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VIBRATIONAL RELAXATION OF HF(v = 3, 4)

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The vibrational relaxation of pure HF(v = 3 and v = 4) has been studied by pumping HF directly from v = 0 to v = 4. The relaxation rates of v = 3 and v = 4 were determined to be $k_T^3 = (2.8 \pm 0.4) \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1} and $k_T^4 = (7.2 \pm 0.5) \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1} at 293°K. It is shown that single quantum energy transfer can account for all of the vibrational relaxation.

1. INTRODUCTION

The vibrational relaxation of HF has been the subject of much work, both because of its importance for the modelling of chemical lasers and for the testing of theories of energy transfer. Recent interest has centered on the relaxation rates of the second and higher levels.

Theoretical studies have attempted to model the relaxation of HF using a collision complex model [1, 2], classical trajectory calculations [3, 4], and an information theory synthesis [5, 6].

The experimental study of these higher vibrational levels has proved difficult. The experiments have produced HF in levels with vibrational quantum numbers $v \geq 2$ by two different methods. In the first, highly vibrationally excited HF is produced in a chemical reaction. Quenching of HF chemiluminescence by added gas is monitored to deduce vibrational relaxation rates. This method has been used by Smith and co-workers [7, 8] and by Kwok and Wilkins [9]. The second method is to use laser excitation followed by vibrational up-pumping to study the kinetics of levels with $v > 1$. Bott [10] has measured the relaxation rate of $v = 2$ in this way. Osgood et al have used sequential pumping of $v = 1$, $v = 1$ and 2 and $v = 1$, 2 and 3 to obtain relaxation rates of levels $v = 2 - 4$ [11]. In all these experiments several vibrational levels are populated simultaneously resulting in relatively complicated kinetic schemes.

This letter reports a new method for the study of the relaxation of HF(v = 3, 4). The method is an extension of the laser-excited vibrational fluorescence technique. Hydrogen fluoride is pumped directly from v = 0 to v = 4. The populations of v = 3, 4 are monitored by observing second overtone fluorescence ($\Delta v = 3$) in the near infrared with a photomultiplier. The greatly simplified kinetic scheme enables measurement of the relaxation rates with good accuracy and without the uncertainties of previous methods. It is also shown that HF(v = 4) molecules relax by losing a single quantum, yielding HF(v = 3).

2. EXPERIMENTAL

Hydrogen fluoride was handled in a monel vacuum line and fluorescence cell. The cell and line were passivated by filling with 600 Torr of HF for 24 hours. The monel fluorescence cell was 28 cm long and 2.5 cm in diameter. Calcium fluoride windows at Brewster's angle were mounted at each end with Viton O-rings. To reduce scattered light a single conical optical baffle of the type described by Pruett and Zare [12] was placed in each arm of the cell 8 cm from the viewing region. Fluorescence was viewed through a 2.5 cm diameter sapphire window.

Matheson HF was used (stated purity of the liquid phase 99.9%). In all experiments HF was frozen at 77°K and pumped on to remove noncondensibles (typically a few percent of

the total pressure). This was done twice. To test for the possibility that the measured rates might be affected by water contaminating the HF, two experiments were done in which the HF was dried. In the first HF was distilled twice from - 30°C to 77°K [11]. In the second HF was dried over anhydrous CoF_3 [13]. No systematic changes in the rate constants were observed among these experiments. It is concluded that water made a negligible contribution to the decay rates. Hydrogen fluoride was flowed slowly through the fluorescence cell (flow speed ~ 2 cm s^{-1}). Cell pressures were measured with a 0 - 10 Torr MKS Baratron. During a fluorescence measurement the cell pressure remained constant to within ± 2%.

A CMX-4 flashlamp-pumped dye laser was used to excite the R(2) line of the v = 0 to v = 4 transition at 6703 Å (pulse energy ~ 2 mJ; linewidth ~ 0.2 cm^{-1} FWHM). The laser beam was collimated with a lens and passed through the cell twice.

Fluorescence (Δv = 3) was focused onto the photocathode of a Varian VPM-159 photomultiplier tube operated at -25°C. Optical filters at the entrance to the photomultiplier housing blocked scattered laser light and passed the fluorescence from either v = 3 or v = 4. The v = 4 fluorescence was passed by a filter with center wavelength 926 nm and full bandwidth at half maximum of 46 nm (1% T at 79 nm bandwidth). Fluorescence from v = 3 was passed by a filter with a center

wavelength of 880 nm and a full bandwidth at half maximum of 28 nm (1% T at 52 nm bandwidth). A second filter designed to reflect scattered light but transmit fluorescence was placed over the viewing window of the cell.

The laser was tuned to the absorption line by maximizing the signal from a spectraphone. A few hundred fluorescence photons were collected from a single laser pulse. To produce a decay curve, two thousand laser shots were averaged with a Tektronix R-7912 transient digitizer and PDP-11/10 computer. The scattered light was then recorded and subtracted from the total light. Scattered light intensity was less than half the v = 4 fluorescence intensity. Fluorescence decay curves for v = 3 and 4 are shown in Fig. 1. The fluorescence from v = 3 is weaker mainly due to a lower Einstein A coefficient.

3. RESULTS

We allow for the possibility of multiquantum energy transfer in our kinetic scheme, Eqs. (1) - (3).

$$HF(v = 4) + HF(v = 0) \xrightarrow{k_3^4} HF(v = 3) + HF \qquad (1)$$

$$HF(v = 4) + HF(v = 0) \xrightarrow{k_v^4} HF(v = 0 - 2) + HF \qquad (2)$$

$$HF(v = 3) + HF(v = 0) \xrightarrow{k_T^3} HF(v < 3) + HF \qquad (3)$$

Process (1) represents single quantum relaxation of HF(v = 4) by HF(v = 0) to produce v = 3. The rate constant k_3^4 includes both V → V and V → T, R processes. Equation (2) corresponds

to removal of v = 4 by multiquantum processes and includes all mechanisms producing HF in levels v < 3. The rate constant k_v^4 is the rate constant for multiquantum relaxation. Equation (3) and the rate constant k_T^3 represent relaxation of v = 3 by all possible V → V and V → T, R processes.

The corresponding rate equations yield

$$N_4(t) = N_4(0)\ e^{-k_T^4\ P_{HF}t} \tag{4}$$

$$N_3(t) = \frac{k_3^4\ N_4(0)}{k_T^4 - k_T^3} \left\{ e^{-k_T^3\ P_{HF}t} - e^{-k_T^4\ P_{HF}t} \right\} \tag{5}$$

where $N_4(t)$, $N_3(t)$ are the populations of v = 4, v = 3 at time t respectively and P_{HF} is the pressure of HF. Here $k_T^4 = k_3^4 + k_v^4$. The rate constant k_T^4 is the rate constant for removal of v = 4 by all processes.

From Eq. (4), the population of v = 4 decays exponentially with rate (1/lifetime) $k_T^4\ P_{HF}$. After an initial rise the population of v = 3 decays with a rate $k_T^3\ P_{HF}$. A plot of these decay rates for v = 4, 3 vs pressure yields lines with slopes k_T^4, k_T^3 respectively. Figure 2 shows one such plot. The results of six experiments were averaged to give $k_T^4 = (7.2 \pm 0.5) \times 10^{-11}$ cm^3 molec^{-1} s^{-1} [$(2.4 \pm 0.2) \times 10^6$ s^{-1} Torr^{-1}]. The average of four experiments gives $k_T^3 = (2.8 \pm 0.4) \times 10^{-11}$ cm^3 molec^{-1} s^{-1} [$(9.4 \pm 1.2) \times 10^5$ s^{-1} Torr^{-1}]. The error estimate in each case is two standard

deviations of the mean* and includes an additional 2% for uncertainty of the pressure.

To test for possible multiquantum relaxation, the fraction of HF(v = 4) which becomes HF(v = 3) is determined. From Eqs. (4) and (5)

$$k_3^4/k_T^3 = \int_0^\infty N_3(t)\,dt \;/\; \int_0^\infty N_4(t)\,dt$$

and the desired fraction k_3^4/k_T^4 is calculated from the measured k_T^3 and the ratio of integrated fluorescence intensities.

Fluorescence intensities were converted to relative populations using the rotationless Einstein transition probabilities of Sileo and Cool [14] and the vibration-rotation interaction factors of Meredith and Smith [15]. A thermal rotational distribution was assumed. After correcting for filter transmissions and detector sensitivity the average of eight pairs of measurements (v = 3, 4) gives $k_3^4/k_T^3 = 2.40 \pm 0.23$. The error estimate is two standard deviations of the mean. Taking k_T^3 as $(2.8 \pm 0.4) \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1} we calculate $k_3^4 = (6.8 \pm 1.1) \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1}. The fraction of molecules leaving v = 4 and reaching v = 3 is thus $k_3^4/k_T^4 = 0.95 \pm 0.15$. To well within our experimental uncertainty single quantum energy transfer accounts for all the relaxation of v = 4. Using the Einstein

*i.e. $2\sigma/\sqrt{N}$ where $\sigma^2 = \sum_{i=1}^{N} (X_i - \overline{X})^2/(N - 1)$,

transition probabilities of Herbelin and Emmanuel [16] or Meredith and Smith [15] we calculate that $k_3^4 = (7.3 \pm 1.1) \times 10^{-11}$ cm^3 molec^{-1} s^{-1} or $k_3^4 = (7.2 \pm 1.1) \times 10^{-11}$ cm^3 molec^{-1} s^{-1}, respectively, in even closer agreement with our total relaxation rate k_T^4.

4. DISCUSSION

Table 1 compares our results with the experimental results of others. The disagreement among these results reflects the difficulties inherent in the previous methods.

In the experiment of Kwok and Wilkins [9] v = 4 was populated by V - V up-pumping from lower vibrational levels. This coupling together of the vibrational levels was not considered in their kinetic analysis and may have caused significant error. The interpretation of their experiment is further complicated by the necessity of modelling the fast flow in their apparatus.

The results of Poole and Smith [8] are in fair qualitative agreement with our data. They show that v = 4 relaxes roughly two times faster than v = 3. The absolute rates are somewhat smaller. The experiments of Poole and Smith measure the ratio of the rate of relaxation by an added quencher (HF in this case) to the total decay rate of HF in the absence of quencher. They argued that with no added quencher, the decay rate is purely radiative. Some additional

collisional relaxation may have occured, however. This would lead to the calculated rates being low and lead to a somewhat smaller increase in the reported v = 4 rate over the v = 3 rate. Our result for v = 4 is in better accord with the earlier work of Airey and Smith [7].

The agreement with the data of Osgood et al. [11] is only fair even considering their rather large error estimates. The uncertainties of their data result from the complexity of pumping several vibrational levels simultaneously. In their experiment it was necessary to produce an initial vibrational temperature. The difficulty of doing this was greatest for the experiments determining the relaxation rates of v = 3, 4.

The experimental method described in this letter suffers none of the problems of these other techniques. The decay rates give the absolute rate constants directly and the interpretation is straightforward.

Table 2 compares our rates with previous theoretical values for these rates and for the ratio k_3^4/k_T^4.

The rates of Shin and Kim for HF $2 \leq v \leq 5$ are calculated by considering two mechansims; a long-lived collision complex and a direct V - R relaxation [2]. Since the ratio of the v = 4 to v = 3 rate is not well predicted by their theory the agreement for the v = 3 rate is likely to be fortuitous. The first order perturbation theory of Shin and Kim predicts that single quantum energy transfer will predominate, hence $k_3^4/k_T^3 = 1.0$.

Wilkins has performed a full three-dimensional classical trajectory study of HF vibrational relaxation [4]. The calculated rates for removal of HF(v = 3, 4) are not in good agreement with this experiment. On the basis of his calculation, Wilkins proposes that the vibrational relaxation of HF(v = 4) will occur through fast multiquantum V → R relaxation followed by slower R - T relaxation. The mechanism proposed by Wilkins cannot be entirely correct. We find no evidence for large multiquantum rates (Table 2). Rapid V → R transfer and R → V back transfer followed by slower R → T transfer would result in non-exponential decays from v = 4. Our decays are exponential over at least 3 lifetimes. Fluorescence from the high rotational levels of v = 3 ($J \gtrsim 5$) is not passed by our optical filter. Since we see that 95 ± 15% of the HF that leaves v = 4 appears in v = 3 with $J \lesssim 5$, there cannot be a large population in the high rotational states of v = 3.

Clendening et al. [5] have attempted to compute HF energy transfer rates from an information theory "synthesis." They assumed that a single surprisal parameter was sufficient to describe the ratio of the information theoretic prior rates to the actual rates for all possible V → V and V → R, T processes. The one parameter was fixed by the HF(v = 1) V → R, T rate. Large multiquantum V → V rates were calculated which are clearly inconsistent with the single quantum transfer observed for v = 4. It is not surprising that more

than one parameter should be required to describe all V → V and V → T, R processes for HF.

The fast relaxation of HF observed in these experiments is undoubtedly a result of the strong HF - HF attraction. Since we find no evidence for large multiquantum energy transfer rates it is unlikely that a collision complex is formed which is sufficiently long-lived that randomization of the available energy occurs. Gait [17] has shown that an attractive potential can give rise to "orbiting" trajectories which make a large contribution to V - V energy transfer probabilities. Small changes in rotational quantum numbers can easily absorb the energy defect to give large relaxation rates for these levels.

We plan to extend this technique to study higher vibrational levels and to study vibrational relaxation and chemical reaction of HF with other collision partners.

5. ACKNOWLEDGMENTS

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Table 1

Comparison of experimental rates for relaxation of HF(v = 2 - 5)[a]

Reference	v = 2	v = 3	v = 4	v = 5
Bott [10]	1.6			
Kwok Wilkins [9]	1.6 ± 0.5	2.6 ± 0.9	2.7 ± 1.0	0.9 ± 0.5
Poole Smith [8]	1.3	1.9	3.2	4.6
Airey Smith [7]	1.6	1.7	≥ 4.4	≥ 6.5
Osgood et al [11]	2.5 ± 0.7	4.9 ± 1.5	4.3 ± 1.8	
This work		2.8 ± 0.4	7.2 ± 0.5	

a) All rates in units of 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}.

Table 2

Comparison of theoretical rates with this work[a]

Reference	v = 3	v = 4	k_3^4/k_T^4
Shin and Kim [2]	2.41	1.91	1.0
Wilkins [4]	8.0 ± 0.76	8.8 ± 0.7	0.38
Clendening et al. [5]	2.11	2.16	0.49
This work	2.8 ± 0.4	7.2 ± 0.5	0.95 ± 0.15

a) All rates in units of 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}.

Figure 1. Typical fluorescence decay curves for v = 3 and v = 4. The HF pressure was 0.144 Torr for both traces.

Figure 2. HF relaxation rate vs pressure for v = 3 (▲) and v = 4 (●).

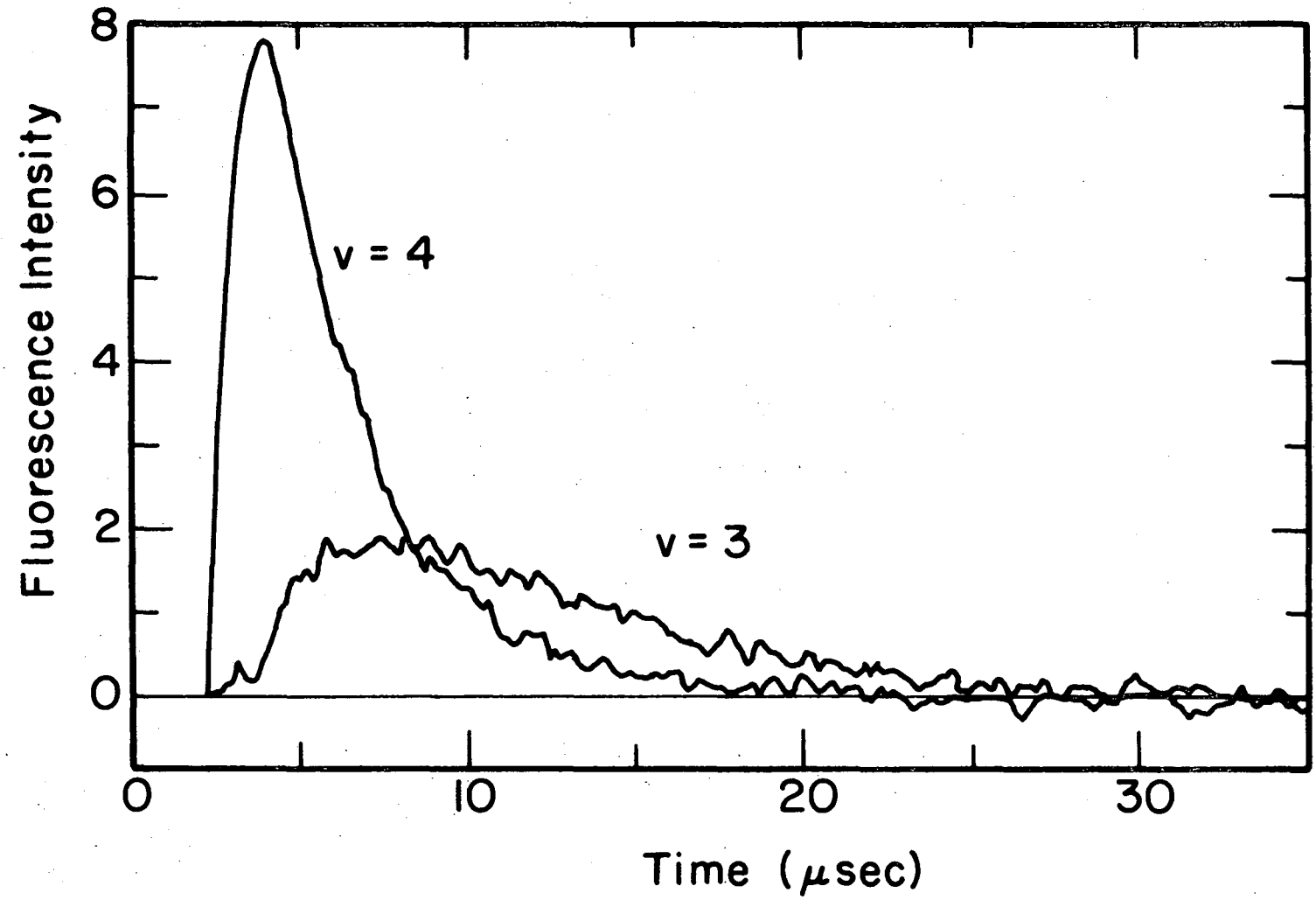

Fig. 1

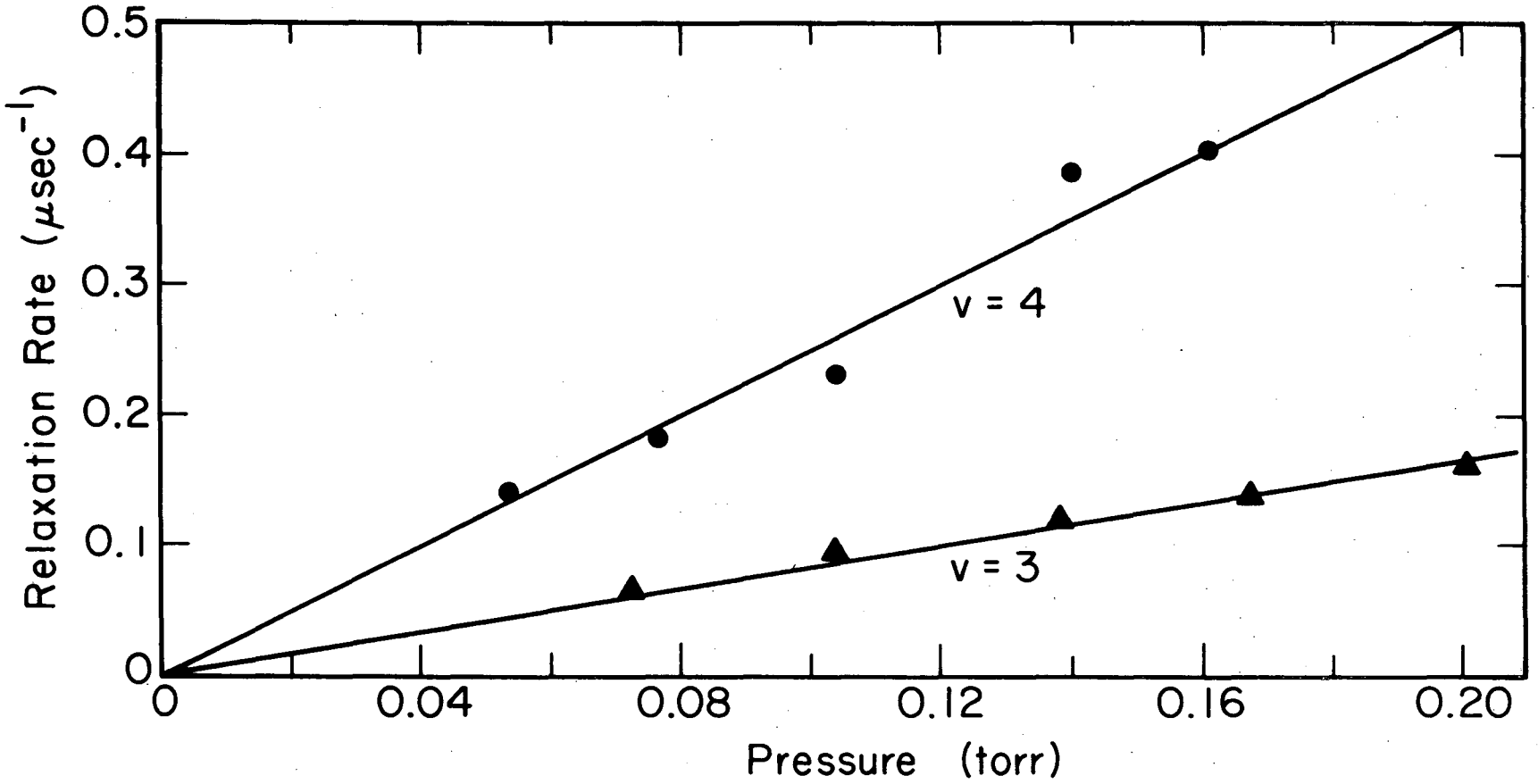
0.5
0.4
0.3
0.2
0.1
0
Relaxation Rate (μsec^{-1})
v = 4
v = 3
0
0.04
0.08
0.12
0.16
0.20
Pressure (torr)

Fig. 2

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