God. Jugosl. cent. kristalogr. **16** (1981) 52—53

DERIVATION OF STRUCTURAL INFORMATION ABOUT CRYSTALLOHYDRATES BY THE METHODS OF VIBRATIONAL SPECTROSCOPY*

BOJAN ŠOPTRAJANOV

Hemiski fakultet, Univerzitet »Kiril i Metodij«, 91000 Skopje

Received June 11, 1981

Owing to the fact that they both reflect the shape of the potential-energy hypersurface, the arrangement of the atoms in a crystal (i. e. the crystal *structure*) on the one hand and the vibrational *frequencies* on the other are mutually related. This interdependence lies in the basis of all spectra-structure correlations, including those for crystallohydrates. The relations are not always simple, however, and thus only qualitative or, at best, semi-quantitative structural information can be derived from the analysis of the vibrational spectra. On the other hand it has been shown that the accuracy of the determined atomic positions could be improved if spectroscopically-determined data are taken into account (A. Eriksson *et al., J. Mol. Struct.* **52** (1979) 107).

In the case of crystallohydrates relatively reliable information about the $O_w \ldots O$ distances could be derived from the observed ν_{OD} frequencies of isotopically isolated HDO molecules. The normal modes of an isolated (gas-phase) HDO molecule, namely, are essentially *OH* and *OD* stretching motions as well as HOD bending and in the case of HDO molecules in a crystal in which they are surrounded almost exclusively by H_2O molecules (crystals with low deuterium content) the complications arising from vibrational coupling of identical oscillators are virtually absent. The spetroscopic and diffraction data on a number of crystallohydrates have been correlated (B. Berglund *et al., J. Mol. Struct.* **43** (1978) 169), an exponential relation between ν_{OD} and $R_{O_W \cdots O}$ being found. The comparison (and thus correlation) between the frequencies (as a rule determined at low temperatures) and the diffraction data about the distances is not always straightforward, however. A number of factors such as the difference in the time-scale of the two kinds of experiments; the fact that the ν_{OD} frequencies reflect the H-bond strength which may not be a simple function of the donor-acceptor distance; the difference (if present) in the temperature of the two experiments and the structural changes accompanying the change of temperature etc. cause an appreciable scatter of the points on the ν_{OD} *vs.* $R_{O_W \cdots O}$ diagram and give rise to an appreciable uncertainty of the estimated, on the basis of the observed OD stretching frequencies, $O_w \ldots O$ di-

* The abstract of a general lecture presented at the *16th Conference of the Yugoslav Centre of Crystallography* held in Skopje and Kavadarci on 10th to 12th June 1981.

stances. Examples are given showing the comparison of the experimental and estimated donor-acceptor distances for crystallchydrates studied in our laboratory.

In favourable cases the number of crystallographically distinct water molecules can nicely be deduced from the number (and relative intensities) of bands in the OD stretching region of isotopically isolated HDO molecules, but when a large number of different types of water molecules is present in the unit cell (as is often with higher hydrates) the overlap of bands makes this task difficult. Both situations are illustrated by comparing the infrared spectra with available diffraction data.

Attention is paid to the appearance of the spectra in the OH stretching region of crystallohydrates containing water molecules which form strong hydrogen bonds.

An asymmetric surrounding of the water molecules (e. g. water molecules belonging to the *H* or *J* type in the classification of Ferraris and Franchini-Angela, 1972) is often associated with appearance of multiple bands in the HOH, HOD and/or DOD bending region, but such bands are observed also in cases (as in alums) where the surrounding is *not* asymmetric.

In the case of crystallohydrates which are salts of relatively simple acids (e. g. phosphates, sulfates etc.) the degree of asymmetry of the anion could be estimated (at least qualitatively) from the number and separation of the bands originating from the stretching or bending vibrations of the anion. It is dangerous, however, to make far-reaching conclusions, for example about the mode of bonding (monodentate, chelate etc.) of the anion on this base as illustrated by the examples given.