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RICE UNIV HOUSTON TEX DEPT OF CHEMISTRY  
INVESTIGATION OF MULTIQUANTUM RELAXATION IN HCL.(U)  
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INVESTIGATION OF MULTIQUANTUM  
RELAXATION IN HCl

RICE UNIVERSITY, HOUSTON, TEXAS

1 OCTOBER 1976

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INVESTIGATION OF MULTIQUANTUM RELAXATION IN HCl

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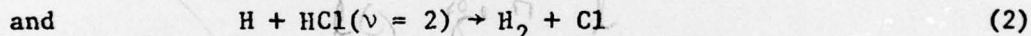
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Second Quarterly Report

During the past quarter progress has been made in three important areas: (1) the apparatus has been tested and calibrated, and several preliminary experiments have been performed, (2) various computations have displayed the degree of sensitivity of HCl( $v = 1$ ) and HCl( $v = 2$ ) to the mechanism of de-excitation, and (3) the reactions:



have been studied with some precision. In addition much useful information on the overall HCl( $v$ )/H system has been acquired through conversations with Dr. J. Wolfrum of the Max-Plank-Institut für Strömungsforschung, Göttingen.

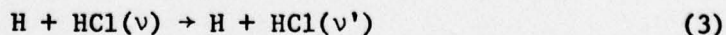
The optical and electronic layout of the apparatus in its final form is shown in Fig. 1. Chemiluminescence from the reactor passes through a sapphire window and is focused by a CaF<sub>2</sub> lens onto the entrance slit of a small fast monochromator. Radiation emerging from the exit of the monochromator is refocused onto a liquid N<sub>2</sub> cooled InSb PV detector. The signal from this detector, after amplification, is fed into a phase sensitive detector. The reference for this is obtained from the chopper wheel mounted immediately adjacent to the flow reactor. In some experiments, the monochromator is replaced by one of a set of interference filters chosen so as to isolate a single vibration-rotation band. The

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experimentally measured bandwidths (30% of maximum transmission) of the various filters are shown in Fig. 2. For comparison, the spectra of HCl is included on this figure. It is clear that filter 1 isolates the HCl(1 → 0) band, and that filter 3 isolates the HCl(3 → 2) band. In order to isolate HCl(2 → 1), filter 2 is used in conjunction with an HCl cold-cell that completely absorbs all radiation in the HCl(1 → 0) band. The apparatus described above has been used in a number of preliminary experiments. Unfortunately, wall deactivation of HCl(v) is proving to be a troublesome interference, and recent experiments have been directed towards finding wall coatings that are relatively inert to vibrationally excited HCl.

Computation has shown that HCl(v = 1) is particularly sensitive to the choice of de-excitation model. This is illustrated in Fig. 3. For this computation, (H)<sub>0</sub> was chosen as  $3 \times 10^{13} \text{ cm}^{-3}$ , and (Cl<sub>2</sub>)<sub>0</sub> as  $6 \times 10^{12} \text{ cm}^{-3}$ . The rate constant for the reaction,  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ , was assumed to be that measured by Niki *et al.*<sup>1</sup>; namely,  $3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , and the initial vibrational distribution of HCl was assumed to be that measured by Polanyi and coworkers<sup>2</sup>; namely  $f_0 : f_1 : f_2 : f_3 : f_4 = 0 : 0.28 : 1.00 : 0.92 : 0.08$ . Three different deactivation mechanisms were investigated:

- (a) a mechanism containing only single quantum transitions, that is, the reaction



occurred with  $v = v' \pm 1$ ;

*Letter on file*

- (b) a mechanism with all transitions ( $v \rightarrow v'$ ) occurring, and being equally probable; and
- (c) a mechanism containing only transitions to  $v' = 0$ .

The deactivation rate constants were chosen to conform with the measurements of Wolfrum and Arnoldi<sup>3</sup> for deactivation of  $\text{HCl}(v = 2)$  and  $\text{HCl}(v = 1)$ . The total rate of deactivation of  $\text{HCl}(v = 3)$  was assumed to be three times that for  $\text{HCl}(v = 1)$ . Wall deactivation was assumed to be slow. As can be seen from Fig. 3, the three different mechanisms are easily distinguishable if the concentration of  $\text{HCl}(v = 1)$  is measured.  $\text{HCl}(v = 2)$  is not so sensitive to the deactivation mechanism as can be seen from Fig. 4.

Reactions (1) and (2) were not included in the above computations because recent measurements in this laboratory have shown them to be of little importance in this system. These measurements were a continuation of those described in the first quarterly report. The method used was identical to that described in the previous report, except that measurements were made at higher pressures in order to reduce the possibility of wall de-excitation of  $\text{HCl}(v)$ . A careful analysis of our results showed that less than 15% of the total deactivation of  $\text{HCl}(v = 3)$  and  $\text{HCl}(v = 2)$  by atomic hydrogen occurred via reactions (1) and (2).

During the last three months, I have visited the laboratories of Dr. Jurgen Wolfrum at Göttingen, and have spoken to him further at the Combustion Symposium which was held August 21-25 at M.I.T. He has continued his studies of the  $\text{HCl}(v)/\text{H}$  system that were described in Chemical Physics Letters in 1974<sup>3</sup>, and has several new results that bear on the research performed under this contract. His main findings

are listed below:

(a) Activation Energy for  $\text{HCl}(\nu = 1) + \text{H} \rightarrow \text{HCl}(\nu = 0) + \text{H}$

For this reaction, he has measured the rate constant over the temperature range 220-400 K, as:

$$k = 1.32 \times 10^{-10} \exp(-1600 \text{ cal/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

This activation energy is a little higher than that obtained by Brown, Glass and Smith in their preliminary experiments.

(b) Rate constant for  $\text{HCl}(\nu = 2) + \text{H} \rightarrow \text{products}$

The rate of total deactivation was measured at 295 K as

$$k = (2.5 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

(c) The Exchange Reaction,  $\text{D} + \text{HCl}(\nu = 1) \rightarrow \text{DCl} + \text{H}$

Less than 10% of the total deactivation of  $\text{HCl}(\nu = 1)$  occurred via exchange. This finding is to be expected in view of the high barrier to exchange found by Endo and Glass.<sup>4</sup>

(c) The Reaction  $\text{H} + \text{HCl}(\nu = 1) \rightarrow \text{H}_2 + \text{Cl}$

The rate of this reaction was measured as less than  $1.33 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  at 295 K. Thus excitation of  $\text{HCl}$  to  $\nu = 1$  increases the rate of this reaction by less than a factor of 4.<sup>5</sup> This observation is consistent with that described earlier in the report; namely, that excitation of  $\text{HCl}$  to  $\nu = 2$  or  $\nu = 3$  does not greatly increase the rate of this reaction.

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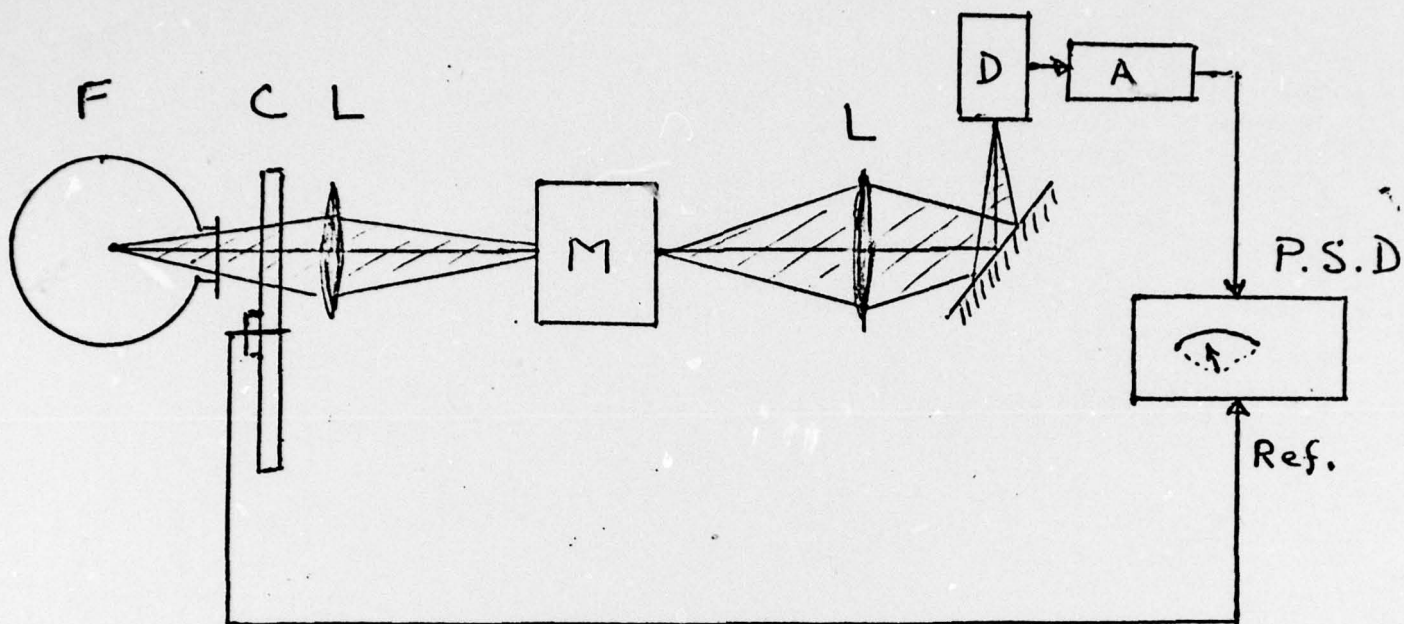
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FIGURE CAPTIONS

- Fig. 1: Diagram of apparatus.
- Fig. 2: Measured bandwidth of various interference filters as compared to the HCl emission spectra.
- Fig. 3: The concentration of HCl( $\nu = 1$ ) vs. reaction time computed using three different deactivation mechanisms. The abscissa is given as a fraction of  $(Cl_2)_0$ . For comparison purposes the HCl( $\nu = 3$ ) concentration, which is invariant to mechanism, is included.
- Fig. 4: The concentration of HCl( $\nu = 2$ ) vs. reaction time.

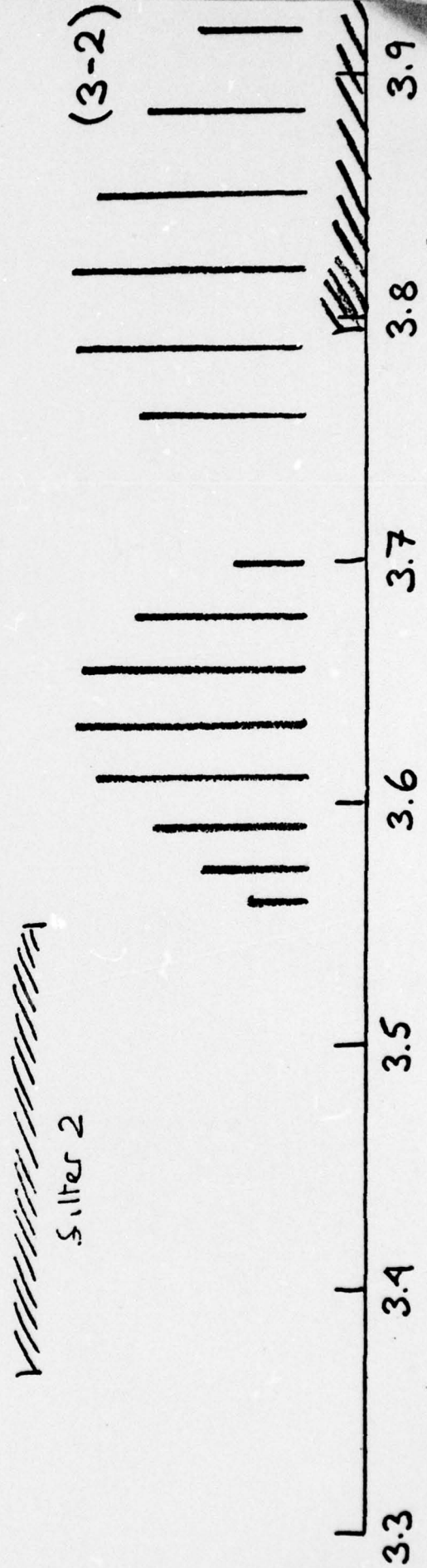
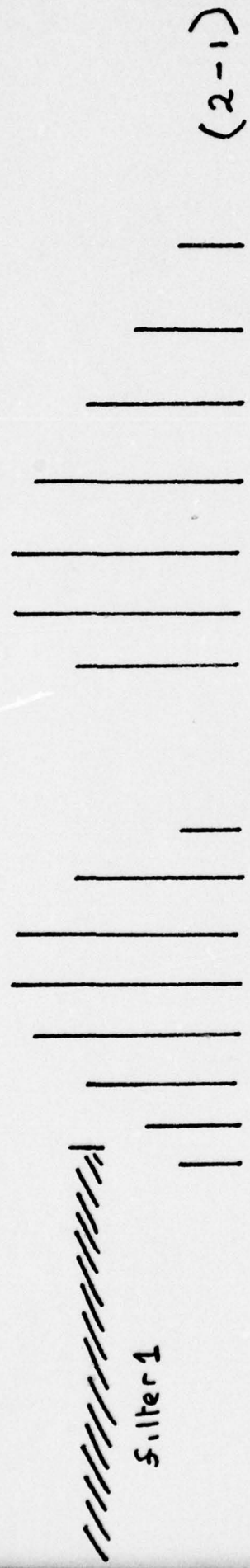
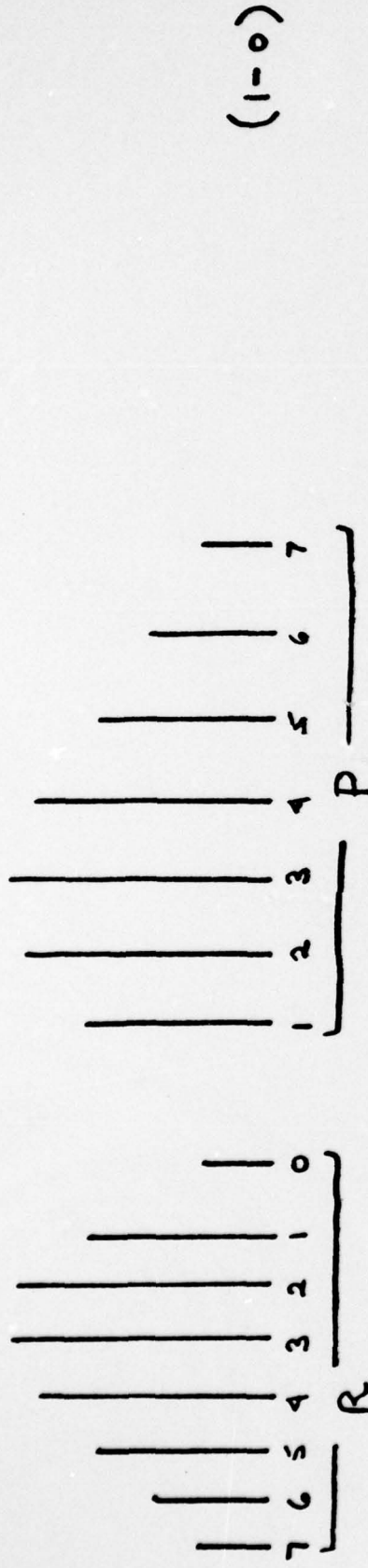
SCHEMATIC OF APPARATUS

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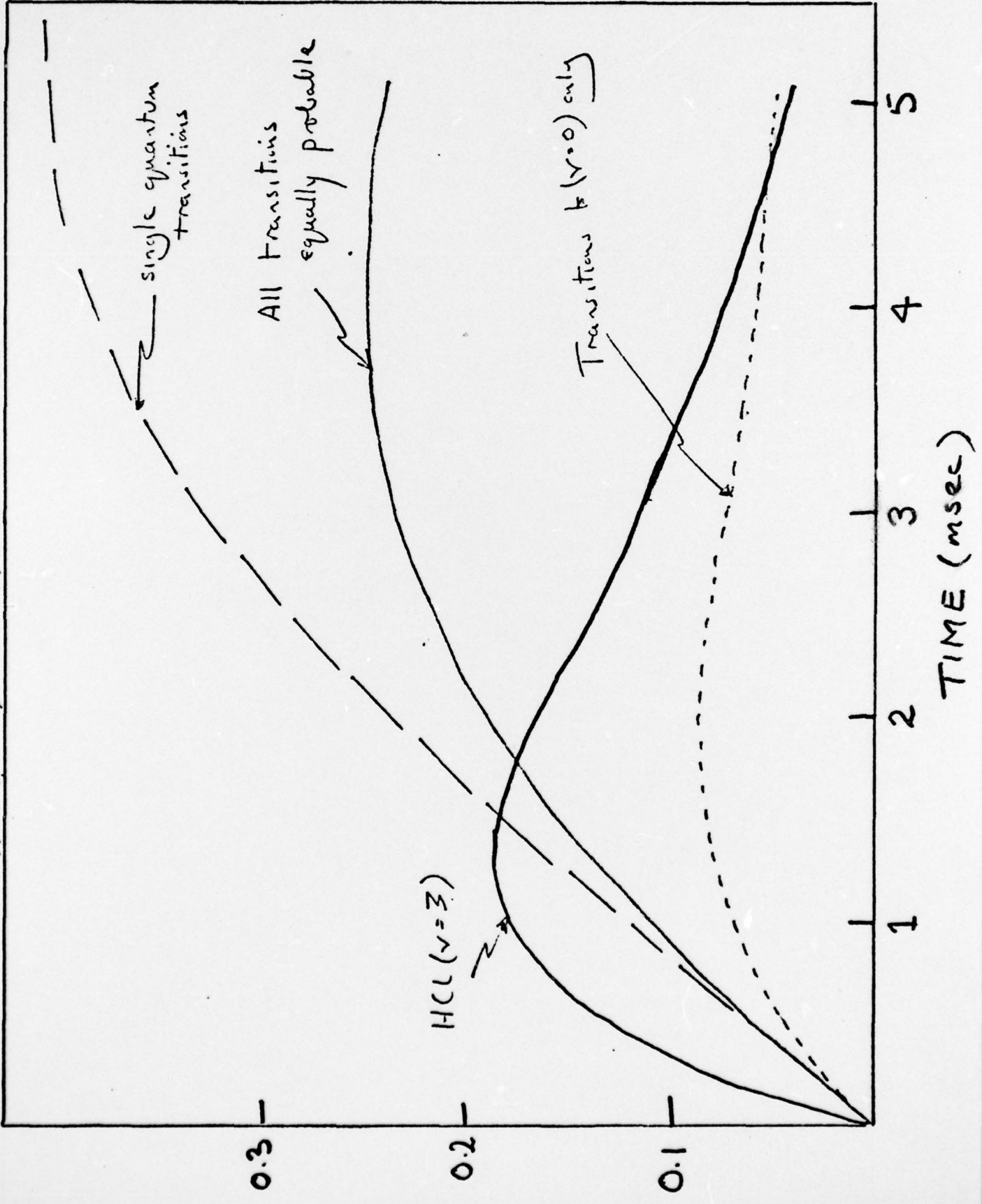


- F = Flowtube reactor
- C = Chopper wheel
- L = 1" dia, 50 mm F.L  $\text{CaF}_2$  lens
- M = f/3.7 Monochromator
- D = Indium Antimonide, PV, detector
- A = Amplifier
- P.S.D. = Phase Sensitive Detector

# HCl Spectra



HCl ( $v=1$ ) vs Reaction Time



HCl ( $v=2$ ) vs Reaction Time

