Supporting Information

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Dynamics and Infrared Spectroscopy of the Protonated Water Dimer

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Supporting Information

1 Brief description of MCTDH

The quantum-dynamical problem is solved in the time-dependent picture using the multiconfiguration time dependent Hartee method (MCTDH)\cite{1}. MCTDH is an efficient algorithm to solve the time-dependent Schrödinger equation by means of a variationally optimal multiconfigurational expansion of the wavefunction. Each configuration is given by a Hartree product of functions depending on a single or a group of degrees of freedom, the so-called single-particle functions (SPF). Both the multiconfigurational expansion coefficients and the SPF are allowed to vary simultaneously in time, which dramatically reduces the amount of configurations necessary to achieve a converged propagation as compared to the standard, numerically exact, propagation method. By controlling the number of configurations, MCTDH can be made as close to exact as desired, at the cost of an increased computational effort. The MCTDH program is also capable of using the time-independent picture, allowing for the convergence to eigenstates and eigenenergies of the Hamiltonian at hand. The algorithm that implements this feature is called improved relaxation \cite{2}. This algorithm is essentially a multiconfiguration self-consistent field approach that takes advantage of the MCTDH machinery. Several eigenenergies and eigenstates have been calculated using improved relaxation. They are invaluable in the assignments of some bands coming from the time-dependent calculation of the IR spectrum, and provide a total characterization of the corresponding states in terms of their fully-correlated wavefunctions. All the reported simulations were performed with the Heidelberg MCTDH package of programs \cite{3}.

2 Representation of the Potential Energy Surface

As outlined above, the wavefunction is represented by products of SPFs which in turn are represented by discrete variable representation grids. The total primitive product-grid consists of \(1.3 \times 10^{15}\) points. This number makes clear that the potential must be represented in a more compact form to make calculations feasible. We choose to represent the PES as follows: the coordinates are divided in five groups, \(g_1 \equiv [x, y, z, \alpha]\), \(g_2 \equiv [\gamma_a, \gamma_b]\), \(g_3 \equiv [R, \beta_a, \beta_b]\), \(g_4 \equiv [r_{1a}, r_{2a}, \theta_a]\) and \(g_5 \equiv [r_{1b}, r_{2b}, \theta_b]\) (The same mode combination is used in the MCTDH calculations). The potential is then
expanded as \cite{4}:

\[
\hat{V}(c) = \hat{v}^{(0)} + \sum_{i=1}^{5} \hat{v}^{(1)}_i (g_i) + \sum_{i=1}^{4} \sum_{j=i+1}^{5} \hat{v}^{(2)}_{ij} (g_i, g_j) + \hat{v}^{(3)}_{z,2,3} (z, g_2, g_3)
\]  

(1)

where \( c \equiv [g_1, \ldots, g_5] \). The \( \hat{v}^{(0)} \) term is the energy at the reference geometry. The \( \hat{v}^{(1)}_i \) terms are the intra-group potentials obtained by keeping the coordinates in other groups at the reference geometry, while the \( \hat{v}^{(2)}_{ij} \) terms account for the group-group correlations. The potential with up to second-order terms gives already a very reasonable description of the system. The \( \hat{v}^{(3)}_{z,2,3} \) term accounts for three-mode correlations between the displacement of the central proton, the distance between both water molecules and the angular wagging and rocking motions. This PES representation may be sequentially improved in a convergent series by adding more correction terms where coordinates belonging to three or more different groups are allowed to vary simultaneously. However, the PES in \cite{1} is found to reproduce the full potential very well, providing a converged zero-point energy of 12376.3 \( \text{cm}^{-1} \), 16 \( \text{cm}^{-1} \) below the reported Diffusion-Monte-Carlo result \cite{5} on the full potential. A detailed discussion on the construction and accuracy of the potential energy representation will be given in a forthcoming publication.

References

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