

IR laser fragmentation of the molecular ion CF_3I^+

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Experiments reveal that the maximum of the dissociation spectrum of the molecular ions CF_3I^+ shifts toward a shorter wavelength of the fragmenting IR radiation as the intensity of this radiation is raised. It is concluded that the distribution of the vibrational energy of the molecular ions produced by electron impact is not at equilibrium.

Experiments have been carried out on the fragmentation of vibrationally excited small polyatomic molecules by electron impact and by UV radiation¹⁻³ in accordance with the suggestion of Ref. 4, in an effort to study the possibility of a bond-selective laser dissociation of molecules. Correspondingly, there is interest in the IR laser fragmentation of molecular ions.

In this letter we are reporting the first observation of a shift of the spectral maximum of the essentially collisionless multiphoton dissociation of the molecular ions CF_3I^+ , produced by electron impact (60 eV), toward shorter wavelengths (a blue shift). The nature of the fragmentation of the ion has been studied as a function of the frequency and energy density of the laser pulse. The elementary mechanisms for the decay of the ion in an intense ($\cong 50\text{-MW/cm}^2$) laser field have been identified. The data obtained indicate that the distribution of vibrational energy in a term of the electronic ground state of the ion may not be an equilibrium distribution.

The experimental apparatus includes a pulsed TEA CO_2 laser with discrete tuning of the output frequency over the CO_2 lines and a "mass-reflectron" time-of-flight mass spectrometer.⁵ The laser light is concentrated by a mirror-lens telescope and coupled into the ion source of the reflectron. It provides an energy density up to 10 J/cm^2 in the region of the electron beam ($12 \times 5 \times 1.5\text{ mm}$). The pressure of the CF_3I gas in the ion source is 10^{-5} Torr. This gas is bombarded with pulses of 60-eV electrons with a length of $1\ \mu\text{s}$. The molecular ions resulting from this bombardment are fragmented by an IR pulse 100 ns long, delayed 300 ns with respect to the end of the ionization. The fragmentation products are expelled into the drift volume of the mass spectrometer by an electric field pulse $2\ \mu\text{s}$ long, applied $1\ \mu\text{s}$ after the electron-ionization pulse. Ion packets formed by the "soft mirror" of the mass reflectron⁵ are detected by an assembly of microchannel plates with an amplification of 10^8 . The measured pulse heights are processed by a procedure which provides the fraction of the ion current corresponding to each fragment in the total current of the mass spectrum. The results are averaged over 20 realizations. The currents of the main dissociation fragments, CF_3I^+ , CF_3^+ , I^+ , and CF_2I^+ , are taken into consideration in the total

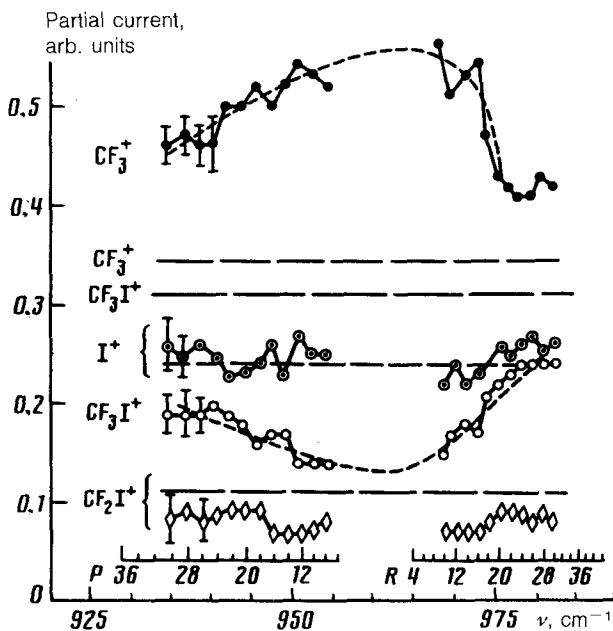


FIG. 1. Spectrum of the partial currents of the basic fragments of the photodissociation of CF_3I^+ at an energy density $\Phi = 4.4 \text{ J/cm}^2$. Straight dashed lines— $\Phi = 0$.

ion current. The currents of the other fragments amount to less than 5% of the total current. Their magnitude remains constant within the measurement error.

Figure 1 shows the partial ion currents of the main fragments versus the wavelength of the dissociating light near $10 \mu\text{m}$ for an irradiation energy density of 4.4 J/cm^2 . We found no effect of a dissociation of CF_3I^+ in the $9\text{-}\mu\text{m}$ output band of the CO_2 laser. The horizontal dashed lines in Fig. 1 show the amplitudes of the mass peaks found in the absence of the laser irradiation. When the laser field is applied, it dissociates the CF_3I^+ ion, in a process accompanied by an increase in the yield of the CF_3^+ fragment. The pathways for the monomolecular decay of the CF_3I^+ ion which lie at low energies are^{6,7} $\text{CF}_3\text{I}^+ \rightarrow \text{CF}_3^+ + \text{I} - 1.04 \text{ eV}$ and $\text{CF}_3\text{I}^+ \rightarrow \text{CF}_3 + \text{I}^+ - 2.45 \text{ eV}$. However, the circumstance that the relative yield of the fragment I^+ does not change, within the measurement error, during the laser dissociation of the CF_3I^+ ion is unambiguous evidence for the first of these pathways.

Figure 2 shows the evolution of the CF_3I^+ fragmentation spectrum as the irradiation energy density is raised from 0.3 to 4.4 J/cm^2 . Also shown here are data from Ref. 8 on the yield of the CF_3^+ fragment in the single-photon dissociation of CF_3I^+ by continuous irradiation at an intensity of 2 W/cm^2 . In addition, this figure shows data from Ref. 7 on the dissociation, at an energy density of 0.8 J/cm^2 , of CF_3I^+ ions confined in an interaction volume by an ion cyclotron resonance. We believe that some secondary ion-radical reactions, including heterophase reactions, could have occurred under the conditions of Ref. 7; it is difficult to rule out an effect of such reactions.

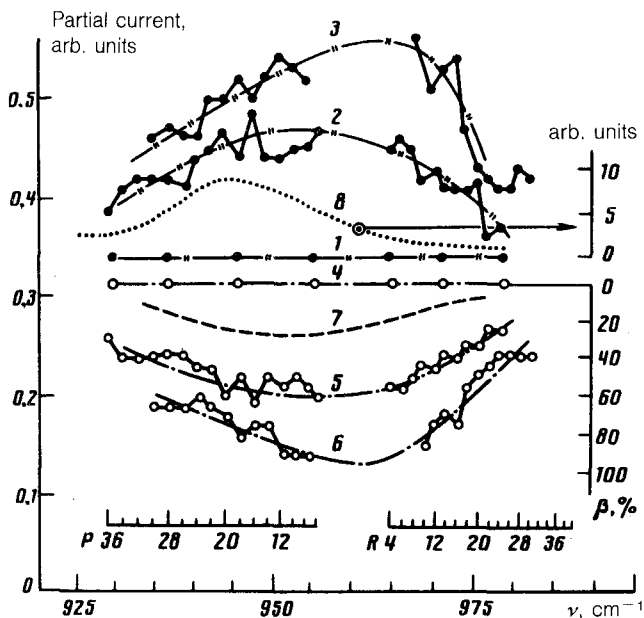


FIG. 2. Spectrum of the partial currents of the fragments at various energy densities of the laser irradiation, Φ . 1-3— $\Phi = 0, 0.3$, and 4.4 J/cm^2 , respectively, CF_3^+ ; 4-6—the same, but for CF_3I^+ ; 7—data of Ref. 7, $\Phi = 0.8 \text{ J/cm}^2$; 8—data of Ref. 8, power density of 2 W/cm^2 . The β axis shows the relative number of CF_3I^+ ions that dissociate, found with allowance for the filling factor of the working volume: $V_{\text{irrad}}/V_{\text{ioniz}} = 0.6$.

The curves in Fig. 2 demonstrate a shift of the maximum of the dissociation spectrum toward shorter wavelengths with increasing energy density of the radiation causing the fragmentation. A possible explanation for this behavior is that as the energy density is increased, there is an increase in the contribution to the total dissociation yield from those particles which, after the formation of the CF_3I^+ ion but before the application of the laser pulse, are in low-lying, not completely stochastic vibrational levels of the electronic ground term of the CF_3I^+ ion. The pronounced vibrational anharmonicity of this relatively shallow term would then be responsible for the blue shift of the maximum of the fragmentation spectrum of the CF_3I^+ ion. An alternative explanation might be the appearance during the ionization of the molecule of a bimodal distribution of the ions in vibrational energy (cold and hot ensembles of ions), with an equilibrium distribution of energy among the vibrational modes of each of the ions. However, we believe that the significant size of the shift ($\approx 20 \text{ cm}^{-1}$), which is comparable to the half-width of the dissociation spectrum, is evidence that the distribution of vibrational energy among the modes of the original ion is not an equilibrium distribution.

Further research on the blue shift as a function of the intensity of the radiation causing the fragmentation and the method for preparing the ions to be fragmented (preliminary vibrational excitation of a neutral molecule below and above the bound-

ary of the region of stochastic vibrational motion²; ionization by UV radiation; etc.) will provide more-detailed and more-specific information on the structure of the electronic terms of the CF_3I^+ ion and will make it possible to evaluate the possibility of carrying out bond-selective processes involving this ion.

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