Interferometric Study of Rotational Motion of Hydrogen Halides Trapped in Low-temperature Matrices

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Summary The rotation of HCl and DCl in argon matrices at 20° K has been verified and the frequencies of the $J = 1 \leftarrow J = 0$ transitions measured; rotation does not occur in a nitrogen matrix.

THE $J = 1 \leftarrow J = 0$ rotational transitions of HF and DF in noble-gas matrices have been reported[1] but, although HCl, DCl, HBr, and DBr isolated in these matrices have been examined in the far i.r.[2] the $J = 1 \leftarrow J = 0$ transitions were not observed because the frequencies were below the lower limit (33 cm.$^{-1}$) of the particular spectrometer used.

In order to verify that these molecules rotate in argon matrices, but not in nitrogen, as inferred from studies of the vibration–rotation spectral regions,[3] a R.I.I.C. FS-720 Fourier spectrophotometer was used in conjunction with an Air Products and Chemicals, Inc. AC-2 "Cryo-Tip." The interferometer sample compartment lid was modified to provide an O-ring seal round the vacuum shroud of the cryostat. This is, we believe, the first use of an interferometer for spectral studies of matrix-isolated species.

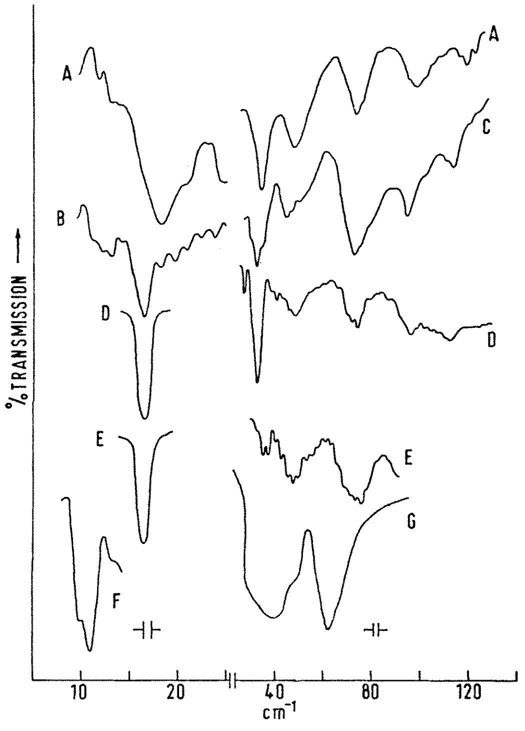

FIGURE. *Far i.r. spectra of* (A) HCl, M : A = 1000, 17 *μmole;* (B) HBr, M : A = 500, 62 *μmole;* (C) HBr, M : A = 500, 143 *μmole;* (D) HI, M : A = 300, 210 *μmole;* (E) HCN, M : A = 500, 122 *μmole;* (F) DCl, M : A = 1000, 51 *μmole;* (G) Xe (55° K) M : A = 200 (*redrawn from ref.* 5); *in argon at* 20° K. *The structure on the bands is due to the residual effects of interference fringes from the support window.*

The samples of HX in argon, which were deposited on a silicon window at 20° K, were examined at M : A (matrix : absorber) ratios of 1000 and 500. Multimer absorptions[4] at *ca.* 200 cm.$^{-1}$ and a complex series of absorptions from 120 to 20 cm.$^{-1}$ were observed. The latter bands exhibit considerable similarity irrespective of the nature of the solute molecule (Figure) and are tentatively assigned to phonon bands activated by the trapped species.[5] As the polarity of the solute molecule decreases, the overall intensity of the absorptions decreases markedly; on increasing the solute concentration, these bands become weaker and tend to merge into a broad absorption. The peaks occur at *ca.* 34, 48, 73, 97, and 115 cm.$^{-1}$; the first two coincide roughly with pure rotational lines reported for H_2O in argon,[6] but we observed no absorption due to water in the vibrational region and also the behaviour of these bands does not fit such an interpretation. Jones and Woodfine[5] observed phonon band maxima at *ca.* 42 and 64 cm.$^{-1}$ for argon, *i.e.* in the same region as the three lower-frequency bands that we observed. While the spread of the phonon bands out to 120 cm.$^{-1}$ is surprising, it is difficult to find an alternative explanation. Since the band at *ca.* 73 cm.$^{-1}$ appears for HI and HCN, as well as for HCl and HBr, this absorption must be due to an activated phonon band rather than to a localised mode.[2]

Below 20 cm.$^{-1}$, strong absorptions were observed for HCl, DCl, and HBr in argon at 18·6, 10·9, and 16·2 cm.$^{-1}$, respectively (Figure), which could reasonably be assigned to the $J = 1 \leftarrow J = 0$ transitions. However, a medium-intensity band was observed at 16·5 cm.$^{-1}$ for HI and HCN (presumably, like the higher-frequency absorptions, a phonon band), thus casting some doubt on the assignment for HBr. Also, the frequencies of the $J = 1 \leftarrow J = 0$ transitions of HF, HCl, and DCl are similar to the values of $[R(0) - P(1)]/2$ derived from the vibration–rotation spectra in argon matrices, whereas the value of 16·2 cm.$^{-1}$ for HBr is considerably larger than expected (Table).

TABLE. *Rotational transitions of hydrogen halides in argon matrices*

HX	Gas $J=1 \leftarrow J=0$	Ar matrix $J=1 \leftarrow J=0$	Ar matrix $[R(0) - P(1)]/2$
HF	41·9	44·0[a]	43·5
DF	22·0	27·3[a]	—
HCl	20·9	18·6	17·0
DCl	10·8	10·9	9·9
HBr	16·7	16·2(?)	9·5
DBr	8·5	—	4·4

[a] Ref. 1.

There was no detectable absorption at lower frequency for HBr nor was a band observed for DBr, although in the latter case the frequency could be below the range of these measurements.

Although it had generally been thought that rotation does not occur in a nitrogen matrix,[7] Harvey and Shurvell[8] recently reported the presence of rotational features for HCl and HBr in this matrix. A reinvestigation of HX in nitrogen[3] suggested that rotation is *not* occurring; in the present work HCl in a nitrogen matrix showed no absorption below 20 cm.$^{-1}$, confirming this result.

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