Experimental and Theoretical Investigations of the Dissociation Energy (D_0) and Dynamics of the Water Trimer, $(H_2O)_3$

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1. Vibrational density of states of $(H_2O)_2$

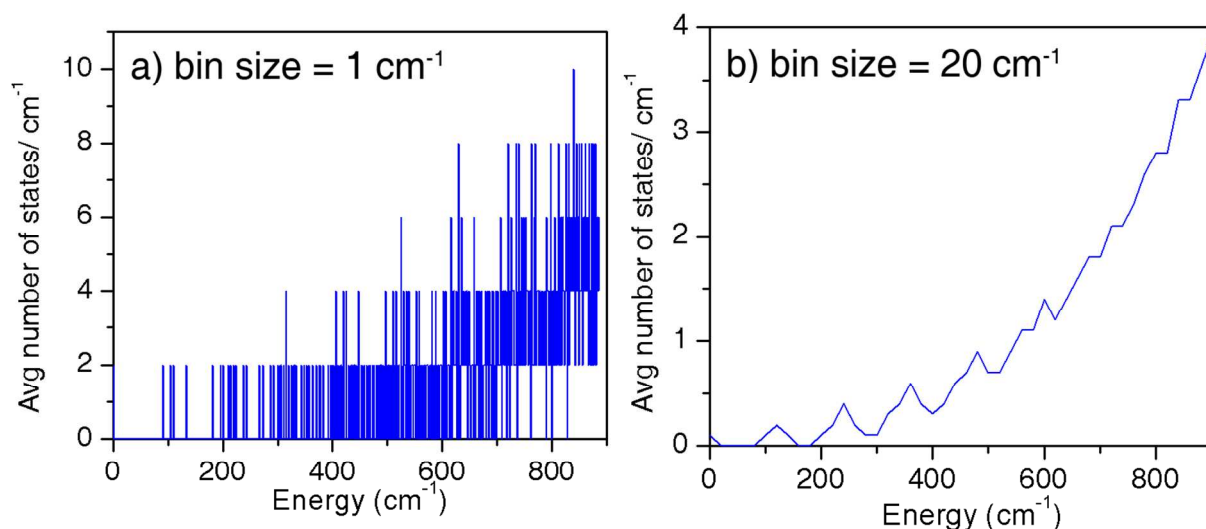**Figure S1.** Vibrational density of states of $(H_2O)_2$ in the range $0 - 900$ cm^{-1}, calculated by Beyer-Swinehart algorithm[1,2] using bin size of a) 1 cm^{-1} and b) 20 cm^{-1} and published intermolecular mode fundamental frequencies.[3]

2. (H₂O)₃ speed distributions and simulations using smooth functions

For comparison, speed distribution fits using an exponential function, e^{-CE_T}, where C is a fitting parameter and E_T is the center-of-mass translational energy, were carried out. Due to the lack of unique structures in the images, fittings using various combinations of rovibrational populations gave equally good fits. For example, using $D_0 = 2640$ cm^{-1}, the images can be well fit assuming that the (H₂O)₂ cofragment is only in the ground vibrational state but with high rotational excitation (Figure S2). As shown in Figure S2, high rotational states of the (H₂O)₂ cofragment must have large populations in order to fit the velocity distribution. Such high rotational excitation of levels of ($J'' > 40$) in vibrational predissociation are unlikely. Likewise, a good fit can be obtained by using the fundamental levels of all the intermolecular vibrational modes, where each vibrational mode is scaled by $e^{CE_{vib}}$, and optimizing C in the rotational energy distributions (Figure S3). While it is impossible to determine the separate rotational and vibrational energy distributions unambiguously, it is clear that in order to fit the velocity profiles (high translational energy parts) of the images with values near the calculated D_0, low rovibrational states of the dimer, including the ground vibrational state must be populated. For the low translational energy parts of the images, it is impossible to distinguish between cases in which high frequency intermolecular vibrational modes, overtones and combination bands are populated, as well as cases where the populations are dominated by high rotational energies. Fortunately, the QCT calculations provide additional information, reinforcing the interpretation of statistical-like distributions.
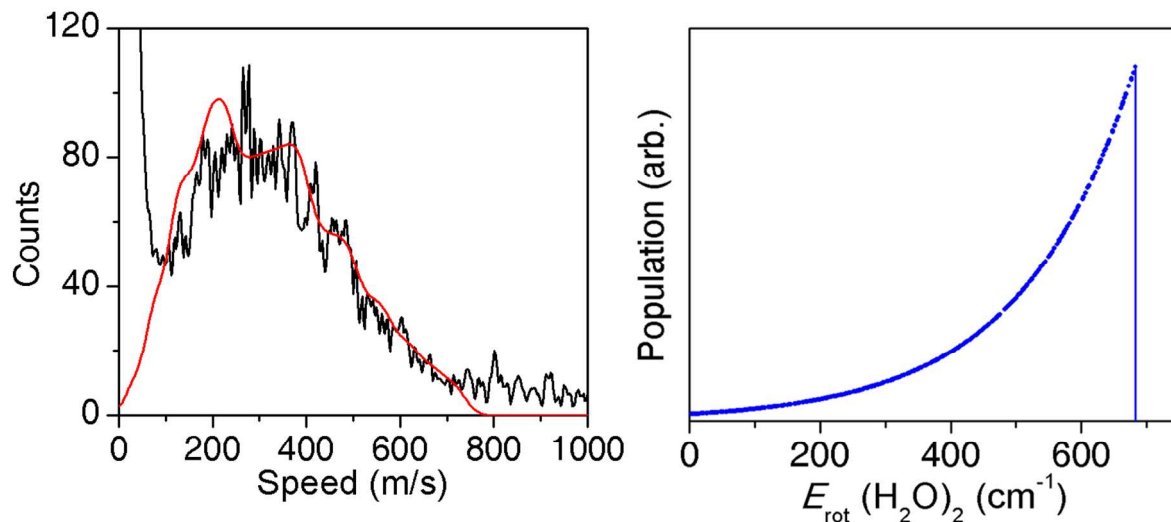
Figure S2. Speed distributions from reconstructed images obtained by monitoring H_2O fragments in the $J''_{KaKc} = 3_{2,1}$ level. Black curves show experimental measurements and red curves correspond to the total integrated simulations using $D_0 = 2640$ cm^{-1}. The fit is accomplished by using an exponential decaying function, e^{-CE_T} for the rotational populations and assuming that only the ground vibrational state of the $(H_2O)_2$ fragment is populated. The blue curve shows the population as a function of $(H_2O)_2$ rotational energy that corresponds to the simulation.
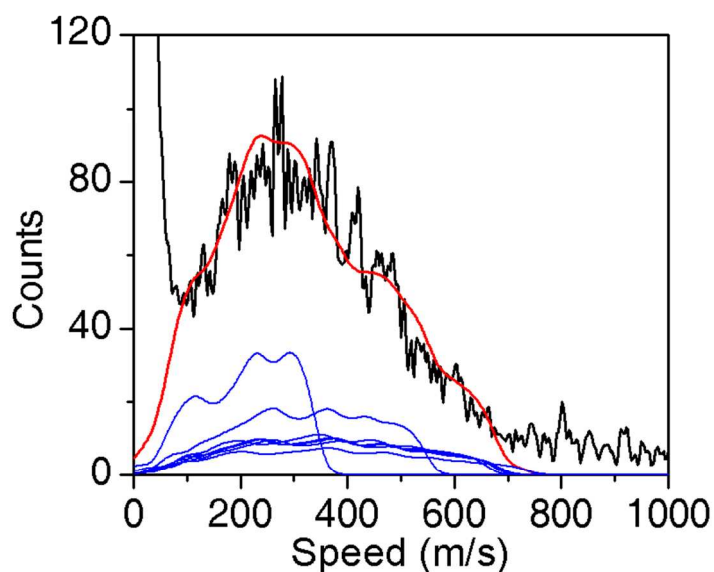

Figure S3. Speed distributions from reconstructed images obtained by monitoring H_2O fragments in the $J''_{KaKc} = 3_{2,1}$ level. Black curves show experimental measurements and red curves correspond to the total integrated simulations using $D_0 = 2640$ cm^{-1}. The fit is accomplished by using an exponential decaying function, e^{-CE_T} for the rotational populations and assuming all the $(H_2O)_2$ fragment intermolecular mode fundamentals are populated. The vibrational populations are scaled by an exponential function, $e^{CE_{vib}}$ and blue curves show the integrated populations for each vibrational mode.

REFERENCES

(1) Beyer, T.; Swinehart, D. F. *Commun. ACM* **1973**, *16*, 379.

(2) Baer, T.; Hase, W. L. *Unimolecular Reaction Dynamics: Theory and Experiments*; Oxford University Press, Inc.: New York, 1996.

(3) Kalescky, R.; Zou, W.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **2012**, *554*, 243-247.