Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

A quantum description of the proton movement in an idealized hydrogen bridge

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Supplementary Material

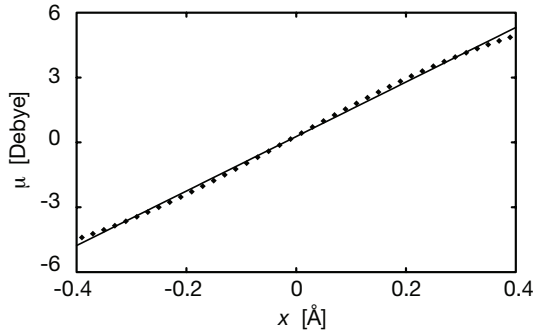

Figure S.1: Molecular dipole moment of the completely optimized $(Dih)_2H^+$ cation calculated with G03 (points) and the corresponding linear fit.

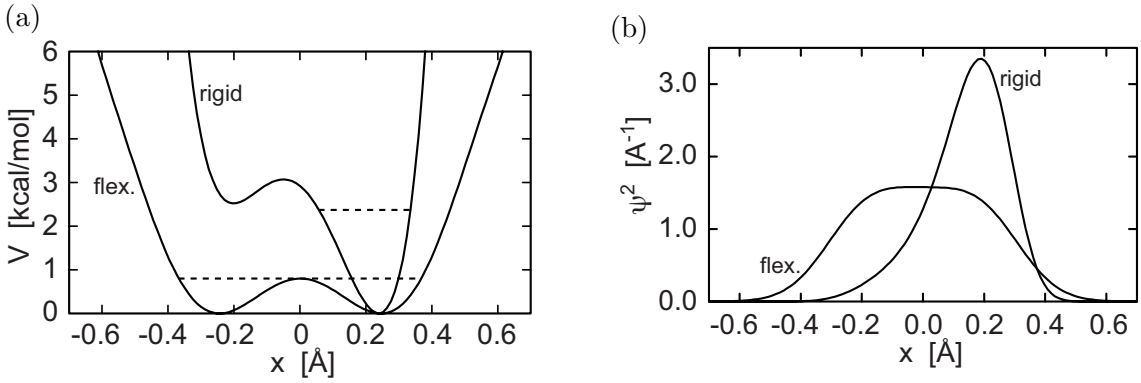

Figure S.2: Testing the scan conditions on the $(Dih)_2H^+$ cation. rigid: Rigid framework approximation as used in main body of the paper, flex: complete geometry optimization of the $(Dih)_2H^+$ ion under the constrains of a linear NHN^+ hydrogen bridge and a fixed H^+ position. a) Potential energy functions $V(x)$ [solid lines] and ground state energies ϵ_0 [dashed lines]. b) Squared ground state wave functions $\psi^2(x)$.

run	1	2	3	4
time	4000	4059	4108	4000
$\overline{T}$	297.5	301.7	295.1	80.8
$\sigma_{\overline{T}}$	34.3	36.5	34.7	9.2
$\sigma_{\overline{E}_{\mathrm{tot}}}$	0.11	0.12	0.12	0.03
$\overline{E}_{\mathrm{kin}}$	20.4	20.7	20.2	5.54
$\sigma_{\overline{E}_{\mathrm{kin}}}$	2.35	2.50	2.38	0.62
short	225	248	326	0
hops	7	13	11	0

time: total simulation time, $\overline{T}$: average temperature, $\sigma_{\overline{E}_{\mathrm{tot}}}$: standard deviation of $\overline{T}$, $\sigma_{\overline{E}_{\mathrm{tot}}}$: standard deviation of the average total energy, $\overline{E}_{\mathrm{kin}}$: average kinetic energy, $\sigma_{\overline{E}_{\mathrm{kin}}}$: standard deviation of $\overline{E}_{\mathrm{kin}}$, short: number of conformers with $d_{\mathrm{NN}} < 2.57$ Å, hops: number of observed changes in the general proton position. All times in fs, all energies in kcal/mol, all lengths in Å, all angles in degrees, all frequencies in cm^{-1}.

Table S.1: Selected properties of the BOMD simulations.

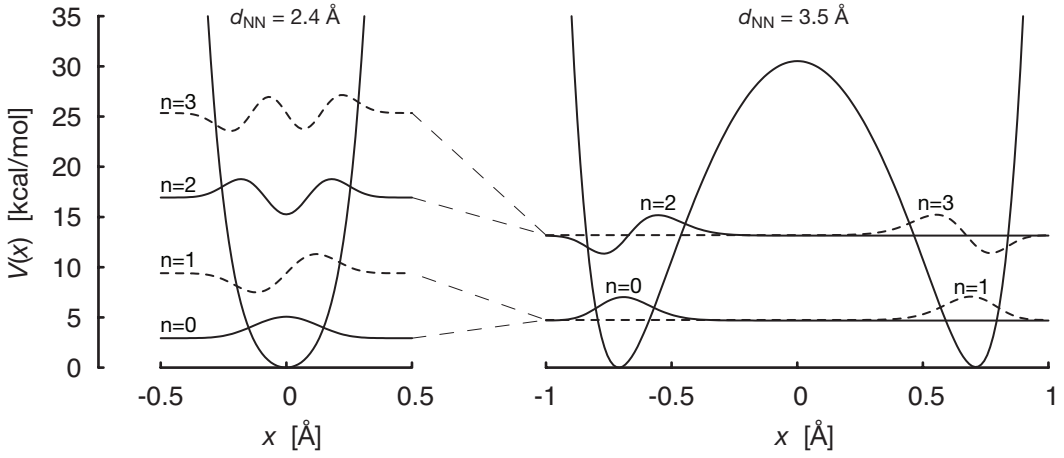

Figure S.3: Potential energy function $V(x)$ and the unscaled wave functions of the first 4 proton states at different heavy atom distances d_{NN}.

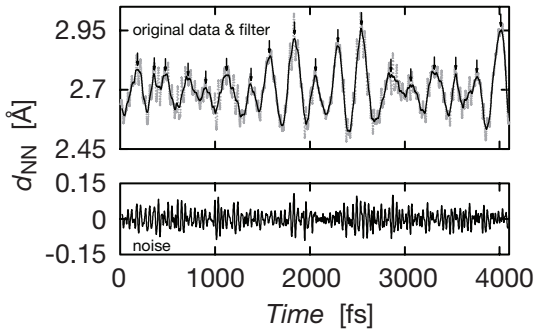

Figure S.4: Time series decomposition of the of the NN distance in $(Dih)_2H^+$ during run number 3 (295.1 K). grey dots: original data from the BOMD run, black solid line: filtered results from a floating average algorithm (symmetric average of 39 fs) and noise, small black arrows: 18 maxima used for the calculation of the periodicity.

Figure S.4 summarises the time series decomposition of d_{NN} in run number 3. The analysis showed that most of the noise in the d_{NN} values originates from a 15 fs disturbance, which can be linked to the movement of the linking proton, and second process with a estimated periodicity between 38 and 40 fs possibly originating from Dih ring vibrations in the 800 cm^{-1} region. The subsequent decomposition with a symmetric time averaging interval of 39 fs suggests a periodicity of 225.3 fs for the NN stretch vibration, which perfectly reproduces a periodicity of 225.4 fs from the harmonic frequency analysis. A repetition of this analysis on all three runs yielded values of 222.5 and 223.6 fs in good agreement with the harmonic frequency analysis. In summary, the BOMD simulations reproduce correctly the periodicity results from the harmonic frequency analysis and thereby link seamlessly to the previous quantum calculations.