

A LASER INDUCED FLUORESCENCE STUDY OF VIBRATIONAL ENERGY TRANSFER IN DIDEUTEROMETHANE

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V-V and V-T/R rates of ν_1 , ν_2 , ν_3 , ν_6 , ν_8 , and ν_9 of CH_2D_2 were measured and are reported. The deactivation efficiencies of rare gas collision partners were measured and calculated by SSH theory, the results are reported and discussed. Possible V-V pathways are presented and discussed.

1. Introduction

In recent years, a wealth of information has been uncovered about vibration to vibration (V-V) and vibration to translation/rotation (V-T/R) energy transfer processes in polyatomic molecules, much of it by the technique of laser induced fluorescence [1,2].

The substituted methanes have been the subject of extensive research in this area. With respect to energy transfer pathways, some of the better understood molecules are: the symmetric top, monosubstituted methyl halides [2] and the spherical top, methane [3,4]. In the symmetric top methyl halides, all vibrational transitions are allowed by dipole selection rules. In CH_2D_2 the C_{2v} symmetry results in some dipole non-allowed transitions e.g., the small energy gap, $\nu_7 \leftrightarrow \nu_9$ transition*. Hence it was felt that an understanding of the vibrational energy transfer processes in CH_2D_2 could make a valuable contribution to existing knowledge and yield information with respect to the potential role of symmetry on the rates of V-V processes.

A preliminary report of this work has been previously presented [5].

* CH_4 has dipole non-allowed transitions namely $\text{A}_1 \leftrightarrow \text{A}_1$ and $\text{A}_1 \leftrightarrow \text{E}$. Therefore any dipole non-allowed V-V step would involve ν_1 , e.g. $\nu_1 \leftrightarrow \nu_2$, but since ν_1 to ground is also infrared non-allowed, its behavior has not been directly investigated.

2. Experimental

The basic experiment consists of monitoring the time dependence of fluorescence originating from all of the infrared active fundamentals of CH_2D_2 except for the initially pumped fundamental, the ν_7 mode (see fig. 1). The details of the experimental method and apparatus have been reported previously [6], therefore only a brief description is included here.

Strong fluorescence from CH_2D_2 can be observed following irradiation of the gas with the output of a CO_2 laser operating on the R(22) line of the 9.6μ band. Weaker fluorescence is observed when the laser is operated on a variety of other lines, including the R(40), R(8), P(20), P(30) and P(34) lines of the 9.6μ band. The laser is Q-switched at 100 Hz and produces a pulse of approximately 3 mJ, as measured by a calibrated thermopile. The detectors used vary as a function of the fluorescence wavelength to be observed. For 3-5 μ fluorescence, ν_1 , ν_6 , ν_2 and ν_8 , an In : Sb detector was used. The response of the detector and entire electronic chain was 0.9 μs [6]. For 6.8 μ fluorescence, ν_3 , a Au : Ge detector was used, most measurements were done with a 5 k Ω load resistor, which produced a 1.2 μs response time for the detector and following electronic chain. For fluorescence in the 8-10 μ region, ν_9 and ν_4 , a Cu : Ge, liquid He cooled detector was used with a 5 k Ω resistive load yielding a response time of approximately 1 μs .

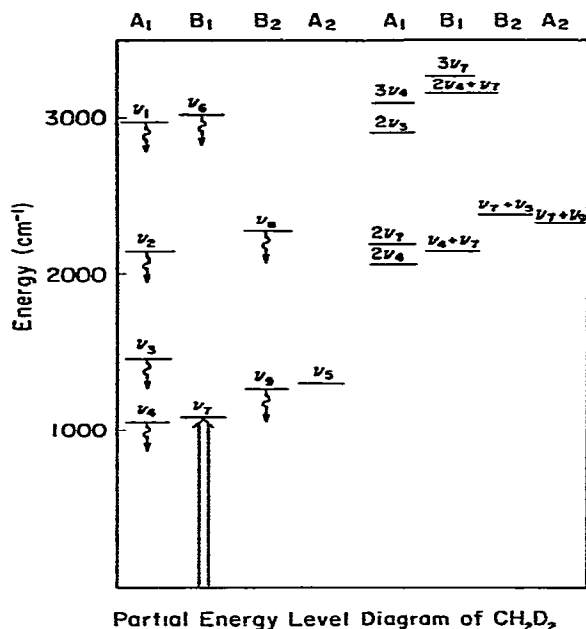


Fig. 1. Vibrational energy levels of CH_2D_2 are arranged according to their symmetries. The first four columns show the fundamentals; some overtones and combination bands are shown in the second four columns. The solid arrow indicates the laser pumped state and the wavy arrows indicate the observed states.

CH_2D_2 of 98 at. % minimum nominal purity was obtained from Merck and Co. A mass spectrometric analysis showed a CH_2D_2 content of >99% with the major impurities being other deuterated methanes. The gas was thus used without further purification.

3. Results

All experiments reported on in this paper were done using the R(22), 9.6μ CO_2 laser line at 1080 cm^{-1} which overlaps the ν_7 band of CH_2D_2 . Fluorescence was observed from the levels shown in fig. 1. Interference filters were used to isolate fluorescence from a single level (or set of closely coupled levels) and to verify that the levels were in the appropriate wavelength region.

Fluorescence from ν_1 and ν_6 was not separated, due to their proximity and extensive rotational overlap. For the same reason they are assumed to be fully equilibrated on the timescale of V-V processes in the

molecule and therefore will be treated as a single state, $[\nu_1; \nu_6]$.

ν_2 and ν_8 fluorescence was monitored through three different filters or filter combinations: 4.7μ band pass, 4.8μ long pass and sapphire, and 4.5μ long pass and sapphire. The 4.7μ b.p. and 4.8μ l.p. filters are expected to isolate primarily the ν_2 state from ν_8 while the 4.5μ l.p. and sapphire would be expected to transmit emission from both states. All V-T and V-V measurements with these filter sets were identical and for the purposes of this paper the states are considered to behave identically. However, efforts are being made to completely isolate each state using narrow band pass filters [7].

The ν_3 state is easily isolated in the 6.8μ region and the ν_9 state was also isolated as was the P branch of the ν_4 state. However laser scatter precluded accurate measurements being performed on the ν_4 state and greatly complicated attempts at the measurement of ν_9 risetimes at low pressures.

The ν_5 transition at 1300 cm^{-1} was not observed. It is an infrared non-allowed transition by strict dipole selection rules though it has been observed as a weak band in the absorption spectrum and its presence is attributed to Coriolis coupling [8].

The V-T/R relaxation rates of all reported states were measured at pressures ranging between 0.1 and 25 torr. All relaxation signals were single exponential and a plot of relaxation rate versus pressure was linear from approximately 0.5 to 25 torr. Below 0.5 torr, diffusion to the cell walls and subsequent deactivation of the molecules became important [9].

All measured V-T/R rates were the same within experimental error (see table 1) indicating that, as expected, the vibrational manifold is fully equilibrated on the V-T/R timescale. V-T/R rates were also measured in rare gas mixtures by monitoring fluorescence from ν_3 and ν_9 . The measured rates from the two different states were the same within experimental error. A linear dependence of $1/\tau$ versus rare gas pressure was observed in all cases, with excellent correlation of the intercepts with the deactivation rate of the CH_2D_2 component of the mixture. Rare gas deactivation rates of CH_2D_2 and other relevant rare gas parameters are reported in table 2. Relative deactivation rates of CH_2D_2 -rare gas collisions were calculated via Stretton's modification of SSH theory [10,11]. These are presented in table 2. Normalized probabilities are plotted in fig. 2.

Table 1
Experimentally determined V-V and V-T/R rates in CH₂D₂

| State ^{a)} | Symmetry | Energy (cm ⁻¹) | V-V rate (ms ⁻¹ torr ⁻¹) | V-T/R rate (ms ⁻¹ torr ⁻¹) |
|---------------------|----------------|----------------------------|--|--|
| ν_4 | A ₁ | 1033 | c) | c) |
| ν_7 | B ₁ | 1090 | | pumped state |
| ν_9 | B ₂ | 1234 | 263 ± 12 | 0.96 ± 0.5 |
| ν_5 | A ₂ | 1300 | | IR inactive mode |
| ν_3 | A ₁ | 1450 | 212 ± 21 | 1.03 ± 0.05 |
| ν_2 | A ₁ | 2139 ^{b)} | 291 ± 29 | 1.02 ± 0.05 |
| ν_8 | B ₂ | 2234 | | |
| ν_1 | A ₁ | 2976 | 130 ± 13 | 1.03 ± 0.05 |
| ν_6 | B ₁ | 3013 | | |

a) State assignment as of Wilmshurst and Bernstein [21].

b) 2139 cm⁻¹ accepted instead of 2202 of ref. [21] according to the recommendation of Hiller and Straley [22].

c) Observed but not measured due to interference from laser scatter.

Table 2
Deactivation of CH₂D₂ by rare gas collision partners

| Collision partner | $\mu^a)$ (au) | $\epsilon/K^d)$ (K) | $\sigma^d)$ (Å) | Experimental | | | Theoretical |
|--------------------------------|------------------|------------------------|--------------------|--|------------------------------|---|---|
| | | | | $1/\tau$ (ms ⁻¹ torr ⁻¹) | $Z_{1-0}^e)$ (collisions) | $P_{1-0}^f)$ (collision) ⁻¹ | $P_{1-0}^g)$ (collision) ⁻¹ |
| He | 3.27 | 10.22 | 2.56 | 0.935 | 15000 | 1 | 1 |
| Ne | 9.52 | 35.7 | 2.789 | 0.147 | 61000 | 2.5×10^{-1} | 6.05×10^{-3} |
| Ar | 12.37 | 124 | 3.418 | 0.102 | 92000 | 1.7×10^{-1} | 1.41×10^{-3} |
| Kr | 14.8 | 190 | 3.61 | 0.067 | 135000 | 1.1×10^{-1} | 5.44×10^{-4} |
| Xe | 15.8 | 329 | 4.055 | 0.053 | 185000 | 8.2×10^{-2} | 2.01×10^{-4} |
| CH ₂ D ₂ | 9.01 | 225 ^{c)} | 3.82 | 1.01 | 13300 | 1.15 | 4.76×10^{-3} |

a) Reduced mass of collision pair, CH₂D₂-rare gas.

b) Lennard-Jones parameter from ref. [23].

c) Obtained from ref. [24].

d) Hard sphere diameters obtained from ref. [23], for CH₂D₂ that of CH₄ is used.

e) Number of collisions required for deactivation: $Z_{10} = 2530[(\sigma_a + \sigma_b)/2]^2(\mu)^{-1/2}\tau$, for σ in Å, μ in au, and τ in ms torr.

f) Probability of deactivation per collision relative to He: $P_{1-0} = (Z_{1-0})_{\text{He}}/(Z_{1-0})_{\text{X}}$.

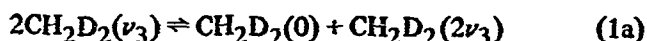
g) Relative probability of deactivation per collision calculated by SSH theory [10,11] and normalized to He.

Rates of rise of population in the fundamentals of CH₂D₂ are reported in table 1 as best fits to a single exponential rise. All $1/\tau$ versus pressure plots were linear over the region reported on and all intercepts were zero within experimental error.

4. Discussion

An ultimate aim of vibrational energy transfer

studies is detailed information about pathways of energy flow. Based on considerations of the magnitude of the energy gap and information gained via studies of methyl halides, the likely pathways for filling the [ν_1, ν_6] states in CH₂D₂ can be narrowed to two:



and subsequently

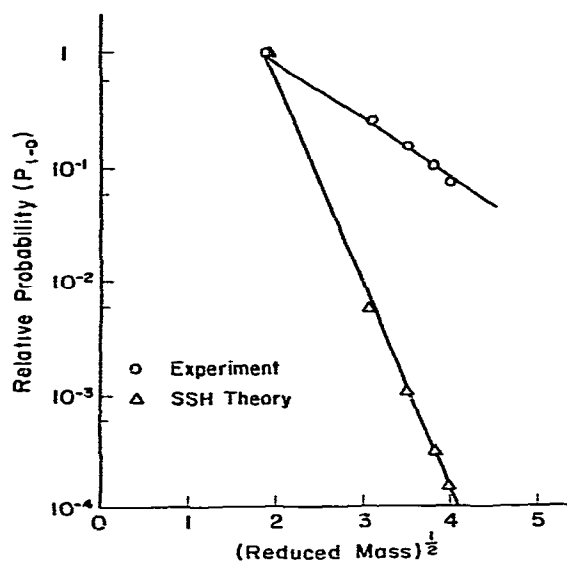
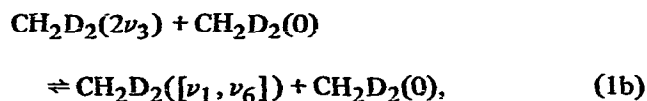
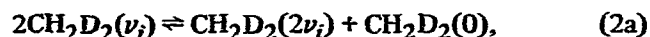


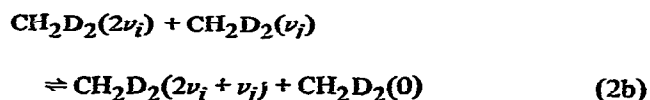
Fig. 2. Semilogarithmic plot of relative deactivation probability per collision, P_{1-0} versus (reduced mass of collision partners)^{1/2}. For the SSH calculations a breathing sphere parameter of 1 was used. The probabilities were normalized by taking $P_{1-0} = 1$ for $\text{CH}_2\text{D}_2 - \text{He}$. The experimental rates were converted to P_{1-0} as indicated in the footnote to table 2, and normalized to He.



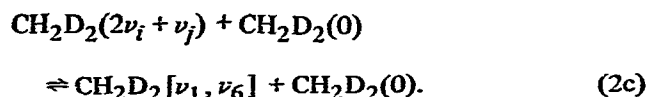
where ν_3 could be filled by any of the processes discussed below, or $[\nu_1, \nu_6]$ may be filled by an "up the ladder" process involving an overtone of one of the states in the 1000 cm^{-1} region ($2\nu_i$) colliding with another excited molecule in the same region to yield a triply excited state ($2\nu_i + \nu_j$) near 3000 cm^{-1} , e.g. $3\nu_4$. A collision of the triply excited state with a ground state molecule would yield a $[\nu_1, \nu_6]$ molecule. This can be represented as follows:



followed by

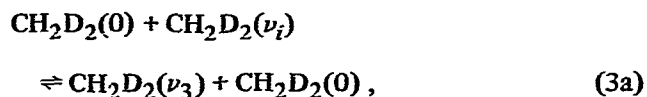


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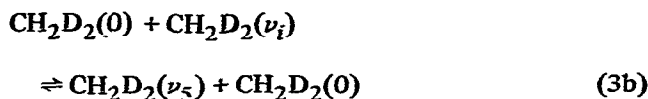


As a result of preliminary studies involving the rare gas dependence of the rate of rise of the $[\nu_1, \nu_6]$ states, which will be reported on in detail in a future publication [12], process (1) seems most likely as leading to the equilibration of the $[\nu_1, \nu_6]$ modes with the initially pumped mode, though we cannot yet totally rule out process (2).

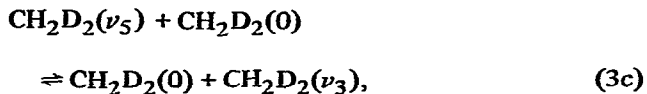
Filling of the ν_3 state can also be limited to a few plausible pathways: ν_3 can fill from below via a process of the type



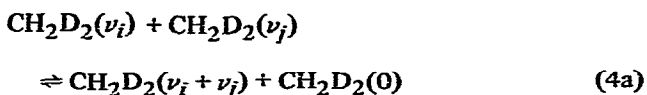
or



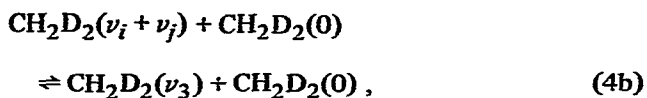
and



or it can fill from above via a process of the type



and



where $i, j = 4, 7, 9$. A variety of intermediate steps are possible in (4b). For example, ν_3 may be filled through ν_2 which is filled via a ν_i combination band.

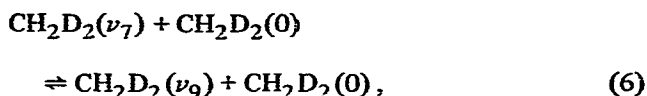
If $[\nu_1, \nu_6]$ fills via a process like that in (2) then ν_3 could fill from above via the process



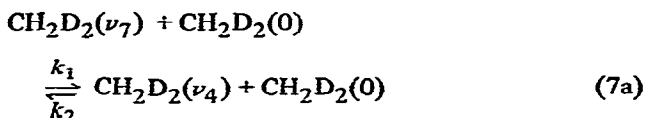
Again, due to preliminary results of the dependence of the rise rate of the ν_3 state on rare gas pressure, a pro-

cess of the type illustrated in eq. (4) seems most likely [12].

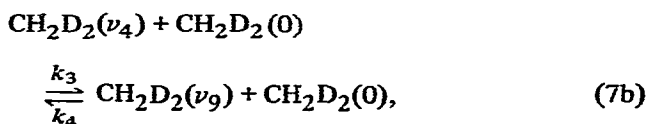
The filling of ν_9 represents an interesting point regarding symmetry effects on (V-V transfer) rates. The transition $\nu_7(B_1) \rightarrow \nu_9(B_2)$ is forbidden according to dipole selection rules in the C_{2v} group*. For small energy gaps, it has been shown that dipole-dipole terms, when present, normally dominate higher multipolar terms in their contribution to the energy transfer process [13,14]. One can then consider whether ν_9 would be expected to fill via the dipole non-allowed process



or via an intermediate state



and



where all steps are allowed by dipole selection rules. For the pressure range observed to date (0.4 to 3 torr) and within the limits of our signal to noise level we see only a single exponential rise for the ν_9 population following laser excitation of ν_7 . While an induction time reflecting a consecutive kinetic process would be expected if k_1 is comparable to k_3 , it has been found by mathematical simulation of the signal, that the induction time would not be observable under our experimental conditions if $k_1 \gtrsim 3k_3$. This is not an unreasonable expectation considering the small energy gap between ν_7 and ν_4 and the overlap of their rotation levels. Further studies are underway in an effort to improve signal to noise level via TE laser pumping of ν_7 and an effort is being made to pump ν_4 and to observe the resulting rise of population of ν_7 and ν_9 which

* The restriction may be relaxed if mixing due to Coriolis forces is sufficient to change the symmetry types of the fundamentals involved.

will allow direct determination of the rate constants in eqs. (7a) and (7b) [12]. This will then allow for the evaluation of the role of symmetry in these processes.

4.1. V → T/R rates

It is again evident, as in many previous studies, that SSH theory is insufficient to describe the variation of the deactivation rate of methane or a substituted methane as a function of rare gas collision partner [2]. For the methyl halides consideration of the combined deactivation effects of translational degrees of freedom as described by SSH theory [10,11] and rotational degrees of freedom as described by V → R theory result [15,16] in a qualitative reproduction of the features present in the experimental data [2,17]. The most striking feature being a leveling off of the deactivation probability as a function of increasing reduced mass of the collision pair. This behavior has also recently been reproduced for a number of the methyl halides by use of a unified V → T/R theory [18].

In CH_2D_2 this leveling behavior is not observed. The deactivation rate continues to decrease significantly as a function of reduced mass. The behavior observed in CH_2D_2 has also been observed in CH_4 [19] and in CHD_3 [20]. As indicated in fig. 2 this behavior is not predicted by SSH theory. Nor would it be reproduced by simple V → R theory which would predict no variation or a very slight variation of rate as a function of reduced mass of the collision partner. It is also doubtful whether a simple synthesis of predictions of V → T and V → R theories could produce this behavior assuming reasonable scaling factors for V → T and V → R contributions [17]. This behavior should present an interesting challenge for a unified V → T/R theory.

5. Conclusions

Following excitation of CH_2D_2 with the R(22) line of the 9.6 μ CO_2 laser transition, fluorescence is observed from 7 of the 8 infrared active fundamentals of CH_2D_2 . All states exhibit a V-T/R rate of 1 ms^{-1} torr^{-1} . V-V rates are measured for 6 of the fundamentals with the 3 μ [ν_1, ν_6] modes likely filling via a resonant process involving two quanta in the ν_3 mode. The ν_3 mode most likely fills from the modes in the 2000 cm^{-1} region while these modes are most likely

filled via a resonant process involving two quanta in the modes at 1000 cm^{-1} . The possible role of symmetry effects in filling the ν_9 state is discussed. The rates of deactivation of CH_2D_2 by rare gases were measured and the dependence of the deactivation of CH_2D_2 on rare gas reduced mass cannot be reproduced by simple SSH V-T or V-R theories or a simple superimposition of the two as was found applicable for the methyl halides.

In a future publication we intend to present a much more detailed discussion of the V-V pathways in this system [7].

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