

Determination of the boundary for randomization of vibrational motion by a method of IR laser excitation and electron impact

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The boundaries of the regions of randomization of the vibrations of CF_3I and SF_6 molecules have been detected. The dependence of these boundaries on the excitation frequency has been determined. The fractions of molecules that go into the randomization region have been determined for various excitation frequencies.

The nature of the fragmentation of molecules caused by electron impact depends on their vibrational state.¹ If the vibrational motion is stochastic, the fragmentation should not depend on the particular method by which the vibrations are excited. Consequently, a study of the fragmentation of vibrationally excited molecules as a function of the excitation frequency and the absorbed energy may yield information about the position of the randomization boundary.

In this letter we report the first observation of the randomization boundary for the vibrational motion of molecules. We have also determined the spectral dependence of this boundary. The experiments were carried out for CF_3I and SF_6 molecules, which differ in symmetry, in the apparatus described in Ref. 1. The laser excitation of these molecules was carried out in the absorption bands of the vibrational modes ν_1 and ν_3 , respectively. An acoustooptic method was used to determine the absorbed energy.

To avoid any effect of a change in the fraction of excited molecules with varying frequency and intensity of the laser beam, we used the following procedure to analyze the experimental results. The electron impact causes a fragmentation of both excited and unexcited molecules. The signal (A_i) representing the ion current of fragment i consists of the signals coming from excited and unexcited molecules. The increment in the current upon excitation is proportional to the fraction of excited molecules, q , and to the change in the cross section for the production of charged fragments with increasing energy of the molecule, E : $\Delta A_i \sim q\{\sigma_i(E) - \sigma_i(0)\}$. This value of q also determines the relationship between the average absorbed energy W , measured by the acoustooptic method, and the energy of the excited molecules, E : $W = qE$. The ratios $(\Delta A_i/W) \sim [\sigma_i(E) - \sigma_i(0)]/E$ do not depend on q and are determined exclusively by the energies of the excited molecules and the nature of their fragmentation. These ratios can accordingly be selected as parameters that describe the state of the molecules. If the vibrational motion has become stochastic, then the values of these parameters, at a fixed energy E , are the same for all frequencies of the exciting IR field. Although we do not know E , its logarithm differs from that of the measured quantity, W , by an additive increment of $\ln q$. If, by choosing this additive increment appropriately, we manage to bring all the curves of $\ln W$ versus the parameter $\Delta A_i/W$ for the various excitation frequencies into coincidence at large E , we can thereby determine not only the randomization boundary but also the fraction of excited molecules.

We used this procedure for CF_3I molecules (using the fragments CF_3I^+ , CF_2I^+ , I^+ , CF_2^+ , CF_3^+ , and CF^+) and for SF_6 molecules (SF_5^+ and SF_3^+S^+). The ion currents of the remaining fragments were measured with a low relative accuracy, so that the corresponding parameters for these fragments agreed in all cases. Figure 1 shows $\ln E$ versus $\tan^{-1}(A_i^{(t)} - A_i^{(0)})/W$ for the case of SF_6 for the fragments SF_5^+ and SF_3^+ , found for the output lines from P_{12} to P_{24} from a CO_2 laser. The coincidence was reached by displacing the curves along the ordinate. Figure 2 shows the boundaries (found in this manner) of the region in which the vibrations become stochastic, along with the spectra of the fraction of excited molecules, q . For an absolute calibration of the ordinate in units of photons per molecule, we used the data of Ref. 2 found for the P_{20} line. We assume that the results of Ref. 2 refer to the excitation of a molecule in a collisional regime with a q factor of approximately unity. Shown for comparison are the line absorption spectra of gaseous SF_6 and CF_3I at 300 K. The curves in Fig. 2 are evidence that the vibrational motion in molecules with a cubic anharmonicity (CF_3I) becomes stochastic in a manner different from the corresponding process in molecules with a fourth-order anharmonicity (SF_6). In the latter case the intermode coupling is weaker, as can be seen in particular in the stronger spectral dependence of the randomization boundary.

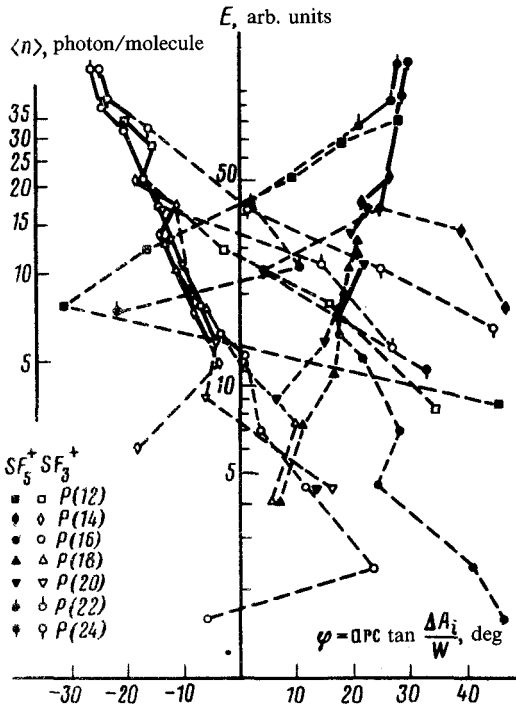


FIG. 1.

The spectral dependence of the randomization boundary of the SF_6 molecule corresponds qualitatively to the theoretical boundary in terms of position, typical shape, and value at the minimum.³ It is, however, more difficult to make a quantitative comparison because of our imprecise knowledge of the constants of the intramodal and intermodal anharmonicity and the crudeness of the model of two ensembles — of

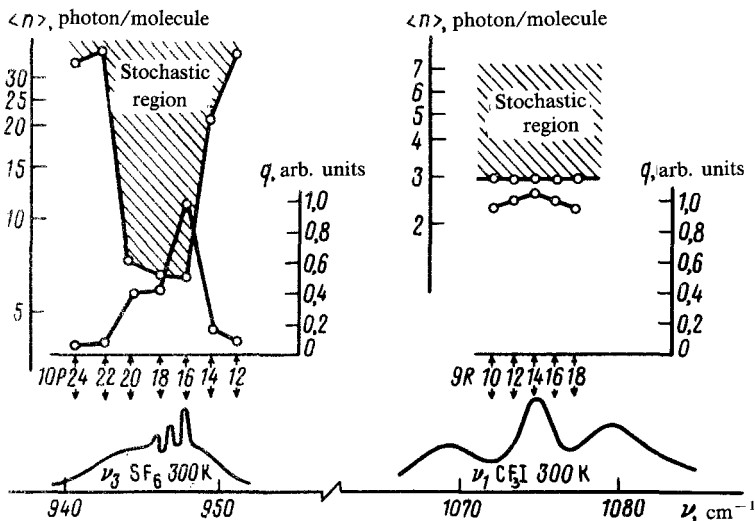


FIG. 2.

unexcited and highly excited molecules. We might note that the use of a CO₂ laser with a continuously tunable frequency would make it possible to determine the boundary of the stochastic region more accurately.

These results refer to the randomization that occurs upon the excitation of one of the IR-active modes. It would be interesting to study the randomization of the vibrational motion during excitation in various modes, with multifrequency excitation (IR-IR, IR-UV, etc.). Such studies would be completely feasible by the new method reported here.

¹V. M. Akulin, V. D. Vurdov, G. G. Esadze, N. V. Karlov, A. M. Prokhorov, A. A. Susanin, and É. M. Khokhlov, *Pis'ma Zh. Eksp. Teor. Fiz.* **40**, 53 (1984) [*JETP Lett.* **40**, 783 (1984)].

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³V. M. Akulin and N. V. Karlov, *Zh. Eksp. Teor. Fiz.* **79**, 2104 (1980) [*Sov. Phys. JETP* **52**, 1063 (1980)].

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