

1200.⁸ A measurement to 1 part in 10^3 would then give a value of α with a precision of 4.2 in 10^7 . This is significantly more precise than the present 1.6 in 10^6 determination of α from measurements using the ac Josephson effect.

The determination of the fine structure of the He^+ ion gives an even more fertile field for the multiple-quantum-transition technique. In helium there is no hyperfine structure and one can envision using a multiple-quantum transition in the $n=6$ state with a Q of 10^4 to 10^5 for determination of the fine-structure constant.

We wish to acknowledge the assistance of Mr. David A. Van Baak during the early phases of this work.

*Research supported by the National Science Foundation under Grant No. GP-22787.

†Polaroid Foundation Graduate Fellow, 1973-1974.

¹Indirect measurements of the fine-structure constant such as the hydrogen hyperfine structure, the muonium hyperfine structure, the helium fine struc-

ture, the electron $g-2$, and the ac Josephson effect all have possible ambiguities in their interpretation.

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³Measurements of related high- Q fine-structure transitions through level-crossing techniques have been reported by T. G. Eck and R. J. Huff [*Phys. Rev. Lett.* **22**, 319 (1969)] and by H. J. Beyer *et al.* [*Phys. Rev. Lett.* **28**, 263 (1972), and *J. Phys. B: Proc. Phys. Soc., London* **4**, L129 (1971)]; M. Glass-Maujean, *Opt. Commun.* **8**, 260 (1973).

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⁷The apparatus and technique are similar to that described in C. W. Fabjan and F. M. Pipkin, *Phys. Rev. A* **6**, 556 (1972).

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Observation of Momentum Transfer in Rotationally Inelastic Molecular Collisions of CO_2 with H_2 , He , CO_2 , and $\text{Kr}^\dagger$

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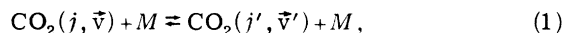
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(Received 14 January 1974)

We present an experimental technique enabling a direct observation of the momentum transfer distribution generated by rotationally inelastic molecular collisions of CO_2 with H_2 , He , CO_2 , and Kr . The observations indicate that the rotational transition results primarily from peripheral collisions which are effective in transferring angular momentum, but which communicate a relatively small linear momentum transfer. The *mean* change in the z component of velocity is presented for CO_2 - H_2 collisions.

We report initial experimental observations of the momentum-transfer distribution generated by rotationally inelastic molecular collisions of CO_2 with H_2 , He , CO_2 , and Kr . The general process under examination is



where the pair $(j, \vec{v})$ labels, respectively, the rotational quantum number and velocity of the CO_2 molecule, and M represents the appropriate col-

lision partner. Previous studies examining the velocity dependence of collisions of atomic and molecular systems have involved molecular-beam experiments,¹ coherent spectroscopy,² treatment of collisional effects on spectral line profiles,^{3,4} determination of infrared pressure-broadening coefficients,⁵ the role of velocity cross relaxation on the Lamb dip,⁶ and two-photon, double-resonance studies of collisionally redistributed populations.⁷ In the technique de-

scribed below, the methods of saturation spectroscopy are utilized to detect the velocity distribution arising from rotationally inelastic collisional processes and therefore provide an evaluation of the mean change of one component (z component) of the molecular velocity, viz., $(\vec{v} - \vec{v}')_z|_{\text{ave}} \equiv \langle \Delta v_z \rangle$, in these collisions. These data provide direct information on the characteristics of the intermolecular forces⁸ and supplement the findings of alternative methods such as pressure broadening and kinetic studies.⁹

Basically, the experimental technique involved the generation of a perturbed velocity distribution of a particular rotational level and the detection of the collisional transfer of this perturbation to a nearby rotational state using the apparatus illustrated in Fig. 1. Two pairs of stable single TEM₀₀-mode CO₂ sources¹⁰ (1, 2) and (3, 4) were used; the two labeled 1 and 4 served as local oscillators stabilized¹¹ to the centers of their respective $P(j)$ and $P(j')$ operating transitions. The beams from oscillators 2 and 3, with intensities of 20 and 2 W/cm², respectively, were passed collinearly through an absorption cell which contained a gaseous mixture of CO₂ and the collision partner M . Part of the beams ω_2 and ω_3 were heterodyned with their respective local oscillators, establishing the frequency measurements $|\omega_1 - \omega_2|$ and $|\omega_3 - \omega_4|$. The 4.3- μ m fluorescence

arising from the $00^0_1 - 00^0_0$ transition in the CO₂ contained in the cell falls on a liquid-nitrogen-cooled InSb detector and is observed by mechanically chopping the ω_2 beam at 780 Hz and the ω_3 beam at 540 Hz, and detecting synchronously at the sum frequency of 1320 Hz as oscillator 3 was scanned in frequency. The 4.3- μ m intensity and the frequency of oscillator 3 were simultaneously recorded on magnetic tape for subsequent numerical data reduction.

Figure 2 illustrates typical data obtained with this experimental method for pure CO₂ at a pressure of 30 mTorr. In Fig. 2, trace *a*, a narrow resonance is exhibited when both lasers 2 and 3 are operated on the 10.6- μ m $P(20)$ transition. The full width at half-maximum (FWHM) of this resonance is 1.7 ± 0.1 MHz and is primarily de-

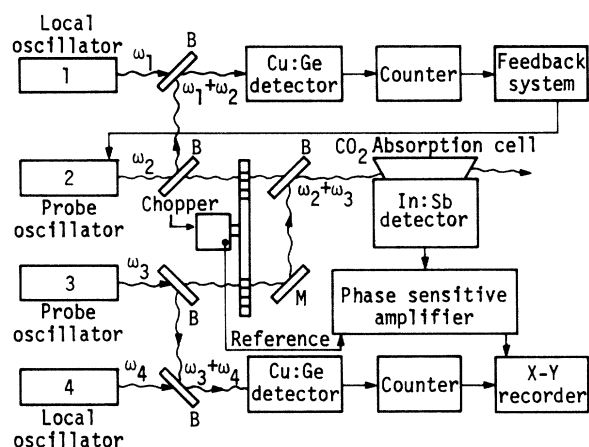


FIG. 1. Schematic diagram of the experimental apparatus illustrating the two pairs (1, 2) and (3, 4) of stable probes and local CO₂ oscillators operating on $P(j)$ and $P(j')$ transitions, respectively. The probe beams ω_2 and ω_3 are combined by a beam splitter (B) and pass in spatial coincidence through the absorption cell. Modulation of the two probe beams is provided by the chopper. The oscillator frequencies are established by heterodyne techniques.

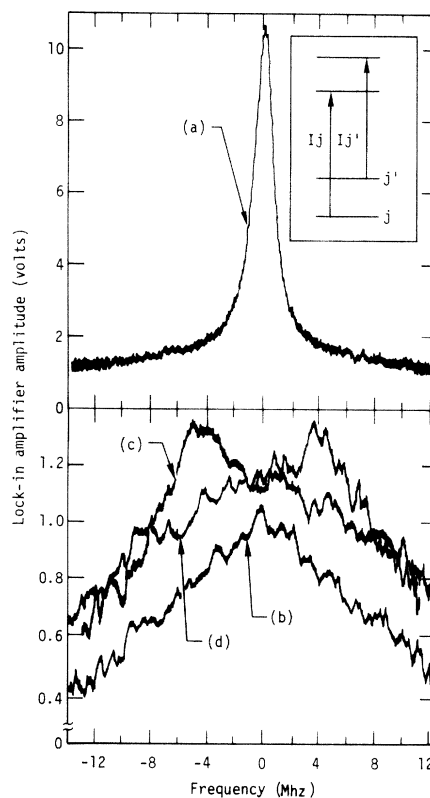


FIG. 2. Saturated resonance observed in the 4.3- μ m CO₂ fluorescence using the apparatus of Fig. 1. The abscissa is the frequency $\omega_3 - \omega_4$. Trace *a*, oscillators 2 and 3 both set on the 10.6- μ m $P(20)$ line. Curves *b*, *c*, and *d*, oscillators 2 and 3 operating, respectively, on the 10.6- μ m $P(20)$ and $P(18)$ transitions. Oscillator 2 is locked ($\omega_2 - \omega_1$) 0.1 MHz below the $P(20)$ line center in *b*, 5 MHz below in *c*, and 5 MHz above in *d*. Trace *b* has been depressed slightly for clarity. Inset, levels involved for the lower data traces.

terminated by power broadening. This width is a measure of the velocity spread of the radiatively produced perturbation of the molecular population. The lower three traces of Fig. 2 exhibit the nature of the signal when the sources 2 and 3 are operating on the 10.6- μm $P(20)$ and $P(18)$ transitions, respectively. In the trace labeled *b*, oscillator 2 was locked 100 kHz below the $P(20)$ line center; in traces *c* and *d*, source 2 was set, respectively, at 5 MHz below and 5 MHz above the $P(20)$ center frequency. The fact that the widths of these resonances are significantly greater than that of Fig. 2, trace *a*, and the fact that the location of the peak of the resulting resonance is determined by the frequency setting of oscillator 2 clearly establishes the velocity selective property of the collisional transfer between the two rotational levels in the lower $10^0 0$ level. Under the conditions of this experiment, it can be shown that the influence of the populations in the upper $00^0 1$ level is negligible. This aspect was verified experimentally by the absence of any detectable effect when oscillator 2 was operated on the 10.6- μm $P(20)$ transition and oscillator 3 was operated on the 9.6- μm $P(18)$ transition.¹²

The pressure dependence of the four-level res-

onance for CO_2 in collision with H_2 was investigated; and by fitting the resulting data with a Lorentzian plus an appropriate background signal, a zero-pressure intercept FWHM of 9 ± 4 MHz was obtained.

A brief investigation has also been made of the dependence of the four-level, collision-induced resonance on the value of $|j - j'|$. For the case of CO_2 in collision with H_2 , the velocity-selective resonance has been observed for¹³ $|j - j'| = 2$ and 4, but was not detected for $|j - j'| > 4$. This observation is related to data obtained from line-broadening studies¹⁴ which can be used to estimate the maximum orbital angular momentum l_{max} operative in the collision. For CO_2 - H_2 collisions at 300°K, $l_{\text{max}} \simeq 4$, a value which is consistent with our observations.

In an attempt to describe these four-level, collision-induced resonances, we are employing an analysis similar to that of Freed and Haus,⁶ but generalized to include rotationally inelastic collisions. Ignoring the roles of particle diffusion and polarization effects,¹⁵ we may write the equations of motion for the velocity-distribution functions $f_j(\vec{v})$ and $f_{j'}(\vec{v})$ of the lower two levels, including the influence of the saturating radiative fields I_j and $I_{j'}$, as

$$\partial f_j(\vec{v})/\partial t = \sum_{i=j,j'} \left\{ \int d^3v' [K_{ij}(\vec{v}'\vec{v})f_i(\vec{v}') - K_{ji}(\vec{v},\vec{v}')f_j(\vec{v})] \right\} + g_j(\vec{v}, I_j, \omega_j) + R_j(\vec{v}) - \gamma_j(\vec{v})f_j(\vec{v}). \quad (2)$$

A similar equation for $\partial f_{j'}(\vec{v})/\partial t$ is obtained with the interchange $j \rightarrow j'$. The quantity $K_{rs}(\vec{v}, \vec{v}')$ is the collisional matrix of which the off-diagonal elements ($r \neq s$) describe rotationally inelastic scattering and which are directly related to the angle-dependent forces occurring during a collision. The functions $g_j(\vec{v}, I_j, \omega_j)$ describe the perturbation generated by the radiation field of the $P(j)$ transition at frequency ω_j with intensity I_j . Since the transitions are Doppler broadened, the radiative excitation is highly selective in velocity space as indicated by the narrow resonance illustrated in Fig. 2, curve *a*. The quantities $R_j(v)$ and $\gamma_j(v)$ describe, respectively, the excitation and decay processes coupling the population of the j th level to all other molecular states exclusive of j' . The resulting steady-state distribution derived by equating Eq. (2) to zero is established by the competition between the strong velocity-selective perturbing influence of the radiation fields I_j and $I_{j'}$ and both elastic and inelastic collisions which tend to restore the equilibrium Boltzmann distribution. For all other conditions

fixed, an increase in the perturber gas pressure enables the collisional redistribution to compete more effectively with the selective radiative processes, causing the width of the observed resonance to broaden linearly with increased density. The zero-pressure intercept indicates the minimum observable width of the collisionally transferred population and is a measure of the mean change of the z component of the molecular velocity in a rotationally inelastic collision. With power broadening and the influence of CO_2 - CO_2 collisions taken into account, the intercept of the CO_2 - H_2 data indicate a value of $\langle \Delta v_z \rangle \simeq (3 \pm 2) \times 10^3$ cm/sec for $j = 20 \rightarrow j' = 18$ collisions.

Considerable velocity selectivity was observed for CO_2 in collision with light perturbers such as H_2 and He, as well as the more massive systems CO_2 and Kr. For the latter case this suggests that the rotationally inelastic collisions are mainly peripheral encounters occurring at a large interaction radius, favoring the transfer of angular momentum with a relatively small linear momen-

tum transfer. We note that at sufficiently large intermolecular separations, allowing the neglect of exchange forces arising from electron overlap, the main contributions to the angle-dependent interaction will arise from anisotropic dispersion forces in $\text{CO}_2\text{-He}$ and $\text{CO}_2\text{-Kr}$ scattering and the quadrupole-quadrupole interaction in addition to the anisotropic dispersion forces for $\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-CO}_2$ scattering.¹⁶ Finally, the $\text{CO}_2\text{-CO}_2$ case has the additional possibility of exchange processes. The details of these effects with a wide variety of collision partners are currently under study.

In summary a new experimental technique has been developed enabling a direct observation of the momentum-transfer distribution in rotationally inelastic molecular collisions. With this method, velocity-selective rotational transfer has been detected for CO_2 in collision with H_2 , He , CO_2 , and Kr . Specifically, for H_2 the data indicate a value of $\langle \Delta v_z \rangle \approx (3 \pm 2) \times 10^3$ cm/sec for $j = 20 \rightarrow j' = 18$ transitions at 300°K , a quantity which is far less than the mean thermal speed. These data provide direct information on the anisotropic component of the intermolecular interaction and also demonstrate that collision-induced transitions between closely spaced levels can occur with a small effect on the molecular velocity for states that have no transition dipole moment. This is an extension of the conclusion reached by Anderson¹⁷ for cases involving a transition dipole moment. Finally, we note that the extension of this experimental technique to three spatial dimensions will enable studies equivalent to molecular-beam scattering investigations in the examination of differential scattering cross sections.

The authors gratefully acknowledge many helpful conversations with H. A. Haus, P. W. Hoff, J. R. Murray, and W. J. Stevens, and the expert technical assistance of B. R. Schleicher.

†Work performed under the auspices of the U.S. Atomic Energy Commission.

*Hertz Foundation Fellow.

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