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Lifetimes of metastable spherical carbon cluster dianions

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Semiclassical calculations are made of the lifetimes of metastable spherical carbon cluster dianions using a model potential based on electrostatics. The metastability is attributed to shape resonances resulting from the combination of the long range Coulomb repulsion and the shorter range electron–molecule interaction. Results for fullerene dianions show a strong dependence of the lifetimes on the molecular size. The transition from stable to metastable dianions is estimated to occur when the radius of the spherical molecule is about 5.5 Å. This simple model potential might provide a starting point for experimental and theoretical searches for the existence of stable dianions.

1. Introduction

Singly charged negative ions in the gas phase are of fundamental importance in atomic and molecular physics, and have attracted considerable experimental and theoretical attention over recent decades [1–11]. With the advancement of spectroscopic and theoretical methods, new atomic ions have been found to be stable, such as Ca^- and Sr^-, with small electron affinities of about 40 meV [13, 14]. However, the existence of gas phase doubly charged atomic negative ions has remained a matter of some controversy [8]. Small dianions such as O^{-2} or CO_3^{-2} are very common in solution and solid state chemistry, but are unstable in the gas phase [8, 12]. This instability is due to the strong Coulomb repulsion between the excess negative charges. Theoretically, Lieb [15] formulated an upper bound for the maximum number of electrons, N_c, that can be bound to an atomic nucleus of charge Z, $N_c \leq 2Z + 1$. This inequality, gives the first proof that H^{-2} is not stable, which is in agreement with experiment [16] and many *ab initio* studies [6].

Recently, we introduced a simple effective interaction potential to calculate the critical nuclear charges of stable atomic anions [17]. This potential approximates both the short-range potential of a negative ion core with $Z = N - 1$ electrons and the partially screened long range Coulomb potential for $Z \neq N - 1$. The critical charge can be found from the equality, $E_I(Z_c) \equiv E(N, Z_c) - E(N-1, Z_c) = 0$, where E_I is the extrapolated ionization energy. Results for the critical charges [17], for atoms with $2 \leq N \leq 18$ were in good agreement with both the *ab initio* multireference configuration interaction calculations of Hogreve [18] and the critical charges extracted by us [17] from Davidson's figures of isoelectronic energies [19]. In order to have a stable atomic dianion one should require the surcharge $S_e(N) \equiv N - Z_c(N) \geq 2$. We have found that the surcharge never exceeds 2 [17]. Clearly the results of the surcharges exclude the existence of any stable atomic dianions in the gas phase, and confirm the previous speculations that, at most, only one electron can be added to a free atom in the gas phase.

For molecular systems, there is still an open question concerning the smallest molecule that can bind two or more excess electrons with both electronic stability (against electron detachment) and thermodynamic stability (against fragmentation) [20]. A number of multiply-charged anions with relatively large size, more than 10 atoms, have been observed in the gas phase. However, experimentally there are only a few stable small dianions [8], consisting of less than 10 atoms, including $C_n^{-2} (n = 7–9)$ [21–23], SiC_6^{-2} [24], $S_2O_6^{-2}$ [25], four penta-atomic dianions, PtX_4^{-2} and PdX_4^{-2} ($X = Cl$ and Br) [20, 26], and dianions such as $Be_2C_6^{-2}$ [27], BeF_4^{-2} and MgF_4^{-2} [28]. Cederbaum and coworkers examined the stability of alkali halides (MX_3^{-2}) ($M = Li$, Na, K; $X = F$, Cl) [29, 30] and mixed beryllium carbon dianions BeC_4^{-2} and BeC_6^{-2} [31], Simons and coworkers [32–34] predicted $Mg_2S_3^{-2}$ to be a stable linear dianion and MX_8 ($M = Se$, Te; $X = F$, Cl). Ortiz and coworkers [35] examined the structure and stability of small carbon clusters, Bartlett [36] studied the linear carbon cluster dianions C_n^{-2} ($n = 2–10$). Sommerfeld and Child investigated the lifetimes of the vibrational states of LiF_3^{-2}

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[37]. Yannouleas and Landman [38] studied multiply charged anionic metal clusters.

In this paper, we present the calculations of the lifetimes of metastable spherical carbon cluster dianions using a model potential based on electrostatic considerations. Our interest in spherical molecules is motivated by the experimental and theoretical works on fullerenes [8, 12, 30, 39–51].

2. Model potential for spherical molecular dianions

For systems with covalent bonds, the stability of the molecular dianions is limited by electron detachment rather than molecule dissociation [37]. As a typical reference for spherical molecular dianions, let us examine the stability of the C_{60}^{-2} molecule.

The C_{60} molecule is of I_h symmetry, has 60 carbon atoms with 120 core electrons and 240 sp^2 electrons, 90 σ-type CC bonds and 30 inter-pentagonal π-type CC bonds [52]. The σ electrons produce strong covalent bonds and almost homogeneously fill in the inner space of the sphere, and the π electrons produce a spherical shell of weaker covalent bonds on the outside of the structure. As an approximation, it can be modelled as a neutral dielectric sphere with relative dielectric constant $\epsilon = 4.4$ [42]. C_{60}^{-1}, which is the product of electron tunnelling from the metastable states of C_{60}^{-2}, may be treated as a singly negatively charged dielectric sphere. The metastability of C_{60}^{-2} can be attributed to a shape resonance resulting from the long range Coulomb repulsion combined with the shorter range electron–molecule interaction. This simple model can be used to investigate, in a systematic way, the stability of spherical molecular dianions as a function of their sizes.

From classical electrostatics, the electrostatic potential between an electron ($q = e$) and a dielectric sphere of radius R is given by [53]

$$\varphi(\mathbf{r}) = \frac{q}{|\mathbf{r}-\mathbf{r}'|} - \sum_{l=0}^{\infty} q\frac{(\epsilon-1)l}{(\epsilon+1)l+1}\frac{R^{2l+1}}{r^{l+1}r'^{l+1}}P_l(\cos\theta), \tag{1}$$

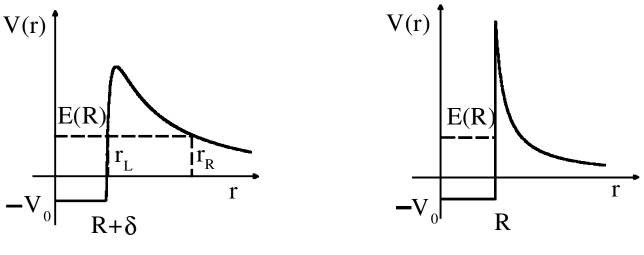

Figure 1. Interaction potential $V(r)$ of an electron at distance r from a singly negative sphere of radius R (left) compared with a pure Coulomb repulsive potential (right).

where ϵ is the relative dielectric constant, $\mathbf{r}'$ is the position of the electron and $\mathbf{r}$ is an arbitrary point outside of the sphere, $P_l(\cos\theta)$ is the lth Legendre polynomial and θ is the angle between the vectors $\mathbf{r}'$ and $\mathbf{r}$. In Equation (1) the first term is the direct Coulomb term from the electron and the terms in the summation correspond to the different polarized fields of the sphere induced by the electron. In the first-order approximation, taking the leading term in the summation $l = 1$, the interaction potential between an electron at a distance $r > R$ and a negatively singly-charged sphere can be obtained using the method of images [54],

$$\begin{aligned} V(r) &= -V_0 && r < R, \\ V(r) &= -\frac{(\epsilon-1)R^3}{2\,(\epsilon+2)r^2(r^2-R^2)} + \frac{1}{r} + \frac{l(l+1)}{2r^2} && r > R, \end{aligned} \tag{2}$$

where the constant $-V_0$ is an average attractive field inside the sphere. This potential was used to estimate the lifetime of the highly fluorinated chiral C_{3h} molecule $C_{60}F_{48}$ [55]. The shape of this model potential is shown in the left side of figure 1. The polarized term in equation (2) can be simplified as

$$\frac{1}{2}\frac{(\epsilon-1)}{(\epsilon+2)}\left(\frac{R}{r^2} + \frac{1}{2\,(R-r)} + \frac{1}{2\,(R+r)}\right), \tag{3}$$

which has corrections to the Coulomb term $\frac{1}{r}$ with the interactions of the form R^3/r^4 and R/r^2 at large r. If we neglect the polarized term, we obtain the repulsive Coulomb potential as shown in the right side of figure 1:

$$\begin{aligned} V(r) &= -V_0 && r < R, \\ V(r) &= \frac{1}{r} + \frac{l(l+1)}{2r^2} && r > R. \end{aligned} \tag{4}$$

This simpler model potential has a sharp potential barrier, and is used to estimate the lifetimes of non-spherical molecules such as MX_4^{-2} [20].

Figure 2 compares the pure Coulomb potential ($l = 0$), $14.4/r$ in units of eV, with the model potential for the dielectric sphere, equation (2), for fixed $\epsilon = 4.4$ and $R = 5.01$ Å for different values of $l = 0, 1, 2, 3$. Generally, the potential shape is described by a set of parameters, potential height $V_{\max}(R)$, potential width $W(R)$, starting point $r_s(R)$. They vary with R. For a Coulomb potential the starting point is $r_s(R) = R$, while for the dielectric model $r_s(R) = R + \delta$, where δ is a small number.

3. Lifetimes of spherical dianions using the WKB approximation

As stated above, the metastability of spherical dianions can be attributed to a shape resonance. The resulting Coulomb barrier is analogous to that which gives rise to α-particle decay from the

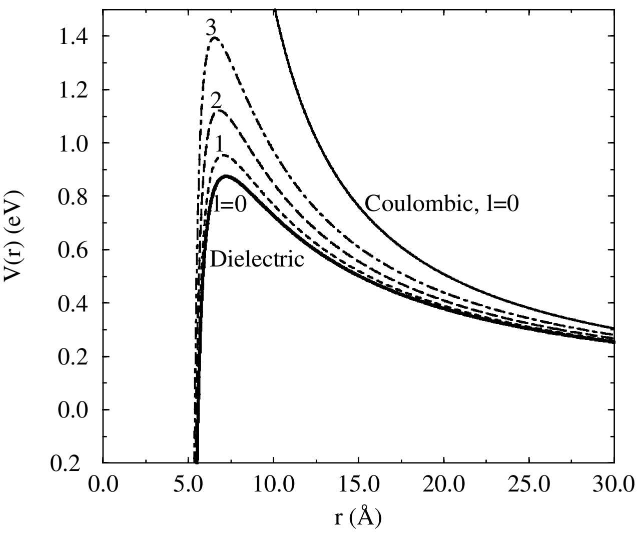

Figure 2. Effective radial interaction potential $V(r)$ with the centrifugal part at different orbital angular momenta $l = 0, 1, 2, 3$ as a function of the distance r for given $\epsilon = 4.4$ and $R = 5.01$ Å, corresponding to C_{60}^- plus an electron.

nucleus. The lifetimes of the metastable states are usually determined from the energy width using exact square integrable (L^2) methods, such as the complex scaling technique [56, 57]. However, an approximate method such as the semiclassical WKB (Wentzel, Kramers, and Brillouin) [58] theory can be used to estimate the lifetimes of the metastable states.

We consider the electron tunnelling through a potential barrier as the electron energy satisfies $0 < E \leq V_{\max}$; the zero energy is chosen as the energy at infinite separation between the sphere and the electron. The two classical turning points r_{Left} and r_{Right} are determined by $E = V(r)$ which divide $\{r : R, +\infty\}$ into three regions: two classically allowed $R < r < r_{\mathrm{L}}$ and $r_{\mathrm{R}} < r < +\infty$ for $E > V(r)$, and one classically forbidden $r_{\mathrm{L}} < r < r_{\mathrm{R}}$ for $E < V(r)$, as shown in figure 1.

The transmission coefficient T_{r} is defined as the ratio of current density of the outgoing wave χ_{trans} $(r > r_{\mathrm{R}})$ to the incident wave χ_{inc} $(r < r_{\mathrm{L}})$ [58]

$$T_{\mathrm{r}} = \frac{|\,\chi_{\mathrm{trans}}(r)\,|^2\, v_{\mathrm{trans}}}{|\,\chi_{\mathrm{inc}}(r)\,|^2\, v_{\mathrm{inc}}}. \tag{5}$$

Here v_{trans} and v_{inc} are the velocity of the outgoing and incident waves, respectively. According to the WKB theory, the transmission coefficient T_{r} can be written as [58]

$$T_{\mathrm{r}} = \frac{4}{\left(2f + \dfrac{1}{2f}\right)^2}, \qquad f = \mathrm{e}^{\int_{r_{\mathrm{L}}}^{r_{\mathrm{R}}} \kappa(r)\mathrm{d}r},$$

$$\kappa(r) = \left[\frac{2\mu}{\hbar^2}(V(r) - E)\right]^{1/2}, \tag{6}$$

where μ is the reduced mass of the sphere and the electron, which is approximately equal to the mass of the electron, and E is the energy of the electron inside the well. The lifetime τ can be estimated as

$$\tau = \frac{1}{\mathrm{rate}} = \frac{2r_{\mathrm{s}}}{T_{\mathrm{r}} v_{\mathrm{inc}}}, \tag{7}$$

where v_{inc} is the velocity of the incident electron at kinetic energy E, as determined by $v_{\mathrm{inc}} = (2E/m)^{1/2}$.

4. Short range interactions and the electron energy inside the well

To estimate the energy inside the well, as shown in figure 1, we generalize the expression derived by Smith [59] for successive ionization potentials of aromatic hydrocarbons to the case of spherical molecules. The basic idea is that the large polynuclear aromatic molecules ionize like fragments of graphite, and their ionization potentials approach the sum of the graphite work function and the electrostatic work of charging a conductor of the size and shape of the molecule. In the limit of large size, the approximate work (SI units) to remove n electrons is given by [59]

$$W_n(R) = n\left(w + \frac{\alpha}{R}\right) + \frac{n^2\beta e}{2C} \tag{8}$$

Here $n = 1, 2, 3, \cdots$, w, α, β are adjustable parameters, R is the radius of the spherical molecule and C is the capacity of the dianion. For spherical dianions, C has the form $4\pi\epsilon_0 R$, with ϵ_0 being the absolute dielectric constant in vacuum.

The nth ionization energy, $E_{\mathrm{I}}^n = W_n - W_{n-1}$, is given by

$$E_{\mathrm{I}}^n = w + \frac{\alpha}{R} + \frac{14.4\beta}{2R}(2n - 1), \tag{9}$$

and the $(m-1)$th electron affinity energy, $E_{\mathrm{A}}^m = W_{-m+1} - W_{-m}$, has the form

$$E_{\mathrm{A}}^m = w + \frac{\alpha}{R} - \frac{14.4\beta}{2R}(2m - 1), \tag{10}$$

with E_{I} and E_{A} given in eV and R in Å.

The radius of the spherical molecule R can be related to the number of atoms N inside the sphere. If we assume that the molecule has the same spherical structure as C_{60}, with an inner sphere of radius $R_0 = 3.55$Å [52, 60] and a spherical shell of π electrons with

$\Delta R = 1.46$ Å, then $R = R_0 + \Delta R$. This result is consistent with distance D between two nearest neighbour molecules in the C_{60} lattice, $D = 2R = 10.02$ Å [60]. Since the number of atoms is approximately proportional to the surface area of the inner sphere $N \sim 4\pi R_0^2$, and we obtain

$$R = \frac{\sqrt{N}}{7.746} R_0 + \Delta R. \tag{11}$$

5. Results

We use the negative value of the electron affinity energy given by equation (10) at $m = 2$, i.e. $-E_A^2$ for the electron energy inside the well. In equation (10) there are three parameters w, α and β which may be determined from the known values of the electron affinities (E_A^m) of three molecules. For this work, we use the experimental results $E_A^1 = 2.666 \pm 0.001$ eV of C_{60} [43] and $E_A^1 = 2.676 \pm 0.001$ eV of C_{70} [43], and $E_A^2 = -0.3$ eV of C_{60} which was determined by the generalized gradient approximation [42]. After fitting the values of the three parameters in equation (10), we obtain

$$E_A^1 = 2.8521 - \frac{0.9325}{R}, \tag{12}$$

$$E_A^2 = 2.8521 - \frac{15.7922}{R}. \tag{13}$$

To calculate the lifetime of a dianion, we used $-E_A^2$ as the estimated value of the resonance energy inside the well. The zero-point energy was chosen as the threshold for autodetachment fragments, an anion plus a free electron, as shown in figure 1. When $-E_A^2$ is located between the barrier height and the threshold, the electron will tunnel through the barrier at a certain rate. But electron autodetachment will occur when $-E_A^2$ is larger than the barrier height. As $-E_A^2$ decreases below the threshold, we have a zero tunnelling rate and hence an infinite lifetime. As the value of $-E_A^2$ becomes closer to the well depth V_0, classically there will be a strong short range interaction between the tunnelling electron and the anion. Based on this analysis, we can approximate the constant V_0 as the mean field potential of the anion. For a specific dianion we may obtain V_0 by the angular and radial averages of the corresponding 3-dimensional potential. Of course, different dianions may have different V_0. Considerations of interactions inside the anion and interactions of the anion with the tunnelling electron have been given by Dreuw and Cederbaum [31, 61].

The present two potential models, equations (2) and (4), are different in that the Coulomb model allows τ to decrease to near zero while the dielectric sphere model has a cutoff point at small R corresponding to $N = 6$ atoms. This may be understood from examining the change in the height of the two barriers compared with the energy inside the well. Numerical calculations show that it is possible to find two classical turning points for the Coulomb potential for $R \geq R_t = 0.48$ Å, and for the dielectric spherical model turning points occur at $R \geq R_t = 2.63$ Å with $N = 6$. But when the electron energy inside the well becomes larger than the height of the barrier, for the region $R < R_t$, no turning points exist and classically the dianion is unstable.

For C_{60}^{-2} the two excess electrons occupy the t_{1u}^2 LUMO (the lowest unoccupied molecular orbital), which give rise to $^3T_{1g}$, ^1H_g, ^1A_g electronic states in strict analogy with the low lying ^3P, ^1D, ^1S multiplets of carbon (p^2) atom [41]. The ground state of C_{60}^{-2} is $^3T_{1g}$ with total angular momentum $l = 1$, while the higher energy states are ^1H_g with $l = 2$, and ^1A_g with $l = 0$. The lifetimes were calculated using the WKB approximations, equation (7), the radius of a given molecule was estimated from equation (11), and the first and second electron affinities were estimated from equations (12) and (13). Figure 3 presents a comparison of the calculated lifetimes of the spherical dianions, using the WKB approximation, as a function of both N and R using the dielectric sphere model, equation (2), and the Coulomb model, equation (4) , with $l = 1$. For small R or N, the lifetime is short and increases as R or N increases. The cutoff values of R_c and N_c, where the transitions between metastable and stable occur, are $R_c = 5.52$ and $N_c = 78$ for the pure Coulomb model and $R_c = 5.53$ and $N_c = 79$ for the dielectric sphere model. In table 1, we compare the lifetimes of carbon cluster dianions with the available experimental and theoretical results. The results indicate the strong dependence of the lifetimes on the molecular size and the general trend of increasing stability as the molecule size increases.

Due to the reported different values of E_A^2 for the C_{60} molecule, we examine the effect of varying E_A^2 or the energy inside the well on the lifetimes of the different spherical dianions. From the calculated lifetimes for $E_A^2 = -0.4, -0.3, -0.2, -0.1$ eV, we can combine the two experimental results and our calculated value to narrow down the possible values of E_A^2 for C_{60}. Hettich *et al.* [39] reported the lifetime of C_{60}^{-2} as long lived, $> 10^{-3}$s, while Wang *et al.* [40, 62] showed that there are no C_{60}^{-2} signals at the timescale of 0.1s. Thus, the lifetime of C_{60}^{-2} is expected to be between the two experimental values, $0.001 \text{ s} < \tau < 0.1 \text{ s}$. Our estimated lifetime from the dielectric spherical model is 1.1×10^{-5}s at $E_A^2 = -0.3$ eV and 0.168 s at $E_A^2 = -0.2$ eV. Therefore we further narrow down the difference in the elec-

Table 1. Calculated WKB lifetimes (in s) of spherical molecular dianions from both models: the dielectric and Coulombic potentials. For comparison the available experimental and theoretical calculations are given. An entry of the form 2.7 (−15) means 2.7×10^{-15}.

Spherical molecular dianions	Lifetime						Exp. (E), Theor. (T)
	Dielectric			Coulombic			
	$l = 0$,	1,	2	$l = 0$	1,	2	
C_{20}^{-2}	2.7 (−15),	5.2 (−15),	2.0 (−14)	8.6 (−14),	2.0 (−13),	9.3 (−13)	> 10 μs E [21]
C_{40}^{-2}	1.8 (−12),	3.9 (−12),	1.7 (−11)	8.3 (−11),	1.9 (−10),	9.7 (−10)	
C_{60}^{-2}	5.0 (−06),	1.1 (−05),	5.2 (−05)	2.8 (−04),	6.5 (−04),	3.4 (−03)	< 0.1 s, E [40, 62] 50 μs − 5 s, E [43] 4×10^7 year, T [65] > 10^{-3} s, E [39] 3 min, E [64]
C_{64}^{-2}	2.1 (−03),	4.7 (−03),	2.2 (−02)	1.2 (−01),	2.8 (−01),	1.5 (+00)	
C_{68}^{-2}	1.7 (+01),	3.8 (+01),	1.8 (+02)	9.8 (+02),	2.3 (+03),	1.2 (+04)	
C_{70}^{-2}	1.2 (+04),	2.6 (+04),	1.3 (+05)	6.8 (+05),	1.6 (+06),	8.6 (+06)	50 μs − 5 s, E [43] > 10^{-3} s, E [39] 3 min, E [64] Stable, T [66]
C_{74}^{-2}	1.0 (+14),	2.3 (+14),	1.1 (+15)	6.2 (+15),	1.5 (+16),	8.0 (+16)	Stable, T [66]
C_{78}^{-2}	1.3 (+58),	2.9 (+58),	1.4 (+59)	8.0 (+59),	1.9 (+60),	1.0 (+61)	Stable, T [66]
C_{82}^{-2}	∞,	∞,	∞,	∞,	∞,	∞,	Stable, T [66]
C_{84}^{-2}	∞,	∞,	∞,	∞,	∞,	∞,	Stable, T [66] 60 μs, T [67]
$C_{86}^{-2}, C_{88}^{-2}, C_{90}^{-2}$	∞,	∞,	∞,	∞,	∞,	∞,	Stable, T [66]

tron affinity energy to, $-0.246 \text{ eV} < E_A^2 < -0.204$ eV. The variation in the lifetimes with the different values of E_A^2 over the range [−0.25, −0.20] is shown in figure 4.

Now, let us consider the case of $l = 0$. It is interesting to compare the calculated lifetimes of small dianions using the models described above with the available exact *ab initio* calculations. We choose C_2^{-2} which has electronic states ${}^1\Sigma_g^+$. It is a small dianion with axial symmetry, quite different from the present spherical model of interaction potentials with O_3 symmetry. Table 2 compares the results for the dimer C_2^{-2} obtained using the Coulomb model (the dielectric spherical model can be used only for molecules with at least six atoms) with the calculations using a complex absorbing potential in conjunction with a multireference configuration interaction wavefunction [63]. In the Coulomb model, we took the inner sphere diameter $2[R - \Delta R]$ (see equation (11)) as an approximation of its bond length. The estimated range shown in table 2 and obtained from the numerical results in figure 3 relates to the range in R that corresponds to $N = 2$. The results are encouraging for such a small system. For the dimer C_2^{-2} there are only two atoms; therefore the two excess electrons have to be separated along the molecular axis. From a dynamic point of view, as one electron tunnels through the barrier, Coulomb repulsive forces always push the other electron towards the opposite side of the sphere along the tunnelling coordinate. This tunnelling picture is consistent with the real geometry of axial diatomics. This might explain why the spherical model gives good results for such a small dianion.

Table 2. Estimated parameters for $C_2^{-2}({}^1\Sigma_g^+$ and $l = 0)$ using the WKB approximation, compared with the exact *ab initio* calculations [63].

	Pure Coulomb model	Exact [63]
Energy	4.2 ± 0.2 eV	3.52 eV
Number of atoms	2	2
Bond length	1.35 ± 0.15 Å	1.265 Å
Lifetime τ	$1.2(\pm 0.4) \times 10^{-15}$ s	2.2×10^{-15} s(0.3 eV)

Finally, we extend the lifetime studies from $l = 0$ and $l = 1$ to higher orbital angular momentum $l = 2, 3$ with fixed $E_A = -0.3$ using the dielectric spherical model. There are no large changes in the lifetimes, but results for $l = 1$ show no cutoff point at small R compared with results for $l = 0$ where the cutoff point is $R_t = 2.63$ Å.

6. Conclusion

We used the WKB approximation to estimate the lifetimes of spherical carbon cluster dianions using a simple model potential: an electron interaction with a singly

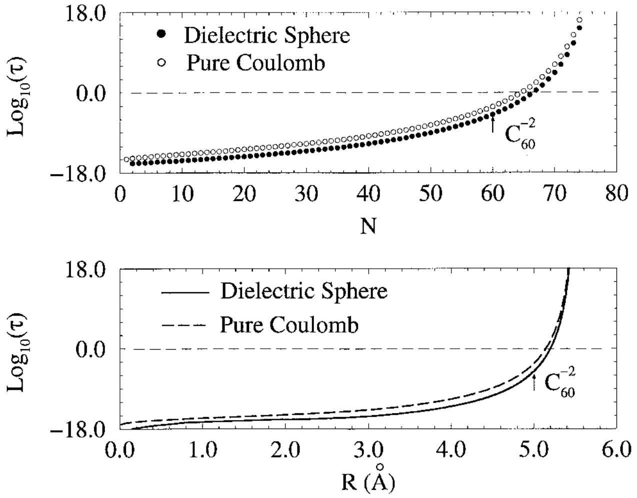

Figure 3. Logarithmic lifetimes (in s), $\log_{10}[\tau]$ as a function of the number of atoms N (upper) and radius R(Å) (lower) of spherical dianions; thin dashed line corresponds to $\tau = 1$ s.

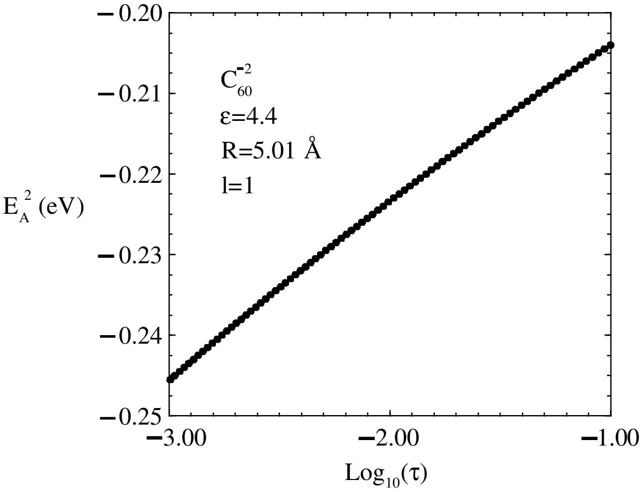

Figure 4. Possible values of the second electron affinity energy E_A^2 as a function of the logarithmic lifetime $\log_{10}[\tau]$ for dielectric constant $\epsilon = 4.4$, radius $R = 5.01$ Å and orbital angular momentum $l = 1$ for C_{60}^{-2}.

negatively charged dielectric sphere. In this model the metastability of a given dianion is attributed to a shape resonance resulting from the long range Coulomb repulsion combined with the shorter range electron–molecule interaction. For carbon clusters, the dielectric constant was fixed at $\epsilon = 4.4$, corresponding to C_{60}^{-2}; the first and second electron affinities were estimated using equations (12) and (13), as the size of the cluster varies and the radius of the sphere was estimated from equation (11). Although the results of this simple model compare well with the experimental results for large carbon clusters, we can rely only on the fact that these results give us a general trend in the increasing stability as the size of the dianions increases. Results for fullerene dianions show a strong dependence of the lifetimes on the molecular size, as shown in table 1.

We estimate the transition, from stable to metastable dianions, to occur when the radius of the spherical molecule is about $R_c = 5.5$, which corresponds to $N_c = 78$. Since there is still an open question concerning the smallest molecule that can bind two or more excess electrons in the gas phase, this simple model potential might provide a starting point for experimental and theoretical searches using accurate *ab initio* methods for the existence of stable dianions. It is interesting to note the large discrepancies between different experiments and between experimental investigations and theoretical calculations concerning the lifetimes of large molecular dianions. This shows the need for more accurate calculations for large molecular dianions.

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