Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres

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Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres

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Abstract. Quantum mechanical scattering calculations are carried out for gas-phase molecules of anthracene, an aromatic system with three condensed aromatic carbon rings, in collision with low-energy electrons. They reveal the presence of various metastable (resonant) anionic states of this prototype species belonging to the larger polycondensed aromatic hydrocarbons deemed to be present in various regions of the interstellar medium. These resonances are analysed in terms of their most likely paths to stabilization into bound anionic molecules or aromatic fragments, while the important role of threshold virtual states is also discussed within the same context.
1. Introduction

The large series of aromatic molecules that go under the name of polycyclic aromatic hydrocarbons (PAHs) are made up of fused rings of aromatic carbon structures with five or six members that eventually form very large ensembles of carbon-rich molecules. They have been proposed to be the carriers of unidentified infrared bands by several authors [1–3] since they exhibit the characteristic emission wavelengths of aromatic hydrocarbons (see, e.g., [4]). At a similar level, the diffuse interstellar bands (DIBs), which are the broad absorption bands that span from the far infrared to the near ultraviolet [5], have also been attributed to PAHs even though the specific identification of the molecular carriers has proven to be difficult. To date more than 400 DIBs have been detected [6], but none of them has been unequivocally assigned to molecular carriers of the PAH class [7].

The inclusion of chemical processes involving PAHs in the astrophysical models on the evolution and composition of interstellar clouds and protoplanetary atmospheres has, however, been found to have significant consequences. For example, those models [8, 9] which included the formation of anionic PAHs have found marked effects in the chemistry of interstellar clouds: in dense clouds, in fact, free electrons are surmised to efficiently attach to PAHs, thereby replacing the latter with anionic PAHs, which then can become the principal carriers of negative charge. Likewise, the fraction of ionized atomic species is reduced in diffuse and dense clouds, where the recombination rates between atomic cations and PAH anions increase when compared to the cation–electron recombination rates [10].

However, models that include PAHs neglect to include the dehydrogenated neutral and anionic derivatives of the above molecules, although the dehydrogenated PAH anions may become more stable in the interstellar and circumstellar media (ISM and CSM) because of the larger electron affinities of these radicals (>1 eV) as compared to the parent hydrocarbons (0.5–1.0 eV) [11]. In our previous studies of anions of smaller members of the PAHs [12–14], we have indeed found that the formation of metastable complexes, the transient negative ions (TNIs), on the attachment of free electrons could lead to both the stabilization of the full anion or to the subsequent detachment of an H atom with final stabilization of the anionic radicals [15]. We therefore suggest that astrophysical models should include anionic PAHs and also dehydrogenated, carbon-rich species for a more realistic description of CSM evolution processes. Within that context, one further needs to assemble realistic estimates of the rates of
formation for the above species, a process that thus requires the previous evaluation of total, integral scattering cross sections for

\[
e^{-} + \text{PAH}_{(n)} \rightarrow [\text{PAH}_{(n)}]^{*} \rightarrow \begin{cases} (\text{PAH}_{(n-1)})^{+} + \text{H}, \\ \text{PAH}_{(n)}^{-}, \end{cases}
\]  

(1.1)

In the present study, we therefore wish to analyse in some detail how one can obtain the above cross sections over the relevant range of electron energies and how the TNI structures are identified and related to the likely occurrence of the above processes.

The paper is organized as follows. Section 2 briefly outlines our computational method and the numerical evaluation of the scattering observables for a specific system, the anthracene (An) molecule, C_{14}H_{10}, formed by three linearly condensed aromatic rings.

Section 3 reports the locations and identification of low-energy attachment complexes in the form of resonances and virtual states, while our present conclusions are given in section 4.

2. An outline of the present computational model

When the scattering event is described for a fixed nuclear configuration, one represents the total wavefunction of the ‘target + e^{-}’ as an antisymmetrized product of electronic wavefunctions that parametrically depend on the positions of the nuclei. The scattering process under investigation is here initially limited to elastic channels; therefore no electronic excitations are considered, and the N-bound electrons of the target are assumed to be in a specific molecular electronic state (ground state) which is taken to remain unchanged during the scattering. In our equations the occupied molecular orbitals (MO) of the target are expanded on a set of symmetry-adapted angular functions with their corresponding radial coefficients represented on a numerical grid so that any arbitrary three-dimensional function describing a given electron, either a bound or a scattering electron, is expanded around the centre of mass of the molecule, where the origin of the body-fixed frame is placed. The single centre expansion is then given by

\[
F^{p\mu}(r, \hat{r}|\mathbf{R}) = \sum_{\ell_m} \frac{1}{r} f^{p,\ell_m}_{\mu}(r|\mathbf{R}) \chi^{p\mu}_{\ell_m}(\hat{r}),
\]  

(2.1)

where the indexes refer to the \(\mu\)th component of the \(p\)th irreducible representation (IR) of the point group of the molecule at the nuclear geometry \(\mathbf{R}\). The angular functions \(\chi^{p\mu}_{\ell_m}\) are symmetry-adapted angular functions given by a proper combination of harmonics \(Y_{\ell_m}(\hat{r})\) [16]

\[
\chi^{p\mu}_{\ell_m}(\hat{r}) = \sum_{m} b^{p\mu}_{\ell_m h} Y_{\ell_m}(\hat{r}).
\]  

(2.2)

The coefficients \(b^{p\mu}_{\ell_m h}\) are discussed in the literature and can be obtained from a knowledge of the character tables of the relevant molecular point group. The coupled partial integro-differential scattering equations take the form

\[
\left[\frac{d^2}{dr^2} - \frac{\ell (\ell + 1)}{r^2} + 2 (E - \epsilon_\alpha) \right] f^{p,\ell\alpha}_{\chi h}(r|\mathbf{R}) = \sum_{\ell'h'} \int dr' V^{p,\mu',\ell'h'}_{\chi\ell\ell'}(r, r'|\mathbf{R}) f^{p,\mu',\ell'h'}_{\chi\ell'h'}(r'|\mathbf{R}),
\]  

(2.3)

where \(E\) is the collision energy and \(\epsilon_\alpha\) is the electronic eigenvalue for the \(\alpha\)th asymptotic state so that \(k_\alpha^2/2 = E - \epsilon_\alpha\), where \(k_\alpha\) is the asymptotic momentum of the electron with the target in a
state \( \alpha \). The \((p\mu\alpha)\) indices in (2.3) now label the symmetry and corresponding target state of the continuum wavefunction, and refer to the kernel of the integral operator \( \hat{V} \), a sum of diagonal and nondiagonal terms that, in principle, fully describe the electron–molecule interaction for the molecular ground state geometry \( \mathbf{R} \). Introducing the further assumption of having only a local \( \text{e}^-\)–molecule interaction (as we shall discuss below), one can again simplify the form of the coupled equations

\[
\left[ \frac{\partial^2}{\partial r^2} - \frac{\ell_i (\ell_i + 1)}{r^2} + k^2 \right] f_i (r|\mathbf{R}) = \sum_j V_{ij}^{p\mu} (r|\mathbf{R}) f_j^{p\mu} (r|\mathbf{R}) ,
\]

where the indices \( i \) or \( j \) represent the ‘angular channel’ \((\ell, h)\) and the potential coupling elements are given by

\[
V_{ij}^{p\mu} (r|\mathbf{R}) = \langle \chi_i^{p\mu}|V (r|\mathbf{R}) \chi_j^{p\mu} \rangle = \int d\mathbf{\hat{r}} \chi_i^{p\mu}(\mathbf{\hat{r}}) V (r|\mathbf{R}) \chi_j^{p\mu}(\mathbf{\hat{r}}) .
\]

The exchange contribution to the operator in (2.5) is an energy-dependent local exchange potential discussed by the authors many times before [17]. We further include the dynamical short-range correlation through the addition of a local energy-independent potential which is obtained by defining an average dynamical correlation energy of a single electron within the formalism of the Kohn and Sham variational scheme. The functional derivative of such a quantity with respect to the SCF \( N \)-electron density of the molecular target provides a density functional description of the required short-range correlation energy as an analytic function of the target electron density [16]. The latter contribution is finally connected with the long-range dipole polarizability term providing the additional polarization potential contribution. The main focus of this paper is on the mechanism and qualitative characteristics of possible low-energy, one-electron resonances. This requires a model which is simple enough to be computationally attractive but which includes sufficient details of the full scattering problem to reproduce the essential features of the physics involved. Thus, we locate the low-energy resonances by using a simple, purely local model potential that we have called the static-model-exchange-correlation (SMEC) potential, \( V_{\text{SMEC}} \) [16]. We start by noting that an alternative basis expansion is provided by new angular eigenfunctions obtained by diagonalizing the angular Hamiltonian at each radius \( r \). These distance-dependent angular eigenstates are referred to as the adiabatic angular functions \( Z_k^{p\mu}(\theta, \phi, r) \) which, at each radial value, are linear combinations of the symmetry-adapted ‘asymptotic’ harmonics

\[
Z_k^{p\mu}(\theta, \phi, r) = \sum_{\ell h} \chi_{\ell h}^{p\mu}(\theta, \phi) C_{\ell h, k} (r) ,
\]

where the expansion coefficients are solutions of the matrix eigenvalue equation

\[
\sum_{\ell h} V_{\ell h', \ell h} (r) C_{\ell h, k} (r) = C_{\ell h', k} (r) V_k^{A} (r) .
\]

The eigenstates \( V_k^{A} (r) \) now form an adiabatic radial potential for each index \( k \) over the selected range of the \( \text{e}^-\)–molecule distances. The spatial extent of the resonant wavefunction can be determined from the well and angular momentum barrier of such adiabatic potential terms, and the physical mechanism for the resonance is that of a trapped electron tunnelling through the potential barrier. In order to represent the nonadiabatic coupling terms between adiabatic curves,
we actually employ a piecewise diabatic (PD) representation of the potential whereby the radial coordinate is divided into a number of regions so that sector $i$ is defined as $r_{i-1} < r < r_i$, with $r_0 = 0$. In each radial region, we average the coupling potential $V_{\ell h, \ell h'}(r)$ over $r$ and the resulting averaged potential is diagonalized as in (2.7) to yield a set of angular functions $Z_{\ell, i}^{\ell h}(\theta, \phi)$. Then, in region $i$ the scattering potential is transformed into the new representation in which it is nearly diagonal. The resulting equations are solved using the full scattering potential in each region with the further approximation of ignoring the off-diagonal couplings in that region: to solve the radial equations using the PD approach requires matching of the radial functions and their derivatives at the boundary between radial regions. The transformation of the radial functions from one region to the next is given by the transformation matrix $U_{i+1 \leftarrow i \ell h, \ell h'}$ defined by

$$U_{i+1 \leftarrow i \ell h, \ell h'}^{i+1-i} = \sum_{\ell h} C_{\ell h, k}^{(i+1)} C_{\ell h, k', i}^{i}.$$  

When the size of the angular momentum eigenfunction basis used is larger than the size of the diabatic angular basis set, the transformation matrix $U_{k, k'}$ is not in general unitary. We accomplish the unitarization of $U_{i+1 \leftarrow i \ell h, \ell h'}$ using simple Graham–Schmidt orthonormalization on the columns of $U_{i+1 \leftarrow i \ell h, \ell h'}$ as described earlier by the authors in [16]. The actual resonance features (i.e. energy position and width) are obtained from the scattering calculations either by fitting the eigenphase sums to a Breit–Wigner behaviour or via the properties of the poles in complex space of the scattering $S$ matrix. The calculations described in the following will take advantage of various pieces of information obtained from scattering calculations:

1. the nodal structures and the antibonding features of the resonant wavefunctions associated with the excess electron as the nuclear geometry of the equilibrium structure is initially considered;
2. the resonant state location

$$E_{i}^{\mathrm{TNI}}(\mathbf{R}_i) = E_{i}(\mathbf{R}_i) + \frac{i}{2} \frac{\Gamma(\mathbf{R}_i)}{2},$$  

where TNI labels the specific transition negative ion produced by the resonance in question.

In the present analysis, the only nuclear set of geometries that we shall consider is that of the equilibrium configuration of anthracene, the latter being computed by the authors and in fair agreement with experiments [18]. The resonance evolutions as the molecular geometries change, as implied by equation (2.9), will be analysed in a subsequent, separate work.

3. Locating ‘resonant’ anionic species

3.1. Threshold behaviour: finding a virtual state

The presence of virtual states for collision systems at very low scattering energies has been studied for a long time (see, e.g., [19, 20]). In qualitative terms, the phenomenon occurs very close to the zero-energy threshold and for overall attractive potentials of some strength: in the present system, the polarization potential plays this role since the system presents a fairly large value for its spherical dipole polarizability: $\alpha_0 = 188 \text{ bohr}^3$ [21]. The states in question are characterized by very large elastic cross sections at vanishing energies [22] and large and negative scattering lengths, indicating an amplitude increase of the scattering state near the origin: in such cases, the scattered electron increases its wavefunction amplitude [19] close to
the molecular partner and is therefore expected to couple more strongly with the molecular vibrational modes. Since we know that radiative stabilization probabilities depend inversely on the relative collision energy between the electron and the target molecule, as well as directly on the third power of the energy gap \[ E^3 \], then the occurrence of virtual states at zero energies would maximize the probabilities of energy losses by photon emission with formation of a bound anion through a more efficient coupling with vibrational modes.

The role of these states is thus significant for the present context since, if the PAH in question were to have a virtual state at threshold, then the collisionless environment of the ISM could allow the bound anion to be formed by radiative stabilization, in efficient competition with the autodetachment channel \[ 24 \]. Another important feature of a virtual state formation is the dominance of s-wave scattering, and hence of an isotropic distribution of scattered electrons \[ 19 \] over the molecular spatial region.

The presence of virtual state formation during electron scattering from anthracene has been suggested in experiments \[ 22, 25 \] that measured backward scattering processes down to meV of collision energy. It therefore seems interesting to try to verify this suggestion by following the scattering features using quantum scattering calculations as already performed successfully for benzene \[ 25 \]. The angular distributions, calculated over a broad range of energies and down to \( 1 \times 10^{-6} \text{ eV} \), are reported by the data of figure 1.

One clearly sees a strong forward peaking exhibited by all cross sections as the collision energy decreases, whereas at ultralow scattering energies the distribution becomes nearly isotropic, as expected from the dominance of the \( \ell = 0 \) partial wave in the scattering event.

Other effects of the virtual state formation could be seen in the data reported in figure 2.

Such data are very interesting in documenting the effects of a virtual state formation on scattering observables: the upper panel of the figure shows the dramatic increase at zero energy of the elastic, integral cross sections. This corresponds to a drop in the eigenphase sum (lower panel) very close to vanishing energies and to an increase of the latter up to a maximum as one moves away from the threshold: the maximum of dephasing is followed by a rapid decrease.

**Figure 1.** Computed differential cross sections (DCS) for e\(^-\)–anthracene scattering down to \( 10^{-6} \text{ eV} \) of collision energy.
Figure 2. Computed integral, elastic cross sections (upper panel) in the totally symmetric IR $A_{1g}$. The corresponding eigenphase sum behaviour is seen in the lower panel of the figure. See the text for further details.

Table 1. Computed scattering length for scattering in the $A_{1g}$ IR.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Scattering length $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>$-12.53$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>$-12.52$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>$-12.40$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>$-11.40$</td>
</tr>
<tr>
<td>$0.5 \times 10^{-2}$</td>
<td>$-8.72$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-2}$</td>
<td>$-6.96$</td>
</tr>
</tbody>
</table>

that crosses the zero at an energy corresponding to the Ramsauer–Townsend feature in the cross section of the upper panel ($\sim 0.15$ eV). After that energy, the eigenphase remains negative and decreasing, indicating the presence of an attractive potential that allows formation of a virtual state at threshold [19, 24].

Table 1 reports the behaviour of the scattering length as a function of collision energy: it slowly decreases as a negative quantity, indicating again the presence of a virtual state or of a zero-energy resonance [20].

In a series of earlier studies on ultralow energy scattering experiments [22, 25], it was shown that both the total cross sections, $\sigma_{\text{tot}}$, and the backward scattering cross sections, $\sigma_{\text{back}}$, exhibit a marked increase in size at vanishing collision energies, thereby confirming the presence of a temporary anion as a virtual state. The data for the anthracene are provided in the two panels of figure 3, where we compare them with the present calculations.
Figure 3. Upper panel: backward scattering cross sections versus integral cross sections. The experimentally determined [22] backward cross sections, as obtained after integrating the corresponding DCSs from 90° to 180°, are given by the lozenges (and labelled as expt). The corresponding calculations are given by $\sigma_{\text{back}}$, while the integral cross sections are given by the calculations labelled $\sigma_{\text{tot}}$. Lower panel: computed ratios between the $\sigma_{\text{back}}$ and $\sigma_{\text{tot}}$ values from the present work.

One clearly sees the following interesting points from the data in that figure:

- both $\sigma_{\text{tot}}$ and $\sigma_{\text{back}}$ (upper panel) show unequivocally their strong increase at vanishing energies, as also reported by experiments that refer only to $\sigma_{\text{back}}$, and therefore should be compared with our computed green curve. Our data start increasing at lower energies than those of the experiments. Moreover, we agree very well with them down to about 100 meV, and their trend is clearly the one indicated by our calculations: given the approximation of our model potential, the accord is rather good;

- the ratio between $\sigma_{\text{back}}$ and $\sigma_{\text{tot}}$ should go to 1/2 at vanishing energies, since the distribution of electrons for dominant s-wave scattering is isotropic in the space frame. Thus, one should see if at nearly zero energy (in our case: 10 $\mu$eV) that ratio is reached by our calculations as it has been by experiments in the case of benzene [25] where our calculations also produced that value of 0.5, hence confirming for that molecule the existence of a virtual state at vanishing collision energies. The data in the lower panel of figure 3 only come from our computations and indeed also surmise the occurrence of
Table 2. Computed resonance locations and widths for the single-particle resonance of anthracene below 10 eV. All the values are in eV.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Energy (eV)</th>
<th>Width (eV)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{3u}$</td>
<td>1.16</td>
<td>0.035</td>
<td>$\sim 0.6$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>2.46</td>
<td>0.098</td>
<td>$\sim 1.5$</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>2.91</td>
<td>0.510</td>
<td>$\sim 1.67$</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>3.76</td>
<td>1.974</td>
<td>$\sim 1.80$</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>4.81</td>
<td>0.360</td>
<td>$\sim 2.67$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>7.77</td>
<td>0.982</td>
<td>–</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>10.46</td>
<td>2.218</td>
<td>–</td>
</tr>
</tbody>
</table>

such an effect for the anthracene molecule, although no direct measurements are available for the latter.

We can therefore conclude with some confidence that the anthracene molecule forms a threshold negative ion via the occurrence of a virtual state for vanishing scattering energies. This feature is obviously very important for establishing the likely presence of anthracene anions in the ISM, since the negligible excess energy of such metastable compounds combined with the relative small, positive electron affinity (EA) for this system ($\sim 0.53$ eV, [26]) can be expected to have a higher probability of being dissipated via radiative stabilization and therefore to provide a successfully competing channel with respect to autodetachment of the electron: a more efficient coupling of the electron motion as a virtual state with the nuclear motions should also occur here, thereby helping further the stabilization of an $[\text{An}]^-$ bound state.

3.2. Going up in energy: resonant states and metastable orbitals

Several shape resonances were also found at various energies below 10 eV for different symmetries, two of them at low energies and very narrow. The resonances identified from the analysis of the cross section behaviour were further verified by checking that the eigenphase sums showed a change by $\pi$ at the resonance energy. Following the Breit–Wigner formula, the resonance energy and the width were determined from that behaviour, and the results are shown in table 2.

The calculated elastic, integral cross sections are reported in figure 4, where each of the contributing IRs that were found to have a low energy resonance is shown over the same range of energies from threshold up to about 10 eV.

The lowest resonant state, the $^2B_{3u}$ state of anionic metastable anthracene, is located around 1 eV and turns out to have a very narrow width. It is interesting to note that the lowest virtual MO obtained from a minimal basis set (MBS) calculation of the Hartree–Fock energy for the equilibrium geometry also indicates the latter to be of $b_{3u}$ symmetry, although located much higher in energy. A comparison of their spatial shapes is reported in the two panels of figure 5 and show a strong similarity between the two wavefunctions.

The data reported in the figure also allow us to make the following comments:

(i) the first resonance corresponds to a $\pi^*$-type orbital with a nodal plane at the locations of the molecular nuclei; the corresponding density of the extra electron is chiefly on the ‘external’
carbon atoms, with no extra density on the H atoms or onto the more ‘linked’ internal C atoms;
(ii) the very old experiments reported on electron transmission spectra by Burrow et al [26, 27] also indicate a resonance feature around 0.6 eV, i.e. in reasonable agreement with our findings. These authors, however, could make only an ad hoc estimate of its
symmetry as no scattering angular distributions were available, although they recognized it as a $\pi^*$-type resonant state. One can thus say that, besides the threshold-energy virtual state, anthracene molecules exhibit also another path to anionic stabilization: a very narrow resonant state at about 1 eV of energy which is only weakly coupled to nuclear structures via its $\pi^*$ property and has no extra density over the H atoms of the ring structure.

The next resonance occurs around 2.46 eV and is also fairly stable (see the widths in the third column on the right of table 2). The earlier experiments of Burrow et al found also a second resonance around 1.5 eV, which is again downshifted with respect to our data as it occurred with the previous resonance [26, 27]. One should note here that the model potentials employed in our scattering calculations are known to show only semi-quantitative agreement with available experiments (see, e.g., [16, 17, 25]) although always being able to locate all the ones experimentally observed. Thus, given the presence of only very old experimental data [26, 27] the agreement with them is as can be expected. The symmetry is now $a_u$, as in the second virtual orbital from the MBS calculations, and the excess electron again shows a marked $\pi^*$ character, i.e. localized on all C atoms and with a symmetry plane over their equilibrium geometry.

It is interesting to note that this second, low-energy resonance again follows the symmetry of the virtual orbital from a standard quantum chemistry calculation, as shown in figure 6. However, the actual energy position in the continuum is very different from that given by the more realistic dynamical modelling of our quantum scattering study.

The computed partial cross sections of figure 4 additionally report three further resonances that appear in the low-energy range and with widths that suggest realistic stability for them: they correspond to metastable negative ions of anthracene, which have, respectively, $^2B_{1g}$, $^2B_{3u}$ and $^2B_{2g}$ symmetry. The earlier experiments [26, 27] also indicate three additional structures after the two associated with the previous resonances of figures 5 and 6: one centred at 1.67 eV, another around 1.80 eV and a third resonance at 2.67 eV. Even earlier estimates [27, 28] of
Figure 7. Computed wavefunctions (real part) for the resonant electron in anthracene for the three symmetries at higher energies. Their locations and widths are given (in eV) and the corresponding spatial maps of the virtual orbitals are also listed.

the anionic states of anthracene suggested also the 1.80 and 2.60 eV as possible negative ions. Our calculations place the three resonances shifted down in energy between 1 and 2 eV, as expected from the various approximations introduced by our interaction model, but their symmetries follow the sequence of the corresponding virtual orbitals, and therefore our scattering calculations, unlike the experiments, are able to provide the symmetries of such resonances and to estimate also their lifetimes. Figure 7 collects the spatial distributions of
the three extra electrons and compares them with the corresponding virtual orbitals: here again
the quantum chemical calculations place the virtual states much higher in energy but follow the
symmetry sequence proposed by the scattering calculations, which confirm in this case the
expected physical features of the metastable states of $C_{14}H_{10}^-$ lying in the lower continuum of
energy.

The group of resonances found up to about 5 eV of energy in the continuum of the electron
attachment spectrum for anthracene has the following common properties, of interest in the
present discussion:

(i) all resonant states indicate an essentially $\pi^*$-type nature, i.e. strong localization on the
carbon atoms along some specific bonds but essential absence of excess electron density
on the terminal H atoms;

(ii) our earlier calculations of $\pi^*$-type resonances in polycondensed aromatic rings (see, e.g.,
[24]) had indicated that such resonances are rather weakly coupled to the nuclear motions
of the neutral partner and therefore are not likely to lead to ring-breaking fragmentations,
while possibly causing instead diffuse energy rearrangements within the molecular mode
prior to autodetachment;

(iii) the absence of any extra charge located on any of the H atoms also suggests that a possible
fragmentation path could be the one often observed in aromatic systems [28, 29]: one of
the external H atoms detaches and leaves behind a dehydrogenated anionic radical $C_{14}H_9^-$. Given
the marked preferential localization of the excess charge (on all resonances) on the
PAH’s rings in this molecule, the tunnelling out of the H atom, driven by the excess energy
from the attached electron that gets redistributed into other vibrational modes [29, 30]
could therefore be a realistic possibility in the present system.

4. The present conclusions

In the quantum scattering analysis of the features of low-energy electrons interacting with gas-
phase anthracene, we have detected two main characteristics of the present system: (i) the
presence of a virtual scattering state at vanishing energies, whereby the small energy release
which could occur via radiative emission would be more likely to stabilize the anionic molecule
(EA $\sim$0.53 eV, [26]) as discussed before and (ii) the existence of several shape resonances at
energies between 1 and 4 eV where the excess electron is chiefly localized onto the condensed-
ring framework of C atoms but not on the terminal H atoms of anthracene.

The above features bear interesting consequences for the possible role of this molecule as
an electron-soaker in dark interstellar clouds or in protoplanetary atmospheres. The virtual state
formation, in fact, is a property also found for other polycondensed aromatic ring systems (see,
e.g., [14, 24]) and provides a possible path to radiative stabilization of unfragmented anionic
species since, for most of the neutral PAHs, their positive electron affinities are quite small, so
that the total energy release on stabilization of virtual states into bound states remains fairly
small and could therefore provide an efficient evolution path with respect to both dissociative
attachment and autodetachment channels. An actual dynamical calculation would, however,
require the coupling of the electron’s motion with that of the bound molecular atoms and is
currently not possible for large polyatomics. On the other hand, the present findings make the
above evolution a reasonable conjecture.
Additionally, the existence of several other resonances at higher energy, but still within a realistic range of electron energies (e.g. up to 50 000 K at most), has been characterized by temporary anionic states where the excess electron densities are localized on the polycondensed rings and not on any of the terminal H atoms. This indicates that the excess energy release on electron attachment will have to chiefly occur via intramolecular vibrational rearrangement (IVR) paths since radiative stabilization would not be competitive with the electron detachment process or with other fragmentating attachment channels. As a consequence, the rearrangement paths would be conceivably guided by the extent and strength of spatial couplings between the metastable electron and the atomic network of the neutral molecular partner. Since, in the present case, we found that all the resonances exhibit excess electron wavefunctions with a node on the molecular plane (due to their $\pi^*$-type character) and with no extra density on the terminal H atoms, it is reasonable to assume that IVR processes will not be very efficient and would not be able to lead to ring-breaking processes. On the other hand, the possible release of one of the external H atoms could occur by resonant tunnelling of the latter (e.g., see also [30, 31]) that would leave a stable anion of the dehydrogenated anthracene.

In conclusion, the analysis of the scattering features at low energy from electron collision events indicates rather strongly that the anthracene molecule, when found, could possibly evolve into two types of molecular anions: the unfragmented \([\text{An}]^-\) species and various types of dehydrogenated anions \([\text{An}–\text{H}]^-\), all very likely to stem from the currently identified metastable anionic intermediates.

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References
