

Dependence of the rate of vibrational-translational relaxation in SF₆ on the intensity of selective laser excitation

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Nonlinear effects of vibrational-translational ($V-T$) relaxation in an SF₆ molecule excited by intense radiation of a CO₂ laser were experimentally investigated. It is shown that at high excitation levels the ($V-T$) relaxation time becomes substantially shorter.

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1. The purpose of this article is to describe the results of an experimental investigation of the rate of vibrational-translational ($V-T$) relaxation in SF₆ gas under conditions of intense selective excitation of the molecule oscillations by radiation from a pulsed CO₂ laser. At intensities exceeding 10³ W/cm², the dependence of the ($V-T$) relaxation time on the intensity becomes strongly manifest; at an SF₆ pressure ~ 1 Torr, an increase of the intensity of the selective excitation from 10³ to 10⁶ W/cm² is accompanied by a decrease of the time of the ($V-T$) relaxation by a factor 6-7. Experiments with pure SF₆ and with an SF₆+Ar mixture (excited molecules in an inert-gas thermostat) have made it possible to separate effects of the acceleration of the ($V-T$) relaxation as a result of the heating of the gas (the Landau-Teller mechanism) and the anharmonicity that manifests itself substantially at larger vibrational temperatures.

2. Studies of selective pulse excitation of vibrational-rotational transitions have led to the discovery of a number of new nonlinear phenomena in molecules (see the recent review^[1]). Particular interest attaches here to radiative excitations of higher vibrational levels of polyatomic molecules, effects of collisionless bleaching in a strong optical field, etc.. It is natural to expect that at intensities as high as 10³-10⁸ W/cm² the nonlinear effects can manifest themselves also in relaxation processes; these nonlinearities can greatly influence many photophysical and photochemical phenomena.

We have investigated the nonlinear effects for the ($V-T$) relaxation process. Some of the data on this subject were obtained earlier for diatomic molecules in shock-tube experiments.^[2] On the other hand, under selective laser excitation, which offers the greatest possibilities for the study of the phenomena in question, ($V-T$) relaxation has heretofore been investigated only at low excitation levels.

3. A block diagram of the experimental setup is shown in Fig. 1. The SF₆ at pressures ~ 1 Torr and room temperature was excited by the radiation of a pulsed CO₂ laser operating on the $P(20)$ line ($\tau_p \approx 500$ nsec), and at a radiation power density ranging from 10³ to 10⁶ W/cm². The ($V-T$) relaxation process was monitored either against the time variation of the refractive index, determined by the translation temperature (interferometry method) or by absorption at one of the selected frequencies of the vibrational-rotational spectrum ("trial-beam method"). The measured relaxation times greatly exceed the times of the vibrational-rotational and rotational relaxations.

4. The experimental results are given in Figs. 2 and 3. Measurements of the relaxation time τ

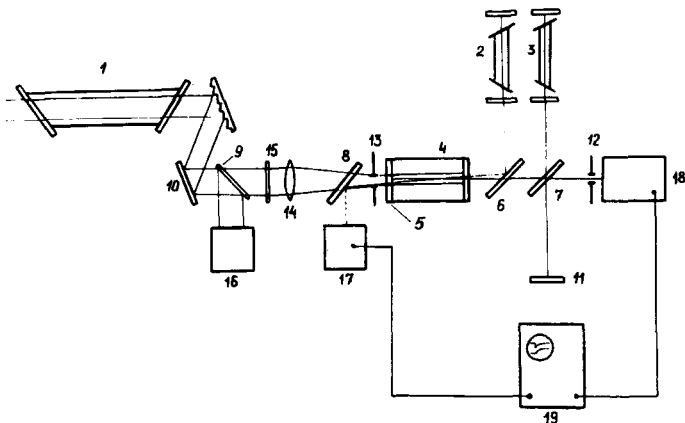


FIG. 1. Block diagram of experimental setup: 1—pulsed CO₂ laser; 2—cw CO₂ laser; 3—He-Ne laser ($\lambda=0.63 \mu\text{m}$); 4—cell with gas; 5—germanium mirror; 7—semitransparent mirror for $\lambda=0.63 \mu\text{m}$; 6, 8, 9—NaCl plates; 10, 11—total-reflection mirrors; 12, 13—diaphragms; 14—NaCl lenses; 15—attenuating filter; 16—calorimeter; 17—Ge-Au IR receiver; 18—photomultiplier; 19—two-beam oscilloscope S8-11 with memory.

were performed in pure SF₆ at a pressure 1–2 Torr (under these conditions, at the employed experimental geometry, the nonstationary processes accompanying the establishment of the density are inessential^[4]) and in a mixture of SF₆ with Ar. The data obtained by the interferometry method and by the two-beam method are in good agreement.

It is seen that at intensities $I > 10^3\text{--}10^4 \text{ W/cm}^2$ the (V — T) relaxation process is not described by a constant characteristic time; the quantity τ is a function of the time elapsed from the instant t of excitation ($\tau > \tau_p$ in all our experiments) and of the intensity I .

Figures 2 and 3 therefore show plots of $\tau = \tau(t)$ at fixed I (or at the corresponding maximal vibrational temperatures T_v) and the plots of $\tau = \tau(0, I)$, with $\tau(0, 0)$ corresponding to the relaxation time measured at small deviations from the equilibrium state.

5. Proceeding to a discussion of the experimental data, we note first that the values of τ obtained at $I \leq 10^3 \text{ W/cm}^2$ ($T_v \approx 300 \text{ K}$) agree well with the previously published data (according to^[3], $\tau(0, 0) = 122 \pm 8 \text{ sec-Torr}$ for pure SF₆).

The shortening of the (V — T) relaxation time is due, in our opinion, to the joint influence of the anharmonicity of the oscillations and the heating of the gas (the Landau-Teller mechanism), which manifest themselves at high excitation levels. In a single-component system of anharmonic oscillators, the time of (V — T) relaxation decreases with increasing vibrational temperature T_v , which in turn is a function of the intensity) like (see^[2,5])

$$\tau_{\text{anh}} = \tau_{\text{har}} \left[\frac{1 - \exp\left(-\frac{E_1}{T_v} + \delta\right)}{1 - \exp\left(-\frac{E_1}{T_v}\right)} \right]^2, \quad (1)$$

where τ_{har} is the (V — T) relaxation time for harmonic oscillators, E_1 is the energy of the lower vibrational levels, and δ is a factor that takes into account the influence of the anharmonicity on the probability of the single-quantum transitions:

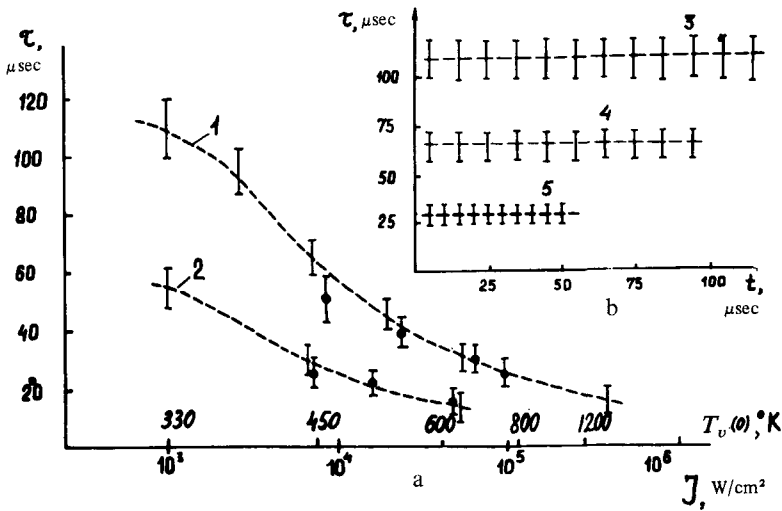


FIG. 2. Results of measurements of the ($V-T$) relaxation time as a function of the intensity I of the exciting radiation in pure SF_6 ($\tau = \tau(0, T_v) = \tau(0, I)$) at pressures 1 Torr (curve 1) and 2 Torr (curve 2) (a). The figure shows also the corresponding values of the maximum vibrational temperature $T_v(0)$. b) Plots of $r = r(t, I = \text{const})$, $I = 10^3, 10^4, 10^5$ W/cm 2 (curves 3, 4, and 5, respectively) for three values of I . The values of τ marked by dark circles were obtained by an interferometry method, and those without circles by a trial-beam method.

$$\delta \approx 4 \left[\left(\frac{0.32}{\alpha} \right)^{2/3} \left(\frac{\mu}{T} \right)^{1/3} E_1^{2/3} \left(\frac{\Delta E}{E_1} \right) \right] - \left(\frac{\Delta E}{T} \right),$$

where μ is the reduced mass of the colliding particles, α is the constant in the exponential potential $\sim \exp(-\alpha r)$ of the intermolecular interaction (in \AA^{-1}), T is the gas temperature (in $^{\circ}\text{K}$), and ΔE is the anharmonicity of the vibrations (in $^{\circ}\text{K}$).

In purest form, the effect of the anharmonicity should manifest itself for SF_6 in a thermostat. Therefore Fig. 3(b) shows, besides the experimental points, also a theoretical curve calculated in accordance with (1). To determine the parameter δ in accordance with the ($V-T$) relaxation model in SF_6 , the necessary data for the ν_6 mode were taken to be:

$$E_1 \approx 522\text{K}, \quad \frac{\Delta E}{E_1} \approx 7.5 \times 10^{-3}, \quad \mu = 28.6 \text{ at. mass un.}, \quad \alpha^{-1} = 0.4 \text{\AA},$$

$$T = 300\text{K}.$$

Of course, to assess conclusively the quantitative agreement between calculations based on (1) and experiment for polyatomic molecules it is necessary to have a more abundant experimental material; relation (1) was obtained for a single-mode model. Yet it is possible to advance on the basis of Fig. 3 certain hypotheses concerning the predominant relaxation channel. The behavior of τ in pure SF_6 can be attributed to simultaneous action of the anharmonicity (which plays the principal role at small t , when the difference between T_v and T is appreciable) and the gas heating, which plays a major role at the end of the relaxation process. The action of these two processes is the

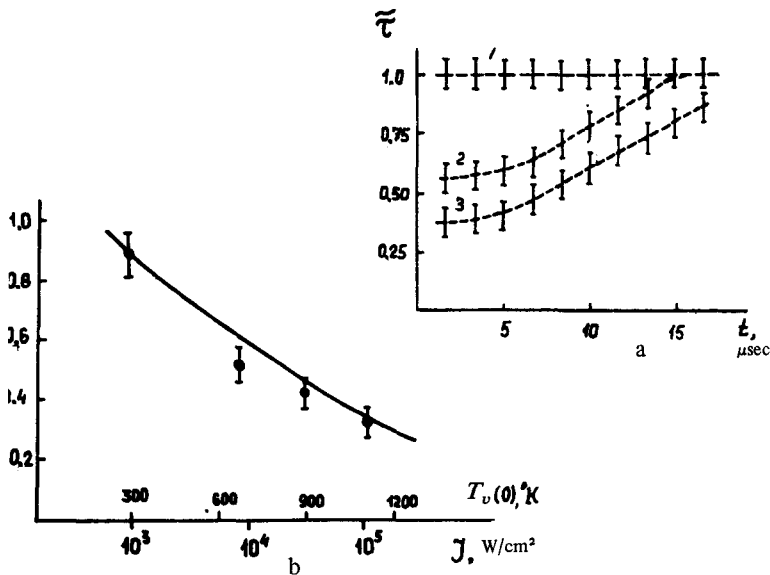


FIG. 3. Measured values of the ($V-T$) relaxation time τ as a function of the intensity I in a mixture of SF_6 (1 Torr) and Ar (40 Torr). a) For three values of the intensity $I = 10^3, 10^4, 10^5$ W/cm^2 (curves 1, 2, and 3 respectively) we show the plots of $\tau = \tau(t)$. b) The points show the experimental value of the ratio $\tau = \tau(0, I) / \tau(0, 0)$. The solid curve is a plot of formula (1) and represents the theoretical dependence of $\tau = \tau_{\text{anh}} / \tau_{\text{har}}$ on the vibrational temperature.

use of the weak $\tau = \tau(t)$ dependence; a similar situation obtains in experiments with shock tubes.^[2]

6. The described nonlinear effects in the ($V-T$) relaxation must be taken into account in many problems of laser photochemistry.

A detailed quantitative comparison of the data on ($V-T$) relaxation of strongly perturbed molecules placed in a thermostat, on the one hand, and theory, on the other, can be used to identify the relaxation channels; at high excitation levels, an appreciable contribution can be made by multiphoton processes and mode interaction; dissociation processes become significant.

Finally, the nonlinear phenomena can manifest themselves also in relaxation processes of other types; selective laser excitation offers extensive possibilities for their study.

R.V. Ambartzumyan and V.S. Letokhov, *Chemical and Biochemical Applications of Lasers* 2, 200 (1977), ed. by C.B. Moore, Academic Press, 1977.

S.A. Losev, O.P. Shatalov, and M.S. Yalovik, *Dokl. Akad. Nauk SSSR* **195**, 585 (1970) [*Sov. Phys. Dokl.* **15**, 1037 (1971)].

J.I. Steinfeld, J. Burak, D.E. Sutton, and A.W. Nawak, *J. Chem. Phys.* **52**, 5421 (1970).

V.M. Gordienko, A.V. Mikheenko, and V.Ya. Panchenko, *Kolebatel'no-postupatel'naya relaksatsiya v SF_6 pri bol'shikh urovnyakh selektivnogo vzbuzhzhdeniya* (Vibrational-Translational Relaxation in SF_6 at High Selective-Excitation Levels), Paper at Fifth All-Union Vavilov Conf. on Nonlinear Optics, Novosibirsk, June 15-19, 1977.

B.F. Gordiets, A.I. Osipov, E.V. Stupochenko, and L.A. Shelepin, *Usp. Fiz. Nauk* **108**, 655 (1972) [*Sov. Phys. Usp.* **15**, 759 (1973)].