

ROTATIONAL RAMAN SPECTRA OF HCl, DCl, AND HBr IN SOLUTION

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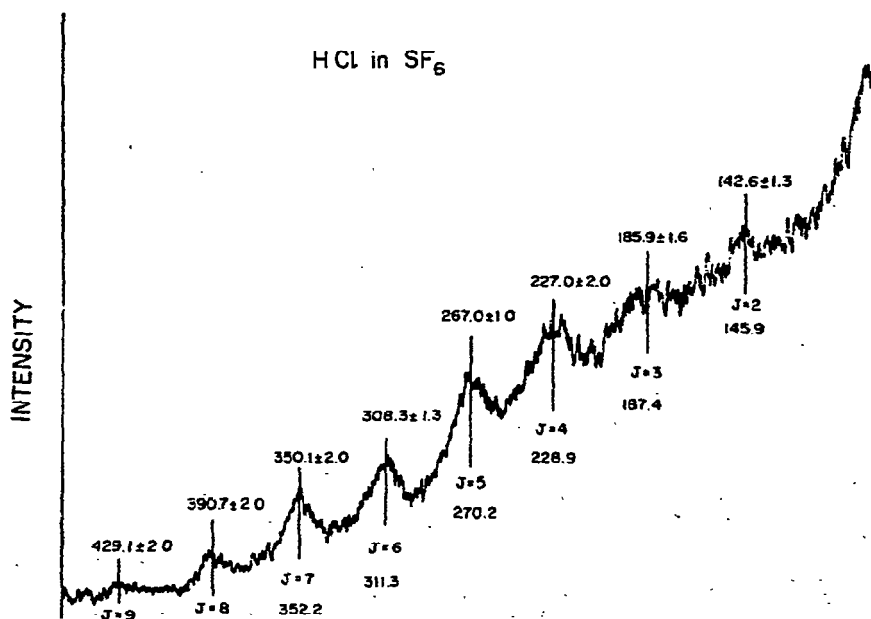
The low frequency Raman spectra of dilute solutions of HCl, DCl, and HBr dissolved in liquid SF_6 and C_2F_6 consist of partially resolved features corresponding to the gas phase rotational lines. Transitions from $J = 1$ for HBr and $J = 2$ for HCl were identified. These results and those from far infrared spectra are examined in terms of existing theories.

Study of Raman spectra of diatomic molecules dissolved in various organic solvents has allowed us to observe the phenomenon of "quasi free rotation" in the liquid phase, and thus to extend some recent infrared results [1,2]. We present

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here Raman spectra of HCl, DCl and HBr dissolved in liquid SF_6 and C_2F_6 at about 1:15 mole fraction. Each of these solvents weakly perturbs the vibrational frequency of the solute diatomic molecules.

Near the exciting line (4880 Å of the argon ion laser) we have observed series of maxima with frequencies close to those of the pure rotational



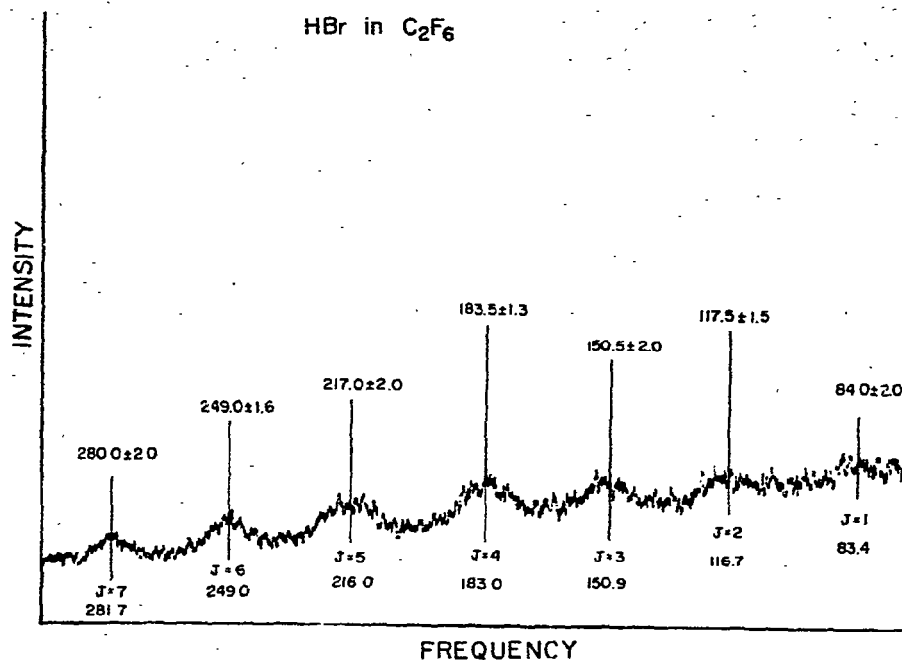


Fig. 2. The pure rotational Raman spectrum (Stokes) of HBr dissolved in liquid C_2F_6 at $288^\circ K$. The observed frequency (above the curve), the J value of the initial state, and the corresponding calculated gas frequency (below) are given for each band. The latter were obtained by using the following rotational constants [6, 7]: $B_0 = 8.34 \text{ cm}^{-1}$, $D_0 = 386 \times 10^{-6} \text{ cm}^{-1}$.

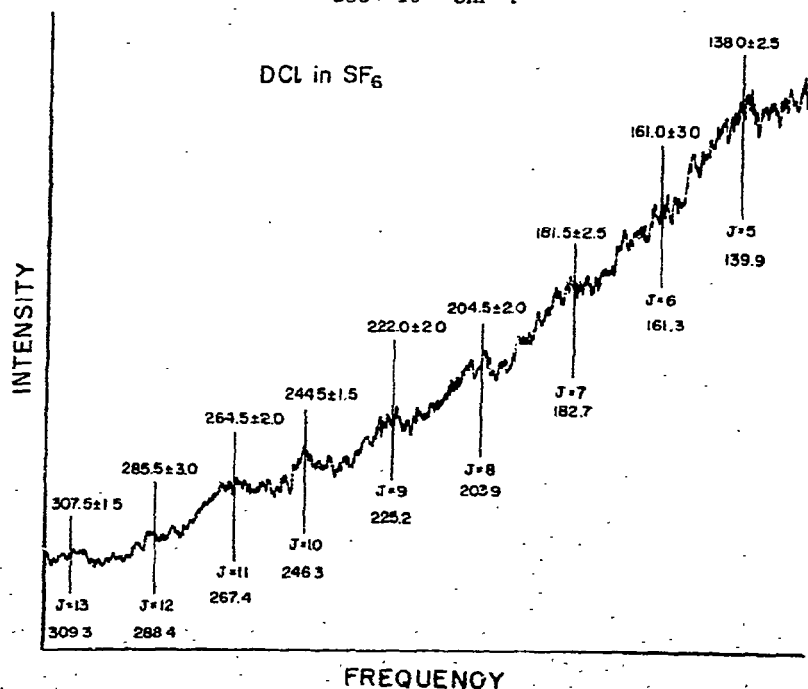


Fig. 3. The pure rotational Raman spectrum (Stokes) of DCl dissolved in liquid SF_6 at $293^\circ K$. The observed frequency (above the curve), the J value of the initial state, and the corresponding calculated gas frequency (below) are given for each band. The latter were obtained by using the following rotational constants [6, 8]: $B_0 = 5.39 \text{ cm}^{-1}$, $D_0 = 140 \times 10^{-6} \text{ cm}^{-1}$.

gas spectra (see figs. 1, 2 and 3). Each frequency measurement was repeated at least three times for two different sample cells and the quoted error limits indicate the entire range. The profiles of these bands are very much broader than those obtained for the gases, which are usually determined by the spectral slitwidth. For example the apparent half band widths for HCl and HBr dissolved in C_2F_6 , observed with a slitwidth of 4 cm^{-1} , are respectively 20 ± 2 and $14 \pm 2\text{ cm}^{-1}$. Moreover, if we compare the peak height of the strongest rotational line to that of the vibrational Q branch, we find a ratio of roughly 1:1 for the gases and less than 1:10 for the solutions.

In these and other solutions we observed a solvent dependent broadening of the vibrational Q branch; this will be the subject of a subsequent paper.

If we compare our experimental Raman results for HCl in solution to those obtained in IR by Birnbaum and Ho [1], we see that a larger number of transitions has been observed in the Raman spectrum, in particular for low J values. Our DCl rotational spectra were less easily resolved (fig. 3) because of the bandwidth and the smaller frequency spacing.

The comparison of infrared and Raman data yields new information about rotation of polar molecules in the liquid phase. These data do not support the idea [3] of the existence of two kinds of molecules; those with high energy which are freely rotating, and those with rotational energy below a barrier hindering rotation. This hypothesis leads to the contradiction that a barrier of about 200 cm^{-1} is obtained from infrared data

(since the first observed transition is $4 \rightarrow 5$) while a value of 60 cm^{-1} is calculated from the Raman data (since we are able to observe the $2 \rightarrow 4$ transition). Further, the observation of the $2 \rightarrow 4$ transition for HCl, and $1 \rightarrow 3$ for the HBr, close to their respective gas frequencies seems to indicate that the low rotational energy levels for these molecules are not perturbed as much as predicted by the calculations of Galatry and Robert [4]. Finally, in contrast to the J dependence of the frequencies of the rotational lines observed in the infrared vibration rotation spectrum of HF in SF_6 [2], we have observed no J dependence for the molecules studied here.

It appears that the existing theories are unable to explain both the infrared and Raman results.

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