Intense nonlinear-optics excitation of completely symmetric vibrations of polyatomic molecules: Study of the Fermi resonance and other anharmonic interactions

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(Submitted 30 March 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **35**, No. 9, 381–383 (5 May 1982)

Intense two-frequency laser pumping has been used for the selective excitation of up to 35% of the CO_2 and SF_6 molecules in the samples from the ground state to completely symmetric vibrational states. It has been shown by a direct experiment, for the first time, that the Fermi-resonance states 10^00 and 02^00 of CO_2 molecules are not strongly bound kinetically. The kinetics of the collisional excitation of 02^20, 03^10, 03^30, etc., states of CO_2 has been studied, and the corresponding reaction rates have been determined.

PACS numbers: 33.10.Gx, 33.80.Be

1. We are reporting here the first direct experimental study of the various mechanisms and rates for the "thermalization" of vibrational energy. We studied CO_2 molecules; the energy was initially in the vibrational excitation of the completely symmetric mode ν_1 (the 10^00 state) or an overtone of the deformation mode ν_2 (the 02^00 state). A substantial selective population of these CO_2 states (up to 35% of the total number of molecules was achieved from the ground state through two-photon Raman excitation in the visible range (the same result was achieved for the levels of the ν_1 mode of SF_6).

The primary purpose of these experiments was to determine whether there is a "kinetic" manifestation of the Fermi resonance between the states CO_2 (10^00) and CO_2 (02^00). According to a widely held opinion,[1–4] a Fermi resonance should cause a rapid collisional energy exchange between these states, despite the large energy defect (103 cm^{-1}). Our data show, however, that this exchange occurs quite slowly.

A second purpose of these experiments was to determine the role played by overtones of the deformation mode (02^20, 03^30, and also 11^10, 03^10, etc.) in the de-excitation of the 10^00 and 02^00 states. Our results show that these states play the major role here, apparently because of the small energy defects of the corresponding collisional-exchange reactions.

Despite the obvious importance of these questions, their resolution has remained unclear, primarily because of the ambiguity in the interpretation of data obtained by the experimental methods which have previously been used, both for exciting the CO_2 (10^00) and CO_2 (02^00) states (electric discharges, electron beams, and shock tubes[2,4]) and for diagnostics of the collisional relaxation of these states (IR luminescence[3] and IR absorption[1,4]).

2. In the present experiments a highly nonequilibrium ("excess") population of the vibrational level of interest (with the frequency Ω_R) was produced through two-phonon Raman excitation in oppositely directed, focused beams of the second harmonic from a Nd:YAG laser (at the frequency ω_1) and from a dye laser (ω_2) with $\omega_1 - \omega_2 = \Omega_R$ (Ref. 5). In the experiments we detected saturation of the Raman transitions excited in CO_2 (00^00-10^00 and 00^00-02^00): The differences between the populations of the corresponding levels decreased by a factor greater than 3 when the two-photon combination excitation was begun.

The populations of the level excited by the pump and of the levels coupled to that level by collisional exchange were studied by coherent active Raman spectroscopy (CARS).[5,6] The excitation and probing pulses had a length $\tau = 20$ ns. The appearance of populations in levels which are not populated under equilibrium conditions at $T \approx 300$ K was detected as "hot" lines in the CARS spectrum.

3. We were able to observe 16 new lines in the CARS spectrum of the CO_2 molecule during the two-photon Raman excitation of the 10^00 and 02^00 levels. These lines correspond to transitions which begin from the following states: 10^00, 02^00, 01^10, 02^20, 03^10, 03^30, 11^10, and 12^20. The accuracy of this identification of the hot lines, which was based on the energy level diagram of the CO_2 molecule,[7] was no worse than 1 cm^{-1} at the probing resolution ~1 cm^{-1}.

When the 10^00 state was pumped at a gas pressure in the range $p = 0.1$-1 atm, hot lines appeared in the CARS spectrum which corresponded to the population of the states 10^00, 01^10, 02^20, 11^10, and 12^20, but even at $p = 1$ atm there were no lines corresponding to any of the allowed Raman transitions beginning from the 02^00 state. On the other hand, when the 02^00 state was pumped, we observed hot lines coming from the states 02^00, 01^10, 02^20, 03^30, and 03^10, but we observed no lines coming from the 10^00 state.

Figure 1 shows part of the CARS spectrum of pure CO_2 at $p = 1$ atm at a frequency shift of about 1265 cm^{-1} in the presence and absence of the two-photon Raman excitation. The resonance at 1265 cm^{-1} corresponds to the 01^10-03^10 transition, and that at 1263 cm^{-1} corresponds to the 02^00-04^00 transition. The latter resonance arises only during Raman pumping of the 02^00 level. From curve 3 we find that in the two-photon Raman excitation of the 10^00 state at $p = 1$ atm for a time $\tau = 20$ ns the filling of the 02^00 state due to collisional relaxation is at least an order of magnitude less than the filling of the 01^10 state. It then follows, in view of the results of Ref. 5, that the rate constant K_1 for the reaction

$$CO_2(10^00) + CO_2(00^00) \overset{K_1}{\rightleftarrows} CO_2(02^00) + CO_2(00^00) + 103\ cm^{-1} \qquad (1)$$

is quite small: $K_1 \lesssim 7 \times 10^4\ s^{-1} \cdot Torr^{-1}$. This result seems natural, since reaction (1) has a large energy defect. Nevertheless, it has been asserted in Refs. 1 and 3, as well as in several other places (see the citations in Refs. 1-3 and 7), on the basis of indirect data that the rate constant K_1 lies in the range 3×10^5-$10^6\ s^{-1} \cdot Torr^{-1}$.

4. We can determine the role played by the 02^20 level in the de-excitation of the 10^00 and 02^00 levels by studying how the hot line at 1425 cm^{-1} (which corresponds to

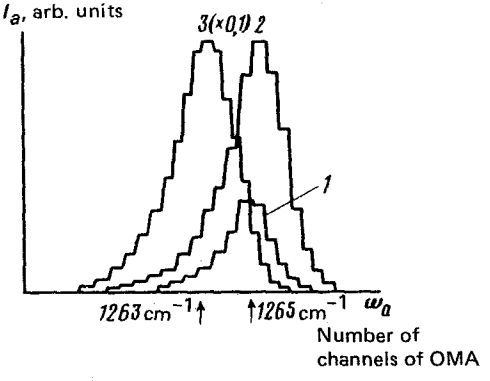

FIG. 1. The CARS spectrum of gaseous CO_2 at $p = 1$ atm and $T = 300$ K obtained with an optical multichannel analyzer (OMA) by the method of CARS with broad-band pumping (see Chapter VI in Ref. 6). 1–Unexcited gas; 2–with Raman excitation of the $10^0 0$ level; 3–with Raman excitation of the $02^0 0$ level (the ordinate scale is reduced by a factor of 10 for this curve). The width of a channel of the OMA is 0.34 cm^{-1}; the instrumental width is ~1.2 cm^{-1}.

the transition $02^2 0$–$12^2 0$) varies with the gas pressure. Curve 2 in Fig. 2 shows the population of this level as a function of the pressure during pumping of the $10^0 0$ level. We conclude from these results that the reaction

$$CO_2(10^0 0) + CO_2(00^0 0) \underset{\leftarrow}{\overset{K_2}{\rightarrow}} CO_2(02^2 0) + CO_2(00^0 0) - 50\ \text{cm}^{-1} \qquad (2)$$

goes with a rate constant $K_2 \gtrsim 4 \times 10^5$ s^{-1} · Torr^{-1} (cf. curve 1 and the results of Ref. 5).

A corresponding conclusion follows from data obtained during pumping of the $02^2 0$ level. We thus see that the $02^2 0$ state plays an important role, along with the $01^1 0$ state, in the de-excitation of the $10^0 0$ and $02^0 0$ states.

The hot lines at 1423 cm^{-1} (corresponding to the $11^1 0$–$21^1 0$ transition) and 1249 cm^{-1} (the $03^1 0$–$05^1 0$ transition) carry information about the populations of the $11^1 0$ and $03^1 0$ states. The pressure dependence of the $03^1 0$ and $11^1 0$ populations is shown by curves 3 and 4, respectively, in Fig. 2, from which we conclude that the processes which populate these levels are quite rapid, having rate constants $K_{3,4} \gtrsim 7 \times 10^5$ s^{-1} · Torr^{-1}. The sole mechanism which could be suggested to explain such rates is the collision of molecules excited by the Raman pumping with thermally excited molecules:

$$CO_2(10^0 0) + CO_2(01^1 0) \underset{\leftarrow}{\overset{K_3}{\rightarrow}} CO_2(11^1 0) + CO_2(00^0 0) - 22\ \text{cm}^{-1}, \qquad (3)$$

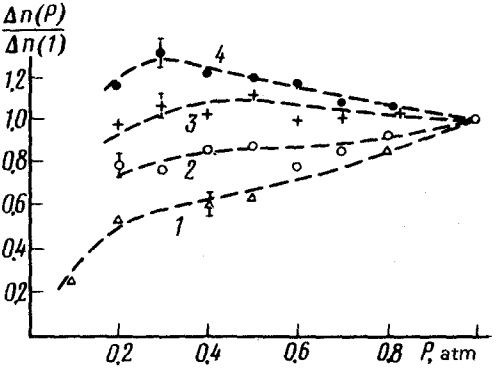

FIG. 2. Dependence on the gas pressure (the gas is pure CO_2) of the excess level populations (the extent to which the populations exceed their equilibrium values). 1–The $01^1 0$ level; 2–$02^2 0$; 4–$11^1 0$ with Raman excitation of the $10^0 0$ level; 3–$03^1 0$ with excitation of the $02^0 0$ level. The curves are normalized to the same value at $p = 1$ atm and $T = 300$ K. The efficiency of the two-photon Raman excitation of the corresponding levels is held constant as the gas pressure is varied.

$$CO_2(02^00) + CO_2(01^10) \overset{K_4}{\rightleftarrows} CO_2(03^10) + CO_2(00^00) + 19\ cm^{-1}. \quad (4)$$

We believe that these processes were responsible for the changes in the populations of the 10^00 and 02^00 states at a rate $\sim 10^6\ s^{-1} \cdot Torr^{-1}$, noted in Ref. 3.

5. The method of two-photon Raman excitation joins IR excitation as a universal method for producing nonequilibrium distributions of polyatomic molecules in vibrational levels. In some separate experiments we managed to highly excite the completely symmetric ν_1 mode of the SF_6 molecule, and we observed hot lines in the CARS spectrum corresponding to transitions between overtones of the ν_1 mode and other modes.

We wish to thank S. A. Akhmanov for support of this work and for useful discussions. We also thank A. M. Brodnikovskiĭ, V. N. Zadkov, V. D. Lysov, and A. N. Mezentsev for cooperation in these experiments.

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Translated by Dave Parsons
Edited by S. J. Amoretty