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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 10.6μ 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; and because of this, the energy stored in these levels is coupled to the C. W. power output of the 10.6μ laser oscillation (but not necessarily to the Q-switch power output). The 10.6μ 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 4.3μ. The relaxation studies are done both in the presence of a D. C. 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 a pair of electrodes which allows D. C. discharge excitation when desired. The laser discharge tube is much longer in length than the sample tube, and in this way, 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. Accordingly, the sample tube introduces only a small perturbation on the performance of the laser system.

Consider the laser operating in the Q-switch mode on the $(10^{0}0) \leftarrow (00^{0}1)$ rotation-vibration transition of CO_2 at 10.6μ, (see Fig. 1). The high intensity Q-switch beam introduces rapid radiative 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 of each Q-switch pulse and results in sudden changes in level populations of $(10^{0}0)$ and $(00^{0}1)$ states. After the pulse, the level populations slowly relax to their steady state values. The change in level populations 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 infrared monochromator is placed in front of the side window, and the output of the monochromator is detected by a fast response infrared detector.

In this experiment, we have studied the fluorescence of nearly overlapping spontaneous emission bands arising from transitions within the asymmetrical stretch vibrational levels, $(00^{0}v-1) \leftarrow (00^{0}v)$, (see Fig. 1). These bands fall at about 2300 cm^{-1}(4.5μ). The monochromator may be tuned in this region to select the emission originating primarily from individual $(00^{0}v)$ levels.

The rate of volume quenching and diffusion of the ($00^{0}1$) levels was studied with the sample tube at room temperature and without a discharge. In this case, the steady state level populations are in thermal equilibrium at room temperature. The Q-switch laser pulse suddenly increases the population of the ($00^{0}1$) level and results in a rapid rise in the spontaneous emission from this band. The decay of this emission signal back to its steady state value is found to be a pure exponential. Fig. 2 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 ($00^{0}1$) levels 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 inch). Analysis of the curve in Fig. 2 gives a rate of volume quenching for the ($00^{0}1$) level due to collisions with the ground state CO_2 molecules. This is 385/sec/mm corresponding to a cross section of $\sigma = (3.3 \pm .3) \times 10^{-19} cm^2$. The analysis of this curve at low pressure gives a cross section for the self diffusion coefficient for diffusion of excitation of the ($00^{0}1$) state to the wall. This is $0.50 cm^2/sec$ normalized to one atmosphere. In this latter, estimate, we have not included the possibility that a collision with the wall may not necessarily lead to an immediate decay of the excitation of the molecular vibration. This effect may readily be studied by repeating the experiment with different types of walls for the sample tube. Furthermore, the non-cylindrical geometry of the tube, caused by the presence of the side window, also introduces an uncertainty in the exact value of the diffusion length. As a result, the measured value of the diffusion coefficient is correct to within a factor of two. The linear portion of the curve in Fig. 2, when extended, does not go through the origin. This is caused by the radiative decay of the $(00^{0}1)$ level. However, to deduce from this an exact value of this radiative lifetime, the effect of self trapping of resonance radiation must be included.

In the above experiment, the decay of the fluorescence signal is observed by direct display of the detector output on an oscilloscope. The signal to noise may be improved considerably by using standard electronic circuitry to achieve long integration times. This is expected to make possible observations at very low pressures of CO_2 and detailed studies of the effects of various buffer gases on the vibrational relaxation.

Let us now consider relaxation and collisional coupling between various levels in the presence of a D. C. discharge in the sample tube. In this case, the densities of the excited vibrational levels are so large that collisions between molecules in excited vibrational levels play important roles. Because of these collisions, the relaxation of a level depends on the exact densities of a number of collisionally coupled levels and hence is a complex function of the current through the discharge tube. The collisional coupling between the $(00^{0}v)$ levels may be studied by observing the spontaneous emission side light originating from these levels as the sample tube is subjected to C. W. or Q-switch pulses of 10.6μ laser radiation. Using a very narrow Q-switch pulse, one finds that, as the population of the $(00^{0}1)$ is suddenly changed, those of the higher $(00^{0}v)$ levels also suffer an appreciable change, but with a time delay. The change of the spontaneous emission signal due to population changes in the ($00^{0}v$) levels is roughly half as large as the steady state spontaneous emission signal in the absence of 10.6μ laser radiation. The time delay in the spread of excitation among these levels is less than ten microseconds. This was measured in a discharge consisting of a mixture of He-N_2-CO_2 and under conditions of near optimum gain for the 10.6μ transition. This indicates the presence of a large rate of upward excitation among the ($00^{0}v$) levels. (Note that the energy spacing between adjacent ($00^{0}v$) vibrational levels is about 2300 cm^{-1}). Such an excitation may be accounted for by considering collisions between two vibrationally excited molecules causing further excitation of one and de-excitation of the other. This may occur in collisions between two CO_2 molecules or possibly a CO_2 and a N_2 molecule. The energy defect in such a collision is small and the corresponding cross section is expected to be large.

In order to inspect the degree of importance and the consequences of the above collisional couplings, it is important to know the relative populations of adjacent ($00^{0}v$) vibrational levels in the discharge tube. To establish this, the intensity profile of the nearly overlapping emission band of the ($00^{0}v$-1) $\leftarrow$ ($00^{0}v$) transition was analyzed in detail. This was studied both with the sample discharge tube subjected to 10.6μ C.W. laser radiation as well as without the laser irradiation. It was found that the ratio of the population of adjacent ($00^{0}v$) vibrational levels remained the same in both cases. Furthermore, the ratio was found to be close to unity for a number of low lying (00^0v) levels corresponding to relatively high positive temperature among them. This was found to hold for levels up to and including v = 4. For larger v, the level populations fall drastically. (In these measurements, it was important to allow for the effect of self trapping of the $(00^0 0) \leftarrow (00^0 1)$ transition). This observation, together with that of the presence of tight collisional couplings between the (00^0v) levels have a number of important consequences:

1. While the unsaturated gain of the 10.6μ transition is determined only by the populations of the $(10^0 0)$ and $(00^0 1)$ levels, the laser output power, which corresponds to saturated gain at the laser transition, is determined by the populations of at least three additional (00^0v) levels. Accordingly, the energy stored in the populations of at least four of the low lying (00^0v) levels is coupled to the C. W. 10.6μ laser output, and each of these levels contributes more or less by the same amount to the total 10.6μ laser power.
2. The steady state distribution of population among the (00^0v) levels are non-inverted. However, immediately after the application of a Q-switch 10.6μ laser pulse, where the population of the $(00^0 1)$ level is suddenly decreased, an inverted population may be obtained among the (00^0v) levels. This will occur in a time of the order of a few microseconds determined by the relaxation time constant discussed above. Accordingly, the 10.6μ Q-switch laser pulse "switches" on a sizable gain at a different frequency. A search was made for new laser oscillations induced by Q-switching of the 10.6μ transition. A

strong pulse was detected at 4.3μ in a He-CO_2-N_2 discharge. The molecular rotation vibration parameters of the excited ($00^{0}v$) levels are not accurately known, but the best fit of the measured wavelengths to the known molecular parameters suggests a tentative assignment to P(31) transition between levels ($00^{0}2$), ($00^{0}1$). The overall behavior of the 4.3μ pulse follows the mechanism described above. For instance, if the pulse length of the 10.6μ laser oscillation is increased to a value in excess of a few microseconds, the 4.3μ pulse occurs only at its onset and its pulse length cannot be extended by any means. Finally, it should be pointed out that the conditions for obtaining optimum output power coupling for the 10.6μ pulse are appreciably different than those for the 4.3μ pulse. This should be allowed for in obtaining optimum output power of the 4.3μ pulse.

3. In a Q-switch system where the 10.6μ laser transition alone is allowed to oscillate, the population of the higher ($00^{0}v$) 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 between adjacent ($00^{0}v$) levels.

It should be noted that other excited vibrational levels of the CO_2 molecules may also be tightly coupled to the laser levels. These may be studied by observing the influence of 10.6μ Q-switch laser radiation on the infrared emission originating from excited bending modes or the symmetrical stretching mode.

The induced fluorescence technique used in the above experiments is an extension of that technique applied earlier in studies of the thermalization of a number of closely spaced levels in excited atomic Ne(3). The relaxation studies described above give information related to the behavior of individual vibrational levels which is not readily obtainable from shock tube studies. Furthermore, in a gas discharge, the behavior of the induced fluorescence signal may be interpreted, in a manner which is free from additional complexities generally encountered in other experimental methods. This is because, in the induced fluorescence techniques, the presence of excitation processes which are unaffected by the laser field do not appear in the final measurements. However, in an experimental method such as afterglow emission studies of pulsed discharges, the decay of other sources of excitation of molecular levels, for example, cascade transitions from a long lived excited electronic state, may lead to ambiguities in the interpretation of the observed behavior.

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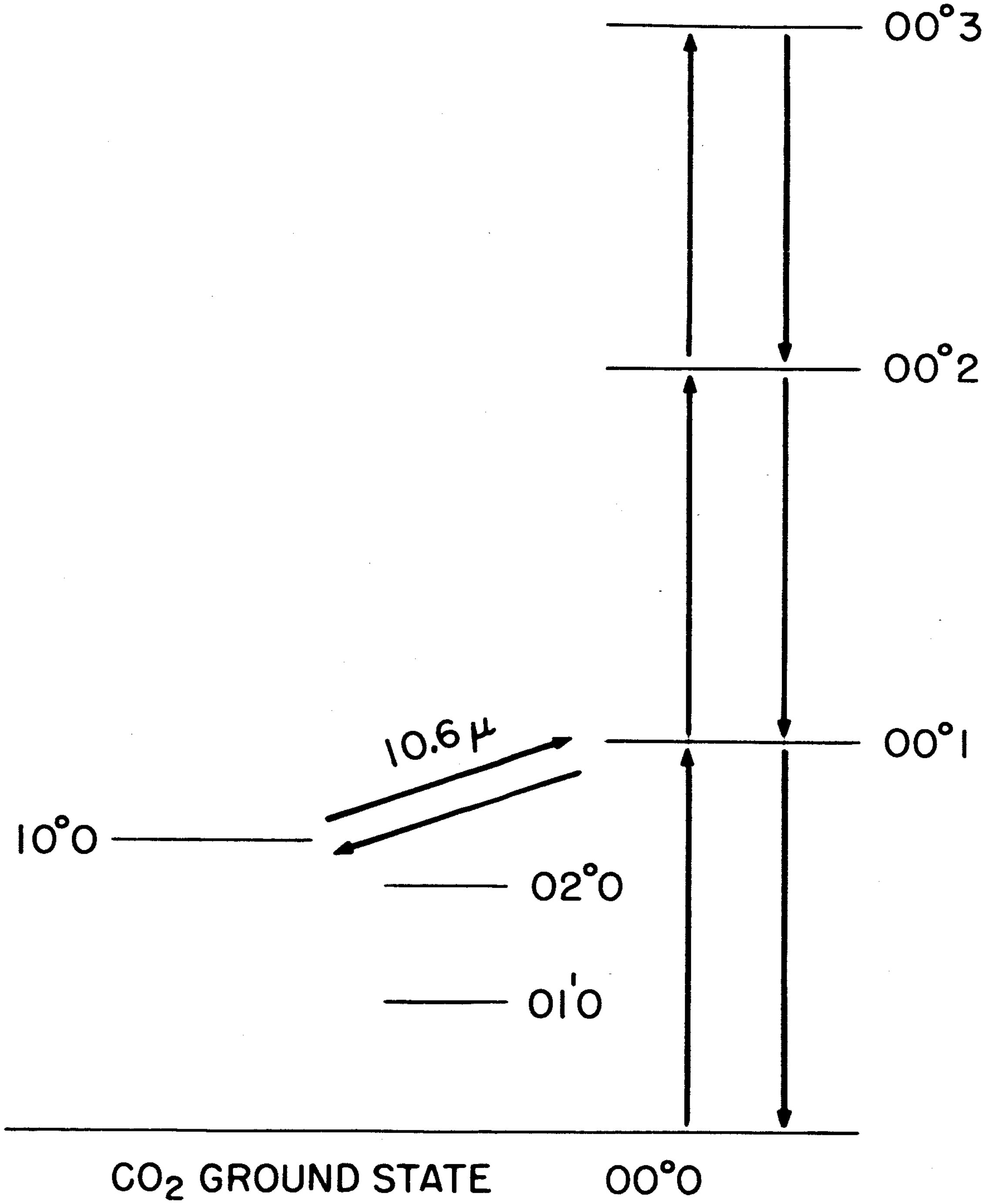
References

1. M. A. Kovacs, G. W. Flynn, and A. Javan, Applied Physics Letters, 8, No. 3, p. 62 (1966).

2. G. W. Flynn, M. A. Kovacs. C. K. Rhodes, and A. Javan, Applied Physics Letters, 8, No. 3, p. 63-65 (1966)

3. J. H. Parks and A. Javan, Phys. Rev., 139, No. 5A, A1351-1358 (1965).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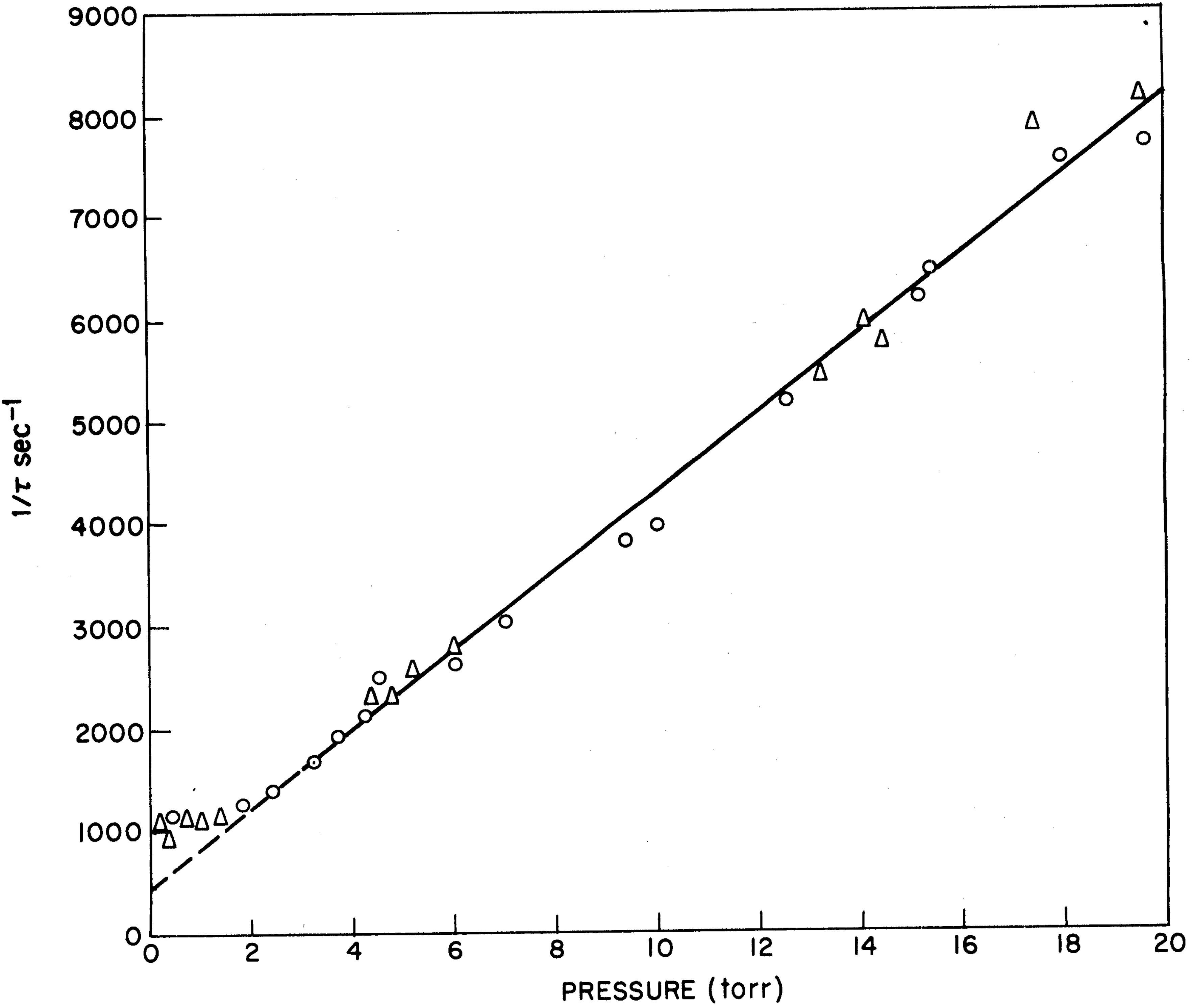
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