Resonance Capture of Electrons by Molecules near the Threshold of Ionization

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Abstract—Physical processes that result in the production of positive and negative ions are found to be interrelated. Evidence of this relationship is a correlation between the energies of molecule ionization and resonance production, found for a number of polycyclic aromatic hydrocarbons via the mass spectrometry of negative ions in resonance electron capture.

INTRODUCTION

Positive ions are produced if a molecule is bombarded with electrons whose energy E_e exceeds that of ionization. Electrons with lower energies E_e ranging from 10–15 eV to ~0 eV are captured by molecules to produce negative ions (NIs) that exist for a certain period (resonances, temporary, or transient NIs). Resonance electron capture (REC) occurs at strictly defined energies corresponding to the discrete energy levels (orbitals) or transitions between them that are characteristics of every compound.

Three mechanisms of the deceleration and capture of electrons are known [1, 2]: (1) vibrationally-excited (or nuclear-excited) Feshbach resonance (VEFR), which drives the capture of the slowest, thermal electrons ($E_e \sim 0$ eV) by molecules with positive electron affinity (EA); (2) the shape resonance (SR) characteristic of faster incident electrons ($0 < E_e < \sim 4$ eV), created by the potential barrier that retains the incoming electron; and (3) electron-excited (or core-excited) Feshbach resonance (EEFR), where the incident electron expends its energy on electronic excitation of a molecule to be bound as part of a molecular NI, which is energetically more stable than the (parent) electron-excited neutral molecule.

The EEFR electron configuration is such that the captured electron is placed with the antiparallel spin on the same vacant molecular orbital (MO), to which own electron of the molecule was excited. From the formal viewpoint there is no difference between the ways in which this configuration was obtained: the electron with freely-directing spin is added either to a singlet- or to triplet-excited molecular predecessor (i.e., to a molecule in which electron spins on partially occupied MOs are oriented in the same direc-

tion). The energetically lower-lying triplet-excited parent states appears to be more preferable, thus the energies of the EEFR would seem that they should correlate with triplet states. However, such expectations have failed [3, 4], and theoretical calculations cast doubt on whether valence excited states can ever form bound states with additional electrons [5]. Over time, for many classes of compounds [3, 4, 6–10] a strict correlation has been revealed between energies of NI resonance peaks and the energies of the first lowest-energy bands of optical UV absorption spectra, which are known to be of a singlet-excited nature. This correlation was associated with the existence of another, fourth type of resonances, referred to as inter-shell [11]. An additional electron is positioned on the electron configuration of these electron-excited resonances not on the same (valence) orbital but on another (quasi-Rydberg) orbital [11]. It should be noted that the configuration in which electrons are excited to and captured on different vacant levels was known earlier for electron-excited type-II shape resonances [2]. Distinctive features of inter-shell resonance are that they (1) arise in the fields of singlet-excited states with positive electron affinity [5] and (2) only emerge for molecular objects whose dipole momentum μ exceeds critical value $\mu_{min} = 1.625$ Debye, which was predicted as early as the 1950s by E. Fermi [12] (according to refined data, $\mu_{min} = 2.4$ Debye [13]). It was found later that the REC supported by dipole-bound states is characteristic of not only electron-excited molecules but of molecules in the ground state as well, an observation that has recently begun attracting the interest of researchers [14–16].

In this work, we report an observation for NIs that form as a result of the resonance capture of electrons at energy E_e, which is close to that of molecule ioniza-
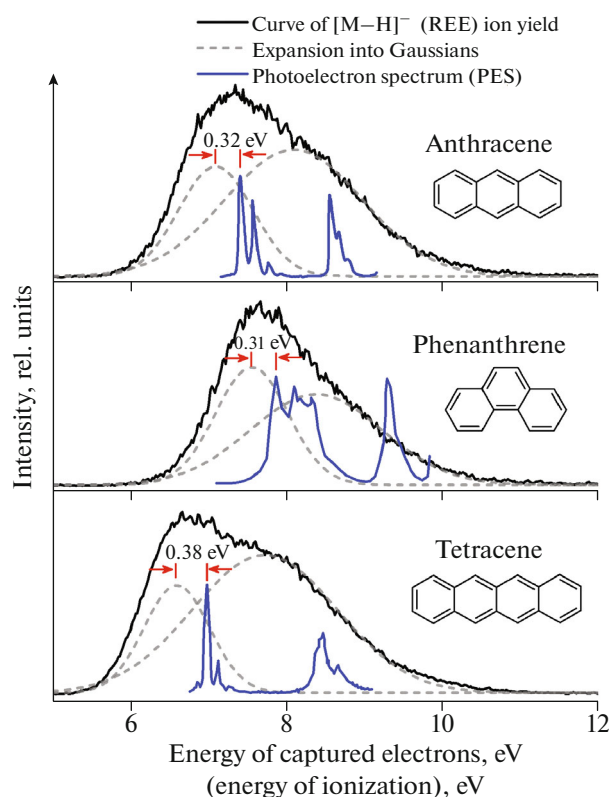
Fig. 1. Resonance curves of the effective yield of negative ions $[M-H]^-$ from some PAH molecules as a function of electron energy E_e (data of [20]) and photoelectron spectra of the same compounds obtained using ultraviolet photoelectron spectroscopy (PES) (digitalized data of [27, 29, 30]; the scale of ionization energy is matched with that of E_e).

tion (i.e., at an energy much higher than the minimal energies sufficient for optical excitation). This phenomenon was discovered in exploring polycyclic aromatic hydrocarbons (PAHs). The considered set of PAHs included cata-condensed ones whose structure contained three to five condensed benzene rings: anthracene and its isomer phenanthrene; tetracene and its isomers, tetraphen, chrysene, and triphenylene; and pentacene and its isomer, dibenzo[a,c]anthracene.

RESULTS AND DISCUSSION

According to the data from experiments [17–21] carried out by the method of resonant electron capture negative ion mass spectrometry (RECNI MS), the resonance capture of electrons by PAH molecules occurs in a wide range of electron energies: $E_e = 0$– 12 eV. Like PAH precursors benzene and naphthalene, phenanthrene and triphenylene do not form long-lived molecular NIs. This confirms the data on the negative or too small positive adiabatic electron affinity of these molecules [21, 22]. The remaining PAHs, whether cata- or pericondensed molecules, form long-

lived (detectable by mass spectrometry) molecular NIs (M^-) at the thermal energy of electrons ($E_e \sim 0$ eV) due to the VEFR [21] mechanism.

In compounds with stronger adiabatic electron affinity $EA_a > 0.7$ eV (tetracene, pentacene, phenyl-anthracene, and perylene), M^- ions are also observed at higher, epithermal energies E_e of up to ≈ 4 eV. In [21], tetracene was used as an example to show that the energies of the maxima in the series of resonance M^- peaks in the range of $0 < E_e < 4$ eV are very close to the energy of π^* shape resonances detected via electron transmission spectroscopy [23]. SRs are considered to be short-lived with respect to the autodetachment of an electron with the typical lifetime of $\tau_a = 10^{-15}$–10^{-10} s [2]. In this case, however, they become long-lived ($\tau_a > 10^{-6}$ s), due presumably to a radiationless transition (internal conversion) to ground electron state M^-, which is accompanied by the conversion of excess electron energy into vibrational energy [24]. This can be interpreted as a conversion of SR into VEFR.

The resonance capture of electrons with higher energies $E_e > 4$ eV results in the dissociative decay of PAHs. Resonance peaks are in this case observed on the effective yield curves (EYCs) of fragment ions [25, 26]. The only channel of M^- fragmentation for the entire series of PAHs is the detachment of a hydrogen atom with an intense release of de-protonated products $[M-H]^-$ in high-energy range $E_e = 5$–12 eV [17, 18, 20]. As an example, Fig. 1 shows the EYCs of $[M-H]^-$ ions from some PAHs as a function of E_e. The EYC of $[M-H]^-$ ions for other compounds in the considered series are generally very similar, but the positions of the maxima on the E_e scale differ.

The average energy of maximum yield of these ions from compounds throughout the considered series lies around E_e 7.5 eV. A broad, asymmetric, and complicated profile suggests the presence of no fewer than two resonance peaks below the EYC envelope; this becomes apparent when they are presented as decomposition to Gaussian functions (see Fig. 1). The mechanism of electron capture for these resonances in PAHs has yet to be identified, so we performed a comprehensive analysis using available data obtained by complementary methods.

The energy positions of the pairs of resonance peaks discerned in this way vary broadly from compound to compound. This is illustrated by the energy chart in Fig. 2, which shows the positions of their maxima. The same chart also shows the positions of two or three lowest-energy bands in the photoelectron spectra (PE spectra) of corresponding compounds (see the example of segments of PE spectra displayed in Fig. 1 along with the EYC of $[M-H]^-$ ions) [27–30]. The chart shows that the energies of maxima of the first
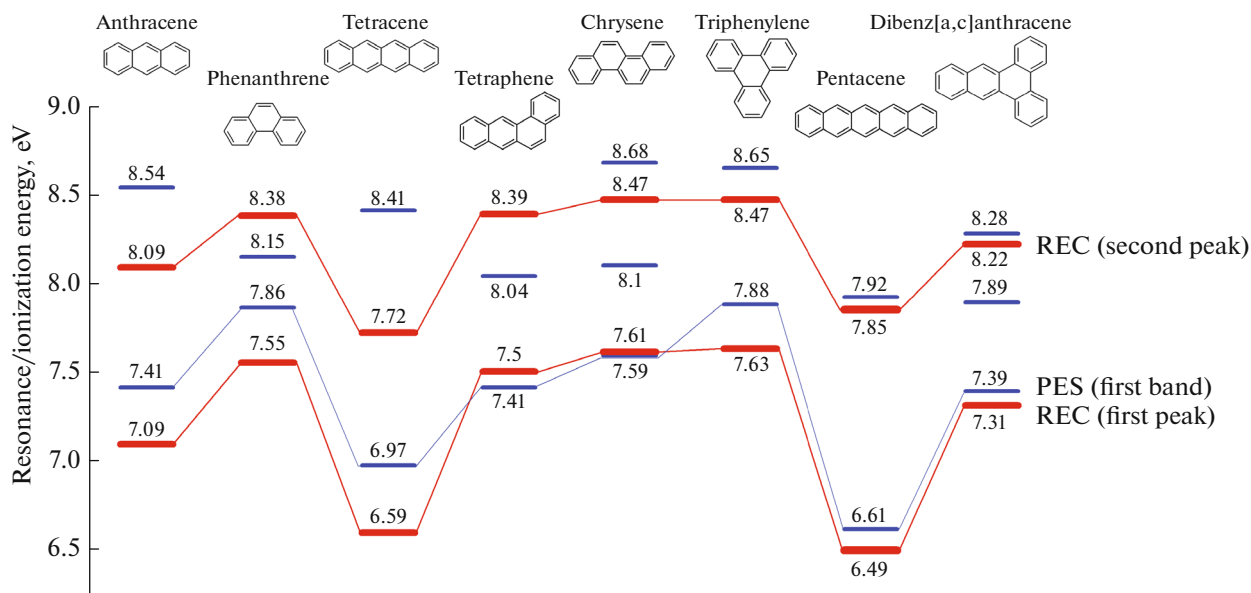
Fig. 2. Correlations between the energies of high-energy resonance states of negative PAH ions (data of RECNI MS [20]) with lower energies of ionization (PE spectra [27−30]).

resonance peaks correlate with the first (lower) ionization energies of molecule being 0.1−0.4 eV[1] lower. Figure 2 also shows a similar correlation for the second resonance peaks of the Gaussian deconvolution, which are 0.5−1.3 eV higher than the first bands of the PE spectrum. However, the correlation between the second and third bands of the PE spectrum is not apparent (see Fig. 2).

Data from optical UV absorption spectroscopy [32−36] show that electron (triplet) excitation can occur in PAH molecules at energies as low as 1.5−2 eV. There is no doubt that the considered resonances in the high-energy range of 5−12 eV in PAHs can be identified as electron-excited resonances [2]. Such resonance occurs if an electron from an occupied MO is excited to a vacant orbital with the concurrent capture of an incident electron on the same or other vacant MO. As shown above (Figs 1 and 2) for PAH molecules, the energies of the considered resonances are very close to the thresholds of molecule ionization. We may therefore conclude that these resonances are due to the capture of an electron by a highly-excited molecule, for which the energy of the incident electron is too low to induce ionization. Since the correlating first (lowest in energy) PE spectrum band is associated with the detachment of an electron of the molecule from an highest occupied molecular orbital (HOMO), the excitation of an electron of a PAH molecule presumably comes from the (π-type) HPMO to

a higher-lying vacant quasi-Rydberg orbital (2s or 3s) that is immediately adjacent to ionization continuum. The incident extra electron is probably captured to the same quasi-Rydberg orbital, which is then twice occupied. Such electron NI configurations are quite viable, since parent quasi-Rydberg electron-excited states can contain additional electrons in a bound state [5]. The correlation diagram (Fig. 2) shows the considered resonances are mostly 0.1−0.4 eV lower than the corresponding PE bands (i.e., below the "underionized" highly-excited states of molecules), that may serve as an indication of the positive electron affinity *EA* of the latter.

CONCLUSIONS

Using PAH as an example, we found a correlation between characteristic energy parameters of the production of positive ions and the resonance formation of negative ions. The significance of the energy of molecule ionization over the energy position of the resonances clearly indicates the existence of a relationship between (grandparent) positive ions, (parent) electron-excited molecules, and (daughter) electron-excited resonances [37]. Based on this correlation for the PAH molecules, we determined the most probable electron configuration of the resonances (temporary-living NIs) that form in high-energy region $E_e = 5$−12 eV, and thus the mechanism of the resonance capture of electrons: the electron-excited Feshbach resonance.

PAHs are of practical interest, especially in organic electronics [38]; on the other hand, they are hazardous to human health and are thus monitored in the environment using a variety of analytical means. It has been shown for many classes of compounds that the

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[1] A similar correlation with PE spectra was discovered recently for a series of high-energy resonances in the REC spectrum of benzoic acid [31]. For the correlation to be observable, however, the PE spectra were shifted to lower energies in the E_e scale by a considerably higher value of 3.9 eV.

RECNI MS technique is a powerful tool for structural and analytical studies [25, 26, 39−43]. A critically important condition for this technique to be used as part of gas chromatography combined with mass spectrometry (GC/MS) [44−48] for chemical analysis is the choice of the optimal energy of ionizing electrons that ensures the obtainment of the strongest electron signal and the characteristic NI mass spectra. Since not all molecules in the PAH series form long-lived molecular NIs, mass-spectrometric identification of these compounds can be based on detecting de-protonated molecules [M−H]⁻. Our analysis of the energy position of resonance [M−H]⁻ peaks allows us to choose the optimum energy of ionizing electrons for recording 2D REC NI mass spectra for the entire PAH series: 7.5 eV.

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