UV many-photon ionization of vibrationally excited polyatomic molecules

V. M. Akulin, V. D. Vurdov, G. G. Esadze, N. V. Karlov, A. M. Prokhorov, and
É. M. Khokhlov
Institute of General Physics, Academy of Sciences of the USSR

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Experiments reveal that vibrational excitation of polyatomic molecules influences their UV many-photon conversion accompanied by the formation of molecular ions and charged fragments. When various conversion pathways come into play, and when switches occur between these pathways, there are some observable consequences. Changes are also observed in the number of photons involved in the corresponding processes upon a change in the vibrational state of the molecule.

Vibrational excitation of molecules changes the positions of their electronic absorption bands[1] and thereby significantly increases the capabilities of classical UV photochemistry. There are known cases[2] of a switching of a UV photochemical reaction by the IR field which excites vibrations of a definite mode composition of a CF_2Cl_2 molecule. The mechanism for this effect has not been studied at the level of the elementary event.

In this letter we report observation of the elementary event of many-photon ionization of CF_3I and CF_2Cl_2 molecules by the light from a KrF laser. We have studied the effect of IR vibrational excitation on this process. The experiments are carried out in a time-of-flight mass spectrometer. The IR beam from a pulsed TEA CO_2 laser[3] enters the working chamber of the ion source of the spectrometer, which contains molecules of the gas under study at a pressure $\sim 5 \times 10^{-6}$ Torr. The ionization is performed by the focused beam from a KrF excimer laser (wavelength of 248 nm), in a pulse 30 ns long with an energy density of 4 J/cm^2.

Figure 1 shows the heights of the peaks representing the current of ion fragments of the CF_2Cl_2 molecule versus the energy absorbed by the ν_1 mode, which corresponds to valence vibrations involving C–F bonds. During excitation of the mode ν_8, which corresponds to a vibration involving a C–Cl bond, we do not observe a decay of the molecule into charged fragments (at the sensitivity level of the ion detector, which is 10^{-7} of the number of bombarded molecules). This result is evidence that a stochastic situation does not occur at the excitation levels reached. Further evidence for this conclusion comes from experiments on electron-impact fragmentation of the molecule, carried out by the method described by us in Ref. 4. It is interesting to note that the heights of the ion peaks remain in the same proportions as the absorbed energy is varied and also as the excitation frequency is varied within the ν_1 band. This result is apparently a consequence of the excitation of only one of the terms of the molecular ion, which corresponds to dissociation with fixed proportions of the decay products.

A qualitatively different behavior of the heights of the ion peaks of the charged fragments is seen in the case of the CF_3I molecule (Fig. 2). Since the vibrational motion

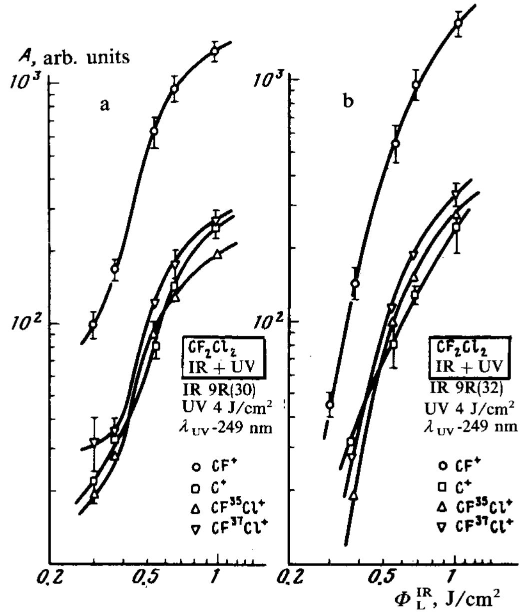

FIG. 1.

of this molecule becomes stochastic starting at only the third or fourth level of the ν_1 mode,[4] we do not observe a frequency dependence of the fragmentation in the UV field in this case. For this molecule, on the other hand, there are changes in the relative heights of the ion peaks for the CF^+ fragment, on the one hand, and the height of the ion peak of the CF_3I^+ fragment, on the other. The latter ion appears during the laser bombardment only after a preliminary vibrational excitation of the molecule. The change in the fragmentation proportions is evidence that the UV light performs its ionization through a transfer over several (at least two) terms of the molecular ion

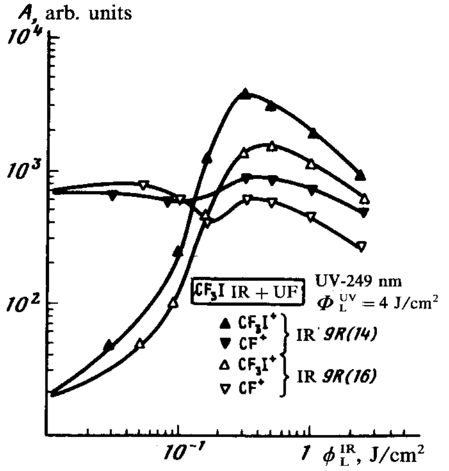

FIG. 2.

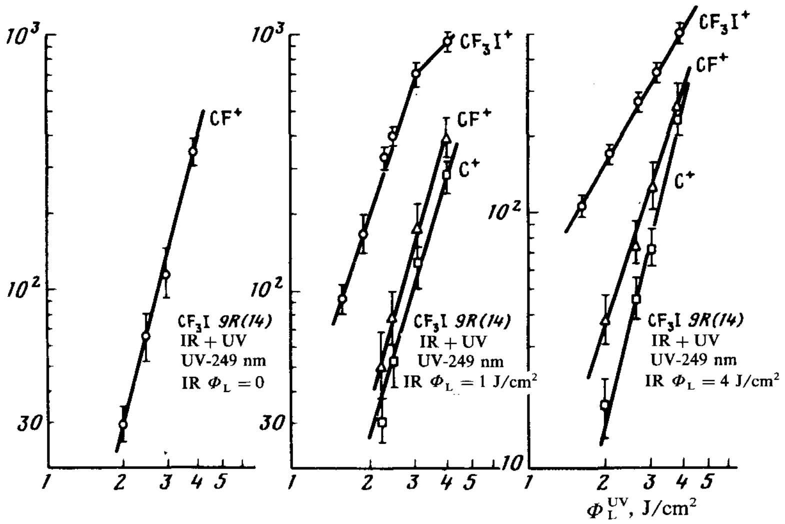

FIG. 3.

CF_3I^+, one of which corresponds to a bound state, and the other to an unstable state. The same conclusion is implied by the observation of a dependence of the fragment formation probability on the UV intensity (Fig. 3). The number of photons involved in the process involving the formation of the CF^+ ion is four and is independent of the vibrational excitation level; only the cross section for this process changes. The number of photons involved in the transition accompanied by the formation of the CF_3I^+ ion changes both with an increase in the reserve of vibrational energy and with an increase in the UV intensity.

We believe that the results found on the UV many-photon photoionization of vibrationally excited molecules can be explained qualitatively in the following way. The ionization of the molecule by the UV light occurs through intermediate states corresponding to vibrational levels of excited electronic terms. Upon a change in the vibrational state of the electronic ground term, which is the starting point for the UV process, due to the IR excitation, there are changes in the frequencies of Franck–Condon transitions to intermediate terms, so that there is a change in the structure of the intermediate resonances which changes the cross section for the many-photon transition. The same explanation can be offered for the behavior observed for the CF_2Cl_2 molecule. To explain the effects that occur in the CF_3I molecule, we should take into account the possible existence of different pathways for the UV excitation, corresponding to processes involving different numbers of photons. A change in the starting level causes different small changes in the intermediate levels for the various pathways, thereby changing the relative probabilities for the formation of various ion fragments. In polyatomic molecules, whose vibrational motion is inherently multidimensional, the number of intermediate states involved in a Franck–Condon transition is large, and their density is high. For this reason, the many-photon transitions do not go through isolated intermediate levels but through zones of levels formed by the vibrational substructure of the electronic terms. Consequently, in intense fields, in which the condition for the existence of a quasicontinuum is satisfied (the Stark broadening of the levels is greater than the characteristic distance between the adjacent states), we should expect changes in the power-law dependence of the ion formation probability on the UV intensity. We are apparently observing such a change in the formation of the CF_3I^+ ion during vibrational excitation of the CF_3I molecule to the level $3\nu_1 \approx 3000\ \mathrm{cm}^{-1}$.

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