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VIBRATIONALLY EXCITED MOLECULES FOR CHEMICAL LASER

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"Vibrationally Excited Molecules for Chemical Laser"

by

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"Vibrationally Excited Molecules for Chemical Laser Development"

As detailed in our original proposal, our research efforts undertaken during the brief tenure of this contract have followed two separate avenues of investigation. In the first aspect of these studies, we proposed to study elementary, exothermic, atom-molecule reactions in the hopes of discovering basic features of chemical reaction systems which would help us to optimize the channeling of the heat of reaction into specific internal energy vibrational modes of the reaction products. The long-range goal of such studies would hopefully be the prediction of specific chemical reactions which might be promising candidates for chemical laser systems. In the second aspect of our work, we proposed to investigate the efficiency of vibrational energy transfer from excited diatomics in the $V = 2$ vibrational levels. The rationale behind these studies was the fact that eventual optimization of power output from chemical laser systems will require very precise knowledge of energy transfer mechanisms and efficiency, including energy transfer data from vibrational states above $V = 1$. The progress and results obtained in each of these studies are discussed below.

1. Infrared Chemiluminescence Studies of Chemically Reacting Systems.

In order to determine the fraction of the heat of reaction which was converted to vibrational excitation of the product species, the technique known as infrared chemiluminescence was employed. In these studies, reactions are carried out in a low pressure fast flow reactor and the emission of vibrational fluorescence from vibrationally excited product molecules is monitored. From the distribution and intensity of this fluorescence one can then attempt to calculate the initial distribution of vibrationally excited product molecules produced in the reaction. Because of the exceedingly low signal levels involved in these studies, sensitive infrared detection systems are required. In our particular case, we employ the phase sensitive, lock-in-amplifier technique to increase the signal-to-noise level.

Almost the entire portion of the one year of this contract was devoted to the construction and subsequent improvement of a high speed flow system and the development of the necessary electronic monitoring systems to analyze the infrared emissions. A 4-inch quartz flow tube reactor equipped with three 1 1/2 inch diameter infrared transmitting windows was constructed. The length of this flow tube is 2.5 feet and the windows are spaced 3 inches apart in the center of this tube. High speed pumping was achieved by using a 4-inch NRC oil diffusion pump backed by a mechanical Welch duo-seal pump of 10 cfm capacity. A low impedance 4-inch cold trap was inserted between the flow tube and the diffusion pump in order to protect the pump oil from the corrosive compounds to be employed in some of our work. A gate valve was inserted between the trap and the diffusion pump to permit vacuum distillation of the condensate from the cold trap without subjecting the pump oil to exposure to these materials.

The other end of the flow tube was connected to the two gas inlets, one being used for the atomic reactant and the other for the stable reactant. Atoms were produced by electrodless microwave discharge using a Raytheon 110 watt discharge unit. The flow rates of the various reactants were determined using calibrated flow meters and the pressure in the reactor was measured with a Granville-Phillips capacitance manometer.

The infrared fluorescence from the reaction cell is chopped mechanically at a frequency of 450 cycles per second. The emitted light is focused by a CaF_2 lens into a Perkin-Elmer monochromator and exits into a Pb S detector. A Princeton Applied Research Corp. lock-in-amplifier (PAR, Model 124) was employed to magnify this signal and the amplified signal was fed to a Mosely 1 mv recorder.

Upon completion of this apparatus, the remainder of the contract year has been devoted to a systematic attempt to improve the detection capability so as to permit us to investigate reactions at as low a pressure as possible. This is an extremely important point if we are to minimize collisional relaxation and hence obtain initial vibrational energy distributions. These studies involve investigation of the effect of flow velocity, chopping frequency, microwave power variations used to produce atoms and test of several monochromators as they effect the signal-to-noise ratio. Although the apparatus has now been refined and we are quite pleased and optimistic about reaching our initial research objectives, the contract year has expired and we regret our inability to have discovered any new reactions which might serve as potential chemical laser systems. However, we are hopeful of obtaining continuation outside funding so that we might continue these studies and thus capitalize on the research and effort devoted to the construction of our apparatus.

2. Vibrational Energy Transfer Studies from the V = 2 State of HBr.

This phase of the research was carried out in Dr. Hao-Lin Chen's laboratories. The research involves the study of laser excited vibrational fluorescence in which valuable data concerning energy transfer efficiency are obtained. Prior to the work reported here, this particular technique had been employed with good success to the study of energy transfer from the V = 1 to V = 0 state for various diatomic molecules. In the current study, the energy transfer processes and relaxation rates have been studied for the reaction:

$$2HBr(V = 1) \rightleftarrows HBr(V = 2) + HBr(V = 0) + \Delta E = 90\ cm^{-1}.$$

In view of the anharmonicity of vibrational quantum states, the mechanism of relaxation and excitation of vibrational states above V = 1 is of considerable interest. The knowledge obtained from these studies is of direct importance in considering the kinetics of chemical lasers as well as the theory of unimolecular decompositions.

The exact techniques employed and the results obtained are described in the reprint of the journal article appended to this report. Also shown in this paper are the details of the experimental apparatus employed. Because of this publication, it would be redundant to supply additional description of this work here.

It is fair to say that, as a result of this work, our knowledge of the mechanism of vibrational energy transfer has been increased substantially and it is clear that the laser induced fluorescence technique can be employed profitably to investigate energy transfer from vibrational states above $V = 1$. One can anticipate additional valuable work in this area in the years ahead using this particular method.

Publications to Date Resulting from Work on Contract N00019-72-C-0236

1. B. M. Hopkins and H. L. Chen, Chemical Physics Letters, 17, 500 (1972).

Enclosure: Reprint of above publication.

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VIBRATIONAL EXCITATION AND RELAXATION OF HBr($V = 2$) STATE

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Vibrational fluorescence from the $V = 2$ to the $V = 1$ state is observed following excitation by a pulsed HBr chemical laser. The time dependence of the fluorescence is used to determine the rate of near-resonant vibration-to-vibration energy transfer, HBr($V = 1$) + HBr($V = 1$) $\rightleftharpoons$ HBr($V = 2$) + HBr($V = 0$) + $\Delta E = 90\ \mathrm{cm}^{-1}$. The cross section for this reaction in the exothermic direction at room temperature has been found to be $(1.1 \pm 0.2) \times 10^{-16}\ \mathrm{cm}^2$.

1. Introduction

Vibrational relaxation rates of vibrationally excited molecules have been studied by the laser excited vibrational fluorescence technique [1]. To date most experiments [2, 3] have concerned energy transfer from the $V = 1$ to $V = 0$ state. Recently using this technique we measured the vibrational relaxation rate of the HCl molecule in its $V = 2$ state [4]. Here we present a similar study of the HBr molecule.

In this experiment we have observed the building up of the $V = 2$ state population of the HBr molecule through the rapid V → V energy exchange process,

$$2\mathrm{HBr}(V = 1) \rightleftharpoons \mathrm{HBr}(V = 2) + \mathrm{HBr}(V = 0) + \Delta E = 90\,\mathrm{cm}^{-1}.$$

The mechanism of the relaxation and the excitation of anharmonic oscillators by this type of single quantum exchange process has been of considerable interest in the past. Knowledge of the rates of relaxation of upper vibrational states could give useful information concerning the principles of unimolecular decomposition and the kinetics of chemical lasers. The experimental results of our study have been compared with theoretical predictions based on different interaction potentials in order to more fully understand the dynamics of vibrational energy transfer.

2. Experimental

Laser pulses generated by the reaction

$$\mathrm{Br}\cdot + \mathrm{HI} \rightarrow \mathrm{HBr} + \mathrm{I}\cdot + \Delta H = -16.1\ \mathrm{kcal/mole}$$

were used to vibrationally excite molecules in a quartz fluorescence cell. The experimental arrangement is shown in fig. 1. It is quite similar to the set up already described [3]. However in order to populate a significant portion of the HBr molecules in the $V = 1$ state, the fluorescence cell was put partially inside the laser cavity. In addition to the gold-coated mirror and Ge flat used in previous experiments, a third reflector, another gold-coated mirror, was used to collect the unabsorbed laser beam and send it back to the laser cavity. No significant enhancement in fluorescence intensity was observed for samples containing high concentrations of HBr molecules in the mixture, whereas for mixtures with lower HBr mole fractions, an increase in the fluorescence signal of a factor greater than two was observed.

For monitoring the fluorescence intensity, a Ge:Au photoconductor was used. Measurements of 2 → 1 vibrational fluorescence were screened by a HBr cold cell with atmospheric pressure so that only 2 → 1 fluorescence signals and some transitions from higher states were seen by the detector. Fluorescence signals from higher states were much weaker in intensity so that only signals from 2 → 1 transitions were significant. The signals were amplified, displayed on a Tektronix 545 oscilloscope, and

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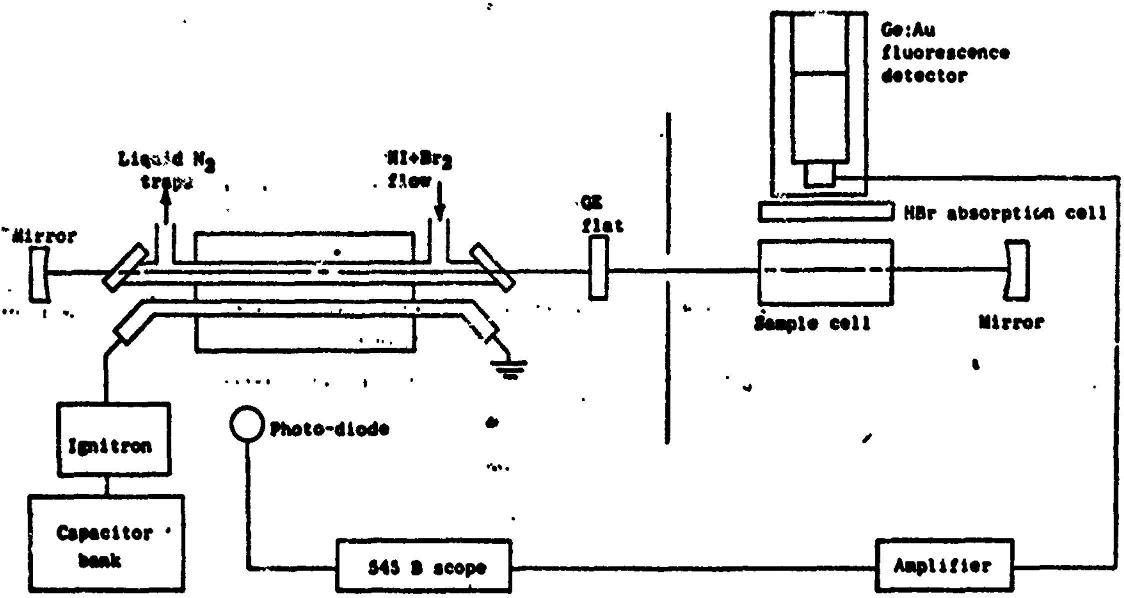

Fig. 1. HBr laser-excited vibrational fluorescence apparatus for observing $V = 2$ to $V = 1$ emissions.

photographed. The overall detection response time was less than 2.5 μsec.

Hydrogen bromide of 99.8% specified minimum purity obtained from the Matheson Company was used and purified by degassing and by repeated distillation in a closed vacuum line from traps at −120° to −180°C. Matheson research grade gases: He (Ne < 0.2 ppm, $N_2 < 0.5$, $O_2 < 0.1$, Ar < 0.1, $H_2 < 1$, $CH_4 < 0.5$, $CO_2 < 0.5$, $H_2O < 1$) and Ne (He < 50 ppm, $N_2 < 1$, $O_2 < 0.1$, $H_2 < 5$, Ar < 1, CO < 0.5, $CH_4 < 0.5$, $H_2O < 1$) were used without further purification. Research grade Kr (Xe < 25 ppm, $N_2 < 25$, $O_2 < 4$, Ar < 4, $H_2 < 5$, $CH_4 < 10$, $H_2O < 1$) was frozen in liquid N_2 and pumped in order to remove possible CH_4 contamination. Measurements were carried out at a total gas pressure between 40 and 80 torr. The cell temperature was 23 ± 3°C.

3. Kinetic scheme

Following excitation by the HBr chemical laser, there are five possible rate processes governing the excitation and relaxation of the $V = 2$ and the $V = 1$ states in HBr–M gaseous mixtures:

$$\mathrm{HBr}(V=1) + \mathrm{HBr}(V=1) \underset{k_e'}{\overset{k_e}{\rightleftharpoons}} \mathrm{HBr}(V=2) + \mathrm{HBr}(V=0) + \Delta E = 90\ \mathrm{cm}^{-1}, \quad (1)$$

$$\mathrm{HBr}(V=1) + \mathrm{HBr}(V=0) \xrightarrow{k^{1\to0}_{\mathrm{HBr-HBr}}} 2\mathrm{HBr}(V=0) + \Delta E = 2559\ \mathrm{cm}^{-1}, \quad (2)$$

$$\mathrm{HBr}(V=1) + \mathrm{M} \xrightarrow{k^{1\to0}_{\mathrm{HBr-M}}} \mathrm{HBr}(V=0) + \mathrm{M} + \Delta E = 2559\ \mathrm{cm}^{-1}, \quad (3)$$

$$\mathrm{HBr}(V=2) + \mathrm{HBr}(V=0) \xrightarrow{k^{2\to1}_{\mathrm{HBr-HBr}}} \mathrm{HBr}(V=1) + \mathrm{HBr}(V=0) + \Delta E = 2469\ \mathrm{cm}^{-1}, \quad (4)$$

$$\mathrm{HBr}(V=2) + \mathrm{M} \xrightarrow{k^{2\to1}_{\mathrm{HBr-M}}} \mathrm{HBr}(V=1) + \mathrm{M} + \Delta E = 2469\ \mathrm{cm}^{-1}. \quad (5)$$

The Boltzman factor $k_e/k'_e = \exp(\Delta E/kT) = 1.55$ relates the rate constants for vibrational energy exchange. Deactivation is due only to collisions since the radiative lifetimes for both the $V = 1$ and the $V = 2$ states are relatively long compared with the measured relaxation times so that these radiative processes are neglible.

Representing HBr($V = 1$) by x and HBr($V = 2$) by y, the differential equations for the time rate of change of x and of y are:

$$\dot{y} = a_1 x^2 - b_1 y, \quad (6)$$

$$\dot{x} = -a_2 x^2 + b_2 y - c_2 x, \quad (7)$$

with

$$a_1 = k_e, \quad (8)$$

$$b_1 = k'_e[\mathrm{HBr}] + k^{2\to 1}_{\mathrm{HBr-HBr}}[\mathrm{HBr}] + k^{2\to 1}_{\mathrm{HBr-M}}[\mathrm{M}], \quad (9)$$

$$a_2 = 2a_1, \quad (10)$$

$$b_2 = k'_e[\mathrm{HBr}] + b_1, \quad (11)$$

$$c_2 = k^{1\to 0}_{\mathrm{HBr-HBr}}[\mathrm{HBr}] + k^{1\to 0}_{\mathrm{HBr-M}}[\mathrm{M}], \quad (12)$$

where the brackets denote gas concentrations. It is extremely difficult to solve these simultaneous nonlinear differential equations. Their solution has been previously explained for the HCl($V = 2$) system. Following the same arguments as ref. [4], one finds

$$y = \{x_0^2/(0.65[\mathrm{HBr}] + 4x_0)\} \times \{1 - \exp[-0.65 k_e([\mathrm{HBr}] + 6.15 x_0)t]\}. \quad (13)$$

Since $x_0 < 0.05$ [HBr] and $y < x$ eq. (13) can be written as

$$y = \{1.55 x^2/[\mathrm{HBr}]\}\{1 - \exp(-0.65 k_e[\mathrm{HBr}]t)\}, \quad (14)$$

$$x = x_0 \exp\{-(k^{1\to 0}_{\mathrm{HBr-HBr}}[\mathrm{HBr}] + k^{1\to 0}_{\mathrm{HBr-M}}[\mathrm{M}])t\}. \quad (15)$$

Therefore, the solution for the time dependent differential equation for HBr($V = 2$) has the form

$$y = \{1.55 x_0^2/[\mathrm{HBr}]\}\{1 - \exp(-0.65 k_e[\mathrm{HBr}]t)\} \times \exp\{-2(k^{1\to 0}_{\mathrm{HBr-HBr}}[\mathrm{HBr}] + k^{1\to 0}_{\mathrm{HBr-M}}[\mathrm{M}])t\}. \quad (16)$$

Eq. (16) may overestimate the rate constant k_e by less than 20%.

4. Results

When HBr($V = 1$) molecules are produced in the mixture by absorption of a laser pulse, vibrational energy is rapidly exchanged between the HBr($V = 1$) molecules according to eq. (1). Since the backward reaction is 90 cm^{-1} exothermic, energy is shuffled from HBr($V = 1$) to the ($V = 2$) state until the final concentration relation

$$[\mathrm{HBr}(V=2)] = \{[\mathrm{HBr}(V=1)]^2/[\mathrm{HBr}(V=0)]\}(k'_e/k_e)$$

$$= 1.55\,[\mathrm{HBr}(V=1)]^2/[\mathrm{HBr}(V=0)] \quad (17)$$

is reached. After this rapid rise of HBr($V = 2$), the system is returned to equilibrium through various V → T,R relaxation processes [such as eq. (2) through eq. (5)]. A typical 2 → 1 fluorescence signal with 48.4 torr of a HBr/Ne mixture with mole fraction of HBr as 1.78×10^{-3} in the cell is shown in fig. 2. The fluorescence intensity increases initially, then decreases slowly to zero. The rapid rise can be interpreted by eq. (14). The slow decay is a simple exponential. The best values of the fast and slow relaxation times are given in table 1. The rate constant for transfer of a quantum from one HBr($V = 1$) molecule to another for populating the

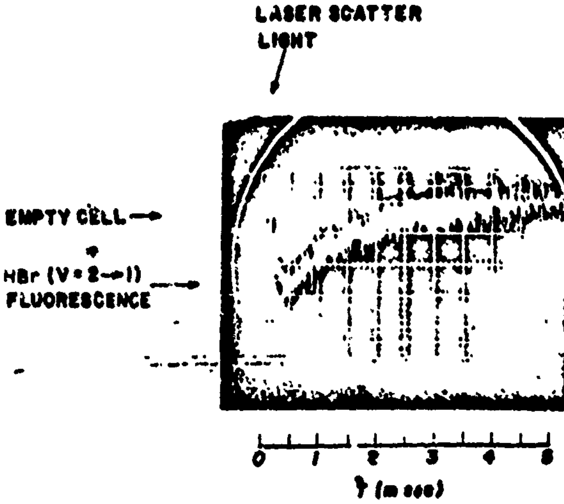

Fig. 2. $V = 2$ to $V = 1$ vibrational fluorescence from a HBr–Ne mixture. The rapid rise after the laser pulse is due to the V→V energy transfer process described in eq. (1) in text. The slow decay is mainly due to the deactivation of $V = 1$ state of the V→V energy-exchange-equilibrated system. The sample pressure is 48.4 torr with [HBr] = 1.78×10^{-3}, [Ne] = 0.9982 and $\tau_{\mathrm{rise}} = 1.0 \times 10^2$ µsec, $\tau_{\mathrm{decay}} = 1.1 \times 10^3$ µsec.

Table 1
Vibrational relaxation rates in HBr mixtures

M	X_{HBr}	X_M	$(P\tau_{rise})^{-1}$ (sec^{-1} $torr^{-1}$)	$(P\tau_{decay})^{-1}$ (sec^{-1} $torr^{-1}$)	k_e [a] (sec^{-1} $torr^{-1}$)
He	1.16×10^{-3}	0.9988	113 ± 20	17.3 ± 2.0	$(1.43 \pm 0.25) \times 10^5$
Ne	1.78×10^{-3}	0.9982	217 ± 30	18.3 ± 2.0	$(1.54 \pm 0.21) \times 10^5$
Kr	1.57×10^{-3}	0.9984	165 ± 30	4.1 ± 1.0	$(1.49 \pm 0.27) \times 10^5$

[a] Calculated by eq. (13) in text.

HBr($V=2$) state is $k_e = (1.47 \pm 0.30) \times 10^5$ sec^{-1} $torr^{-1}$ and the rate constant for endothermic energy transfer from the HBr($V=2$) state to form two HBr($V=1$) states is $k_e' = (0.95 \pm 0.19) \times 10^5$ sec^{-1} $torr^{-1}$.

Depopulation of the ($V=1$) state of the V→V energy-exchange-equilibrated system and depopulation of the $V=2$ state by V→T,R relaxation processes like eq. (4) and eq. (5) contribute to the slow decay of HBr($V=2 \rightarrow V=1$) fluorescence.

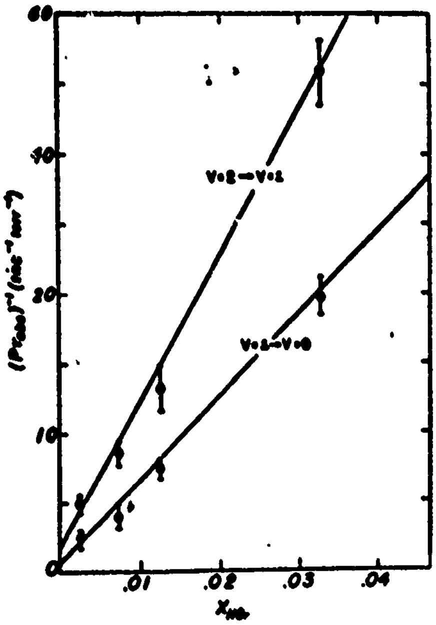

Fig. 3. Observed $V=2$ to $V=1$ and $V=1$ to $V=0$ vibrational fluorescence decay rates for HBr–Kr mixtures as a function of HBr mole fraction. Note that the slope and intercepts for 2→1 plot can be reproduced by doubling the 1→0 values. However, due to the possible impurities involved, the intercepts may only serve as the lower limits for $P\tau_{HBr-Kr}$ value.

The number of HBr($V=2$) molecules populated by this technique is a very small fraction of the $V=1$ state molecules so that one could approximate the relaxation of the HBr($V=2$) state as

$$[\mathrm{HBr}(V=2)] = \frac{1.55\,[\mathrm{HBr}(V=1)]_{t=0}^2}{[\mathrm{HBr}]} \times \exp\{-2(k_{\mathrm{HBr-HBr}}[\mathrm{HBr}] + k_{\mathrm{HBr-M}}[\mathrm{M}])t\}. \quad (18)$$

Direct comparison on semi log plots between 2→1 and the square of 1→0 signals, shows that the decay of 2→1 fluorescence is equal to that of the square of the 1→0 signals. In fig. 3 observed fluorescence decay rates for HBr–Kr mixtures are plotted as functions of HBr mole fractions. The intercept for the 2→1 plot is equal to twice that of the 1→0 plot. The same relations are found for both HBr–Ne and HBr–He mixtures. We therefore conclude that reactions one through five are the major processes involved in the decay of the HBr ($V=2$) state.

5. Discussion

Various theoretical approaches [5–8] have been developed to calculate the probability of V→V transfer between molecules. Two types of intermolecular forces contribute to the intermolecular potentials used in these predictions. They are (1) short range repulsive forces and (2) long range attractive forces. The short range SSH theory [5] predicts a probability of 6×10^{-3} for the process

$$\mathrm{HBr}(V=1) + \mathrm{HBr}(V=1) \rightarrow \mathrm{HBr}(V=2) + \mathrm{HBr}(V=0) + \Delta E = 90\ \mathrm{cm}^{-1}.$$

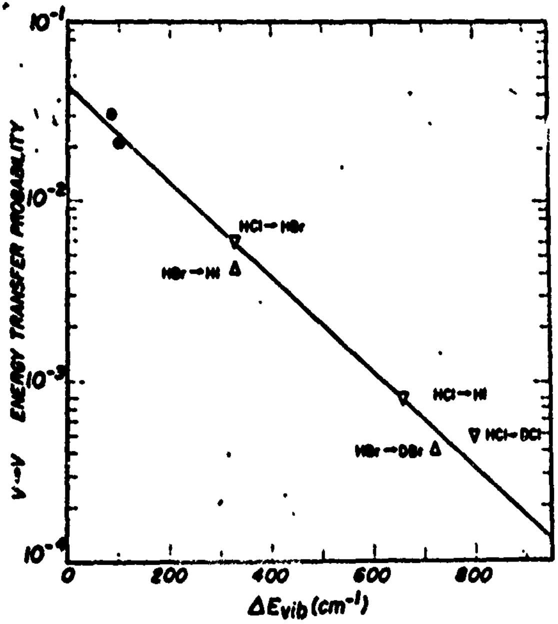

Fig. 4. Probability of V→V energy transfer between hydrogen halides versus energy discrepancy ΔE: ▿, data for process involving HCl; ▵, data for process involving HBr; ○, data for V→V energy exchange between HCl ($V = 1$) molecules and ●, data for V→V energy exchange between HBr($V = 1$) molecules. All are presented in the exothermic direction.

Another theory, that of Rapp and Englander-Golden [6], which assumes a purely repulsive intermolecular potential for near resonant V→V energy transfer between molecules in collision predicts a probability of 4×10^{-2} for the same process. An elaborate model for near resonant V→V energy transfer due to dipole–dipole long-range forces has been developed by Sharma and Brau [7], and Stephenson et al. [8]. This theory, in which the contribution from each individual rotational state of the colliding molecules is included and the averaged probability is computed by summing over the thermal rotational distribution, gives a probability which is too small in order of magnitude when compared to our experimental probability of $(3.1 \pm 0.6) \times 10^{-2}$. Fig. 4 shows a plot of log P versus ΔE for single quantum V→V energy exchange between hydrogen halide molecules which we have obtained previously [2, 3]. Extrapolation of this experimentally determined line to $\Delta E = 90\ \mathrm{cm}^{-1}$ gives a probability of 2.5×10^{-2} which is in reasonable agreement with our experimental results as are the calculations based on short range forces. Thus we conclude that the short range, multipole–multipole interactions, are dominant in this V→V energy exchange process.

6. Conclusion

This experiment has demonstrated the pumping of an upper vibrational state $V = 2$ of the HBr molecule by V→V energy exchange from a lower excited state $V = 1$. The decay of this V→V exchange equilibrated system was found to be dominated by the relaxation of the $V = 1$ state. The observations made are consistent with completed studies of the HF ($V = 2$) molecule [9] and of the HCl ($V = 2$) molecule [4]. The technique may still be applied to other systems such as DF, DCl, CO, NO, etc. A more complete understanding of the dominating interaction potential involved could be obtained by a temperature variation study of these rates.

Acknowledgement

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