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FEATURE ARTICLE

Interpretation of Atomic Displacement Parameters from Diffraction Studies of Crystals

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Anisotropic Gaussian displacement parameters (ADP's), routinely obtained from crystal structure analyses, define the second moments of atomic probability distribution functions and hence provide information about averaged displacements of atoms from their mean positions in crystals. From the ADP's alone it is not possible to derive rigorous conclusions about crystal or molecular vibrations, but simple models involving correlated motions of groups of atoms are often capable of reproducing the observed ADP's and their temperature dependence. The possibilities and limitations of such models are discussed. Judiciously exercised and interpreted, the analysis of ADP's can yield quantities such as mean-square libration amplitudes that are not easily obtainable by other physical methods.

Introduction

The idea that atoms and molecules move in crystals—indeed, move sometimes with large amplitude—would have struck most chemists of earlier generations as outlandish. Professor Leopold Ruzicka once opined to one of us that "a crystal is a chemical cemetery". We know what he meant: long rows of molecules, interred in a rigid geometrical arrangement, lifeless compared with the molecular mazurkas that can be imagined to occur in solution. The view that Ruzicka expressed in his characteristically vivid and outspoken manner is perhaps still widely shared among chemists and even (we suspect) among some crystallographers. It should not be. In 1913, only a few months after the discovery of X-ray diffraction, Debye² showed in detail how increasing the temperature should reduce the diffraction intensities, especially

at large scattering angles, by increasing the extent of vibration of the atoms about their average positions.

Crystallographers have been confronted by anisotropic "vibration parameters" since they began to use three-dimensional diffraction data in the early 1950s. In 1956, Cruickshank showed how such quantities for anthracene and naphthalene could be interpreted in terms of molecular rigid-body motion³ and thus related to the spectroscopic and thermodynamic properties⁴ of the crystals. Nowadays, with improvements in the precision and accuracy of intensity measurement, it has become possible to detect quite subtle effects arising from the motion of molecules, and portions of molecules, in crystals.

What were originally termed anisotropic "vibration parameters" or "thermal parameters" are more precisely described as anisotropic Gaussian displacement parameters, U^{ij} , called here ADP's.

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