

Supplementary Material for:

HOD on Ni(111): Ab Initio Molecular Dynamics Prediction of Molecular Beam Experiments

Davide Migliorini^{1,a}, Francesco Nattino^{1,†}, Ashwani K. Tiwari² and Geert-Jan Kroes^{1,b}.

¹Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

²Indian Institute of Science Education and Research Kolkata, Mohanpur, 741246 West Bengal, India.

† current address: Theory and Simulations of Materials (THEOS) and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

a) email: d.migliorini@lic.leidenuniv.nl

b) email: g.j.kroes@chem.leidenuniv.nl

Convergence Tests

The setup has been tested with respect to the number of layers, the supercell size (N), the K-points grid and the cutoff energy. The results are reported in Table SI.

Table SI. Details of the convergence tests. E_b^p and E_b^v are the barrier with respect to the parallel or the vertical gas-phase geometry, respectively. ΔE_b^p and ΔE_b^v are the differences with the setup used in the paper (highlighted in gray).

Layers	N	K-points	Cutoff / [eV]	E_b^p / [eV]	ΔE_b^p / [eV]	E_b^v / [eV]	ΔE_b^v / [eV]
4	3x3	4x4x1	350	0.689	0.000	0.676	0.000
5	3x3	4x4x1	350	0.702	0.013	0.689	0.013
6	3x3	4x4x1	350	0.682	-0.007	0.669	-0.007
7	3x3	4x4x1	350	0.693	0.004	0.680	0.004
4	2x2	4x4x1	350	0.761	0.072	0.690	0.014
4	3x3	4x4x1	350	0.689	0.000	0.676	0.000
4	4x4	4x4x1	350	0.686	-0.003	0.685	0.009
4	3x3	3x3x1	350	0.706	0.017	0.694	0.018
4	3x3	4x4x1	350	0.689	0.000	0.676	0.000
4	3x3	7x7x1	350	0.692	0.003	0.679	0.003
4	3x3	11x11x1	350	0.692	0.003	0.679	0.003
4	3x3	4x4x1	300	0.656	-0.033	0.645	-0.031
4	3x3	4x4x1	350	0.689	0.000	0.676	0.000
4	3x3	4x4x1	400	0.698	0.009	0.685	0.009
4	3x3	4x4x1	450	0.700	0.011	0.687	0.011
4	3x3	4x4x1	600	0.703	0.014	0.690	0.014

Vibrational modes and artificial IVR

The harmonic frequencies of the vibrational modes of the three water isotopologues H₂O, HOD and D₂O, computed with the set up used in the paper, are reported in Table SII together with the experimental fundamental frequencies. The larger differences between the energy associated with the vibrational modes makes HOD less prone to artificial IVR and therefore more suitable for AIMD rather than H₂O or D₂O. This can be seen in Fig. S1 where the average energy of 20 HOD molecules in the ($\nu_{OH}=1, \nu_{OD}=0, \nu_{bend}=0$) state is reported. The energy imparted in the ν_{OH} state stays localized in the OH stretch mode throughout the 200 fs AIMD-QCT simulation without redistributing among the other vibrational modes.

Table SII. Vibrational modes for the different water isotopologues. ν_{asym} and ν_{sym} are the antisymmetric and the symmetric stretch, respectively, and ν_{bend} is the bend mode. For HOD ν_{OH} and ν_{OD} are the vibrational modes localized on the OH and on the OD stretch, respectively. The harmonic frequencies computed with the set up used in the calculations (SRP32-vdW) are reported together with the experimental values of the fundamental frequencies. The experimental data are taken from Ref. 1.

Isotopologue	mode	SRP32-vdW [cm ⁻¹]	Experimental [cm ⁻¹]
H ₂ O	ν_{asym}	3752.0	3755.8
	ν_{sym}	3639.5	3657.1
	ν_{bend}	1603.8	1594.8
D ₂ O	ν_{asym}	2747.6	2787.7
	ν_{sym}	2620.7	2668.1
	ν_{bend}	1173.8	1178.4
HOD	ν_{OH}	3697.9	3707.5
	ν_{OD}	2682.2	2782.0
	ν_{bend}	1405.9	1402.2

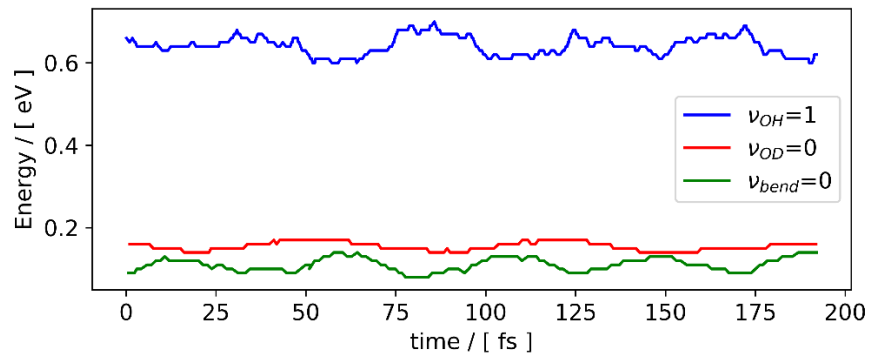


Figure S1. Average energy of 20 HOD molecules in the $(\nu_{OH}=1, \nu_{OD}=0, \nu_{bend}=0)$ state during a 200 fs QCT-AIMD propagation.

Ground state reactivity

The ground state ($\nu=0$) reactivity has been computed and compared with the laser-off S_0 . The results reported in Fig. S2 show that, at the large $\langle E_i \rangle$ investigated, the ground state reactivity does not significantly differ from the laser-off one.

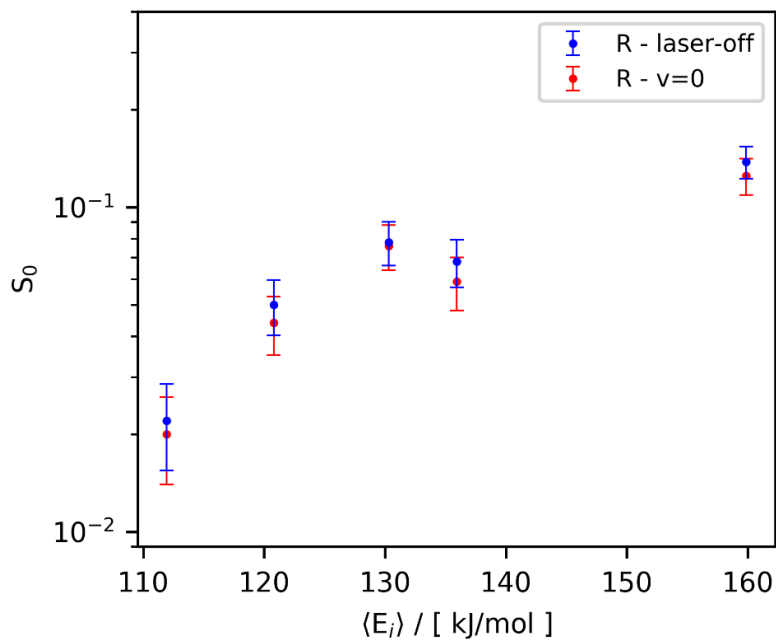


Figure S2. S_0 for laser-off and $\nu=0$ simulations in blue and red, respectively.

Angular distributions

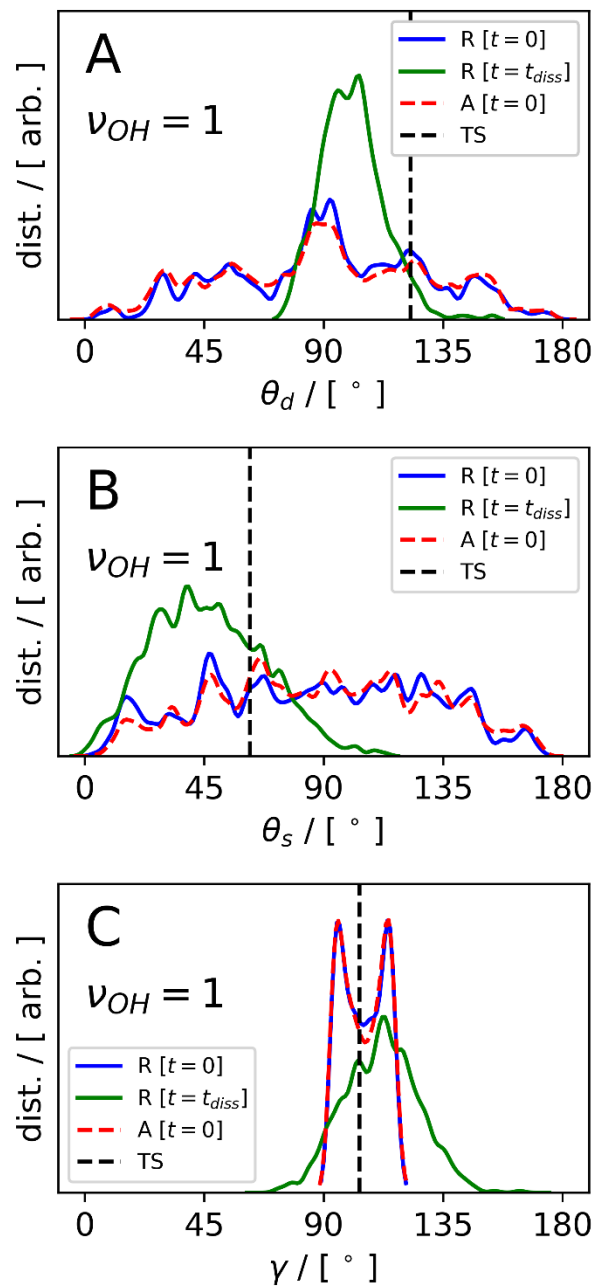


Figure S3. Same as Fig. 7 in the main paper but for $\nu_{OH} = 1$.

Initial Orientation

The $\nu_{OH}=1$ molecules have been simulated in the ($J=2, K_a=0, K_c=2$) state while sampling all the experimentally accessible M values (i.e., $M = -2, -1, 0, 1, 2$). In principle the transition we are simulating would also excite the molecule in $K_c=-2$. However, when $K_a=0$, the initial orientation of the molecule is independent on the sign of K_c . To show this (Figure S4) we prepared 10 sets containing 5000 molecules each in the states ($J=2, K_a=0, K_c=\pm 2$) for all the accessible values of M .

For each set the orientation of the OH and the OD bonds have been evaluated by computing the angle θ that the bonds make with the surface normal z . Fig. S4 shows that the initial distribution of θ , and therefore the molecular orientation, does not depend on the sign of K_c .

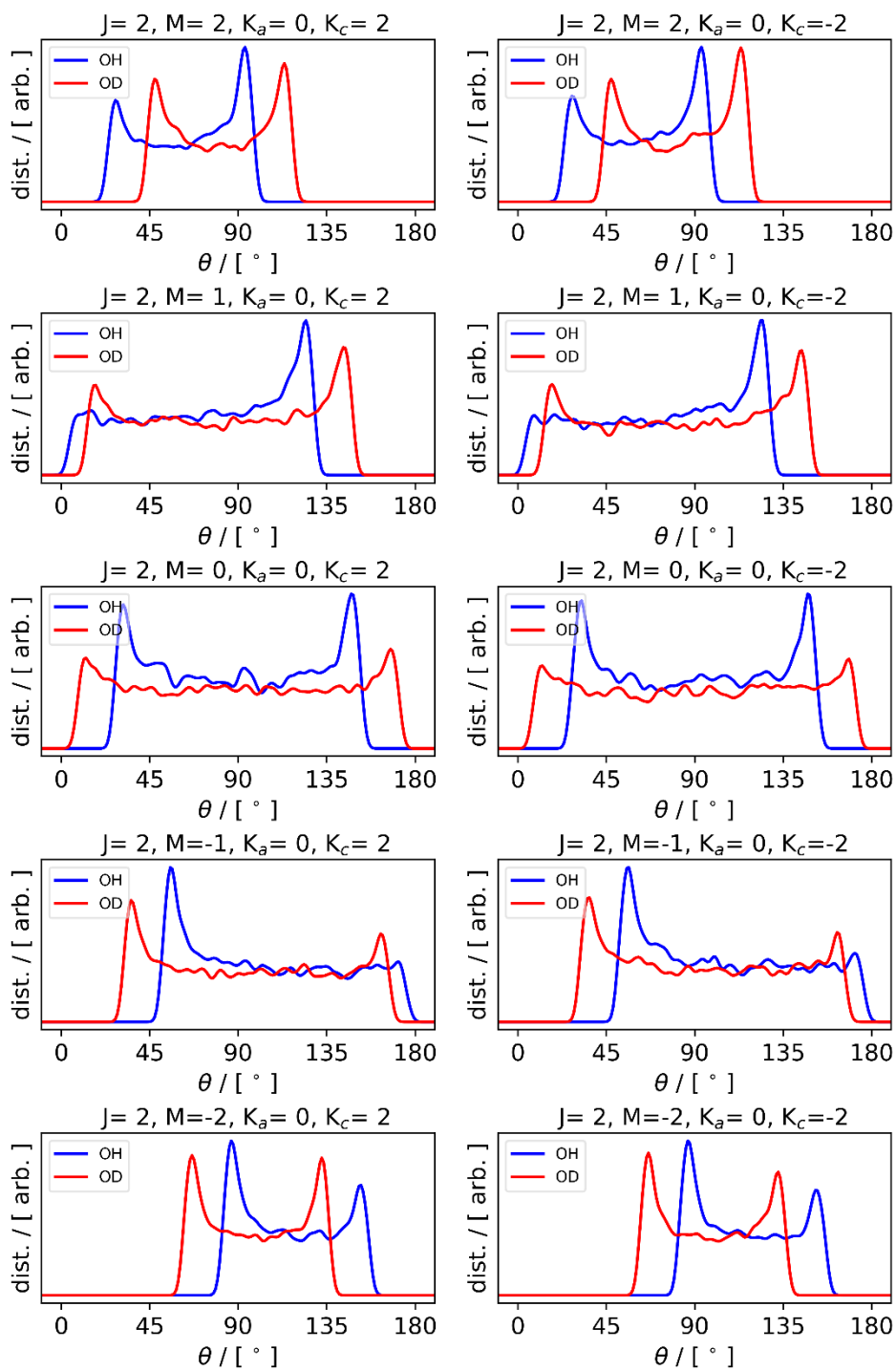


Figure S4. Distribution of the initial angle θ for the OH (blue) and the OD (red) bond. Different plots refer to different rotational states. Plots on the same line refer to rotational states that only differ in the sign of K_c .

References

1. Herzberg, G. *Molecular Spectra and Molecular Structure Volume II: Infrared and Raman Spectra of Polyatomic Molecules*. (Krieger Publishing Company, 1991).