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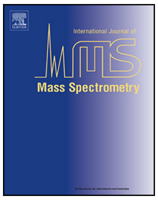

Attaching electrons to a 3-ring acene: Structures and dynamics of anions in gas-phase anthracene

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This work is affectionately dedicated to Prof. Dr. Tilmann Maerck, a good friend and a great scientist.

ABSTRACT

The existence of metastable anions, formed in the gas-phase by electron scattering off anthracene molecules is investigated via both quantum dynamics calculations and quantum chemical structure calculations. The differences in the sign of the experimentally known electron affinity (EA), positive small for anthracene, and of its values obtained from different methods employed to estimate it in the present work, are shown to be related to level of computations and to the increasing effects from electron–electron dynamical correlation (as well as the all-important bound-continuum exchange) which act to selectively stabilize the attaching electron in this three-ring acene, the first of the polycyclic aromatic hydrocarbons (PAHs) to exhibit stable anions in the gas phase.

1. Introduction

In the early 1970s, the first spectra of some of the brightest infrared sources in the interstellar and circumstellar spaces revealed the unexpected presence of strong emission features from 3.3 to 8.6 μm (e.g.: see [1]) and references given therein). Since then, several types of observations have shown that these features dominate the spectra of almost all objects, including the H II regions, the reflection nebulae, the young stellar objects, the post-AGB objects and the general interstellar medium (ISM) of the Milky Way and of other galaxies (e.g. see Ref. [2] as an example). It is now well established that these IR emission features are due to the vibrational relaxation of UV-pumped polycyclic aromatic hydrocarbons molecules (PAHs) with sizes ranging from 20 to 100 carbon atoms [3]. Furthermore, rapid advances in computational power and experimental resolution have allowed to suggest in the forest of diffuse, unidentified infrared bands (DIBs) the presence of radicals, charged cationic and anionic species as the IR emitters of choice [4–6].

It is therefore of great current interest to be able to understand, at the molecular level, the sequence of processes which can lead to photoionization or to chemical charge exchange on such systems, as well as to the formation of stable and metastable anions by interactions with the environmental electrons [7].

The possible role of free electrons generated by photoionization of the most abundant species of the ISM (H, D, He) has been discussed many times in the literature over the years [8,9] and our group has analyzed in some detail the end-line of such processes when applied to aromatic species like coronene [10], benzene [11], and phenyl [12], where in fact the possible role of transient negative ions (TNIs) in the continuum has been shown to be linked to the stabilization of anionic species with significant sizes of attachment rates [13]. Such possibilities are particularly intriguing for the anthracene molecule since its capability of forming stable anionic species sits at the apposite side of the energy range with respect to its smaller predecessors in the series: benzene and naphthalene have, in fact, negative EA values [14]; moreover, the anthracene's EA is shown by experiments to be rather small: +0.530 ± 0.005 eV [15,16]. Hence, while the smaller acenes are expected to only have metastable anions, which then decay either by autodetachment or by dissociative electron attachment (DEA) driven by more complicated fragmentations [14], anthracene only forms barely bound anions after the metastable attachment of near-threshold electrons [17].

Additionally, recent high-level computational studies of condensed rings aromatic acenes [18,19] have pointed out that, from the analysis of the composition of their multiconfigurational wavefunctions, the topologies of the natural orbitals in symmetry-unrestricted CASSCF calculations indicate that such systems exhibit

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a ^1A_g closed-shell electronic ground state and, at the same time, indicate the diradical and polyradical character of the acenes with more polycondensed aromatic rings. In other words, the highest occupied molecular orbitals require increasingly smaller amounts of energy for the singlet–triplet gap as the acenes get bigger in size, thus causing single occupancy of both the highest occupied natural orbital (HONO) and the lowest unoccupied natural orbital (LUNO). This diradical character therefore changes the correlation contributions as the anion is being formed, i.e. the corresponding extra-electron will become, or will not manage to become, a bound electron in the stable anion depending on the extent of the correlation effects included in the calculations. The previous discussion therefore points at the computational difficulties which exist for the realistic evaluation of the structural features of the bound anions of anthracene as well as for the reliable assessment of the dynamics for electron attachment rates to this system, i.e. on the effective role that the formation of resonant, metastable anions plays on controlling the final efficiency of low-temperature attachment rates to PAHs, a feature of importance for their modelling in dark clouds and in circumstellar envelopes [13].

The present study therefore intends to revisit our earlier study on the anthracene metastable anions [17] by employing increasingly more sophisticated treatments of correlation forces in both quantum chemistry studies and scattering calculations. In the latter instance we shall also improve on the treatment of bound-continuum exchange interactions. We shall therefore analyse in some detail the possible existence of metastable anions for anthracene as well as the actual structures of a bound anion in its ground electronic state. The structural features of the electronically excited anionic configurations will be also linked with the resonant anionic complexes obtained from quantum scattering calculations in the low-energy range.

The following section will briefly describe the cross-section quantum calculations. We shall employ a multichannel scattering approach used by us many times before so that only a brief outline of the method will be given, together with relevant references where further details could be obtained. We shall also report here the details of the new and varied structure calculations employed for the analysis of its anions.

Section 3 shall give our results from all calculations and compare our findings from both the dynamics and structure studies, while Section 4 will summarize our conclusions.

2. Computational methods

2.1. An outline of the scattering calculations

Since the quantum dynamical equations used for this study have been described in detail many times before [20,21], we only present here a brief outline of it and refer the reader interested in more details to those publications.

The total $(N+1)$-electron wave function is constructed as an antisymmetrized product of one-electron wave functions obtained from Hartree-Fock orbitals of the neutral ground state molecular target, considering the N bound electrons in their ground-state configuration during the whole scattering process: thus, no core-excited resonances are allowed in our modelling. Each of the three dimensional wave functions describing a given electron is then expanded around the molecular center of mass (Single Center Expansion, SCE) so that for each of the bound molecular electrons we have

$$\phi_i^{p\mu}(r,\hat{\mathbf{r}}|\mathbf{R}) = \sum_{\ell h}\frac{1}{r}u^{p\mu}_{\ell h,i}(r|\mathbf{R})\chi^{p\mu}_{\ell h}(\hat{\mathbf{r}}) \tag{1}$$

and for the scattered particle

$$\psi^{p\mu}(r,\hat{\mathbf{r}}|\mathbf{R}) = \sum_{\ell h}\frac{1}{r}f^{p\mu}_{\ell h}(r|\mathbf{R})\chi^{p\mu}_{\ell h}(\hat{\mathbf{r}}) \tag{2}$$

In the above SCE representations, the superscripts label the μth irreducible representation of the pth symmetry group to which the molecule belongs at the fixed nuclear geometry $\mathbf{R}$, and the subscripts refer to each of the angular channels under considerations; the radial coefficients $u^{p\mu,\alpha}_{\ell h}$ for the bound molecular electrons are numerically evaluated by a quadrature on a radial grid [22]. The angular functions $X^{p\mu}_{\ell h}$ are given as

$$\chi^{p\mu}_{\ell h}(\hat{\mathbf{r}}) = \sum_{m} b^{p\mu}_{\ell mh} Y_{\ell m}(\hat{\mathbf{r}}). \tag{3}$$

where the coefficients $b^{p\mu}_{\ell mh}$ are described and tabulated in Ref. [23]. The ensuing coupled partial integro-differential quantum scattering equations evaluate the unknown radial coefficients $f^{p\mu}_{\ell h}$ for the (N+1)th continuum electron:

$$\left[\frac{d^2}{d^2r} - \frac{\ell(\ell+1)}{r^2} + 2(E-\epsilon)\right] f^{p\mu}_{\ell h}(r|\mathbf{R})$$
$$= 2\sum_{\ell' h'}\int dr' V^{p\mu}_{\ell h,\ell' h'}(r,r'|\mathbf{R}) f^{p'\mu'}_{\ell' h'}(r'|\mathbf{R}) \tag{4}$$

where E is the collision energy and ϵ is the electronic eigenvalue for the ground state energy so that $k^2/2 = E - \epsilon$, k being the asymptotic momentum of the elastically scattered electron.

For a target which has a closed shell electronic structure, with $n_{occ} = N/2$ doubly occupied molecular orbitals, the static-exchange (SE) potential has the following form:

$$V_{SE} = \sum_{\gamma=1}^{M}\frac{Z_\gamma}{|\mathbf{r}-\mathbf{R}_\gamma|} + \sum_{i=1}^{n_{occ}}\left(2\hat{J}_i - \hat{K}_i\right) = V_{st} - \sum_{i=1}^{n_{occ}}\hat{K}_i \tag{5}$$

where $\hat{J}_i$ and $\hat{K}_i$ are the usual static potential and the non-local exchange potential operator, respectively. We further model the correlation and polarization effects via the following optical potential:

$$V_{cp} = V_{Corr}(r), \quad r \le r_{match} \tag{6}$$

$$V_{cp} = V_{Pol}(r), \quad r > r_{match} \tag{7}$$

employing density related models which have been described before for the short-range correlation effects [20,21]. We then generate the exchange interaction with the Free-Electron-Gas-Exchange model proposed by Hara (HFEGE [24]), V_{HFEGE}:

$$V_{HFEGE}(\mathbf{r}|\mathbf{R}) = -\frac{2}{\pi}K_F(\mathbf{r}|\mathbf{R})\left[\frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left(\frac{1+\eta}{1-\eta}\right)\right]. \tag{8}$$

When dealing with closed-shell systems as the present case, the electronic density $\rho(\mathbf{r}|\mathbf{R})$ is given as

$$\rho(\mathbf{r}|\mathbf{R}) = \int |\det||\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\ldots\phi_{n_e}(\mathbf{x}_{n_e})|||^2 \quad d\mathbf{x}_2 \quad d\mathbf{x}_3\ldots d\mathbf{x}_{n_e} \tag{9}$$

is evaluated by assigning 2 as the occupation number of each of doubly occupied MOs in the neutral targets of the present study. In other words, the scattered electron initially interacts with the neutral molecular targets at the fixed geometry of their equilibrium structures. This final potential provides the so-called static-model-exchange-correlation-polarization (SMECP) potential accounting for the interaction forces between the impinging free electron and

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