Supplementary Information for: HCl–H$_2$O dimer: An accurate full-dimensional potential energy surface and fully coupled quantum calculations of intra- and intermolecular vibrational states and frequency shifts

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1 Reduced Probability Density Contour Plots

The set of coordinates $\mathbf{Q} = (r_0, \beta_A, \gamma_A, \beta_B, \tilde{\alpha})$, where $\tilde{\alpha} \equiv (\alpha_A - \alpha_B)$, that we use to solve for the eigenstates of $\hat{H}_{inter}$ (see Sections 3.1.1 and 3.1.2 of the text) are not ideal ones with which to visualize the spatial properties of these states with the aim of assigning them to particular vibrational modes. A set of coordinates better suited to this task are those which specify the position of the HCl moiety with respect to a dimer-fixed axis system that is parallel to the water-fixed axes MF_A. Unfortunately, the latter coordinates are not well-suited to the calculation of the intermolecular eigenstates. What one can do, however, is to start with the intermolecular eigenstates computed as functions of $\mathbf{Q}$, transform them to coordinates referred to the MF_A axes, and examine their spatial characteristics as a function of the latter. We outline here the procedure by which we have done this to produce the contour plots presented in Figs. 7 and 8 of the text.

We are specifically interested in the reduced probability densities (RPDs) associated with the projections of the water c.m.-to-HCl c.m. vector, $\mathbf{r}_0$ onto the MF_A axes $\hat{x}_A$ and $\hat{y}_A$. We define these projections as

$$x \equiv \mathbf{r}_0 \cdot \hat{x}_A \tag{1}$$

$$y \equiv \mathbf{r}_0 \cdot \hat{y}_A \tag{2}$$

To obtain a wavefunction RPD as a function of (x, y) we first compute the values of x and y associated with each point on a 5D grid of $\mathbf{Q}$ values like that employed to evaluate $V_{inter}|\psi\rangle$ in the diagonalization of $\hat{H}_{inter}$ (see Section 3.1.2 of the text). We then assign each (x, y) value to the nearest point on a grid of such points (x_i, y_j), where $x_i = i\Delta x$, $i = -i_{\max}, -i_{\max} + 1, \ldots, i_{\max} - 1, i_{\max}, y_j = j\Delta y, j = -j_{\max}, -j_{\max} + 1, \ldots, j_{\max} - 1, j_{\max}$, and Δx and Δy are constants. In this way we obtain a mapping between each point on the $\mathbf{Q}$ grid and a point on the (x_i, y_j) grid. That mapping depends only on the values of r_0, β_A, and γ_A associated with the $\mathbf{Q}$ grid point. It is independent of the values of the coordinates $(\beta_B$ and $\tilde{\alpha})$ that describe the angular orientation of the HCl. The mapping is also such that

more than one set of (r_0, β_A, γ_A) values might map to a particular (x_i, y_j) point. We keep track of the number of such sets that map to each (x_i, y_j) and denote that number $N_{i,j}$.

Next, we transform the intermolecular eigenstate of interest, $|\kappa\rangle$, from the basis-set representation $|\Gamma\rangle \equiv |s, j_A, k_A, m, j_B\rangle$ to the $\mathbf{Q}$-grid representation

$$\langle \mathbf{Q}_k | \kappa \rangle = \sum_{\Gamma} \langle \mathbf{Q}_k | \Gamma \rangle \langle \Gamma | \kappa \rangle \tag{3}$$

where $\mathbf{Q}_k$ denotes one point on the $\mathbf{Q}$ grid.

Finally, we compute the RPD at each grid point (x_i, y_j) as

$$\rho(x_i, y_j) = \frac{1}{N_{i,j}} \sum_{s,t,u} f_{s,t,u}^{i,j} \sum_{v,w} |\langle r_{0,s}, \beta_{A,t}, \gamma_{A,u}, \beta_{B,v}, \tilde{\alpha}_w | \kappa \rangle|^2 \tag{4}$$

where $f_{s,t,u}^{i,j} = 1$ if $(r_{0,s}, \beta_{A,t}, \gamma_{A,u})$ maps to (x_i, y_j) and $f_{s,t,u}^{i,j} = 0$ if it does not. We include the factor of $N_{i,j}^{-1}$ in Eq. (4) so as to take the average RPD at grid point (x_i, y_j) in cases where more than one set of $(r_{0,s}, \beta_{A,t}, \gamma_{A,u})$ values map to it.

The fidelity with which the procedure above produces an accurate RPD contour plot depends on the density of the $(r_{0,s}, \beta_{A,t}, \gamma_{A,u})$ portion of the $\mathbf{Q}_k$ grid. To produce the contour plots in the text we worked with a grid containing twenty r_0 points, one-hundred β_A points, and one-hundred-twenty γ_A points. This, given the values of Δx and Δy (0.3 bohr and 0.4 bohr, respectively) and $i_{\max}$ and $j_{\max}$ (20 and 20, respectively), ensured the mapping of at least one set of $(r_{0,s}, \beta_{A,t}, \gamma_{A,u})$ values to 99% of the (x_i, y_j) grid points, and those that were not mapped to are on the periphery of the grid.