

11.4-8 CORRELATION OF INTERNAL LIBRATIONAL MOTION WITH OVERALL MOLECULAR MOTION\*. By V. Schomaker and K. N. Trueblood, Department of Chemistry, University of Washington, Seattle, WA 98105 and Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90024, USA

The Dunitz-White (1973) treatment of internal librations included only a single parameter for each librating group, its librational amplitude, and in applications of this model, the possible correlations of this motion with the overall translation and libration of the entire molecule have been ignored (e.g., Dunitz, J. D. and White, D. N. J. (1973) *Acta Cryst.* **A29**, 93; Trueblood, K. N. and Dunitz, J. D. (1983) *Acta Cryst.* **B39**, 120). We have formulated these correlations and altered the computer program THMV to take them into account. When the librational axis does not lie on a symmetry element, six additional parameters are needed for each librating group (for correlation with overall libration and overall translation). If the position of a given atom is affected by two or more internal librations, additional parameters are needed for their pairwise correlations and these have been included.

We have applied the revised program to a number of molecules containing internally librating groups. In all cases so far examined, the effects on  $I$ ,  $I$ ,  $S$  and the group librational amplitude of including these new correlations have been far smaller than the e.s.d.'s of these quantities. In only a few instances have correlations between the librational amplitudes of groups that contain atoms in common been significant.

The implications of different site symmetries of the libration axes have been considered; they may be related directly to those applying more generally to overall molecular motion (V. Schomaker and K. N. Trueblood (1968) *Acta Cryst.* **B24**, 63). These symmetry considerations will be discussed, together with comparisons of the results of applying this model with those found from the simple one-parameter Dunitz-White model.

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11.4-9 LATTICE DYNAMICAL CALCULATION OF THERMAL DIFFUSE SCATTERING IN PHENOTHIAZINE. By A. Criado, A. Conde & R. Márquez, Dpto de Optica y Centro Coordinado del C.S.I.C., Facultad de Física, Sevilla, SPAIN.

Lattice dynamics in monoclinic phenothiazine is studied within the harmonic approximation and using the Born-von-Kármán formalism where the force constants are calculated analytically from the crystal structure. The external formalism is used, considering the molecule as a rigid body with six degrees of freedom, three translations and three rotations, and the crystal potential function is assumed to be in a pairwise form as a sum of interatomic interactions, each one in a Buckingham potential:  $V(r) = -A/r^6 + B \exp(-Cr)$  where A, B and C are parameters depending on the atom pair involved. Thermal crystallographic parameters are obtained performing a sampling through the Brillouin zone and are compared with experimental ones.

The Brillouin zone is sampled and the eigenvalues and eigenvectors of the dynamical matrix are stored in order to calculate thermal diffuse scattering intensity. A division of 25 parts along each reciprocal unit vector has been chosen, yielding a total of 8125 points, considering time reversal symmetry. First-order TDS in-

tensity is calculated both in an exact calculation, including optic and acoustic branches, and in the long-wave approximation allowing for dispersion (LWD), and the results are compared. First-order TDS correction factors  $\alpha_1(\vec{H})$ , are calculated in both modalities for different reflections and their values are discussed as a function of the dispersion of the acoustic modes from the long-wave limit behaviour. A Fourier difference synthesis with Bragg intensities plus TDS contribution is performed in order to reveal directly the influence of TDS intensity over electronic density maps and, later, a least-squares refinement process is carried out to find the effect of TDS intensity over variable parameters.

Second-order TDS intensity is obtained and the different contributions, acoustic-acoustic, acoustic-optic and optic-optic to the intensity through a Bragg reflection are separated in order to compare their contributions to the second-order TDS correction factor  $\alpha_2(\vec{H})$ .

Second-order TDS factors are calculated both in the exact calculations from lattice dynamical results and using the LWD approximation in order to study the reliability of this approximation. Similarly to the first-order case, a difference Fourier synthesis with intensities containing second-order TDS contribution is performed to study the differences in density maps.

11.4-10 NUMERICAL STRUCTURE FACTOR CALCULATIONS OF ORIENTATIONALLY DISORDERED MOLECULES: THE PLASTIC PHASE OF CBr<sub>4</sub>. By D. Hohlwein, Institut für Kristallographie der Universität Tübingen, West-Germany.

The structure factor of molecules with broad orientational distribution functions can be calculated with symmetry adapted spherical harmonic functions (e.g. Press, Hüller, *Acta Cryst.* (1973) **A29**, 252; Vogt, Prandl, J. Phys. C (1983) **16**, 4753) or as proposed recently (Hohlwein, *Acta Cryst.* (1981) **A37**, 899) with Gaussian or other appropriate functions around equilibrium orientations. In our case the structure factor has to be calculated numerically.

The method has been applied to neutron diffraction data of CBr<sub>4</sub> in the plastic phase. The probability distribution of 24 Br atoms on the surface of a sphere (6 equilibrium orientations of the molecule) is described by two parameters: the mean-square librational angles around two axes passing through the center (C-atom) and being perpendicular to each other. The distributions are Gaussian in the polar angle  $\theta$  and elliptical in the azimuth. The directions of the librational axes are determined by symmetry.

These two parameters, together with an isotropic temperature factor, give a final  $R_w = 0.078$ . The librational angles are 15.5(7) and 8.5(8) degrees. This large anisotropy can only be explained by a coupling of translation and rotation. In the difference Fourier map a reorienting molecule is detected. Refinement with a population factor  $p$  for this molecule yields  $R_w = 0.042$  and  $p = 0.12(2)$ . A simple dynamical model for the reorientation process is proposed and compared with inelastic neutron measurements.