

**22.2-02** SHORT-RANGE ORDER IN DIFFERENT MODELS OF WATER. B. J. Gellatly and J. E. Quinn, Crystallography Department, Birkbeck College, Malet Street, London, WC1E 7HX, England.

Several models of the water-water interactions are currently used in studies of liquid water, ices, solutions and water-biomolecule interactions. Although each model has its own advantages, none appears entirely satisfactory. For example, the ST2 (Stillinger and Rahman; J. Chem. Phys. 60, 1545(1974)) and central force (CF) (Stillinger and Rahman; J. Chem. Phys. 68, 666(1978)) models can account for many thermodynamic properties, yet a comparison of predicted neutron radial distributions with experiment suggest the first neighbour angular correlations are too strong. Lie and Clementi's CI potential (J. Chem. Phys. 64, 5308(1976)) is fitted to points on the water dimer surface calculated by ab initio methods including configuration interaction; although rescaling the temperature results in a relatively successful model, the complete failure to reproduce the second virial coefficient - itself a dimer property - is strange. The polarisable electropole model (PE) of Barnes et al (Nature 282, 459(1979)) is remarkably successful in handling known cooperative effects, and can predict good experimental quantities in vapour, crystal, and liquid phases; its radial distribution function is not completely satisfactory and it appears the potential may underestimate the strength of the local angular correlations.

In order to throw some light on these different models, we have examined in some detail sections of the dimer surfaces of ST2, CI and PE models, and these results will be discussed in terms of surface plots obtained using an interactive computer graphics system. The overtetrahedrality of the ST2 model shows itself in a separation of the energy wells corresponding to the (stable) trans,

In contrast, the corresponding CI surface shows a single well with a minimum energy somewhere between the two. The PE surface sits between these two extremes, showing little more than a plateau at the cis orientation, separated from the trans well by a shoulder rather than a peak. The PE surface appears to give the best fit to the well shape obtained from the ab initio calculations.

A further major feature concerns the repulsive region of the dimer surface corresponding broadly to close approaches of hydrogens on the two molecules. The barriers for ST2 and PE are too low ( $\sim 4.5$  and  $+3$ Kcal mole<sup>-1</sup> respectively compared to a theoretical  $\sim +7$ Kcal mole<sup>-1</sup>). The CI surface, however, is dramatically repulsive at  $\sim +19$ Kcal mole<sup>-1</sup>, apparently a consequence of fitting an analytical form to a set of calculated points which fail to sample this region adequately. These results are discussed in terms of the possible consequences for the local structures of the simulated liquid and solutions.

The perturbation of the PE dimer surface by 3 and 4 body effects has been examined for sample configurations, and these results also will be presented. As expected, the three-body contribution to the energy of a cluster can be significant (typically 5-10% of the total energy) and strongly variable. In contrast, the four body contribution rarely exceeds 0.1% and would appear to be negligible. This suggests that cooperative effects in water are best approached in computer simulations by initially using analytical forms for 2 and 3 body energies.

**22.2-03** INVESTIGATIONS ABOUT THE EXISTENCE OF A LIQUID-TYPE QUASI-CLOSE-PACKING IN CONCENTRATED AQUEOUS SOLUTIONS OF ALUMINIUM AND INDIUM SALTS. By M.I. Cabaco, M.I. de Barros Marques, M.A. Oliveira, M. Alves Marques, I. Física e Matemática (INIC)2 Gama Pinto 1699 Lisboa Portugal

The existence of correlations of position taken up by heavy ions in concentrated aqueous solutions was demonstrated using X-ray diffraction (J.A. Prins and R. Fonteyne, Physica 2, 1016(1935)). Experimental data obtained for a number of different ionic solutions were then interpreted by considering the interference of the X-rays scattered by the heavy ions assumed as arranged in a liquid-type quasi-close-packing. Later others have admitted, too, the presence of ion-ion correlations in their X-ray diffraction investigations of the structure of concentrated aqueous solutions (A.K. Dorosh and A.F. Skryshenskii, Zh. Strukt. Khim., 5, 6, 911 (1964)). The existence of a local close-packing of hydrated light or heavy ions filling up almost completely the volume occupied by the solution has been suggested by the present authors (M. Alves Marques and M.I. de Barros Marques, Proc. K. Ned. Akad. Wet. B77, 286(1974)) for interpreting diffraction patterns of concentrated aqueous solutions of inorganic salts of metallic cations. In the X-ray patterns of concentrated aqueous solutions of salts of aluminium and indium near  $s=1\text{\AA}^{-1}$  ( $s$ , momentum transfer divided by  $\hbar$ ) a maximum of intensity is observed; the value of  $s$  corresponding to these interference maxima diminishes when the concentration of the cation diminishes according to the hypothesis of considering the aqueous solution as a close-packing of large diffraction units; these diffraction units are the cations surrounded, predominantly, by hydration water molecules. X-rays diffracted by interstitial anions interfere destructively at  $s=1\text{\AA}^{-1}$ : of course, if the nitrate anion (32 electrons) is replaced by the perchlorate anion (50 electrons) the intensity of the above mentioned interference maximum diminishes drastically in the X-ray pattern of equimolecular concentrated solutions of indium salts. Authors indicate a range of the value of the molarity of the investigated solutions corresponding to the  $s$  values which are in good agreement with the assumed close-packing:

SOLUTE SALT	MOLARITY RANGE	H <sub>2</sub> O per cation	$s_{\text{exp}}$ ( $\text{\AA}^{-1}$ )	$s_{\text{calc}}$ ( $\text{\AA}^{-1}$ )
Al(NO <sub>3</sub> ) <sub>3</sub>	2.67M	17.0	0.80	0.81
	0.94M	55.7	0.54	0.57
AlCl <sub>3</sub>	3.07M	16.4	0.82	0.84
	0.97M	54.3	0.58	0.60
In(NO <sub>3</sub> ) <sub>3</sub>	3.96M	9.4	0.93	0.92
	2.24M	20.4	0.81	0.76

The X-ray pattern of the 0.88M solution of indium nitrate gives  $s_{\text{exp}}=0.80\text{\AA}^{-1}$  in notorious disagreement with  $s_{\text{calc}}=0.56\text{\AA}^{-1}$ ; then the close-packing hypothesis of the indium complexes is not plausible for this aqueous solution. A large disagreement was observed, too, for the 1.23M solution of indium chloride between  $s_{\text{exp}}=0.87\text{\AA}^{-1}$  and  $s_{\text{calc}}=0.63\text{\AA}^{-1}$ . A general discussion of the structural models idealized by the authors for these ionic solutions will be given.