

Mechanism for nondissociative capture of electrons by molecules in two energy regions with the formation of long-lived negative ions

Yu. V. Vasil'ev and V. A. Mazunov

Physics Department, Bashkir Science Center, Ural Branch of the Academy of Sciences of the USSR

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The attachment of epithermal electrons to azobenzene molecules occurs through an electronically excited Feshbach resonance.

The formation of negative molecular ions at thermal energies ($\sim kT$) of the electrons is generally believed to occur by the mechanism of a vibrationally excited Feshbach resonance.¹ On the other hand, we do not yet have an explanation for a few experimental observations^{2,3} of a nondissociative capture of epithermal electrons

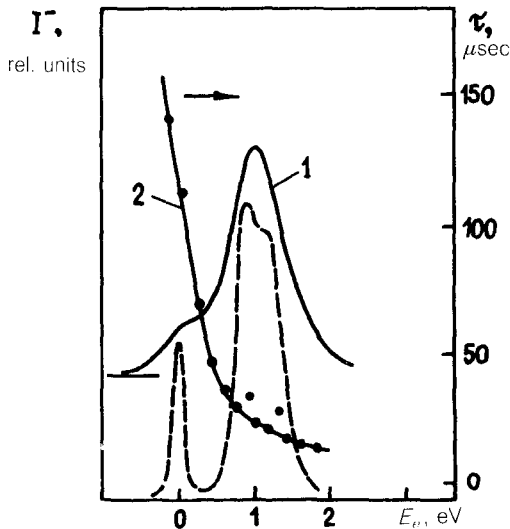


FIG. 1. 1—Current of negative molecular ions from azobenzene versus the electron energy; 2—lifetime of these ions versus the electron energy; dashed line—the same as 1, but measured with an electron monochromator ($\Delta E_{1/2} = 0.005$ eV).

($kT \ll E_e \lesssim 1.5$ eV) by molecules accompanied by the formation of long-lived ions ($\tau > 10^{-6}$ s), which are important from the standpoint of the thermalization of electrons in media and gas insulators and in other problems. One way to establish the mechanism for the formation of long-lived negative molecular ions at $E_e \sim 1$ eV is to search for a series of compounds in which a variation of substituents with various donor-acceptor properties would not result in the disappearance of the resonance peak at epithermal E_e . A search of this sort has led to the class of substituted azobenzenes. Working by the method of mass spectrometry of the resonance capture of electrons,¹⁾ we have established that the molecules of all the substituted azobenzenes (we studied 21 compounds with $R = \text{CH}_3, \text{NO}_2, \text{Hal}$, etc., in the *para*-position) capture electrons in two energy regions, 0 and $\lesssim 1$ eV. The position of the higher-energy resonance varies with R in the series. The average lifetimes (τ) of the negative molecular ions with respect to the self-detachment of an electron are also different at the peaks of the resonances, but this lifetime is always longer for the first resonance. The curve of the effective yield of negative molecular ions from azobenzenes plotted at the standard width of the electron energy distribution, $\Delta E_{1/2} \sim 0.3$ eV, consists of two overlapping resonances (Fig. 1). Measurements of τ in the region 0–2 eV have revealed an exponential dependence on E_e . The points on this curve suggest that there are two resonance states in the peak at epithermal energies (more on this below).

According to Ref. 4, the photoelectron spectra obtained in the present study show that the energy intervals between the bands of the photoelectron spectra and the peaks of the negative-ion yield curves are the same if the first band of photoelectron spectrum is placed not at the lowest-energy peak but at the peak in the emission of negative molecular ions at an epithermal energy. The correlation found (see Fig. 2 for the azobenzenes) is the first to be established for such a wide energy interval (~ 7 eV), extending to deep ionization energies at 14–15 eV. According to a calculation carried

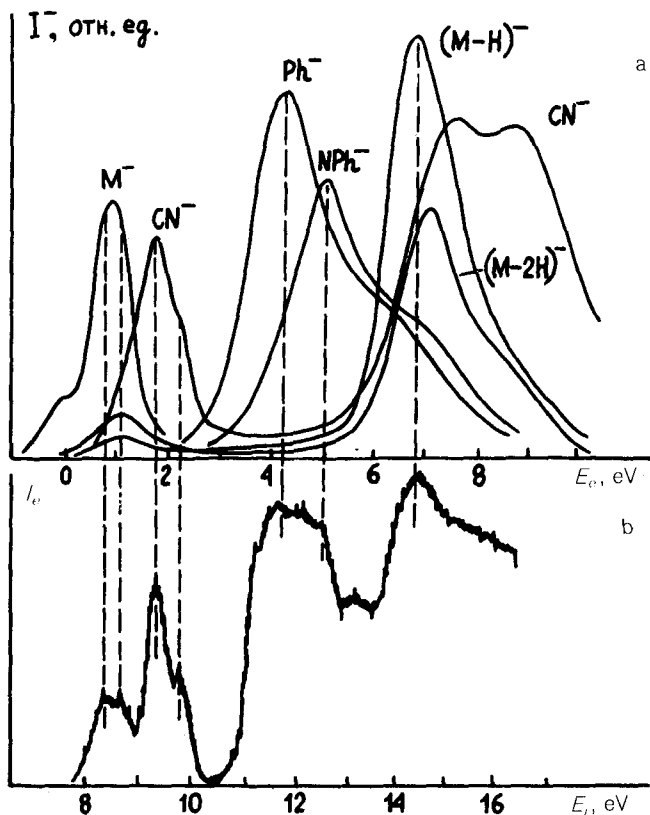


FIG. 2. a—Effective yield of negative ions of azobenzene; b—photoelectron spectrum of azobenzene. The energy scales have been shifted in such a way that the first band of the photoelectron spectrum coincides with the second resonance peak of molecular ions.

out by the MPDP method, this interval corresponds to the removal of electrons from more than 15 doubly filled orbitals. This fact is unambiguous evidence for the mechanism of the capture of electrons of epithermal energy by molecules of substituted azobenzenes: an electronically excited Feshbach resonance. In other words, this is the capture of an electron accompanied by a transfer of an electron from an occupied molecular orbital to a vacant one. The relatively low energy of the resonance, ~ 1 eV, is not surprising since the energies of the low-lying triplet and singlet transitions are 1.5 eV (Ref. 5) and 2.79 eV (Ref. 6), respectively.

Analysis of the photoelectron spectra of the entire series of compounds, including a determination of the integral intensities of the bands, and also quantum-chemical calculations by the MPDP and MChPDP/3 methods have shown that the first band of the photoelectron spectrum of the azobenzenes in the region 8.4–8.8 eV corresponds to the ionization of two overlapping molecular orbitals: a loosely bound combination of

unshared pairs of nitrogen atoms, $a_g(n_-)$, and a π orbital of symmetry a_u . In this case the second peak of negative molecular ions should contain two resonances, corresponding to the excitation of electrons from the $a_g(n_-)$ and a_u orbitals. Indeed, a special experiment in which we used an electron monochromator (with a resolution of 0.05 eV) made it possible to observe these two states (Fig. 1). [The resonance state of the negative molecular ion determined in this manner, which is formed through the excitation of an electron from an $a_g(n_-)$ orbital, refutes the suggestion that the peak at the epithermal energy is due to a shape resonance, although resonances of this type do formally lie above the mother state but below the Feshbach resonances.]¹

The operation of the mechanism of an electronically excited Feshbach resonance does not by itself mean that the negative molecular ions should be long-lived. In a conservative system consisting of a molecule and an electron, there can always be a redistribution of the energy brought in by the extra electron, with the result that there is a rapid self-detachment of an electron. We would suggest that this state is stabilized as the result of a radiationless transition from an excited state to the ground state of the negative molecular ion, accompanied by a strong excitation of vibrational modes. This explanation would explain the fact that the dependence of τ on E_e persists over a wide range, as shown in Fig. 1. Because of the coupling of the electronic and nuclear motions, the process would become far slower than the self-detachment processes due to the Coulomb interaction. According to the orbital-correlation principle established in Ref. 7, the captured and excited electrons for azobenzenes should be in two different molecular orbitals: a π orbital and a σ orbital. Otherwise, the fragment ions would have formed from all resonance states for which this process would have been possible from the energy standpoint. Furthermore, a low-lying vacant orbital of the π type is mostly localized at N atoms, while a σ orbital is localized primarily at the rings. This circumstance may also be responsible for a weak value of the Coulomb interaction and thus the intensification in the radiationless transition to the ground state of the negative molecular ion.

We note in conclusion that the difference ~ 1 eV between the absorption maximum of the azobenzene anion radicals in the region⁸ 550–600 nm and the resonance at the epithermal energy serves as an estimate of the electron affinity of the azobenzenes, since the excitation energy was reckoned from the ground state of the anion radical in Ref. 8, while in the present study it was reckoned from the ground state of the molecule. An estimate of the electron affinity by the MPDP method yields 1.18 eV. We wish to thank V. I. Khvostenko for a discussion of these results.

¹The mass spectra of negative ions were recorded on the modified instrument described in Ref. 3. The electron energy scale was calibrated on the basis of the peak corresponding to SF_6^- from SF_6 and the peak corresponding to $C_6H_5^-$ from C_6H_6 (~ 0 and 8 eV, respectively).

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