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THE HCl STRETCHING VIBRATION IN HCl/DCl MIXED CRYSTAL

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ABSTRACT The HCl stretching vibration in HCl/DCl mixed crystals has been studied using model intermolecular potentials.The contribution of electrostatic and atom-atom interactions are discussed.

In a recent paper [1] we have discussed the intramolecular vibration of orthorhombic HCl crystal using an intermolecular potential that includes interactions among dynamic molecular dipoles and quadrupoles. All the features of the infrared spectrum (Davidov and TO-LO splitting,band shape) could be satisfactorily explained. The intermolecular potential was parametrized to fit the crystal data with inclusion of long range effects. It can be of interest to check if the potential is also suitable to explain the infrared absorption in mixed HCl/DCl crystals where dynamic interactions are confined to the limited region of clusters of the guest molecules and dynamic long range effects are absent. This check may be of interest also in connection with studies of HCl clusters in inert matrices [2]. In fact in matrix isolated HCl there is the simultaneous problem of the static (equilibrium configuration) and vibrational properties of the clusters while in isotopic mixed crystals the possible structure of the clusters is rigorously known from the crystal structure determination.

THE HCl/DCl MIXED CRYSTAL

This study will be confined to the low temperature phase where HCl and DCl are isomorphic [3] . Since the bond lenghts of the isotopic molecules are not greatly different we can safely assume that the HCl molecules arrange in the DCl lattice without substantial distortion of the host lattice.We will concentrate the attention in the HCl stretching region of mixed crystals with approximate HCl/DCl ratio 7:100 since the spectra of crystals with this composition have been carefully measured by Brunel [4,5] .In this range of composition we must deal essentially with isolated molecules and with a distinct concentration of dimers of the guest molecules,while the concentration of trimers is negligible [6] .Since DCl crystallizes in a slightly distorted face centered cubic structure [3] there are twelve nearest neighbour positions to be considered about a given origin molecule. The molecular arrangement is shown in Fig.1 where it can be seen that the twelve HCl dimers can be arranged into four distinct types differing for the mutual molecular orientation or intermolecular separation. This is summarized in Table 1. It is reason

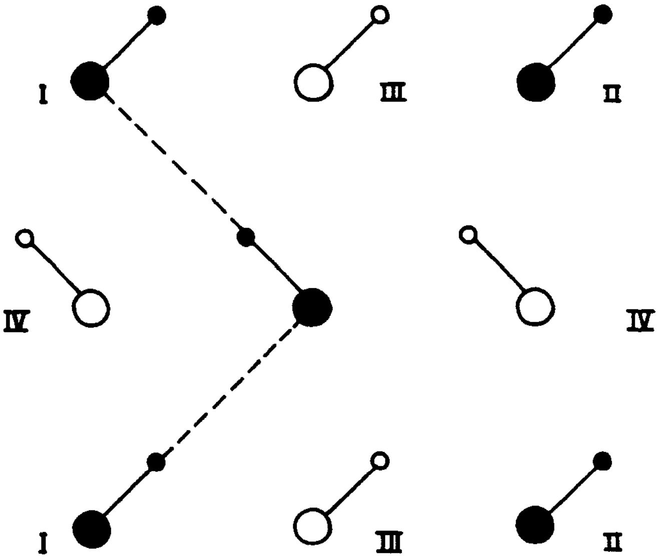

Fig.1- Structure of DCl viewed along the c axis showing nearest neighbours of a central origin molecule.Solid circles indicate atoms at $z=\pm c/2$,open circles indicate atoms at $z=0$.

able to assume that the 12 HCl dimers have the same probability of occurence in the DCl lattice. As matter of fact,whichever the structure of the dimer,the same number and type of hydrogen bonds will be present in the crystal.

THE HCl DIMER SPECTRUM

In the concentration range of interest in the present study,the major problem for the interpretation of the infrared absorption of the mixed crystal is the calculation of the vibrational frequencies of the dimer. Calculation are easily performed with the exciton model already used for the pure crystal [1] considering the much simpler two molecule system. Using an electrostatic potential with resonant dipole-dipole, dipole-quadrupole and quadrupole-quadrupole terms the calculated splittings for the various possible dimers reported in Table 2 are obtained. The relative contributions of the various electrostatic terms are quite different than in the neat crystal [1] . It is seen from the table that only for the hydrogen bonded dimer of type I the splitting is appreciable. Therefore the absorption for type I dimer shuld be distinct from the monomer band while the absorption from the other dimers should overlap with that of the monomer. This is in fact observed experimentally. In the infrared spectrum only two

Table 1- Intermolecular distances,cell indices and relative orientations of nearest neighbours in the DCl lattice.

Type	Distance (Å)	Cell indices of 2nd molecule §	relative orientation
I	3.6767	(-1-1 0),(-1-1-1)	perpendicular
II	3.7463	(0 0 0),(0 0-1)	perpendicular
III	3.9756	(-1 0 0),(-1 0-1) (0-1 0),(0-1-1)	perpendicular
IV	3.8655	(1 0 0),(-1 0 0) (0 1 0),(0-1 0)	parallel

§Indices of the primitive lattice.Origin molecule is in the (0 0 0) cell.

Table 2- Electrostatic contribution to the frequency shift (cm^{-1}) of the symmetrical mode of the HCl dimer.

Type	d-d	d-q	q-q	total
I	- 0.51	- 3.22	- 3.17	- 6.90
II	- 0.30	2.81	- 2.92	- 0.41
III	- 1.74	0.08	- 0.19	- 1.85
IV	1.11	0.00	- 1.02	0.09

d-d= dipole-dipole; d-q = dipole-quadrupole; q-q = quadrupole-quadrupole

side peaks are observed,symmetrically displaced with respect to the monomer peak [4,5]

The calculated splitting for type I dimer is,however, only of about 14 cm^{-1} compared to the experimental observation of 22 cm^{-1} [4,5] There are various possible sources of the observed discrepancy. The first can be a temperature effect. In fact the crystal structure has been determined at 100°K and the infrared experiment has been performed at 40°K and 20°K [4,5] . In the high temperature phase there is an appreciable temperature variation of the lattice constant [7] A similar variation can be expected for the low temperature crystal,also by comparison with known data on the other simple crystals. With the reduction of the intermolecular separation,the electrostatic interation could consequently increase.As a matter of fact in crystalline HCl and DCl some effect of the temperature on the factor group splitting has been found experimentally [4,8,9].

It is difficult to estimate a priori the extent of variation of unity cell parameters in DCl. However,in the temperature range from 100°K to 40°K a 4% decrease of the nearest neighbours distance is reasonable and would lead to a 2.5 cm^{-1} increase of the dimer splitting. The unit cell contraction can thus have an effect on the splitting but cannot fully explain the observed discrepancy between calculated and observed values.

We also investigated the contribution to the dimer splitting of short range interactions represented by atom-atom potentials. A special atom-atom was used for the hydrogen bonded Cl··· H contact. Alternatively,the interaction of the hydrogen-bonded pair was represented by a Morse potential. The parameters of the potentials were taken from lattice dynamics calculation on pure HCl crystal [10,11] .

The atom-atom cntribution is appreciable only for type I dimer,as discussed below.

In an isolated two molecules system the atom-atom interaction gives rise to a splitting of the order of 15-20 cm^{-1} depending on the type of potential used. This splitting is asymmetric in the sense that it is mainly due to differences in the diagonal terms of the interaction matrix, since the intermolecular interaction in an isolated dimer is essentially asymmetric.

The splitting due to atom-atom interactions of an HCl dimer embedded in a linear chain of DCl molecules is on the contrary small and symmetrical with respect to the frequency of the monomer,the value being of the order of 1-2 cm^{-1},a result comparable to that obtained for the pure crystal.

These calculations assumed that the HCl···HCl and HCl···DCl potentials were identical. On the basis of the results obtained for an isolated dimer it can be guessed that a larger atom-atom contribution would be obtained by assuming that the interaction of an HCl molecules with an identical or with an isotopic molecule are not identical. This is not unconceivable for the hydrogen-bond contacts [12] . We have made attempts to make reasonable changes in the parameter of the Morse potential representing the minimum of potential curve. A splitting as large as 4 cm^{-1} can be obtained.

In conclusion it is seen that if the effects of the temperature lowering and short range contribution are includes as described above a dimer splitting of 20 cm^{-1} can be obtained,in good agreement with experimental observations.

INTENSITY DISTRIBUTION IN THE INFRARED SPECTRUM

The calculation described above show that the infrared spectrum of the HCl trapped in the isotopic crystal should

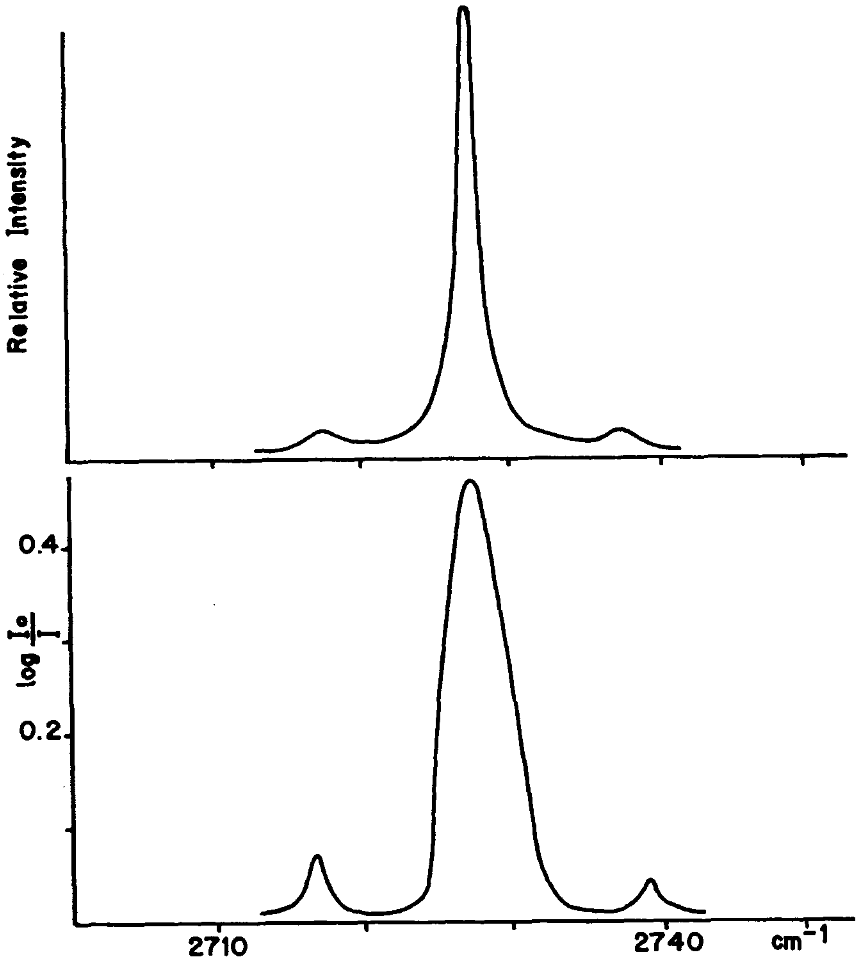

Fig.2- Calculated (upper curve) and observed (lower curve) infrared absorption in HCl/DCl mixed crystals,with composition 7.5 :100

consist of a central peak,due to the monomer and to type II, III,IV dimers,and two side peaks due to type I dimer.In the infrared spectrum it is found that the "monomer" peak has an half width of 5 cm^{-1} compared to a half width of 1.5 cm^{-1} for the dimer peaks. The larger width of the "monomer" peak can be explained as arising from overlap of different bands. We have calculated the infrared spectrum of the mixed crystal in the HCl stretching region with the following assumptions:

a) the half width of the bands is 1.5 cm^{-1};

b) the type I dimer splitting is 20 cm^{-1} including electrostatic and atom-atom contribution, as discussed above;

c) the relative abundance of the monomer with respect to the dimers follows the distribution law reported by Behringer [6];

d) the intensity of the dimer peaks has been calculated in the oriented gas approximation [1].

The observed and calculated spectra are compared in Fig.2, where it can be seen that the agreement is reasonable.

The calculated ratio of the central to the side peaks intensity is approximately 15 to be compared with an extimated experimental ratio of 10.

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