Supplementary material (ESI) for PCCP

Reaction dynamics simulations of the identity S_N2 reaction H_2O + $HOOH_2^+ \rightarrow H_2OOH^+$ + H_2O. Requirements for reaction and competition with proton transfer

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Optimized geometries (MP2/6-31G(d)) in Å, energies (including ZPVE) in Hartree at 0 K, and frequencies in cm^{-1} scaled by a factor of 0.9434 (Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.)

H_2O, -76.175371

```
 H     0.020305     0.000000     0.000942
 O    -0.026185     0.000000     0.968516
 H     0.901548     0.000000     1.247209
1637.3
3561.4
3694.8
```

H_2OOH^+, -151.354775

```
 H     0.073521     0.000000     0.031203
 O    -0.007541     0.000000     1.018592
 O     1.410155     0.000000     1.381922
 H     1.504247     0.815651     1.951919
 H     1.504247    -0.815651     1.951919
412.6
859.3
1041.5
1133.7
1403.9
1571.8
3236.4
3318.3
3393.6
```

H_3O^+, -76.440456

```
 O    -0.041778    -0.089800    -0.029541
 H    -0.060871    -0.032109     0.959476
 H     0.884312    -0.032109    -0.377215
 H    -0.498821    -0.907427    -0.352720
910.2
1633.6
1633.7
3319.4
3425.8
3425.8
```

$HOO(H)\cdots H\text{-}OH_2^+$, -227.595778

```
 H     0.214219     0.004569    -0.040393
 O     0.151304     0.279270     0.901453
 O     1.403194    -0.284670     1.418407
```

H	1.744923	0.837134	2.177252
H	1.073413	-1.054092	1.939736
O	1.893711	1.778596	2.707581
H	2.778501	2.175621	2.548342
H	1.194915	2.428120	2.468733

104.5
138.2
333.7
355.7
480.4
534.4
679.0
879.3
1192.4
1286.9
1352.5
1550.1
1686.9
1868.0
3426.0
3439.4
3466.6
3528.2

TS S_N2, -227.546715

O	0.000000	0.000000	0.133587
H	0.000000	0.000000	1.116810
O	1.784433	0.000000	0.210445
O	-1.784433	0.000000	0.210445
H	1.990098	-0.789789	-0.338704
H	-1.990098	-0.789789	-0.338704
H	1.990098	0.789789	-0.338704
H	-1.990098	0.789789	-0.338704

-240.0
172.2
270.5
296.9
446.8
472.8
719.3
736.2
780.8
847.9
1249.0
1571.0
1576.1
3386.6
3414.6
3512.8
3525.5
3527.7

HOOH, -151.103862

O	0.058365	0.020177	-0.000086
O	0.002724	0.061694	1.467225
H	0.953117	-0.057102	1.653206
H	-0.326108	0.897410	-0.186067

318.0
875.8
1247.5
1381.0

```
3526.0
3528.1

H2OO, -151.018991
 O    -0.040757     0.070594     0.059826
 O     0.036357    -0.062972     1.569785
 H     0.904874     0.000234    -0.181472
 H    -0.452640    -0.783527    -0.181472
731.6
895.8
917.5
1581.6
3442.6
3564.9
```

RRKM Calculations

The procedure employed for the variational RRKM calculations has been described in detail by Grabowy and Mayer (Grabowy, J. A. D.; Mayer, P. M. *J. Phys. Chem. A* **2004**, *108*, 9726.). Unimolecular rate constants, $k(E)$ were obtained from the expression

$$k(E) = \frac{\sigma}{h}\frac{N^{\neq}(E, E_0, R^*)}{\rho(E)} \tag{1S}$$

where σ is the reaction symmetry number, h the Planck's constant, E_0 is the 0 K activation energy, $\rho(E)$ is the reactant ion density of states, and $N^{\neq}(E,E_0,R^*)$ is the sum-of-states at a O···H separation R^* using the general RRKM program by Zhu and Hase (*General RRKM Program*; Quantum Chemistry Program Exchange (QCPE) No. 644, Indiana University, 1993.).

The transition state for the dissociation of the protonated hydrogen peroxide water complex is obtained by identifying the O···H separation R^* with the lowest sum-of-states. Upon dissociation, six internal modes in the cluster are transformed into three translational and rotational modes. One out of these vanishing mode is the reaction coordinate, R. The torsion around the O···H-O bond in the dissociating complex is treated as a free rotor. The four remaining vanishing frequencies were then scaled in analogy to Grabowy and Mayer by

$$v'(R) = v(R_{\mathrm{eq}})\mathrm{e}^{-\alpha(R-R_{\mathrm{eq}})} \tag{2S}$$

where $v'(R)$ is the frequency at a O···H separation R, R_{eq} is the equilibrium O···H bond distance and α is an adjustable parameter. Equation 2S is based on the assumption that the four modes will vanish exponentially to zero along the reaction coordinate. The parameter α was determined by comparing the corresponding vibrations at the complex structure with those at 5.0 and 8.0 Å and then averaged. Here, the values for α were 0.20, 0.17, 0.43, and 0.38 for the first, third, fifth, and sixth-lowest mode in the complex. The second lowest mode was the torsion and the fourth lowest mode the reaction coordinate.

For the remaining 12 modes, the transition state frequencies were chosen to be the average of the complex frequencies and the frequencies of free HOOH and H_3O^+. This approximate approach of the transition state is illustrated in Figure S1.

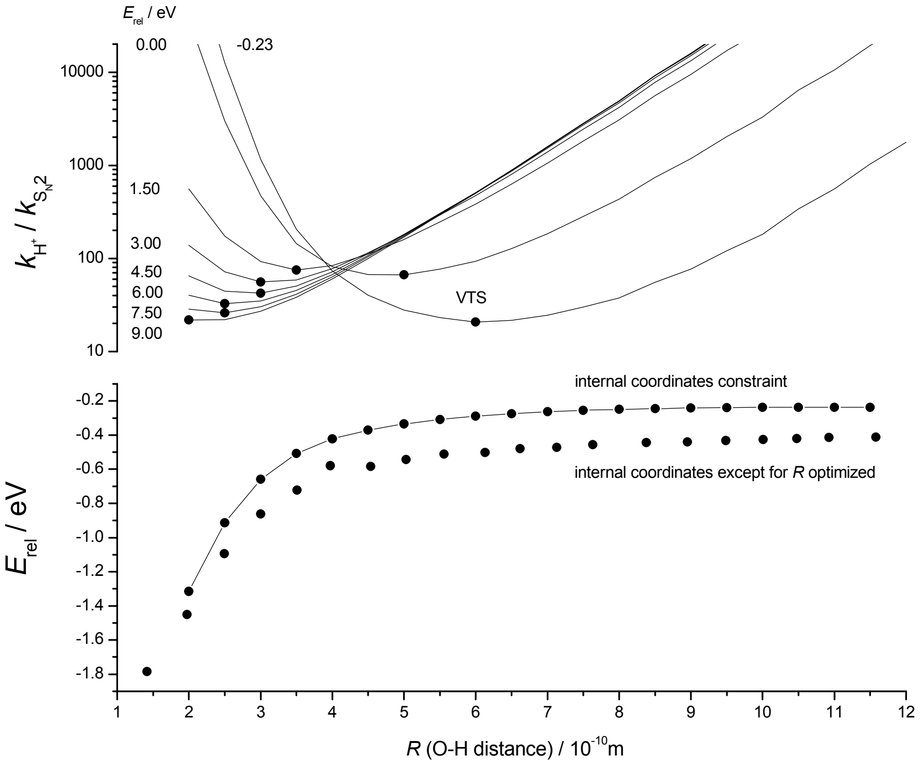


Figure S1. Plot of the relative rates of the identity S_N2 reaction, $k(S_N2)$, and the proton transfer reaction, $k(H^+)$, versus the O···H bond distance at various energies showing the variational transition state (VST), top, and the potential energy surface for the dissociation of HOO(H)···H-OH_2^+ at the MP2/6-31G(d) level relative to free H_2O and $HOOH_2^+$, bottom.

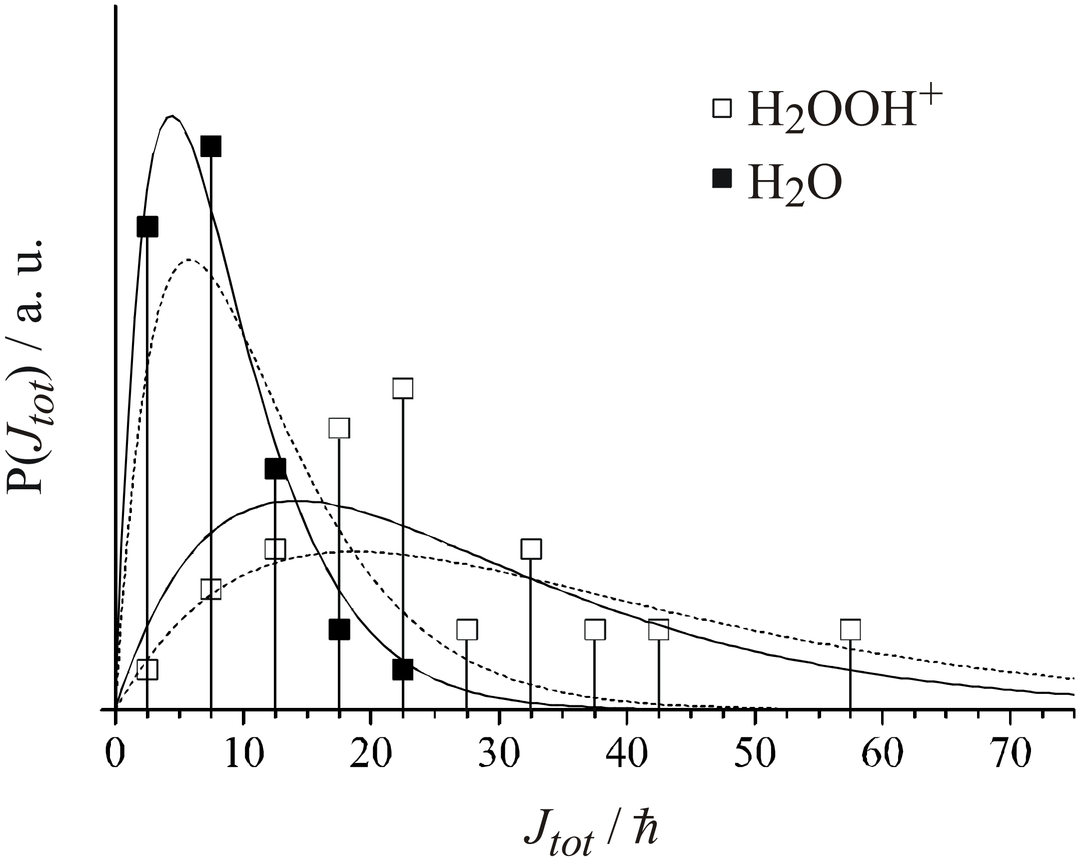
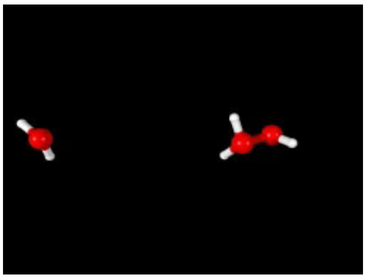


Figure S2. Total angular momentum for H_2O and $HOOH_2^+$ at a centre-of-mass distance of 8Å after starting from the TS, HOO(H)···H-OH_2^+, and adding 1.5eV kinetic energy to the releasing water molecule. The solid lines are Maxwell-Boltzmann distributions fitted to the data. The dashed lines are the corresponding distributions for free H_2O and $HOOH_2^+$ at 298K. Although there is an observable directed rotation of the releasing $HOOH_2^+$ molecule, it is not statistically significant ($J_x = 7.0 \pm 6.4$, $J_y = -5.9 \pm 5.2$, $J_z = -2.3 \pm 3.5$).

mpeg4 movies

Proton transfer

Movie 1 is an example for a thermal collision of H_2O with $HOOH_2^+$, no extra kinetic energy is added to the fragments. The fragments collide and form the metastable HOO(H)···H-OH_2^+ complex. At this stage, the proton is mostly bound to the water fragment. After 3ps, dissociation of the complex into protonated water and hydrogen peroxide.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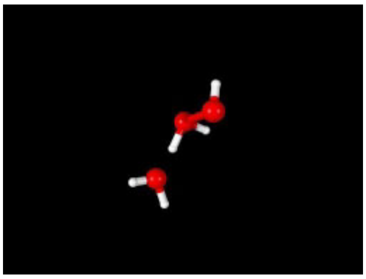
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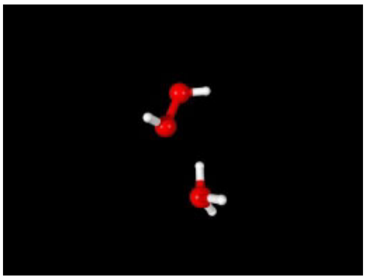
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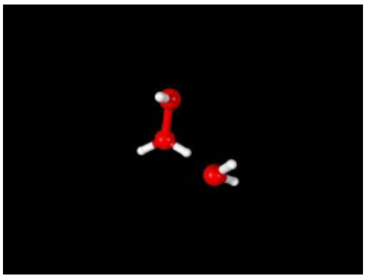
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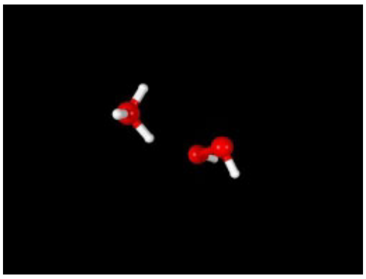
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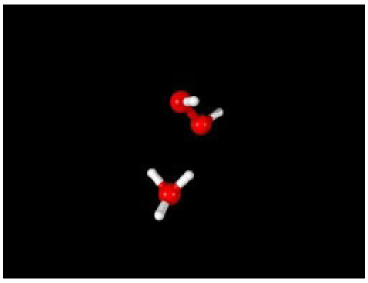
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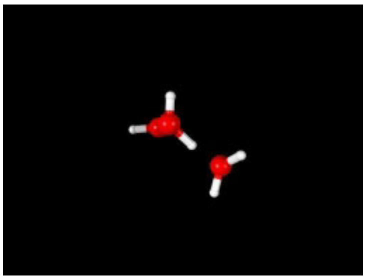
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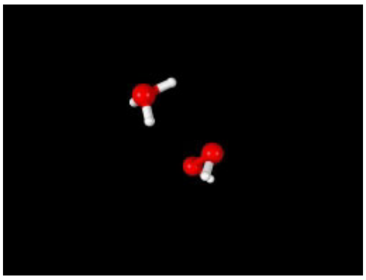
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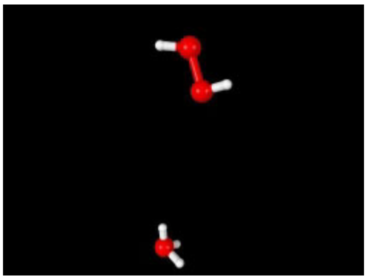
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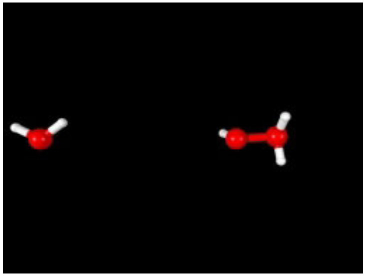
Identity S_N2

The kinetic energy and the relative orientation of the fragments are critical for a productive collision, Movie 2. The kinetic energy is partly transferred into the O-O stretch. The O-H bond in the OH fragments becomes also excited which is due to temporary hydrogen bonding to the dissociating water molecule.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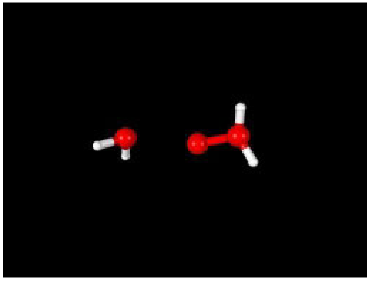
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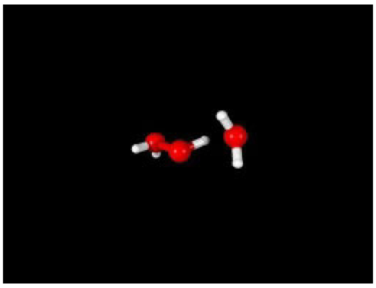
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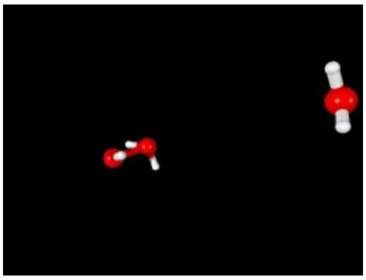
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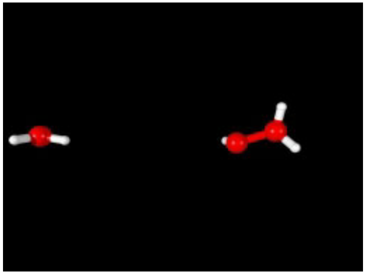
No identity S_N2

The molecules are upon collision perfectly aligned for an identity S_N2 reaction, but the translational motion and the phase of the vibration do not match, such that the intermediate TS like complex dissociates again towards the reactants side, Movie 3.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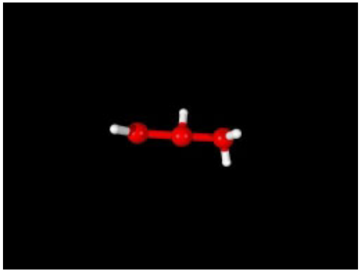
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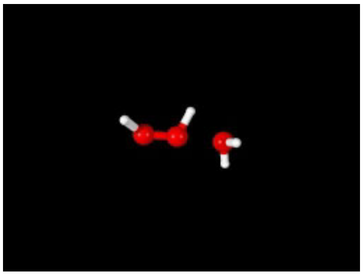
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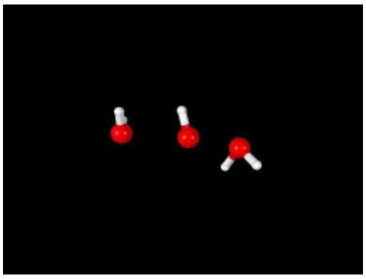
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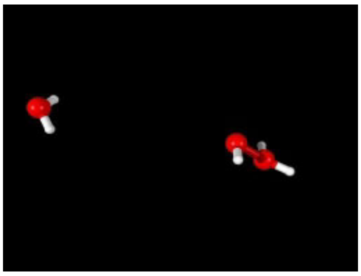
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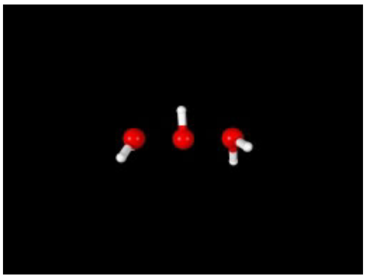
Low energy reaction channel

In Movie 4, the integration of the trajectory was started from the TS and 1.5eV kinetic energy were added to one of the water molecules. During the dissociation, a high rotational momentum is induced into the $HOOH_2^+$ fragment. A minor contribution to the rotational momentum is due to addition of kinetic energy along the O-O bond rather then along the proximate centre of mass vector between the fragments. However, during the initial stages of the dissociation, there is strong interaction between the water and the remaining $HOOH_2^+$, and at a given distance the HO part of $HOOH_2^+$ is hydrogen bonding to the water oxygen. This forces the H_2O fragment to move up and induces a counter-clockwise rotation of $HOOH_2^+$. For conservation of rotational momentum, the total system has to rotate counter-clockwise. Movie 4 shows how intimately rotation must be coupled to relative translation to accommodate successful passage through the S_N2 TS at low collisional energies. The rotational motion of the total system is not shown in Movie 4, since all frames are projected along the centre-of-mass of the fragments.



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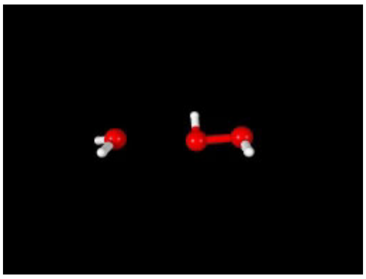

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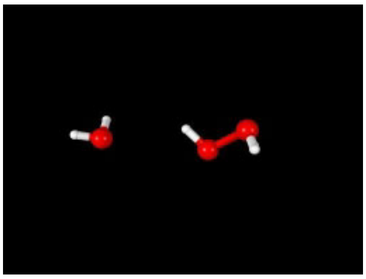

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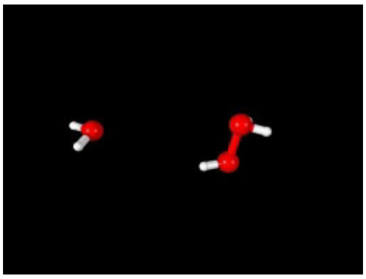

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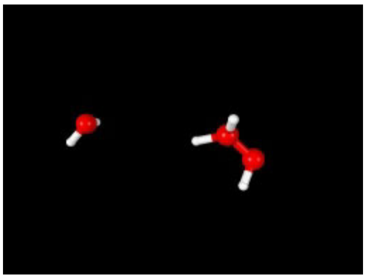

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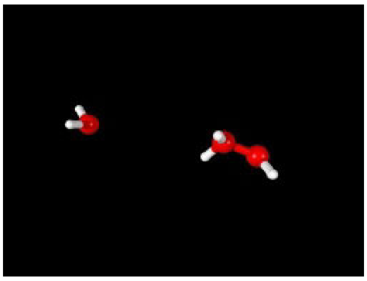

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