

Direct observation by the RLS method of the randomization of the vibrational energy in molecules during interaction with a strong laser IR field

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The Raman light scattering (RLS) spectroscopy method has been used for the first time for diagnostics of the molecular excitation process in a laser IR field. The randomization of the vibrational energy in CF_3I and SF_6 molecules has been investigated.

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In studies of the interaction process of polyatomic molecules with a laser IR field considerable attention has been focused on the question of the energy distribution among the various vibrational degrees of freedom. At the present time it is universally accepted¹ that for a sufficiently strong molecular excitation the vibrational energy is distributed in a statistically balanced manner among the modes. This is caused² by the

complicated (stochastic) character of the motion of the nuclei in a highly excited molecule. In papers dealing with the interaction of molecules with an IR field this energy region is usually called the vibrational quasicontinuum. At the same time, during the excitation of the low molecular transitions only that mode should be efficiently excited whose frequency is in resonance with the laser radiation. It is obvious that for understanding the IR photoexcitation process the question of the location of the boundary between the stochastic region of the vibrational motion and the low-energy region, where the motion is customarily described in terms of vibrational modes, is exceptionally interesting.

In our work we have used the RLS spectroscopy method for the first time for directly observing the randomization in the the process of IR photoexcitation of molecules. The physical concept of using this method is quite simple. During the resonance excitation of only the one vibrational mode ν_{IR} active in IR absorption, the anti-Stokes component of the RS signal in some other mode ν_{RS} , active in the RS, should be absent. The anti-Stokes signal I_A will appear only when the excitation process affects the ν_{RS} mode.¹⁾ This can occur both as a result of the interaction with the IR field itself and as a result of collisional vibrational relaxation, occurring after the laser flash. Any changes in I_A are extremely simple to interpret since, as is easily shown,³ its value, integrated over the spectrum near ν_{RS} , is proportional to the average energy in this mode and does not depend on the distribution function.

CF_3I and SF_6 molecules were investigated. Excitation was accomplished with a CO_2 laser flash with a base-line duration of 20–25 nsec. The radiation frequency was tuned to the Q -branch of the ν_1 mode of the CF_3I molecule (1074.6 cm^{-1}) and the ν_3 mode of the SF_6 molecule (944.7 cm^{-1}). The radiation was focused at the cell by a cylindrical lens (see Fig. 1). The second harmonic of a ruby laser with a flash duration $\tau_{\text{UV}} \approx 20$ nsec was used as the source for obtaining the RS spectrum. A synchronization circuit made it possible to vary continuously the delay τ between the two flashes. The accuracy of the synchronization was 15 nsec. The probing radiation was focused down to a 0.2-mm diameter neck coaxially with the 1-mm thick neck of the CO_2 laser

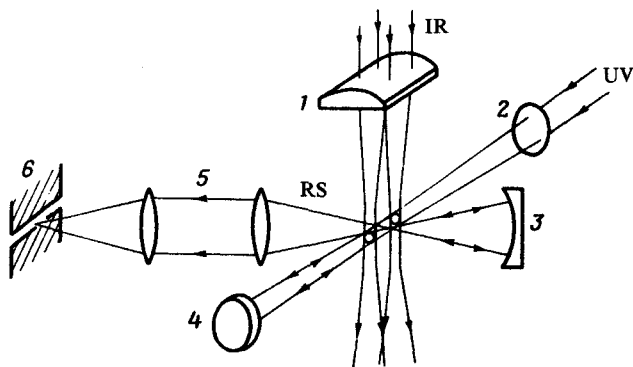


FIG. 1. Optical schematic of experiment: 1—cylindrical NaCl lens, 2, 5—quartz lenses, 3, 4—mirrors to collect scattered light, 6—entrance slit of triple monochromator.

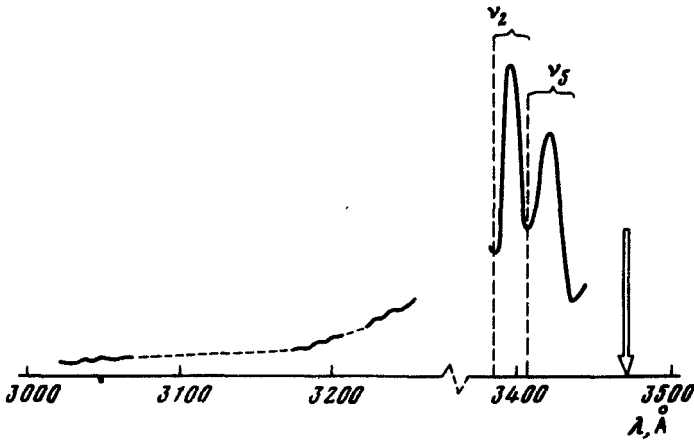


FIG. 2. Portions of the anti-Stokes RS spectrum in CF_3I for the following conditions: pressure $p = 3.5$ Torr. Energy density of IR flash is $\Phi = 1.2 \text{ J/cm}^2$. Delay between IR and UV flashes is $\tau = 1.2 \mu\text{sec}$. Dashed lines denote harmonic locations of lines. Arrow indicates RS excitation frequency.

radiation. A system⁴ including a triple monochromator and a multichannel television recording system, operating in the photon counting regime, was used to record the RS spectra.

A portion of the spectrum in the anti-Stokes region of vibrationally excited CF_3I molecules is shown in Fig. 2. It is seen that two modes ν_2 and ν_3 , active in RS, are clearly evident in this portion of the spectrum, and even for very strong excitation of

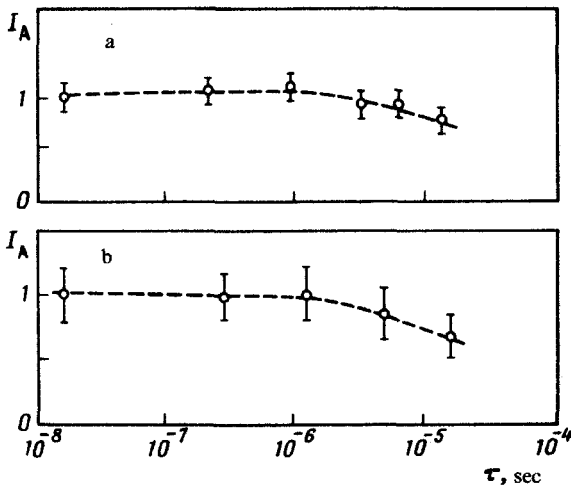


FIG. 3. Dependence of integral anti-Stokes RS signal on the delay τ between IR and UV flashes: a— SF_6 , $\Phi = 0.28 \text{ J/cm}^2$, $p = 0.5$ Torr, b— CF_3I , $\Phi = 0.30 \text{ J/cm}^2$, $p = 0.5$ Torr.

the CF_3I molecules the RS spectrum is concentrated near the frequencies of these modes. The maxima of the bands, however, are shifted toward the long-wavelength side because of anharmonic effects. The dependence of the intensity I_A of the anti-Stokes signal in the individual modes on the delay τ for different excitation levels was measured in order to investigate the randomization of the vibrational energy. To do this the portion of the spectrum within which the anti-Stokes scattering in a given mode is concentrated is isolated by the monochromator, and the signal was recorded by a PMT. The measurements were made at a gas pressure $p = 0.5$ Torr.

Figure 3 shows the relationship $I_A(\tau)$ for both molecules at the minimum CO_2 laser energy density $\Phi = 0.3 \text{ J/cm}^2$ at which the sensitivity of the recording system was still able to measure the RS signal reliably. It is seen that the signal does not change as the delay is changed from the minimum value (0–15) nsec to a value of $\approx 1 \mu\text{sec}$. (The observed fall-off for $\tau > 1 \mu\text{sec}$ is due to the diffusion of molecules from the excitation region.) The minimum delay corresponds to times much shorter than the vibrational-vibrational relaxation time. Analogous results were obtained in portions of the spectrum corresponding to other modes, active in RS. The nature of the behavior did not change as Φ was increased to 1.2 J/cm^2 and p to 10 Torr.

The results obtained indicate unequivocally that under the conditions of the experiments for $\Phi \geq 0.3 \text{ J/cm}^2$ and $p \geq 0.5$ Torr randomization of the of the vibrational energy occurs even in the very process of interaction with the IR field. An upper estimate on the limiting random energy $\overline{\mathcal{E}}_{\text{st}}$ of the vibrational motion can be given from the measurement of the characteristics of the IR photoexcitation process for CF_3I and SF_6 molecules. For example, for CF_3I molecules for $\Phi = 0.3 \text{ J/cm}^2$ a fraction $q = 0.4$ of the molecules⁵ is excited into the quasicontinuum, and the absorbed energy per molecule amounts to $\overline{\mathcal{E}} = 4 \times 10^3 \text{ cm}^{-1}$. Thus, the average energy of the molecules, excited in the quasicontinuum, amounts to $\overline{\mathcal{E}}_q = \overline{\mathcal{E}}/q = 10^4 \text{ cm}^{-1}$. It can be concluded from this that $\overline{\mathcal{E}}_{\text{st}} < 10^4 \text{ cm}^{-1}$. For the SF_6 molecule, as follows from the data of Ref. 6, the estimate gives $\overline{\mathcal{E}}_{\text{st}} < 7 \times 10^3 \text{ cm}^{-1}$. A more precise determination of the $\overline{\mathcal{E}}_{\text{st}}$ values requires a higher recording equipment sensitivity, which, in our opinion, is completely realistic within the limits of one and one-half to two orders of magnitude.

In conclusion, let us note that the use of the RLS method is also promising for solving many other problems, arising in the study of IR photoexcitation and photodissociation processes. By recording the spectra of not only the anti-Stokes but also the Stokes components of the RS one can obtain information about the energy distribution of the molecules themselves as well as the radicals that are formed, and can also investigate the vibrational energy relaxation processes for highly excited molecules.

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⁵This constitutes the fundamental difference between the proposed method and methods associated, for example, with absorption probing.

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