

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 $\text{O}\dots\text{S} = 3.19\text{-}3.55 \text{ \AA}$, $\text{H}(\text{D})\dots\text{S} = 2.25\text{-}2.59 \text{ \AA}$ and angles $\text{O-H}(\text{D})\dots\text{S} = 153\text{-}180^\circ$;

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

(c) hydrogens with $H(D)\dots S > 3.1 \text{ \AA}$ [$H(D)\dots O > 2.70 \text{ \AA}$], far outside the usual hydrogen bond range.

Vibrational spectroscopic investigations on isotopically dilute (H and D) single crystals, measured at 295 K and 75 K, showed uncoupled O-H(D) stretching frequencies in the range $\tilde{\nu} = 2345\text{--}2665$ (3145-3620) cm^{-1} . According to the Badger-Bauer rule these frequencies would correspond to hydrogen bond energies of 5-40 kJ mol^{-1} . Reasonable assignments of the observed frequencies to the individual hydrogen bonds could be made. For the approximately linear O-H(D) \dots S type bonds with $H(D)\dots S = 2.35 \text{ \AA}$ ($O\dots S = 3.3 \text{ \AA}$) uncoupled O-H(D) frequencies of $\tilde{\nu} = 2400\text{--}2520$ (3220-3410) cm^{-1} were observed, the specific values depending significantly on the chemical nature of the S acceptor atoms. Despite large $H(D)\dots S$ distances (2.71-2.85 \AA) the bifurcated O-H(D) $\dots S_2$ bonds show stretching frequencies which are similar to those of linear O-H(D) $\dots S$ bonds with $H(D)\dots S = 2.35 \text{ \AA}$. The type (c) hydrogen atoms observed in $\text{Na}_3\text{PS}_4 \cdot 8\text{H}_2\text{O}$ and $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$ exhibit O-H(D) frequencies of $\tilde{\nu} = 2665$ (3620) cm^{-1} which indicate some crystal field interactions with the surrounding atoms.

04.6-03 X-RAY AND NEUTRON DIFFRACTION STUDIES OF THE HYDROGEN BONDING IN HYDROXYBENZOPHENONES. By E.O. Schlemper and M.S. Hussain, Department of Chemistry, and Fred Ross, Research Reactor Facility, University of Missouri, Columbia, Missouri, U.S.A. In order to examine hydrogen atom positions in O---O hydrogen bonds of intermediate strength, we have undertaken diffraction studies of several hydroxybenzophenones. The crystal structure of 2,4-dihydroxybenzophenone (Liebich, Acta Cryst. (1979) B35, 1186) revealed an intramolecular O---O hydrogen bond (2.55 \AA). We have completed a neutron study of that compound and will present accurate hydrogen positions as well as an X-N deformation density study of the hydrogen bond. In addition X-ray studies of 2,2',4,4'-tetrahydroxybenzophenone and 2,2'-dihydroxybenzophenone will be presented. In the former there are two symmetry independent molecules in space group $P\bar{1}$. Each has two unique intramolecular O---O hydrogen bonds involving the carbonyl oxygen with the 2 and 2' hydroxy groups. The O---O distances are 2.52, 2.58, 2.62, and 2.72 \AA at the present stage of refinement ($R=0.034$). In addition there are intermolecular hydrogen bonds involving the hydrogen atoms of the 4 and 4' hydroxy groups. These involve O---O distances of 2.76, 2.76, 2.87, and 3.01 \AA , and O-H---O angles from 145 up to 175 $^\circ$. Whereas the two six membered aromatic rings in 2,4-dihydroxybenzophenone are nearly mutually perpendicular, those in 2,2',4,4'-tetrahydroxybenzophenone are more nearly coplanar (dihedral angles of 42 and 44 $^\circ$) because of the intramolecular hydrogen bonding between the carbonyl oxygen and both the 2 and 2' hydroxy groups.

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04.6-04 THE CRYSTAL STRUCTURE OF THE ADDITION COMPOUND OF FLUOROSILICIC ACID WITH UREA. By Ze-Ying Zhang, Mei-Cheng Shao, Xiao-Jie Xu and You-Chi Tang, Institute of Physical Chemistry, Peking University, Beijing, China; Yu-Qin Tu, Institute for Plant Protection Research, Chinese Academy of Agricultural Sciences, Beijing, China.

The addition compound $((\text{NH}_2)_2\text{CO})_4 \cdot \text{H SiF}_6$ crystallizes in tetragonal space group $P 4_12_12$ with lattice parameters $a=9.263(4) \text{ \AA}$, $c=17.898(6) \text{ \AA}$ and $Z=4$. The structure was solved by direct method and refined for 1362 independent $\text{MoK}\alpha$ counter data. The R index is 0.052 and $R_w=0.032$. The result reveals that the crystal structure consists of octahedral fluorosilicate anions and ureated protons $((\text{NH}_2)_2\text{CO} \cdots \text{H}^+ \cdots \text{OC}(\text{NH}_2)_2)$. The structure formula is $((\text{NH}_2)_2\text{CO} \cdots \text{H}^+ \cdots \text{OC}(\text{NH}_2)_2)_2 \cdot (\text{SiF}_6)^-$. The two protons of a fluorosilicic acid molecule are captured by two pairs of urea molecule and form two strong hydrogen bonds O-H-O respectively of 2.424 \AA and 2.443 \AA in length. The center of each such hydrogen bond sits on a two-fold axis. All F and N atoms are involved in forming hydrogen bonds F \cdots H-N. Such hydrogen bonds have certainly reinforced the framework of the crystal. This addition compound has been found to be an effective and practical agent for prevention and control of plant diseases such as wheat stem rust. The capture of the acidic protons by urea molecules through hydrogen bonding has made the fluorosilicic acid less harmful, more convenient to store and transport, and its effect more persistent.

04.6-05 HYDROGEN BONDING IN $(\text{NH}_4)_2\text{TiF}_6$. By Z. Tun and I.D. Brown, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada. L8S 4M1.

A recent study (Knop, Westerhaus and Falk, 1980 *Can. J. Chem.*, 58, 867) of infrared spectra of the ammonium ion in $(\text{NH}_4)_2\text{TiF}_6$ at different temperatures shows that the stretching frequency of all N-H bonds increases with decreasing temperature. The negative values of dv/dT for the N-atoms have been explained by supposing that at low temperatures the hydrogen atoms form trifurcated bonds as required by the space group symmetry but that at higher temperatures the ammonium ion is rotationally disordered to form stronger hydrogen bonds with particular F atoms. In order to examine this hypothesis we have used x-ray diffraction to refine the structure of $(\text{NH}_4)_2\text{TiF}_6$ at room temperature and at 153K to $R = 0.02$. The crystal is trigonal, space group $P\bar{3}m1$ with $Z = 1$, $a = 5.920(2)$, $c = 4.702(1) \text{ \AA}$ (153K) and $a = 5.972(2)$, $c = 4.822(1) \text{ \AA}$ (290K).

Although hydrogen atoms were included with anisotropic temperature factors in both refinements, a difference map showing the electron density of the H atoms shows the inadequacy of the conventional model. At 153K the H atoms are well localised with one on the 3 fold axis and 3 on mirror planes but at room temperature the unique H atom appears to be disordered off the threefold axis. The relation of this disorder to that proposed by Knop *et al.* will be discussed.