

center of mass of one of the molecules encountered the boundary . The boundary distance of 36Å was adjusted to reproduce the experimental density of water at room temperature. The equations of motion were solved using an implicit quaternion method¹¹ for the rotations and a Leap frog method for the translations. The timestep used was 1 fsec.

In our simulation we neglected electrostatic interactions with solvent outside the cube. We calculated the missing contribution to the solvation energy from a simple PCM model¹². The simulated box was put into a cubic cavity in a dielectric continuum and the contribution to the solvation energy was calculated from the interaction between the charges within the box and the induced surface charges. It gave 13% of the total solvation energy. This value stayed rather constant along the trajectory. Therefore we assume that the essential changes of interaction with solvent molecules in the immediate surroundings are taken into account sufficiently.

The force field was designed to reproduce the local electrostatic interactions properly, which is especially important for the large sized PIC molecule with its extended π -electron system. It is based on a simplified version of the effective fragment model¹³⁻¹⁵. The charge distribution is approximated by distributed multipoles which were calculated with GAMESS on the basis of TZV/HF wavefunctions¹⁶. For the simulation only point charges q_i and dipoles \vec{p}_i were used which are centered at the positions of the nuclei and the bond centers. The Coulombic interaction energy is

$$V_{ij}^{Coul} = \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}} + \frac{\vec{R}_{ij}(q_i \vec{p}_j - q_j \vec{p}_i)}{4\pi\epsilon_0 R_{ij}^3} + \frac{R_{ij}^2 \vec{p}_i \vec{p}_j - 3(\vec{R}_{ij} \vec{p}_i)(\vec{R}_{ij} \vec{p}_j)}{4\pi\epsilon_0 R_{ij}^5} \quad (1)$$

The values of point charges and dipoles are given for the symmetry unique atoms in Table I.

The electronic spectra were calculated on the ZINDO/CI-S level¹⁷ including the point monopoles and dipoles of all water molecules. The two lowest excited states of the dimer are to a large extent linear combinations of the lowest monomer excitations with only very small admixture of higher monomer excitations and of charge resonance states. Therefore we use a simple 2-state model to analyze the delocalized dimer states in terms of the local excitations A^* and B^* . The interaction matrix is

$$\begin{pmatrix} \bar{E} - \Delta/2 & V \\ V & \bar{E} + \Delta/2 \end{pmatrix} \quad (2)$$