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Internal Conversion as the Main Stabilization Mechanism for Long-Lived Negative Molecular Ions

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Abstract—The temperature dependence of the mean lifetime of Ph–N=N–Ph[−] azobenzene negative molecular ions on the captured electron energy is studied with a static mass spectrometer by the method of resonance electron capture. A family of respective experimental dependences is calculated accurate to 2–10%. It is shown that the molecular anions in the epithermal electron energy range can be stabilized through internal conversion, namely, a series of fast radiationless transitions without change in the multiplicity.

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INTRODUCTION

It is known that in the case of thermal electrons ($0 \leq \varepsilon \leq kT$), the vibrational Feshbach resonance is the basic mechanism of generating long-lived (more than 1 μ s) negative molecular ions (NMIs). Under such conditions, the NMI lifetime to the electron autodeachment (τ_d) is directly related to molecular anion excess vibrational energy E_i [2], which, in turn, is a sum of three terms: kinetic energy ε of an incident electron, adiabatic electron affinity EA_a , and the initial margin of vibrational energy E_v in a target molecule. Being distributed over vibrational degrees of freedom, the excess energy produces an electron autodeachment delay mechanism; that is, some time must elapse before the excess energy accumulates on the degree of freedom that is responsible both for the formation of an autodeachment state and for its decay [1, 3]. It is generally accepted that exactly this mechanism comes into effect when long-lived NMIs result from thermal electron capture by molecules with a positive electron affinity.

Unlike the case of thermal electron capture, the mechanism behind the generation of long-lived NMIs due to the capture of “epithermal” electrons ($\varepsilon \gg kT$) has not been fully understood. In fact, all resonances known in this energy range are short-lived. The lifetime of shape resonances, which depends on the time of electron tunneling through a potential barrier, equals 10^{-15} – 10^{-10} s [4], while the lifetime of electronically excited Feshbach resonances cannot exceed a characteristic radiative time on the order of 10^{-8} s. Obviously, a fast relaxation mechanism is needed to convert the initially short-lived state of NMIs to a long-lived state.

Several hypotheses for such a relaxation mechanism have been put forward: (i) electron capture

induced by the electronically excited Feshbach resonance (EEFR) with subsequent NMI stabilization via a radiationless transition to the ground electronic state [5, 6], (ii) electron capture by the shape resonance mechanism with subsequent internal conversion of NMIs to the ground electronic state [7, 8], (iii) EEFR-induced electron capture with subsequent ion doublet–ion quartet transformation through inter-combinative conversion [9], and (iv) electron capture with plasma mode excitation [10]. Hypotheses (i)–(iii) explain the existence of long-lived NMIs in several (most often two) resonance peaks in the energy interval from 0 to ~ 4 eV. Hypothesis (iv) substantiates the extremely wide and almost continuous range of electron energies (0–15 eV) in which long-lived NMIs of fullerenes [11, 12] and their substituted analogs [12, 13] arise in the gas phase. In [10], an essentially new type of resonance in the cross sections of electron scattering by molecules is discussed: an incident electron spends nearly all energy on the excitation of plasma oscillations (plasmons) and, having an almost zero energy, is captured by a molecule. It is obvious, however, that such a mechanism by no means provides the existence of long-lived NMIs: the fact is that the plasmon lifetime is on the order of 10^{-15} – 10^{-14} s [14]. Unfortunately, the authors of this model say nothing of what happens with fullerene anions after the electron capture. At the same time, they recognize [15] that the electron autodeachment rate constant is entirely determined by the excess energy of NMIs. This means that it is the ground electronic state that is long-lived in anions of fullerene (and its derivatives).

The above analysis of experimental data demonstrates that however important the mechanism of initial electron capture, the final long-lived electronic state of NMIs, rather than their initial state, is respon-

Table 1. Mean lifetime τ_a of Ph–N=N–Ph[−] ions in the maxima, ε_m , of resonance states (from electron transmission spectroscopy data [21])

ε_m , eV	τ_a , μ s		
	363 K	423 K	483 K
0	150	150	134
0.88	42	36	30
1.29	17.5	17.5	17.5

sible for the anomalously long lifetime of molecular anions in the epithermal range. Most authors think that the ground electronic state is the final state. It results from the initial short-lived electronic state through a series of fast (10^{-14} – 10^{-12} s [16, 17]) radiationless transitions without change in the multiplicity. In this case, energy losses by radiation are not observed and the excess energy of NMIs is totally converted to the vibrational energy. The state thus formed is similar to the state of long-lived NMIs arising from the thermal electron capture through the vibrationally excited Feshbach resonance. In addition, this state is akin to the self-ionization state of fragment ions with the vibrational state energy exceeding the electron affinity of radicals [1].

The basic argument in favor of the above mechanism of NMI stabilization is the monotonic and rather fast drop of the electron energy dependence of the NMI mean lifetime [6, 8]. Indeed, if energy losses by radiation are absent, the NMI excess energy grows with the captured electron energy and accordingly the lifetime will decrease. The only serious objection against this argument is the amount of the excess energy. For example, in several resonance states of anthraquinone, it may reach 4 eV [8] (the “effective” vibrational temperature is $T_{ve} \approx 1200$ K) and for NMIs of fullerene and its derivatives, it may be as high as 20 eV [11, 12] ($T_{ve} \approx 1950$ K). Will NMIs with such a high excess vibrational energy be long-lived?

To answer this question, we for the first time studied experimentally and then calculated (in terms of the Illenberger–Smirnov–Kompaneits model [3, 18–20]) the dependences of the azobenzene NMI mean lifetime on the captured electron energy for different temperatures in the collision chamber. The aim of this work was to show that if NMIs are stabilized by means of internal conversion, calculated and experimental families of these curves nearly coincide. Azobenzene molecules were chosen as test objects for two reasons. First, there is still little agreement among researchers about how these molecules produce long-lived NMIs [6, 21]. Second, these “classical” objects have been extensively investigated by other physical methods [21], so that the respective results can be used as references in lifetime computation.

EXPERIMENTAL

The lifetime of Ph–N=N–Ph[−] ions were measured with a MI-1201 static spectrometer adapted for negative ion detection in the resonance electron capture (REC) mode. The detailed description of the spectrometer is given elsewhere [22]. Similar experiments conducted by the method of dissociative electron attachment spectroscopy are described in [23]. In short, a focused beam of quasi-monochromatic electrons is passed through a collision chamber filled with an analyte gas to a pressure sufficient for pairwise collisions. The currents of the resulting negative ions were detected mass-spectrometrically (in a sector magnetic field) in the incident electron energy range 0–15 eV. The half-width of the electron energy distribution at a half-height was 0.4–0.5 eV; the electron current, 1 μ A; and the accelerating voltage, 4 kV. The electron energy scale was calibrated against maxima in the effective yield curves (EYCs) for CF₆[−] ions from SF₆ (0 eV) and C₆H₅[−] ions from C₆H₆ (8 eV).

To measure temperature effects, the chamber was heated to a desired temperature. Analyte molecules reached thermal equilibrium after multiple collisions with the walls of the chamber. The technique for measuring the mean lifetime to autodetachment was described many times [12, 18, 19, 22]. It allows one to measure time τ_a in the interval 1–1000 μ s at collision chamber temperatures ranging from 80 to 220°C.

Quantum-chemical computation was performed in terms of the density functional theory using the Gaussian software suite [24]. The B3LYP functional and standard basis set 6-31G(d) were applied to optimize the geometry of the Ph–N=N–Ph molecule and its anion and calculate their vibration frequencies and force constants.

RESULTS AND DISCUSSION

Figure 1 shows EYCs for Ph–N=N–Ph[−] negative ions and their corresponding neutral component [12] at collision chamber temperatures of 363, 423, and 483 K.

It is easy to see that azobenzene molecules capture electrons in two energy bands with maxima at about 0 and 0.85 eV. It was demonstrated [6, 21] that the latter band consists of three closely spaced resonance states. In the electron transmission spectrum, they show up as two peaks at 0.88 and 1.29 eV [21]. Comparing the EYCs and the electron energy dependences of the azobenzene lifetime, $\tau_a(u)$, one can contrast the resonances and their mean lifetimes (Fig. 2, Table 1).

The family of curves $\tau_a(u)$ has a number of features. First, the lifetime decreases monotonically with increasing energy of captured electrons at a given temperature in the collision chamber. Second, temperature effect $\tau_a(T)$ fades out with increasing resonance energy.¹ Third, at energies above the energy of the

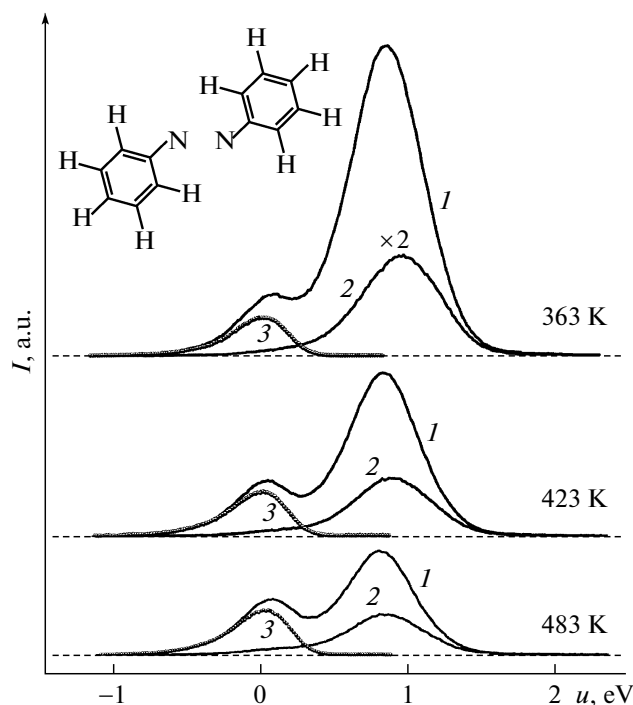


Fig. 1. Experimental EYCs at temperatures of 363, 423, and 483 K in the collision chamber. (1) Current I of long-lived Ph–N=N–Ph[−] azobenzene NMIs vs. energy u in the maximum of the electron energy distribution, (2) dependences $I(u)$ for the Ph–N=N–Ph neutral component, and (3) dependences $I(u)$ for sulfur hexafluoride anions (SF₆[−]) demonstrating the form of the electron energy distribution (shown for comparison).

third resonance, the lifetime of azobenzene NMIs becomes almost independent both of the temperature in the chamber and of the captured electron energy. Fourth, the temperature effect in the maximum of the first resonance is unexpectedly small for thermal electrons: in the interval 363–483 K, it is nearly the same as in the second resonance ($Pt \approx 0.13 \mu\text{s}/\text{K}$) and tends to zero in the interval 363–423 K ($Pt \approx 0$).

The first two features are easy to explain in terms of the above mechanism: NMI stabilization through internal conversion. As energy ε of the captured electron grows, so does excess energy $E_i = EA_a + E_v + \varepsilon$ of the resonance, as a result of which the NMI mean lifetime drops. In this expression, only the second term (energy E_v of target molecule vibrational excitation) depends on temperature. With a rise in the electron temperature, the contribution of this terms decreases. Therefore, the temperature effect fades out to complete disappearance [19]. The third and fourth features

¹ Hereinafter, the amount of the temperature effect at given electron energy ε in given temperature interval ΔT will be described by the expression $Pt = \left(\frac{\Delta\tau}{\Delta T}\right)_{\varepsilon = \text{const}}$, where $\Delta\tau$ is the mean lifetime of NMIs.

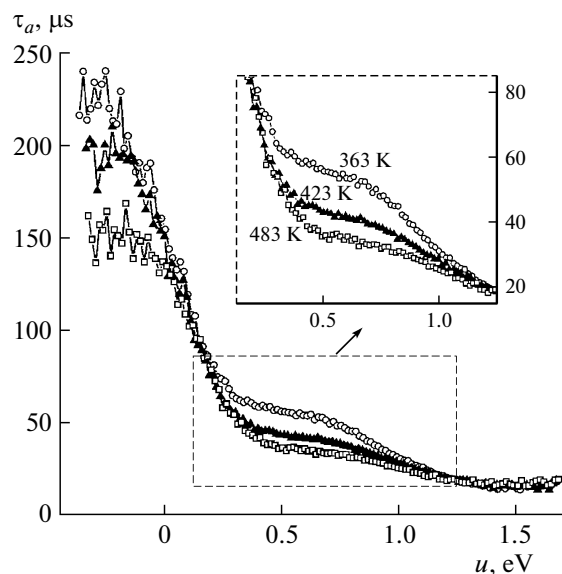


Fig. 2. Experimental time to the autodetachment of the electron from the long-lived azobenzene NMI, τ_a , vs. incident electron energy u (in the maximum of the distribution curve) at different temperatures in the collision chamber.

cannot be explained in simple terms. These effects are “finer” and call for detailed computation. Such computation was carried out in [18–20]. However, the computational accuracy did not suffice to unambiguously indicate the origin of the tail in curves $\tau_a(u)$, which is essentially independent of the chamber temperature and electron energy. As for the minor temperature effect in the case of thermal electrons, we did not observe it before.

MEAN LIFETIME OF AZOBENZENE MOLECULAR ANIONS

The NMI lifetimes were calculated using the Illenberger–Smirnov–Kompaneits model [3]. In terms of this model, the NMI lifetime to electron autodetachment is given by

$$\tau_a = \tau_0 \frac{n(R^-)}{n(R_m)}. \quad (1)$$

Here, τ_0 is the characteristic time of variation of the distribution function over vibrational states, $n(R_m)$ is the number of vibrational states for the nucleus configuration responsible for electron capture, and $n(R^-)$ is the number of vibrational states for the nucleus configuration providing a maximal binding energy of the electron (in other words, the numbers of vibrational states for the molecule and ion, respectively).

For the simplest statement of the model, its basic parameters (the characteristic time of variation of the distribution function over vibrational states, the number of vibrational states in NMIs and in the target molecule as a function of the target’s vibrational state)

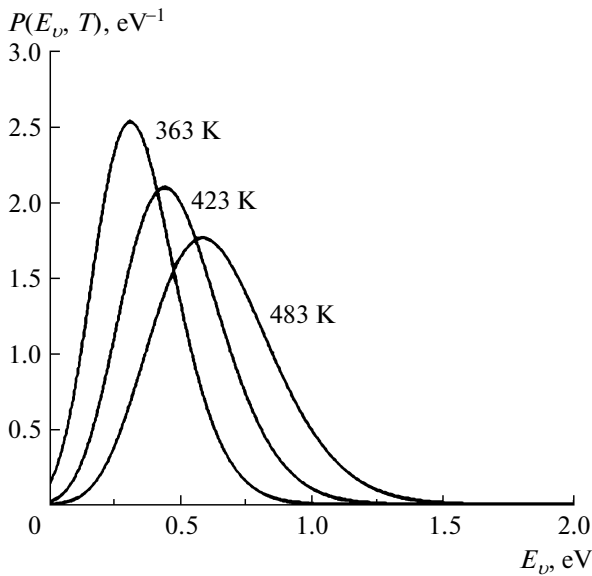


Fig. 3. Initial Boltzmann distribution $P(E_v, T)$ of target azobenzene molecules over the total vibrational energy at different temperatures in the collision chamber.

were determined in [18]. Using this model, it was shown that the decay of NMIs is multiexponential and the NMI lifetime depends on the temperature in the collision chamber and on the size and boundaries of the time window of the experiment (or, in other words, on the observation time). The primary reasons for the multiexponentiality are (i) the Boltzmann distribution of neutral target molecules over vibrational states [18] and (ii) the presence of the instrument distribution function of electron energies in the ion source. The latter reason was taken into account in [19, 20].

In this work, the Illenberger–Smirnov–Kompaneits model was considerably modified. The number of vibrational states of the molecule and ion, $W(E)$, with energies up to E was determined by direct count [25] on a computer in the Mathcad software environment. We used an approximation method to cut the computational time. At the early stage, number $W(E)$ of vibrational states for a small number of oscillators was calculated exactly; then, at each subsequent step, when one more oscillator was involved, function $W(E)$ was approximated by the function

$$W(E) = \exp \left[y_0 + A_1 \exp \left(-\frac{E}{t_1} \right) + A_2 \exp \left(-\frac{E}{t_2} \right) + A_3 \exp \left(-\frac{E}{t_3} \right) \right], \quad (2)$$

where y_0 , A_1 , t_1 , A_2 , t_2 , A_3 , and t_3 are the energy-independent parameters of the approximation.

The desired computational accuracy ($<0.1\%$) was determined at each step of calculation, the final result being checked in two ways: by comparing with (i) reference points at relatively low energies E (for which

computation is still possible) and (ii) the results of the same calculations carried out using the less accurate (about 1%) Whitten–Rabinovitch algorithm [25]. Proceeding in such a way, we managed to determine the number of vibrational states of the molecule and ion through density functions $\rho_n(E)$ and $\rho_i(E)$ of the respective energy states and use the Illenberger–Smirnov–Kompaneits model in the form

$$\tau_a(E_v, \varepsilon) = \tau_0 \frac{\rho_i(EA_a + E_v + \varepsilon)}{\rho_n(E_v + \varepsilon)}. \quad (3)$$

This form, as before, assumes [18] that the autodetachment of a captured electron takes place at an almost zero energy irrespective of its initial energy. The initial Boltzmann distribution of target molecules over the vibrational energy (Fig. 3) was calculated by the formula

$$P(E_v, T) = \frac{\rho_n(E_v) \exp \left(-\frac{E_v}{kT} \right)}{\prod_{i=1}^{3N-6} \left(1 - \exp \left[-\frac{hc\omega_i}{kT} \right] \right)^{-1}}, \quad (4)$$

where N is the number of atoms in molecule, ω_i is the frequency of an i th vibration in a molecule (cm^{-1}), h is the Planck constant, c is the speed of light, and k is the Boltzmann constant.

To calculate the averaged lifetime, it is necessary to know, along with functions $\tau_a(E_v, \varepsilon)$ and $P(E_v, T)$, the NMI formation cross section. Strictly speaking, electron capture cross section $\sigma(\varepsilon, E_{v1}, E_{v2}, \dots, E_{vn})$ depends on many variables: electron energy ε and the energies of $n = 3N - 6$ normal vibrations of the molecule. Amount N_i of resulting molecular anions is proportional to the product

$$N_i \propto \sigma(\varepsilon, E_{v1}, E_{v2}, \dots, E_{vn}) P(E_{v1}, E_{v2}, \dots, E_{vn}, T), \quad (5)$$

where $P(E_{v1}, E_{v2}, \dots, E_{vn}, T)$ is the Boltzmann distribution over vibrational states. In general, it depends on many variables, namely, on the energies of normal vibrations of the molecule and temperature. In such a “multidimensional” representation, the NMI lifetime is impossible to calculate today. In this work, product (5) is approximated as

$$N_i \propto \sigma(\varepsilon) P(E_v, T), \quad (6)$$

where $\sigma(\varepsilon)$ is the electron energy dependence of the capture cross section, $P(E_v, T)$ is the Boltzmann distribution of molecules over total vibrational energy $E_v = \sum_{i=1}^{3N-6} E_{vi}$. The form of functions $\sigma(\varepsilon)$ and $P(E_v, T)$ depends on the electron capture mechanism and therefore differs in the thermal and epithermal ranges of electron energies.

We think that generally the $P(E_v, T)$ versus E_v dependence in the thermal range has a threshold: $P(E_v, T) = 0$ at $0 \leq E_v \leq E_{vt}$. In approximation (6), the threshold is embodied in the specific (latent) dependence of σ on E_v . The calculation of vibrational fre-

quencies (B3LYP/6-31G(d)) show that the optimal geometries of an azobenzene molecule and an azobenzene NMI belong to the same point symmetry group C_{2h} and also that the molecule and NMI have almost the same normal vibrational frequencies ω_i and respective normal coordinates Q_i . For instance, Fig. 4 demonstrates typical sections of the potential energy surface (PES) for the azobenzene molecule and its respective NMI: Q_1 (totally symmetric vibration) and Q_2 (non-totally symmetric vibration).

These sections, constructed using the calculated force constants and the adiabatic electron affinity of the azobenzene molecule (EA_a), are normal parabolas. It is seen from Fig. 4 that after the electron capture, the equilibrium position of the normal totally symmetric vibrations in the NMI shifts (coordinate Q_1) compared with the molecule. At the same time, the equilibrium positions of the nuclei of the non-totally symmetric vibrations (coordinate Q_2) remain unchanged. According to the energy conservation law, the capture of an electron with an almost zero energy is expected to increase energy E_v in the NMI by EA_a compared with the molecule. Then, according to the Frank–Condon principle, transitions not changing vibrational quantum number ν will be the most probable for non-totally symmetric vibrations, while transitions changing ν will be the most probable for totally symmetric ones. This means that only totally symmetric vibrations may increase the vibrational energy to a level necessary for the vertical capture of a thermal electron. Moreover, the amount of this increase explicitly depends on the initial vibrational energy of the molecule. For example, when an azobenzene molecule captures a thermal electron that is in the ground vibrational state, energy E_v grows by as little as 0.21 eV. For azobenzene, $EA_a = 1.378$ eV and therefore the process being discussed may take place only for non-vertical capture the probability of which rapidly drops with increasing quantum number ν . This example substantiates the assumption of the existence of non-zero threshold energy E_{vt} for azobenzene molecule vibrational excitation. From the sections of the ion and molecule PESs constructed along all the normal coordinates, we estimated E_{vt} for an azobenzene molecule. It turned out that this energy falls into the interval 0.2–0.5 eV.² The value of E_{vt} and the form of the $P(E_v, T)$ curve at $E_v > E_{vt}$ were refined based on the target molecule initial Boltzmann distribution by varying parameters β and $E_{v, \max}$. Here, $E_{v, \max}$ is the energy of the maximum in the $\beta P(E_v, T)$ curve and β is the aspect ratio. As has been mentioned above, ther-

² If threshold energy E_{vt} is sufficiently high (the PESs of NMIs shift relative to those of molecules insignificantly), the capture of thermal electrons will be improbable even if the temperature of target molecules is very high. This may be a reason why some molecules with a high positive electron affinity do not capture thermal electrons, as exemplified by a para-benzoquinone molecule ($EA_a = 1.89$ eV) [8].

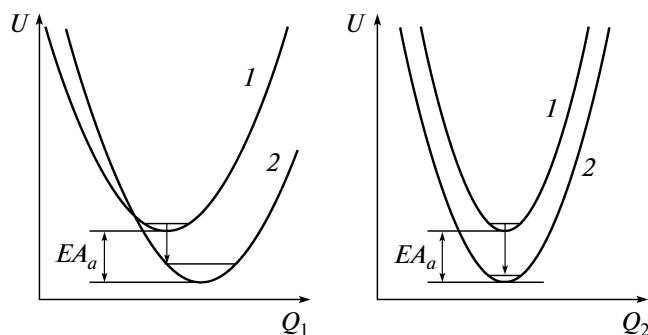


Fig. 4. Typical sections of the PESs for the (1) azobenzene molecule and (2) azobenzene NMI along normal coordinates Q_1 (totally symmetric vibration) and Q_2 (non-totally symmetric vibration). EA_a is the adiabatic electron affinity. The vertical capture of a thermal electron by an azobenzene molecule that is in the ground vibrational state is shown by an arrow.

mal electron capture cross section $\sigma(\varepsilon)$ can be fairly accurately approximated by the δ function. Therefore, $\sigma(\varepsilon)$ in this energy interval was simulated by a normalized rectangular function about 10^{-5} eV wide (pseudo- δ function).

In the epithermal energy range, electrons are captured by the shape resonance mechanism [21]. An extra electron is temporarily held by the molecule owing to a combination of attractive forces (polarization and exchange interaction) and repulsive forces [1]. Then, as we think, the initial vibrational excitation of a target molecule does not have a considerable influence on the NMI generation cross section and therefore the form of the $P(E_v, T)$ curve coincides with the initial Boltzmann distribution of target molecules over vibrational states. In this energy range, electron capture cross section $\sigma(\varepsilon)$ is simulated by a superposition of Gaussian curves over the spectrum of transmitted electrons [21]. The values of σ_{\max} and ε_{\max} in the maxima of respective resonances and the FWHM values of the resonance peaks are summarized in Table 2.

Possible competition between the processes of electron autodetachment and internal conversion in the epithermal energy range (from the time of generation of an NMI to the time of its transition to the ground electronic state) was taken into account by introducing parameter α . With parameter α , we took into account the fraction of anions that “have survived” into the transition to the ground electronic state (provided that these competing channels are independent of each other). With this in mind, the final formulas for the mean lifetime take the form

Table 2. Calculated parameters and the respective method of computation

Calculated parameters					Calculation method
Vibrational frequencies of the azobenzene molecule and anions					Gaussian [24], B3LYP/6-31G(d) method, scaling [26] over IR spectrum [27]
$EA_a = 1.378$ eV					Photoelectron spectroscopy data for Ph–N=N–Ph [−] anions [28]
$t_1 = 27.9$ μs, $t_2 = 6.7$ μs					Calibration with SF ₆ [−] ions [29]
$f(\varepsilon, u)$					Simulated from the EYC for SF ₆ [−] ions [19, 20]
Electron capture cross section in the epithermal energy range					Simulated by a superposition of Gaussian curves taken from the electron transmission spectrum [21]
σ_{\max} , a.u.	4.07	3.325	5.077	2.0	
ε_{\max} , eV	0.8	0.98	1.24	1.98	
FWHM, eV	0.231	0.283	0.518	0.471	
$\rho_i(E), \rho_n(E)$					Direct computation [25]
$P(E_v, T)$	Thermal energy range				Found from target molecule initial Boltzmann distribution $P(E_v, T)$ by varying parameters $E_{v, \max}$ and β , where $E_{v, \max}$ is the energy of maximum in the $\beta P(E_v, T)$ curve and β is the aspect ratio
	Epithermal energy range				Calculated by formula (4)
$\tau_0 = 444.8$ fs					Estimated as the frequency-averaged lifetime of one vibration in an NMI [18]. Adjustable parameter
$\alpha = 1$					α , adjustable parameter

$$N_{i2}(T, u) = \int_0^{\varepsilon_i} \int_{E_{v1}}^{\infty} N_0 j f(\varepsilon, u) \sigma(\varepsilon) P(E_v, T) \times \exp\left(\frac{-t_1}{\tau_a(E_v, \varepsilon)}\right) dE_v d\varepsilon \quad (7)$$

$$+ \alpha \int_0^{\infty} \int_{\varepsilon, 0}^{\infty} N_0 j f(\varepsilon, u) \sigma(\varepsilon) P(E_v, T) \exp\left(\frac{-t_1}{\tau_a(E_v, \varepsilon)}\right) dE_v d\varepsilon,$$

$$N_{i1}(T, u) = \int_0^{\varepsilon_i} \int_{E_{v1}}^{\infty} N_0 j f(\varepsilon, u) \sigma(\varepsilon) P(E_v, T) \times \exp\left(\frac{-(t_1 - t_2)}{\tau_a(E_v, \varepsilon)}\right) dE_v d\varepsilon \quad (8)$$

$$+ \alpha \int_0^{\infty} \int_{\varepsilon, 0}^{\infty} N_0 j f(\varepsilon, u) \sigma(\varepsilon) P(E_v, T) \exp\left(\frac{-(t_1 - t_2)}{\tau_a(E_v, \varepsilon)}\right) dE_v d\varepsilon,$$

$$t(T, u) = \frac{t_2}{\ln\left(\frac{N_{i1}}{N_{i2}}\right)} \quad (9)$$

In formulas (6)–(8), t_1 and t_2 are the times ions take to reach the detection system and the drift area (field-free area before the ion detector [22]), respectively; ε_i is the upper energy boundary of thermal electron capture; $f(\varepsilon, u)$ is the Maxwellian–Gaussian instru-

ment electron energy distribution function depending on the captured electron energy [19, 20]; N_0 and j are the number of target molecules in the ion extraction region and the electron flow density, respectively (both parameters are set arbitrarily and do not influence calculation data); $N_{i2}(T, u)$ is the number of ions recorded by the detector as a function of the temperature in the collision chamber and of the energy corresponding to the maximum of the instrument electron energy distribution function; $N_{i1}(T, u)$ is the number of ions at the entrance to the drift area; and $t(T, u)$ is the molecular anion measured lifetime.

EXPERIMENTAL RESULTS VERSUS CALCULATION DATA

Figure 5a shows the calculated dependence of mean lifetime $\tau_a(u)$ of Ph–N=N–Ph[−] molecular anions on the captured electron energy at a temperature in the collision chamber of 423 K. EYCs $I(u)$ for Ph–N=N–Ph[−] anions and their neutral component Ph–N=N–Ph at the same temperature are depicted in Fig. 5b. Also, Figs. 5a and 5b show the respective experimental data for comparison. All parameters used in the calculations, along with the method of their calculation, are listed in Table 2.

Having compared calculated and experimental curves $\tau_a(u)$ and $I(u)$, we found that they coincide accurate to 2–10%. The maximal discrepancy (about 10%) is observed at the ends of the curves, where the relative experimental error is nearly the same. In the mid-

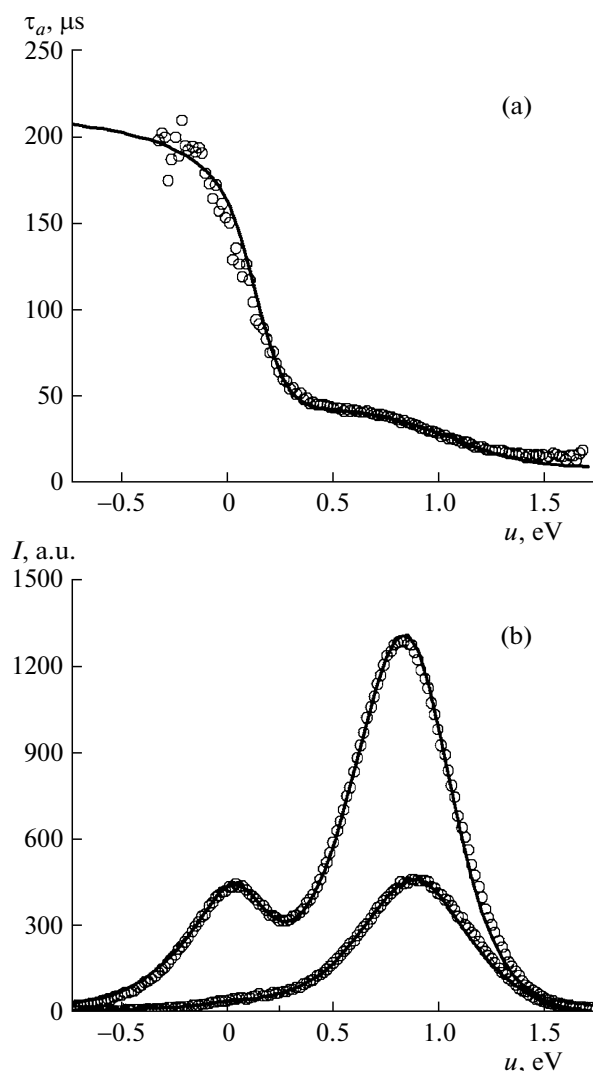


Fig. 5. (a) Ph–N=N–Ph[−] anion lifetime τ_a vs. captured electron energy u and (b) EYCs for the Ph–N=N–Ph[−] NMI and its neutral component Ph–N=N–Ph at a temperature in the collision chamber of 423 K. Continuous lines, calculation; empty circles, experimental data.

dle of the electron energy interval ($u = 0$ – 1.25 eV), the calculation inaccuracy is also within the experimental error and does not exceed 2–5%. With the parameters used in the calculation being the same, the computational accuracy remains high for other temperatures in the collision chamber (363 and 483 K). The high accuracy of calculations substantiates all the features observed in the family of curves $I(u)$ and $\tau_a(u)$ (Figs. 1, 2).

The minor temperature effect exhibited by lifetimes in the thermal electron range can be qualitatively explained based on the calculated azobenzene molecule distribution over vibrational states, $P(E_v, T)$ (Fig. 6).

As expected, this distribution has a clear-cut threshold ($E_{vt} = 0.30$ – 0.35 eV). To estimate quantity

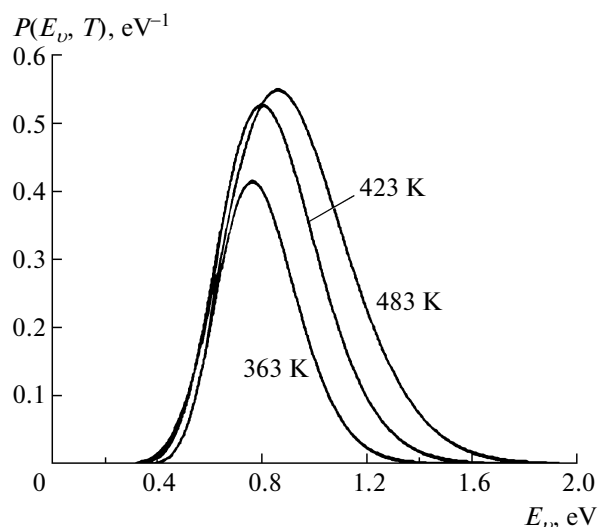


Fig. 6. Azobenzene target molecule distribution $P(E_v, T)$ over vibrational states responsible for the thermal electron capture at different temperatures in the collision chamber.

Pt , it is necessary to calculate the mean vibrational energy of the azobenzene molecule,

$$\bar{E}_v(T) = \frac{\int_{E_{vt}}^{\infty} E_v P(E_v, T) dE_v}{\int_{E_{vt}}^{\infty} P(E_v, T) dE_v}.$$

At temperatures of 363, 423, and 483 K, this energy equals 0.80, 0.85, and 0.92 eV, respectively. It follows from formula (3) that at $\varepsilon = 0$, the NMI lifetime depends only on E_v . Therefore, the temperature effect is almost zero ($Pt \approx 0$) in the temperature interval 363–423 K and is insignificant in the interval 423–483 K ($Pt \approx 0.13$ $\mu\text{s}/\text{K}$). If “thermal” electrons had been captured by molecules with any vibrational excitation, energy \bar{E}_v would have been equal to 0.350, 0.490, and 0.645 eV at the same temperatures and quantity Pt would have grown almost by three orders of magnitude ($Pt \approx 70$ $\mu\text{s}/\text{K}$) in the interval 363–483 K, according to our estimates. Such a “pronounced” temperature effect seems to have been observed by us earlier in the case of anthraquinone molecules [19].

The origin and the physical meaning of the tail in the family of the $\tau_a(u)$ curves, which is almost independent of the collision chamber temperature and electron energy, are easy to understand if molecules with a vibrational excitation of >0.25 eV are omitted from lifetime calculations (Fig. 7).

With this condition fulfilled, the calculated tail in the $\tau_a(u)$ curves coincides with that observed experimentally. This means that target molecules with a low

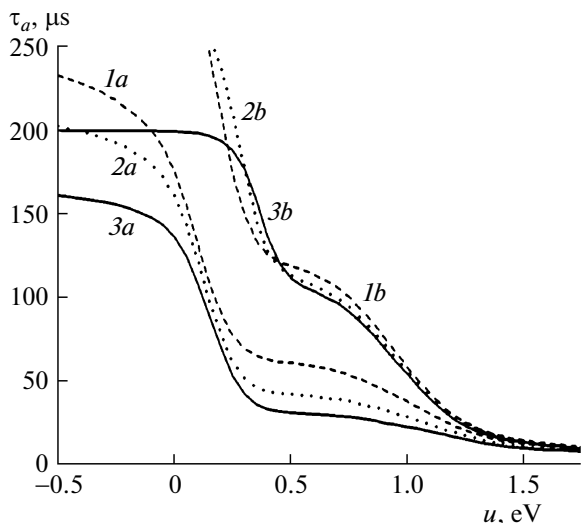


Fig. 7. Interpretation of the tail in the experimental temperature dependences $\tau_a(u)$. Curves $1a$ – $3a$ and $1b$ – $3b$ are dependences $\tau_a(u)$ calculated, respectively, with and without considering molecules with vibrational excitations >0.25 eV. Dashed lines $1a$ and $1b$ are constructed for 363 K; dotted lines $2a$ and $2b$, for 423 K; and continuous lines $3a$ and $3b$, for 483 K.

vibrational energy ($0 \leq E_v \leq 0.25$ eV) are main contributors to the measured lifetime within the tail.

CONCLUSIONS

Thus, at temperatures of 363, 423, and 483 K in the collision chamber, the calculated family of $\tau_a(u)$ curves and EYCs for azobenzene NMIs coincide with the respective experimental curves accurate to 2–10%. Such a high computational accuracy allows us to conclude that the principles underlying the calculations are valid. Namely, we relied upon the Illenberger–Smirnov–Kompaneits statistic model and assumed that NMIs produced through the capture of epithermal electrons become stable by means of internal conversion: a series of fast (10^{-14} – 10^{-12} s) nonradiative transitions without changing the multiplicity. A molecular anion thus produced has a considerable margin of excess vibrational energy. It is distributed over many vibrational degrees of freedom, and whether the NMI will hold the electron for >1 μ s depends mainly on the electron affinity of the molecule and on the number of its vibrational degrees of freedom. Obviously, each NMI is characterized by the critical energy of its own, or which the lifetime to autodetachment becomes shorter than 1 μ s. Note that the critical energy per vibrational degree of freedom bears more information that the critical energy itself and thereby makes it possible to correctly compare the stability of different molecular anions. We estimated the stability of azobenzene anions as 0.05 eV (cf. with

0.10 eV for fullerene anions and 0.07 eV for anthraquinone).

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