VIBRATIONAL RELAXATION MEASUREMENTS IN CO_2 USING AN INDUCED-FLUORESCENCE TECHNIQUE*

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This Letter is a summary of preliminary experimental studies of a number of relaxation processes involving excited vibrational levels of the CO_2 molecule. These studies involve the use of a new technique in which infrared fluorescence, induced by the application of intense pulses of Q-switched 10.6-μ laser radiation,[1,2] is used to obtain an accurate measure of the rate of volume quenching of the first excited asymmetrical stretching mode (00^01) of the CO_2 molecule. We have also shown that a number of widely spaced vibrational levels of this molecule are highly coupled through collisions; because of this, the energy stored in these levels is coupled to the cw power output of the 10.6-μ laser oscillation (but not necessarily to the Q-switch power output). The 10.6-μ oscillation occurs on a transition involving only one pair of these collisionally-coupled vibrational levels. The time constant involved in this collisional coupling is such that for a few microseconds after application of Q-switched radiation, an inversion of population may be obtained among these vibrational levels. This has enabled attainment of a new Q-switched laser oscillation at 4.3 μ. The relaxation studies are done both in the presence of a dc discharge current and without a discharge where the steady-state level populations are at room temperature.

In this experiment, a short sample tube is placed within the resonator of a Brewster-angle laser system with infrared transmitting windows. An additional infrared window is provided on the side of the sample tube, which is connected to a gas-handling system that allows varying amounts of CO_2 together with other gases to be introduced into the tube. The sample tube is equipped with electrodes which allow a dc discharge excitation when desired. The laser discharge tube is much longer than the sample tube; thus the gain or attenuation of the sample tube at the laser frequency is kept at a level considerably lower than the gain of the laser tube. The sample tube introduces only a small perturbation on the performance of the laser.

Consider the laser operating Q-switched on the $(00^01) \rightarrow (10^00)$ rotation-vibration transition of CO_2 at 10.6 μ [see Fig. 1(a)]. The intense Q-switch beam introduces rapid transitions between the corresponding levels of the CO_2 molecules in the sample tube. This occurs during a very short time corresponding to the pulse-length[3] of each Q-switch pulse and results in sudden changes in population of the (10^00) and (00^01) states. After the pulse the level populations slowly relax to their steady-state values. The change in population may be monitored by viewing the infrared spontaneous emission from CO_2 levels through the side window of the sample tube. For this purpose, a grating monochromator is placed in front of the side window, and the output detected with a Au:Ge detector.

The rate of volume quenching and diffusion of the (00^01) levels was studied with the sample tube at room temperature and <u>without</u> a

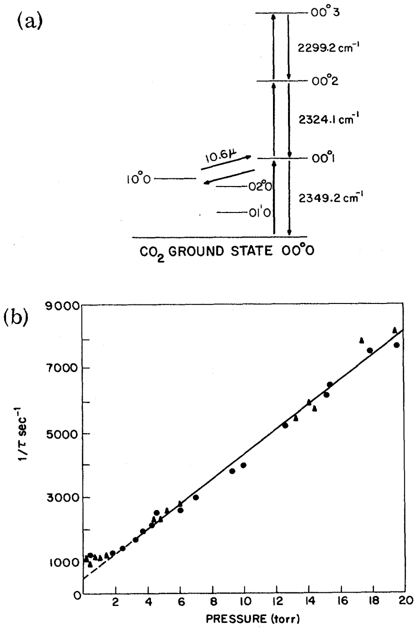

FIG. 1. (a) CO_2 vibrational energy levels. (b) Rate of volume quenching and diffusion for (00^01) level of CO_2. The triangles and circles represent data taken on two separate occasions.

discharge. In this case, the steady-state populations are in thermal equilibrium at room temperature. The Q-switch pulse suddenly increases the population of the (00^01) level and results in a rapid rise in the spontaneous emission originating from this level. Observations were made by detecting the emission band arising from the $(00^01) \rightarrow (00^00)$ transitions.[4] The center of this band falls at 4.26 μ. The decay of this emission signal back to steady state is found to be a pure exponential. Figure 1(b) gives the measured rate of decay of this signal as a function of CO_2 pressure in pure CO_2. The diffusion of excitation of the (00^01) level to the walls of the sample tube is responsible for departure from linear dependence at low pressure. (The average diameter of the sample tube was about 1 in.) Analysis of the curve in Fig. 1(b) gives a rate of volume quenching for the (00^01) level due to collisions with the ground state CO_2 molecules. This is 385 $\sec^{-1}$ mm^{-1} corresponding to a cross section of $\sigma = (3.3 \pm 0.3) \times 10^{-19}$ cm^2. The analysis of this curve at low pressure gives a cross section for the self-diffusion coefficient for diffusion of excitation of the (00^01) state to the wall. This is 0.50 cm^2/sec normalized to one atmosphere. In this estimate the possibility that a collision with the wall may not lead to immediate decay of the excitation of the molecular vibration is not included. This effect may be studied by varying the wall material in the sample tube. Furthermore, the noncylindrical geometry of the tube, caused by the presence of the side window, introduces an uncertainty in the value of the diffusion length. The uncertainty in the measured value of the diffusion coefficient due to the latter source of error is about 50%. The linear portion of the curve in Fig. 1(b), when extended, does not go through the origin. This is caused by the radiative decay of the (00^01) level. However, to deduce from this an exact radiative lifetime, the effect of self-trapping of resonance radiation must be included.

Consider now relaxation and collisional coupling between various levels in the presence of a dc discharge in the sample tube. In this case, the densities of the excited vibrational levels are so large that collisions between molecules in the excited vibrational levels play important roles. Thus, the relaxation of a level depends on the densities of a number of collisionally-coupled excited levels and hence is a complex function of the discharge current. The collisional coupling between the antisymmetric stretching vibrational levels may be studied by observing the spontaneous emission arising from the nearly overlapping emission bands $(00v) \rightarrow (00\,v-1)$ which fall at around 4.4 μ. The monochromator may be tuned in this region to allow observation of emission originating predominantly from various vibrational levels.[5] The 4.4-μ emission bands were studied while the sample tube was subjected to cw or Q-switched 10.6-μ laser radiation. Using a narrow Q-switch pulse, one finds that, as the population of the (00^01) is suddenly changed, the populations of the higher vibrational levels also change appreciably, but with a time delay. The change in spontaneous emission signal due to population changes in the higher vibrational levels is roughly half as large as the steady-state spontaneous-emission signal in the absence of 10.6-μ laser radiation. The time delay in the spread of excitation among these levels is less than ten microseconds. This was measured in a discharge mixture of He-N_2-CO_2 with near optimum gain at 10.6 μ corresponding to pressures in the millimeter range. This indicates that a sizable rate of excitation of the higher (00^0v) levels originates from collisions involving (00^01) levels. Such an excitation may arise from collisions between two vibrationally excited CO_2 molecules (or an excited CO_2 and an excited N_2 molecule) causing further excitation of one and de-excitation of the other.

To inspect the importance and consequences of the above collisional couplings, it is important to know the relative populations of adjacent (00^0v) vibrational levels in the discharge tube. To establish this, the intensity profile of the nearly overlapping emission bands of the $(00^0v) \rightarrow (00^0\,v-1)$ transitions was analyzed in detail. This was studied with the sample discharge tube subjected to 10.6-μ cw radiation as well as without the laser irradiation. It was found that levels as high in energy as $v = 4$ were heavily populated. However, the populations of the higher energy levels fall drastically. Furthermore, in the presence of cw 10.6-μ radiation, the intensity profile of all of these emission bands decreased by about a factor of 2. Also, the relative intensity distributions of the emission bands remained the same with or without cw laser irradiation. Lastly, the steady-state intensity distribution of the 4.4-μ emission bands corresponded to a relatively high positive vibrational temperature.[6] Accordingly, the ratio of the steady-state populations of two adjacent (00^0v) levels is close to unity[6]; but not so close as to allow[7] cw laser oscillation on the $(00v) \rightarrow (00\,v-1)$ transitions. (In these measurements, the effect of self-trapping of the $(00^01) \rightarrow (00^00)$ transition was allowed for.) The presence of a hot vibrational temperature and the existence of tight collisional coupling between higher vibrational levels have a number of important consequences:

(1) While the unsaturated gain of the 10.6-μ transition is determined only by the populations of the (10^00) and (00^01) levels, the cw laser-output power, which corresponds to saturated gain at the laser transition, is determined by the populations of a number of additional vibrational levels. The energy stored in the populations of levels as high as (00^04) is coupled to the cw 10.6-μ laser output, and each of these levels contributes appreciably to the total 10.6-μ laser power.

(2) The steady-state distribution of the population among the (00^0v) levels is noninverted, preventing oscillation at $(00v) \rightarrow (00\,v-1)$ transitions. However, immediately after application of a Q-switch 10.6-μ laser pulse, the population of (00^01) is suddenly decreased, and an inverted population may be obtained among the low-lying rotational states of adjacent $(00v)$ vibrational levels. This occurs in a time on the order of a few microseconds determined by the relaxation time discussed above. The 10.6-μ Q-switch pulse is capable of "switching on" sizable gain at a different frequency. A search was made for new laser oscillations induced by Q-switching of the 10.6-μ transition. A strong pulse was detected in a He-CO_2-N_2 discharge at 4.350 ± 0.002 μ corresponding to the $P(31), (00^02) \rightarrow (00^01)$ transition. Weaker transitions corresponding to $P(33)$-$P(47)$ lines were also observed (details of the Q-switch system used will be described elsewhere). The over-all behavior of the 4.3-μ pulses follows exactly the mechanism described above; if the pulse length of the 10.6-μ oscillation is increased to a value in excess of about 10 μsec, the 4.3-μ pulse occurs only at the onset of the 10-μ pulse, and the 4.3 pulse length cannot be extended by any means.

(3) In a Q-switch system where the 10.6-μ laser transition alone is allowed to oscillate, the population of the higher vibrational levels are no longer coupled to the laser field. This is because the duration of a pulse is generally less than the time constant of the collisional coupling discussed above.

Other excited vibrational levels[6] are also tightly coupled to the CO_2 laser levels. Additional studies can also be made by observing the influence of 10.6-μ Q-switch radiation on the emission originating from excited bending modes or the symmetrical stretching mode.

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[1] M. A. Kovacs, G. W. Flynn, and A. Javan, Appl. Phys. Letters 8, 62 (1966).

[2] G. W. Flynn, M. A. Kovacs, C. K. Rhodes, and A. Javan, Appl. Phys. Letters 8, 63 (1966).

[3] In an optimum system, the pulse length measured with a properly matched fast detector (Au:Ge) was about 20 nsec, in complete agreement with an indirect determination discussed in Refs. 1 and 2. However, a pulse width of a few hundred nsec is sufficiently short to allow unambiguous determination of relevant relaxation times discussed here.

[4] Because of rapid thermalization of the rotational levels, the entire 4.26-μ band appears in fluorescence. Accordingly, the identities and the number of simultaneously oscillating rotation-vibration transitions of the Q-switch laser are unimportant. This is valid for all the experimental conditions discussed throughout this paper.

[5] A number of additional low-lying emission bands arising from $(v_1, v_2, v_3) \rightarrow (v_1, v_2, v_3-1)$ transitions are also present and fall in the 4.4-μ region. Their intensities are dependent on the conditions of the discharge and various partial pressures in the CO_2-N_2-He mixture.

[6] An additional proof for the presence of a large positive temperature within the low-lying (00^0v) levels is: For a few microseconds after a Q-switch pulse, the transient populations of the (00^02) and (00^01) levels are very nearly inverted. (See the later discussion in the text.) This occurs when the population of the (00^01) level is suddenly decreased by a factor of 2. From this, one obtains a steady-state population ratio given by $n(002)/n(001) > \frac{1}{2}$, or a vibrational temperature, $T > 3000°\mathrm{K}$. The exact determination of this temperature from an analysis of the $(00v) \rightarrow (00\,v-1)$ emission bands is somewhat obscured because of the overlapping of a number of additional bands from $(v_1, v_2, v_3) \rightarrow (v_1, v_2, v_3-1)$ transitions. These additional levels are also found to be coupled to the (00^01) level.

[7] C. K. N. Patel, Phys. Rev. Letters 12, 588 (1964).