Two-photon Raman excitation of molecular vibrations; a new approach to the study of vibrational relaxation in polyatomic gases

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The new approach to the study of the manners and rates of relaxation of vibrational energy in an ensemble of polyatomic molecules consists of using two-photon Raman excitation (TRE) of Raman-active vibrational-translational transitions (resonance condition $\omega_1 - \omega_2 = \Omega$, where ω_1 and ω_2 are the frequencies of the components of biharmonic laser emission and Ω is the frequency of the vibrational-rotation transition from the ground state which is allowed in Raman scattering), to produce a strongly nonequilibrium redistribution of the molecules among the quantum levels and to observe the subsequent restoration of the thermal equilibrium. The means and rates of vibrational relaxation are probed by (coherent) active Raman-scattering spectroscopy (CARS). With H_2, CO_2, and SF_6 as examples it is shown experimentally that TRE is highly effective for selective energy input to the internal degrees of freedom of polyatomic degrees of freedom of polyatomic molecules, comparable with the effectiveness of direct IR excitation of dipole-allowed transitions. Strong saturation of the vibrational and rotational transitions in TRE is recorded directly for the first time. The TRE-CARS method is distinguished by its high selectivity of excitation and probing, by the possibility of investigating all molecules (including homonuclear diatomic ones that cannot be investigated by IR spectroscopy) and the arbitrary Raman-active transitions, as well as high spectral, temporal and spatial resolution. The TRE-CARS method was used to investigate the channels and measure the rate constants of collisional energy exchange in the system of lower vibrationally excited states of the CO_2 molecule, and to reveal the important role of dipole-active overtones of the deformation mode of this molecule in the deactivation of the excitation energy of the lower laser levels. The great importance of the symmetry of the states of the collision partners for the realization of vibrational exchange is demonstrated experimentally. It is observed that the first excited state of the completely symmetrical mode of the SF_6 molecule is long-lived: $\tau_r p \gtrsim 15$ μsec · Torr.

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§1. INTRODUCTION

1.1 Ensembles of molecules that are selectively excited into definitive vibrational states play an important role in laser photophysics and photochemistry, and are widely used in research on physical and chemical kinetics.[1–3] They were usually produced by acting directly on the vibrations of the chosen mode with IR laser radiation that is at resonant in frequency with the corresponding dipole-allowed transition in the molecule. However, the difficulties of obtaining intense IR radiation that can be continuously tuned in frequency in a sufficiently wide band, and the presence of selection rules that "forbid" IR excitation from the ground state of fully symmetric and other Raman-active vibrational modes to a large number of molecules ("alternative hindrance"[4]), impose certain restrictions on this method. Two-photon Raman excitation (TRE) of vibrational Raman modes in a biharmonic field of a high-power laser in the UV, visible, or near-IR band ($\omega_1 - \omega_2 = \Omega$, where ω_1 and ω_2 are the frequencies of the laser pump and Ω is the frequency of the excited mode) constitute an additional method of preparing ensembles of selectively excited molecules, besides the one described above.

The pump in a TRE system can be an effective, tunable in a wide range (up to several thousand reciprocal centimeters), an organic-dye-solutions laser (ODSL), or a parametric light generator that can cover which is in conjunction with a laser of fixed frequency the entire region occupied by the states of the normal vibrations of polyatomic molecules ($0 \leqslant |\omega_1 - \omega_2|/2\pi c \leqslant 4500$ cm^{-1}). The high peak power of such lasers and the possibility of using "hard" focusing make it possible, as will be shown below, to reach exceedingly high efficiencies of the TRE, comparable with the efficiency of direct IR excitation.

TRE can be used to excite fully symmetrical and other IR inactive molecular vibrations, including vibrations of diatomic homonuclear molecules (H_2, O_2, N_2, etc.). All this indicates that the TRE is definitely a promising method.

1.2 The first to observe population of an excited vibrational level in the course of stimulated Raman scattering (SRS) of a high-power ruby-laser pulse in hydrogen gas were de Martini and Ducuing[5]; they registered the spontaneous anti-Stokes Raman scattering of a probing light beam. In several later experiments[6,7] the SRS technique was used to induce a small increase of the population in the state $v = 1$ of simple diatomic molecules in pure gases and in mixtures, as well as (with the aid of SRS of picosecond pulses) in completely symmetric vibrational states of polyatomic molecules in liquids. Owyoung and Esherick[9] used two-photon Raman saturation of a vibrational transition in D_2 for spec-

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troscopy of SRS amplification, free of Doppler broadening (the theory was developed in Ref. 10). Finally, recently Byer and co-workers[11] recorded broadening of the spectral line of a signal of coherent active Raman-scattering spectroscopy (CARS)[1)] in acetylene, which they attributed to saturation of the Raman transition in the two-frequency pump field. In the experiments of Owyoung and Esherick and of Byer there was no independent monitoring of the population of the upper level of the excited transition.

In our preceding paper[13] we reported, for the first time ever, strong (up to 20% of the total number of molecules) selective population of the states. $CO_2(10^00)$ and $CO_2(02^00)$ of carbon dioxide gas on account of TRE, and the appearance of an "excess" population on the lower level $CO_2(01^10)$ as a result of vibrationally inelastic collisions (see also Ref. 14).

1.3 The present article is devoted to an experimental investigation of the limiting characteristics (primarily, efficiency) of two-photon Raman excitation of vibrations and rotations of diatomic and polyatomic molecules in the gas phase (with H_2, CO_2, and SF_6 as examples) and to the development of a new method, based on TRE, of investigating vibrational relaxation in molecular gases. The latter consists of direct sounding, with the aid of coherent CARS, of the changes of the populations of vibrationally-rotational states of the investigated molecules in the course of collision V-V exchange with the state subjected to the TRE.

§2. ESTIMATE OF THE EFFICIENCY OF TWO-PHOTON RAMAN EXCITATION OF A VIBRATIONAL TRANSITION

The perturbation of the population of vibrational levels of a molecular gas in a biharmonic optical field

$$\mathbf{E}(t)={}^1/_2(\mathbf{E}^{(1)}e^{-i\omega_1 t}+\mathbf{E}^{(2)}e^{-i\omega_2 t}+\text{c.c.}) \tag{1}$$

can be calculated exactly within the framework of the two-level model, assuming that $\omega_1-\omega_2\approx\Omega$ is the frequency of the selected molecular vibration. The steady state solution of the equations for the coherent amplitude Q of the molecular vibrations and normalized difference of the populations of the vibrational levels n (see Ref. 12, §2, Chap. V), is of the form

$$Q(t)={}^1/_2Q_0e^{-i(\omega_1-\omega_2)t}+\text{c.c.},\qquad n=n_0, \tag{2}$$

$$Q_0\approx\frac{T_2}{4M\Omega}\left(\frac{\partial\alpha}{\partial Q}\right)_0 n_{\text{ther}}E^{(1)}E^{(2)*}\frac{i-\Delta}{1+G+\Delta^2}, \tag{3}$$

$$n_0=n_{\text{ther}}[1+G/(1+\Delta^2)]^{-1}. \tag{4}$$

Here $\Delta=(\omega_1-\omega_2-\Omega)T_2$ is the dimensionless detuning, T_1 and T_2 are respectively the "longitudinal" and "transverse" relaxation times, α is the electronic polarizability of the molecule, n_{ther} is the equilibrium population difference, M is the reduced mass of the molecules, $G=I_1I_2/I^2_{\text{sat}}$ is the parameter of two-photon saturation, $I_{1,2}=(c/8\pi)|\mathbf{E}^{(1,2)}|^2$, and I^2_{sat} is the square of the intensity of the saturation, which can be conveniently expressed in terms of the differential cross section $d\sigma/do$ for Raman scattering (RS) in the following form:

$$I^2_{\text{sat}}=(\pi c\hbar)^2(\lambda_1^4T_1T_2d\sigma/do)^{-1}. \tag{5}$$

The homogeneous width of the molecular resonance at the level 0.5, as can be seen from (3), increases with increasing G:

$$\Delta\Omega=2(1+G)^{1/2}/T_2. \tag{6}$$

The nonstationary solution for $n(t)$ and $Q(t)$ is similar in form to the so-called Torrey solution, which is well known in the theory of saturation of magnetic resonance (see, e.g., Ref. 15), with the linear polarizabilities of the transitions replaced by the Raman polarizabilities (see Ref. 12, §2, Chap. V and Ref. 16). We shall need later a general expression for $n(t)$ at $\Delta\omega=\omega_1-\omega_2-\Omega=0$ for the case of "rectangular" pump pulses, which are turned on at the instant $t=0$:

$$n(t)=\frac{n(0)}{1+G}\left[1+Ge^{-t/T}\left(\text{ch}\,\tilde\Omega t+\frac{1}{\tilde\Omega T}\text{sh}\,\tilde\Omega t\right)\right], \tag{7}$$

where

$$\tilde\Omega=[T^{-2}-(G+1)/(T_1T_2)]^{1/2},\qquad T^{-1}={}^1/_2(T_1^{-1}+T_2^{-1}).$$

It is obvious that at $G>T_1T_2/T^2-1$ ("coherent regime") the function $n(t)$ is subject to oscillations, which are the analogs of single-photon optical nutation.

The pump-wave intensities needed to saturate Raman transitions in molecules in the gas phase can be relatively easily obtained in experiment. For example, in carbon dioxide at atmospheric pressure, where $d\sigma/do=4.5\cdot10^{-31}$ cm^2/sr for $\lambda\approx500$ nm,[17] $(\pi T_2)^{-1}=150$ MHz,[18] and $\Omega/2\pi c=1388$ cm^{-1} approximately 25% of the molecules in the interaction volume turn out to be in the excited state in a biharmonic field of the form (1) at $I_1=I_2=0.9\cdot10^9$ W/cm^2 within a time $\tau=20$ nsec. This still does not cause breakdown of the gas[19] and/or other undesirable side effects.

We note at Eqs. (3)–(7) can be used also in the calculation of the saturation of purely rotational Raman-active transitions.

§3. LASER SPECTRUM-ANALYSIS ASSEMBLY FOR EXPERIMENTS BY THE TRE-CARS METHOD; EXPERIMENTAL PROCEDURE

A block diagram of the experimental setup is shown in Fig. 1.

The emission of the Nd:YAG master oscillator ($\lambda=1.06$ μm, $\tau\approx20$ nsec) is amplified in Nd:YAG amplifiers A1–A3. After doubling the frequency in nonlinear CDA crystals, part of the radiation is used to pump the TRE-CARS system at frequency $\omega_1(\lambda_1=0.53$ μm), and the second part of the second-harmonic radiation is used to excite tunable dye lasers at frequencies ω_2 and ω_3. The Raman-active transitions were excited by opposing collinear focused beams of frequencies ω_1 and ω_2. The powers of the corresponding beams reached 3 and 0.8 MW respectively at a spectral width less than 0.2 cm^{-1} at the 0.5 level of each of the pulses. The ω_2 radiation was amplified in a dye-filled cell K, pumped "head-on" by the ω_1 beam.

The populations of the excited states of the molecules were probed by the CARS method using "co-moving" propagating almost collinear beams of frequencies ω_1 and ω_3; the frequency of the recorded anti-Stokes CARS signal is $\omega_a=2\omega_1-\omega_3$. No time delay was introduced between the exciting (TRE) and probing (CARS) pulses. The kinetics of the collisional V-V processes manifested itself in a pressure

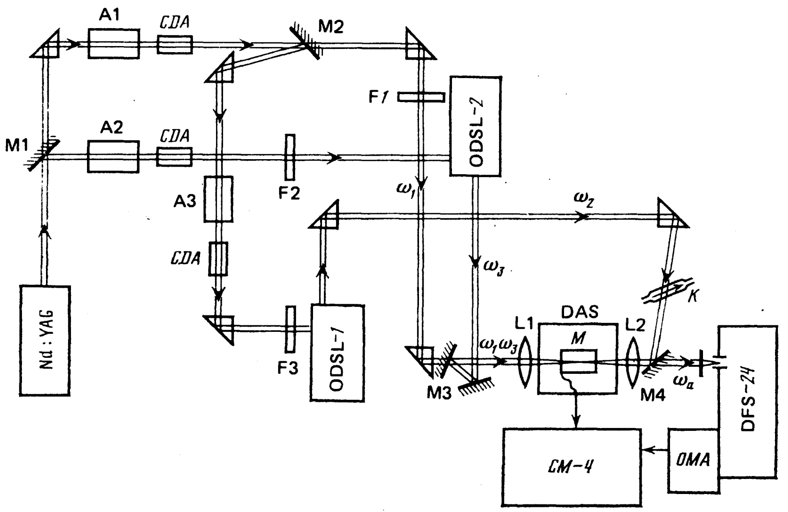

FIG. 1. Diagram of spectrum-analysis assembly developed for experiments on TRE-CARS of molecular gases; M1—semitransparent beam-splitting mirror; M2–M4—dichroic mirrors; M2 reflects radiation with $\lambda = 1.06\,\mu$m and passes radiation with $\lambda = 0.53\,\mu$m, while M3 reflects the tunable radiation $\omega_3(\lambda_3 = 555–580$ nm) and passes radiation with $\omega_1 = 0.53\,\mu$m; M4 reflects the beams ω_1 ($\omega_1 = 0.53\,\mu$m) and $\omega_2(\lambda_2 = 555–580$ nm) and passes the anti-Stokes CARS signal ($\omega_a = 2\omega_1 - \omega_3$; F1–F3 are SZS-21 light filters; OMA—optical multichannel analyzer (OMA-1 model of the PARC firm).

dependence of the relative intensities of the "hot" lines in the CARS spectra.

In the experiments we used broad band CARS probing of the excited molecules. To this end, the probing laser ODSL-2 had a line width $\geqslant 10$ cm^{-1}. The CARS spectrum was recorded in this case with the aid of an optical multichannel analyzer (OMA), located at the exit from the double monochromator DFS-24. The spectral resolution of such a system in these experiments was approximately 1 cm^{-1}. To improve the signal/noise ratio, 50–100 optical pulses were accumulated in each measurement.

A cylindrical condenser microphone M, equipped with an amplifier, was placed in the cell with the gas (OAS). This made possible optical-acoustic spectroscopy of the Raman scattering (OASRS), see Refs. 13 and 20–22). The OASRS was used to monitor the accuracy of the tuning of the pump-frequency difference ω_1–ω_2 to the frequency Ω of the excited mode.

The microphone signal, after first passing through a gated pulse-stretching amplifier[23] and the OMA were fed to a CM-4 minicomputer through matching modules in the CAMAC standard. Also fed to these modules were signals from the photodiodes (not shown in Fig. 1), two of which recorded the energies of the pump pulses ω_1 and ω_2 in each laser flash, and one of the energy of the measuring Fabry-Perot etalon ring, by the same token monitoring the frequency ω_2 of the tunable laser. The entire process of gathering, reduction, documentation, and feeding the experimental results to a display and/or a plotter was controlled by the computer in accordance with a set program.

§4. INVESTIGATION OF THE SATURATION OF TWO-PHOTON RAMAN-ACTIVE TRANSITIONS IN H_2, CO_2, and SF_6.

The presence of excitation of the vibrational-rotational Raman-active transitions in TRE and the appearance of saturation of these transitions were registered simultaneously by two methods: with the aid of CARS and OASRS.

The intensity of the coherent-CARS signal on the transition subjected to TRE with the aid of independent sources is given by

$$I_{AS} \propto (N_a - N_b)^2 (d\sigma/do)^2 \Delta\Omega^{-2}, \tag{8}$$

where N_a and N_b are respectively the densities of the molecules on the lower and upper levels of the investigated transition, and $\Delta\Omega$ is defined in (6). In the experiment one measures the energy of the anti-Stokes CARS pulse

$$W_{AS} \propto \int_0^\tau dt \int_V dV I_{AC}, \tag{9}$$

where V is the interaction volume.

The measured acoustic signal in the OASRS scheme (the peak value of the alternating voltage from the microphone) is proportional to the total number of molecules in the interaction volume, which are raised during the biharmonic-pump pulse to the excited state:

$$W_{OA} \propto \int_{(V)} dV N_b(\tau). \tag{10}$$

We investigated in the experiment the dependences of the signals W_{AS} and W_{OA} on the TRE level, $G \propto I_1 I_2$; the latter varied because of the variation of the intensity of the pump radiation with frequency ω_2. After the end of the measurement cycle, the computer arranged, in accordance with a special program, the aggregate of the measured values of W_{AS} and W_{OA} in accordance with the measured value of the product of the pump-pulse energy, and delivered the results in the form of a corresponding plot.

Figure 2 shows characteristic plots of $W_{AS}(G)$ and $W_{OA}(G)$ for the case of an investigation of the purely rotational transition $J = 3$ $J = 1$ (the line $S_0(1)$ in hydrogen gas; $\Omega/2\pi c = 587.5$ cm^{-1}. The measured values of $I_1 I_2$ were renormalized to the square of the "effective" saturation intensity $I^e_{sat} = (1.6 \pm 1.0) \times 10^{10}$ W/cm^2, namely $G = I_1 I_2 / (I_{sat}{}^e)^2$. The deviation of the $W_{OA}(G)$ dependence and the decrease of $W_{AS}(G)$ with increase of G, which are clearly seen in Fig. 2, attest to the equalization of the populations in the ground ($J = 1$) and excited ($J = 3$) states with increasing TRE, i.e., to saturation of the corresponding transitions.

The solid lines in Fig. 2 shows the results of a numerical

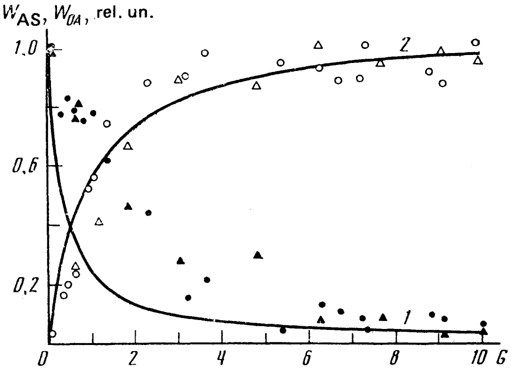

FIG. 2. Experimental (points) and theoretical (solid curves) dependences of the CARS signals (W_{AS} (curve 1, points ▲, ●) and OASRS signals—W_{OA} (curve 2, points Δ, ○ in the transition $S_0(1)$ of hydrogen ($p = 0.4$ atm, $T \approx 300$ K on the normalized product of the intensities of the components of the biharmonic pumping that produces the TRE of this transition; $G = I_1I_2/(I_{sat}^{e})^2$. The experimental points, in the form of markers with different shapes, were obtained in different experimental runs. They were plotted with a computer; the data are averaged over 100 pulses. CARS and the OASRS signals were normalized to the corresponding maximum values; the normalization along the abscissa scale is different for the experimental and theoretical curves (see the text).

solution of the equations for $n(t)$ and $Q(t)$ with allowance for (7), (9), and (10). Corresponding to the maximum value $G = 10$ shown in Fig. 2 is TRE of 45% of all the molecules initially located on the level $J = 1$ into the state with $J = 3$. the products I_1I_2 on the calculated plots were normalized to the square of the saturation intensity, calculated from the formula (5): $I_{sat}^{T} = 2.6\times10^8$ W/cm² (the value $d\sigma/do = 1.6\times10^{-30}$ cm²/sr was taken from Ref. 17, while $T_2 = 2\times10^{-9}$ sec and $T_1 = 10^{-7}$ sec were taken from Ref. 24). The difference between the values of I_{sat}^{e} and I_{sat}^{T} is due primarily to the fact that the spectral width of each of the pump waves (≈ 0.2 cm^{-1}) was ~ 20 times larger than the width of the investigated Raman transition (≈ 0.01 cm^{-1}), and also to geometric factors which were not taken into account in the calculation.

Figure 3 shows results of similar experiments on the line ν_1 of the SF_6 molecule ($\Omega/2\pi c = 774.5$ cm^{-1}, $p = 0.4$ atm). An estimate of the maximum value of the perturbation of the populations of the initial states on account of the TRE, based on the data on the decrease of the CARS signal, amounts to approximately 30%. For the transitions 10°0 ← 00°0 and 02°0 → 00°0 of the CO_2 molecule the analogous quantity was respectively approximately 35 and 30%.

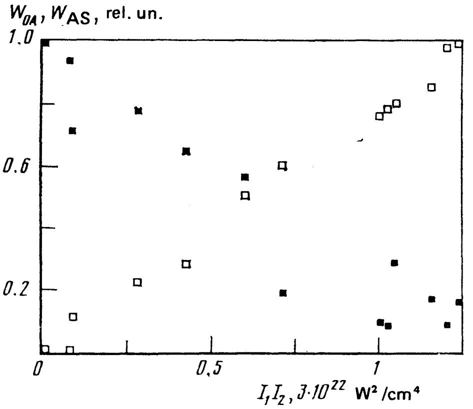

FIG. 3. Experimental dependences of the CARS signals (W_{AS} (the points ■) and of the OASRS signals W_{OA} (points □) in the transition 100000 ← 000000 of sulfur hexafluoride ($p = 0.4$ atm) on the product of the intensities of the components of the biharmonic pump that produces the TRE of the same transition.

§5. INVESTIGATION OF THE VIBRATIONAL RELAXATION IN CARBON DIOXIDE BY THE TRE-CARS METHOD

In experiments by the TRE-CARS method we have investigated in detail the vibrational exchange and the "thermalization" channels of selective excitation of fully symmetric states in the CO_2 molecule. The results of the preliminary experiments were briefly reported in Ref. 14. Kinetics of the collisional population and deactivation of the upper CO_2(00°1) laser level has by now been quite completely established (see Refs. 3, 25, 26, and the bibliography therein).

However, data pertaining to each of the two lower laser levels, CO_2(10°0) and CO_2(02°0), are known with much lower accuracy. Until recently the rate constant of the collisional exchange of energy between the lower laser levels, proceeding in accordance with the reaction.

$$CO_2(10^00)+CO_2(00^00)\leftrightarrow CO_2(02^00)+CO_2(00^00)+103\ \text{cm}^{-1}, \tag{11}$$

was estimated from data of various experiments to range from $\sim 10^3$ (Ref. 27) to $\sim 10^6$ (Refs. 28–31) sec^{-1}. Torr^{-1}. The most substantial causes of such large errors are[25,29] the relatively slow response of the photodetectors for the registration of the IR spectra, the low spectral resolution of the dispersion instruments in the middle and far IR, which make it difficult to classify the transitions, and finally the circumstance that neither the states 10°0 and 02°0 themselves nor the neighboring state 02^20 can be selectively populated, in accordance with the selection rules, from the ground state by direct IR excitation.

The TRE-CARS method is not subject to any of the foregoing restrictions. The sufficiently high spectral resolution of TRE-CARS both during the excitation stage (~ 0.2 cm^{-1} in our experiments) and in the probing state (~ 1 cm^{-1} makes it easy to identify the "hot" lines that appear in the CARS spectra, and the transitions corresponding to them. The positions of the energy levels of the vibrational states of CO_2 were taken from Ref. 32.

Figure 4 shows the dependence, on the pressure p, of the excess (over the equilibrium value at $T \approx 300$ K) populations of certain levels populated by collisions in TRE of the state 10°0 or 02°0 (the curves were normalized to their values at $p = 1$ atm). These populations were taken to equal $W_{AS}^{1/2}/p$ [cf. Eq. (9)]; for the 01^10 level, account was taken of the equilibrium population (8.1% at $T \approx 300$ K).

The excitation of the numerical values of the rate constants of the collision-exchange reactions from the data shown in Fig. 4 is not a simple task, inasmuch as the action of the Raman excitation continues during the probing. They can be used to determine reliably the relative rates of the collision processes with participation of different states, but provide only a rough estimate of their absolute values.

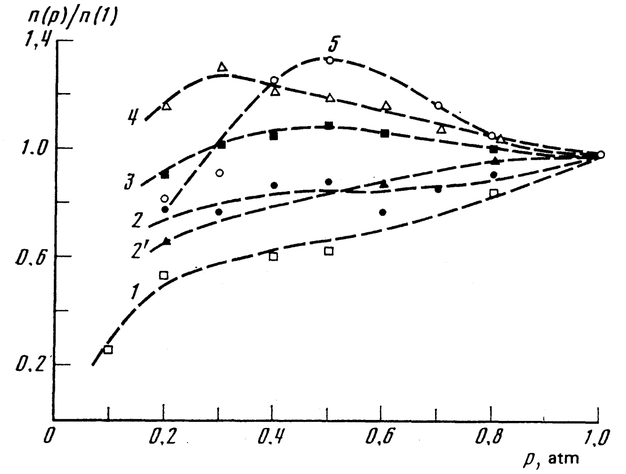

FIG. 4. Dependences, on the gas pressure, of the excess population of the equilibrium value for the levels 01^10 (curve 1), 02^20 (curves 2 and 2′), 03^10 (curve 3), 11^10 (curve 4), and 12^20 (curve 5) of CO_2 in the case of TRE of 10^00 (curves 2, 4, 5) and 02^00 (curves 1, 2′, 3). When the gas pressure was varied the TRE effectiveness (per molecule) of the corresponding levels was maintained constant.

It can be seen from the presented data that the most rapidly populated (with a rate constant $K \geqslant 7\times 10^5$ $\text{sec}^{-1}\cdot\text{Torr}^{-1}$) are the states 11^10 and 03^10 (cf. Ref. 14). The slower reactions, with rate constants $K \approx (4\text{–}7)\times 10^5$ $\text{sec}^{-1}\cdot\text{Torr}^{-1}$ are

$$CO_2(10^00)+CO_2(00^00) \leftrightarrow CO_2(02^20)+CO_2(00^00)+53\ \text{cm}^{-1}, \quad (12)$$

$$CO_2(02^00)+CO_2(00^00) \leftrightarrow CO_2(02^20)+CO_2(00^00)-50\ \text{cm}^{-1}. \quad (13)$$

The excess 02^20 population remains in this case, at all the investigated pressures, smaller by several times than the excess 01^10 population, whereas the reactions that populate the latter state proceed somewhat more slowly, with $K = (2\text{–}4)\times 10^5\ \text{sec}^{-1}\cdot\text{Torr}^{-1}$ (see Ref. 13 and Fig. 4). It follows therefore that the population of the state 01^10 at the TRE of 10^00 or 02^00 proceeds apparently not directly but via the level 02^20, followed by rapid deactivation of the latter through the channel

$$CO_2(02^20)+CO_2(00^00) \leftrightarrow 2CO_2(01^10)+0.3\ \text{cm}^{-1}. \quad (14)$$

We noted that precisely this method of energy degradation from the states 10^00 and 02^00 was predicted by Sharma from theoretical considerations.[33]

The exchange reaction (11), as follows from Ref. 14, is rather slow, with a rate constant $K \lesssim 7\times 10^4\ \text{sec}^{-1}\cdot\text{Torr}^{-1}$. This confirms indirectly the conclusion that the exchange reaction (14) is quite rapid, for otherwise the exchange $CO_2(10^00) \leftrightarrow CO_2(02^00)$ could be effected sufficiently rapidly via the state $CO_2(02^20)$ (see the reactions (12) and (13).

The collisional V-V exchange in the CO_2 molecule, observed in our experiments, are illustrated in Fig. 5 by wavy arrows. It can be seen that the deformation mode ν_2, which has the lowest energy quantum, plays an important role in the thermalization of the completely symmetrical states 10^00 and 02^00. The equilibrium is established most rapidly within the deformation mode, and furthermore among those of its overtones (and composite tones) which are not completely symmetric. Under the conditions of the described experiments, no manifestations whatever were observed of the reactions

$$CO_2(10^00)+CO_2(10^00) \leftrightarrow CO_2(20^00)+CO_2(00^00)-33\ \text{cm}^{-1}, \quad (15)$$

$$CO_2(02^00)+CO_2(02^00) \leftrightarrow CO_2(04^00)+CO_2(00^00)+22.5\ \text{cm}^{-1},$$

although they do have small energy defects, and the density of the excited molecules in our experiments was high enough. The low rate of these reactions can be attributed to the fact that the vibrational states that participate in the exchange have no dipole moments.

§6. STRONG RAMAN EXCITATION AND CARS PROBING OF THE MODE IN SF_6 GAS

The SF_6 molecule serves as a model in experiments on multiphonon excitation and dissociation of molecules in a strong resonant IR laser field.[1,2] It is of interest to assess the extent to which TRE via the completely symmetrical mode ν_1 can be used for multiphoton excitation and possibly for dissociation of this molecule with the aid of biharmonic pumping.

Upon excitation of completely symmetrical oscillations in SF_6 molecules (the mode ν_1), the difference between the frequencies of the emission of the Raman pumping $\omega_1-\omega_2$ were tuned to resonance with the frequency of these oscillations $\Omega/2\pi c = 774.5\ \text{cm}^{-1}$.

Figure 6 shows the spectra of the CARS probing of the mode ν_1 at different detunings $\Delta\omega = \omega_1-\omega_2-\Omega$ of the exciting pair of frequencies from exact resonace. It can be easily seen that as $\Delta\omega \to 0$ there is produced in the ν_1 spectrum a new band whose maximum is shifted by $1.8\ \text{cm}^{-1}$ from the position of the maximum of the unshifted line. The anharmonicity of the ν_1 mode amounts in this case exactly $1.8\ \text{cm}^{-1}$ (Ref. 34). Obviously, the new band is the hot line corresponding to the transition between the states $v_1 = 1$ and $v_1 = 2$. The very existence of this new line is an indication that in the investigated pressure range $p = 0.2\text{–}1$ atm the

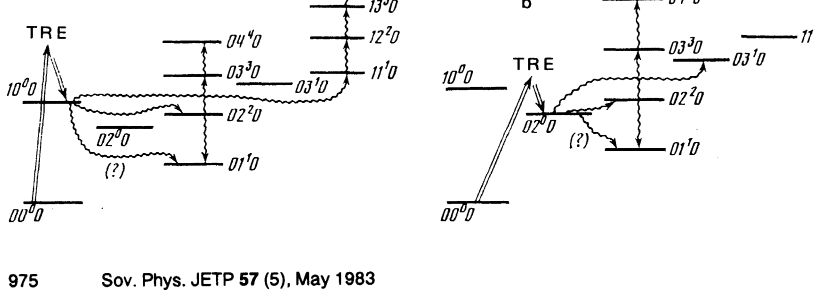

FIG. 5. Diagrams illustrated the most rapid channels (wavy arrows) of excitation energy transfer from the completely symmetrical states 10^00 (a) and 02^00 (b), populated from the ground state with the aid of TRE (shown by the double arrows). The level energies correspond approximately to their height above the 00^00 level.

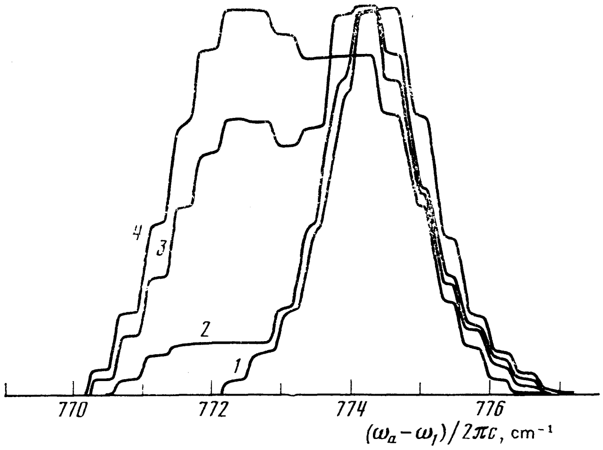

FIG. 6. Modification of the CARS spectrum of the ν_1 mode of the SF_6 molecule (gas pressure $p = 0.2$ atm) by a change of the conditions of the TRE of the transition $v_1 = 1 \leftarrow v_1 = 0$. For the curves 1, 2, 3, 4 the values of $\Delta\omega/2\pi c = (\omega_1 - \omega_2 - \Omega)/2\pi c$ are respectively 5, 3, 1, and 0 cm^{-1}. The curves were normalized to their maximum values. The spectral widths of both pump components do not exceed 0.2 cm^{-1}.

vibrational energy of the state $v_1 = 1$ relaxes more slowly than the energy input into it from the pumping laser.

The rate of laser pumping, determined in experiment, is $(\dot{n}/n)_{\rm TRE} \approx 5\times10^7$ sec^{-1}, therefore we obtain a relaxation time $\tau_r^{-1} \lesssim 5\times10^7$ sec^{-1}, i.e., $K = (\tau_r p)^{-1} \leqslant 7\times10^4$ sec$^{-1}\cdot$Torr^{-1}. This rate constant is substantially lower than the corresponding constant for the mode ν_3 $K \approx 10^6$ sec$^{-1}\cdot$Torr^{-1} of the SF_6 molecules: (Ref. 35). The apparent reason is that in the course of the ν_1 vibrations the SF_6 molecule retains its spherical symmetry, and its dipole moment is in this case zero (cf. the result of §5).

At the same time it can be seen that the states of the mode $\nu_1 = 1$ are not radiatively populated by the TRE. Obviously, the obstacle here is the relatively large anharmonic shift.

The character of the change of the CARS spectrum of the ν_1 mode under the influence of the TRE becomes different when one of the pumping waves of the TRE is not the radiation of a narrow-band ($\Delta\nu \approx 0.2$ cm^{-1}) dye laser but a broad-band ($\Delta\nu \approx 5$ cm^{-1}) laser having the same peak power (see Fig. 7). At optimal tuning of the central frequency of the broad band laser, the maximum intensity of the CARS spectrum of the ν_1 mode decreases by a factor ≈ 5 compared with the case when there is no TRE, and in place of the narrow line, shifted by 1.8 cm^{-1}, which appears under narrow-band excitation, one can see here a less pronounced broad wing, that extends into the low-frequency side from the center of the unshifted line all the way to ≈ 5 cm^{-1}.

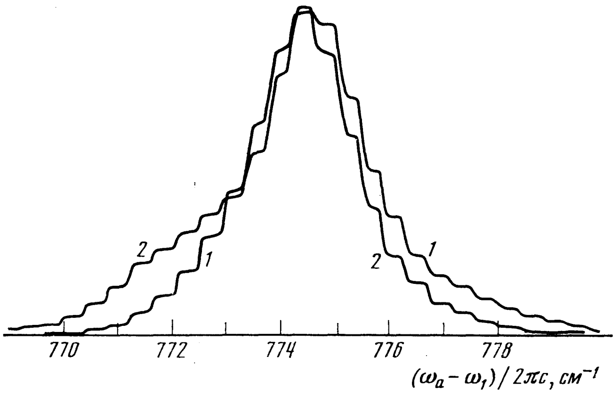

FIG. 7. Modification of the CARS spectrum of the ν_1 mode of SF_6 gas ($p = 1$ atm) in broad-band two-photon Raman excitation of the entire Q band of this transition—curve 2; curve 1 shows the CARS spectrum of the unexcited gas. The spectra are normalized to their maximum values.

It is natural to connect the appearance of this wing with the presence of hot lines in the CARS spectrum, lines corresponding to population of the states ν_1, $2\nu_1$, $\nu_1+\nu_6$, $\nu_1+2\nu_6$, etc. under the influence of the broad-band TRE. The anharmonic shift of the frequencies is compensated in this case automatically, on account of the broad band excitation.

§7. CONCLUSION

Thus, we have demonstrated experimentally that with the aid of Raman biharmonic pumping in the form of nanosecond pulses it is possible to excite effectively, all the way to saturation, dipole-forbidden transitions in polyatomic molecules in the gas phase (H_2, CO_2, SF_6).

There are grounds for assuming that the use of a more powerful multifrequency dye laser than in the present experiment will make possible radiative excitation of poly-atomic-molecule states that lie higher than $v_1 = 1$. In this case multifrequency pumping consisting of several narrow equidistant spectral lines separated by the anharmonic shift of the excited mode ensures selectivity of the excitation. The use of shorter and more powerful nanosecond laser pulses will make it possible to observe coherent effects in Raman-active transitions[16,36,37]—the analog of optical nutations, of photon echo, of self-induced transparency, etc., which were previously investigated in experiments on nonstationary excitation of dipole-allowed transitions. The first reports of experiments in this direction have already been published.[38,39]

Investigation by active RS spectroscopy, of the energy relaxation in nonequilibrium molecular ensembles produced with the aid of TRE, is the essence of a new approach to the investigation of vibrational relaxation of polyatomic molecules. The combined TRE-CARS method is outstanding for the following reasons: It is selective with respect to the excitation and probing levels. It is universal (all molecules, including homonuclear diatomic molecules have RS-active vibrational-rotational transitions suitable for excitation as well as for probing; all RS-active transitions with frequencies in the range 0–4500 cm^{-1} can be investigated with the same experimental setup without any substantial revamping or readjustment of the apparatus). It has no intensity or molecule-density threshold. It has high spectral, temporal, and spatial resolution (determined respectively by the width of the spectral line, by the pulse duration, and by the dimensions of the caustic of the focused beams of the high-power lasers in the visible range). It has high excitation efficiency (in the incoherent regime, up to 50% of the total number of molecules on the initial level, and in the coherent regime up to 100%) and probing efficiency (determined by the known advantages of coherent CARS). TRE-CARS methods were used to investigate means and rates of collisional exchange of energy in the system of first vibrationally excited states of molecules of carbon dioxide, to elucidate the substantial role played by dipole-active overtones of the deformation mode of this molecule in the deactivation of the excitation of the lower laser levels, and to prove experimentally the importance of the symmetry of the states of the partners in the collision for the realization of vibrational exchange. It was observed that the first excited state of the ν_1 mode in the SF_6 molecule is long-lived: in contrast to the dipole-active excitations *f* the mode ν_3, which decay at a rate $\sim 10^6$ $\sec^{-1} \cdot \text{Torr}^{-1}$, it becomes deactivated with a rate constant $K \leqslant 7 \times 10^4 \sec^{-1} \cdot \text{Torr}^{-1}$.

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[1)] The anti-Stokes variant of CARS is called also spectroscopy of coherent anti-Stokes scattering of light—see Ref. 12.

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