Analysis of Atomic Displacement Parameters

MS11.06.01 NORMAL MODE ANALYSIS FROM ELASTIC DIFFRACTION DATA IS POSSIBLE! WHY AND HOW?
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It is generally believed that atomic mean square displacement parameters (ADP) obtained from an elastic diffraction experiment provide information on the motion of individual atoms, but cannot say anything on the cooperative displacements of groups of atoms unless assumptions of questionable validity are made. This opinion is correct with respect to ADP’s pertaining to a single temperature; it is untenable, however, when ADP’s at several temperatures are available. Why is this so?

ADP’s can be considered as a superposition of the contributions from many normal modes. The absolute atomic displacements of a mode depend on its energy (v), its effective or reduced mass (m), on temperature (T) and on relative displacement (A) according to $A^2 h^2 / (8 \pi^2 m^2 \nu^2 v^2) \coth (h \nu / (2 k_B T))$. At sufficiently low temperatures this expression can be approximated by $A^2 h^2 / (8 \pi^2 m^2 \nu^2 v^2)$. At sufficiently high temperatures the corresponding approximation is $A^2 k_B T (4 \pi^2 m^2 \nu^2 v^2)$.

Now, suppose that a mean squared displacement U is the result of a superposition of two normal modes only and that it has been measured at a low and at a high temperature; then $U(\text{low T}) = A^2 h^2 / (8 \pi^2 m^2 \nu^2 v^2) + A^2 h^2 / (8 \pi^2 m^2 \nu^2 v^2)$ $U(\text{high T}) = A^2 k_B T (4 \pi^2 m^2 \nu^2 v^2) + A^2 k_B T (4 \pi^2 m^2 \nu^2 v^2)$.

From the two independent observations the two normal frequencies can be determined, provided A1 and A2 are known. This simple argument can be generalized to more than two frequencies and to the corresponding relative displacements if the coth-dependence and the three-dimensional information contained in the ADP’s are taken into account. In practice, ADP’s need to be measured at a sufficient number of appropriate temperatures.

MS11.06.02 MODELLING THE THERMAL MOTION OF FREELY ROTATING MOLECULES. R. T. Downs and L. W. Finger, Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. N.W., Washington D.C. 20015, phone: (202) 686-2410 x 2469, e-mail: downs@gl.ciw.edu

All molecular gas-phases become crystalline when subjected to sufficient pressure. Spectroscopic studies show that the molecules are freely rotating while near the freezing point for many of these phases. As pressure increases the motion is constrained and a lowering of symmetry occurs. In order to model the freely rotating molecule we calculated molecular electron-density wave functions using the Gaussian92 program for energy-optimized model molecules. The electron-density was then spherically averaged in order to mimic the rotations. The Fourier transform of this spherically averaged electron density provides the scattering factor for the rotating molecule. The displacement parameters obtained from the structure refinement then provide estimates of translational motion.

MS11.06.03 LATTICE-DYNAMICAL CALCULATION OF ATOMIC DISPLACEMENT PARAMETERS (ADPs). Carlo M. Gramaccioli and Francesco Demartin, Università degli Studi, Via Botticelli 23, I-20133, Milan, Italy, Tullio Pilati, CNR-CSRSRC, Via Golgi 19, I-20133 Milan, Italy

ADPs comparable with the corresponding values obtained from crystal structure refinement can be derived from Born-von Karman lattice dynamics. A rigid ion model has been assumed, where atomic charges and VFF parameters have been deduced from best fit to the vibrational frequencies of a series of similar compounds, either molecular crystals or even ionic, non-molecular