

Controlling the electron-impact fragmentation of molecules through IR-laser excitation of vibrational modes

V. M. Akulin, V. D. Vurdov, G. G. Esadze, N. V. Karlov, A. M. Prokhorov,
A. A. Susanin, and É. M. Khokhlov

Institute of General Physics, Academy of Sciences of the USSR

(Submitted 23 May 1984)

Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 2, 53–55 (25 July 1984)

The monomolecular fragmentation of the vibrationally excited molecules CF_3I , CF_3Br , and CF_2Cl_2 by electron impact has been studied. It has been found possible to effectively control the composition of fragmentation products. A mechanism for this control effect is proposed.

Study of the effect of intense IR laser beams on the vibrational degrees of freedom of molecules has demonstrated that the molecules can be selectively excited and selectively dissociated by mechanisms involving an equilibrium thermal decomposition.^{1,2} Although there has been no study of the possibility of a nonthermal decomposition of molecules by IR laser beams, it would seem that this process could be implemented in a small number of molecules which have a particular valence-bond structure.

In general, electronic degrees of freedom must be involved in a change in the nature of the fragmentation of a molecule, i.e., in a change in the composition of the primary products of the decomposition of the molecule. These degrees of freedom can be influenced by electron impact, which causes a breakup of a molecule by a variety of mechanisms, including mechanisms involving the formation of charged fragments. It thus becomes possible to use the methods of conventional mass spectrometry to visualize the products of the elementary collision events between the vibrationally excited molecule and the electron.³ We would like to study that range of energies of the incident electron which would cause an electronic transition in the molecule in accordance with the Franck-Condon principle. The high sensitivity of mass spectrometry

makes it possible to obtain information on the primary decomposition products at a pressure range which clearly rules out any effect of collisions.

For the present study of the fragmentation of a vibrationally excited molecule by electron impact we used an apparatus consisting of an MSKh-4 time-of-flight mass spectrometer modified to allow injection of the laser beam and equipped with a micro-channel-plate device for detecting ions (46 mm in diameter, $K_{\text{ampl}} = 10^8$) and with a pulsed electron gun (pulse length of 1 μs , electron energy on the order of 80 eV). The molecules in the working volume of the mass spectrometer were vibrationally excited by the beam from a pulsed TEA CO_2 laser which was discretely tunable over the CO_2 emission lines by means of a diffraction grating with 100 lines/mm. The laser pulse length, which was monitored by a photon-drag detector, was 100 ns at the 0.1-maximum level. The pulse energy was measured with a pyroelectric calorimeter and was varied over the course of the experiments with a calibrated CaF_2 attenuator. The laser beam was coupled into the working volume of the mass spectrometer through a BaF_2 window by a cylindrical NaCl lens with a focal length of 20 cm. This lens formed a caustic with a cross section of $15 \times 2.5 \text{ mm}^2$. The change in the cross section over a distance equal to the diameter of the aperture in the ejecting electrodes did not exceed 10%. The plane beam from the pulsed electron gun was transported in the plane of the laser beam in the bombardment region. An effusion beam of the test gas at a temperature of 300 K entered the working volume of the mass spectrometer along the axis normal to the plane of the laser beam. The pressure in the working chamber was 7×10^{-6} torr. The heights of the peaks in the mass spectra were measured with an S8-2 oscilloscope. The average height of each peak and the relative measurement error were determined by measuring the mass spectra ten times at each of the fixed laser energy densities.

We selected the gases CF_3I , CF_3Br , and CF_2Cl_2 to study the dependence of the nature of the fragmentation of the molecules on the degree of their vibrational excitation. The experimental results are shown in Figs. 1 and 2.

The CF_3I and CF_3Br molecules have identical spatial structures; they have a C_{3v} symmetry and approximately equal normal-vibrational frequencies. When these molecules are excited at frequencies corresponding to the Q branches of the fundamental bands of the ν_1 mode (1074 cm^{-1} and 1084 cm^{-1} , respectively), the degrees of vibrational excitation of these molecules by identical laser pulses are equal in order of magnitude. It can be seen from Fig. 1a that the vibrational excitation substantially changes the nature of the fragmentation of the molecules. Furthermore, the particular way in which the nature of the fragmentation changes with the energy density of the laser pulse is qualitatively different in the cases of CF_3I and CF_3Br . The differences can be seen most clearly by comparing the probabilities for the production of CF_3^+ and I^+ ions from the CF_3I molecule with the probabilities for the production of CF_3^+ and Br^+ ions from the CF_3Br molecule. It should be noted that the effect observed here reaches a maximum at laser-beam energy densities considerably lower than the threshold for dissociation in single-frequency bombardment. Consequently, during excitation of the ν_1 mode of the CF_3I and CF_3Br molecules (this mode corresponds to valence vibrations of C-F bonds), despite the identical symmetry and approximately equal spatial structures and spectral structures of the vibrational bands, the effect of

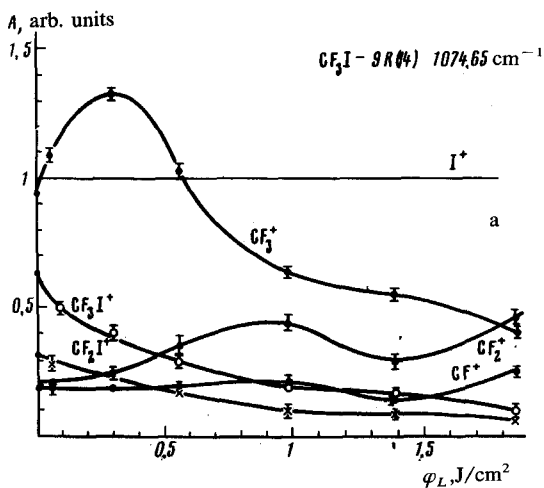
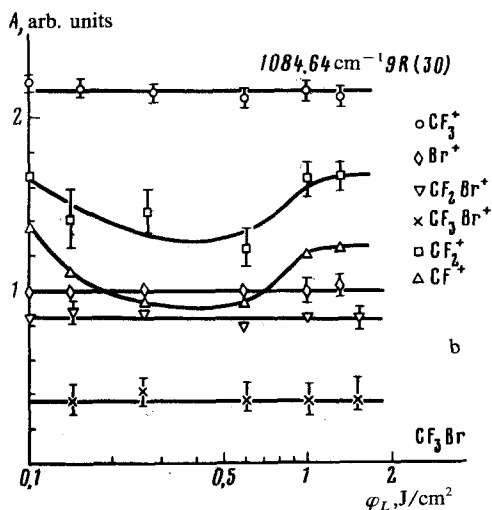


FIG. 1.



the excitation on the nature of the fragmentation during electron impact is different for these two molecules.

To study the effect of the distribution of vibrational energy among modes on the nature of the fragmentation, we used the CF_2Cl_2 molecule. Figures 2a and 2c show the yields of the various ion fragments during excitation of this molecule at the frequencies ν_1 and ν_8 , respectively, which correspond to pumping of vibrations of the C-F and C-Cl bonds. Comparison of these figures shows that the curves corresponding to the excitation of the molecules in different vibrational bands are qualitatively different. In other words, the nature of the fragmentation of the molecule is sensitive to the mode composition of the vibrational excitation. Comparison of Figs. 2a and 2b show that

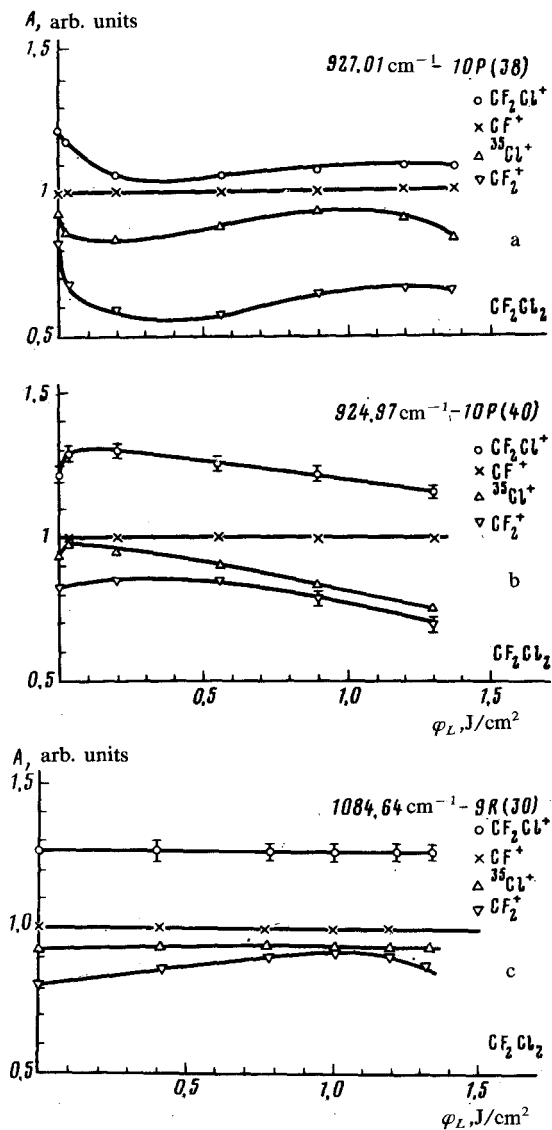


FIG. 2.

there are also some more subtle trends, which reflect changes in the nature of the fragmentation upon changes in the frequency structure of the radiation within a single vibrational band.

These facts show that the nature of the fragmentation of the molecule caused by electron impact depends strongly on the vibrational state of the molecule. We believe that these experimental results can be explained in the following way. It can be shown that, according to the Franck-Condon principle, the probability for transitions between molecular terms by electron impact is dominated by those points of the trajectory at which the coordinate, momentum, and force parameters of the vibrational motion are equal. When the vibrational state of the molecule is changed by the laser

pulse, the probability amplitude for finding the molecule at these points changes, changing the probability for the fragmentation of the molecule by the mechanism corresponding to the given pair of terms. It is also obvious that by changing the nature of the vibrational wave function at these points through laser bombardment one can control the magnitudes and directions of the momenta of the nuclei, and again the consequence will be a change in the nature of the fragmentation of the molecules.⁴

Two conclusions of practical importance can be drawn from these results. First, the combined effects of IR light and electron impact on a molecule open up the possibility of controlling the process—producing certain ions and radicals as desired—and optimizing this process. There is the further possibility of controlling the composition of ion beams. Second, refinement of this method will make it possible to determine the isotopic selectivity of the elementary photodissociation even under clearly collisionless conditions. Third, the results of this study raise the hope that the method proposed here may prove a reliable method for determining the nature of the vibrational motion of polyatomic molecules and the extent to which this motion is stochastic.

We wish to thank E. K. Karlova for assistance in this study.

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