SELECTIVE EXCITATION THROUGH VIBRATIONAL ENERGY TRANSFER AND OPTICAL MASER ACTION IN N_2-CO_2

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In all the presently known two-component gas optical masers,[1,2] where selective excitation of the upper maser level is reported, the transfer of energy takes place between electronic states of the two component gases. We wish to report selective excitation of CO_2 molecules through transfer of vibrational energy of nitrogen molecules in the $v = 1$ vibrational level of their ground electronic state $^1\Sigma_g{}^+$, and resulting optical maser action on the rotational transitions (near 10.6 μ) of the 00^01-10^00 vibrational band of CO_2 in a continuous-flow N_2-CO_2 system. (Optical maser action on the 00^01-10^00 and 00^01-02^00 vibrational-rotational transitions of CO_2 in a pulsed as well as a cw discharge in pure CO_2 has been reported recently.[3]) The selective excitation of the CO_2 molecule from its ground state to the 00^01 state takes place during a two-body collision involving a CO_2 ground-state molecule and a vibrationally excited N_2 molecule in its ground electronic state. Hereafter, we shall refer to the ground electronic state N_2 molecule in vibrationally excited levels as $N_2{}^*(v = 1, 2, 3,$ etc.). Again, there are a large number of chemical reactions through which one can produce various diatomic molecules in vibrationally excited levels,[4] and hence the selective excitation through vibrational-energy transfer may be generally applicable for obtaining cw optical maser action on vibrational-rotational transitions of polyatomic molecules.

A discharge in low-pressure nitrogen results in a very effective production of $N_2{}^*(v = 1, 2, \cdots)$.[5] Since N_2 has a zero permanent dipole moment, the nitrogen molecules excited to vibrational levels of the ground electronic state cannot decay to the $v = 0$ vibrational level through electric-dipole radiation. Thus, under laboratory conditions the effective lifetimes of these states are governed by deactivation through collisions with other molecules and walls. Morgan and Schiff[6] report a total deactivation rate of 8.8/sec, including wall collisions at pressures of a few Torr. [Hence, vibrationally excited ground-state nitrogen molecules are ideal for selectively exciting another species of molecules to an upper maser level, since high population density of the $N_2{}^*(v = 1)$ can be easily obtained.] Very strong quenching of $N_2{}^*(v = 1)$ by CO_2 and N_2O has also been reported by Morgan and Schiff.[6] Recently, Legay and Legay-Sommaire[7] have observed the vibrational-rotational emission spectrum of CO in the ground electronic state, up to $v = 4$, in a system where vibrational-energy transfer from $N_2{}^*$ to CO is believed to be responsible. (They also suggest the possibility of maser action on vibrational-rotational bands of CO and CO_2 through selective excitation during vibrational-energy transfer from $N_2{}^*$.)

Figure 1 shows a partial energy-level diagram of N_2 and CO_2.[8] The potential-energy curves as a function of internuclear separation in N_2 have not been shown. Rotational levels for all the vibrational levels have been omitted for simplicity. The energy-level diagram has been drawn with respect to the ground state of $N_2(v = 0)$ and $CO_2(00^00)$. Various radiative transitions (including the maser transitons) have been indicated. It can be seen that $N_2{}^*(v = 1)$ at 2330.7 cm^{-1} is in very close coincidence with the 00^01 vibrational level of CO_2 at 2349.16 cm^{-1}. The energy discrepancy is ~18 cm^{-1} (to be compared with average thermal energy, kT, of the molecules,

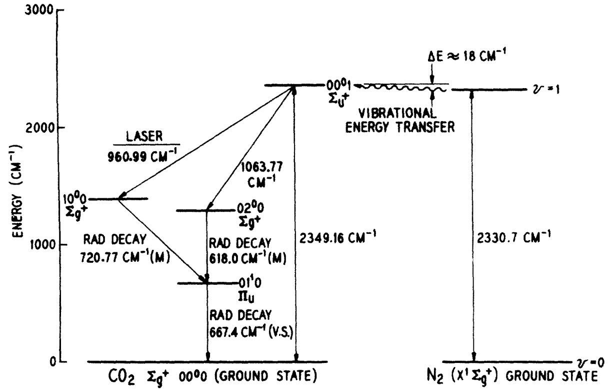

FIG. 1. Energy-level diagram showing pertinent vibrational levels of CO_2 and N_2 (from reference 8). Rotational levels for the vibrational levels have not been shown for simplicity.

which at room temperature is about 210 cm^{-1}). Thus a collision of the second kind, which may be written as

$$\begin{aligned} &N_2^*(v=1)+CO_2(00^00) \\ &\quad \rightarrow N_2(v=0)+CO_2(00^01)-18\ \text{cm}^{-1}, \qquad (1) \end{aligned}$$

can have a large cross section because of the near-perfect coincidence. The lower maser level (10^00), on the other hand, is removed from $N_2^*(v=1)$ by more than 900 cm^{-1}, and hence the cross section for exciting the CO_2 ground-state molecules to the lower maser level during a collision with $N_2^*(v=1)$ will be much smaller than that for the reaction described in Eq. (1). In addition, the excitation of CO_2 (00^00) molecules to the lower maser level (10^00) involves a reaction in which both the transitions, viz. $N_2^*(v=1)\rightarrow N_2(v=0)$ and $CO_2(00^00)\rightarrow CO_2^*(10^00)$, are optically forbidden. We can see from the theoretical treatment by Bates[9] of the collisions of the second kind that for such a reaction with the same energy discrepancy as that in Eq. (1), the cross section is smaller than that for the case of excitation of CO_2 to the upper maser level described in Eq. (1), in which only one of the transitions is optically forbidden. Thus, when $N_2^*(v=1)$ molecules are allowed to mix with CO_2, a selective excitation of CO_2 ground-state molecules to the 00^01 levels takes place. From the experiments on optical maser action in pure CO_2 discharges,[3] we know that the lifetimes of the 00^01 levels are longer than the lifetimes of the 10^00 levels. Hence, the required conditions for obtaining maser action on the 00^01-10^00 transitions are fulfilled. The same argument also applies to the 00^01-02^00 transitions, though in the present experiment no optical maser action on any of these transitions was detected.

Figure 2 shows the experimental setup. It is a continuous-flow system with linear flow rates of the order of 500 cm/sec. Nitrogen, better than 99.99% pure, flows in through its inlet port and passes through the region where a discharge is excited by a vhf (27-Mc/sec) generator. It should be emphasized at this point that there is <u>no</u> discharge anywhere else in the system. In the discharge region, electron-ion recombinations and atom-atom recombinations as well as cascades produce the nitrogen molecules in the vibrational levels of the ground electronic state. Due to the long lifetimes of $N_2^*(v=1)$, these can be transported from the generation region into the interaction region without appreciable loss. In the interaction region, CO_2 and the products of the N_2 discharge mix. There is a rapid deactivation[6] of $N_2^*(v=1)$, and the mixed gases are then pumped out through the central port. The distance between the discharge region in N_2 and the port at which the discharge products are admitted into the interaction region is approximately 20 cm, and it is expected that all the atomic and electron-ion recombination will have taken place by the time the discharge products reach the interaction region. CO_2 and N_2 flow rates are adjusted to be nearly equal with a total pressure of 0.8 Torr in the interaction region. The interaction chamber which forms a part of the optical maser structure is 25 mm i.d. The optical maser structure has been described by Faust <u>et al.</u>[11] The end mirrors, which are coated opaque with vacuum-deposited gold, are spaced 1.3 meters apart and are nearly confocal. Energy is coupled out from the resonator through a 0.5-mm aperture in the center of the output mirror.[11] A Ge:Hg photoconductor (4.2°K) was used as the detector.

Table I lists the wavelengths at which maser

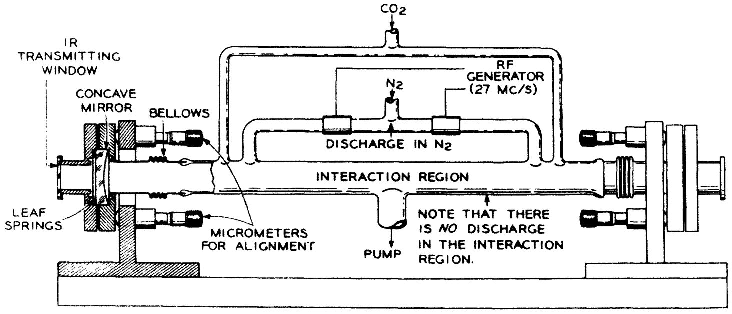

FIG. 2. Experimental apparatus for obtaining optical maser action in N_2-CO_2, due to vibrational-energy transfer from $N_2^*(v=1)$ to CO_2. (Drawing is not to scale.)

Table I. Measured vacuum wavelengths, frequencies, and identification of the CO_2 optical maser transitions obtained from a continuous-flow N_2-CO_2 system.

Measured wavelength (vacuum)[a] (μ)	Frequency (cm^{-1})	Identification[b] 00^01-10^00 vibrational band
10.5322	949.47	$P(14)$
10.5519	947.70	$P(16)$
10.5716	945.93	$P(18)$
10.5915[c]	944.15	$P(20)$
10.6119	942.34	$P(22)$
10.6327	940.49	$P(24)$
10.6537	938.64	$P(26)$

[a] Absolute wavelength accuracy ±3 Å (measured with a 1-meter Jarrell-Ash spectrometer).

[b] See reference 3 for a detailed discussion on the identification.

[c] Strongest maser transition, $P_{\text{out}} > 1$ mW.

oscillation was obtained. These are seen to be the P-branch rotational transitions belonging to the 00^01-10^00 vibrational band of CO_2 from $P(14)$ to $P(26)$. The strongest transition occurs at 10.5915 μ and a cw power output in excess of 1 mW has been obtained. The rf power required to generate the discharge in N_2 to obtain this power output is less than 100 watts. This should be compared with about 1000 watts required to obtain the same power output from CO_2 in a 5-meter-long pure CO_2 discharge.[3] (Thus the efficiency of a two-component system using N_2-CO_2 is much higher than the one using CO_2 alone.)

The gas temperature (i.e., molecular temperature and also the rotational temperature of CO_2) in the interaction region can be taken to be about 300°K. Thus, with the help of analysis given in reference 3, the results of the present experiment lead us to conclude that the ratio of total population densities in the vibrational level 00^01 and 10^00 is about 1.12. The ratio N_{00^01}/N_{10^00} for the case of pure CO_2 discharge maser was reported to be 1.05 (reference 3). This gives us an indication of the effectiveness of the selective transfer of vibrational energy from $N_2^*(v=1)$ to CO_2.

An interesting observation can be made due to the absence of discharge in the interaction region where maser action is produced. The $1/D$ dependence (D is the diameter of the interaction region) of optical gain found in other gas masers[10,12] is not expected to hold in the N_2-CO_2 system. Since none of the energy levels involved in CO_2 depend upon the presence of walls for depopulation, the optical gain should reflect the diameter dependence of $N_2^*(v=1)$. Thus increasing the diameter of the interaction chamber should leave the optical gain unchanged, or at the most the optical gain should be a slowly increasing function of diameter in contrast with other gas masers.[10,12]

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