Observation of proton and electron detachment from an anthracene molecule during pronounced IR many-photon superexcitation

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The detachment of a proton and an electron from a large polyatomic molecule (anthracene) has been observed (for the first time) during pronounced IR many-photon superexcitation of the molecule above the dissociation boundary in the electronic ground state.

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1. The many-photon excitation of polyatomic molecules by intense pulsed IR laser beams is an effective method for giving molecules a large vibrational energy E_{vib}. An upper limit $E_{\text{vib}}^{\max}$ is usually set on the vibrational energy by the dissociation energy of the molecule, D_0. At a high rate (w) of many-photon excitation (in a very strong IR field), however, and at a limited rate of unimolecular decay (if the molecule has a large number of atoms), there may be a pronounced superexcitation of the polyatomic molecule above the dissociation boundary: $E_{\text{vib}}^{\max} - D_0 > D_0$. The effect is described quantitatively by the RRKM statistical theory of unimolecular decay.[1] In the semiclassical approximation of this theory ($E_{\text{vib}}^{\max} \gg E_0$, where E_0 is the zero-point energy of the molecule) the following formula can be derived:

$$\frac{E_{\text{vib}}^{max} - D_0}{D_0} = \left(\left(1 - \frac{w}{\mathcal{K}}\right)^{1/(s-1)}\right)^{-1} - \frac{E_0}{D_0} - 1, \tag{1}$$

where s is the number of vibrational degrees of freedom, and $\mathcal{K}$ is a frequency factor, which appears in the expression for the unimolecular decay rate in the semiclassical approximation. It is on the order of 10^{15} s^{-1}. During IR many-photon excitation it is a simple matter to achieve a rate[2] $w \approx 10^9$ s^{-1}. According to (1), a pronounced vibrational superexcitation of the molecule can be achieved for a molecule with $s \gg \ln(\mathcal{K}/w)$.

This letter reports an attempt to achieve pronounced IR many-photon superexcitation of the anthracene molecule ($C_{14}H_{10}$, $s = 66$, $D_0 = 4.8$ eV), for which expression (1) yields $(E_{\text{vib}}^{\max} - D_0)/D_0 \approx 3$. At these large values $E_{\text{vib}}^{\max} \approx 19$ eV we can expect to excite high-lying electronic states by virtue of the nonadiabatic coupling of the electronic and vibrational motion. These high-lying states would lead, in particular, to ionization of the molecule ($I = 7.4$ eV). The observation of charged particles during IR laser bombardment of anthracene will thus be direct evidence of a pronounced vibrational superexcitation of this molecule.

2. A time-of-flight mass spectrometer is used in the present experiments to observe the charged particles produced during the IR many-photon excitation. An anthracene powder in the chamber of a mass spectrometer is heated along with the entire spectrometer to 30–40 °C during continuous vacuum pumping by an oil-free pump. The saturation vapor pressure of anthracene at this temperature is $P_{\text{sat}} \simeq 4 \times 10^{-6}$ Torr; the residual air pressure does not exceed 10^{-7} Torr. This mass spectrometer is described in more detail in Ref. 3.

The pulsed beam from an atmospheric-pressure CO_2 laser is focused into the ionization region of the mass spectrometer by an NaCl lens with a focal length of 14 cm. The frequency of the laser output, $\nu = 949.48$ cm^{-1}, lies near one of the most intense lines in the IR absorption spectrum of the anthracene molecule.[4] Experiments were carried out with IR laser pulses of two lengths: "short," $\tau_{\text{IR}} = 70$ ns, and "long," $\tau_{\text{IR}} = 1$ μs. The mass spectrometer was calibrated with the help of the molecular ion $C_{14}H_{10}^{+}$, which is produced during two-photon ionization of anthracene vapor by the beam from a KRF excimer laser ($\lambda = 249$ nm, $\tau_{\text{UV}} = 20$ ns) (Ref. 3; see Fig. 1 of the present paper).

3. Figure 1a is a representative mass spectrum of the positively charged particles produced during the bombardment of anthracene molecules by the "short" pulse from the CO_2 laser at a beam energy density $\Phi = 55$ J/cm^2. The heaviest ion observed in this mass spectrum is $C_{14}H_{10}^{+}$; the lightest is the hydrogen ion, H^+. The threshold for the formation of ions during bombardment with the "short" IR pulse corresponds to $\Phi_{\text{thr}} \simeq 35$ J/cm^2.

No ions could be detected during bombardment of the anthracene molecule with "long" pulses at energy densities up to $\Phi = 80$ J/cm^2.

To resolve the possible role played by the formation of ions on the various surfaces in the mass spectrometer when struck by IR light, we carried out a control experiment in which the beam leaving the mass spectrometer was reflected onto the

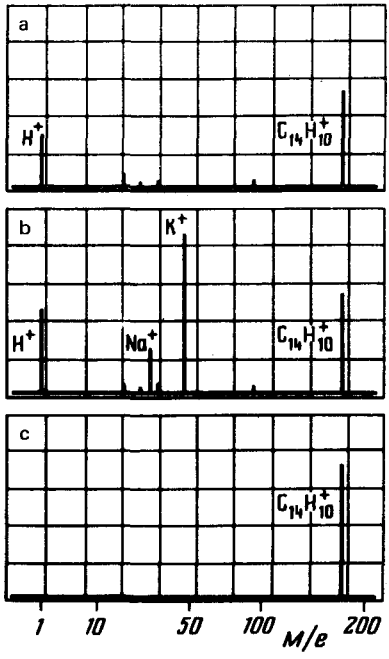

FIG. 1. Mass spectra of the positive ions produced under various conditions. a—Bombardment of anthracene molecules by a "short" pulse from a CO_2 laser, $\Phi = 55$ J/cm^2; b—during reflection of the IR pulse onto an electrode in the mass spectrometer; c—during two-photon UV ionization of anthracene molecules.

surface of an electrode directly below the ionization region.[3] The resulting mass spectrum revealed additional peaks corresponding to Na^+ and K^+ ions (Fig. 1b), which are desorbed from the surface of the copper electrode as a result of heating caused by the IR pulse. When a corresponding control experiment was carried out with a "long" IR pulse, we found only Na^+ and K^+ ions in the mass spectrum.

4. These experiments show unambiguously that collisionless IR many-photon excitation of anthracene molecules is accompanied by the ionization of these molecules and the detachment of a proton. For these reactions to occur, the internal energy of the molecule must exceed the energies of the corresponding reaction channels. The energy diagram in Fig. 2 shows the thresholds for certain possible decomposition reactions of the anthracene molecule.[5] The ionization threshold is 7.4 eV; the thresholds for proton production in the reactions in Fig. 2 are 16.3 eV and 18.4 eV. The observation of proton and electron detachment during IR bombardment of the anthracene molecule is direct evidence that this molecule has been given a pronounced vibrational superexcitation above the dissociation boundary in the electronic ground state. The observed superexcitation levels and the governing role played by the beam intensity (and thus by the excitation rate w) confirm that expression (1) gives a realistic estimate of the possible superexcitation of large molecules.

For molecules with comparatively few atoms, SF_6 and BCl_3, for example, at the typical pulse lengths $\tau_{IR} = 10^{-7}$–10^{-6} s, the maximum possible vibrational superexcitation above the dissociation boundary is only slight, $(E_{vib}^{max} - D_0)/D_0 \ll 1$, according to

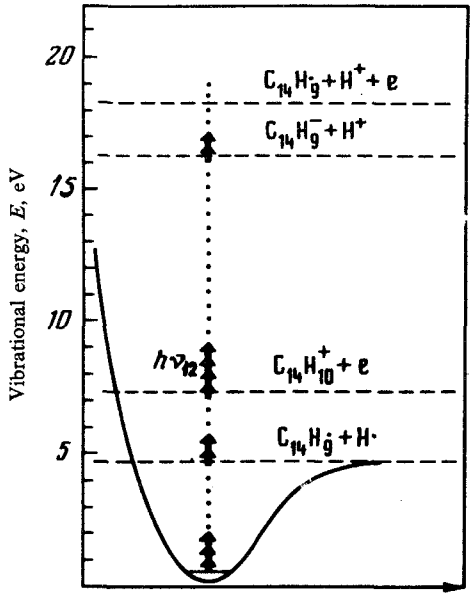

FIG. 2. Energy diagram for certain possible reactions involving dissociation and the formation of charged particles for a highly excited anthracene molecule.

the predictions of the RRKM theory and direct observation.[6] Consequently, the IR many-photon ionizaiton of few-atom molecules in the electronic ground state is improbable.

The formation of charged particles during the vibrational excitation of neutral molecules is one manifestation of a nonadiabatic coupling of the electronic and vibrational motion in highly excited molecules; other pieces of evidence (observed previously) are the inverse electronic relaxation,[7] the detachment of an electron from a negative ion,[8] and electronic predissociation.[9] We might note that pronounced IR many-photon superexcitation of molecules gives us a new technique for exciting molecules to high-lying states. This technique may make it possible to observe processes (proton detachment, for example) which are not observable during UV excitation.

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