is obtained from the one-dimensional radial Schrödinger equation

$$-\frac{1}{2} \frac{d^2}{dr^2} \chi(r) + (\varepsilon_{ad}(r) + E_b) \chi(r) = 0, \quad \chi(r)$$

being the corresponding reduced radial wave function. As in the case of DB anions [7], we have verified that this approximation is valid by a comparison with direct full calculations of $V_{ad}(r)$ and E . It clearly shows that the non-Born-Oppenheimer effects are non negligible only for very weakly bound species, *i.e.* if the molecular rotor constant B is of the same order as $1/2r^2$. For standard rotor constants of about 0.1 cm^{-1} this sets an upper limit to the spatial extend of the excess electron radial wave function at about 1000 a.u.

In the basis set $\{Y_m^l\}$ the matrix elements of H' to calculate are:

$$\begin{aligned} H'_{lm'l'm'} &= (l(l+1)f(r) + f_0(r)) \delta_{ll'} \delta_{mm'} \\ &\quad + f_1(r) \langle Y_{m'}^{l'} | \cos(\theta) | Y_m^l \rangle \\ &\quad + f_2(r) \langle Y_{m'}^{l'} | 3 \cos^2(\theta) - 1 | Y_m^l \rangle \end{aligned}$$

with $f(r) = B + 1/2r^2$ and $f_2(r) = f_2^Q(r) + f_2^{\alpha}(r)$

$$\begin{aligned} \langle Y_{m'}^{l'} | \cos(\theta) | Y_m^l \rangle &= (-1)^{m'} \sqrt{(2l+1)(2l'+1)} \\ &\quad \times \begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & 1 \\ m & -m' & 0 \end{pmatrix} \end{aligned}$$

and

$$\begin{aligned} \langle Y_{m'}^{l'} | 3 \cos^2(\theta) - 1 | Y_m^l \rangle &= (-1)^{m'} \sqrt{4(2l+1)(2l'+1)} \\ &\quad \times \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & 2 \\ m & -m' & 0 \end{pmatrix}. \end{aligned}$$

These matrix elements are non zero only if $m = m'$ and it has been verified that those terms corresponding to non zero values of m do not lead to the lowest eigenvalue of H' . As in the case of DB anions [3, 7] $\varepsilon_{ad}(r)$ is then only determined from the sub-matrix elements with $m = 0$ and an approximate analytical expression can be obtained by considering only the three first basis functions with $l = 0, 1$ and 2 which bring the major contribution to $\varepsilon_{ad}(r)$ [15]. The matrix H' reduces to

$$\begin{pmatrix} f_0 & f_1/\sqrt{3} & 2f_2/\sqrt{5} \\ f_1/\sqrt{3} & f_0 + 2f + 4f_2/5 & 2f_1/\sqrt{15} \\ 2f_2/\sqrt{5} & 2f_1/\sqrt{15} & f_0 + 6f + 4f_2/7 \end{pmatrix}$$

and its eigenvalues $\lambda + f_0$ verify the equation

$$\lambda^3 + a_1 \lambda^2 + a_2 \lambda + a_3 = 0$$

with

$$\begin{aligned} a_1 &= -8 \left(f + \frac{6}{35} f_2 \right), \\ a_2 &= 12f^2 + \frac{208}{35} f f_2 - \frac{3}{5} f_1^2 - \frac{12}{35} f_2^2, \\ a_3 &= 2f f_1^2 + \frac{8}{5} f f_2^2 - \frac{12}{35} f_1^2 f_2 + \frac{16}{25} f_2^3. \end{aligned}$$

The lowest eigenvalue $\lambda_{min} + f_0 = \varepsilon_{ad}(r)$ is then analytically calculated as

$$\varepsilon_{ad}(r) = f_0 + \frac{8}{3} \left(f + \frac{6}{35} f_2 \right) - \sqrt{\frac{-4p}{3}} \cos \left(\frac{\pi}{3} - \varphi \right)$$

with

$$\cos(3\varphi) = \sqrt{\frac{-27q^2}{4p^3}}, \quad \varphi \in \left[0, \frac{\pi}{6} \right]$$

and $p = a_2 - \frac{a_1^2}{3}$, $q = \frac{2}{27} a_1^3 - \frac{a_1 a_2}{3} + a_3$. The corresponding angular wave function Y which depends only on the polar coordinate θ is given as with

$$Y(\theta) = (Y_0^0 + c_1 Y_0^1 + c_2 Y_0^2) / \sqrt{1 + c_1^2 + c_2^2}$$

with

$$c_1 = \frac{\sqrt{3} f_1 (\varepsilon_{ad} - f_0 - f_2)}{f_1^2 + 3f_2 (\varepsilon_{ad} - f_0 - 2f - 4f_2/5)}$$

and

$$c_2 = \frac{\sqrt{5} ((3\varepsilon_{ad} - f_0)(\varepsilon_{ad} - f_0 - 2f - 4f_2/5) - f_1^2)}{2 (f_1^2 + 3f_2 (\varepsilon_{ad} - f_0 - 2f - 4f_2/5))}.$$

Three particular theoretical cases of interest are those of a pure dipolar, a pure quadrupolar or a pure polarization interaction. In the first hypothetical case of a non-rotating pure point dipole, we have $f_0 = f_2 = 0$ and $B = 0$ *i.e.* $f = 1/2r^2$. It is then well known [16] that the radial Schrödinger equation with a potential energy of the form $-\gamma/2r^2$ allows for bound states only if $\gamma > 1/4$ so that the critical dipole moment then corresponds to $\varepsilon_{ad}(r) = -1/8r^2 = -f/4$. Since ε_{ad} also verifies the eigenvalue equation with $a_1 = -8f$, $a_2 = 12f^2 - 3f_1^2/5$ and $a_3 = 2f f_1^2$, we obtain the equality $f_1 = -\frac{\mu_{crit}}{r^2} =$

$$-\sqrt{\frac{225}{64} \frac{20}{43}} f \text{ or } \mu_{crit} = \frac{1}{2} \sqrt{\frac{4500}{2752}} = 0.6394 \text{ a.u.} = 1.625 \text{ D.}$$

This value is very close to the exact theoretical value first derived by Fermi and Teller [1]. If we now set $f_1 = 0$ and either $f_0 = 0$ and $f_2 = -Q/4r^3$ for a pure quadrupolar interaction or $f_0 = -\alpha/2r^4$ and $f_2 = -(\alpha_{//} - \alpha_{\perp})/6r^4$ for a pure polarization potential, it is straightforward to get the lowest eigenvalue as the lowest solution of a second order equation involving only the matrix elements corresponding to $l = 0$ and $l = 2$ (sd_{z^2} orbital) as

$\varepsilon_{ad} = f_0 + 3f + 2f_2/7 - \sqrt{(3f + 2f_2/7)^2 + 4f_2^2/5}$. Since $f_0 \leq 0$ it is clearly seen that ε_{ad} is also always negative, *i.e.* the quadrupolar or the polarization interactions are always attractive whatever the sign of Q and thus of f_2 or whatever the values of the molecular polarizabilities. At short distances r , the quadrupolar case for which $|f_2| \gg f$ leads to $\varepsilon_{ad}(r) \approx 0.16Q/r^3$ if $Q < 0$ and $\varepsilon_{ad}(r) \approx -0.31Q/r^3$ if $Q > 0$, so that positive quadrupole moments are more attractive than negative ones. The polarization case for which $|f_2|$ and $|f_0| \gg f$ leads to $\varepsilon_{ad}(r) \approx -\alpha/2r^4 + 0.11(\alpha_{//} - \alpha_{\perp})/r^4$ if $\alpha_{//} < \alpha_{\perp}$ and to $\varepsilon_{ad}(r) \approx -\alpha/2r^4 - 0.20(\alpha_{//} - \alpha_{\perp})/r^4$ if $\alpha_{//} > \alpha_{\perp}$. Since the radial Schrödinger equation with a potential energy of the form $-\gamma/r^n$ with $n > 2$ always allows for bound states for any positive value of γ [16], there is no theoretical critical value of Q or α for the binding of an electron in a pure quadrupolar or polarization potential.

For real molecules and for real pseudopotentials as described above, the presence of the repulsive interaction at short distances must lead to an increase of the critical dipole moment with respect to the theoretical value of 1.625 D and to the appearance of a (positive or negative) critical quadrupole moment and of a critical polarizability, for the stability of the corresponding weakly bound anions. This has been experimentally demonstrated in the case of DB anions, for which the real critical value is $\mu_{crit} \approx 2-2.5$ D [7, 8]. With the help of the available experimental data, the aim of this work is thus to evaluate the proper repulsive interactions in order to obtain a good estimate of the expected real critical values for Q and α .

3 Fit of the experimental data for dipole-bound anions

Within the framework of the above model we are able to give a complete description (energy levels, wave functions...) of any weakly bound anion with only one repulsion parameter C , provided that we know the electrostatic properties of the neutral molecule (μ , Q , α). Due to its physical meaning, *i.e.* the ratio between the repulsion distance and the distance $\alpha^{1/3}$ characteristic of the size of the neutral molecule, the value of C should be always close to 1. We thus compare the results of our calculated electron binding energies $E_b^{C=1}$ using $C = 1$ with as many as possible experimental data E_b^{exp} for DB anions of simple closed-shell molecules for which most of the molecular electrostatic properties (μ , Q , α) are accurately known. Almost all the values of dipole moments μ and of mean polarizabilities α are taken from experimental data [17]. Due to the lack of experimental measurements of quadrupole moments, most of the Q values are only estimates from simple charge distributions on atomic centers which are consistent with the experimental dipole moments [18]. Similarly, $\alpha_{//}$ and α_{\perp} are estimated from standard bond polarizabilities [19] and are made consistent with experimental mean polarizabilities. In the present case of DB species the effects of the quadrupole or of the anisotropic polarization interactions are however of minor importance. Experimental binding energies E_b^{exp} are those deduced from

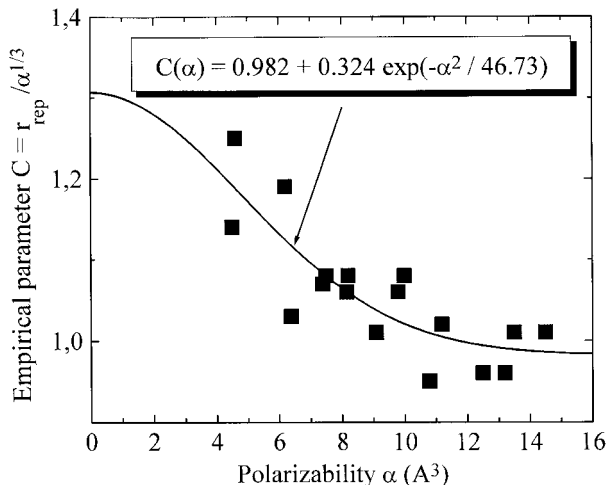


Fig. 1. Repulsion parameters C which fit the experimental electron binding energies E_b^{exp} of DB anions of closed-shell molecules (see Tab. 1) as a function of the molecular mean polarizability α . These 17 points are fitted with the function $C(\alpha)$ as indicated in the inset.

Rydberg electron transfer (RET) experiments and have been confirmed in most cases by field detachment experiments [4, 20] and in the case of thymine by photoelectron spectroscopy experiments [21].

The comparison between $E_b^{C=1}$ and E_b^{exp} in Table 1 clearly shows that $C = 1$ is a rather good value for the larger molecules with the larger mean polarizabilities α but leads to a systematic overestimate of the electron binding energies for the smaller ones. For molecules with $\alpha \leq 10 \text{ \AA}^3$ the relative error $\varepsilon = (E_b^{C=1} - E_b^{exp})/E_b^{exp}$ is always positive and reaches more than 100% for weakly bond DB anions. For molecules with $\alpha > 10 \text{ \AA}^3$, ε is either positive or negative and its absolute value is always below 40%. In order to get more accurate electron binding energies, we have to make C a decreasing function of the polarizability α . For each of the 17 molecules we thus adjust the value of C in order to exactly reproduce the experimental binding energy and the obtained values are plotted as a function of α in Figure 1. They can be reasonably fitted with the function $C(\alpha) = 0.982 + 0.324 \exp(-\alpha^2/46.73)$ so that C goes to a finite value of 1.306 for very small molecules and to the asymptote 0.982 for very large polarizabilities, with a typical uncertainty of about 0.05. This empirical law improves the calculated electron binding energies E_b^{calc} since the absolute value of the relative error $|\varepsilon| = |E_b^{exp} - E_b^{calc}|/E_b^{exp}$ is now always lower than 50% (except for pivaldehyde) and is even lower than 25% in more than half cases (see Tab. 1).

The accuracy of these results are comparable to that of high level *ab initio* calculations [5, 6] which often lead to underestimated E_b^{calc} values as compared to experimental data. As an example the electron binding energy of acetonitrile DB anions has been calculated to be 6.7 meV [5] or 13.4 meV [6] as compared to the present calculation of 15.5 meV and the experimental value of 18.2 meV [4]. A better agreement is however sometimes achieved as for

the DB anions of thymine or the excited DB state of the radical anion C_3H_2 . In the first case, the *ab initio* electron binding energy is 88 meV [5], the present result is 69 meV and the two experimental measurements are 68 ± 20 [7] and 69 ± 7 meV [21]. In the second case, the experimental dipole moment of C_3H_2 is reported to be 4.14 D while *ab initio* calculations [6] lead to a value of 4.48 D and to an electron binding energy of 21 meV, in excellent agreement with the experimental result of 21 ± 6 meV. Using either the experimental or the calculated dipole moment and the calculated quadrupole moment and polarizabilities [22], the present model also leads to a value of either 18 or 27 meV. On the other hand the present model cannot fully take into account the quantum effect of correlation between the excess electron and the electrons of the neutral molecular core. As shown by Gutowski *et al.* in detailed *ab initio* calculations [6], the corresponding binding energy contributions are indeed always as large as the SCF binding energies, independently from their values. This effect is however expected to be important only in the region where the diffuse orbital of the excess electron and the molecular orbitals overlap, *i.e.* at short distances. This may explain why in the present model the empirical repulsion parameter $C(\alpha)$ must be a decreasing function of the polarizability α , independently from the electron binding energy. For larger molecules with larger polarizabilities the size of the overlapping region increases so that the repulsion parameter C must also decrease to empirically allow for more binding interactions.

4 Prediction of electron binding energies for other DB QB or PB anions

Since the present model, using the empirically fitted parameter $C(\alpha)$, is able to reproduce quite accurately the electron binding energies of many different DB anions, we are able to make some quantitative predictions for others DB, QB or PB anions. This is done in Table 2 for various electron binding energies of few DB anions of polar molecules for which no experimental data have been reported so far. Reported E_b^{calc} values are the lower and upper bounds corresponding to $C = C(\alpha) + 0.05$ and $C = C(\alpha) - 0.05$. The results for guanine and cytosine are very close together, *i.e.* $E_b^{calc} \approx 120 \pm 30$ meV and are again much larger than previous *ab initio* results for DB anions of guanine and 1-methylcytosine [5] which respectively amount only to 34 and 32 meV. This is also true for the two weakest DB anions of propanal and formaldehyde for which the reported *ab initio* values were respectively 0.05 and -0.15 meV (unbound excess electron) while the present calculations give 0.9 ± 0.3 and $3.5 \pm 1.5 \cdot 10^{-2}$ meV. This last very weak value again emphasizes the difficulty that one would encounter for the experimental observation of very loosely bound DB anions for molecules with dipole moments close to the practical critical value of $\mu_{crit} \approx 2-2.5$ D. For HF molecules ($\mu = 1.826$ D) we did not find any bound state, even for the lowest repulsion parameter $C = C(\alpha) - 0.05$. On the other hand, HCN

Table 1. Dipole moments μ , quadrupole moments Q , polarizabilities ($\alpha, \alpha_{//}, \alpha_{\perp}$), experimental electron binding energies E_b^{exp} , calculated electron binding energies $E_b^{C=1}$ with $C = 1$ and calculated electron binding energies E_b^{calc} with the empirical repulsion parameter $C(\alpha) = 0.982 + 0.324 \exp(-\alpha^2/46.73)$.

Molecule	μ (D)	Q (a.u.)	$\alpha(\text{\AA}^3)$	$\alpha_{//}(\text{\AA}^3)$	$\alpha_{\perp}(\text{\AA}^3)$	E_b^{exp} (meV)	$E_b^{C=1}$ (meV)	E_b^{calc} (meV)
acetonitrile	3.924	-3	4.5	6.5	3.5	18.2	32	15.5
acetaldehyde	2.75	-3	4.6	5.4	4.2	0.65	2.6	0.95
acrylonitrile	3.87	-7	6.2	8.6	5.0	10.7	22.3	13.2
acetone	2.88	-6	6.4	7.0	6.1	2.8	3.4	1.6
nitromethane	3.46	+2	7.4	9.5	6.3	15	22	14.4
cyclobutanone	2.89	-10	7.5	9.1	6.7	1.8	3.2	1.8
butanone	2.78	-6	8.2	8.7	7.9	1.8	2.9	1.8
butanal	2.72	-9	8.2	9.8	7.4	1.1	2.2	1.3
cyclopentanone	2.88	-13	9.1	11.0	8.2	3	3.2	2.3
pyridazine	3.95	-5	9.8	11.8	8.8	20	26	23.6
pivaldehyde	2.66	-8	10.0	10.6	9.7	1.0	2.0	1.7
cyclohexanone	2.87	-13	10.8	13.4	9.5	5.5	3.4	3.2
thymine	4.10	+11	11.2	13.3	10.2	69	72	69
benzonitrile	4.20	-27	12.5	15.0	11.2	28	23	24.2
adenine	2.50	+10	13.2	16.3	11.6	11.5	7.4	8.1
nitrobenzene	4.20	-10	13.5	17.3	11.6	28	29	30.4
TFMB	2.86	-10	14.5	17.4	13.1	3.8	4.4	4.8

Table 2. Dipole moments μ , quadrupole moments Q and polarizabilities ($\alpha, \alpha_{//}, \alpha_{\perp}$) used for calculating the predicted electron binding energies E_b^{calc} with the fitted parameter $C(\alpha) \pm 0.05$, for several DB anions

Molecule	μ (D)	Q (a.u.)	$\alpha(\text{\AA}^3)$	$\alpha_{//}(\text{\AA}^3)$	$\alpha_{\perp}(\text{\AA}^3)$	E_b^{calc} (meV)
guanine	6.6-7.1	-28	13.7	16.9	12.1	88-150
cytosine	6.5-7.0	-21	10.5	12.6	9.5	90-155
imidazole	3.8	-3	7.0	10.6	5.2	13-19
formamide	3.73	-3	4.2	6.2	3.2	9.5-12.5
HCN	2.984	+4.6	2.6	3.9	1.9	3.3-5
propanal	2.74	-10	6.5	8.3	5.6	0.6-1.2
formaldehyde	2.332	-0.15	2.8	3.7	2.35	$2-5 \times 10^{-2}$

molecules which possess a higher dipole moment and a positive quadrupole moment [23] are definitively able to sustain a DB anion state (see Tab. 2). Contour plots of the excess electron probability density in a plane containing the symmetry (dipole) axis are displayed in Figure 2. It is seen that the orbital is a mixing of s , p_z and d_{z^2} components, illustrating the non-negligible role of the quadrupolar forces for such DB anions.

For pure QB anions, *i.e.* for molecules with null dipole moments and a typical mean polarizability of $\alpha = 10 \text{\AA}^3$, we have calculated the electron binding energies E_b^{calc} as a function of the quadrupole moment Q , for C equal to $C(\alpha)$ and $C(\alpha) \pm 0.05$. These results are displayed in Figure 3 and allow us to set an effective critical quadrupole moment Q_{crit} required for the formation of experimentally observable QB anions. If we set a lower experimental limit to E_b equal to 0.1 meV, we obtain a negative criti-

cal value $Q_{crit} \approx -41 \pm 4$ a.u. or a positive critical value $Q_{crit} \approx +35 \pm 3$ a.u. Due to the difficulty to find closed-shell molecules with such large quadrupole moments, there is only one experimental data for QB anions of succinonitrile molecules [13]. As shown in Figure 3, the upper bound of the present calculations are however in good agreement with this result. The probability density of the corresponding excess electron in a plane which contains the symmetry (quadrupole) axis is also displayed in Figure 4. The orbital is mainly localized perpendicularly to the quadrupole axis, due to the negative value of Q , and it is a mixing of only s and d_{z^2} components, due to the null dipole moment. On the other hand, the present results are in contradiction with the previous calculations for CS_2 [10] which suggest the existence of a stable QB anion state with a binding energy of about 0.7 meV. In this work the repulsion distance has been reduced to as low as 0.3 Å while it is of

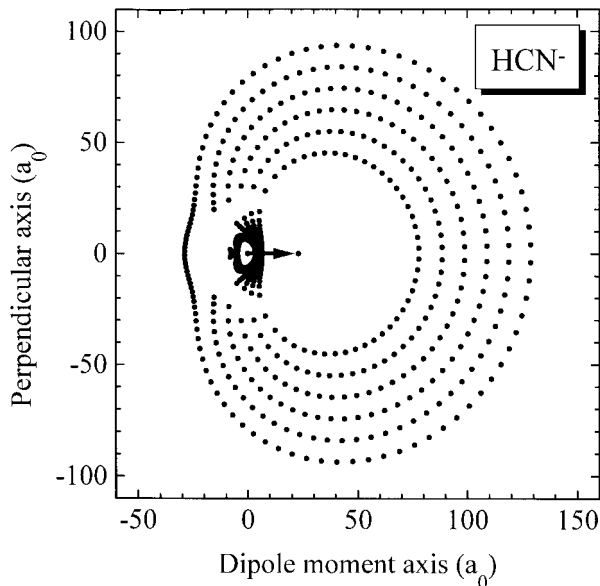


Fig. 2. Contour plots of the excess electron probability density in a plane which contains the symmetry or dipole moment axis for the HCN^- DB anion. The arrow indicates the direction of the dipole moment and its end corresponds to the maximum of the electron probability density. Each successive contour plot then corresponds to a probability divided by a factor of 1.4 and the last one defines the surface inside which 90% of the excess electron is located.

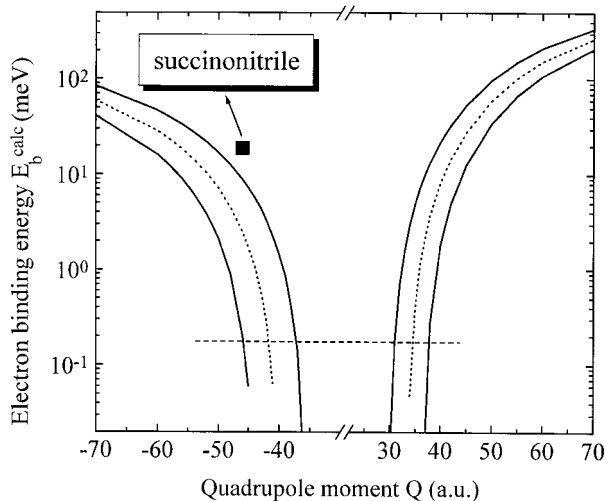


Fig. 3. Calculated electron binding energies E_b^{calc} for QB anions of molecules with null dipole moments and a mean polarizability of $\alpha = 10 \text{ \AA}^3$ as a function of the molecular quadrupole moment Q . The dotted and lower and upper full curves respectively correspond to a repulsion parameter $C(\alpha)$ and $C(\alpha) \pm 0.05$. In order to obtain a binding energy larger than 0.1 meV (dash line), Q must be either lower than the negative critical value $Q_{\text{crit}} \approx -41 \pm 4 \text{ a.u.}$ or larger than the positive critical value $Q_{\text{crit}} \approx +35 \pm 3 \text{ a.u.}$ The only experimental point indicates the recent measurement [13] for the QB anions of succinonitrile molecules ($Q \approx -46 \pm 1 \text{ a.u.}$, $E_b^{\text{exp}} \approx 19 \text{ meV}$).

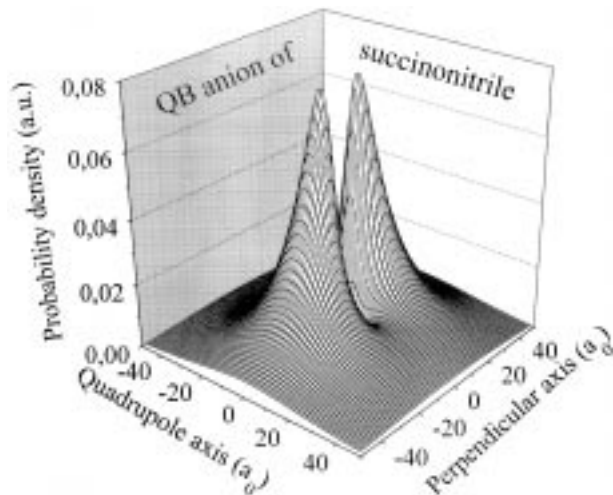


Fig. 4. 3D view of the excess electron probability density in a plane which contains the symmetry or quadrupole axis for the succinonitrile QB anion. Note that, because $Q < 0$, the maximum probability occurs on the axis perpendicular to the quadrupole moment.

the order of 2.1 \AA in the present model, which seems to be a more physical value. Moreover, the quadrupole moment of CS_2 has been calculated to be $+10.5 \text{ a.u.}$ [10] while experimental data and other calculations [23] rather suggest a value of about $+5 \pm 1 \text{ a.u.}$

For pure PB anions, *i.e.* for molecules with null dipole and quadrupole moments, we have also calculated the electron binding energies E_b^{calc} as a function of the polarizability α , for C equal to $C(\alpha)$ and $C(\alpha) \pm 0.05$. These results are displayed in Figure 5 from which an effective critical polarizability α_{crit} required for the formation of experimentally observable PB anions is derived. If we set again a lower experimental limit to E_b equal to 0.1 meV, we obtain $\alpha_{\text{crit}} \approx 60 \pm 20 \text{ \AA}^3$. It is even more difficult to find closed-shell molecules with such very high polarizabilities. One of the only candidates is the C_{60} molecule which polarizability α is about 80 \AA^3 and which possible PB state has been studied in two previous works [11,12]. The reported electron binding energies are in between few and few tens of meV, depending on the choice of α and of the repulsion distance. Within the present model the repulsion parameter C is equal to the asymptotic value of $C(\alpha)$ for such large value of α , *i.e.* $C \approx 0.982$, leading to a repulsion distance of about 4.35 \AA and to an electron binding energy of about 1.4 meV. As demonstrated in a previous work on DB anions [4,7], the presence of a weakly bound anion state leads to a peaked behavior of the anion formation rate constants in RET experiments for a Rydberg quantum number n_{max} which can be calculated within the framework of a simple curve-crossing (or harpooning) model, in very good agreement with experimental data. As recently shown in the case of succinonitrile [13] the same model also holds for QB anions and is here applied to the possible PB state of C_{60}^- . Using $E_b = 1.4 \text{ meV}$ it leads to $n_{\text{max}} \approx 30$ which actually corresponds to the Rydberg quantum number around which a

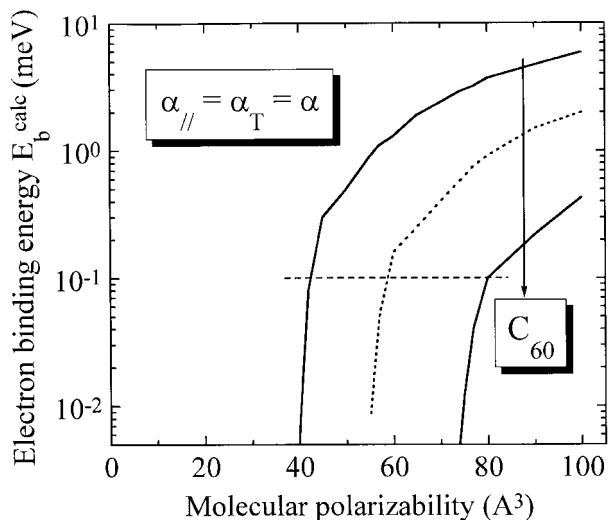


Fig. 5. Calculated electron binding energies E_b^{calc} for PB anions of molecules with null dipole and quadrupole moments as a function of the molecular mean polarizability $\alpha = \alpha_{//} = \alpha_{\perp}$. The dotted and lower and upper full curves respectively correspond to a repulsion parameter $C(\alpha)$ and $C(\alpha) \pm 0.05$. In order to obtain a binding energy larger than 0.1 meV (dash line), α must be larger than the critical value $\alpha_{crit} \approx 60 \pm 20$ a.u. The arrow indicates the value of the polarizability of C_{60} (see discussion in the text).

distinct feature appears in RET experiments [11,12]. Coupled to the valence anion state, the PB state could thus explain the experimental behavior but, as clearly discussed by Hotop and coworkers [12], an alternative explanation involving only the valence state is also possible so that one cannot definitively conclude to the experimental observation of PB C_{60}^- anions. A better test would be to find a molecule with a similar polarizability but with no stable valence anion or with a valence anion state only weakly coupled to the PB state, *e.g.* with a geometry very different from that of the neutral molecule. However such a molecule may not exist since high polarizabilities generally involve many molecular π orbitals which are often able to delocalize and which usually give birth to a stable anion state with a geometry rather similar to the neutral molecule. This remark also holds for small metal clusters which generally possess large polarizabilities but also positive valence electron affinities so that the assignment of PB or image-charge-bound states is also difficult [24].

5 Conclusion

We have shown that a simple electrostatic model is able to give a qualitative and quantitative picture of excess electrons weakly bound to real molecules by dipolar, quadrupolar or polarization forces. The single adjustable repulsive parameter of the model has been fitted to the available experimental data and empirically account for the quantum effects at short distances, such as the repulsive exchange or attractive correlation interactions between the loosely bound excess electron and the valence

electrons of the neutral molecular core. Due to the difficulty to treat very diffuse bound states with quantum methods, we suggest that a fully accurate description of these weakly bound anions may come from hybrid calculations involving an electrostatic description at large distances and *ab initio* calculations at short distances, either with standard methods or with the help of pseudopotential techniques [25].

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14. We use the usual definition of the dipole moment $\mu = \sum_i q_i r_i$ and the traceless definition of the quadrupole moment tensor $Q_{\alpha,\beta} = \sum_i q_i (3r_i^\alpha r_i^\beta - r_i^2 \delta_{\alpha,\beta})$, where r_i^α are the three coordinates of the charge q_i in the center of mass reference frame. Within the cylindrical symmetry around the z axis $\mu = \mu_z$, off-diagonal elements of $Q_{\alpha,\beta}$ are null and $Q_{x,x} = Q_{y,y} = -Q_{z,z}/2$. We thus use $Q = Q_{z,z}$ even for molecules which are only approximate symmetric tops. Atomic units for μ and Q are respectively 1 a.u. = 2.5418 D = 8.478 10^{-30} Cm and 1 a.u. = 1.345 D \AA = 4.487 10^{-40} Cm².
15. Numerical calculations with higher spherical harmonics ($l = 4, 5$) have also been performed in order to test the present analytical approximation. As expected, they lead only to a small increase ($< 10\%$) of the E_b -values for DB anions, even close to the threshold of stability. For QB and PB anions the increase is larger but is only equivalent to an increase of the quadrupole moment Q or of the polarizability α of less than 3%, which is comparable with the experimental or calculated uncertainties on these molecular parameters.
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