

04.5-13 LATTICE-DYNAMICAL EVALUATION OF INTERNAL MODE CONTRIBUTIONS TO TEMPERATURE FACTORS FOR A SERIES OF HYDROCARBONS: A SYSTEMATIC APPROACH. By C.M.Gramaccioli, Institute of Mineralogy, and G.Filippini, Institute of Physical Chemistry, University of Milan, and C.W.R. Centre, I-20133 Milan, Italy.

For rigid organic molecules, deriving temperature factors via a lattice-dynamical Born-von Karman procedure leads to satisfactory agreement with experimental data, and sometimes even a significant improvement with respect to the least-squares fit of molecular tensors to B's can be achieved (Filippini et al., Acta Cryst. (1974), A30, 189). Internal mode contribution is nearly negligible for small rigid molecules, whereas even for a molecule like anthracene it should be accounted for (Scheringer, C., Acta Cryst. (1972) A28, 516; Ishii, M. et al., Acta Cryst. (1979) A35, 613). Whereas calculations on particular single molecules are continuously reported in the literature, here a possible routine procedure for at least a whole group of compounds, such as polynuclear aromatic hydrocarbons, is proposed. In view of the essential rigidity of these molecules, and of the relatively limited accuracy required in dealing with the minor internal contributions to the B's, as a first approximation the contributions of external and internal vibration modes are considered separately; moreover, some generalized valence force fields, which give good results for benzene, naphthalene and anthracene can be safely extended to larger molecules. For instance, for planar vibrations, the simplified valence force field of Neto, Scrocco & Califano (Spectrochimica Acta (1966) 22, 1981) gives good to excellent agreement with experimental frequencies for several hydrocarbons; other generalized force fields for non-planar vibration modes are currently proposed (Evans, J & D.B.Scully, Spectrochim. Acta (1964) 20, 891). Since the 'standard' F-G method essentially involves a laborious elimination of the redundant symmetry coordinates, the Gwinn method (J. Chem. Phys. (1970) 55, 477) permits a generalized approach which can be fully automatized, and which can be easily connected with the usual lattice-dynamical routines applied to molecular crystals.

Examples relative to naphthalene and other hydrocarbons can be easily obtained. Extension to non-rigid molecules, i.e. with mixed internal and 'lattice' modes, is comparatively easy, and -if properly treated- may involve a quite reasonable computing time.

04.6-01 HYDROGEN CORRELATION FUNCTIONS IN Ih ICE. By J.Schneider, Institut für Kristallographie und Mineralogie, Universität München, West Germany

The H-H correlation functions (CFS) of Ih-ice due to the Bernal-Fowler ice rules had been calculated (J.Villain, J.Schneider, in Phys. and Chem. of Ice, Roy.Soc. of Canada, Ottawa 1973) in Q-space by a random walk approximation (RWA). Experimental results of diffuse elastic neutron scattering showed, besides additional diffuse streaks, excellent agreement with predictions of RWA. (J.Schneider, C.Zeyen, J.Phys.C (1980) 13, 4121) This work presents the numerical fourier-transforms of the 3-D Q-space CFS of RWA to show a 3-D R-space image of the local order induced by the ice rules. The 8 O-H-O bonds per unit cell yield 36 H-H CFS which are reduced by symmetry to 2 nonequivalent self-CFS and 6 nonequivalent distinct-CFS. The self-CFS have the shape of double-clubs of rotational symmetry along the respective bonds. The distinct-CFS have the shape of discs whose axis lies in a plane given by the two respective O-H-O bonds and pointing at right angle to the vector joining the two bond centers. The decay of the CFS shows a R^{-5} and thus long range behaviour supporting the 'criticality' of ice shown theoretically. (J.Villain, Sol.St.Comm. (1970) 10, 967)

04.6-02 HYDROGEN BONDS BETWEEN WATER AND SULFUR IN SALT HYDRATES.

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Studies on hydrogen bonds between water and sulfur in hydrated sodium salts have been undertaken in order to find out relationships between the geometry and the energy of O-H(D)...S type hydrogen bonds. Accurate geometrical data from neutron and X-ray diffraction and spectroscopical data are available for O-H(D)...S bonds in $\text{Na}_2\text{S}\cdot 9\text{D}_2\text{O}$, $\text{Na}_3\text{PS}_4\cdot 8\text{H}_2\text{O}$, $\text{Na}_3\text{AsS}_4\cdot 8\text{D}_2\text{O}$, $\text{Na}_3\text{SbS}_4\cdot 9\text{D}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$. Following types of interaction between water and sulfur have been observed in these examples:

(a) approximately linear O-H(D)...S type hydrogen bonds with $0\dots\text{S} = 3.19\text{-}3.55 \text{ \AA}$, $\text{H(D)}\dots\text{S} = 2.25\text{-}2.59 \text{ \AA}$ and angles $\text{O-H(D)}\dots\text{S} = 153\text{-}180^\circ$;

(b) bifurcated O-H(D)...S,S type hydrogen bonds, almost symmetrically branched with $0\dots\text{S} = 3.36\text{-}3.65 \text{ \AA}$ and $\text{H(D)}\dots\text{S} = 2.71\text{-}2.85 \text{ \AA}$;