Laser Cooling by Spontaneous Anti-Stokes Scattering

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Cooling of a three-level system resulting from anti-Stokes scattering of electromagnetic radiation has been observed for the first time. A CO_2 laser was used to lower the temperature of samples of CO_2 and CO_2-Xe mixtures. Satisfactory agreement between theory and experiment was found. The technique's ability to deliver an extremely fast cooling pulse should find application in the study of nucleation dynamics.

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It has long been recognized that optical pumping of a medium accompanied by spontaneous anti-Stokes scattering (SASS) can lead to the lowering of its temperature.[1] Consider a simplified three-level system consisting of a ground state $|0\rangle$, an intermediate state $|1\rangle$, and an uppermost state $|2\rangle$ which has allowed transitions to both $|0\rangle$ and $|1\rangle$ at frequencies ν_{20} and ν_{21}, respectively. Optical pumping from $|1\rangle$ to $|2\rangle$ is then followed by either spontaneous emission to $|1\rangle$ (resonant scattering) or $|0\rangle$ (anti-Stokes scattering) or nonradiative relaxation to those states. If we denote the radiative rate for the $|2\rangle \rightarrow |0\rangle$ transition by A and the total nonradiative relaxation rate of $|2\rangle$ by R, cooling is obtained for $A(\nu_{20} - \nu_{21}) > R\nu_{21}$ provided that equilibrium between the $|0\rangle$ and $|1\rangle$ states is restored predominantly through nonradiative processes. An attempt to demonstrate radiation cooling by SASS was made by Kushida and Geusic in a Nd-doped yttrium aluminum garnet crystal more than a decade ago, but they failed because the cooling was masked by a larger heating effect due to an impurity absorption.[2] As far as we know, the work reported here represents the first observation of net cooling by anti-Stokes scattering.

Recently, another kind of laser cooling has been demonstrated in which the temperature of the system is lowered via resonant scattering of laser radiation by Doppler-down-shifted atoms.[3,4] It is of interest to compare Doppler cooling with SASS cooling here. One may define a cooling efficiency ϵ as the ratio of energy removed per scattering event divided by the photon energy. Then for SASS cooling the limiting efficiency is $\epsilon = T/(T' - T)$, where T is the temperature of the sample and T' the ambient temperature.[5] While the limiting efficiency may be difficult to attain in practice, the present experiment shows clearly that efficiencies exceeding unity are quite feasible for SASS cooling. In contrast, for Doppler cooling the energy removed is typically that corresponding to the Doppler width, i.e., $(2kT/M)^{1/2}h\nu/c$. Therefore, the cooling efficiency there would only be $\epsilon \sim (2kT/M)^{1/2}/c \sim 10^{-6}$. On the other hand, whereas the decrement in temperature achievable with SASS cooling would in practice be limited to a relatively small fraction of the initial temperature (since a sizable portion of molecules must remain in the intermediate state), the final temperature one can achieve with Doppler cooling can approach absolute zero.[3,4] The two radiation cooling techniques, therefore, can be expected to lend themselves to quite dissimilar applications.

In the present work, laser cooling by SASS was accomplished in pure CO_2 and mixtures with Xe with use of the 10.6-μm (100) $\rightarrow$ (001) band as the pump transition and the 4.3-μm (001) $\rightarrow$ (000) band for anti-Stokes reemission, as illustrated in Fig. 1. This particular cooling scheme was chosen for a number of reasons. First of all, the required pump radiation is conveniently provided by the CO_2 laser. In addition, the radiative branching ratio for reemission at 10.6 and 4.3 μm is highly in favor of cooling. Finally, the radiative and nonradiative processes of the system are sufficiently well understood not only to virtually ensure the attainment of net cooling, but also to allow a meaningful comparison between theory and experiment. From the energies of the photons involved it is clear that in the limit of negligible nonradiative quenching of the (001) state the cooling efficiency for the scheme employed here exceeds unity, as we have already alluded to earlier.

The cooling apparatus consists mainly of a pipe with 12.7 cm diameter and 150 cm length heated to 300 °C for the middle 100 cm and to about 250 °C near the windows. The cell diameter was chosen from the following considerations. For a given molecular density and pump power, the temperature drop increases with increasing cell diameter in the absence of trapping of the anti-

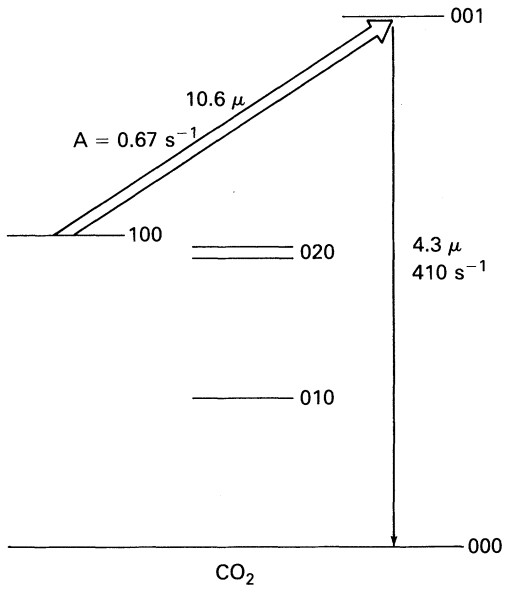

FIG. 1. Radiative transitions utilized in the anti-Stokes cooling of CO_2. Note the large radiative branching in favor of anti-Stokes reemission. The rate of repopulation of the (100) level is primarily controlled by endoergic collisions between CO_2 (000) and CO_2 (000) or Xe which replenish the (010) level.

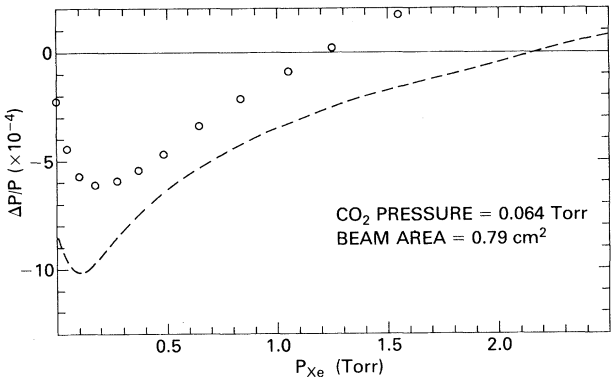

FIG. 2. Pressure-drop data as the Xe partial pressure is varied. The 1-cm-diam pump beam had an intensity of 191 W cm^{-2}. It should be noted, however, that only a small fraction (~1%) of the incident beam was utilized to produce the effects observed because of the small absorption involved. Calculated pressure-drop dependence is given by the dashed curve. See text for assumptions made.

Stokes radiation.[6] The optimum CO_2 density is that for which collisional deactivation of the (001) state just begins to become significant (~10% of the radiative rate). This CO_2 density in turn determines a maximum cell diameter if self-absorption at 4.3 μm is to be avoided. To circumvent reflection of 4.3-μm radiation at the wall, the inside of the pipe was painted with a flat black enamel which effectively absorbed nearly all radiation incident at that wavelength. Any reflected anti-Stokes 4.3-μm radiation would of course be reabsorbed by the gas and have a heating effect on the system.

The pump CO_2 laser produced a TEM_{00} output on the $P(20)$ line of the 10.6-μm band of up to 300 W power. The 1-cm-diam output beam was directed into the absorption cell either as it was or after expansion to a diameter of 10.8 cm. Net cooling or heating of the sample was observed as negative or positive changes in the total pressure. The output of the monitoring capacitance manometer was fed into a chart recorder which facilitated the correction for a small but finite leak. The leak was negligible on the time scale of overall system and instrument response. Measurements were made in both pure CO_2 and mixtures with Xe. The latter was chosen as the dilutent because of its superior thermal insulation properties and its relative inertness in collisionally deactivating the CO_2 (001) state.

Cooling data for the unexpanded pump beam at various Xe partial pressures are shown as open circles in Fig. 2. The trend of the fractional pressure change is influenced by four separate factors here. First of all, as the Xe pressure is increased, the thermal conductivity of the gas mixture is lowered. At the same time, the (100) state becomes better coupled to translational motion, thereby facilitating its repopulation through endoergic collisions. These two mechanisms lead to a larger pressure drop with increasing Xe pressure. However, cooling is produced not in the irradiated region alone for the pump-beam diameter and gas pressures used here. Molecules in the (001) state which have diffused out of that region can also cool the gas. This diffusion process is inhibited by the addition of Xe. Finally, collisional deactivation of the (001) state becomes more important at higher Xe pressures. These last two effects reduce the extent of cooling and result in a heating contribution, respectively. Since these data were taken under highly saturated conditions and since almost all the transport and kinetic parameters needed to model the cooling of the system are known, one is in a position to compare the experimental results with those expected from theory.

To simplify the problem, we assume that the end effects are negligible in the experiment. We further assume that the pump transition is fully

saturated within a cylinder of radius r_0 (corresponding to the radius of the pump beam) along the axis of the absorption cell. The density of CO_2 molecules in the (001) state outside the pumped region is then given by

$$n(r) = n_0 \frac{K_0((\gamma/D)^{1/2} r)}{K_0((\gamma/D)^{1/2} r_0)}, \quad (1)$$

where n_0 is the corresponding saturated density in the pumped region [assumed to be the thermal density of CO_2 molecules in the (100) state], γ is the net deactivation rate of the (001) state, D is the diffusion coefficient, and K_0 stands for the zeroth-order modified Bessel's function of the second kind. The volumetric rate of cooling is therefore

$$\Phi(r) = \begin{cases} n_0 \, dQ/dt, & 0 < r < r_0 \\ n_0 [K_0((\gamma/D)^{1/2} r)/K_0((\gamma/D)^{1/2} r_0)] \, dQ/dt, & r_0 < r < a. \end{cases} \quad (2)$$

with

$$dQ/dt = -Ah\Delta\nu + (\gamma_{CO_2} + \gamma_{Xe}) h\nu,$$

where a is the radius of the cell, A the radiative rate for the 4.3-μm transition, $h\Delta\nu$ the energy of the (100) level, γ_{CO_2} and γ_{Xe} are the quenching rates of (001) by CO_2 and Xe, respectively (note that $\gamma_{CO_2} + \gamma_{Xe} + A = \gamma$), and $h\nu$ is the energy of the 10.6-μm pump photons. It can be shown that the radial temperature change with respect to the temperature change at the wall is then given by

$$\Delta T(r) = \frac{2}{a^2} \sum_{n=1}^{\infty} \frac{\bar{\Phi}_J(\alpha_n) J_0(\alpha_n r)}{\kappa \alpha_n^2 [J_1(\alpha_n a)]^2}, \quad (3)$$

with

$$\bar{\Phi}_J(\alpha_n) = \int_0^a r \Phi(r) J_0(\alpha_n r) \, dr,$$

where J_0 and J_1 are Bessel's functions, $\alpha_n a$ are the zeros of J_0, and κ is the thermal conductivity of the gas mixture. In the limit that the temperature deviations are small, it can further be shown that the fractional pressure change in the cell is given by

$$\frac{\Delta p}{p} = \frac{4}{\kappa T_0} \sum_{n=1}^{\infty} \frac{\bar{\Phi}_J(\alpha_n)}{(a\alpha_n)^3 J_1(\alpha_n a)}, \quad (4)$$

where T_0 is the temperature at the wall. Pressure changes due to momentum transfer from the photons to the absorbing molecules, as observed by Mery, Silhouette, and Conrad,[7] can be neglected in our case because of the small amount of power absorbed and the large ratio of tube diameter to laser-beam diameter.

The calculation of $\Delta p/p$ requires a knowledge of the parameters A, γ_{CO_2}, γ_{Xe}, D, and κ. The radiative rate and the collisional deactivation rate constants were taken from Refs. 8–10, respectively. The diffusion coefficient for the CO_2 (001) state in mixture with Xe should not differ substantially from that for the ground state,[11] and was calculated following standard formulas.[12] Similarly, the thermal conductivity for the gas mixture was obtained from available values for the pure gases. The resultant fractional pressure change as a function of Xe partial pressure thus calculated for the case of interest is shown as the dashed curve in Fig. 2. It is seen that the overall agreement between experiment and theory is good. The calculated effect is somewhat bigger than that measured experimentally for a number of reasons. First of all, while power-dependent data showed that at 191 W cm^{-2} the fractional pressure change was nearing a plateau for any given gas mixture, the pump transition was in no case completely saturated as assumed in the model. Second, even if the transition had been fully saturated the density of CO_2 molecules in the (001) state would still have been less than the thermal density of CO_2 (100) as assumed in the calculations because of the finite repopulation rate for CO_2 (100). Finally, at the CO_2 pressure used there is approximately 20% absorption at 4.3 μm across the radius of the cell, and so some heating due to the trapping of anti-Stokes radiation is to be expected. The departure from thermal equilibrium of the (100) state is greater at lower Xe partial pressures, causing a more pronounced discrepancy between theory and experiment there. In fact, when correction is made for the case of pure CO_2 with use of the known self-relaxation rate for the (010) state[13] which controls the repopulation of the (100) state, dramatically improved agreement is obtained. The gap between theory and experiment becomes smaller with increasing Xe pressure and reaches a minimum at approximately 0.5 Torr of Xe. It then widens again since heating due to self-absorption at 4.3 μm becomes more significant with increased collisional quenching of the (001) state induced by the added Xe.

The effect reported here should be distinguished from the kind of transient cooling due to endothermic energy-transfer collisions discussed by

Christiansen and Hertzberg.[14] In their case, no net energy is removed from the system. In fact, the net energy of the system there is increased by the amount of laser energy absorbed.

The axial temperature drop achieved in our experiments is only approximately 1 °C. Significantly larger temperature decrements should be possible in similar schemes based on electronic transitions with much faster radiative rates. We are currently setting up an experiment to cool alkali vapors using electronic transitions in the dimers. It is expected that with a pulsed-dye-laser output of ~100 kW, axial cooling of about 30 °K can be achieved. Cooling of this magnitude should be sufficient to initiate homogeneous nucleation in a saturated vapor. The corresponding cooling rate in these systems would be of the order of 10^8 deg sec^{-1}. This is several orders of magnitude larger than what one can achieve with the cloud-chamber technique. The only other known technique for studying homogeneous nucleation, namely supersonic expansion, gives spatial rather than time-resolved information. Other potential advantages of the anti-Stokes laser-cooling technique include the ease of studying nucleation at elevated temperatures and its favorable geometry for laser-spectroscopic diagnostics. Thus, the technique we are reporting could become a valuable new tool in the study of the difficult subject of nucleation dynamics. Another possible application is the confinement of focused laser beams by the positive lensing effect created by the axial cooling. The ability to keep a beam tightly focused over appreciable distances might offer some advantage in certain nonlinear-optical experiments. Finally, although the practicality of a laser refrigerator might be questionable, mention of this most obvious application should also be made here.

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