

called "solid," both solid and liquid phases may be present (*i.e.*, a "frozen" system). Some observations on such systems may be more related to the liquid part than to the solid part of the total system. For example, nmr signals arising from the minor part of a frozen system have been mistakenly ascribed to the solid phase. Also, interpretations of the decay of esr signals in frozen systems may often require the consideration of liquid-phase free-radical reactions.<sup>33</sup>

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## Laser Studies of Vibrational Energy Transfer

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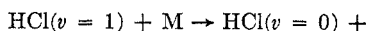
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Powerful, monochromatic beams of laser light<sup>2,3</sup> are opening many new avenues of experimental investigation in chemistry. The laser has been especially useful in studying the redistribution of energy among the vibrational modes of a single molecule and the exchange of vibrational energy between molecules. When a laser wavelength exactly matches a molecular absorption line, it is possible to excite many molecules into a single vibrational energy state. If the concentrations of vibrationally excited molecules can be measured spectroscopically while the laser is pulsed or modulated, rates of vibrational energy transfer processes may be determined. The relative ease of obtaining vibrational relaxation rates and the rapidly growing variety of systems open to experiment make this a rich field for both experimental and theoretical research.

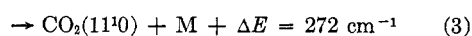
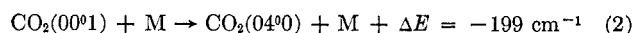
A great variety of vibrational energy transfer processes<sup>4</sup> can occur during bimolecular collisions in gases. A quantum of vibrational energy may be transferred completely into translational and rotational energy of the collision partners (eq 1). Vibrational energy

$V \rightarrow T, R$  transfer

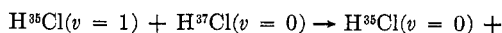


$$\text{M} + \Delta E = 2886 \text{ cm}^{-1} \quad (1)$$

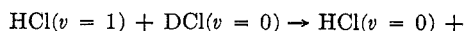
may be transferred from one mode to another within the same molecule with comparatively little energy going into translation and rotation (eq 2 and 3). Intramolecular  $V \rightarrow V$  transfer



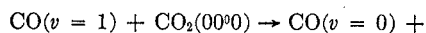
vibrational energy may also be transferred from one molecule into one or more modes of another molecule (eq 4-7). Finally, the quantum transferred may be Intermolecular  $V \rightarrow V$  transfer



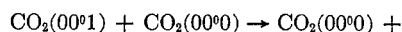
$$\text{H}^{37}\text{Cl}(v = 1) + \Delta E = 2.1 \text{ cm}^{-1} \quad (4)$$



$$\text{DCl}(v = 1) + \Delta E = 775 \text{ cm}^{-1} \quad (5)$$

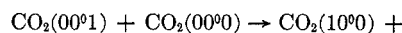


$$\text{CO}_2(11^00) + \Delta E = 65 \text{ cm}^{-1} \quad (6)$$



$$\text{CO}_2(11^00) + \Delta E = 272 \text{ cm}^{-1} \quad (7)$$

shared between the collision partners (eq 8). For each Intermolecular  $V \rightarrow V$  sharing



$$\text{CO}_2(01^00) + \Delta E = 294 \text{ cm}^{-1} \quad (8)$$

type of process there are many different combinations of initial- and final-state quantum numbers. A variety of different intermolecular forces and collision mechanisms may come into play as well.

Two good rules of thumb for vibrational energy transfer may be deduced from theory. They are that

(1) Alfred P. Sloan Fellow.

(2) B. A. Lengyel, "Introduction to Laser Physics," John Wiley & Sons, Inc., New York, N. Y., 1966, provides a good introduction to the properties and uses of lasers.

(3) A. L. Schalow, "Optical Masers," *Sci. Am.*, **204** (6), 52 (1961).

(4) In the energy-transfer reaction equations  $\Delta E$  is the net amount of energy transferred out of vibration into both translation and rotation. When  $\Delta E$  is negative, energy is transferred into vibration. At room temperature  $kT = 200 \text{ cm}^{-1}$ ,  $1 \text{ kcal} = 350 \text{ cm}^{-1}$ . For diatomic molecules the number of vibrational quanta excited is given by  $n$  as in  $\text{HCl}(v = n)$ . The symbol  $\text{CO}_2(X^Y^W)$  denotes a  $\text{CO}_2$  molecule with  $X$  quanta of the symmetric stretch,  $\nu_1$ , excited;  $Y$  quanta of the bending vibrations,  $\nu_2$ , excited with vibrational angular momentum  $z$ ; and  $W$  quanta of the asymmetric stretching vibration,  $\nu_3$ , excited. Figure 3 illustrates this nomenclature clearly. For methane the vibrational quanta excited are indicated in parentheses; *e.g.*,  $\text{CH}_4(\nu_2 + \nu_4)$  is a methane molecule with one quantum each of  $\nu_2$  and  $\nu_4$  excited (Figure 2).

the probability for energy transfer to occur during a collision decreases as more vibrational quantum number changes are required and as more energy must be transferred into translation. Vibrational energy transfer may occur when the energy of interaction between two molecules depends simultaneously on the distance between the molecules and on the vibrational displacements. When translational motion is treated classically, the probability for energy transfer from state  $i$  to state  $f$  to occur during a collision (Figure 1) is<sup>5,6</sup>

$$P_{fi}(v,b) = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} V_{fi}(t) e^{2\pi i \Delta \nu t} dt \right|^2 \quad (9)$$

where  $\hbar \Delta \nu$  is the energy transferred into translation and  $t$  is time. The matrix element  $V_{fi}$  is given by

$$V_{fi}(t) = \int \psi_{\text{vib}}^i \psi_{\text{rot}}^f V[R(t), q_j, \theta_A, \phi_A, \theta_B, \phi_B] \psi_{\text{vib}}^i \psi_{\text{rot}}^i d\tau_{\text{vib}} d\tau_{\text{rot}} \quad (10)$$

where

$$\begin{aligned} V[R(t), \dots] &= \text{the intermolecular potential} \\ &= V_0[R(t)] + \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \dots F_{lm} \dots \\ &[R(t), \theta_A, \phi_A, \theta_B, \phi_B] q_1^l q_2^m \dots \quad (11) \end{aligned}$$

The summations are over all powers of each vibrational coordinate of both molecules, and  $q_1^l$  is the first vibrational coordinate raised to the  $l$ th power. In order for the vibrational integral to be nonzero, one term in  $V$  must contain each vibrational coordinate whose quantum number is changed, raised to the power of the quantum number change. For example, reaction 5 requires a term like  $F_{11} q_{\text{HC1}} q_{\text{DC1}}$  and reaction 2 like  $F_{14}(q_{\text{asym stretch}})(q_{\text{bend}})^4$ . Since vibrational displacements are much smaller than molecular and intermolecular dimensions, the  $F_{lm} \dots$  decrease as the powers of the coordinates increase. Thus the probability of energy transfer decreases rapidly as more quantum numbers are changed. Our second rule follows directly from the behavior of the integral in eq 9. Since  $e^{2\pi i \Delta \nu t}$  oscillates between 1 and  $-1$ , an increase in  $\Delta \nu$  causes the integrand to oscillate faster and the integral to decrease. The integral decreases rapidly for interactions which fall off in a time longer than  $(4\Delta \nu)^{-1}$ . For comparison to the experimentally measured relaxation times,  $P_{fi}(v,b)$  must be integrated over the impact parameter,  $b$ , and over the relative velocity distribution,  $f(v)dv$ . The average probability of energy transfer per hard-sphere kinetic collision is

$$\begin{aligned} P_{fi} &= \frac{\text{rate of energy transfer}}{\text{rate of hard-sphere collisions}} \\ &= \frac{\iint P_{fi}(v,b) 2\pi b db f(v) dv}{\text{rate of hard-sphere collisions}} \quad (12) \end{aligned}$$

Use of the  $\Delta \nu$  and  $\Delta E$  rules to predict relative magnitudes of different  $P_{fi}$  is often risky since neither  $\Delta \nu$  nor  $\Delta E$  may be varied independently from all other molecular parameters. Unexpected changes in interaction potential or in collision trajectory can upset predictions.

Vibrational relaxation processes are important in determining the rates of unimolecular decomposition and atomic recombination.<sup>7</sup> Measurements of the distribution of vibrational energy in newly formed reaction products must eliminate or correct for the effects of vibrational relaxation.<sup>8</sup> Vibrational relaxation rates are important in any nonequilibrium system. They affect gas dynamic processes in shock waves, ultrasonic waves, and expansion flows; they influence the vibrational excitation in electrical discharges. Vibrational relaxation rates govern the inverted populations and hence the properties of vibrational lasers.

The subject of molecular relaxation in gases, and of vibrational relaxation in particular, has been reviewed extensively.<sup>5,7,9-13</sup>  $V \rightarrow V$  energy transfer rates have

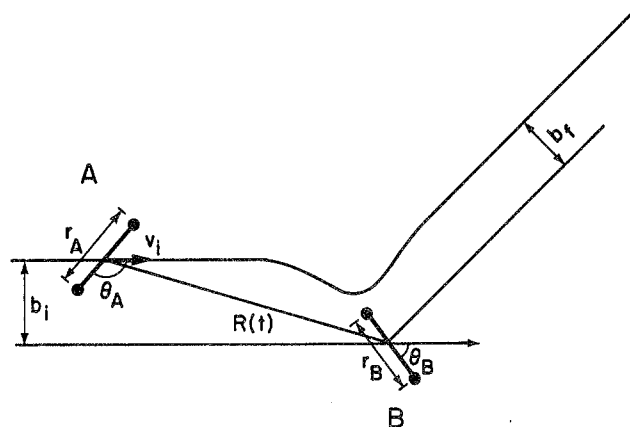


Figure 1. Collision trajectory diagram. Molecule A approaches molecule B with a velocity  $v_i$  and an impact parameter  $b_i$ .  $R(t)$  specifies the distance between the centers of mass of A and B throughout the collision. The molecular rotation angles  $\theta_A$ ,  $\theta_B$ ,  $\phi_A$ , and  $\phi_B$  are defined with respect to space-fixed axes. Angles  $\phi_A$  and  $\phi_B$  are out of the paper. For two diatomic molecules there are only two vibrational coordinates,  $q_A$  and  $q_B$ , the displacements from the equilibrium bond lengths,  $q_A = r_A - r_A^{\text{eq}}$ . The energy of interaction between the two molecules during a collision will depend on all of the internal coordinates as well as on  $R(t)$ . If any of the molecular quantum numbers change during the collision, then energy has been transferred, and  $b_f$  and  $v_f$  will generally be different from  $b_i$  and  $v_i$ .

(5) T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth and Co. (Publishers), Ltd., London, 1961.

(6) These expressions are for first-order perturbation and harmonic oscillator vibrations. Other couplings may occur in higher order perturbation or through anharmonic and Coriolis effects, but with generally much lower probabilities.

(7) B. Stevens, "Collisional Activation in Gases," Vol. 3, Topic 19 of the "International Encyclopedia of Physical Chemistry and Chemical Physics," Pergamon Press, Ltd., Oxford, 1967.

(8) K. G. Anlauf, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Phys. Letters*, **24A**, 208 (1967).

(9) A. B. Callear, *Appl. Opt. Suppl.*, **2**, 145 (1965).

(10) J. D. Lambert, *Quart. Rev. (London)*, **21**, 67 (1967).

been measured previously by flash kinetic spectroscopy,<sup>9</sup> by infrared emission from shock waves,<sup>14</sup> by vibrational fluorescence quenching,<sup>15</sup> and by ultrasonic measurements.<sup>10</sup> In this article we discuss the application of lasers to vibrational energy transfer problems. Since the simultaneous appearance of the original papers on laser-excited vibrational fluorescence<sup>16,17</sup> and on stimulated Raman excitation<sup>18</sup> in 1966, laser studies have allowed several types of  $V \rightarrow V$  energy transfer processes to be observed for the first time and have significantly broadened our knowledge of  $V \rightarrow V$  energy transfer.

## I. Laser Excitation Experiments

**1. Experimental Techniques.** Lasers are excellent excitation sources because they are well collimated, highly monochromatic and usually polarized, and may be modulated or pulsed in times as short as  $10^{-11}$  sec.<sup>19,20</sup> The high degree of collimation of a laser allows all of the output to be collected, focused, and reflected into the best size and shape of sample cell. When absorption coefficients are very low, the sample may be placed inside the laser cavity<sup>21</sup> where the light intensity may be as much as 50 times greater than externally. The polarized output of most lasers is convenient for making fluorescence depolarization measurements of molecular reorientation in collisions.<sup>22</sup> At this time there are more than 20 vibrational bands known which are precisely matched by laser frequencies.<sup>23</sup> For systems such as  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{HCl}$ , where molecular lasers are available, the frequency match between laser emission and molecular absorption is guaranteed. Stimulated Raman excitation does not require frequency matching and may be used on any vibration which exhibits sufficient stimulated Raman gain.<sup>24</sup> Some of the semiconductor injection lasers can be tuned over a fairly wide wavelength range.<sup>25,26</sup> A

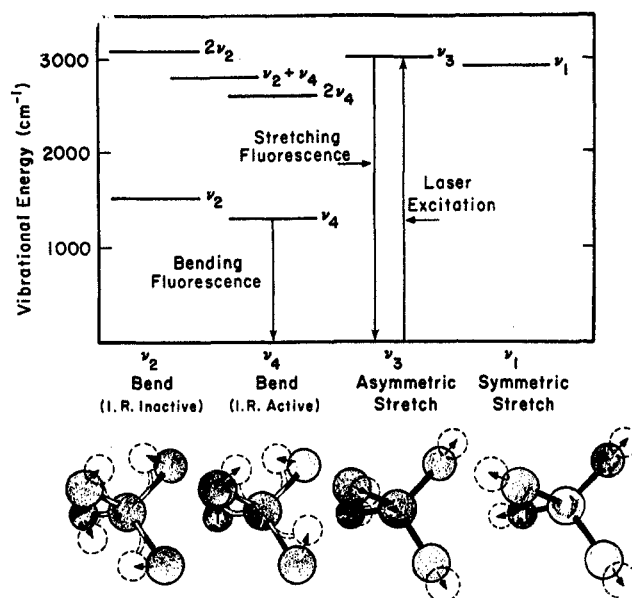


Figure 2. Vibrational energy levels of methane. The laser excitation and fluorescence transitions are indicated.

promising development for the future is the use of parametric oscillators,<sup>27</sup> a type of continuously tunable laser.

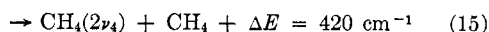
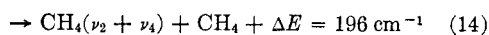
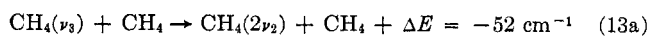
Many spectroscopic methods are available for the measurement of time-dependent energy level concentrations. In laser-excited vibrational fluorescence experiments the infrared emission from vibrationally excited molecules has been monitored by fast photoconductive detectors. Interference filters are used to limit the radiation detected to a single vibrational band. Lines from a molecular laser have been used<sup>28</sup> as sources for measuring concentrations in individual vibration-rotation levels by absorption spectroscopy. Parametric oscillators are a promising source for carrying out rotationally resolved absorption measurements. Laser Raman spectroscopy has been used to measure vibrational excitation in  $\text{H}_2$ .<sup>18</sup> In the future, visible, ultraviolet, or microwave spectroscopy will probably be used on systems for which they give the best detection sensitivity.

**2. Methane.** The He-Ne  $3.39\text{-}\mu$  laser line has been used to excite the asymmetric stretching vibration,  $\nu_3$ , of methane<sup>17,29</sup> (Figure 2). The exciting light is modulated with a mechanical chopper and the phase shift, or time lag, between the excitation and the fluorescence is measured. By measuring the phase shifts of fluorescence from both the bending level,  $\nu_4$ , and the stretching level,  $\nu_3$ , for a wide range of chopping frequencies and pressures both  $V \rightarrow V$  and  $V \rightarrow T$  relaxation times have been measured.

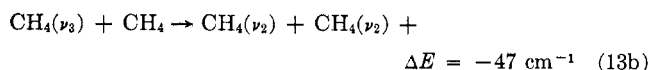
The phase shifts of the  $\nu_3$  fluorescence give the first-order decay rate of the  $\nu_3$  level. All of the  $V \rightarrow V$

- (11) W. H. Flygare, *Accounts Chem. Res.*, **1**, 121 (1968).  
 (12) P. Borrell, *Advan. Molecular Relaxation Processes*, **1**, 69 (1968).  
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 (24) T. A. Wiggins, R. V. Wick, and D. H. Rank, *Appl. Optics*, **5**, 1069 (1967); N. Bloembergen, G. Bret, P. Lallemand, A. Pine, and P. Simova, *IEEE J. Quantum Electronics*, **QE-3**, 197 (1967).  
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 (26) J. M. Besson, J. F. Butler, A. R. Calawa, W. Paul, and R. H. Rediker, *Appl. Phys. Letters*, **7**, 206 (1965).

- (27) R. C. Miller and W. A. Nordland, *ibid.*, **10**, 53 (1967); R. G. Smith, J. E. Geusic, H. J. Levinstein, J. J. Rubin, S. Singh, and L. G. Van Uitert, *ibid.*, **12**, 308 (1968).  
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 (29) J. T. Yardley and C. B. Moore, *ibid.*, **49**, 1111 (1968).

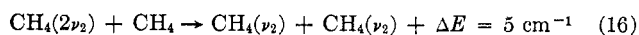


processes may contribute to this rate. In addition, each pair of bending quanta may be shared between the two collision partners (13b). The  $\nu_1$  level may also

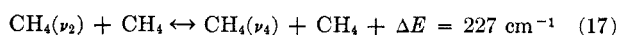


be involved. Energy transfer to other levels is unlikely because of the large  $\Delta E$  required. The over-all probability of  $V \rightarrow V$  transfer out of  $\nu_3$  is found to be  $1.4 \times 10^{-2}$ ; the relaxation time at 1 atm is  $7 \times 10^{-9}$  sec.

The phase shifts of the fluorescence from the  $\nu_4$  bending level at low frequencies give the  $V \rightarrow T$  relaxation time,  $1.9 \times 10^{-6}$  sec at 1 atm, in agreement with ultrasonic data. At high frequencies the short time lag between exciting molecules to the stretching level and their arrival through  $V \rightarrow V$  transfer in the  $\nu_4$  bending level is measured. Energy arrives in the bending fundamental levels by reactions 13–15 followed by reactions such as

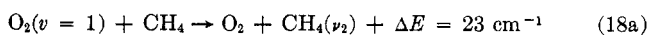


Since these reactions require only one quantum number change in each molecule and since the  $\Delta E$ 's are nearly zero, they are expected to be much faster than reactions 13–15. Finally equilibrium between the two bending fundamentals must be established by



To date, the difference between the measured deactivation rate of the stretch and the population rate of the bend has been smaller than experimental uncertainty. A lower limit on the probability of the  $\nu_2 \leftrightarrow \nu_4$  equilibration of  $10^{-2}$  can be set.<sup>29</sup> We hope to measure this probability directly by laser exciting the  $\nu_4$  vibration. This measurement in conjunction with improvements in the measurements already made would allow the relative importance of (13), (14), and (15) to be established experimentally.

The  $\nu_4$  phase shifts in methane–oxygen mixtures<sup>30</sup> have given a probability of  $2.0 \times 10^{-3}$  for reactions 18.



It should be possible to measure a number of other  $V \rightarrow V$  rates in methane mixtures.

The laser measurements have demonstrated experimentally that  $V \rightarrow V$  energy transfer rates in pure methane are much faster than  $V \rightarrow T$  energy transfer rates. Thus, the populations of all of the excited vibrational levels come into Boltzmann equilibrium with each other rapidly, and the vibrations as a whole relax much more slowly into translation. This has long been thought to be generally true because in nearly

all gases the entire vibrational heat capacity relaxes into translation with a single relaxation time.<sup>5</sup> This follows from the fact that  $V \rightarrow V$  equilibrium can be reached through processes with fairly small  $\Delta E$ 's, whereas  $V \rightarrow T$  energy transfer requires an entire vibrational quantum to be transferred into translation.

In a few cases where fairly small quanta may be transferred into translation and where large quantum number changes inhibit  $V \rightarrow V$  transfer, a  $V \rightarrow V$  process may be slower than the  $V \rightarrow T$  process. In these situations it is often possible to create vibrational population inversions suitable for laser action.

**3. Carbon Dioxide.** The  $\text{CO}_2$  laser operates on the transition between the asymmetric ( $00^01$ ) and symmetric ( $10^00$ ) stretching fundamental levels (Figure 3). Since  $10^{-3}$  of the molecules in room-temperature  $\text{CO}_2$  gas are in the ( $10^00$ ) state, pulsed  $\text{CO}_2$  laser light excites  $\text{CO}_2$  molecules in a cell separate from the laser gas.<sup>16,31–33</sup> The decay of infrared fluorescence from the ( $00^01$ ) level gives the vibrational relaxation time of the asymmetric stretching vibration of  $\text{CO}_2$ . This work has allowed a kinetic analysis of the  $\text{CO}_2$  laser itself.<sup>31</sup>

Javan and his coworkers have found<sup>15,34</sup> the collisional relaxation time of the ( $00^01$ ) level in pure  $\text{CO}_2$  to be  $3.9 \mu\text{sec}$  at 1 atm. This is nearly  $10^3$  times larger than the corresponding time in  $\text{CH}_4$ . By studying the relaxation time at pressures between 1 and  $10^{-3}$  torr, where deactivation occurs at the cell walls, they have made two exciting discoveries.<sup>34</sup> First they found that vibrational excitation diffused through pure  $\text{CO}_2$  less rapidly than did  $\text{CO}_2$  molecules themselves. They suggested that the apparent increase in diffusion cross section,  $91 \pm 10 \text{ \AA}^2$  for vibrationally excited molecules vs.  $53 \pm 1 \text{ \AA}^2$  for ground-state molecules, may be due to the transfer of the vibrational quantum from one molecule to another during a collision. The magnitude of this effect is in good accord with the single-quantum exchange results discussed in section II.2. Secondly, they have found the probability of deactivation of an excited  $\text{CO}_2$  molecule during a collision with the cell wall to be  $0.22 \pm 0.08$ . It is not known whether  $\text{CO}_2$  loses all of its vibrational energy or leaves the wall with some energy still in the symmetric stretching and bending modes.  $\text{N}_2$  ( $4.5 \times 10^{-4}$ )<sup>35,36</sup> and  $\text{CO}$  ( $4 \times 10^{-2}$ )<sup>36</sup> are the only molecules for which comparable data exist. Thus, the field of vibrational deactivation on surfaces is almost untouched.

In mixtures of  $\text{CO}_2$  with rare gases and with some diatomics strictly intramolecular  $V \rightarrow V$  energy trans-

(31) C. B. Moore, R. E. Wood, B. L. Hu, and J. T. Yardley, *ibid.*, **46**, 4222 (1967).

(32) M. A. Kovacs, G. W. Flynn, and A. Javan, *Appl. Phys. Letters*, **8**, 62 (1966); G. W. Flynn, M. A. Kovacs, C. K. Rhodes, and A. Javan, *ibid.*, **8**, 63 (1966).

(33) The equipment used in our laboratory is described in detail in ref 23 and 31. It is essentially the same as that first used in Javan's laboratory.<sup>15,32</sup>

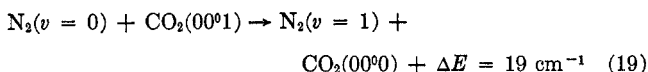
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(36) N. Legay-Sommaire and F. Legay, *J. Phys.*, **25**, 59 (1964).

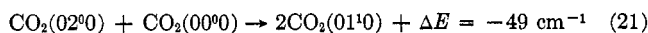
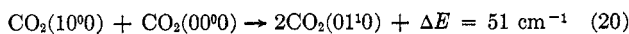
(30) J. T. Yardley and C. B. Moore, *J. Chem. Phys.*, **48**, 14 (1968).

fer has been observed<sup>37</sup> (see section II.1). In some mixtures such as CO<sub>2</sub>-N<sub>2</sub> it has been possible to observe rapid equilibration of energy between CO<sub>2</sub> (00<sup>0</sup>1) and a vibrational degree of freedom in the collision partner.<sup>31</sup> Thus for



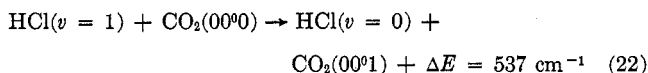
one-half of the vibrational energy is transferred from CO<sub>2</sub> to N<sub>2</sub> in an equimolar mixture. The process is followed by the much slower  $V \rightarrow V$  transfer of energy into symmetric stretching and bending energy in CO<sub>2</sub>. The N<sub>2</sub>O laser system<sup>32</sup> is precisely analogous to the CO<sub>2</sub> system, and some of the same experiments have been done.<sup>33</sup> The  $V \rightarrow V$  energy transfer data on mixtures with CO<sub>2</sub> and N<sub>2</sub>O are discussed in section II.

In another type of laser excitation experiment on CO<sub>2</sub>, Javan's group has used a second CO<sub>2</sub> laser to measure level population changes by absorption spectroscopy.<sup>23</sup> In these experiments energy transfer between the (10<sup>0</sup>0) and (02<sup>0</sup>0) levels is found to take less than ten collisions. The coupling of these two levels to the (01<sup>1</sup>0) level requires about 50 collisions, and is most likely attributed to the processes such as (4).



Reaction 21 is an important type of process since it brings the levels of a single degree of freedom into Boltzmann equilibrium with each other.

**4. Hydrogen Chloride.** Recently, laser-excited vibrational fluorescence experiments<sup>39</sup> have been started using an HCl chemical laser.<sup>40</sup> In HCl-CO<sub>2</sub> mixtures both HCl and CO<sub>2</sub>(00<sup>0</sup>1) fluorescence have been observed.<sup>39</sup> The decay time for HCl fluorescence is found to be equal to the rise time for CO<sub>2</sub> fluorescence. The process



is much faster than the subsequent decay of CO<sub>2</sub>(00<sup>0</sup>1). These rates have also been measured by using the CO<sub>2</sub> laser to excite HCl-CO<sub>2</sub> mixtures. The relative magnitude of these rate constants makes it possible to mix CO<sub>2</sub> into the HCl laser itself and produce CO<sub>2</sub> laser action. This type of experiment has helped in analyzing the mechanism of the HCl chemical laser.<sup>39</sup>

This laser system should make it possible to study reaction 4 as a function of the initial and final rotational quantum numbers. In this way the angular dependence of the interaction potential causing the vibrational energy transfer may be found.

**5. Hydrogen.** DeMartini and Ducuing<sup>13</sup> have focused a Q-switched ruby laser into H<sub>2</sub> gas at pressures

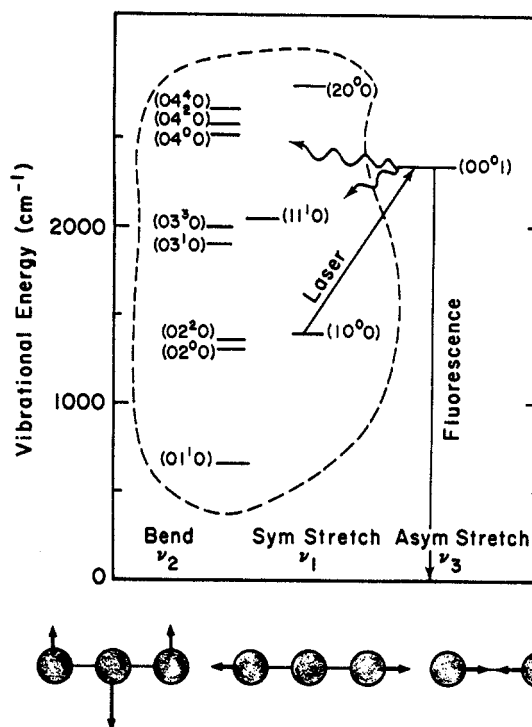


Figure 3. CO<sub>2</sub> vibrational energy levels for the laser-excited vibrational fluorescence experiments.

above 10 atm. The stimulated Raman effect produces approximately  $10^{16}$  vibrationally excited H<sub>2</sub> molecules in 20 nsec. They have observed the  $V \rightarrow T$  relaxation of H<sub>2</sub> by following the decay of the anti-Stokes spontaneous Raman scattering spectrum. This is the only method by which it has been possible to measure the vibrational relaxation time of H<sub>2</sub> near 300°K. Since pressures over 10 atm are required for the stimulated Raman effect, only relaxation times longer than  $5 \times 10^{-7}$  sec at 1 atm may be studied. It should still be possible to measure interesting  $V \rightarrow V$  energy transfer rates in mixtures with H<sub>2</sub>, HD, and D<sub>2</sub>.

## II. $V \rightarrow V$ Energy Transfer Processes

**1. Intramolecular Transfer.** When a vibrationally excited molecule collides with an atom, the only possible  $V \rightarrow V$  energy transfer processes are transitions from one vibrational state to another. The energy difference is transferred into translation and rotation. Figure 4 gives the data from laser experiments on CO<sub>2</sub> and N<sub>2</sub>O mixtures with the rare gases and with diatomic molecules whose vibrational degrees of freedom have been shown not to enter into the mechanism for the rate studied. No other rates have been measured for which the process has been proven to be intramolecular.

Even in the laser experiments it has only been possible to measure the total rate of intramolecular energy transfer out of the asymmetric stretch summed over all possible final vibrational states. We may write reactions similar to eq 2 and 3 leading to all of the levels shown in Figure 3. Some of these processes may be eliminated because they require a large amount of energy to be transferred into translation. For example, the process

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(38) J. T. Yardley, *ibid.*, **49**, 2816 (1968).

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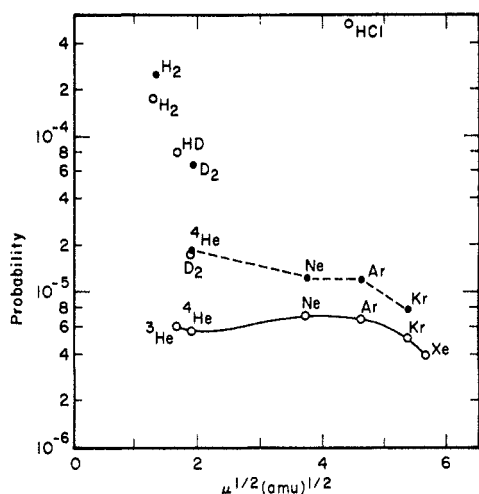
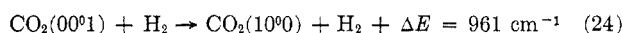


Figure 4. Intramolecular  $V \rightarrow V$  energy transfer probability vs. the square root of the reduced mass of the collision partners. Data are available only for energy transfer within  $\text{CO}_2$  (O) (ref 31, 37, 39, 50) and  $\text{N}_2\text{O}$  (●) (ref 38).



would have a probability near  $10^{-10}$ , on the same order as for  $V \rightarrow T$  energy transfer in  $\text{CO}$ .<sup>15</sup>

The experimental data themselves may also be used to establish limits on the possible values of  $\Delta E$ . The slow change of energy transfer probability with reduced mass and, hence, with velocity for the rare-gas collision partners shows that  $\Delta E$  is not much larger than  $kT$ ; quantitatively the data show that with the rare gases  $20 \text{ cm}^{-1} < \Delta E < 300 \text{ cm}^{-1}$ .<sup>37</sup> For the hydrogen molecule collision partners the situation is qualitatively different. The rapid change of probability with reduced mass indicates that a process with a much larger  $\Delta E$  is important. Reaction 24 is a likely can-



didate. This change of mechanism could result from a change in the interaction potential or perhaps from the influence of molecular rotation.<sup>41</sup> Data on parahydrogen should help decide this point. Measurements of the temperature dependence of these energy transfer probabilities will help to further specify the intermolecular potentials and  $\Delta E$ 's involved.

Quantitative theoretical calculations may also be useful in determining the relative importance of alternate energy transfer paths. Yardley and Moore<sup>37</sup> found that in  $\text{CO}_2$ -rare gas mixtures collisional coupling between energy levels was frequently aided by Coriolis and anharmonic mixing of the normal vibrations. Thus vibrational matrix elements calculated in the harmonic oscillator approximation were found to be orders of magnitude smaller than when couplings were considered. Whenever there is more than a single quantum number change in one molecule such anharmonic couplings must be investigated. For large vibrational quantum number changes the situation is

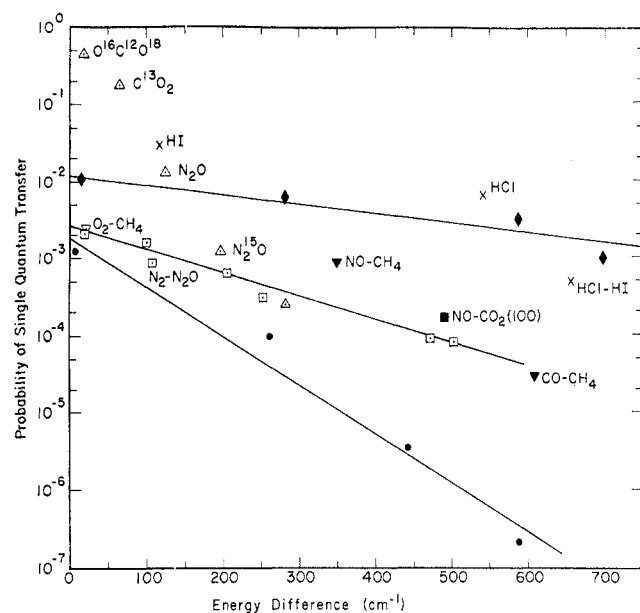


Figure 5. Single-quantum  $V \rightarrow V$  energy transfer probabilities vs. vibrational energy discrepancy,  $\Delta E$ . All probabilities are given for processes in the exothermic direction. For points labeled with only one molecule, energy is exchanged with the asymmetric stretch of  $\text{CO}_2$ . The unlabeled points given from left to right for each symbol are: (◆)  $\text{NO} \rightarrow \text{D}_2\text{S}$ ,  $\text{NO} \rightarrow \text{H}_2\text{O}$ ,  $\text{NO} \rightarrow \text{H}_2\text{S}$ ,  $\text{NO} \rightarrow \text{D}_2\text{O}$  (ref 45); (□)  $\text{CO}_2$  (asymmetric stretch)  $\rightarrow \text{N}_2$ ,  $^{15}\text{N}_2$ ,  $^{12}\text{CO}$ ,  $^{13}\text{CO}$ ,  $\text{NO}$ ,  $^{15}\text{NO}$  (ref 49); (●)  $\text{NO}^* \rightarrow \text{N}_2$ ,  $\text{NO} \rightarrow \text{CO}$ ,  $\text{NO} \rightarrow \text{N}_2$ ,  $\text{CO} \rightarrow \text{O}_2$  (ref 4). The solid points are from flash kinetic spectroscopy and vibrational fluorescence quenching; the remainder are laser data. Other data are from ref 49 ( $\Delta$ ), 39 ( $\times$ ), 30 ( $\nabla$ ), 38 ( $\text{N}_2 \rightarrow \text{N}_2\text{O}$ ), 6 ( $\text{CO}-\text{CH}_4$ ), 45 ( $\text{NO}-\text{CH}_4$ ), and N. Basco, A. B. Callear, and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A260**, 459 (1961) [ $\text{NO} \rightarrow \text{CO}_2$  ( $10^00$ )].

particularly bleak since harmonic oscillator calculations will rarely be useful and spectroscopic data for determining coupling coefficients are rarely available. In any case conclusions drawn from theory must be considered rather tenuous since there are undoubtedly many important facets of  $V \rightarrow V$  energy transfer yet to be understood.

**2. Single-Quantum Exchange.** A great deal of data is now available for the transfer of a single quantum of vibrational energy from one molecule to a single quantum of excitation in another. At first glance, Figure 5 looks very much like a shotgun pattern. Fortunately, closer inspection reveals that among each group of similar collision partners (points denoted by the same shape of symbol) the probability of energy transfer decreases as the energy transferred out of vibration,  $\Delta E$ , increases. The variety of slopes and intercepts exhibited by the lines correlating these points demonstrates that there are several different types of intermolecular forces or collision mechanisms at work here.

In 1964, when only the four data points (● in Figure 5) were available, the situation was much simpler. Callear found<sup>9</sup> that these data could be matched reasonably well by calculations which used the simple repul-

(41) C. B. Moore, *J. Chem. Phys.*, **43**, 2979 (1965).

sive exponential potential<sup>42,43</sup> employed in most  $V \rightarrow T$  energy transfer calculations. Similar agreement was found for high-temperature data on NO-CO and NO-N<sub>2</sub>.<sup>14</sup> The more rapid rates measured when one collision partner was a methane molecule (▼) could reasonably be due to the small reduced mass of the methane vibrations. The rather large probabilities measured for collisions between NO and molecules such as H<sub>2</sub>O show very little decrease with increasing vibrational-energy discrepancy.<sup>44</sup> This could result from a strong hydrogen-bonding type of force between the collision partners or perhaps from the transfer of the energy discrepancy into the rotational degree of freedom. The probabilities are much too large and slowly varying with  $\Delta E$  to be accounted for by the standard theory.<sup>42,43</sup>

Laser experiments on single-quantum exchange from the asymmetric stretch of CO<sub>2</sub> have produced two proofs of the importance of attractive interactions in near-resonant  $V \rightarrow V$  transfer. The probability of  $V \rightarrow V$  exchange between CO<sub>2</sub> and N<sub>2</sub> has been found to decrease by a factor of 3 with increasing temperature between 300 and 1000°K,<sup>45,46</sup> and then to increase above 1000°K.<sup>14,46</sup> Since interactions through the repulsive exponential potential result from collisions with sufficient kinetic energy to climb the repulsive hill, calculations with only this potential yield probabilities which increase with temperature or molecular velocity.<sup>42,43</sup> The observed decrease in probability with increasing molecular velocity may result from interactions within the attractive region of the intermolecular potential if  $\Delta E$  is sufficiently small. In eq 9  $V_{fi}(t)$  will remain nonzero for a longer time with a slower velocity; as long as  $\exp(2\pi i \Delta \nu t)$  does not oscillate during this time, the probability of energy transfer will increase as the velocity decreases. Sharma and Brau<sup>47</sup> have found reasonable agreement between experiment and a calculation using the  $R^{-4}$  attractive interaction between the oscillating dipole moment of CO<sub>2</sub> caused by the asymmetric stretch and the oscillating quadrupole moment of N<sub>2</sub> caused by its vibration. The increase in probability above 1000°K is reasonably attributed to the repulsive exponential interaction taking over at high temperatures.<sup>46</sup>

Near-resonant energy transfer between strongly infrared-active vibrations ( $\Delta$ 's in Figure 5) has been found to be over two orders of magnitude more probable than between inactive or weakly active vibrations in similar molecules<sup>48</sup> ( $\square$ 's in Figure 5). This striking difference is almost certainly due to the  $R^{-3}$  interaction

potential which results from the large vibrational transition dipole moments.<sup>49</sup> Calculations for  $\Delta E = 0$  give about double the probability observed for CO<sub>2</sub>-<sup>16</sup>OC<sup>18</sup>O with  $\Delta E = 18 \text{ cm}^{-1}$ . This is a particularly attractive system for more detailed theoretical calculations since the energy transfer probabilities are so clearly dominated by the  $R^{-3}$  effect and since the interaction potential is quantitatively known from absolute infrared intensity measurements. The problem of attractive interactions in  $V \rightarrow V$  energy transfer has just barely been opened; much more excitement can be expected as new systems are studied, as more temperature dependence data become available, and as more detailed calculations are completed.

**3. Multi-Quantum Exchange and Energy Sharing.** Unfortunately, the  $V \rightarrow V$  energy transfer rates we measure are often sums of the rates of many individual processes. This is almost always the case in situations where multi-quantum exchange and energy-sharing processes such as reactions 6-8 are possible. Equations 13a through 15 for deactivation of the asymmetric stretch of CH<sub>4</sub> are a typical example. An even larger number of processes is possible for the deactivation of the asymmetric stretch in pure CO<sub>2</sub>. To date only one example of multi-quantum exchange has been isolated, and no energy sharing rates have been determined.

By studying the slow relaxation times of CO<sub>2</sub>-N<sub>2</sub>, CO<sub>2</sub>-<sup>16</sup>N<sub>2</sub>, CO<sub>2</sub>-CO, and CO<sub>2</sub>-<sup>13</sup>CO it has been possible to deduce the rate for reaction 6.<sup>50</sup> In this series of molecules the  $\Delta E$  for transfer of a vibrational quantum from the diatomic to the (11<sup>1</sup>0) level of CO<sub>2</sub> decreases from 253 to 19 cm<sup>-1</sup>. The measured rate increases by about a factor of five. The probability with <sup>13</sup>CO is approximately  $3 \times 10^{-5}$ , a factor of 70 less than the corresponding probability for single-quantum exchange with  $\Delta E = 19 \text{ cm}^{-1}$  (Figure 5,  $\square$ 's).<sup>50</sup> This illustrates the effect of requiring two quantum numbers rather than one to be changed in the CO<sub>2</sub> molecule.

### III. Conclusion

Laser experiments have already contributed much new information to the field of vibrational energy transfer. However, a wealth of new  $V \rightarrow V$  energy transfer processes and phenomena are yet to be explored. The rapid pace of laser technology will give us still more new tools for studying vibrational relaxation, and the laser techniques already developed will continue to be productive.

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