ACKNOWLEDGMENTS

I gratefully acknowledge the advice and support of Professor G. W. Robinson. The help and cooperation of Leon Keyser and Hanna Goldring are greatly appreciated.

I. SPECTROSCOPIC OBSERVATION OF DISCRETE SITES IN SIMPLE LIQUIDS

II. INFRARED INTENSITY PERTURBATIONS OF HYDROGEN HALIDE FUNDAMENTALS IN LIQUID XENON

III. ROTATION OF HCl IN SOLID RARE GASES

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1965

(submitted July 1964)

ABSTRACT

Part I

The spectrum of dissolved mercury atoms in simple liquids has been shown to be capable of revealing information concerning local structures in these liquids.

Part II

Infrared intensity perturbations in simple solutions have been shown to involve more detailed interaction than just dielectric polarization. No correlation has been found between frequency shifts and intensity enhancements.

Part III

Evidence for perturbed rotation of HCl in rare gas matrices has been found. The magnitude of the barrier to rotation is concluded to be of order of 30 cm^{-1}.

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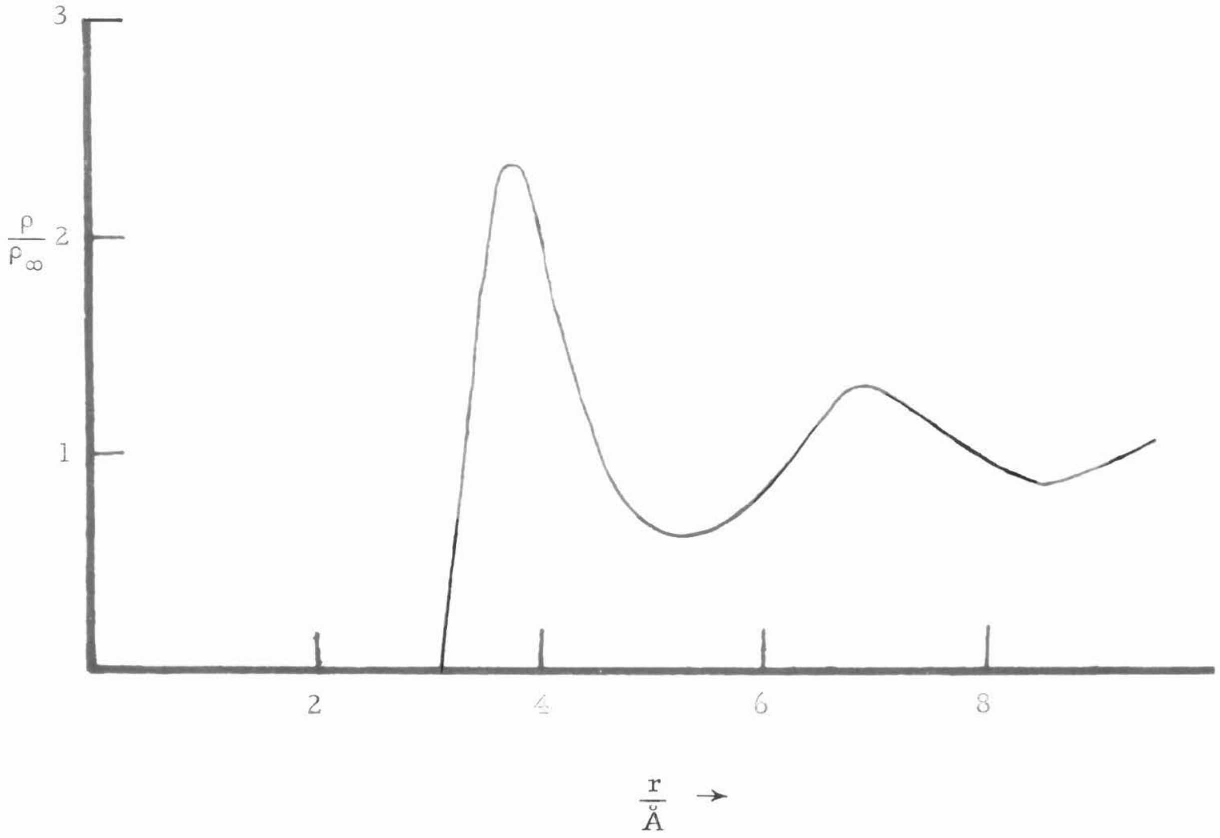
PART I

SPECTROSCOPIC OBSERVATION OF DISCRETE SITES IN SIMPLE LIQUIDS

Introduction and Background

It has been shown by X-ray diffraction(1, 2, 3) as well as by neutron scattering(4, 5, 6) that there exists, in simple liquids, short range order. This information is contained in the radial distribution function such as the one shown in Fig. 1. An important and relevant point to our work is that the characteristic distances in the radial distribution functions are very insensitive to density variations in the liquid.(7) Exact mathematical treatments of liquids reduce, in the limit, to a many body problem. They tend to become so complicated that little enlightenment about liquid state structure can be drawn. To simplify the problem various models have been proposed in order to provide tractable frameworks on which properties of liquids can be calculated. It must be understood immediately that such models are constructed with the evaluation of thermodynamic quantities in mind. These quantities and their measurements are time-averages and do not necessarily directly reflect on the instantaneous structures of liquids. In other words, it is conceivable that many models can give rise to equivalent time-averaged properties. It is not our purpose to evaluate the merits of these models as they relate to thermodynamic calculations. Our chief concern here is the microscopic or local structure in simple liquids. Through a better understanding of such details it is hoped that physically more realistic models may emerge.

TYPICAL RADIAL DISTRIBUTION FUNCTION



$\frac{\rho}{\rho_\infty}$ = ratio of density to overall density

$\frac{r}{\text{Å}}$ = radial distance in angstroms

Fig. 1

Even though the work here is not connected with many of the important aspects of liquid theories, it would facilitate later discussions if we examine very briefly the basic assumptions employed in the well known models. The cell theory,$^{(8)}$ or the theory of Lennard-Jones and Devonshire, divides the liquid volume into identical cells, one for each molecule. The molecules are regarded as moving independently in their cells. It can be seen that this model resembles Einstein's model of the solid state. Actual calculations do give results that agree with the solid data better than liquid data. A typical result of such a calculation is shown in Table I. The tunnel model$^{(8)}$ allows for disorder by regarding the motion of the molecules as beads-on-wire type behavior. This gives better results than the cell theory. There are two types of random hole theories which have been considered. Fundamentally, hole theories suppose the existence of vacancies in the liquid structure. One type$^{(8)}$ does not actually treat the presence of the vacancies as a source of discontinuity, but averages the different environments. This approach is in no better agreement with experiment than the previous models were. The second approach, due to Eyring,$^{(9,10)}$ recognizes the discontinuities in density due to holes which lead to distinctly different potentials in the liquid structure. Eyring considers the existence of two types of environments in the liquid, a solid-like site and a gas-like site. The gas-like property is visualized as originating from the jumping of molecules into the available holes. Those molecules that are not undergoing this process are considered solid-like. For simple

TABLE I[*]

Comparison of Calculated Quantities
with Experimental Results

	Reduced volume V/V_0	Reduced excess energy E'/N_ϵ	Reduced excess entropy S'/Nk	Reduced excess heat capacity C_ν'/Nk
L-J-D or cell theory	1.037	-7.32	-5.51	1.11
Solid argon	1.035	-7.14	-5.33	1.41
Liquid argon	1.186	-5.96	-3.64	0.85

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[*] Reference 8.

liquids, the volume expansion upon melting is usually about 15%. It is therefore assumed that there is this fraction of vacant sites in the liquid structure, giving rise to an equivalent number of gas-like molecules. The calculations are based on a partition function factored into a solid part and a gas part. Results show definite improvements over the previous models. The hole theories possess the significant property that the characteristic distances in the liquid structure are not very sensitive to density variations, in agreement with experiment.

The idea of solid-like sites in liquids is not difficult to accept in view of the slight density changes upon melting. On the other hand, the existence of gas-like molecules in liquids is debatable. As we mentioned before, thermodynamic agreement is not a sufficient condition for deducing the microscopic and instantaneous environments. Therefore, to gain such information, we need a more direct and instantaneous detection scheme.

Detection System

The measuring scheme should satisfy two important requirements. It must be sensitive to local environments such as variation in density, and it must be rapid compared to the rate of change due to local fluctuations. An additional feature, which is rather obvious, is that the scheme must not alter significantly the basic nature of the system under investigation.

We choose our experimental systems to be mercury atoms dissolved in simple liquids: cyclohexane, carbon dioxide, and xenon. The "sensing element" is the 2537 Å resonance absorption spectrum of atomic mercury. This transition has been found to be affected to a measurable degree by the environment of the absorbing atoms.(11) Furthermore, the frequencies of electronic transitions are typically many orders of magnitude faster than diffusion rates in liquids.(12) The spherical nature of the mercury atoms and the inertness of the solvents used should bring about minimal distortions in these liquids. All of these properties seem to indicate that our systems should satisfy the basic requirements already mentioned.

Experimental

In order to withstand the high pressures in some of the experiments, a stainless steel cell was designed and constructed, as shown in Fig. 2. Sapphire windows were preferred over quartz because of transmission and tensil strength.* Teflon gaskets sandwiched the windows. Lead gaskets could not be used due to amalgamation. A torque wrench was used to tighten the flange screws. A drop of triply distilled mercury was placed in the cell before it was closed. It was then evacuated down to the level of the room-temperature mercury vapor pressure (2 μ). The side arm of the cell was then cooled, usually by liquid nitrogen. This enabled the solvent to be distilled into the cell from the glass system at low pressures. After sufficient solvent has been transferred, the high pressure valve to the cell was closed. The cell could now be disconnected from the glass system.

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*Quartz windows of slightly larger diameter than the sapphire windows used failed roughly at 1500 lb./sq. in. air pressure.

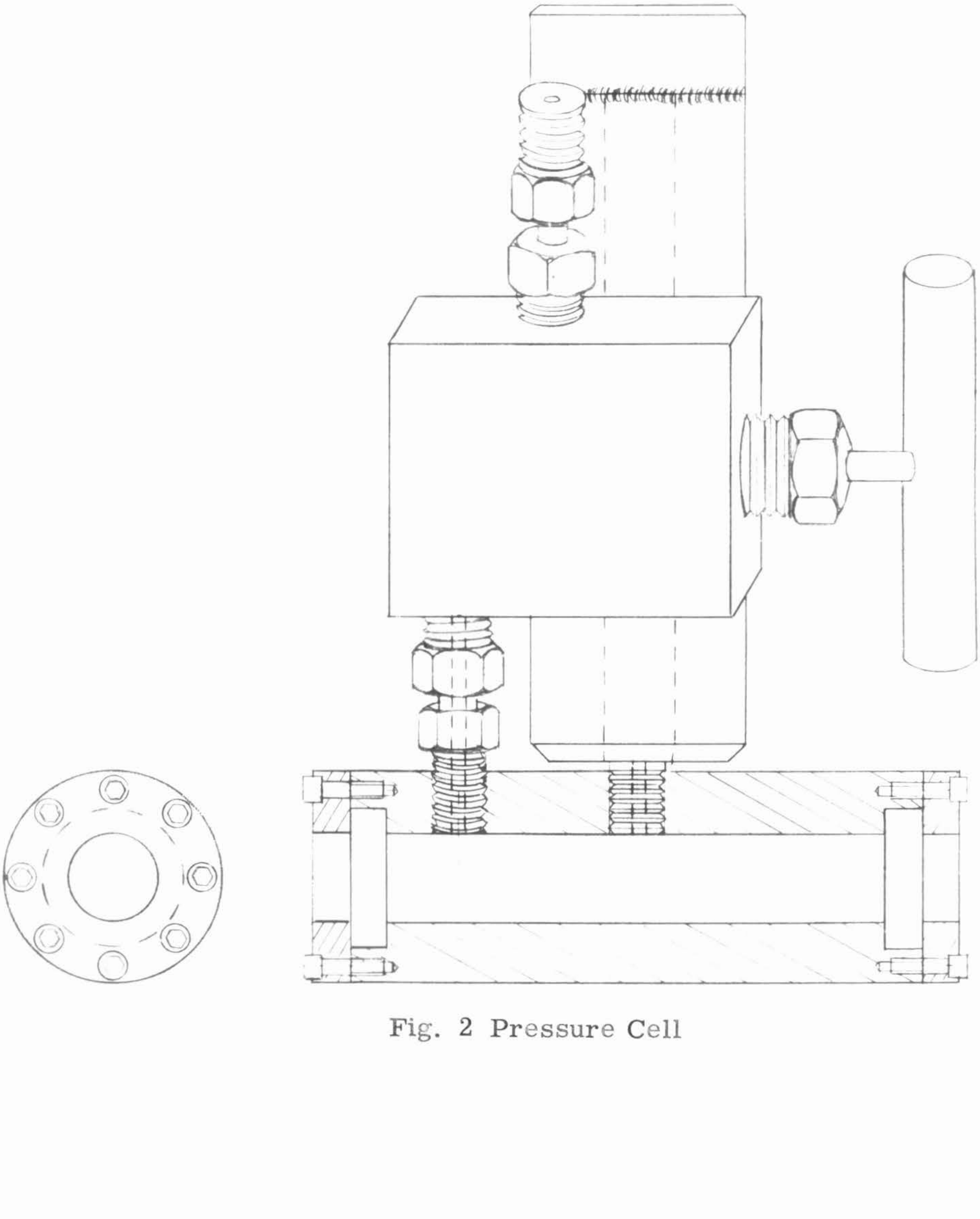


Fig. 2 Pressure Cell

Sufficient time was allowed for the liquefaction and mixing within the cell. The spectra were taken at or close to room temperature on a Cary 14 spectrophotometer. Resolution was not critical due to the broadness of the absorptions. Wave length accuracy was about ± 3 Å. The cyclohexane was spectral grade from the Matheson Co. The carbon dioxide was Coleman grade (99.99%) also from the Matheson Co. The xenon was MSC grade obtained from Linde.

Results and Discussion

The spectra are shown in Figs. 3, 4, and 5. The system neopentane-mercury has previously been investigated by Wright and Robinson.(13) Our work is an extension of this. Before we can analyze these spectra, we must assure ourselves that they belong to mercury atoms dispersed among solvent molecules, because absorption due to aggregates of mercury atoms would make interpretation difficult. The low mol ratio of mercury atoms (less than 10^{-6}) presents a good case for the improbability of mercury clusters. Since the distribution of the mercury atoms depends on the ground states of both Xe and Hg, there is no resonance stabilization of otherwise preferred distributions, such as Hg Hg^*. If there are varying amounts of significant aggregate formation by the mercury in the different liquids, the spectra should reflect this variation. The similarity among the spectra suggests the contrary. We shall assume that interaction among the mercury atoms plays an insignificant role in our systems.

Well resolved doublets can be seen in all three spectra. Since these are instantaneous, space-averaged representations of the

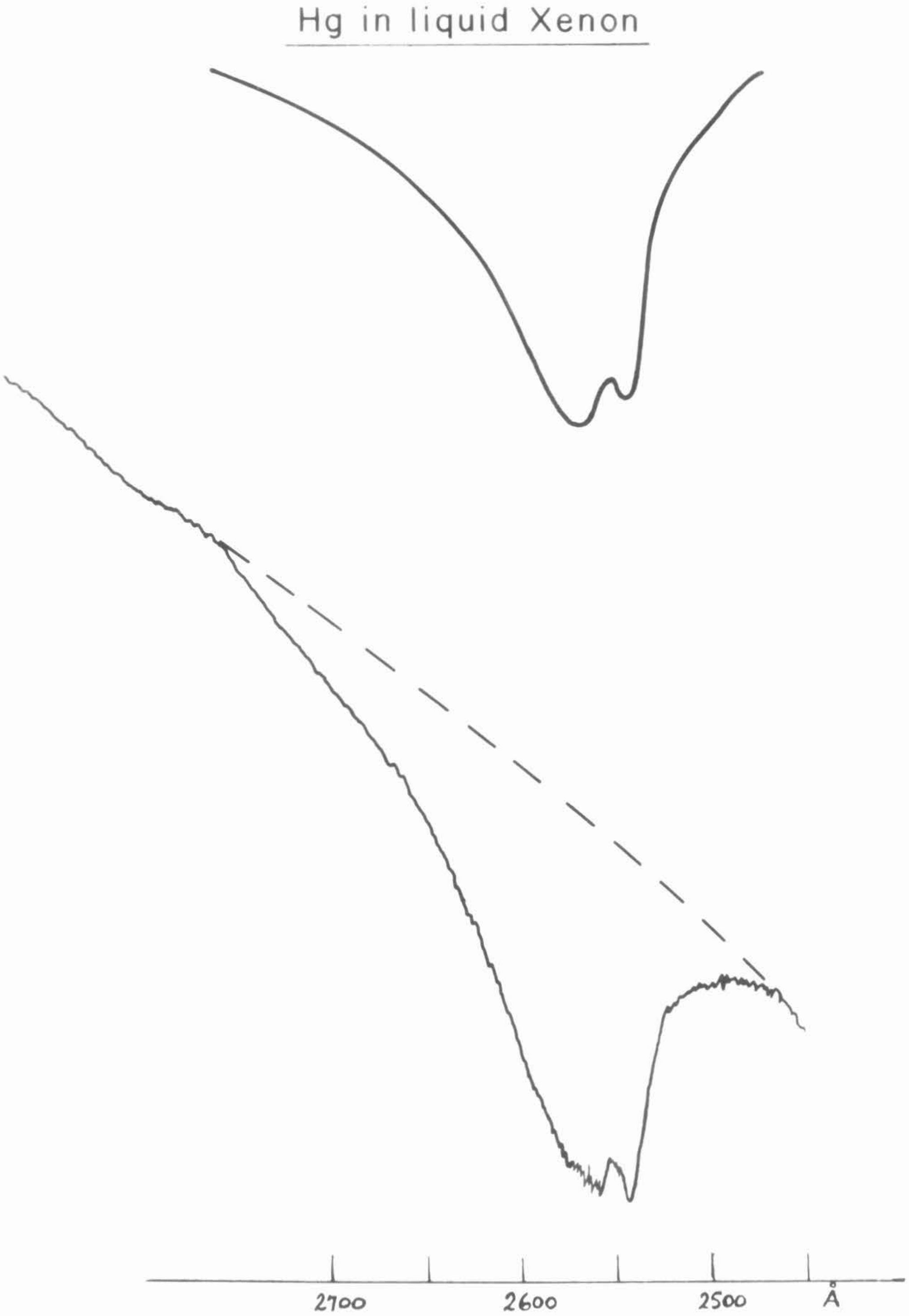
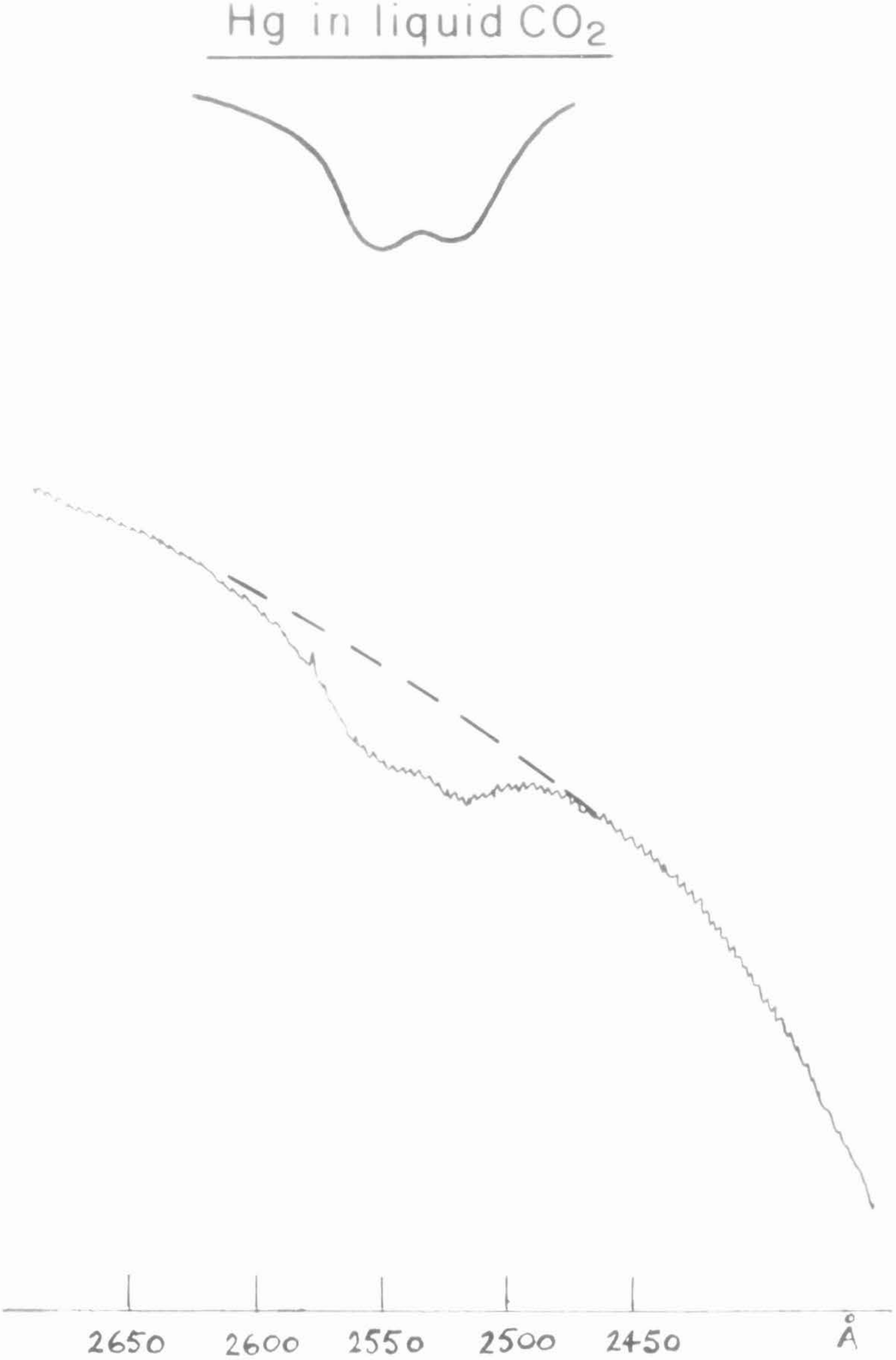


Fig. 3



Hg in liquid CO_2

Fig. 4

Hg in liquid Cyclohexane

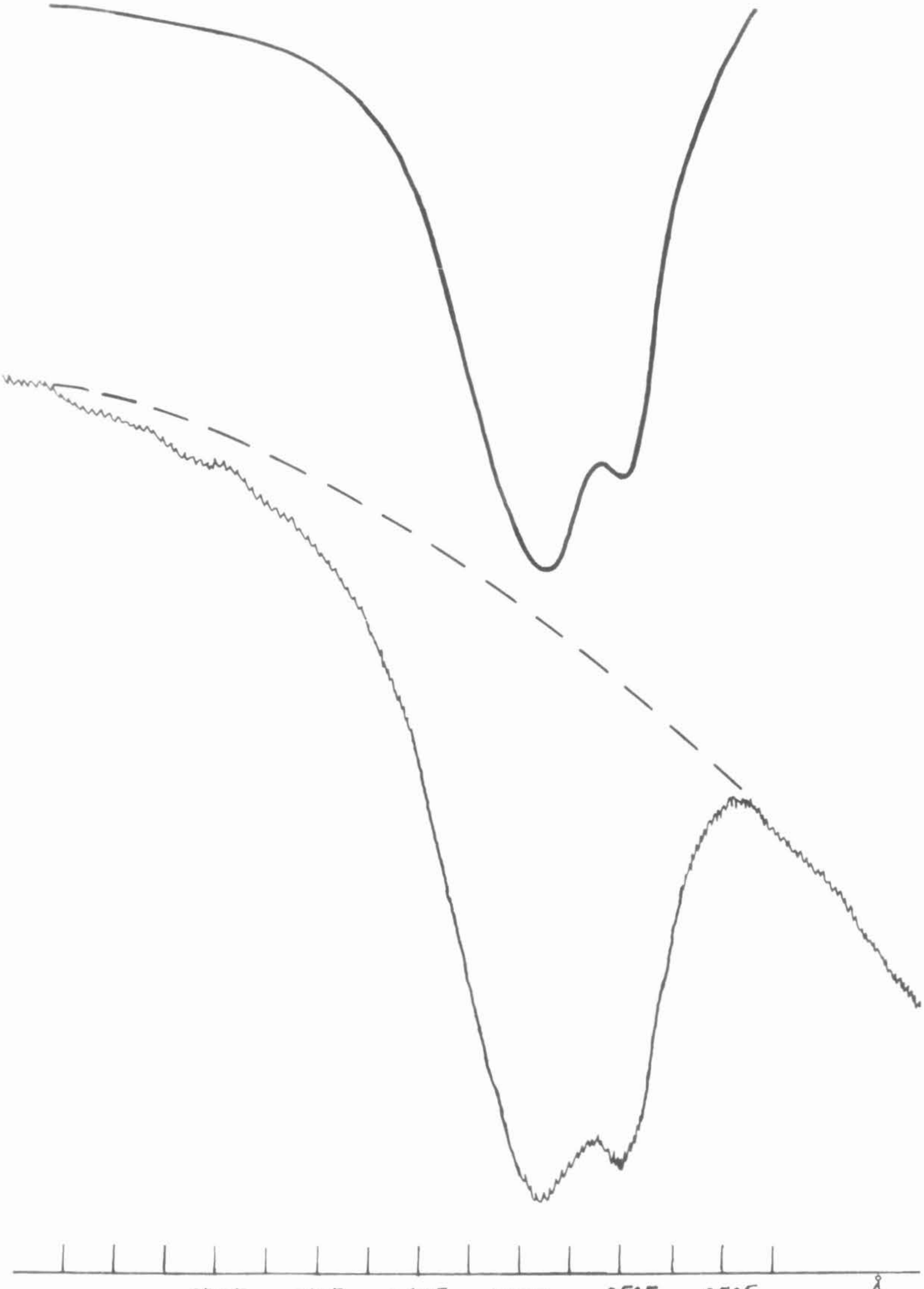


Fig. 5

microscopic nature of the systems, we conclude that there are two overall distinct average environments in these simple liquids. Because of the similarity of the spectra, we limit ourselves to the discussion of the mercury-xenon case. More is known about this system and it seems likely that any general conclusions reached will also apply to the others. Furthermore, the simplicity of this system makes it a prototype. The data are summarized in Table II.

The spectrum of mercury atoms in solid xenon(11) shows that there is some repulsive interaction, at least in the upper state of the transition. This gives rise to a 50 cm^{-1} blue shift in the absorption. This solid spectrum coincides reasonably well with the high frequency component of the doublet in the liquid spectrum. A similar correspondence has been observed in the mercury-argon system,(14) between the highly compressed gas and the solid. This behavior suggests very strongly that a solid-like site exists in the liquid. Due to the extreme sensitivity of repulsive interactions with distance and to the number of nearest neighbors, slight distortions or changes in structure surrounding the mercury atom will produce large changes in potential, leading to different absorption frequencies. This is the proposed origin of the second component in the doublet. An idea somewhat parallel to this has been offered by Michels et al.,(14) based on the experimental work on the Hg/Kr system.(15) There, the essentially doublet spectrum of mercury pressurized by gaseous Krypton at 66.9°C is analyzed in terms of molecular formation between Hg and Kr. Our description may be thought of as an exaggerated case of two

TABLE II

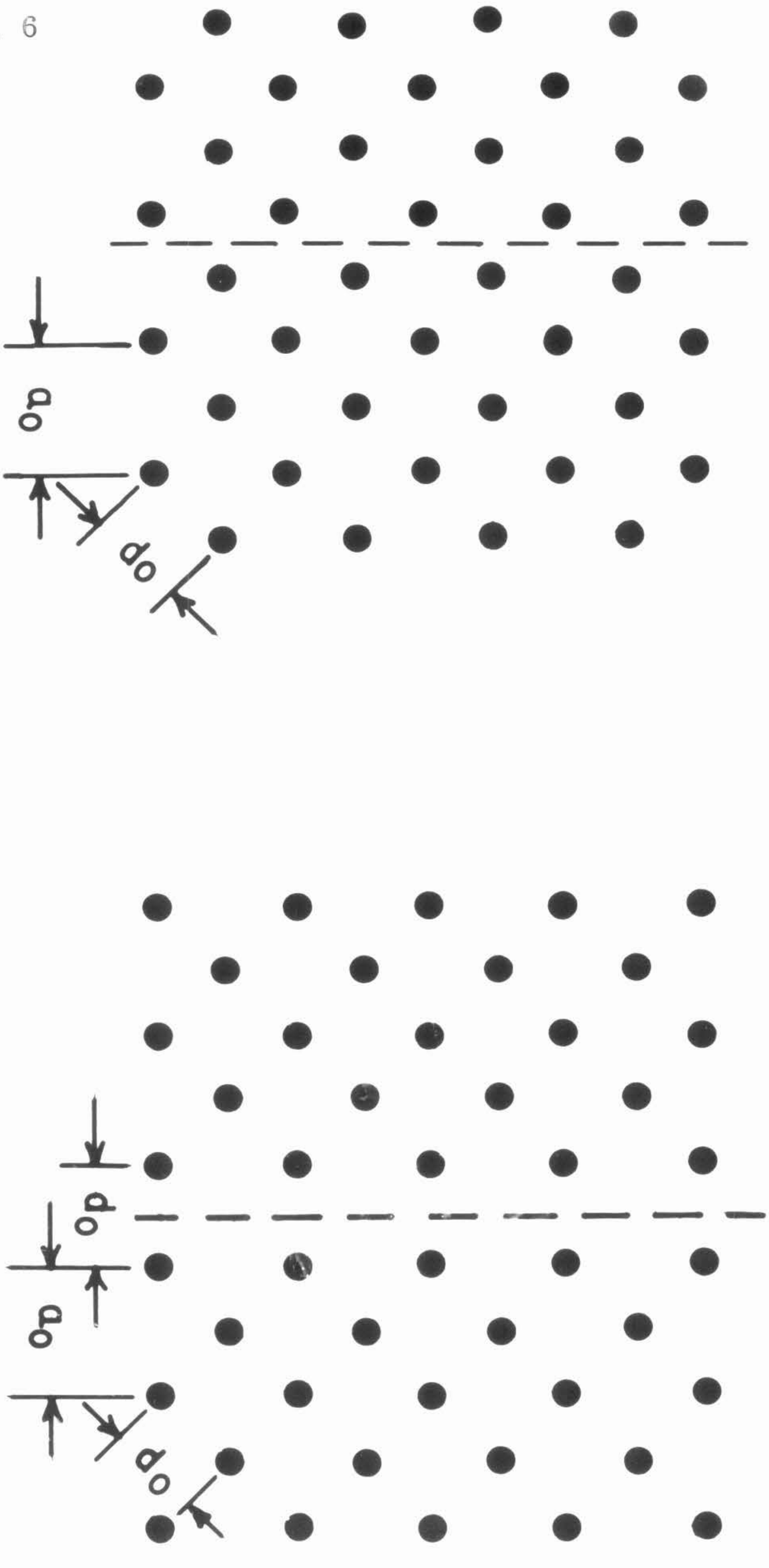
	Peak 1	Peak 2	Approx. Half Width
Xe	2544 Å	2568 Å	1600 cm^{-1}
CO_2	2512 Å	2550 Å	1200 cm^{-1}
Cyclohexane	2545 Å	2575 Å	1300 cm^{-1}

types of molecular species, $HgXe_{12}$ and $HgXe_n$ where $n < 12$. That is, the mercury atoms together with their nearest neighbors are viewed as molecular complexes.

It is possible on the basis of linewidths to make certain crude statements concerning the nature of the "defects" in these liquids. We shall adopt the language of the hole theories for our discussion. If the distribution of holes is really random and if the holes are of molecular size, as suggested by Eyring, practically all of the sites in the liquid will be next to a hole of some sort, single, double, etc. According to our previous arguments, this state of affairs would produce one quasi-continuous absorption, reflecting the numerous possible distributions of holes. Our spectra in view of the double peak character contradict this point of view. Furthermore, it is immediately apparent that a gas-like site does not exist in these liquids due to the absence of any gas-like absorption. The gas-like molecule is therefore more of a mathematical convenience than a physical reality.

As we mentioned before, the hole theories do possess the important property that they correctly refute the idea of uniform expansion of a material on melting. However, we have just pointed out some of the physical drawbacks in the random hole picture, such as the prediction of practically 100% next to hole sites, in disagreement with our experiments. To preserve the idea of discontinuity and to improve on the physical aspects of liquid models, Robinson(17) proposed a two site model consisting of a solid-like site and a surface-like site. Although detailed calculations are still lacking, this model gives a much better account of our experiments. The basic assumption is the formation of clusters separated by interfaces which are the equivalents of holes. In other words, the holes are now ordered. Of course, it is recognized that fluctuations and diffusion are present, but the fraction of time occupied by the transitory configurations is assumed negligible. For simplicity, cubic clusters are assumed. For a given lattice geometry, the size of the clusters determines the fractions of molecules on interior sites and on exterior or surface-like sites. The size of the clusters and the separation between them are shown to be related to the change of molar volume on fusion and the ratio of the enthalpy of fusion to the enthalpy of sublimation. Assuming the additivity of nearest neighbor interactions, the average size of the clusters can be calculated. The average number of nearest neighbors in the liquid is also obtained, which agrees quite well with experiment for several substances: neon, argon, krypton, xenon, and methane. An interesting point that follows from these calculations is that the separation between clusters is very close to the nearest neighbor distance in the solid lattice. This is illustrated in Fig. 6 which is taken from reference 15. Perhaps the most pertinent point about this model relative to the present experimental findings is that there are essentially two distinct sites in the liquid. From Robinson's estimates, it appears that both sites play a significant part in determining the properties of the liquid, the two sites occurring at approximately equal numbers at densities near those at the triple point. The areas under the two components of the doublets seem to support

Fig. 6



a. SOLID

b. LIQUID

this conclusion, provided there are no factors affecting the distribution of the dissolved mercury atoms and their radiative transition probabilities.

A further point of interest is suggested by this model. That is, the transformation from the solid state to the critical state corresponds approximately to a change from face centered cubic structure to a simple cubic one, keeping the nearest neighbor distance the same. The density ratio of these two regions seems to agree with that of the two structures.

Conclusion

From an instantaneous sampling of local environments in simple liquids, we have arrived at the conclusion that two average types of sites exist in simple liquids. Their numbers are approximately equal at triple point densities. From the observation that no feature of our spectra resembles that of a free mercury atom, we can also say that the gas-like description of the non-solid-like sites is without physical basis. We suggest that a surface-like description may be more profitable. A serious difficulty still remains in the determination of a suitable potential for the surface-like site. Until such a task is accomplished and the problems of entropy and correlated motion are treated, we cannot really discuss the subject with completeness.

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PART II

Paper to be submitted by
J. Kwok, H. Goldring, and G. W. Robinson

INFRARED INTENSITY PERTURBATIONS OF HYDROGEN HALIDE FUNDAMENTALS IN LIQUID XENON

Introduction

This work deals with the study of molecular motions of hydrogen halides in a simple solvent, liquid xenon. Since structure in the vibration-rotation band of HCl in liquid xenon has been observed previously,(1) the main object of the present work is to measure the absolute intensities of these systems as well as to determine the band structures of HBr and HI in liquid xenon. Xenon was chosen as a solvent because it is relatively simple but has a high polarizability. Because of this, large effects can be observed without introducing concomitant complications. Furthermore the normal liquid range of xenon occurs at a temperature where hydrogen halide vapor pressures are not too low. Thus there is adequate solubility for spectroscopic investigations.

Existing theories(2, 3) of intensity perturbations on infrared spectra predict intensity enhancements of the order of 20% over the free molecule value. These theories, which are based on Debye's and Onsager's work on dielectric polarization, do not take into account possible perturbations of the active molecule itself. Only the change in electric field intensity is considered in these works. It is well known, however, that when specific interactions occur, intensity enhancements of greater orders of magnitude are found.(4) These effects must be attributed to changes in the active molecules themselves.

Experimental

The Spectrometer. The spectra were taken on a Beckman IR-7 spectrophotometer in single beam. Scattered light was about 1%. In the HI experiment the monochromator was flushed with dry nitrogen to minimize carbon dioxide interference. The spectral slit width was about 2 cm^{-1}. The spectrometer has an automatic slit program which varies the slit width while scanning and is designed so that the amount of light transmitted in the absence of absorption, i.e. the baseline, remains constant. The program however was not perfect, giving a somewhat uneven baseline.

The Cold Cell. The cold cell used was essentially the same as that described previously.(1) An important requirement in our work (and perhaps a convenience generally) is that the cold cell be portable since the spectrometer was situated in another building. Also the cell had to fit into the 5 inch wide sample space of the IR-7, a fact which imposes further restrictions on its design.

An important feature added to the original cell design is a resistor heater wound around the "neck" of the cell.(5) The heating coil consists of ten feet of 25 Ω/ft nichrome wire wrapped directly around the brass cell neck. Electrical insulation between the neck and the wire is maintained by a thin coating of glyptal varnish baked on at 100°C. The nichrome wire is held in place by an additional application of glyptal varnish. The purpose of the heater is to maintain better temperature control of the cell by "bucking" the cooling effect of the heat leak to the liquid nitrogen reservoir. It also serves to invert the cell's normal thermal gradient which is cool on top and warm on the bottom because of the location of the liquid nitrogen cooling reservoir. The inverted thermal gradient prevents bubbling and Schlieren patterns which sometimes cause a high amplitude "noise" when scanning. Roughly 15 V applied from a battery across the heating coil is sufficient in the present cell to keep the temperature about 2°C above the normal xenon boiling point for long periods of time.

Another modification of the cell is the addition of glass side arms of varying volumes connected to the inlet of the cell. The side arm helps in transferring gas mixtures into the cell, and by varying its volume one can tell whether or not any significant fraction of the solute remains as undissolved gas, outside the light path.

Sapphire windows which, because of their hardness are easy to use with pressed indium gaskets, were employed primarily. However, barium fluoride windows, which have better transmission properties in the region of the HI absorption, were used for some of the later HI experiments. Preliminary HI experiments were carried out with a germanium filter inserted between the globar light source of the spectrometer and the cell. The purpose of this was to prevent HI photolysis since the filter has negligible transmission in the visible and ultraviolet but transmits about 30% of the radiation in the region of interest. Subsequently, however, the filter was omitted in order to get stronger signals. The HI in liquid xenon did not undergo detectable photolysis at least for the duration of measurement (2 hours).

Intensity Measurements. The absolute integrated intensity was measured by the Wilson-Wells extrapolation technique.(6) Essentially this means pressurizing the absorbing gas by some inert gas in order to broaden the rotational structure, a requirement which is automatically taken care of in the present experiments. The experimental "band strength" $S_{nn'}$ (which is usually defined, and is so in this paper, as integrated absorption divided by the pressure) for vibrational transition n ↔ n' is found by evaluating the expression,

$$\lim_{p\ell \to 0} \frac{1}{p\ell} \int \ell n \frac{I^{o}_{\nu_{nn'}}}{I_{\nu_{nn'}}} \, d\nu_{nn'} , \qquad (1)$$

where p is the partial pressure of the absorbing gas, ℓ is the path length, fixed in our experiments, and $I_{\nu_{nn'}}$, is the transmitted intensity at the wave number $\nu_{nn'}$ when the incident intensity is $I^{o}_{\nu_{nn'}}$. The integration is carried out over the vibrational band under study. In this paper we choose p in atm (at 300°K), ℓ in cm, and $\nu_{nn'}$ in cm^{-1}, units which facilitate comparison with other measurements. Thus $S_{nn'}$ has units of $cm^{-2}\ atm^{-1}$.

The lowest practical mole ratios for observation of the spectra were found to be of the order:

HCl/Xe: 2×10^{-4}; HBr/Xe: 5×10^{-4}; HI/Xe: 5×10^{-3}.

Many experiments were carried out at these and higher concentrations and it was found that the area under the optical density curve was proportional to the concentration of hydrogen halide molecules. This fact gives assurance that none of the solute was in solid form in the cell. It also pertains to the question of the state of aggregation of the halides in liquid xenon, a point which will be discussed more fully below.

Experimental Difficulties, Sources and Limits of Error

There are quite a few difficulties, not apparent at first glance, involved in carrying out these measurements. Hydrogen halide molecules are adsorbed on the surface of the metal cell, a fact which introduces uncertainty in the concentration. To minimize this effect, gas mixing was carried out in an all glass system using a calibrated 0-800 mm Wallace and Tiernen pressure gauge in conjunction with a set of calibrated bulbs for the concentration determinations. In the case of HI the mixing was carried out in the dark. The gaseous mixture was then quickly solidified in the glass side arm next to the cell. It was stored there until spectra were to be taken at which time the mixture was rapidly liquified in the cold cell. By changing the volume of the glass side arm, as indicated in the Experimental section, it was found that the ratio of the concentration of the hydrogen halides in the gas phase to that in solution was negligibly small, a fact further confirmed by the observed proportionality of integrated absorption and total solute in the mixture. The concentration values which were used in calculating the absolute integrated intensity from the data were therefore based on the total amount of hydrogen halide gas initially in the gaseous mixture. Effects of adsorption on the walls and incomplete solubility would cause these concentration values to be higher, if anything, than the true concentration. This in turn would mean that the values quoted for the band strength are on the low side. If such errors were indeed present, the true intensity enhancements would be even greater than those reported here.

Another source of error lies, of course, in the determination of the base line. This was particularly troublesome in the case of HI where atmospheric CO_2 interference was prominent because the instrument used is not easily flushed. Moreover, as mentioned earlier, the slit program which is supposed to give constant transmission at all wave lengths does not actually do so. Altogether it seems fair to estimate an error of ±20% for the HCl and HBr measurements. In the case of HI, however, the error is probably of the order of ±30%. These measurements will therefore be repeated under better experimental conditions if and when a more useful spectrometer is available to us. In any case the limits of error are not so large that they basically alter the discussion which follows.

Results

Frequency Measurements. The spectra of HCl, HBr, and HI in liquid xenon at 165°K are shown in Figs. 1, 2, and 3. All three hydrogen halides show well defined rotational envelopes. Table I summarizes the frequency measurements. The appearance of a Q-branch is confirmed by Vu and Vodar(7) in their investigation of the shape of the fundamental absorption band of HCl in liquid and highly pressurized N_2, O_2, and Ar. As pointed out by Kwok and Robinson,(1) the fact that the separation between the rotational envelopes is higher than that expected for P–R separation can probably be attributed to the superposition of induced S and O branches which are not resolvable from the P and R branches.

Fig. 1 HCl in LIQUID XENON, 165°K

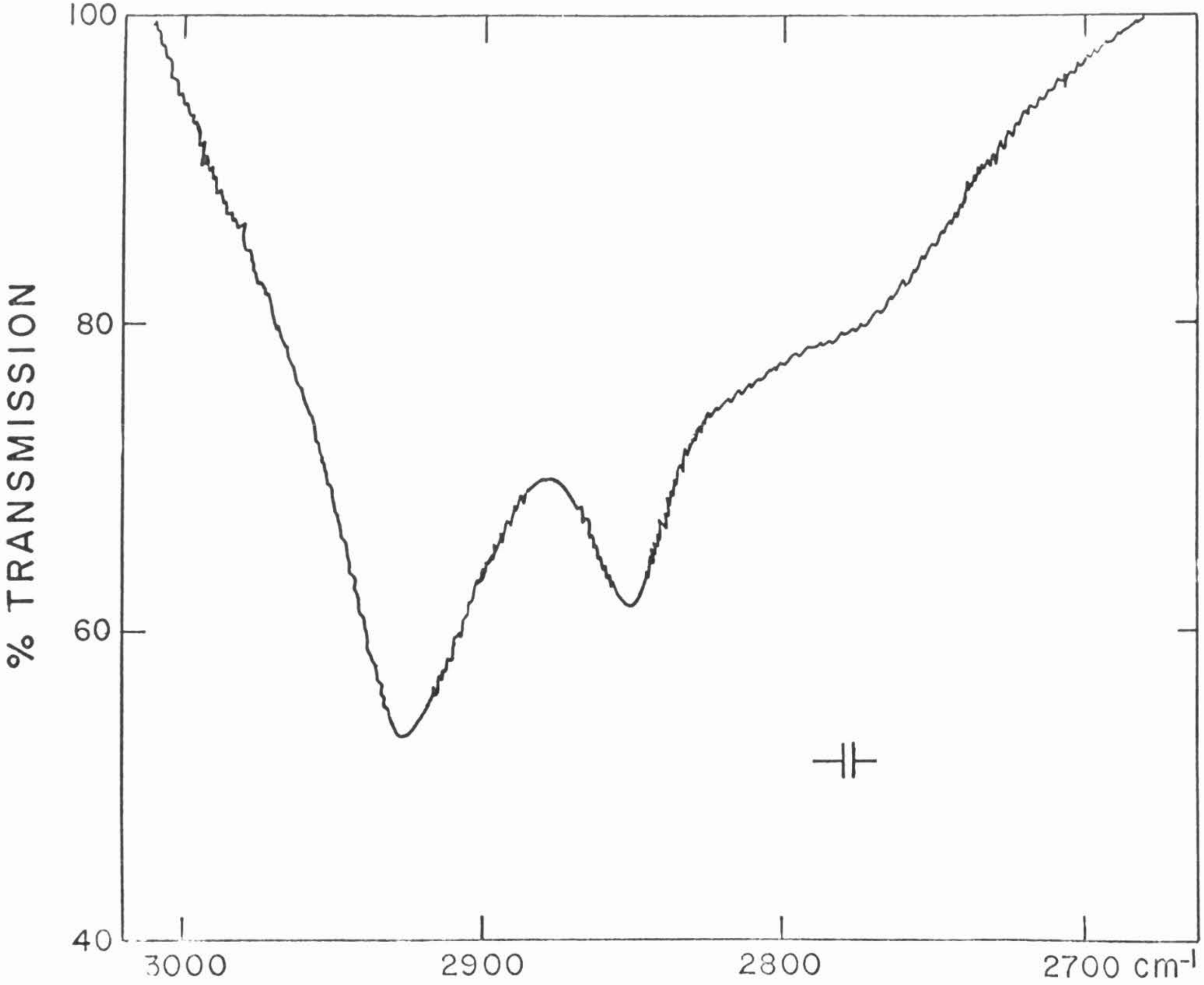

Fig. 2 HBr in LIQUID XENON, 165°K

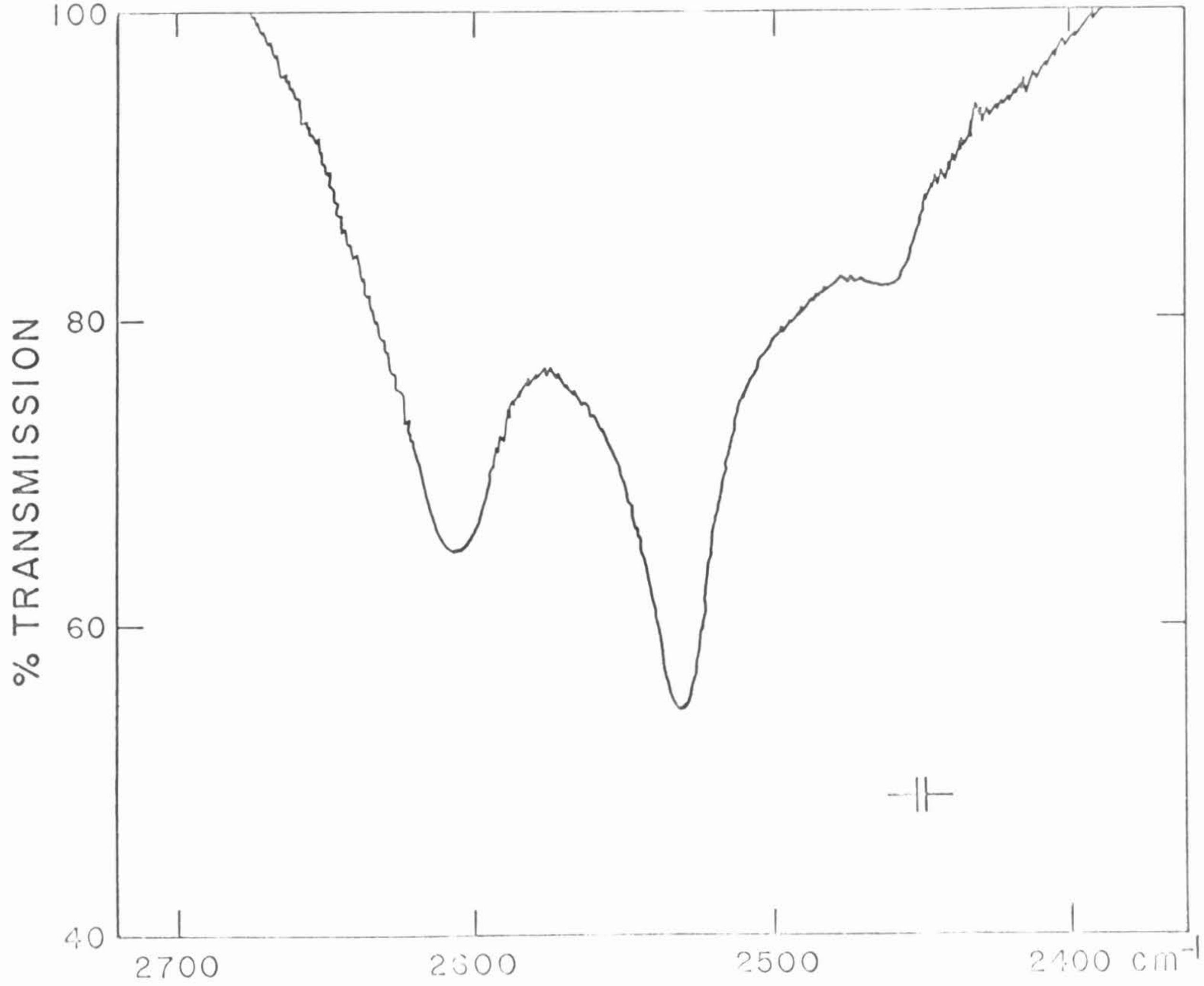

Fig. 3 HI in LIQUID XENON, 165°K

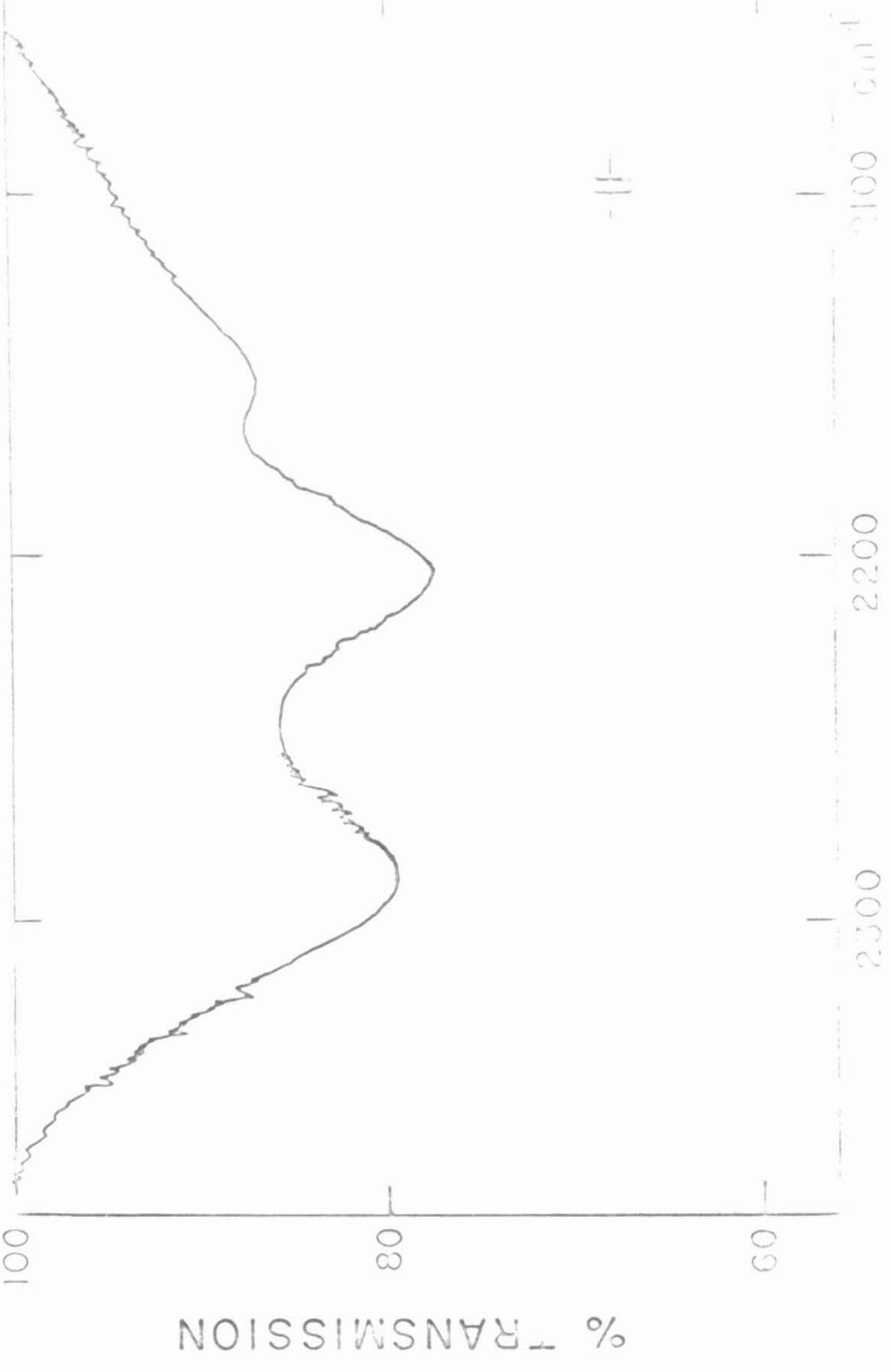

TABLE I

Measured Frequencies and Related Data for Hydrogen Halide Fundamentals*

	Free molecule band origin ν_0^g	Observed Q-branch in liquid xenon ν_0^ℓ	Shift $\nu_0^\ell - \nu_0^g$	Assigned ν_0^s in solid xenon at ~10°K	Calculated approx. P—R separation at 165°K	Observed separation of rotational maxima
HCl	2886	2852	-34	2840	98	150
HBr	2559	2530	-29	—	88	140
HI	2230	2213	-17	—	78	130

*All units cm^{-1}.

Intensities. The most striking feature observed is the increase of absolute integrated band intensities compared with the free molecule values. The results are summarized in Table II. Since the specific mechanisms of frequency shifts and of intensity perturbations are not necessarily the same (vide infra), no simple correspondence is expected nor is observed between the two sets of data.

State of Aggregation

One basic question which arises is whether the spectra observed belong entirely to dissolved monomeric hydrogen halide molecules or to molecules in higher states of aggregation. There is convincing evidence that dimer (or polymer) formation is insignificant. The arguments against dimer formation can be listed as follows:

1) Rank's work. HCl-HCl dimers have indeed been found(11) at 195°K in the gas phase at a density of 0.36 amagat ($p_{HCl} \approx .26$ atm), but their concentration is of the order of one part per fifty thousand that of monomeric HCl! The energy of formation for dimers is found to be 2.14 kcal/mole. From these data it is easy to see that dimer formation is still negligible at 165°K. A thermodynamic estimate,

$$\left(\frac{d\,\ell n\,K_p}{dT}\right)_p = \frac{\Delta H}{RT^2} \tag{2}$$

with $\Delta H = -2.14$ kcal/mole, and ΔH assumed independent of temperature in the range 195-165°K, indicates that the change in equilibrium constant is far from sufficient to account for an appreciable amount of dimerization at the lower temperature. For example, equation (1)

TABLE II

Intensities

	(a) Free molecule band strength cm^{-2}/atm	Free molecule $\left(\frac{\partial M}{\partial r}\right)_{r = r_e}$ Debye/Å	(b) Band strength in liquid xenon cm^{-2}/atm	Dissolved molecule $\left|\left(\frac{\partial M}{\partial r}\right)_{r = r_e}\right|$ Debye/Å	Enhancement ratio (b)/(a)
HCl	140(8)	+.98(8)	336 ± 67	1.52	2.4 ± .5
HBr	38(9)	+.51(9)	103 ± 21	.84	2.7 ± .5
HI	0.37(10)	-.05(10)	16 ± 5	.33	44 ± 13

gives an increase in K_p from about $0.77 \times 10^{-4} \text{atm}^{-1}$ at 195° K to only $2.1 \times 10^{-4} \text{atm}^{-1}$ at 165° K. Of course, we are dealing with HCl molecules dissolved in liquid xenon, not gaseous HCl. There is no compelling reason, however, why dimerization should be enhanced in xenon solution. As a matter of fact, Rank et al.(11) have actually found an HCl-Xe association complex with an energy of formation 1.6 kcal/mole, a value which is of the same order as that for the HCl-HCl dimer. This would imply that the tendency for dimerization of HCl in liquid xenon is less than it is in the vapor phase. Naturally (as predicted by the naive application of Eq. 2) dimer formation becomes important at much lower temperatures.(12)

2) No lines at lower frequencies. Polymerization of hydrogen halides in rare-gas environments usually gives rise to absorption at lower frequencies, e.g., HF in liquid xenon(13) and HCl in solid Xe.(12) In the latter experiments, polymerization of HCl resulted in lines around 2750 cm⁻¹. No absorption maxima were observed in the neighborhood of 2750 cm⁻¹ in the HCl-Xe liquid phase spectrum.

3) Similarity of HCl, HBr, and HI spectra. The tendency to polymerize decreases rapidly in the hydrogen halide series in going from HF to HI. Intuitively then, one would expect HCl to form a much stronger dimer than HI. The simplicity and similarity of the spectra of HCl, HBr, and HI in liquid xenon makes the dimer idea less plausible. The spectrum of HF in liquid xenon on the other hand is quite complex and very different from that of the other halides. In HF dimers and polymers are expected to form and apparently do so to an appreciable extent.

4) Mixture of HI, HBr, and HCl. A mixture HBr, HCl, and HI in liquid xenon was also investigated. No evidence of mixed dimer absorption was found. The spectrum observed was simply a superposition of the three individual spectra.

5) Q-branch shifts. In the spectrum of HCl trapped in solid xenon near 10°K,(12) the missing Q branch of the monomer spectrum shows a -46 cm^{-1} shift from the gas phase. This should be compared with the -34 cm^{-1} shift in the liquid (see Table I). This trend is expected because of the approximate additivity of intermolecular forces and because the ratio of the density of solid Xe at 10°K to that of liquid Xe at 195°K is 1.23. Such a correspondence further supports our interpretation of the solution spectrum as a monomer spectrum.

6) High temperature spectra. The solution spectra of HCl and DCl have been observed at room temperature in solvents such as CCl_4.(14) At room temperature, there is little doubt that the HCl molecules exist in monomeric form. Except for differences in Q branch intensities, such spectra are very similar to the one found in liquid xenon. This fact adds further support to our belief that we are studying dissolved monomeric hydrogen halide molecules.

7) Linear increase of absorption with concentration. Each intensity determination was made on the basis of two or three different concentrations of the hydrogen halide in liquid xenon. Within the limits of experimental error the measured area underneath the optical density curve was proportional to the amount of hydrogen halide present in the solution. This would still be true if all the hydrogen

halide were dimerized, but such a situation seems incompatible with the other arguments presented above. Partial dimerization would give to a region of absorption which is proportional to the square(11) of the concentration of the absorber.

Discussion

Illinger and Smyth(2) have recently treated the problem of intensities of vibrational transitions for dissolved molecules. Their expression for the ratio of the integrated absorption for a vibrational transition n ↔ n' of a dissolved molecule (ℓ) to that of a free molecule (o) in the limit of high vibrational frequencies, low temperatures, and small frequency shift is,

$$\frac{A^{\ell}_{nn'}}{A^{o}_{nn'}} = \frac{|<n|M^{\ell}|n'>|^2 \, F^2_{\ell}}{|<n|M^{o}|n'>|^2 \, E^2_{o}} \tag{3}$$

The band strength ratio $S^{\ell}_{nn'}/S^{o}_{nn'}$ is, of course, identical to the integrated absorption ratio. In equation (3), M is the dipole operator; E_o represents the amplitude of the electric vector of the electromagnetic radiation in vacuum; and F_{ℓ} represents the amplitude of the effective field acting on the dissolved molecule. Following Onsager,(17) F_{ℓ} contains two contributions. One part depends on the field within an empty spherical cavity cut in the solvent dielectric. A second part is dependent upon electric displacements in the dielectric induced by the presence, within the cavity, of the molecule, assumed spherical but polarizable and with a point dipole at its center. The latter contribution to the effective field is known as the "reaction field". Polo and Wilson$^{(3)}$ have shown that within the framework defined by Onsager's assumptions,

$$\frac{F_\ell^2}{E_o^2} = \frac{(n^2 + 2)^2}{9n} \quad , \tag{4}$$

n being the refractive index of the solvent. For xenon, $n \approx 1.4$ and therefore $F_\ell^2/E_o^2 \approx 1.25$, clearly insufficient by itself to explain the large intensity enhancements observed here. Thus one must seek an explanation in the first factor of equation (3), and not solely in the second.

This brings us to the primary motivation for this work, that is, to illustrate that even in simple systems purely dielectric considerations may not be adequate in the discussion of solvent effects on intensities.

We must now consider the perturbations on the dipole matrix element when the molecule is dissolved. Aside from the modification of the electromagnetic radiation due to the dielectric and the cavity, the surrounding molecules can in general give rise to two types of perturbations on the molecular dipole of interest. First, the reaction field mechanism induces an additional dipole moment along the molecular axis. This effectively modifies the dipole moment function and therefore may result in a different value of the dipole derivative, the quantity of importance in intensity considerations. Secondly, the random and fluctuating fields produced by the solvent molecules themselves create induced moments in the molecule independent of its own dipole. This induction is similar to that which gives rise to infrared absorption of compressed or dissolved homonuclear diatomic molecules.

Analysis of these two effects shows that there is an essential difference between them, which is manifested in the selection rules for the rotational transitions, or in band contours in broadened absorptions. As pointed out by Condon,(15) an external electric field will cause a diatomic molecule to exhibit an induced absorption, regardless of whether the free molecule is active or not. This induced absorption is shown to obey Raman selection rules and is superposed onto any original allowed absorption. This effect has been proposed previously by Kwok and Robinson(1) to account for the width of the HCl/Xe absorption and the prominence of its Q branch. On the other hand, the induced dipole along the molecular axis, due to the reaction field, rotates with the molecule. Its presence merely modifies the total absorption, but does not introduce new selection rules.

Since the unperturbed absorption of HI is vanishingly small, it seems to be a good case for distinguishing between these two effects. In synthesizing the experimental absorption by the superposition of O, P, Q, R, and S branches, as was done in our previous work,(1) it is found that the Raman absorptions, O, Q, and S, dominate completely. This is easily seen to be the case by examining Table I. To see if the conclusion that the random field effect is dominant is physically reasonable, one may use the experimental value of the HI dipole derivative in solution (0.33 debye/Å) to estimate the magnitude of the fluctuating fields operating on the molecule. For simplicity, we can use

$$\left(\frac{d\mu'}{dr}\right)_{sol.} = E \left(\frac{\partial \alpha}{\partial r}\right)_{sol.} + \alpha \left(\frac{\partial E}{\partial r}\right)_{sol.} \qquad (5)$$

where μ' is the induced moment due to the external field E, α being the polarizability of HI, and r, the internuclear distance of the molecule. The second term on the RHS of Eq. (5) vanishes because, by assumption, the external field is independent of the internal coordinates of the molecule. For the lack of information, we assume that the polarizability derivative in solution is close to the free molecule value. These derivatives for various diatomic molecules obtained in Raman intensity measurements(16) are typically of the order $1.5 \times 10^{-16} cm^2$. A rough value of the field so obtained is 0.2×10^6 esu/cm^2. This strength of field is quite possible in such dense systems. One might think in terms of instantaneous dipoles of the nearby atoms. This does not mean that there is on the average a field of this magnitude operating on the molecule as a whole. Rather, it reflects on the fields existing at those coordinates of the molecular electron density to which the polarizability derivative is very sensitive. Similar arguments can be presented for HCl and HBr. So we are led to conclude that intensity perturbations even in relatively inert solutions can exceed the limitations of purely dielectric considerations. In our cases, the external or solvent fields seem to play a more important role than the reaction field. This order of importance is also consistent with our estimated magnitude of the fluctuating fields in comparison with that of the reaction fields, calculated according to Onsager's expression.(17) For example,

$$E_r = \frac{2(\epsilon - 1)}{2\epsilon - 1} \frac{\mu}{R^3} \qquad (6)$$

In equation (6), ϵ is the dielectric constant of liquid xenon, approximately 2.0; μ is the dipole moment of the active molecule; and R is the radius of the cavity, assumed roughly 2.2 Å. The calculated values of the reaction fields are less than 0.04×10^6 esu/cm^2. Since the perturbing fields are squared in the intensity expression, it can readily be seen that the effects of the reaction fields are small compared to those of the random fields. That is, the calculated magnitudes of the reaction fields cannot account for the observed intensity increases. Furthermore, as we suggested before, the band contours are more consistent with Raman selection rules which result from the presence of external fields. Therefore, it is understandable that the intensity enhancements due to the reaction field cannot be obtained from our experiments. However, in the absence of fluctuating fields, it may be quite possible to observe the effect of the reaction field, especially in the case of HI. The system of HI dissolved in solid xenon at low temperatures would lend itself to such a study, although there are serious experimental difficulties involved. It is, however, encouraging that our spectra of HCl in solid rare gases (Part III of this thesis) show no detectable signs of Q-branches for the HCl monomer. This fact is consistent with the idea of vanishing fluctuating fields.

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PART III

ROTATION OF HCl IN SOLID RARE GASES

Infrared spectra of condensed substances have been utilized in obtaining information regarding intermolecular interactions as well as for the identification of molecular species. Recently, much work has been done in attempts to prove the existence of rotational or quasi-rotational motions of small molecules in solids by studying their vibration-rotation spectra at low temperatures. Besides the clear-cut case of molecular hydrogen, the systems which have shown signs of rotation include trapped H_2O,(1) NH_3,(2) and CH_4.(3) Simultaneously with our work, HCl in solid argon was investigated.(4) Our work deals mainly with HCl isolated in solid krypton in the temperature range 4.2°K to 30°K, but the spectra of HCl in solid argon and in solid xenon are also reported.

Previous work (Part II of this thesis) has shown that quasi-rotational motion can account for most of the band widths and structures in the hydrogen-halide liquid-xenon systems. Therefore it is natural to inquire whether it is possible to detect individual rotational components in the solid phase of such systems. The conditions for obtaining such evidence are optimized by the low temperature used as well as by the simplicity of the rare gas solids. At these temperatures, the line widths have narrowed to an extent where resolution of the rotational components becomes possible. From the frequencies and temperature dependence of intensities, information concerning the nature and magnitude of possible perturbations on the rotational motion can be derived.

Experimental*

The basic technique used here is generally described as the method of matrix isolation.⁽⁵⁾ The technique has been exploited in both ultraviolet⁽⁶⁾ and infrared spectroscopy.⁽⁷⁾ Fundamentally, it involves the deposition onto a cold window of a gaseous mixture consisting of an excess of non-reactive molecules or atoms plus a small fraction of active molecules. The window must be sufficiently cold so that diffusion is minimized both during deposition and subsequent operations. An outstanding difficulty with such experiments is the control of temperature in this low temperature range where thermal contacts and radiation effects pose problems. Even though these problems are not too difficult to surmount, little attempt seems to have been made in this direction for the kinds of problems to be discussed here. Our immediate task then was the design and construction of a dewar capable of maintaining very low temperatures for long periods of time (of order of hours), while at the same time permitting convenient and accurate temperature changes. A further requirement, peculiar to our laboratories because of the lack of a "local" infrared spectrometer, was that the cooled cell must be easily demounted from the vacuum system and transported from one building to another. It also had to fit into the sample space of the Beckmann IR-7 spectrophotometer, the instrument available to us. At the time

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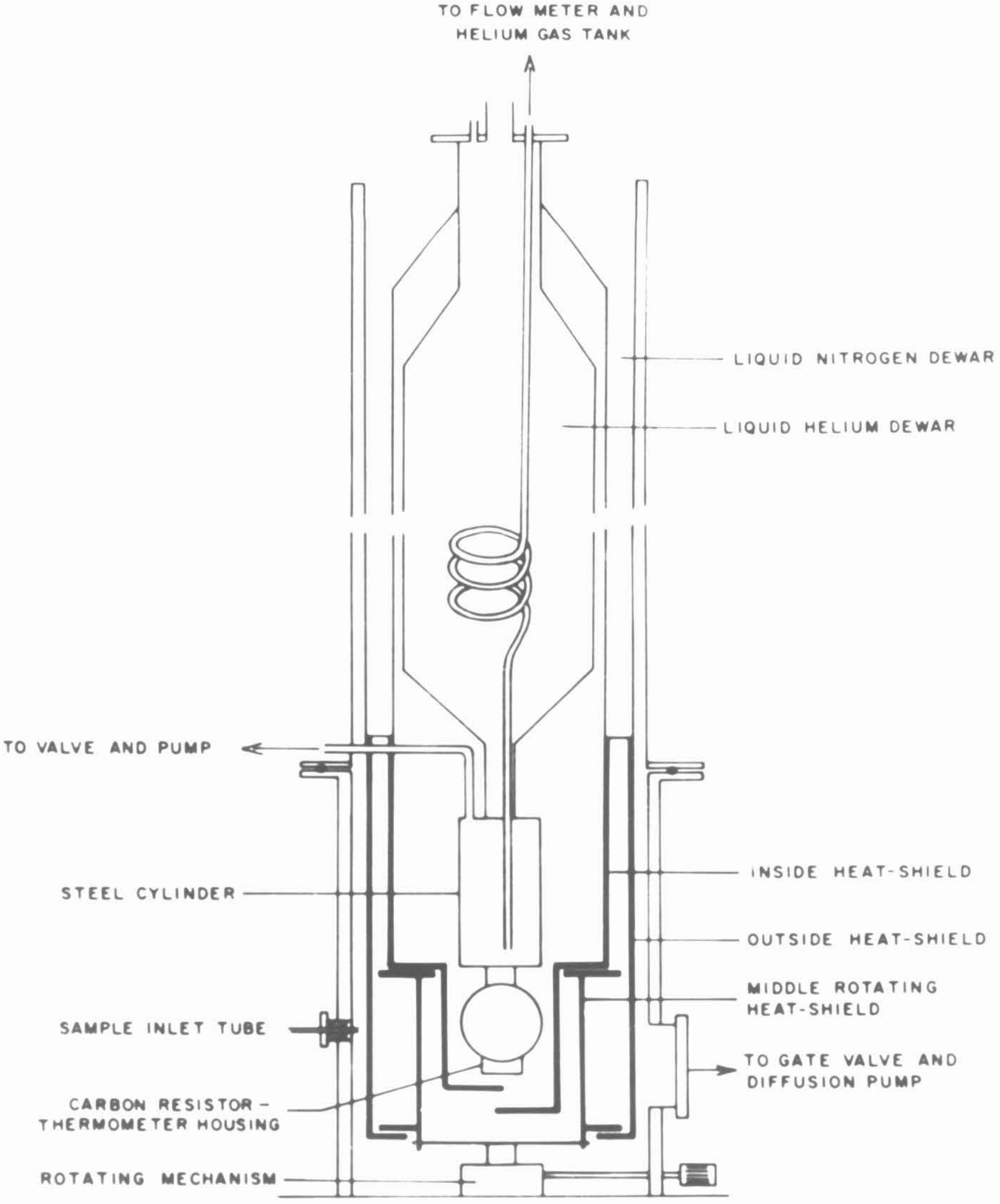
*This part of the work was carried out in cooperation with L. Keyser.

of construction of our cell in 1961, we knew of no apparatus which satisfied all of our requirements. The chief drawback common to previous cells has been the lack of temperature control or the crudeness of it. It has always been a tedious and uncertain maneuver, such as emptying out the coolent from the dewar.

The most significant feature of our cell is the introduction of a thin-walled stainless steel cylinder which acts, in conjunction with a supply of flowing helium gas, as a variable thermal conductor between the liquid helium and the cold window. In other words, the design allows not just conduction, but forced convection as a means of heat transfer. The overall design of the cell is shown in Fig. 1. A stream of helium gas cooled to liquid helium temperature is made to flow from the top of the stainless steel cylinder, directly to the bottom surface. The rate of flow coupled with radiation heating then determines the steady state temperature of the cold finger. A cylinder of the following dimensions was used: 4'' in height, 1.5'' in diameter, and 0.025'' wall thickness. We were able to effect temperature changes of 20 degrees within about 5 min.

The problem of radiation heating is minimized by triply heat-shielding the cold finger, as shown by the cross sectional views in Fig. 2. The rotatable middle shield with windows keeps the cold finger from being exposed directly to high temperature radiators even while spectra are being taken. All of the windows are cesium bromide. A 250 ohm Allen-Bradley carbon resistor, the coating of which had been carefully sandblasted off, is encased in the copper block attached to the cold window and serves as a thermometer.

The thermometer reading is calibrated against a flowmeter in the helium-flow convection system. The flowmeter is operated at close to atmospheric pressure. Typical flow rates are of order of 100 atm.-cc/min. The calibration itself is used only as a rough guide. The precise temperature is monitored and adjustments of flow are continually made to maintain desired temperatures.



TEMPERATURE VARIABLE CELL, 4°K – 40°K

Fig. 1

Fig. 2a

Cross Section of Cell

Alignment for Observation

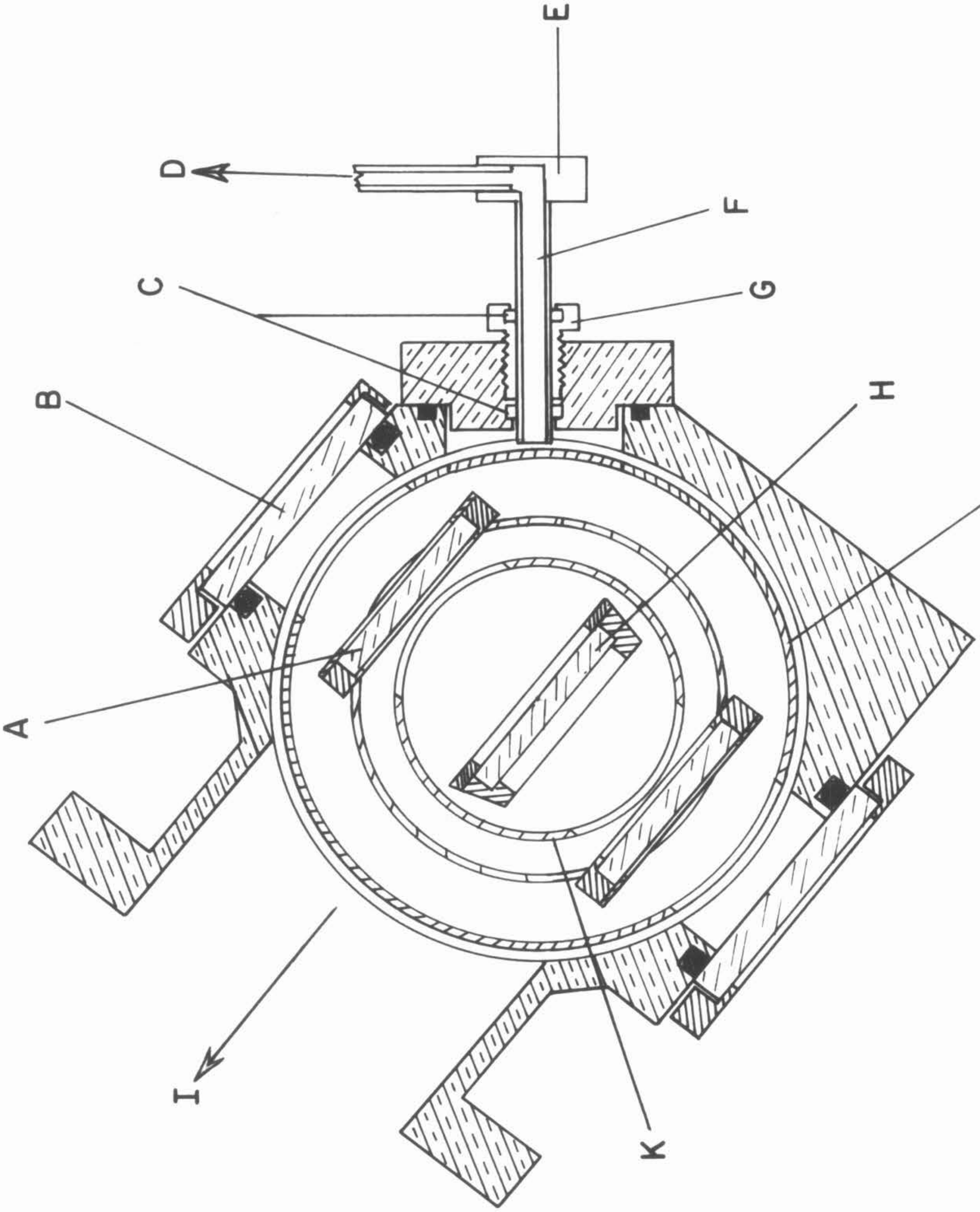


Fig. 2b

Alignment for Deposition

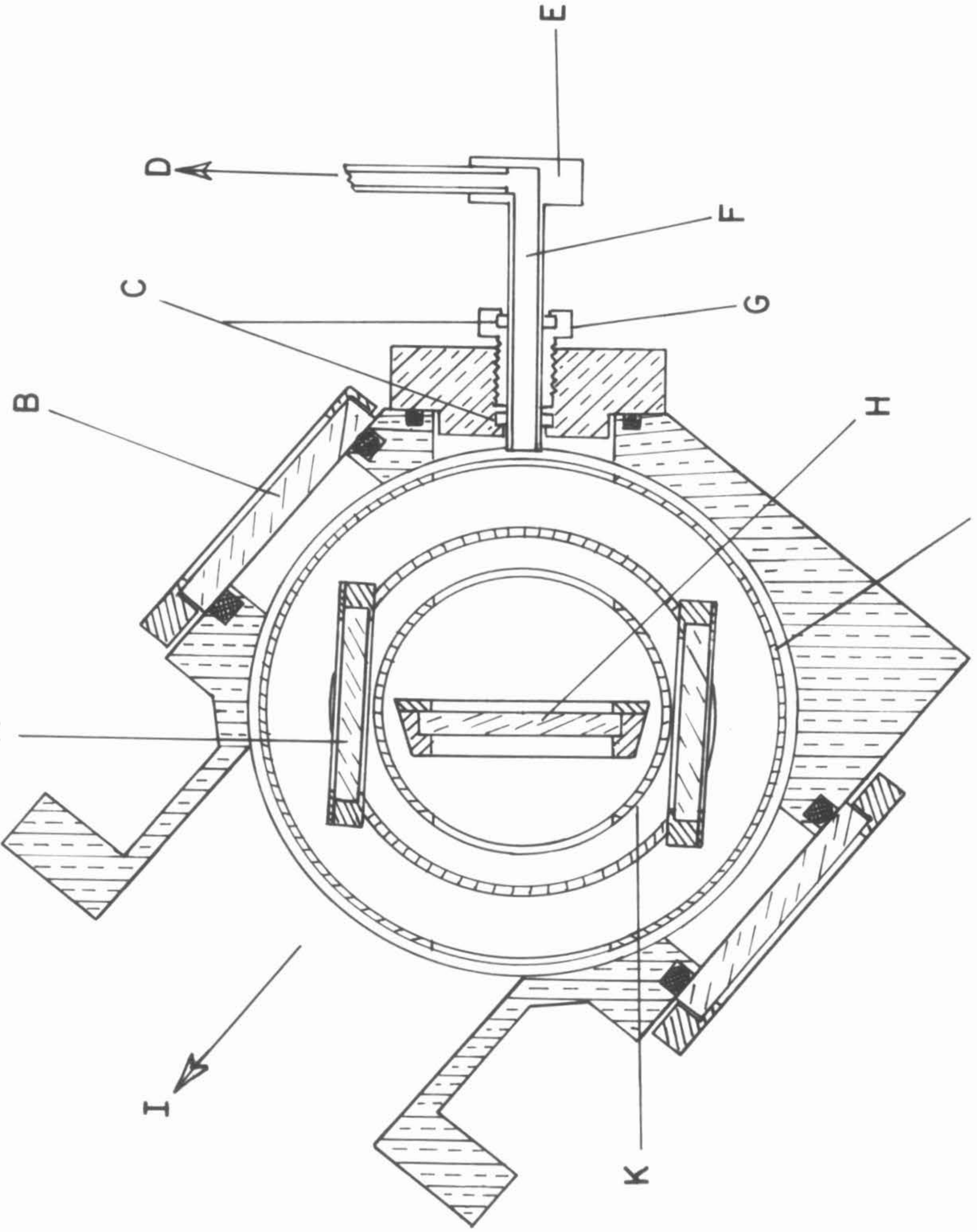


Fig. 2a, b

A. Rotatable middle heat shield with windows

B. Outermost window

C. Teflon gaskets

D. To inlet valve

E. Push stop

F. Inlet tube

G. Pressure screw

H. Cold window

I. To pump

J. Outer heat shield

K. Inner heat shield

Procedure

The first step in a typical experiment is the mixing of gases. This is accomplished in the glass system. Normally only two gases are involved (e.g., HCl, Kr). After the system has been pumped down to about 10^{-3} mm Hg, the gases are allowed to flow into separate calibrated bulbs to obtain the desired nominal ratio of rare gas to hydrogen halide. When the desired pressures in the bulbs are reached, the bulbs are shut by stopcocks. They are then open to a common volume having a sidearm with a removable liquid nitrogen trap. The gases condense quickly into the sidewarm. When the trap is removed, the gases mix in this closed common volume with the aid of a magnetically driven teflon propeller. The mixture is allowed to mix overnight.

After the cell has been pumped to less than 10^{-3} mm Hg, liquid nitrogen is introduced into both the helium and the nitrogen dewars. The convection chamber (the stainless steel container between the cold finger and the liquid helium), which has been evacuated, is now filled to one atmosphere of helium gas. The cell is kept in this condition until the temperature of the cold finger reaches approximately liquid nitrogen temperature. At this point, the residue of liquid nitrogen in the helium dewar is blown out by a steady stream of helium gas. Care must be taken to remove all of the liquid nitrogen from the helium dewar. Otherwise the freezing of nitrogen during liquid helium transfer would cause difficulties. After the excess nitrogen is removed, liquid helium is transferred into the dewar. When the temperature of the dewar has dropped appreciably, the dewar becomes a better pump than the diffusion pump. Therefore, the gate valve to the pump is closed. When liquid helium is actually in the dewar, the pressure in the cell normally drops to about 10^{-6} mm Hg. During the transfer of liquid helium, the convection chamber is open to a supply of helium gas at atmospheric pressure for a few minutes to render the chamber more conducting. This is done in order to achieve quick cooling of the cold finger and is necessary in maintaining low temperatures during deposition.

After the desired temperature is reached, the dewar is rotated relative to its base (see Fig. 2), so that the axis of the sample inlet tube is normal to the cold window. This geometry gives the most efficient and even deposition. The rubber O-ring between the dewar and its base should be well greased to facilitate the turning operation.

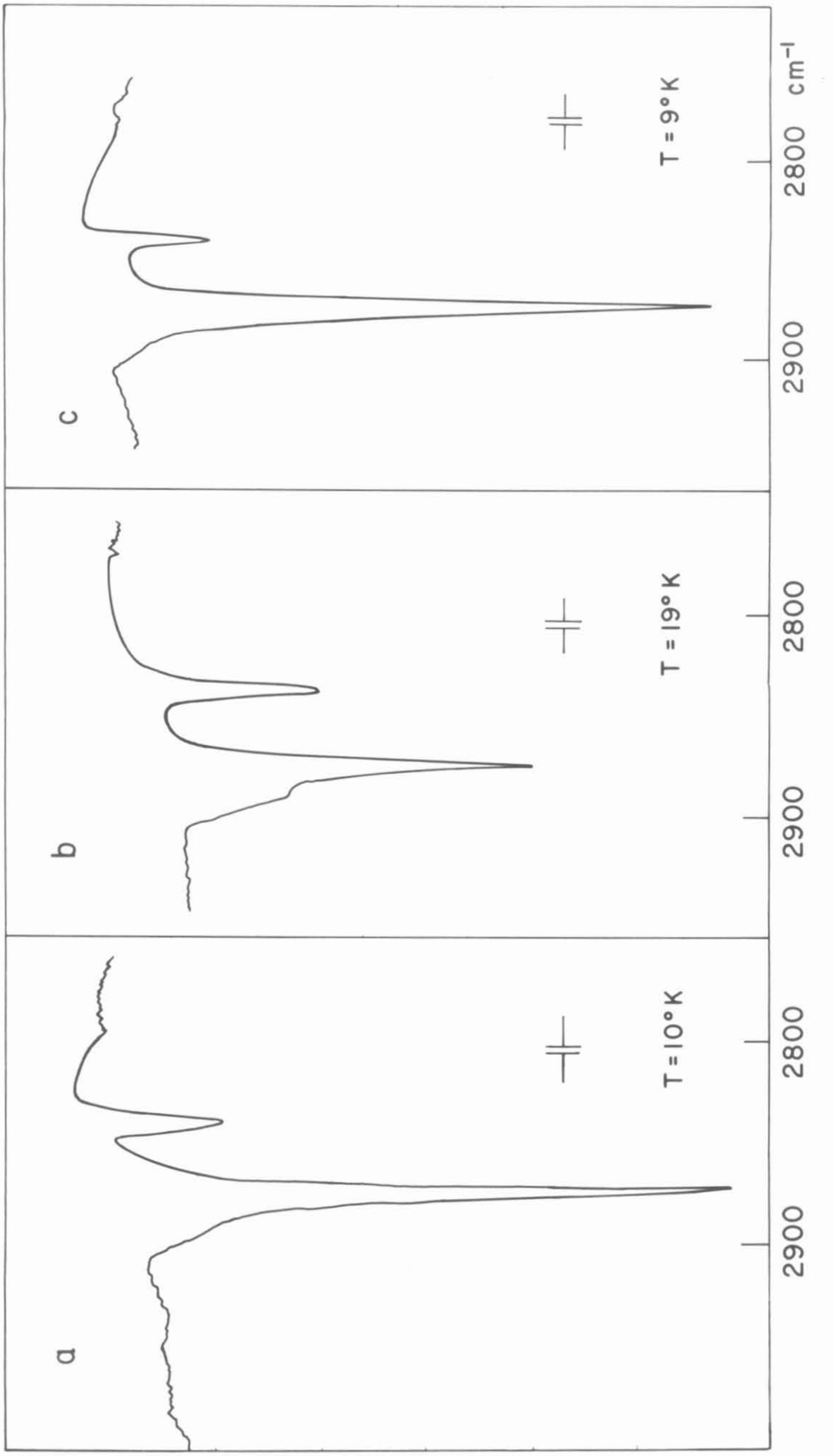
The inlet tube is then pushed in so that the nozzle is about 0.5" from the cold window. Possible leakage accompanying the movement of the inlet tube is prevented by pressed teflon gaskets concentric with the tube. Deposition can now begin. The rate of deposit is roughly one atm.-cc/min., and is controlled by a bellows type valve. A needle valve would be better, but is not absolutely necessary. The temperature of the cold window can be continuously monitored by the carbon resistor thermometer. Of course we are only measuring the temperature of the carbon resistor, but we have good reasons to believe that the temperature of the deposit is very close to the measured value. One indication is that the thermometer response is always instantaneous to operations which affect the deposit or the cold window. These operations may be the rotation of the middle heat shield or the change in depositing rate. The usual temperature during deposition is approximately 10°K. After the deposition, the inlet tube is withdrawn to its original position and the dewar rotated to its original alignment. The cell is now ready for dismounting and transportation to the spectrometer.

Our experiments were carried out on a Beckmann IR-7 spectrophotometer at a resolution of approximately 2 cm^{-1} and accuracy of about 1 cm^{-1}. The temperature range was roughly 4.2°K to 30°K. Beyond 30°K, diffusion of the HCl molecules leading to polymerization limited our working range, although our cell was capable of higher temperatures. The HCl was from the Matheson Co., 99% pure. The rare gases used were MSC grade from the Linde Co. All were used without further purification. Purity was considered sufficient when no detectable impurity spectra were present. Trace impurities were of no great importance in our work.

Results and Discussion

The identification of absorption lines belonging to monomeric HCl molecules is the crucial step in the analysis. This is made difficult by the very intense polymer absorptions, at slightly lower frequencies. Their presence is practically unavoidable in the concentration range used. As will be evident later in the discussion, monomeric HCl molecules should give rise to line intensities and widths dependent on temperature reversibly. On the other hand, polymer intensities are not reversible with temperature since at these temperatures, the monomer-polymer equilibrium favors the polymers. By varying the solvent to solute mole ratio as well as the temperature, we have, by careful sorting, reduced the raw data to the spectra shown in Figs. 3, 4, 5.

First of all, to clarify the problem, we are seeking evidence of rotation or perturbed rotation of hydrogen chloride trapped in an inert matrix. Perhaps it would be more enlightening at this point to consider what one would observe if no rotational motion is present. Besides its internal vibration, an HCl molecule in such a situation can oscillate about its equilibrium position as well as librate about an equilibrium orientation. The oscillation of the whole molecule about its equilibrium position can be dealt with easily. This oscillation can be regarded as translational motion in the deduction of selection rules, because this motion does not alter the internal coordinates of the molecule. From a classical point of view, a light wave of relatively long wave length does not exert a translational force on a neutral collection of



1/100 : HCl/Kr

Fig. 3

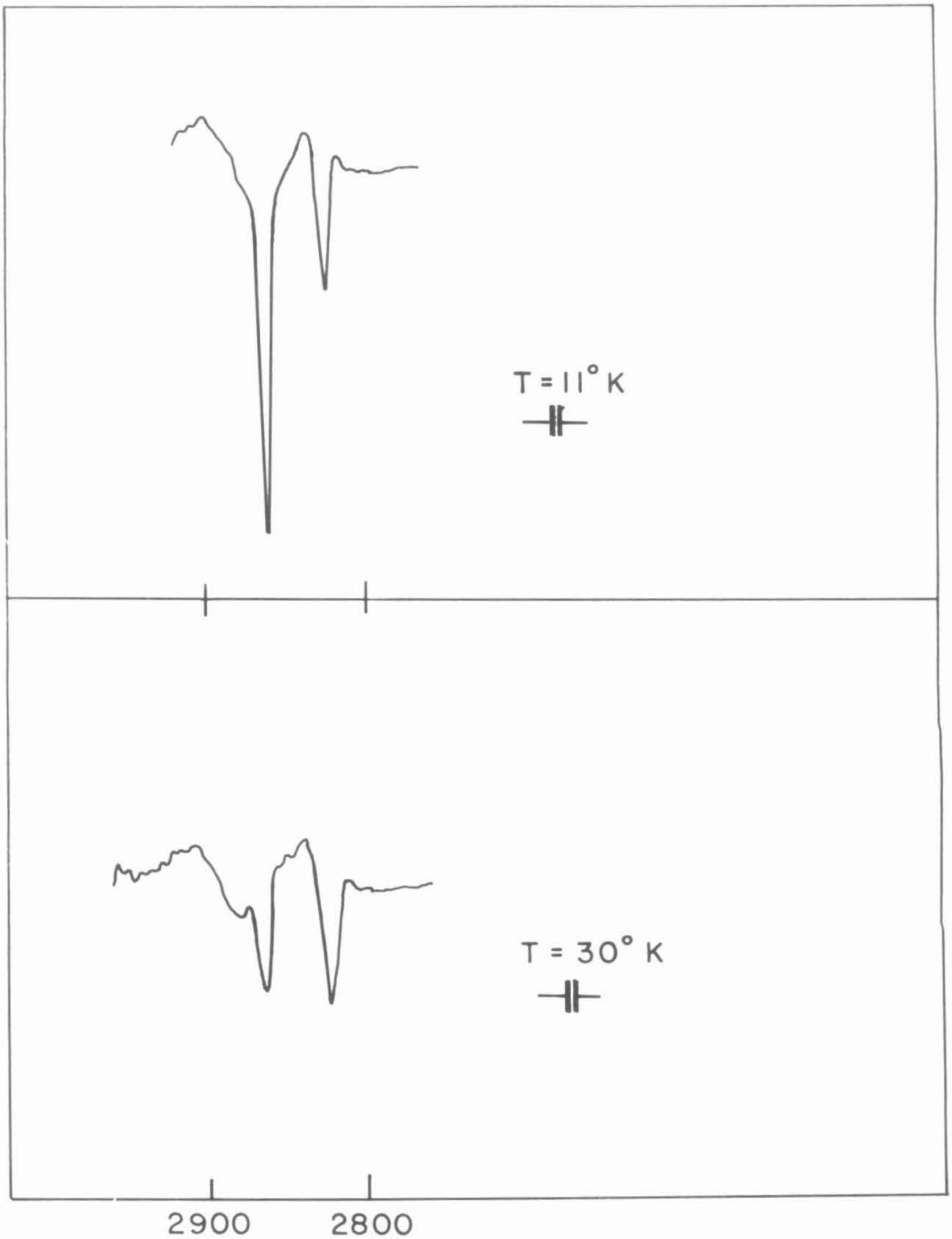
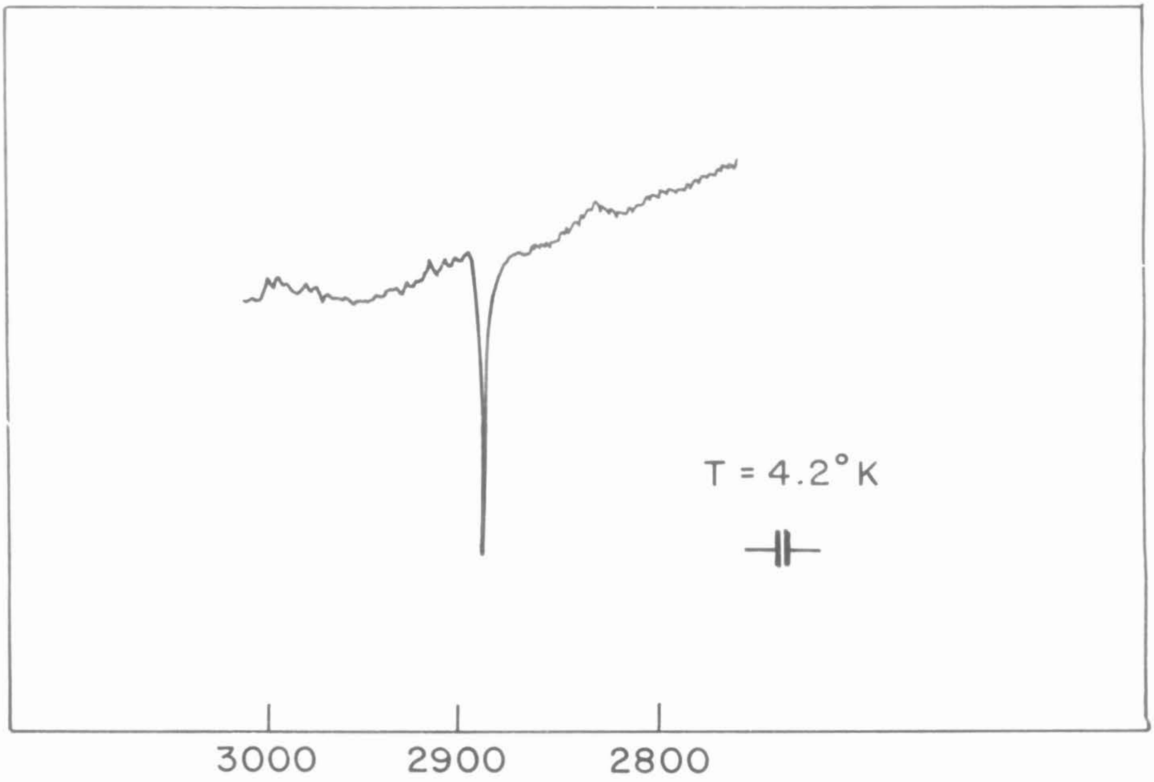


Fig. 4 HCl/Xe : 1/100

Fig. 5



HCl/A : 1/1000

charges. According to the correspondence principle, the light wave cannot induce transitions among energy levels of this motion. We can therefore ignore oscillation of the molecules on their lattice site in our analysis.

A related question which often comes up in spectra of solids is the possibility of phonon combinations. The fact that they are combinations necessarily place them in the category of second order phenomena. We can roughly estimate their degree of importance from the following arguments. Coupling of lattice vibrations with internal vibrations can be formally divided into two types, electrical and mechanical. It is well known that lattice frequencies are usually a couple of orders of magnitude lower than internal vibrations, especially vibrations of hydrogen atoms in molecules. This separation of frequencies results in the lack of mixing of these modes. We can safely discard mechanical coupling. Electrical coupling requires a consideration of mixed terms in the expansion of the dipole moment,

$$\mu = \mu_0 + \frac{\partial \mu}{\partial r} r + \sum_i \frac{\partial \mu}{\partial Q_i} Q_i + \sum_i \frac{\partial^2 \mu}{\partial r \partial Q_i} r Q_i + \cdots$$

In this expansion, μ represents the dipole moment of the combined system, molecule plus lattice. Q_i and r are the approximate normal coordinate of the lattice and the internal coordinate of the molecule respectively. The combination intensities depend on the coupling term, $\left(\frac{\partial^2 \mu}{\partial r \partial Q_i}\right) r Q_i$. Intuitively, the most important contributions to a simultaneous change in dipole moment of the system come from changes in the local coordinates immediately surrounding the HCl molecule. This is because the dominant change in dipole moment of the lattice results from changes in induction due to the HCl dipole. We should therefore focus our attention on some local coordinate, R. In general, R can be described by a linear combination of the normal coordinates of the lattice,

$$R = \sum_j C_j Q_j$$

Then the coupling term becomes, $\sum_i C_i \left(\frac{\partial^2 \mu}{\partial r \partial R}\right) r Q_i$.

The point is that the change in local coordinate giving rise to a change in dipole moment involves all the normal coordinates, weighted by their contribution to the local coordinate. The combination spectrum should consist of a quasi continuous distribution of frequencies, which should be detectable at all temperatures. That is, the lattice modes don't have to be excited in order for the combinations to appear. At very low temperatures where essentially all the lattice modes are in their ground states, we would expect the combinations to appear on the high frequency side of the HCl absorptions. It is not unlike the R-branch of familiar molecular spectra. At higher temperatures where excited configurations of lattice modes are populated, combination absorptions on the low frequency side become possible. The pertinent conclusion to be drawn from this discussion is that if combinations are important, their presence should be observable even at 4.2°K.

Their occurrence would appear as high frequency shoulders on the HCl lines. The spectrum of HCl in argon at 4.2 K shows no obvious sign of this behavior. Therefore, we conclude that lattice combinations are not significant in our systems. We have made the implicit assumption that the coupling of modes is not temperature sensitive.

The libration problem has been dealt with by Hexter and Dows(8) and also by Ewing.(9) Their analysis is based on an approximate quadratic potential for the librational motion. The selection rules so obtained are $\Delta N = 0, \pm 1, \pm 2, \cdots$, in the order of decreasing probability. N here denotes the librational quantum number. If this is the correct physical description of the motion of the trapped HCl molecules, we would observe not one but several absorption lines even at 4.2°K, the $\Delta N = 0$ and $\Delta N = 1$ lines being most intense. As mentioned before, we observe only one line at 4.2°K in argon. Since the situations are similar in all three rare gases, we conclude that libration is not a suitable description here.

We are now left to consider rotation or perturbed rotation as the only reasonable alternative. If there were no perturbations on the rotation of the molecules, the spectra should coincide with that of the free molecule. This is not the case. We might have anticipated this from a consideration of molecular sizes and the distances in the rare gas solids. The relevant information is collected in Table I. Inside a rare gas crystal, it is the maximum "extent" of the molecule that most likely dominates in the consideration of rotational barriers. In view of such close distances it is expected that overlap interactions

TABLE I

	Vander Waals[*] Radius in Angstroms	Lennard-Jones[†] Parameters	
		ϵ/k °K	σ Å
Argon	1.91	124	3.418
Krypton	2.01	190	3.61
Xenon	2.20	229	4.055
HCl	2.48	360	3.305

[*] Taken from: A. Cabana, D. F. Hornig, and G. B. Savitsky, J. Chem. Phys. **39**, 2942 (1963).

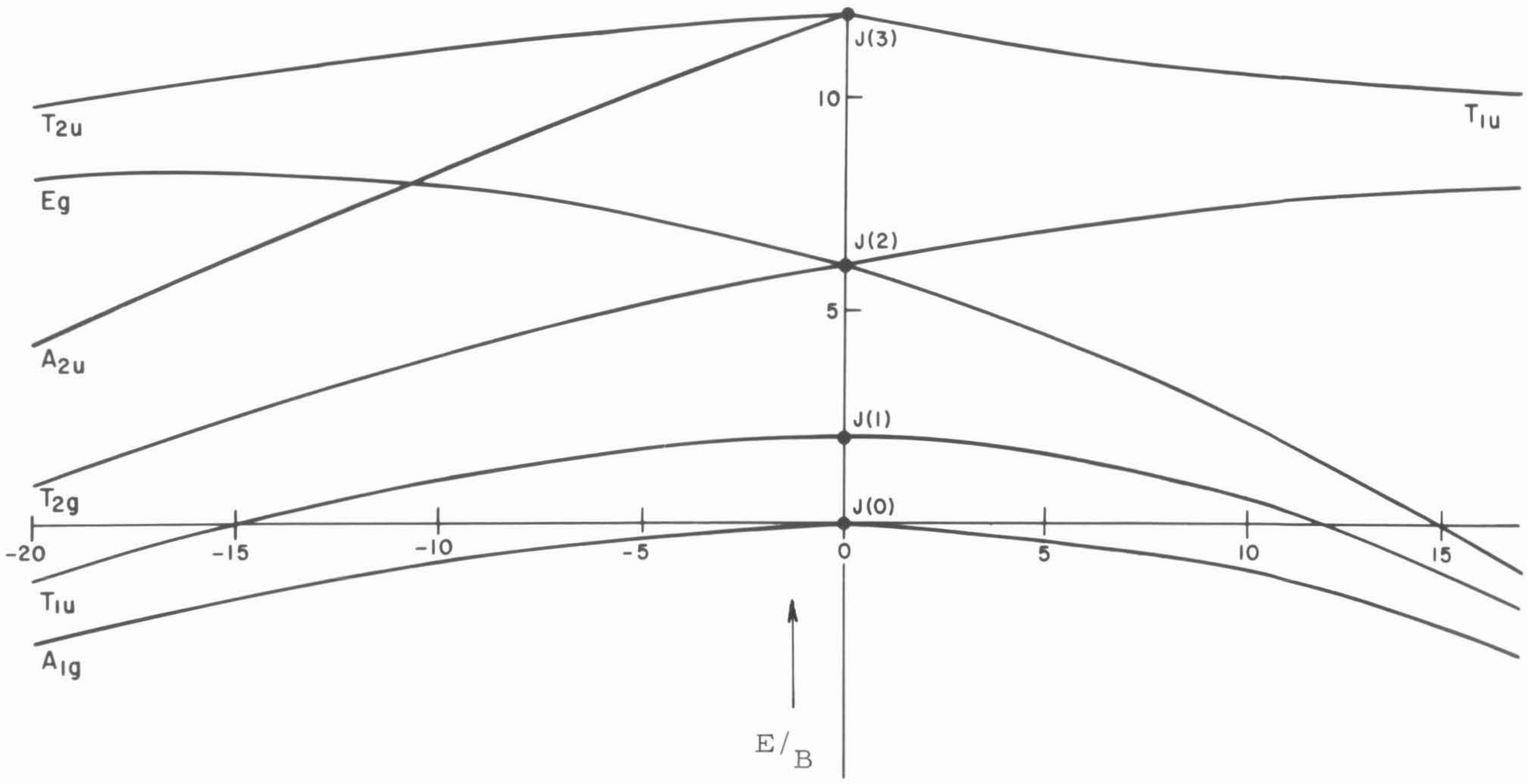
[†] Taken from: J. O. Hirsfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, N. Y., 1954.

play an important role, particularly because perturbations of the rotational motion intuitively originate from peripheral contacts. Since the exact nature of the perturbation is not known, we shall utilize it in parametric terms.

Hindered rotation in solids has been discussed by Pauling,(10) and by Devonshire(11) as well as by others. Devonshire's analysis based on an octahedral potential is directly applicable to our systems, since the substitutional site in the face center cubic structure of the rare gas crystal has octahedral symmetry. Although it is conceivable or even likely that the HCl molecule will distort its surrounding, this distortion still retains the octahedral symmetry as far as the rotation of the molecule is concerned. Devonshire used a potential of the form,

$$V = -K \left\{ P_4^{\,0}(\mathrm{Cos}\ \theta) + \left(\frac{1}{168}\right) P_4^{\,4}(\mathrm{Cos}\ \theta)\ \ \mathrm{Cos}\ 4\phi \right\}$$

where θ and ϕ are the polar and azimuthal angles respectively, and K, the magnitude of the barrier height. The P's are the associated Legendre functions. Simultaneous with our work, Flygare(12) also proposed this model for our systems. The calculation is simply a diagonalization with rigid rotor wave functions, using the potential given above. The energies are plotted in Fig. 6 as a function of K, in units of the rotational constant, B. In order to check on the possible breakdown of selection rules, we also need the approximate wave functions for the low lying states, which are the only ones of interest in our temperature range. The functions, allowed to mix up to the



ENERGY LEVELS vs BARRIER HEIGHT K/B →

Fig. 6

$J = 4$ level, are shown in Table II, for $K \approx 8$ B, a value which is an upper limit to that met in these systems. The states are labeled according to the representations of the octahedral symmetry group. One sees that mixing of different J's is not serious enough to cause breakdown of the rigid rotor selection rules, $|\Delta J| = 1$, $|\Delta m| = 0, 1$. The intensities of individual lines can only be discussed qualitatively because experimentally they are particularly uncertain in this type of work. The frequencies and their possible assignments in the three rare gases are given in Table III. The assignments are made according to the following arguments. At 4°K, only one line appears. This is obviously the R(0) line, or equivalently the $A_{1g}-T_{1u}$ transition, since only the lowest state is appreciably populated. As the temperature is raised, a broad line appears on the high frequency side of the R(0) line and a less broad line on the low frequency side. The lower frequency one should correspond to the P(1) of the gas, whereas the higher frequency one should correspond to an R(1) absorption. Specifically, we shall limit our discussion to the case of HCl in krypton. Referring to the energy diagram (Fig. 6), with $B = 10.59\ \text{cm}^{-1}$ for HCl, one sees that the $A_{1g}-T_{1u}$ (same as the J(0)-J(1)) separation is not very sensitive to barrier height, in the region of low barriers. This is the region of interest as will be evident later. This lack of sensitivity makes it impossible to determine the barrier height, even approximately, from the R(0)-P(1) separation. We have to resort to possible

TABLE II

$$K \approx -8B, \quad \psi_J^m \equiv J(J, J_m)$$

$$A_{1g} = 0.988\,\psi_0^0 + 0.006\,\psi_2^0 - 0.070\,\psi_4^{-4} - 0.117\,\psi_4^0 - 0.070\,\psi_4^4$$

$$T_{1u} = \begin{cases} 0.981\,\psi_1^{-1} + 0.117\,\psi_3^{-1} + 0.151\,\psi_3^3 \\ 0.981\,\psi_1^0 - 0.191\,\psi_3^0 \\ 0.981\,\psi_1^1 + 0.151\,\psi_3^{-3} + 0.117\,\psi_3^1 \end{cases}$$

$$T_{2g} = \begin{cases} 0.704\,\psi_2^{-2} - 0.704\,\psi_2^2 + 0.061\,\psi_4^{-2} - 0.061\,\psi_4^2 \\ 0.996\,\psi_2^{-1} + 0.021\,\psi_4^{-1} + 0.077\,\psi_4^3 \\ 0.996\,\psi_2^1 + 0.077\,\psi_4^3 + 0.021\,\psi_4^1 \end{cases}$$

$$E_g = \begin{cases} -0.010\,\psi_0^0 + 0.986\,\psi_2^0 + 0.076\,\psi_4^4 \\ -0.119\,\psi_4^0 + 0.076\,\psi_4^4 \\ 0.694\,\psi_2^{-2} + 0.694\,\psi_2^2 + 0.133\,\psi_4^{-2} + 0.133\,\psi_4^2 \end{cases}$$

$$A_{2u} = 0.707\,\psi_3^{-2} - 0.707\,\psi_3^2$$

$$T_{2u} = \begin{cases} 0.612\,\psi_3^{-3} - 0.790\,\psi_3^1 \\ 0.790\,\psi_3^{-1} - 0.612\,\psi_3^3 \\ 0.707\,\psi_3^{-2} + 0.707\,\psi_3^2 \end{cases}$$

$$T_{1u} = \begin{cases} 0.191\,\psi_1^0 + 0.981\,\psi_3^0 \\ -0.191\,\psi_1^1 + 0.775\,\psi_3^{-3} + 0.601\,\psi_3^1 \\ -0.191\,\psi_1^{-1} + 0.601\,\psi_3^{-1} + 0.775\,\psi_3^3 \end{cases}$$

TABLE III

Assignments in cm^{-1}

	R(0) or $A_{1g} - T_{1u}$	P(1) or $T_{1u} - A_{1g}$	R(1)* $T_{1u} - T_{2g}$ and $T_{1u} - E_g$	Missing Q Branch or $A_{1g} - A_{1g}$
Ar	2888	2853†	‡	2871
Kr	2876	2838	2892	2857
Xe	2860	2820	2880	2840

*The estimated centers of these unresolved lines are listed here.

†Taken from reference 4.

‡Assignment of this is particularly uncertain.

transitions involving the J(2) states. The J(1)-J(2) or R(1) transition should be split into two components due to the removal of the J(2) degeneracy in the octahedral field. The possibility exists that the barrier height can be estimated from either the splitting in R(1) or the separations of the split components from the R(0) line. Of course, internal consistency is required of these. Assuming a barrier height of the order of -10 B, as suggested by Flygare(12) for the case of argon, we would expect the $T_{1u} - T_{2g}$ line to appear at about 10 cm^{-1} higher than the R(0) line and the $T_{1u} - E_g$ line about another 40 cm^{-1} higher. This is not supported by our observations. Now, if the barrier is low, say near -3 B, the two components would only be split by about 10 cm^{-1}, which may not be resolvable due to the increased linewidths accompanying the elevated temperatures where these transitions can be seen. The center of these unresolved lines would occur at about 20 cm^{-1} higher than the R(0) line. The observed broad line, previously named R(1), fits this description fairly well. A better fit can be achieved by the assumption of a slightly smaller B constant. This idea remains speculative however.

Similar arguments can be made using a positive barrier, with the conclusion that a low barrier of order of 30 cm^{-1} is an apt description in the HCl/Kr system. In entirely the same manner as above, we suggest that the barrier in xenon is no greater than that in krypton, and probably much smaller. Flygare(12) predicted the same R(0)-P(1) as well as R(1)-P(1) separations for HCl in all three rare gases. We cannot fully support these predictions.

As far as the shifts in frequency from the free molecule value are concerned, very little can be said. It has been shown in several cases that a general dielectric consideration is not adequate. The detailed electronic interaction between a particular solute molecule and its solvent with concomitant molecule force constant changes underlies this aspect of the problem. The complexity of frequency perturbations becomes apparent when the spectra of similar molecules trapped in the same solvents are compared. We have summarized such a comparison in Table IV, with the pertinent Lennard-Jones (6-12) parameters listed in Table V.

Polymers

It is worth noting that the polymer absorptions (Fig. 7, 8, 9) in all three rare gas matrices are quite similar in appearance and that their frequencies are reproducible (Table VI). This indicates a certain specificity in the possible configurations of polymers. No clear cut picture of these polymers has been advanced yet. A tentative working hypothesis is that different absorption frequencies correspond either to polymers consisting of different numbers of molecules or more probably to HCl molecules influenced by other HCl molecules situated at various non nearest neighbor distances.

Conslusion

In the area of low temperature spectroscopy, we have successfully built and operated a new and more convenient apparatus, capable of quick and controllable temperature changes. Our search for rotation of HCl trapped in the rare gas solids has resulted in new

TABLE IV

Shifts in cm^{-1}

	CH_4(3)		NO(13)	HCl	CO(14)
	$\Delta\nu_3$	$\Delta\nu_4$	$\Delta\nu_Q$	$\Delta\nu_0$	$\Delta\nu_0$
Ar	+14.9	+1.2	-2.5	-15	+5.5
Kr	- 1.8	-3.9	-5.5	-29	
Xe	-12.7	-6.6	-6.5	-46	

TABLE V

Lennard-Jones Molecular Parameters[†]

	CH_4	NO	HCl	CO
ϵ/k (°K)	144	119	360	110
σ (Å)	3.796	3.599	3.305	3.590

[†] Taken from: J. O. Hirsfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, N. Y., 1954.

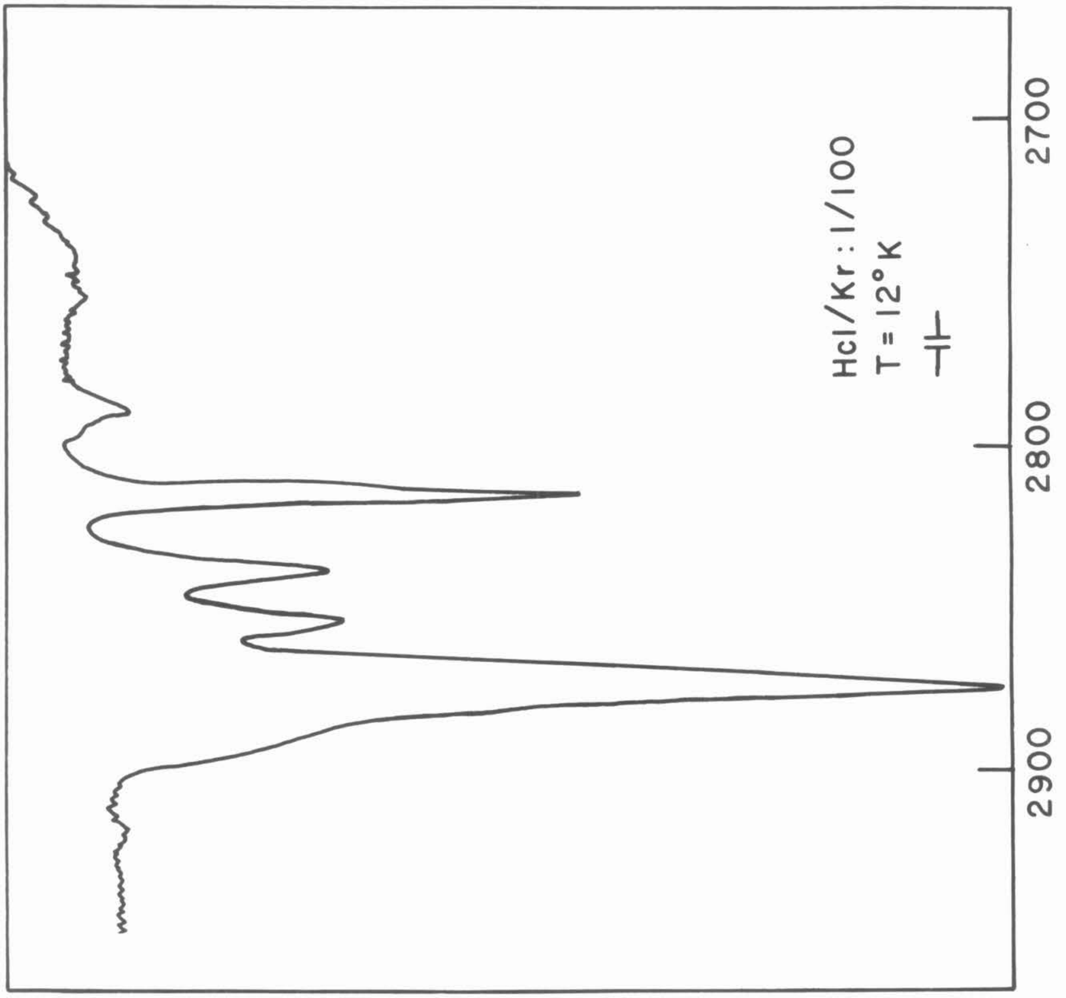


Fig. 7

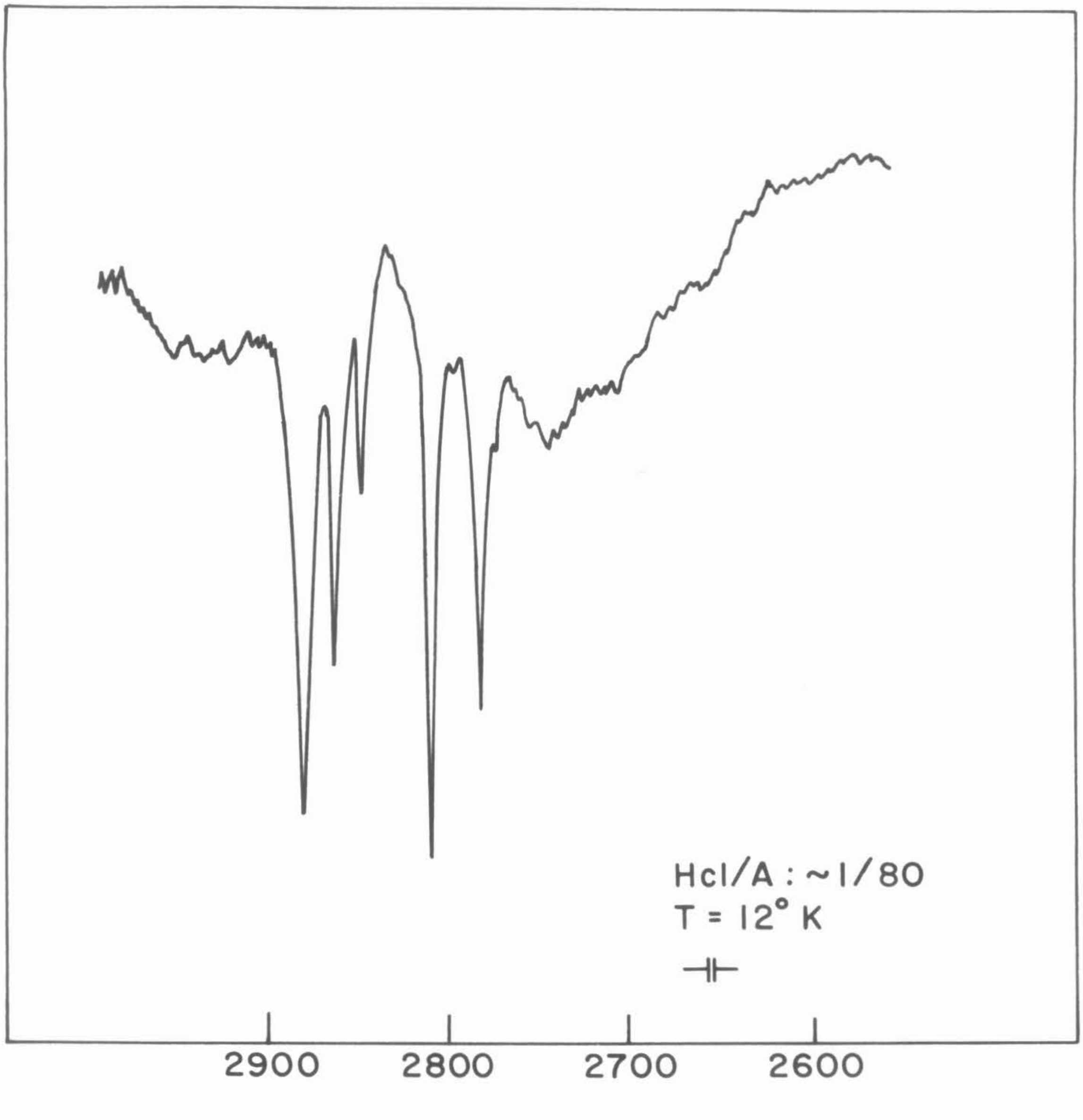


Fig. 8

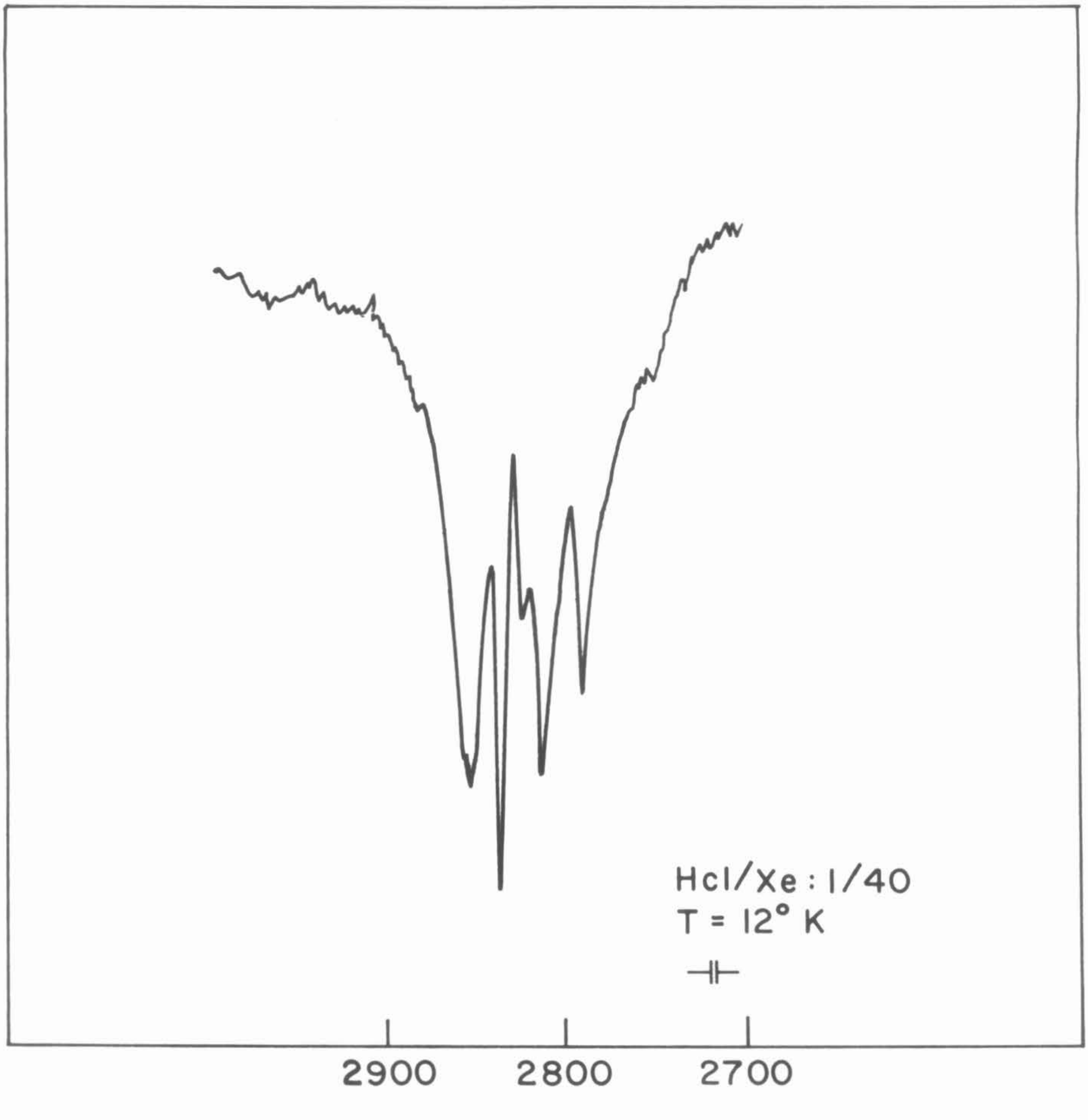


Fig. 9

TABLE VI

Prominent Polymer Frequencies in Cm^{-1}

A	Kr	Xe
2760	2758	2770
2795	2789	2795
2855	2814	2815
2870	2852	2840

support for perturbed rotation. The problem is not completed as it stands because supplementary information can still be gained through isotopic experiments.

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PROPOSITION I

Detection of Microheterogeneity in Liquid Mixtures

Binary liquid mixtures near their critical temperatures exhibit some very unusual properties. Dielectric, acoustical, and optical properties show significant changes in this region. For example, at a few degrees above the critical solution point, there is a large attenuation of acoustical energy as well as a marked increase in dielectric loss. These phenomena are qualitatively explained on the basis of local density fluctuations or structural relaxation near the critical solution temperature. It has been suggested(1,2) that near the critical point, fluctuations in density, short of macroscopic phase separation, cause little free energy change. Therefore, heterogeneity on a microscopic scale should be prevalent.

The physical picture generally accepted is that like molecules form aggregates or clusters with a certain amount of structure as the critical solution temperature is approached. Whereas far from the critical solution, the distribution of molecules in the mixture may be fairly random, it is no longer so in the critical region. A similar picture exists regarding irregular solutions such as those formed between hydrocarbons and perfluorocarbons where the excess free energy is unusually large. The same behavior has been suggested(3) in order to rationalize the discrepancy between calculated and experimental critical temperatures. Small angle X-ray diffraction has shown support for the idea of cluster formation of like molecules in these solutions.

Our experiments on the spectrum of dissolved mercury atoms as a sensing device of local environments present an obvious path of exploration in near critical or irregular solutions. The basic assumption in such an approach is that the minute amount (mol ratio less than 10^{-6}) of dissolved mercury atoms does not significantly perturb the system under investigation, and a random distribution of these atoms is required. We have indicated that the perturbed mercury spectrum can reflect the condition of local surroundings about the atoms. Therefore, in systems where microheterogeneity exists, we should observe essentially the superposition of two spectra. Each of these spectra should be characteristic of the spectrum of dissolved mercury atoms in one of the pure component liquids that make up the solution. On the other hand, if clustering of like molecules is insignificant in these mixtures, we would simply observe a broadened or averaged spectrum, most likely occurring at some intermediate frequency relative to the spectra in the pure liquids.

The optimum situation for this investigation requires sufficient separation in frequency of the mercury spectra in the pure liquids. The temperature of these solutions must also be high enough so that mercury will dissolve to a detectable extent. The hydrocarbon-perfluorocarbon systems seem to be a good case for our purpose. It is known that perfluorocarbons possess unusually strong repulsive interactions and should therefore cause relatively large high frequency shifts in the mercury spectrum. The hydrocarbons normally produce slight low frequency shifts, as in the cases of neopentane and cyclohexane. Thus the possibilities exist for resolution in these systems. Furthermore, the critical temperatures of typical hydrocarbon-perfluorocarbon mixtures are near room temperature which has proved adequate for the observation of the mercury spectrum. A similar system, C_7F_{14}/CCl_4, which satisfies our requirements, should also be interesting.

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PROPOSITION II

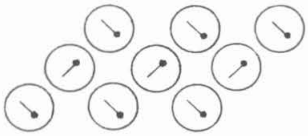
Electrostatic Effect on Vibrational Shift

Impurity spectroscopy in the infrared has been limited, up to now, to systems consisting of an active species isolated in a relatively inert solvent. The reasons behind this are well founded. They center around the simplicity of interaction between solute and solvent.

A rather novel experiment is suggested here where the inertness or simplicity of the solvent is not desired. The purpose of the experiment to be proposed is essentially two-fold, although there may evolve auxiliary interests which can lead to variations on this illustrative example. First, we would like to find and measure the effect of orientation of perturbing fields on the shift in vibrational frequency from the free molecule to the trapped state. Secondly, if such distinct orientations can be found, it would be of great interest to know the magnitude of the activation energy or barrier to the transition from the less stable orientation to the more stable one.

To achieve these ends, the system must allow no rotation of the trapped species and it must make available two orientational positions which are energetically different. We suggest the system CO trapped in HCl or HBr, since these are well known, separately.

The crystal structure of HCl and HBr(1) are thought to contain planes of zigzag chains of the molecule as shown here,



Since the molecular parameters of CO and HCl or HBr are not too different, it is probable that upon quick freezing or deposition at 4.2 K, the CO molecules would be equally oriented in the substitutional sites of the hydrogen halide structure. The two species of CO molecules may then give rise to two resolvable absorptions. Depending on the barrier of reorientation, one of the lines should disappear as the temperature is raised.

A sideline experiment follows from the above considerations. That is, if we use N_2 instead of CO, we may be able to observe the induced absorption of N_2. Furthermore, there should be only one line in this case, due to the symmetry of N_2.

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PROPOSITION III

A Non-equilibrium Effect on the Vibrational Shift of a Trapped Molecule

It is a general phenomenon that the vibrational frequencies of molecules are altered upon entering into solution, both in the solid and liquid states. We are here interested in solid solutions such as the trapping of an active molecule in an inert matrix. The magnitude and direction of the shifts in frequency depend on intermolecular interactions which are categorized, for convenience, into various types, all of which are generally operative.

One type of interaction, which is usually of prime importance in systems interacting repulsively, is visualized as a "cage" or "squeezing" effect. That is, the structure of the surrounding solvent is distorted to accommodate for the foreign molecule. The molecule is in mechanical equilibrium with totality of the solvent, but is not necessarily occupying a point of minimum energy with respect to its nearest neighbors. The force constants of the molecule is determined mainly by the interaction with the nearest neighbors.

Now suppose the active molecule undergoes an electronic transition accompanied by geometric changes. Electronic processes are many orders of magnitudes faster than vibrational relaxation. Therefore the solvent configuration should remain unchanged immediately after an electronic transition of the active molecule. This means that immediately after the transition, the active molecule "sees" a surrounding not in mechanical equilibrium with it. The shifts in vibrational frequencies would therefore be different from those obtained under equilibrium conditions.

To observe this effect, the fundamental frequency of a suitable molecule must be measured in the infrared, in the usual manner. Then the molecule must be excited electronically by whatever means necessary. Electronic relaxation will finally reach a metastable state, say the lowest triplet. Since triplet states are long lived, the surrounding will achieve equilibrium with it before emission. If one can detect the phosphorescent lines to the zero and one vibrational states of the ground electronic state, the effect we seek can be realized.

PROPOSITION IV

The C_2H Radical

Sensitized polymerization of acetylene has been analysed on the basis of free radical processes.(1) Kinetic data suggest strong likelihood of the presence of C_2H. However, no direct evidence of this radical has been established. The interest surrounding this molecule arises not only from the kinetic aspect but also from the electronic and the structural points of view.

Mercury photosensitization of acetylene coupled with the matrix-isolation technique seems to be an obvious approach in the positive identification of this molecule. The experimental conditions employed in photosensitization(2,3) appear quite compatible with those of matrix trapping. A mol ratio of inert gas or matrix material to active molecules in the order of a thousand is quite suitable in both cases. The procedure is simply to illuminate a flowing mixture of acetylene and, say, xenon, which has been exposed to mercury. The 2537 Å light source and the flow system have been described in detail by Lossing et al.(2) After the gas has passed the illuminated zone, it can be immediately deposited onto a cold window (4.2°K) of a low temperature spectroscopic cell, such as ours. The metastable frozen mixture can then be studied spectroscopically, chiefly in the UV region, but conceivably in the IR region also.

The problem of identifying the radical should not be too difficult, if it does occur as an intermediate in the reaction. The absorption due to mercury atoms in solid xenon is well known(4) and is quite localized. Acetylene shows no appreciable absorption above 2000 Å, even in a liquid xenon environment.(5) The C_2H radical is isoelectronic with CN and therefore is expected to absorb near the visible region. A possible complication can come from HgH which has two low lying electronic states. If this difficulty does arise, it may be possible to resolve it through vibrational analysis.

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PROPOSITION V

Possible Interesting Interaction between TCNE and Nitric Oxide

Tetracyanoethylene (TCNE) is known to form charge-transfer complexes with many Lewis bases, for example, the π electron molecules such as benzene and its derivatives.(1) The free energy of formation of these complexes and the frequency of the so-called charge transfer absorption have been shown to be roughly linear functions of the ionization potentials of the bases.(1,2) Mulliken(3) laid the theoretical foundations to the origin of this phenomenon. Briefly, it involves the overlap between the highest filled orbital of the donor and the lowest unfilled orbital of the acceptor. An electron from the donor orbital is supposed to be transferred to the acceptor orbital, giving rise to a kind of resonance stabilization. In effect, the complexing alters the ground electronic distributions of both partners. The perturbed electronic distributions should have a direct effect on the force constants of the bonds associated intimately with the orbitals involved. A simultaneous demonstration of this effect on the vibrations has been difficult. This is because one of the molecules in the complex has usually been an aromatic molecule, its delocalized π orbital being involved. The effect on the ring vibration is therefore relatively small. When the orbital is localized, the effect can be found, as in the halogens. An interesting case of a possible simultaneous observation is proposed here.

TCNE has been proved to be a good acceptor, probably utilizing its central carbon-carbon orbital. On complexing, the carbon-carbon stretching force constant should decrease due to the antibonding acceptor orbital. The delocalization of this orbital is much less than in the aromatic molecules. The effect should be observable. Although, this mode is not IR active, it probably becomes so when the symmetry of the molecule is destroyed upon complex formation. Nitric oxide with its 9.23 ev ionization potential should behave similarly to the aromatics, as far as complexing is concerned. The interesting point about NO in this regard is that its vibrational frequency has been shown to be very sensitive to the electron density in its outermost antibonding orbital.(4) If these arguments are correct, we should expect an increase in the NO frequency with concurrent decrease in the C=C frequency.

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Reprinted from the JOURNAL OF CHEMICAL PHYSICS, Vol. 36, No. 12, 3137–3140, June 15, 1962
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Spectroscopy in Liquid-Rare-Gas Solvents. Infrared Spectra of CH_4 in Argon and of HCl in Xenon*

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(Received November 24, 1961)

A low-temperature cell employing barium fluoride windows and indium metal gaskets has been built and is being used for the study of rotational, vibrational, and electronic motions of molecules in liquid rare gases. The ν_3 fundamental of CH_4 in liquid argon shows a single, relatively sharp Q branch. The P and R branches are probably present but apparently are lost in the wings of the Q branch. The infrared spectrum near 3.5 μ of HCl in liquid xenon shows well-resolved P, Q, and R branches, but the individual rotational lines are not resolved. The O branch is not resolved from the tail of the P branch, but there is some indication of the S branch on the high-frequency side of the spectrum. The Q branch is shifted 36 cm^{-1} to the low-frequency side of its gas-phase position. The appearance of O, Q, and S branches is expected because of the presence of an induced dipole moment through the polarizability of the solvent. The agreement between the observed spectrum and that anticipated on the basis of nearly free rotation gives good evidence for the existence of quantized rotational motions of HCl in liquid xenon.

I. INTRODUCTION

THE primary objective of this work is to obtain information concerning "local environments" in simple, dense fluids, such as argon, krypton, and xenon, through the study of rotational, vibrational, and electronic motions of dissolved solutes. If diffusional processes, i.e., large amplitude or random displacements, are very slow compared with the spectroscopic frequency, then the spectrum of the dissolved molecule is determined by the instantaneous configuration of its local environment. The observed spectrum is, of course, a superposition over the different local environments of all the solute molecules. On the other hand, if the measuring process is slow compared with random fluctuations, then the spectrum will be determined by the time average of the environmental perturbations. Recent neutron diffraction experiments[1] apparently

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* Supported in part by the National Science Foundation and the U. S. Army Research Office.

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‡ Contribution No. 2781.

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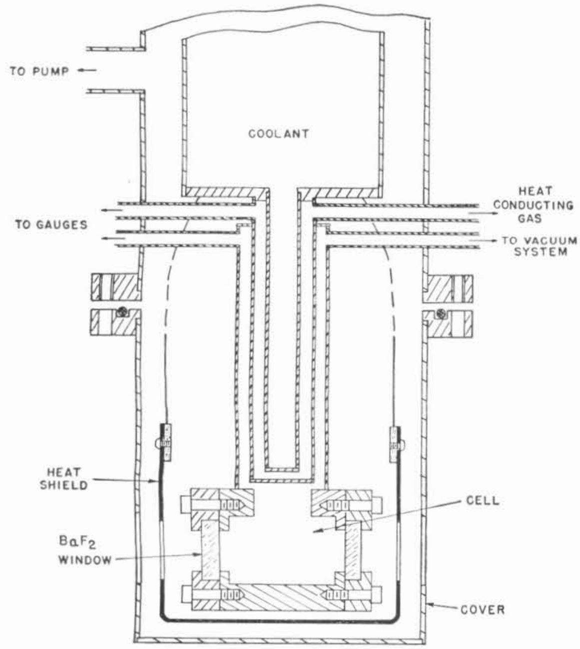

FIG. 1. Low-temperature infrared cell for liquid studies. The temperature of the cell may be adjusted by changing the thermal contacts to the copper heat shield, by varying the pressure of the conducting gas, and by changing the coolant.

indicate that the frequency of local density fluctuations in a liquid is low compared with oscillatory frequencies of the atoms or molecules about equilibrium positions in the liquid structure. This seems intuitively reasonable since the atoms or molecules in a liquid are bound by a potential energy of the order of the heat of vaporization, and this is about ten times larger than kT at the normal melting point of most nonpolar liquids. Thus, it appears that in the present experiments, a good assumption would be that the frequency of the measuring process, i.e., the internal vibrations, is high compared with the frequency of local density fluctuations. There are then four mechanisms responsible for spectral broadening. Different local environments in the fluid provide different intermolecular potentials, and the superposition of spectra of solute molecules in these different fields gives rise to broadening or even to line multiplicity in some instances.[2] In addition, the Franck-Condon effect with respect to quasi-lattice vibrations gives line broadening which results from a superposition of transitions involving the finely spaced vibrational levels of the solvent. In a pure liquid, rapid resonance transfer of vibrational or rotational excitation to neighboring molecules might give an important contribution to line broadening, and uncertainty broadening caused by short vibrational or rotational relaxation times might also contribute a few cm^{-1} to the vibrational or rotational line breadths. Lastly, the splitting of degeneracies due to asymmetric fields may be important.

Quantized rotation in the liquid phase has rarely been reported, not because, necessarily, molecules cannot undergo rotational motions *in the liquid state,* but because the various broadening mechanisms do not allow resolution of the individual rotational lines. It is therefore to be expected that only small molecules having large rotational constants will give resolvable spectra. The case of H_2[3,4] serves as the best example. Structure observed in previous solution spectra of the hydrides NH_3,[5] H_2O,[6,7] HCl,[8–11] and CH_4[12] could also be interpreted as arising from quantized rotational motions. Similar results have been obtained in the gas phase using high pressures.[13,14] The present paper will give further evidence which supports this view in the case of HCl in a very simple liquid solvent.

II. EXPERIMENTAL

A diagram of the apparatus is shown in Fig. 1. For the present experiments barium fluoride windows sealed to the cell by means of flange fittings and indium metal gaskets were employed. More reliable vacuum seals are obtained if the rims of the windows are first coated with platinum or gold[15] and the cell surfaces are "tinned" with indium metal. The cell is capable of withstanding pressures up to at least 15 atm so that the liquid range of the rare gases can be extended substantially beyond that possible at 1 atm. Argon, krypton, and xenon then form a useful set of liquid solvents over the entire temperature range −182° to −55° C. In the present experiments it was found unnecessary to use pressures higher than 6 atm. The path length of the cell is 5 cm, and the solute–solvent mole ratio necessary to obtain adequate absorption was found to be less than 0.001. Because of the small mole

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ratios used, it is not expected that solute–solute interactions play a significant role in the determination of the spectral line shapes.

The cell was constructed so that it would fit in the optical path of either a Perkin-Elmer model 21 or a Beckman IR-7 infrared spectrometer. The Beckman instrument was used to obtain the spectra discussed in this paper. Scanning speeds and slitwidths were chosen so that the instrument resolution was better than 2 cm^{-1}, a value which is more than adequate for resolution of the J structure in the CH_4 and HCl vapor-phase spectra.

As a result of outgassing or an extremely small leak in the vacuum connections to the Dewar, a very small amount of ice condensed on the cell windows. This condensate could not be detected visually, but its presence is revealed by an absorption band in the 3200 cm^{-1} region.

III. CH_4 IN LIQUID ARGON

The 3020 cm^{-1} ν_3 fundamental of CH_4 in liquid argon at $T\approx 100°$ K is shown in Fig. 2 and compared with the theoretical spectrum of the vapor at this temperature. Spin equilibrium is not assumed.[16] In analogy with the vapor-phase spectrum,[17] a strong Q branch occurs. The absorption in the vicinity of the Q branch maximum becomes very broad as the concentration of CH_4 is increased. The P and R branches probably contribute to this broadening, but they are not easily discernible as separately resolved components in the wings of the Q branch. The absence of good resolution of rotational branch structure in this case is therefore probably in part due to the dominance of Q branch intensity in the vicinity of the band origin.

Another reason why the resolution of structure in this system is made difficult may be associated with the fact that the excited level of the transition is triply degenerate. Local fields having low symmetry will remove the degeneracy to an extent depending upon the strength of the field in the region of each methane molecule. If the perturbations are large compared with the rotational line spacing, the rotational lines cannot be resolved.

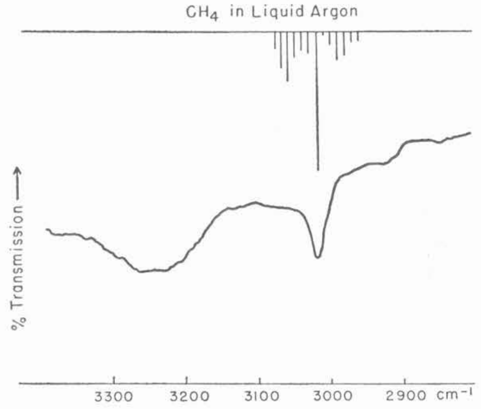

FIG. 2. The infrared spectrum of CH_4 dissolved in liquid argon at $T\approx 100°K$. The absorption near 3200 cm^{-1} is due to ice.

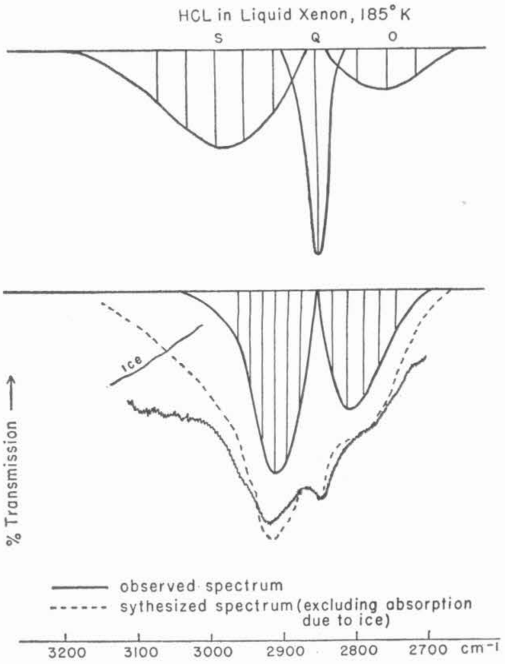

FIG. 3. The infrared spectrum of HCl dissolved in liquid xenon at $T\approx 185°K$. The synthesized spectrum is a superposition of O, P, Q, R, and S branches. The relative intensities of the P and R branches are those for the infrared spectrum of HCl vapor at $T=185°K$. The relative intensities of the S, Q, and O branches are those for the Raman spectrum of the vapor at the same temperature. The relative intensity of the Q branch with respect to the R and P branches was chosen so as to best fit the observed spectrum. The intensities are somewhat approximate, since broadening of the branches and intensity perturbations by the solvent were not taken into account.

Because of the difficulties associated with finding a polyatomic molecule suitable for the study of rotational structure in its solution spectrum, the choice of a diatomic molecule in a rare-gas solvent was made. The infrared spectrum of HCl in liquid xenon is discussed in the next section.

IV. HCl IN LIQUID XENON

The spectrum of HCl in liquid xenon at about 185° K is shown in Fig. 3, where it is compared with a theoretical gas-phase spectrum at the same temperature. The theoretical infrared spectrum is calculated according to formulas given by Herzberg,[18] and the induced spectrum which is Raman-like is obtained from formulas given by Placzek and Teller.[19] The most obvious interpretation of the structure is that it is the

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[18] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950) 2nd ed., p. 126.

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superposition of $O(\Delta J=-2)$, $P(\Delta J=-1)$, $Q(\Delta J=0)$, $R(\Delta J=+1)$, and $S(\Delta J=+2)$ branches associated with the HCl fundamental. Previous work[8–11] carried out on HCl in solution could not so easily lay itself open to such an interpretation, because the solvents were much more complicated than liquid xenon. However, except for variations in the Q-branch intensity, many of the earlier spectra are very similar to the spectrum observed here, and it is very likely that the structure in all cases is caused by "not-too-highly-hindered rotation" of HCl in these solutions. The S and O branches are too spread out to be resolved from the tails of the R and P branches. A slight change of slope observed on the high-frequency side of the R branch is probably caused by the S branch. The appearance of the O, Q, and S branches is expected since the presence of an induced dipole moment in the solute through external fields set up in the polarizable xenon environment can give rise to Raman selection rules.[20] The mechanism is similar to that by which infrared absorption by homonuclear diatomic molecules can occur in a high-density fluid.[13] For HCl, as for CH_4, the J structure is unresolved. Presumably, the presence of a variety of different local fields or the superposition of low-frequency quasi-lattice vibrations is sufficient to broaden lines by an amount which is large compared with the rotational line spacing, but which is not large compared with the separation of the branch maxima.

The Q branch is shifted 36 cm^{-1} to the low-frequency side of its gas-phase position at 2885.9 cm^{-1} [21] due to the usual dipole–induced–dipole and dispersion interactions. Buckingham[22] has given an expression for solvent shifts of vibrational transition energies. His more general expression for the relative change in angular frequency reduces to a power series,

$$\frac{\Delta\omega}{\omega}=C_0+C_1\left(\frac{\epsilon-1}{2\epsilon+1}\right)+C_2\left(\frac{\epsilon-1}{2\epsilon+1}\right)^2+\cdots, \tag{1}$$

in terms of the solvent dielectric constant ϵ when Onsager's[23] model for calculating the reaction field is employed. The term involving C_1 is the so-called Kirkwood–Bauer–Magat formula,[24] and it has been found that this term is adequate to describe shifts of HCl in other solvents.[8]

It is known that reasonably good values for the dielectric constants of liquids, whose molecules interact only weakly, may be obtained from the Clausius–Mossotti equation,

$$\frac{4\pi N}{3}\alpha=\frac{\epsilon-1}{\epsilon-2}\frac{M}{d}, \tag{2}$$

where N is Avogadro's number and M is the molecular weight. If the polarizability[25] α of atomic xenon and the density[26] d of liquid xenon are taken to be 4.0×10^{-24} cm^3 and 3.09 g cm^{-3}, respectively, Eq. (2) gives $\epsilon=1.93$. The reliability of Eq. (2) can be demonstrated for molecules such as CCl_4. It has also been shown experimentally for a rare gas,[27] argon, that deviations from Eq. (2) are indeed slight. Using the calculated value of ϵ and the empirical value of 0.06 for C_1,[8] one obtains a shift of -33 cm^{-1}. A value of 0.088 for C_1 has also been quoted by Josien *et al.*[28] This would give a shift of -48 cm^{-1}. Considering the approximations used, these values agree well with the observed shift of about -36 cm^{-1}. The agreement lends support to the validity of the assignment of the maxima.

One might argue that the maxima in the HCl–Xe spectrum are the result of combination librational or translational frequencies. It is very unlikely that the translational motions can account for the two side bands, since the frequency separations seem too small when account is taken of the high heats of vaporization of xenon and of HCl. Combination bands involving the quasi-lattice modes may occur. The separations of the side bands from the central band are about 75 cm^{-1}, while the Debye maximum frequency in solid xenon is only about 38 cm^{-1}.[29] The maximum lattice frequency for an HCl molecule in a xenon cage may be higher than 38 cm^{-1}, however, since the Debye frequency is of the order of 90 cm^{-1} [29] for pure solid HCl. Therefore, on the basis of the frequency separation in HCl alone, it would be difficult to rule out solvent combination bands as a possible cause of the side bands. However, the fact that the spectrum of DCl in solution[8] shows a decreased separation of the maxima cannot easily be explained on the basis of solvent frequencies.

That the structure is caused by highly hindered rotation of HCl is less likely here than for the case of a molecular solvent, considering the large "cavity" presented by xenon, coupled with the fact that the electronic charge density around each xenon atom is relatively much more simple than that in a molecular solvent. Certainly our arguments here are made stronger by the virtual absence of any side bands in the CH_4–argon spectrum. In addition, the good agreement between the observed spectrum and that anticipated on the basis of nearly free rotation gives, we believe, good evidence for the existence of quantized rotational motions of HCl in liquid xenon.

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