Anomalous low-energy electron attachment in $C_{60}$

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Abstract

We propose that thermal electron attachment to $C_{60}$ should occur preferentially in the p-wave channel, following an analysis of the vibron excitation spectrum of $C_{60}^-$. A very simple model based on this idea is shown to account very well for recent attachment data. The unexplained activation energy of $\approx 0.26$ eV found experimentally is attributed to the p-wave centrifugal barrier. PACS numbers: 34.80.Gs, 61.46.+w
In a recent pair of papers, we have pointed out some remarkable properties of fullerene molecular anions, $C_{60}^{n-}$, $n=1,...,5$ [1,2]. In these ions, a threefold degenerate partly filled $t_{1u}$ molecular orbital (MO) is linearly coupled to two $a_g$ and to eight $h_g$ molecular vibrations, leading to a well-known Jahn-Teller (JT) effect [3–7]. We have made two additional observations, however.

The first is that a static JT description is not really adequate. Zero-point effects are large in $C_{60}$ [8], while at the same time one expects basically no barrier between equivalent JT potential minima, as confirmed, e.g., by Hartree-Fock calculations [7]. A full quantum treatment of ionic motion, typical of the dynamical JT effect is therefore mandatory. As it turns out, fullerene anions constitute a linear weak-coupling case which is easy to solve. In the end, one finds a remarkable enhancement of the true stabilization energies relative to their classical values, which makes the JT effect much more important than believed so far.

The second observation is that for odd $n$ and in particular for $C_{60}^{-}$, the adiabatic coupling of $H_g$ ($L=2$) vibrational coordinates to the $t_{1u}$ ($L=1$) electronic level [9] is affected by a nonzero molecular Berry phase [10]. Its presence, in turn, causes vibron quantization to be anomalous, in qualitative analogy with, for instance Na$_3$ [11]. In that molecule, a strong-coupling $e \otimes E$ dynamical JT case, the Berry phase causes, very unusually, the total pseudorotational angular momentum (excluding spin) to take up half-integer (instead of integer) values [11]. In $C_{60}^{-}$, where $(t_{1u} \otimes H_g)$ coupling is weak, effects appear to be twofold. First, there is always an odd-$L$ state which has energy lower than the even $L$ states in each multiplet of the excitation ladder. In particular, the ground state is $L=1$, and the lowest state on each $m$-vibron excited multiplet is $L=2m+1$. This is the analog of the half-integer effect of Na$_3$. Secondly, $L=0$ states disappear altogether from the low-lying excitation spectrum [12]. For example, each of the eight $H_g$ quadrupolar modes gives rise, after dynamical JT coupling, to a one-vibron multiplet $L=3,2,1$ (in order of increasing energy), followed by a two-vibron multiplet $L=5,3,1,4,2,1,3$ (in order of increasing energy), etc., where in spherical geometry no $a_g$ ($L=0$) state appears. Specifically, the absence of the $L=0$ states can be properly seen as a direct consequence of the absence of $L=1$ states in the overtones of a
quadrupolar harmonic oscillator [13]. Since, moreover, each of the two original $A_g$ ($L=0$) modes gives rise to $t_{1u}$ ($L=1$) vibronic states only, while all other remaining vibrations of different symmetry species [3] are linearly uncoupled to the $t_{1u}$ electronic level of C$_{60}$, no other $L=0$ state is produced. The C$_{60}$ molecule has in addition only a second affinity level, of $t_{1g}$ symmetry, which lies roughly 1 eV above the $t_{1u}$ [14], or 1.7 eV below the ionization level. This higher electronic level is also coupled to molecular vibrations, giving rise to a dynamical JT problem which is easily seen to be formally very similar to that of the $t_{1u}$ level. In particular, therefore, this $t_{1g}$ level again fails to give rise to $a_g$ ($L=0$) vibronic states in its spectrum [15].

In this letter, we point out an unexpected consequence of the above scenario, namely, an anomalous low-energy electron attachment to C$_{60}$. The absence of $L=0$ bound states for C$_{60}^-$, as opposed to a whole set of vibronic $L=1$ states available down to the ground state chemical potential at $E_F=-2.7$ eV [16], suggests that, unlike most common cases, such as, e.g., SF$_6$ [17], electron attachment to C$_{60}$ should proceed by *p-wave instead of s-wave scattering*. We show that this hypothesis allows, via an extremely simple model, to account very well for the observed thermal attachment rate, including its hitherto mysterious activated behaviour [18].

We model the free electron interaction with C$_{60}$ as a short-range scattering event, each partial wave including elastic and inelastic channels. If a channel with nonzero (inelastic) attachment cross section must have bound states in it, then we are led to assume that s-wave attachment can be neglected, and must consider next the p-wave channel. Here, there will be a centrifugal barrier $\frac{h^2}{m_eR^2}$, whose traversal will constitute the major obstacle to attachment. The estimated barrier height at an approximate C$_{60}$ radius of $R \approx 10$ a.u. is $10^{-2}$ Hartrees or 0.27 eV, encouragingly close to the observed and unexplained activation energy for attachment [18].

In order to make quantitative progress, we further model p-wave scattering and attachment as follows. First, we assume that this inelastic process can be replaced by an elastic p-wave scattering across the barrier, followed by an instantaneous, infinitely efficient inelas-
tic electron decay into the $t_{1u}$ bound state. In other words, we assume that once the p-wave electron has crossed the centrifugal barrier it will be attached with probability 1. This assumption seems justified by a very efficient distribution of energy among many degrees of freedom of this large molecule [19]. In conclusion, the attachment cross section to be calculated under this assumption coincides with the elastic p-wave cross section of a real potential $V(r)$. In order to represent the effect of C$_{60}$ on a p-wave thermal electron, this potential must be attractive (with at least a bound state) for $r < R$ and vanish for $r >> R$.

As a first crude attempt we took for $V(r)$ a spherical square well of depth $-V_0$ and radius $R$, with the constraint that is should have a single $L=1$ bound state at $E_I=-2.7$ eV. The p-wave phase shift $\delta_1$ for this potential is [20]

$$\delta_1 = \tan^{-1} \frac{j_1(kR) - \gamma j_1(kR)}{n_1(kR) - \gamma n_1(kR)},$$

$$\gamma = \frac{\chi j_1'(\chi R)}{kJ_1(\chi R)},$$

$$k = \sqrt{2m_eE/\hbar}, \chi = \sqrt{2m_e(E + V_0)/\hbar},$$

where $j_1$ and $n_1$ are Bessel functions of order one. The corresponding attachment cross section $\sigma_A(E) = 12\pi \hbar^2(2m_eE)^{-1} \sin^2 \delta_1$ as a function of incident electron energy $E$ is shown in Fig. 1. The cross section falls off as $E^2$ at small $E$ (due to barrier tunneling) and as $E^{-2}$ at large $E$, with a maximum for $E$ of order of the centrifugal barrier height and a zero due to the p-wave phase shift $\delta_1$ crossing $\pi$, as requested for one bound state. Since the barrier height is considerable, it is clear that p-wave attachment will be very poor at thermal energies. In s-wave, instead, the cross section would have been finite in the $E \to 0$ limit, leading to the large thermal energy attachment normally observed in other large molecules [17,21].

From this cross section, the attachment rate for a thermal distribution with temperature $T$

$$A(T) = \frac{2^{1/2}}{m_e^{1/2}k_B T} \int_0^\infty dE E^{1/2} \sigma_A(E) e^{-E/k_B T}$$

is easily calculated, and the result are plotted in Fig. 2. The choice of $R$ determines
sensitively the correct order of magnitude for the absolute attachment rate. The best fit is with $R=5.27\,\text{Å}$, which is very reasonable for $C_{60}$. The other parameter $V_0=4.68\,\text{eV}$ being fixed by the bound state constraint, we find that the overall agreement with the thermal attachment rates of Smith, Španel and Märk is very good. The approximate activated behaviour is retrieved, and related in our calculation to electrons thermically negotiating the centrifugal barrier. Deviations in excess of a purely activated behaviour seen both experimentally and theoretically at the lowest temperature of 300 K, are found to be due to the $E^2$ quantum tunneling under the barrier. At the highest temperature the calculated attachment rate is slightly smaller than the experiment. This may be due to inadequacy of our simple $V(r)$ as well as of our additional assumptions. The high-energy attachment cross section \cite{21} shows strong peaks in the 1 - 8 eV region interpreted as Feshbach resonances with electronic and vibrational states, which our simple model clearly cannot account for. On the whole, however, we find that this extremely crude model works well enough in the explored region of temperatures to make further improvements unnecessary.

In conclusion, we have given arguments based on a recent dynamical JT study of $C^{-}_{60}$, why low energy electron attachment to $C_{60}$ should occur predominantly in the p-channel. We have furthermore shown that an extremely simple model for that process yields a very good description of the experimental attachment rate, including its anomalous activated behaviour, which is now attributed to crossing of the centrifugal barrier. It is possible that the phenomenon described here could also bear a connection to the failure of the simple Dushman - Richardson formula to account quantitatively for thermionic emission from $C^{-}_{60}$ ions \cite{16}. However, that behaviour is shared by $C^{-}_{70}$ and $C^{-}_{96}$, whose physics is somewhat different in many details. This problem requires a separate investigation.

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This is in contrast with the s-wave channel, where there is no barrier, but no negative energy states available for fast attachment.

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FIGURES

FIG. 1. The $L=1$ cross section for three sets of values of the parameters $R$ and $V_0$ that define the potential well $V(r)$. All choices of parameters satisfy the constraint of a single bound p-state at $E_I=-2.7$ eV. The main peak corresponds roughly to the centrifugal barrier height.

FIG. 2. The electron attachment rate corresponding to three sets of values of the parameters $R$ and $V_0$. The central curve is the best fit of the experimental data points by Smith, Španel and Märk [18]
A graph showing the relationship between energy (E) in electron volts (eV) and cross-section (\(\sigma_A\)) in square ångströms (\(\text{Å}^2\)). The graph includes three curves labeled:

- \(R=5.34\text{Å} V_0=4.62\text{eV}\)
- \(R=5.26\text{Å} V_0=4.68\text{eV}\)
- \(R=5.18\text{Å} V_0=4.73\text{eV}\)
$A \text{ [cm}^3 \text{ s}^{-1}]$

$T^{-1} \text{ [K}^{-1}]$

- $R=5.34\text{Å} V_0=4.62\text{eV}$
- $R=5.26\text{Å} V_0=4.68\text{eV}$
- $R=5.18\text{Å} V_0=4.73\text{eV}$