EXCITATION OF NONPOLAR MOLECULES WITH THE AID OF STIMULATED RAMAN SCATTERING

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1. We have investigated the possibility of obtaining highly excited non-polar molecules with the aid of stimulated Raman scattering.

It is well known that the process of stimulated Raman scattering on vibrational levels of molecules occurs most effectively in liquids. At the same time, the rapid relaxation in the liquid makes it difficult to obtain and to identify highly-excited vibrational levels. To overcome this difficulty, we used the following experimental setup: Radiation of a ruby laser of energy 0.8 - 4 J and pulse duration $\tau = 3 \times 10^{-8}$ sec was focused with a lens of focal length 25 cm into a cell with liquid nitrogen, to obtain the Stokes frequency. Band filters placed at the exit from the cell separated the fundamental and first Stokes components, which were then focused with a lens ($f = 5$ cm) into a cell filled with a mixture 50% O_2 + 50% N_2 or with air at a relatively low pressure (300 Torr). The dimension of the spot at the focus was $\sim$1.5 mm.

Laser radiation $\hbar\omega_L$ directed into a low-pressure cell in the presence of an intense Stokes component $\hbar\omega_s$ should populate effectively the nitrogen level, since the Stokes frequency obtained by scattering from liquid nitrogen satisfies the resonance condition $\omega_s = \omega_L - \Omega$, where Ω is the vibrational frequency of N_2.

The vibrationally excited nitrogen was revealed by the appearance of nitric oxide NO in the mixture as a result of the reaction

$$N_2^* + O_2 \rightarrow 2NO$$
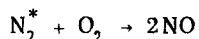
(N_2^* is the vibrationally excited nitrogen). The mixture was analyzed with a mass spectrometer before and after the irradiation. It was established that action of the fundamental and Stokes frequencies on the N_2 + O_2 mixture oxidizes the nitrogen. No nitric oxide was observed when only the fundamental laser frequency acted on the mixture.

2. The process of populating the vibrational level of the nitrogen can be described by the following kinetic equation:

$$\frac{\partial F}{\partial t} = -\frac{\partial}{\partial \epsilon}(I_q + I_{vv} + I_{vT}), \tag{1}$$

where $F(t, \epsilon)$ is the energy distribution function of the molecules,

$$I_q = \Gamma_{01}\hbar\omega\epsilon, \quad I_{vv} = \frac{1}{r_{vv}}\epsilon\left(F + \theta\frac{\partial F}{\partial \epsilon}\right), \quad I_{vT} = \frac{1}{r_{vT}}\epsilon\left(F + T\frac{\partial F}{\partial \epsilon}\right) \tag{2}$$

are respectively the molecule fluxes in energy space produced by the interaction of the molecule with the laser field and by the processes of their vibrational-vibrational and vibrational-translational relaxation, θ is the effective vibrational temperature, T is the translational temperature, $\Gamma_{01} = [6\pi T_2 \hbar^2 c^2/(\hbar\omega_s)^4]q_\Omega q_s Q_0$ is the probability of molecule transition between the ground and first-excited levels as a result of Raman scattering of a flux of photons of fundamental frequency q_L in the presence of a flux of photons of

Stokes frequency q_S, T_2 is the time of transverse relaxation, c is the speed of light, Q_0 is the total Raman-scattering cross section, and τ_{vv} and τ_{vT} are the times of vibrational-vibrational and vibrational-translational relaxation.

The kinetic equation (1) with the fluxes in the form (2) coincides with the analogous equation for the excitation of a dipole molecule by resonant radiation [1, 2]. At a sufficiently long laser-pulse duration ($\tau_{vv} < \tau < \tau_{vT}$), the solution of (1) takes the form $F(t, \varepsilon) = f(\varepsilon)\exp[-\gamma t]$, where γ determines the rate of the chemical reaction. If it is assumed that, owing to anharmonicity, the field excites transitions only between the ground and the first-vibrational levels, then γ and the "vibrational" temperature reach, at sufficiently large radiation fluxes q_S and q_L, their limiting values

$$\gamma_{\infty} \simeq \frac{r}{\tau_{vv}} \left(\frac{\hbar\omega}{\epsilon^*}\right)^2 \ln(\epsilon^*/\hbar\omega), \quad \Theta_{\infty} \simeq \frac{\epsilon^*}{2}\ln(\epsilon^*/\hbar\omega), \tag{3}$$

where ε^* is the activation energy of the reaction $N_2 + O_2 = 2NO$. Since $\varepsilon^* \simeq$ 2 eV [3, 4], $\gamma \simeq 5 \times 10^{-2}/\tau_{vv}$ and $\Theta_{\infty} \simeq 3000°K$. The fluxes required for saturation are $q_S \simeq q_L \simeq q \simeq 10^2$ MW/cm^2 at a gas pressure $\sim$300 Torr, and $T_2 \simeq 10^{-10}$ sec. At $\tau \simeq \tau_{vv}$, $\tau_{vv} \simeq 10^{-6}$ sec, and $Q_0 \sim 10^{-28}$ cm^2, approximately one per cent of the N_2 is oxidized. Since $\tau << \tau_{vv}$ in our experiments, the oxidation of the nitrogen occurs after the termination of the laser pulse, and the number of the reacting molecules is given by

$$\Delta N \simeq N_0 \frac{r\,kT}{\tau_{vv}} \exp\left(-\frac{\epsilon^*}{\Theta_0}\right), \tag{4}$$

where Θ_0 is the vibrational temperature of the nitrogen at the instant of termination of the laser pulse. Assuming that $\hbar\omega/2 < \Theta_0 < \hbar\omega$, and putting $\tau_{vv}/\tau_{vT} \sim 10^{-3}$, we find from (4) that $10^{-6} \lesssim \Delta N/N \lesssim 10^{-2}$. It follows from the experimentally obtained value $\Delta N/N \simeq 0.04\%$ that $\Theta_0 \simeq 0.7\hbar\omega$.

What is the role played by the vibrationally-excited nitrogen molecules in the formation of the nitrogen oxides in our experiments?

It is known that in most reactions in which nitrogen takes part the decisive role is played by the so-called "active" nitrogen. The "active" nitrogen is either atomic nitrogen [3 - 5] or vibrationally-excited molecules that are in the electronic ground state. In thermal methods of nitrogen oxidation, the atomic nitrogen is apparently the main component of the active nitrogen. In electric-discharge methods of obtaining nitric oxide, a considerable fraction of the molecules are in vibrationally-excited states, a circumstance connected with the anomalously large cross sections for the excitation of the vibrational levels of N_2 by electrons [6]. It is most natural to assume that the oxidation of nitrogen in a laser field of fundamental and Stokes frequency occurs with participation of just the vibrationally-excited N_2 molecules. Participation of the atomic nitrogen in the reaction has low probability. The dissociation energy of N_2 is $\varepsilon_D \sim 10$ eV and the very small values of $\Delta N/N$ obtained from (4) at $\varepsilon^* \simeq 10$ eV contradict the experimental results.

Our experiments show that Raman scattering can be useful for a purposeful stimulation of chemical reactions, especially for the study of their kinetic features.

[1] N.G. Basov, E.M. Belenov, E.P. Markin, A.N. Oraevskii, and I.A. Poluektov, Proc. Isfahan Symposium on Laser Physics, 1971.
[2] Yu.V. Afanas'ev, E.M. Belenov, E.P. Markin, and I.A. Poluektov, ZhETF Pis. Red. 13, 462 (1971) [JETP Lett. 13, 331 (1971)].
[3] Ya.B. Zel'dovich and Yu.P. Raizer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavlenii (Physics of Shock Waves and High-temperature Hydrodynamic Phenomena), Fizmatgiz, 1966. [Academic, 1966].
[4] Ya.B. Zel'dovich, P.Ya. Sadovnikov, and D.A. Frank-Kamenetskii, Okislenie azota pri gorenii (Oxidation of Nitrogen by Combustion), AN SSSR, 1947.
[5] R.A. Back, M. Menzies and C.A. Wincler, Canad. J. Chem. 34, 103 (1953).
[6] G.J. Shulz, Phys. Rev. 135A, 988 (1964).

FORMATION OF SUBPICOSECOND UV PULSES BY MULTIPLE NONLINEAR CONVERSION

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1. The purpose of this article is to describe an ultrashort-pulse generator that emits in the wavelength band $\lambda = 0.26 - 0.28$ μ pulses of duration to 0.5×10^{-12} sec and power ~ 10 MW. Such pulses were generated by twofold doubling of the emission of a neodymium-glass picosecond laser. Discrete frequency variation in the UV band was attained through SRS of the fourth-harmonic radiation ($\lambda_4 = 0.26$ μ) in liquid nitrogen. The energy efficiency of the conversion into the fourth harmonic reached 5%.

A major advantage of the method used by us to generate UV picosecond pulses is the improvement, through multiple nonlinear conversion, of the structure of the wave train (suppression of satellites, filtering of the wings of the nonsynchronized spectrum) and reduction of the pulse width.

2. Picosecond pulses in the UV band are of considerable interest as a means of pumping UV lasers, in the determination of the relaxation times of electronic levels, and in the investigation of nonstationary nonlinear effects.

Cascade frequency conversion is at present practically the only way of obtaining sufficiently powerful picosecond pulses in the region $\lambda = 0.26$ μ.

3. The apparatus (Fig. 1) consisted of a picosecond-pulse generator (LGS-1 glass) and two frequency multipliers. In the main laser, the cell with the dye was made integral with the total-reflection mirror; the dye solution was replenished in the cell after each flash.

The generator operated in the lowest transverse mode, which was separated by a diaphragm of 2.2 mm diameter. Typical data on the picosecond pulse train were: total energy of train of 20 pulses $W_1 = 5 \times 10^{-2}$ J; pulse duration (determined from the two-photon luminescence track) $\tau_p = 4 \times 10^{-12}$ sec; peak intensity of unfocused beam $I_1 = 4 \times 10^{10}$ W/cm^2. The first frequency doubler (output frequency $\lambda_2 = 0.53$ μ) used in our experiment was a KDP, ADP, or CDA crystal; in the second doubler (output wavelength $\lambda_4 = 0.26$ μ) we could only use KDP or ADP. An effective quasistatic frequency doubling accompanied by narrowing of the pulse takes place if the length ℓ of the nonlinear crystal is
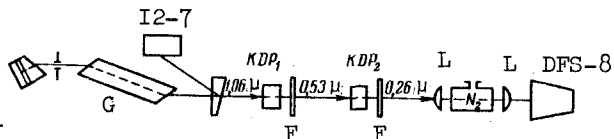

Fig. 1. Experimental setup: G - picosecond pulse generator, KDP$_{1,2}$ - frequency doublers using KDP crystals, F - filters, N$_2$ - liquid-nitrogen cyrostat, I2-7 - oscilloscope and other measuring apparatus.