

## Evidence for the Rotation of HCl in a Solid Nitrogen Matrix

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SINCE the early work of Becker and Pimentel,<sup>1</sup> it has been tacitly accepted that small molecules do not have rotational freedom when trapped in solid nitrogen.<sup>2</sup> We present evidence from infrared absorption studies for rotation of the HCl molecule in a solid nitrogen matrix at liquid-helium temperatures.

Our experiments were carried out using a low-temperature cell of conventional design.<sup>3</sup> Various mixtures of HCl and nitrogen were deposited on a liquid-helium-cooled CsI window and the infrared spectra of the deposits were recorded, using a Perkin-Elmer 112G spectrometer. The Table lists the observed frequencies and absorbances for various temperatures, at two  $N_2$ :HCl ratios. The Figure shows the spectrum of HCl in nitrogen at 5° and 15°K at a matrix-to-solute ratio of 200 to 1.

It is necessary to establish that the observed spectra arise from isolated HCl molecules and not from dimers or higher polymers. This is supported by the frequencies of the observed peaks and their concentration dependence. The gas-phase frequency of  $R(0)$  of HCl is  $2905\text{ cm.}^{-1}$ . In an argon matrix  $R(0)$  occurs at  $2888\text{ cm.}^{-1}$  and in krypton at  $2873\text{ cm.}^{-1}$ .<sup>4-7</sup> Dimers and trimers give rise to absorptions at much lower frequencies.<sup>4,5,8,9</sup> The gas-matrix shifts can be explained satisfactorily in terms of induction, dispersion, and repulsive interactions between the trapped molecule and the surrounding matrix.<sup>4</sup> We have assigned the strong peak at  $2852\text{ cm.}^{-1}$  in the spectrum of HCl in nitrogen to  $R(0)$ . The larger red-shift in the nitrogen matrix arises from an additional electrostatic attraction term, due to interaction of the dipole of HCl with the quadrupole of nitrogen.

The frequencies of the peaks assigned to  $P(1)$  and  $R(1)$  are  $2814$  and  $2875\text{ cm.}^{-1}$  respectively. The intensity of  $R(1)$  is much lower than that of  $P(1)$ . This has also been observed for HCl in the

noble-gas matrices.<sup>4-7</sup> The  $R(1)$ - $P(1)$  separation in the matrix is the same as in the gas phase and the  $R(0)$ - $P(1)$  and  $R(1)$ - $R(0)$  separations are close to the gas-phase values. The concentration-dependence of ratios of absorbances of  $R(0)$  to  $P(1)$  and  $R(0)$  to  $R(1)$  at fixed temperatures are consistent with our assignment of these peaks. The

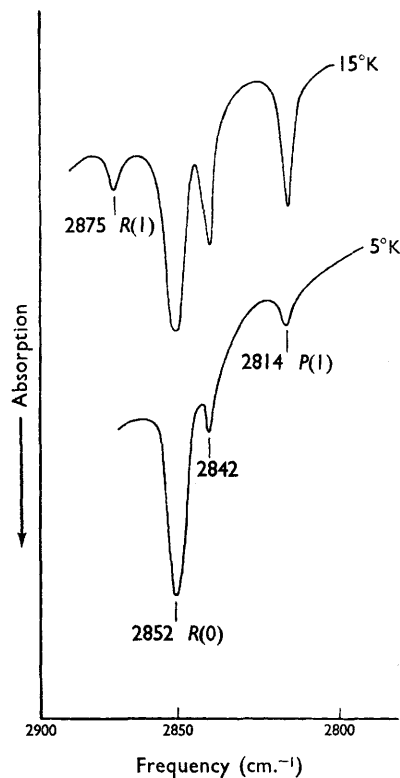


FIGURE. Infrared absorption of HCl in solid nitrogen,  $N_2$ :HCl = 200:1.

TABLE

Infrared absorption of HCl in solid nitrogen

Gas	Frequencies		Absorbance relative to $R(0) = 1.00$				Assignments	
	Gas	Matrix	$\Delta\nu$	$N_2$ :HCl = 200:1		$N_2$ :HCl = 360:1		
				5°K	15°K	5°K	25°K	
2925	2875	-50	—	—	0.09	0.05	—	$R(1)$
2905	2852	-53	1.00	1.00	1.00	1.00	1.00	$R(0)$
—	2842	—	0.03	0.31	—	—	0.29	—
2864	2814	-50	0.04	0.29	—	—	0.19	$P(1)$

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temperature-dependence of these ratios also supports our assignments.

Peaks arising from HCl dimers and higher polymers have been observed in rare-gas matrices at low matrix-to-solute ratios.<sup>4,5,8</sup> The frequency assigned to HCl dimer in an argon matrix was 2818 cm.<sup>-1</sup>,<sup>5</sup> and in a krypton matrix 2815 cm.<sup>-1</sup>.<sup>8</sup> In a nitrogen matrix, dimers, if formed, would be expected to absorb at lower frequencies. Thus it is extremely unlikely that our observed peaks at 2875, 2852, and 2842 cm.<sup>-1</sup> could be due to HCl dimers or polymers. The peak at 2814 cm.<sup>-1</sup> is also above the expected region of dimer absorption.

The peak at 2842 cm.<sup>-1</sup> has not been assigned. A peak has been observed in a similar position,

between  $R(0)$  and  $P(1)$ , in the spectrum of HCl in argon.<sup>4-6</sup> This peak has been called " $Q$ "<sup>5,6</sup> because it occurs in the region of the "forbidden"  $Q$ -branch. However, the alternative suggestion has been made<sup>10</sup> that this peak is due to an interacting pair of HCl molecules in non-nearest-neighbour sites.

HBr and D<sub>2</sub>O have also been studied in solid nitrogen and their spectra show multiplets in the monomer regions. We believe that these multiplets also arise from rotational transitions, but the interpretation of the spectra is not as straightforward as for the HCl case.

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