Supplementary Information for

Photolysis of Nitrophenols in Gas Phase and Aqueous Environment: A Potential Daytime Source for Atmospheric Nitrous Acid (HONO)

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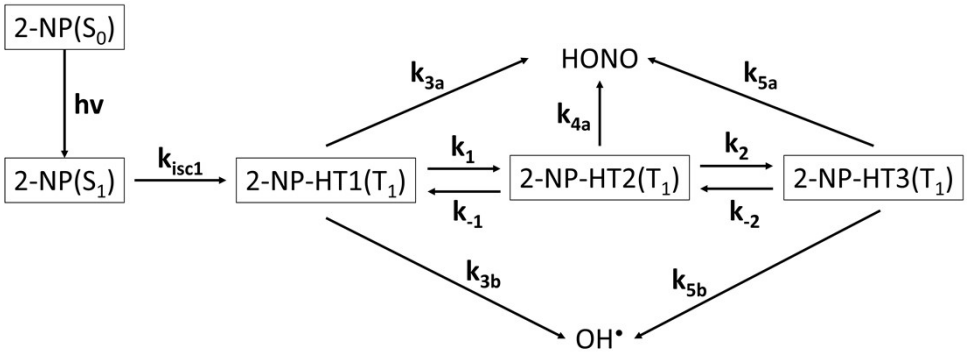
S1. Supplementary Methodology

S1.1 Kinetics Studies for Photolysis of 2-Nitrophenol in Gas Phase

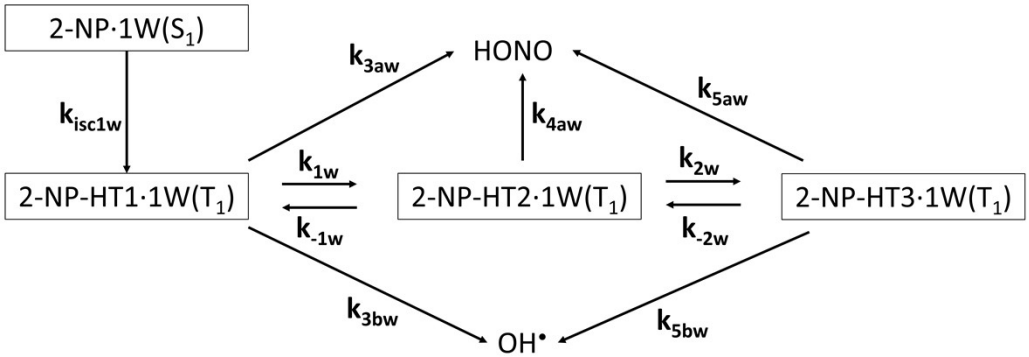
For gas-phase photolysis of 2-nitrophenol (2-NP), HONO and OH· originate from three isomers of 2-NP on T_1 state based on the previous discussions. Therefore, the kinetic model of gas-phase photolysis pathway for HONO and OH· formation from 2-NP are considered as follows:



Scheme S1. Kinetics Model for photolysis reaction of 2-NP for HONO and OH· formation.

where HONO comes from the three isomers of aci-2-NP, while OH· only originates from two isomers. For each isomer on T_1 state, intersystem crossing to hopping back to S_0 state is available, in which the rate constants for 2-NP-HT1(T_1), 2-NP-HT2(T_1) and 2-NP-HT3(T_1) are labelled as k_{isc2}, k_{isc3} and k_{isc4}, respectively. The $S_1 \rightarrow T_1$ transition is not an ultrafast process (see Figure S15 for details), so this transition cannot be ignored in kinetics analysis, and we assume that the rate of ISC is a wavelength and temperature independent value.

In addition, we also investigate the effect of water molecules on the photolysis of 2NP. With the presence of water, the kinetic model is similar with the unimolecular reaction above, which is shown in Scheme S2. The rate constants of gas-phase photolysis from water-aci-2-NP complexes are marked as "w". Here, we assume that 2-NP and water-2-NP complex have the same ISC rate from S_1 to T_1 due to the weak binding energy between two molecules.



Scheme S2. Kinetics Model for photolysis reaction of water-2-NP hydrated complex for HONO and OH· formation.

For water-assisted reactions, the 2-NP forms a hydrated complex first, and the formation of water-2-NP complex can be regarded as an equilibrium, *i.e.,*

$$\text{2-NP}(S_0) + H_2O \overset{\Delta G_1}{\underset{K_{eq1}}{\rightleftharpoons}} \text{2-NP·1W}(S_0) \tag{S1}$$

whose equilibrium constant, K_{eq1}, is written by

$$K_{eq1} = c^o \frac{[\text{2 - NP} \cdot \text{1W}]}{[H_2O][\text{2 - NP}]} = exp(\frac{\Delta G_1}{RT}) \tag{S2}$$

where ΔG is the formation free energy of water-2-NP complex, and c^o is standard molar concentration (1mol/L).

Then, to evaluate the reaction rate of formation of HONO and OH· on T_1 state, the micro-kinetics is implicated by solving the following differential rate equations to characterize the time-dependent variation of concentration of each specie:

$$\frac{d}{dt}[\text{2-NP}] = -k_{isc1}[\text{2-NP}](t) \tag{S3}$$

$$\frac{d}{dt}[\text{2-NP-HT1}] = k_{isc1}[\text{2-NP}](t) - (k_{isc2}+k_1+k_{3a}+k_{3b})[\text{2-NP-HT1}](t) + k_{-1}[\text{2-NP-HT2}](t) \tag{S4}$$

$$\frac{d}{dt}[\text{2-NP-HT2}] = k_1[\text{2-NP-HT1}](t) - (k_{isc3}+k_{-1}+k_2+k_{4a})[\text{2-NP-HT2}](t) + k_{-2}[\text{2-NP-HT3}](t) \tag{S5}$$

$$\frac{d}{dt}[\text{2-NP-HT3}] = k_2[\text{2-NP-HT2}](t) - (k_{isc4}+k_{-2}+k_{5a}+k_{5b})[\text{2-NP-HT3}](t) \tag{S6}$$

$$\frac{d}{dt}[\text{HONO}] = k_{3a}[\text{2-NP-HT1}](t) + k_{4a}[\text{2-NP-HT2}](t) + k_{5a}[\text{2-NP-HT3}](t) \tag{S7}$$

$$\frac{d}{dt}[\text{OH·}] = k_{3b}[\text{2-NP-HT1}](t) + k_{5b}[\text{2-NP-HT3}](t) \tag{S8}$$

Moreover, the photolysis of water-2-NP has the similar issue:

$$\frac{d}{dt}[\text{2-NP·1W}] = -k_{isc1w}[\text{2-NP·1W}](t) \tag{S9}$$

$$\frac{d}{dt}[\text{2-NP-HT1·1W}] = k_{isc1w}[\text{2-NP·1W}](t) - (k_{isc2w}+k_{1w}+k_{3aw}+k_{3bw})[\text{2-NP-HT1·1W}](t) + k_{-1w}[\text{2-NP-HT2·1W}](t) \tag{S10}$$

$$\frac{d}{dt}[\text{2-NP-HT2·1W}] = k_{1w}[\text{2-NP-HT1·1W}](t) - (k_{-1w}+k_{2w}+k_{4aw}+k_{isc3w})[\text{2-NP-HT2·1W}](t) + k_{-2w}[\text{2-NP-HT3·1W}](t) \tag{S11}$$

$$\frac{d}{dt}[\text{2-NP-HT3·1W}] = k_{2w}[\text{2-NP-HT2·1W}](t) - (k_{-2w}+k_{5aw}+k_{5bw}+k_{isc4w})[\text{2-NP-HT3·1W}](t) \quad \text{(S12)}$$

$$\frac{d}{dt}[\text{HONO}] = k_{3aw}[\text{2-NP-HT1·1W}](t) + k_{4aw}[\text{2-NP-HT2·1W}](t) + k_{5aw}[\text{2-NP-HT3·1W}](t) \quad \text{(S13)}$$

$$\frac{d}{dt}[\text{OH·}] = k_{3b}[\text{2-NP-HT1·1W}](t) + k_{5b}[\text{2-NP-HT3·1W}](t) \quad \text{(S14)}$$

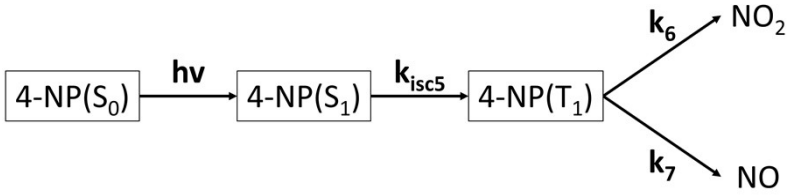
In addition, the concentration of water molecules is relevant to the relative humidity (RH) and temperature, which is defined as

$$[H_2O] = \frac{10^{-3} N_A RH\% p^*_{H_2O}}{RT} (molecules \cdot cm^{-3}) \quad \text{(S15)}$$

where $p^*_{H_2O}$ is the equilibrium vapor pressure of water over a flat pure water surface at a given temperature (7.72×10^{-2} kPa at 250 K and 3.57 kPa at 300 K, respectively), and N_A is the Avogadro's constant. The concentration of water vapors is about $10^{15} \sim 10^{17}$ molecules·cm^{-3} ranging from 10% at 250 K to 100% RH at 300 K (Table S9). Such values are consistent with the previously reported data.[11] Due to the concentration of H_2O being much larger than NPs, we do not consider the concentration changes of water molecules. The concentration of water in different RH are given in Table S9, and the time-dependent evolution of concentration of each product is shown in Figure S16.

S1.2 Kinetics Studies for Photolysis of 4-Nitrophenol in Gas Phase

For gas-phase photolysis of 4-nitrophenol (4-NP), the NO_2 and NO originate from 4-NP on T_1 state based on the previous discussions. Therefore, the kinetic model of gas-phase photolysis pathway for NO_2 and NO formed from 4-NP are considered as the following individual paths:



Scheme S3. Kinetics Model for photolysis reaction of 4-NP for NO_2 and NO formation in gas-phase.

In addition, with the presence of water, the rate constant of gas-phase photolysis from water-4-NP complexes can also obtain the similar kinetic model.

Then, similar with the discussion above, the micro-kinetics to evaluate the reaction rate of formation of NO_2 and NO formation is implicated by solving the following differential rate equations characterize the time-dependent variation of concentration of each specie:

$$\frac{d}{dt}[\text{4-NP}] = k_{isc5}[\text{4-NP}](t) \quad \text{(S16)}$$

$$\frac{d}{dt}[\text{4-NP}(T_1)] = k_{isc5}[\text{4-NP}](t) - (k_{isc6}+k_6+k_7)[\text{4-NP}(T_1)](t) \quad \text{(S17)}$$

$$\frac{d}{dt}[NO_2] = k_6[\text{4-NP}(T_1)](t) \quad \text{(S18)}$$

$$\frac{d}{dt}[NO] = k_7[\text{4-NP}(T_1)](t) \quad \text{(S19)}$$

where k_{isc6} is rate constant the $T_1 \rightarrow S_0$ transition at the minimum of T_1 surface of 4-NP. The related data and calculated results are shown in Figure S17 and Table S6, S12.

S1.3 Kinetics Studies for HONO Formation from 4-Nitrophenol in Gas Phase

Gas-phase HONO formation from 4-NP can be regarded as after the removal of 4-NP, and with the addition of water or oxygen molecules. The reaction routes are in the following thermal reactions:

$$\text{B1} + H_2O \xrightarrow{k_8} \text{B4} + \text{OH}\cdot \quad \text{(S20)}$$

$$\text{B4} + \text{OH}\cdot \xrightarrow{k_9} \text{B5a} \quad \text{(S21)}$$

$$\text{B5a} + NO_2 \xrightarrow{k_{10}} \text{HONO} + \text{P5} \quad \text{(S22)}$$

$$\text{B4} + \text{OH}\cdot \xrightarrow{k_{11}} \text{B5b} \quad \text{(S23)}$$

$$\text{B5b} + NO_2 \xrightarrow{k_{12}} \text{HONO} + \text{P6} \quad \text{(S24)}$$

$$\text{B4} + \text{OH}\cdot \xrightarrow{k_{13}} \text{B5c} \quad \text{(S25)}$$

$$\text{B5c} + NO_2 \xrightarrow{k_{14}} \text{HONO} + \text{P1} \quad \text{(S26)}$$

where k_8, k_9, k_{11}, k_{13} are the adiabatic rate constants, while k_{10}, k_{12}, k_{14} are the non-adiabatic rate constants. To obtain the quantum yields of HONO initiated from the gas-phase photolysis of 4-NP, the following differential rate equations characterize the time-dependent variation of concentration of HONO is solved:

$$\frac{d}{dt}[\text{B1}] = -k_8[\text{4-NP}] \cdot [H_2O] \quad \text{(S27)}$$

$$\frac{d}{dt}[\text{B4}] = \frac{d}{dt}[\text{OH}\cdot] = k_8[\text{4-NP}] \cdot [H_2O] - (k_9+k_{11}+k_{13})[\text{B4}] \cdot [\text{OH}\cdot] \quad \text{(S28)}$$

$$\frac{d}{dt}[\text{B5a}] = k_9[\text{B4}] \cdot [\text{OH}\cdot] - k_{10}[\text{B5a}] \cdot [NO_2] \quad \text{(S29)}$$

$$\frac{d}{dt}[\text{B5b}] = k_{11}[\text{B4}] \cdot [\text{OH}\cdot] - k_{12}[\text{B5b}] \cdot [\text{NO}_2] \quad \text{(S30)}$$

$$\frac{d}{dt}[\text{B5c}] = k_{13}[\text{B4}] \cdot [\text{OH}\cdot] - k_{14}[\text{B5c}] \cdot [\text{NO}_2] \quad \text{(S31)}$$

$$\frac{d}{dt}[\text{HONO}] = (k_{10}[\text{B5a}] + k_{12}[\text{B5b}] + k_{14}[\text{B5c}]) \cdot [\text{NO}_2] \quad \text{(S32)}$$

The initial concentration/population of B1 is obtained from the previous micro-kinetics analysis, which is shown in Figure S17. Here, we use the concentration/population of B1 generated under the 80 kcal/mol irradiation (2.16×10^{-2}) and study the HONO formation under the relative humidity of 10%, 30%, 50%, 70%, 90% and 100% at 250 K and 300 K. The quantum yields of HONO are shown in Figure S18.

S1.4 Kinetics Studies for Photolysis of 4-Nitrophenol in Aqueous Phase

For aqueous-phase (or air-water interfaces) photolysis of 4-NP, the NO_2, NO and HONO originate from 4-NP on T_1 state based on the previous discussions. Therefore, the kinetic model of aqueous-phase photolysis pathway for NO_2, NO and HONO formation from 4-NP are considered as follows:

Path I:

$$\text{4-NP}(S_0, \text{aq}) \xrightarrow{h\nu} \text{4-NP}(S_1, \text{aq}) \quad \text{(S33)}$$

$$\text{4-NP}(S_1, \text{aq}) \xrightarrow{k_{isc7}} \text{4-NP}(T_1, \text{aq}) \quad \text{(S34)}$$

$$\text{4-NP}(T_1, \text{aq}) \xrightarrow{k_{15}} \text{B1(aq)} + NO_2 \quad \text{(S35)}$$

$$\text{4-NP}(T_1, \text{aq}) \xrightarrow{k_{16}} \text{B2(aq)} + \text{NO} \quad \text{(S36)}$$

Path II:

$$\text{4-NP}(S_0, \text{aq}) + H_2O \overset{\Delta G_3}{\underset{K_{eq3}}{\rightleftharpoons}} \text{4-NP·1W}(S_0, \text{aq}) \quad \text{(S37)}$$

$$\text{4-NP·1W}(S_0, \text{aq}) \xrightarrow{h\nu} \text{4-NP·1W}(S_1, \text{aq}) \quad \text{(S38)}$$

$$\text{4-NP·1W}(S_1, \text{aq}) \xrightarrow{k_{isc7w}} \text{4-NP·1W}(T_1, \text{aq}) \quad \text{(S39)}$$

$$\text{4-NP·1W}(T_1, \text{aq}) \xrightarrow{k_{17}} \text{HONO} \quad \text{(S40)}$$

Path III:

$$\text{4-NP}(S_0, \text{aq}) + 3H_2O \overset{\Delta G_4}{\underset{K_{eq4}}{\rightleftharpoons}} \text{4-NP·3W}(S_0, \text{aq}) \quad \text{(S41)}$$

$$\text{4-NP·3W}(S_0, \text{aq}) \xrightarrow{h\nu} \text{4-NP·3W}(S_1, \text{aq}) \quad \text{(S42)}$$

$$\text{4-NP·3W}(S_1, \text{aq}) \xrightarrow{k_{isc7w}} \text{4-NP·3W}(T_1, \text{aq}) \quad \text{(S43)}$$

$$\text{4-NP·3W}(T_1, \text{aq}) \xrightarrow{k_{18}} \text{aci-4-NP·3W}(T_1, \text{aq}) \quad \text{(S44)}$$

$$\text{aci-4-NP·1W}(T_1, \text{aq}) \xrightarrow{k_{19}} \text{HONO} \quad \text{(S45)}$$

$$\text{aci-4-NP·1W}(T_1, \text{aq}) \xrightarrow{k_{20}} \text{OH·} \quad \text{(S46)}$$

In these cases, the NO_2 and NO formation are unimolecular reaction, while the HONO formation requires the participation of water vapors for both bimolecular reactions of 4-NP and unimolecular photolysis of aci-4-NP. Here, we calculated the kinetics of the photolysis reaction of 4-NP in solution under 100% humidity conditions which represents the concentration of water molecules at the air-water interface. The time-dependent variation of concentration of each species are computed as follows:

Path I:

$$\frac{d}{dt}[\text{4-NP}] = -k_{isc7}[\text{4-NP}](t) \quad \text{(S47)}$$

$$\frac{d}{dt}[\text{4-NP}(T_1, \text{aq})] = k_{isc7}[\text{4-NP}](t) - (k_{15}+k_{16}+k_{isc8})[\text{4-NP}(T_1, \text{aq})] \quad \text{(S48)}$$

$$\frac{d}{dt}[NO_2] = k_{15}[\text{4-NP}(T_1)](t) \quad \text{(S49)}$$

$$\frac{d}{dt}[\text{NO}] = k_{16}[\text{4-NP}(T_1)](t) \quad \text{(S50)}$$

Path II:

$$\frac{d}{dt}[\text{4-NP·1W}] = -k_{isc7w}[\text{4-NP·1W})](t) \quad \text{(S51)}$$

$$\frac{d}{dt}[\text{4-NP·1W}(T_1, \text{aq})] = k_{isc7w}[\text{4-NP·1W}](t) - (k_{17}+k_{isc9})[\text{ 4-NP·1W}(T_1, \text{aq})] \quad \text{(S52)}$$

$$\frac{d}{dt}[\text{HONO}] = k_{17}[\text{4-NP·1W}(T_1, \text{aq})](t) \quad \text{(S53)}$$

Path III:

$$\frac{d}{dt}[\text{4-NP·3W}] = -k_{isc7w}[\text{4-NP·3W})](t) \quad \text{(S54)}$$

$$\frac{d}{dt}[\text{4-NP·3W}(T_1, \text{aq})] = k_{isc7w}[\text{4-NP·3W}](t) - (k_{18}+k_{isc10})[\text{4-NP·3W}(T_1, \text{aq})] \quad \text{(S55)}$$

$$\frac{d}{dt}[\text{aci-4-NP·3W}(T_1, \text{aq})] = k_{18}[\text{4-NP·3W}(T_1, \text{aq})] - (k_{19}+k_{20}+k_{isc11})[\text{aci-4-NP·3W}(T_1, \text{aq})] \quad \text{(S56)}$$

$$\frac{d}{dt}[\mathrm{HONO}] = k_{19}[\text{aci-4-NP·3W}(T_1, \text{aq})](t) \quad \text{(S57)}$$

where k_{isc8}, k_{isc9}, and k_{isc10} is rate constant the $T_1 \rightarrow S_0$ transition at the minimum of T_1 surface of 4-NP, 4-NP·1W and 4-NP·3W with the SMD solvation model. To be noticed that the aci-4-NP·3W and aci-4-NP·1W can regard as have the same concentration. The time-dependent evolution of concentration of each product is shown in Figure S19.

S1.5 Photo-absorptions Cross-sections Calculation

The photo-absorption cross-sections are computed with the nuclear ensemble approach (NEA)[1-2] in combination with the TDDFT, performed with the Gaussian 09 software as implemented in the Newton-X package.[3-4] In NEA, the configurations are sampled via the Wigner distributions of a set of independent harmonic potentials, which represent the normal modes under the optimized geometry of the ground state. The corresponding Wigner distribution at 250K and 300K is considered for the sampling. Excitation energies $\Delta E_{0n}(q_i)$ and oscillator strengths $f_{0n}(q_i)$ of the n^{th} excited state are computed for each sampled configuration q_i. Then, the photo-absorption cross-section is defined as (in atomic units)[5]

$$\sigma(E) = \frac{\pi e^2 \gamma}{2mc\varepsilon_0 h} \sum_{l \neq i}^{N_{fs}} \left[\frac{1}{N_p^l} \sum_{k}^{N_p^l} f_{il}(R_k) g(E - \Delta E_{il}(R_k), \delta) \right] \quad \text{(S58)}$$

where the phenomenological line profile g is represented by a normalized Gaussian line shape function centered at each excitation energy $\Delta E_{0n}(q_i)$ with the linewidth of $\delta = 0.1$ eV, which is large enough to suppress the artificial swell of the cross-section curve and small enough to maintain the actual overall shape, and γ is given by[6]

$$\gamma = 1 - exp\left(-\frac{\Delta E}{k_B T}\right) \quad \text{(S59)}$$

S2. Supplementary Figures

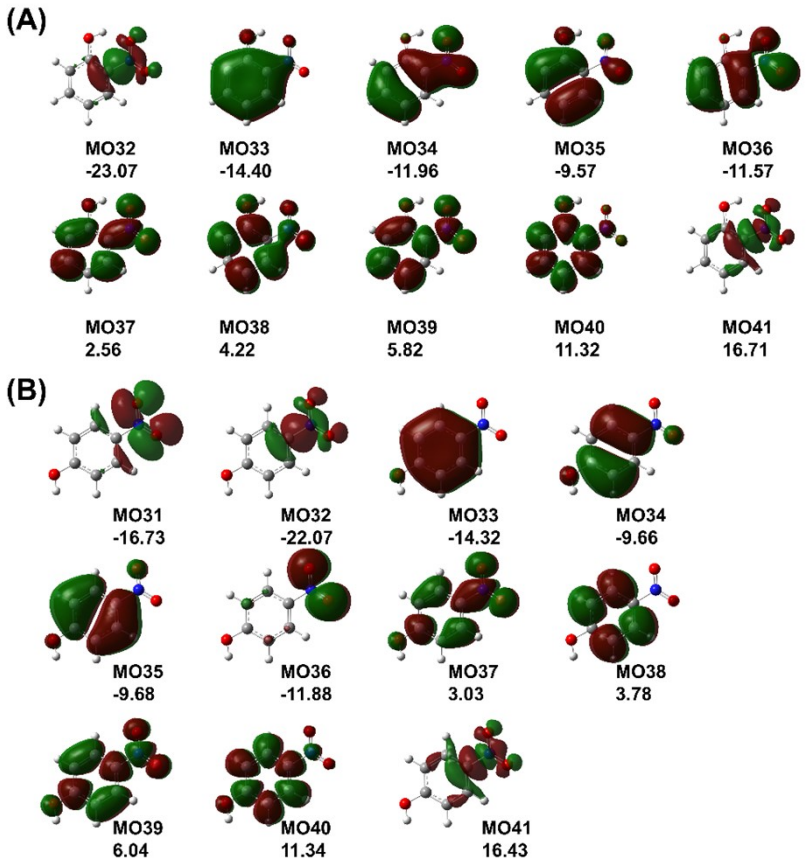


Figure S1. Active-space orbitals used in CASSCF and CASPT2 calculation for (A) 2-nitrophenol and (B) 4-nitrophenol. Each CASPT2 orbital energy (unit: eV) is listed below.

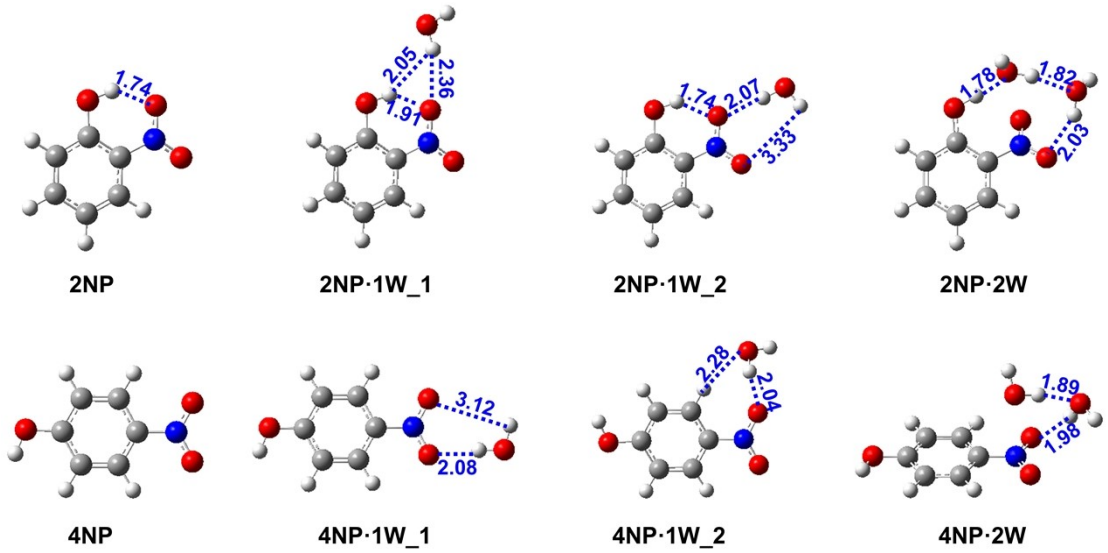


Figure S2. B3LYP/6-311++G(d,p) optimized structures of water-NP hydrated complexes, and the intermolecular distances are also shown (in Å).

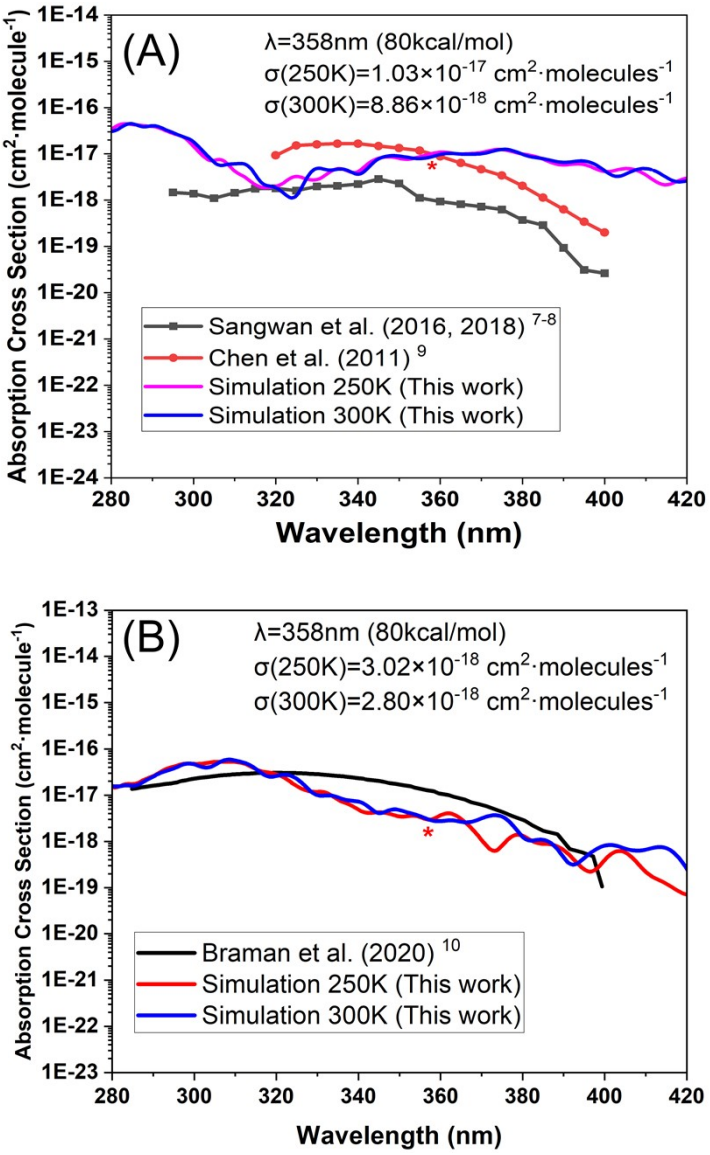


Figure S3. Computed photo-absorption cross-sections (in a unit of $cm^2 \cdot molecules^{-1}$) of (A) 2-NP and (B) 4-NP using the nuclear ensemble approach (NEA) in combination with the time-dependent density functional theory calculation at TD-B3LYP/6-311++G(d,p) level of theory. The value of photo-absorption cross-section of 250K and 300K under 358 nm (E = 80 kcal/mol) wavelength of light are marked on the figure.

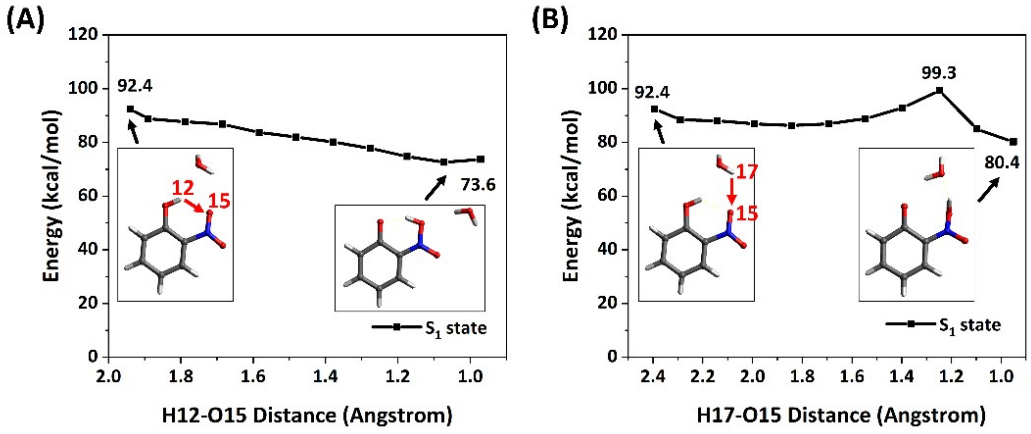


Figure S4. Computed potential energy surfaces (CASPT2//CASSCF/def2-TZVPP) of (A) intramolecular and (B) water-assisted intermolecular excited-state hydrogen transfer of water-2-nitrophenol complex on the S_1 state.

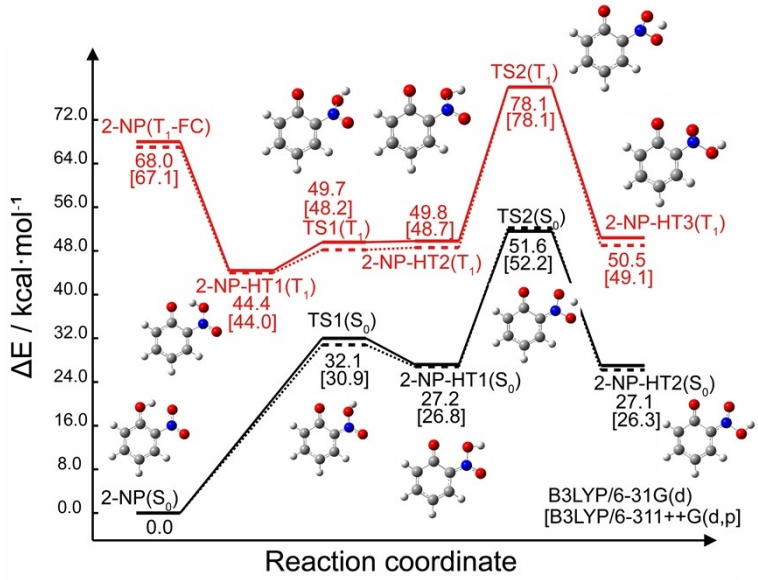


Figure S5. Computed unimolecular hydrogen transfer reaction pathways (at B3LYP/6-311++G(d,p) level) of 2-NP molecule along S_0 and T_1 potential energy surface. The molecular geometries are also shown in the Figure. All the energies are including ZPE correction of each optimized structures. See text for discussions.

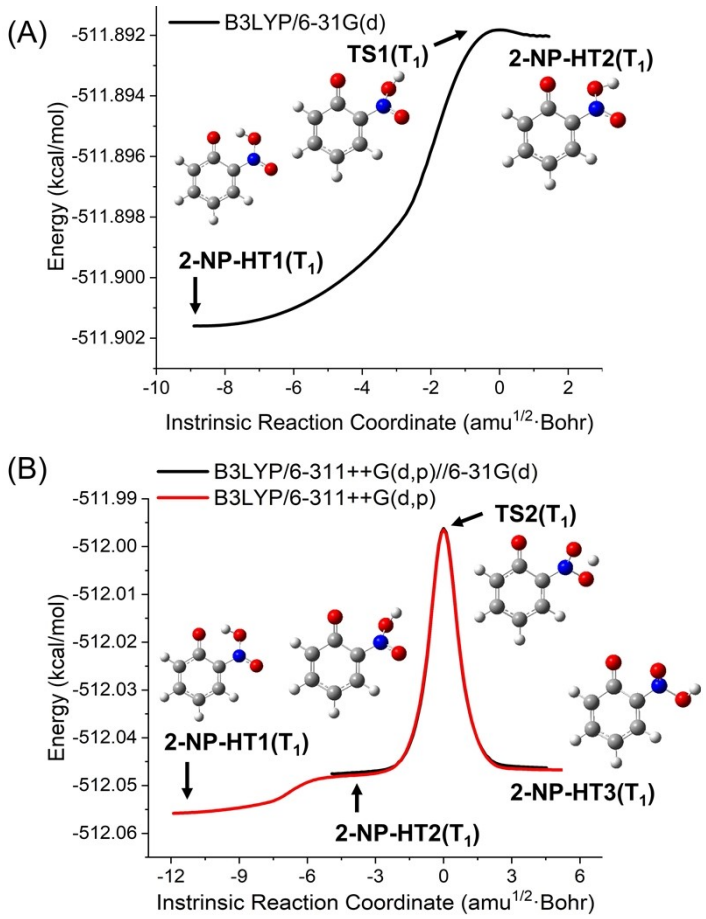


Figure S6. Intrinsic reaction coordinate (IRC) profile for isomerization of 2-NP on T_1 state. The energies are calculated at B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) level.

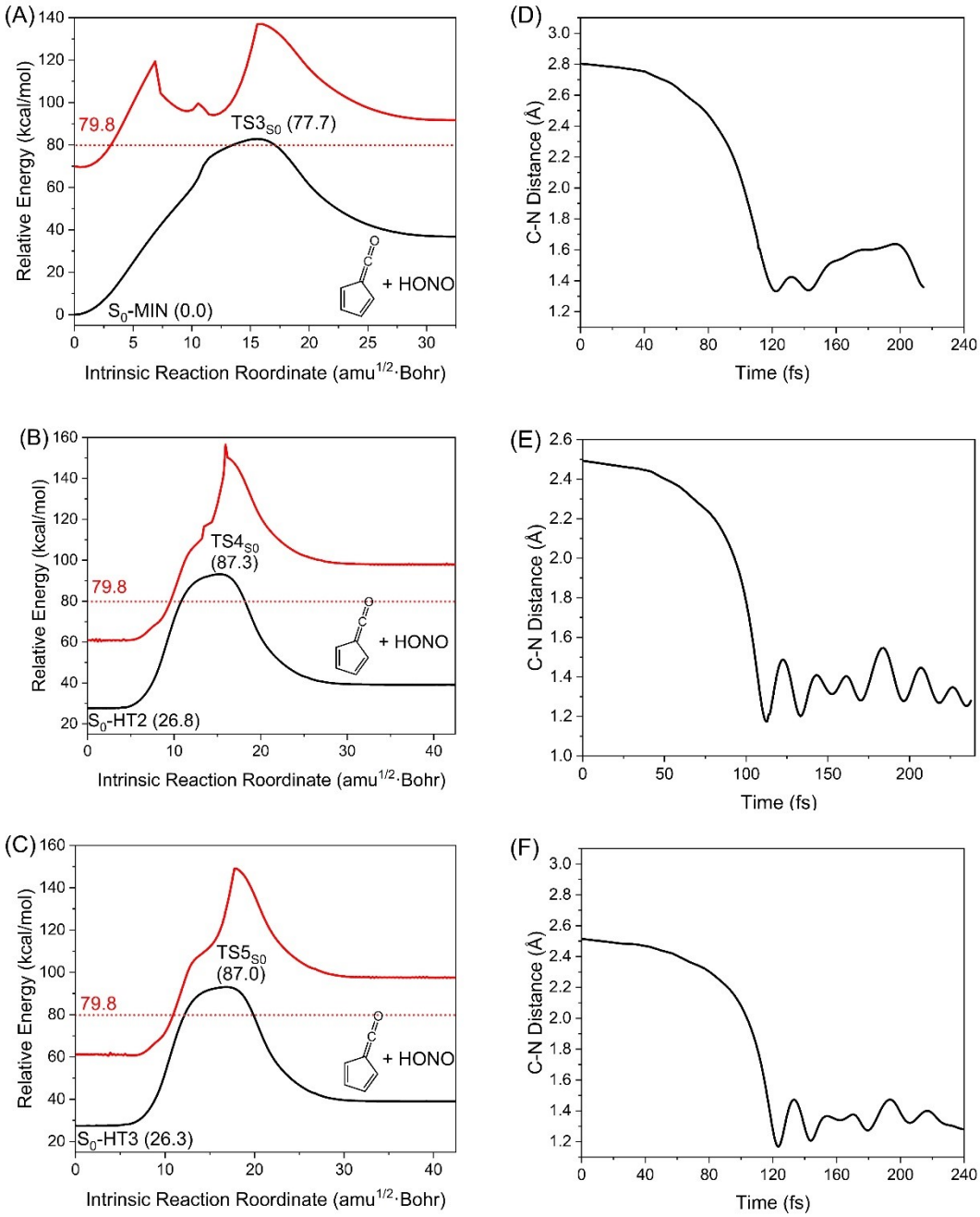


Figure S7. Computed unimolecular C-N dissociation reaction pathways (at B3LYP/6-311++G(d,p) level) of (A) 2-NP, (B) 2-NP-HT2, and (C) 2-NP-HT3 along S_0 potential energy surface for HONO formation. The red dash line refers to the vertical excitation energy of S_1 state in the photolysis. The red and black solid lines stand for energies of T_1 and S_0 state, respectively. The numbers in parentheses indicate the energies of the optimized structures including ZPE correction. (D) ~ (F) represents the distances between the C-N bond length (in) of 2-NP, 2-NP-HT2, and 2-NP-HT3 are plotted as function of time for BOMD trajectories starting from the transition state in the IRC calculations, respectively. See text for discussions.

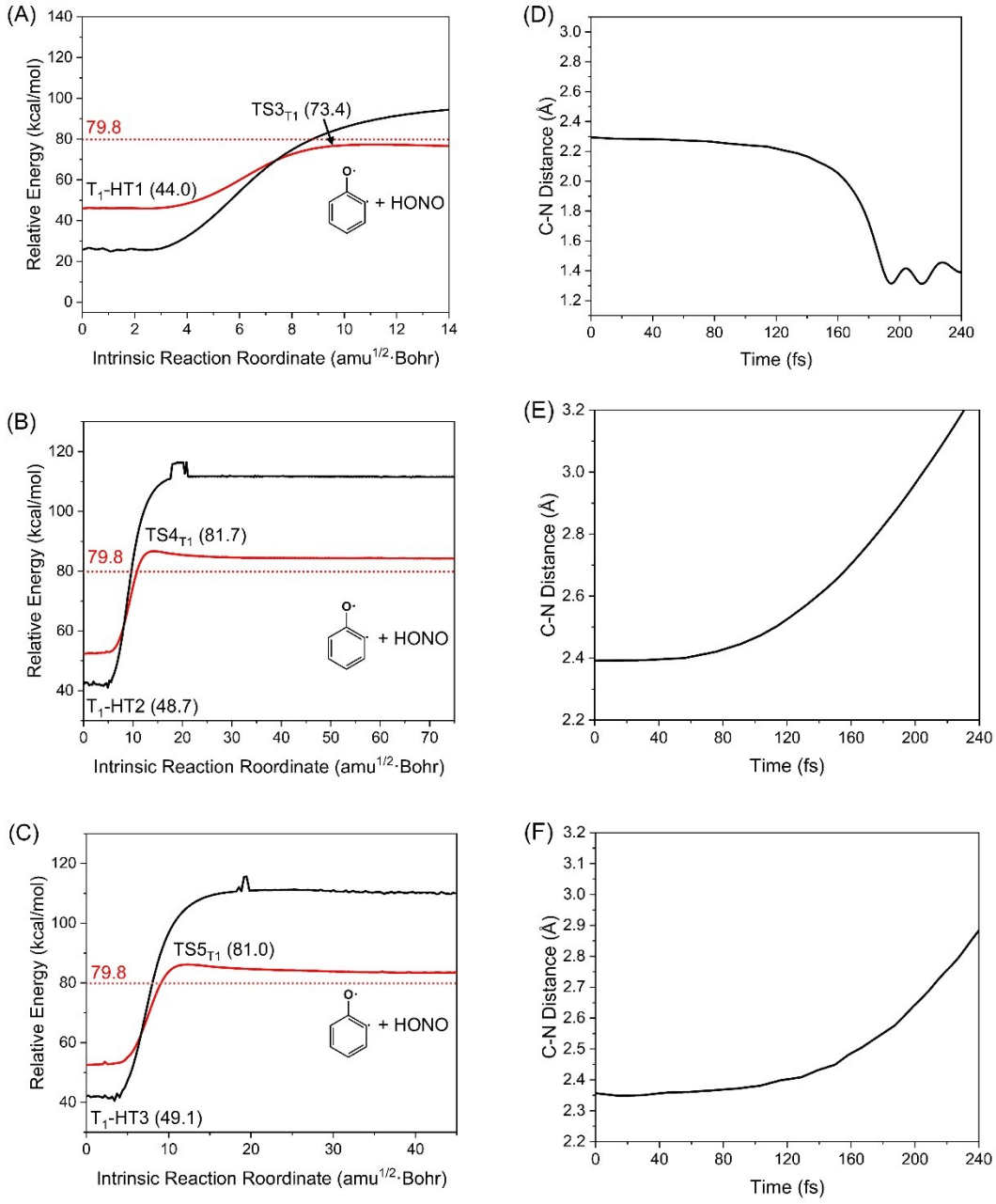


Figure S8. Computed unimolecular C-N dissociation reaction pathways (at B3LYP/6-311++G(d,p) level) of (A) 2-NP-HT1, (B) 2-NP-HT2, and (C) 2-NP-HT3 along T_1 potential energy surface for HONO formation. The red dash line refers to the vertical excitation energy of the S_1 state in the photolysis. The red and black solid lines stand for energies of T_1 and S_0 state, respectively. The numbers in parentheses indicate the energies of the optimized structures including ZPE correction. (D) ~ (F) represents the distances between the C-N bond length (in) of 2-NP-HT1, 2-NP-HT2, and 2-NP-HT3 are plotted as functions of time for BOMD trajectories starting from the transition states in the IRC calculations, respectively. See text for discussions.

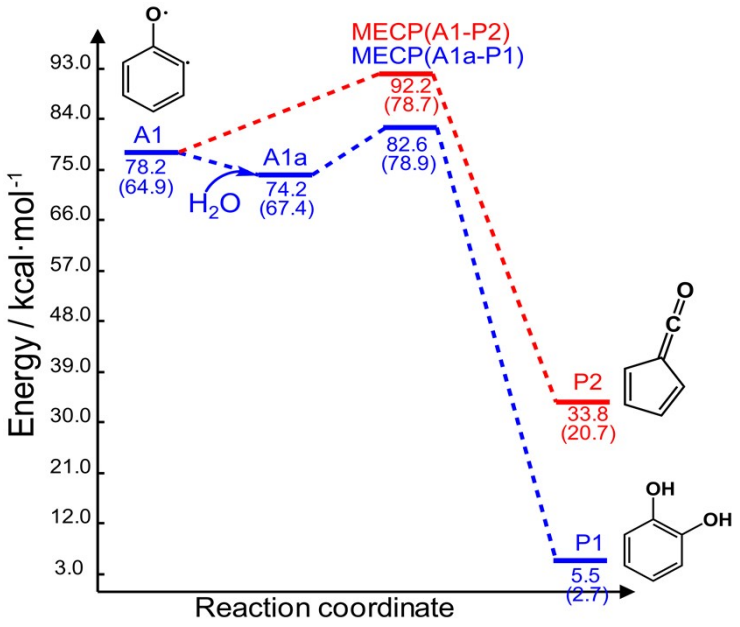


Figure S9. Computed reaction pathways (at B3LYP/6-311++G(d,p) level) for further reaction of catechol formation from the triplet biradical (A1) formed from the photolysis of 2-NP in the presence of water. The ZPE correction is included in the energy values of ΔE.

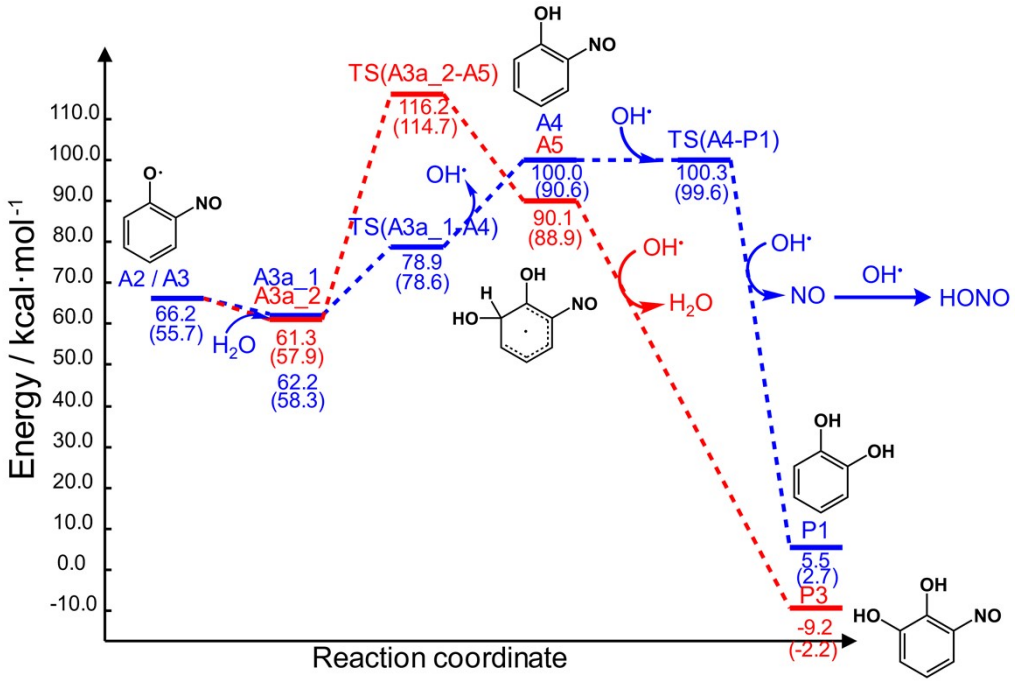


Figure S10. Computed reaction pathways (at B3LYP/6-311++G(d,p) level) for further reaction from the radical (A2&A3) formed from the photolysis of 2-NP in the presence of water. The ZPE correction is included in the energy values of ΔE.

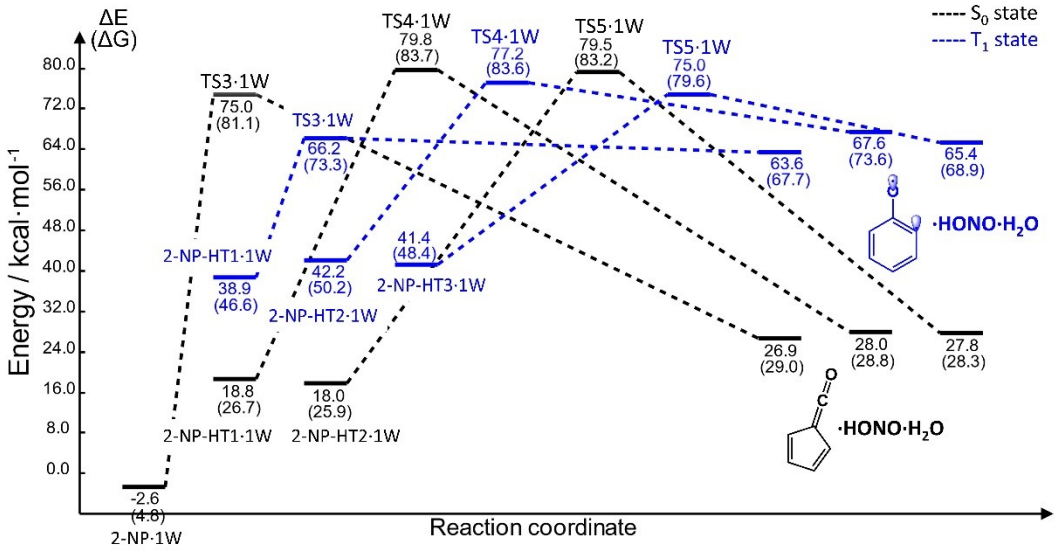


Figure S11. Computed water-assisted C-N dissociation reaction pathways (at B3LYP/6-311++G(d,p) level) of 2-NP and aci-2-NP along the S_0 and T_1 potential energy surfaces for HONO formation. The blue and black solid lines stand for energies of the T_1 and S_0 states, respectively. The numbers in parentheses denote the energies of the optimized structures including ZPE correction.

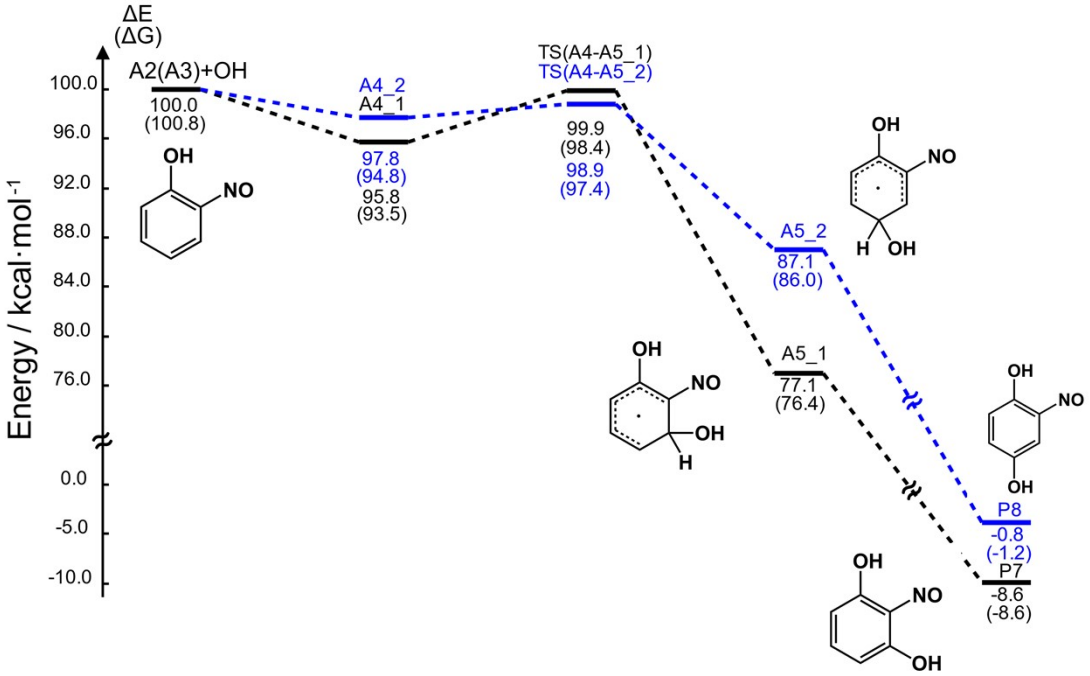


Figure S12. Computed reaction pathways (at B3LYP/6-311++G(d,p) level) for oxidation of 2-Nitrosophenol (A2&A3) by OH· formed from the photolysis of 2-NP in presence of vicinal water, leading to the formation of 2-nitrosobenzene-diols. The ZPE correction is included in the energy values of ΔE.

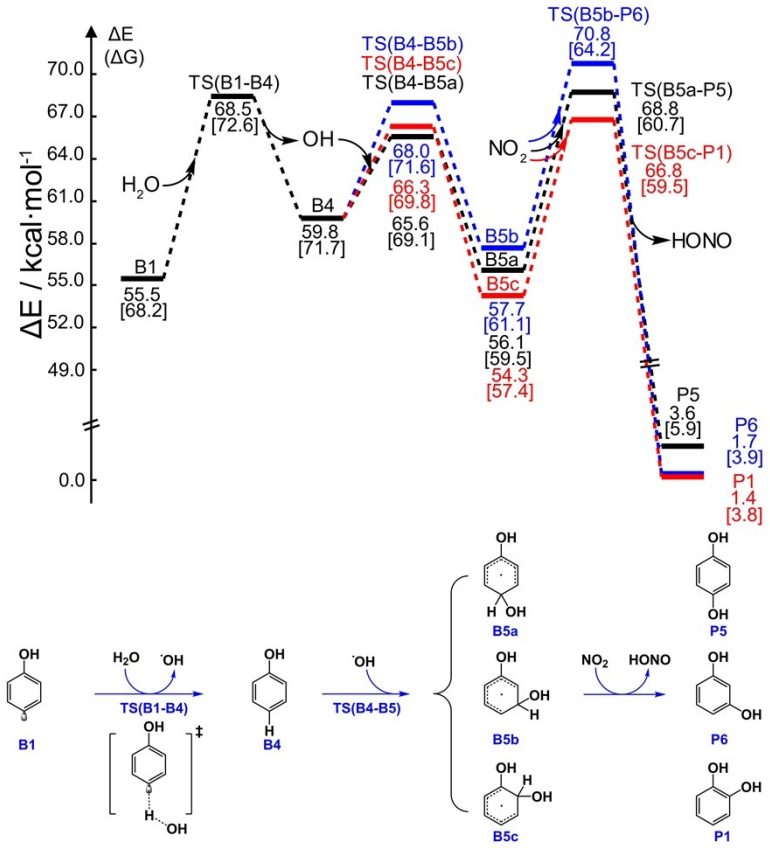


Figure S13. Computed reaction pathways (at B3LYP/6-311++G(d,p) level) for the fate of B1 radical intermediate formed from the photolysis of 4-NP in the presence of water, leading to the formation of HONO and benzene-diols. The ZPE correction is included in the energy values of ΔE. See text for discussions.

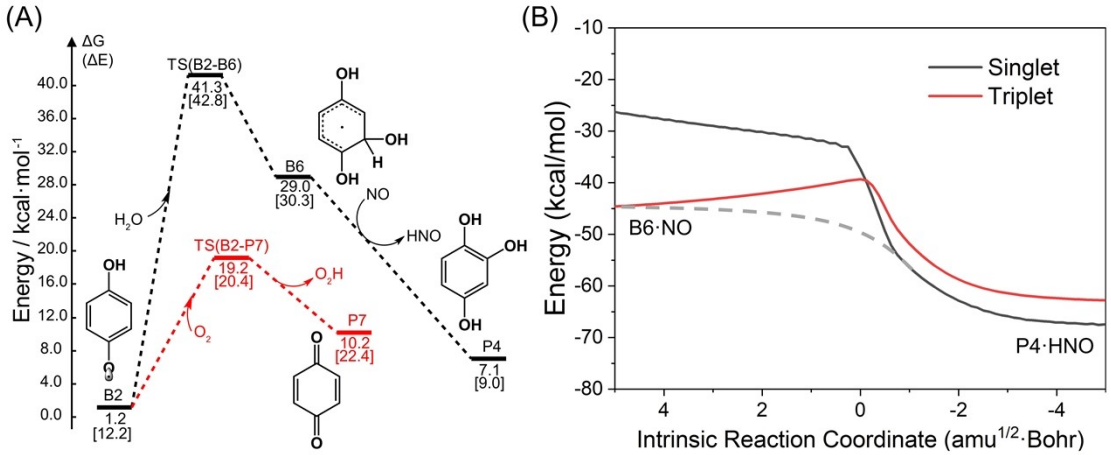


Figure S14. (A) Computed reaction pathways (at B3LYP/6-311++G(d,p) level) for the fate of B2 radical formed from the photolysis of 4-NP in the presence of water. The ZPE correction is included in the energy values of ΔE. (B) The intrinsic reaction coordinate (IRC) of singlet and triplet state for hydrogen transfer between B6 and NO fragments.

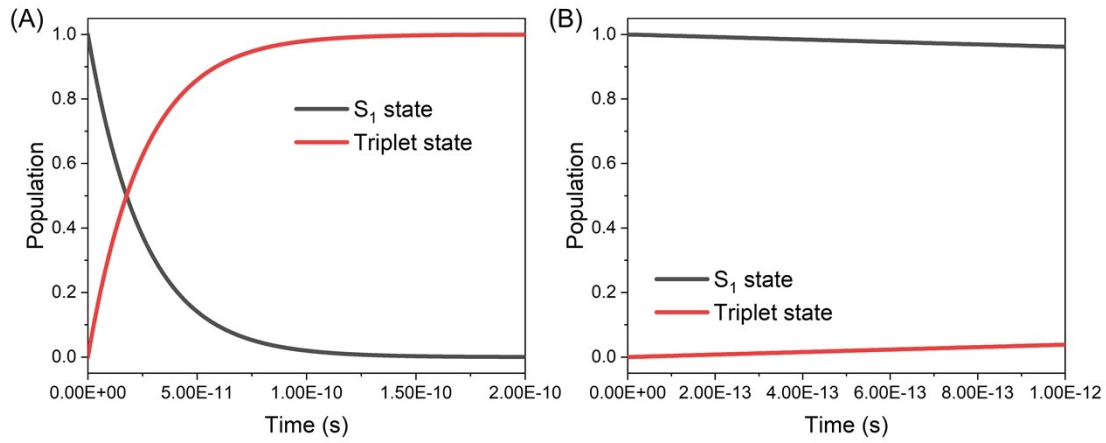


Figure S15. Micro-kinetics for intersystem crossing (ISC) reaction of 2-NP based on the microcanonical rate constants: (A) kinetics with 100% conversion; (B) kinetics within 1 ps.

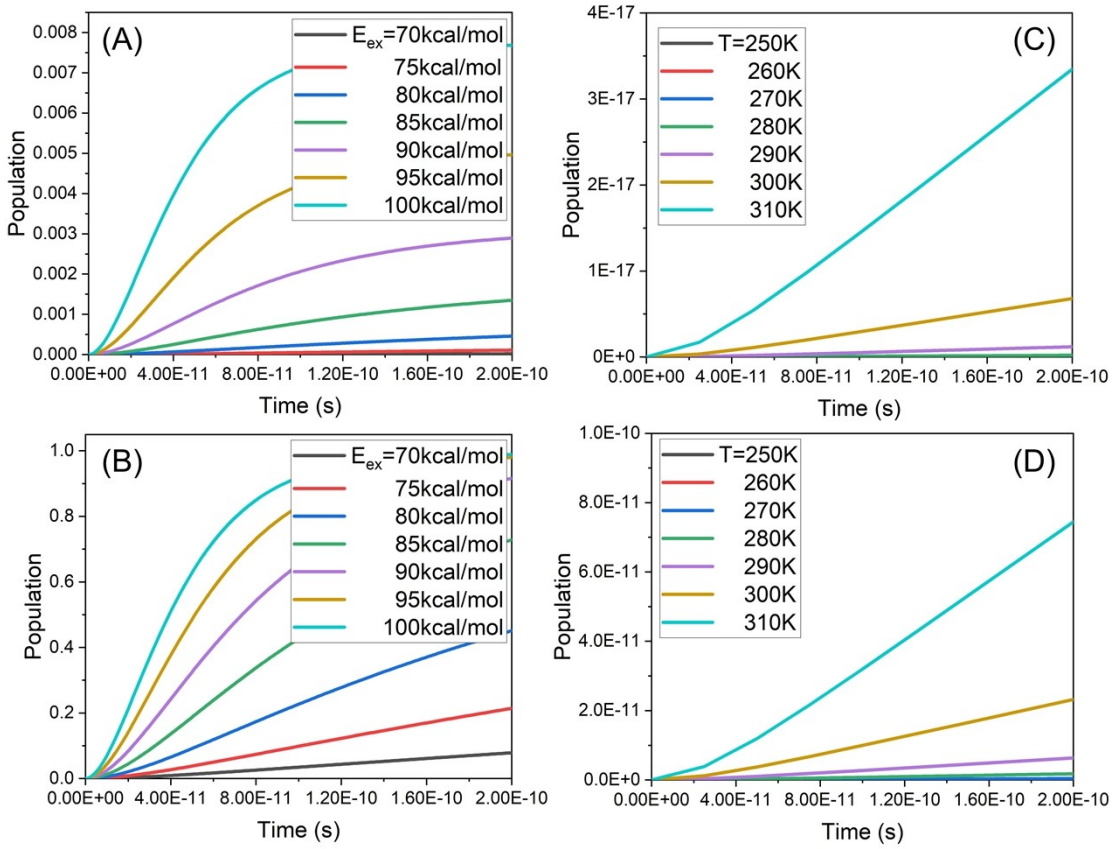


Figure S16. Micro-kinetics for photolysis of 2-NP based on the microcanonical rate constants for (A) HONO and (B) OH· formation as the function of excitation energy of 70 ~ 100 kcal/mol; temperature-dependent micro-kinetics for photolysis pathways of (C) HONO and (D) OH· formation based on the canonical rate constant.

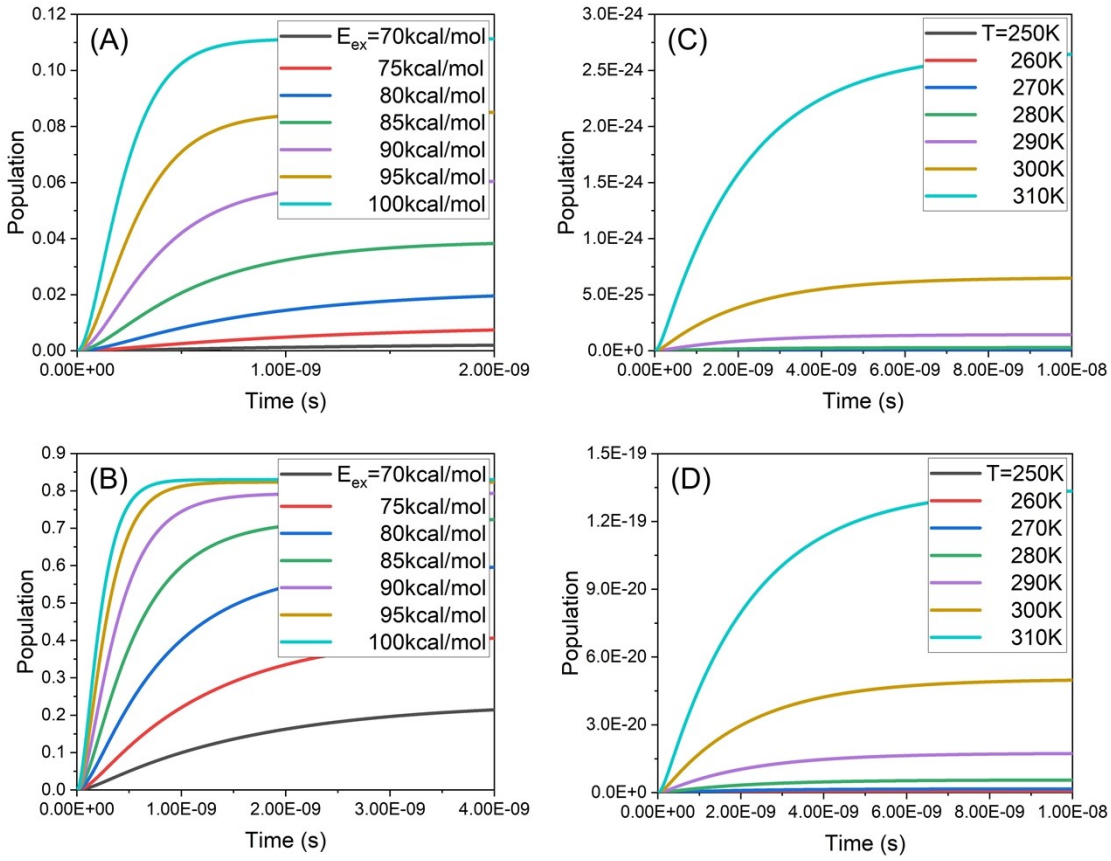


Figure S17. Micro-kinetics for gas-phase photolysis of 4-NP based on the microcanonical rate constants for (A) NO_2 and (B) NO formation as the function of excitation energy of 70 ~ 100 kcal/mol; temperature-dependent micro-kinetics for photolysis pathways of (C) NO_2 and (D) NO formation based on the canonical rate constant.

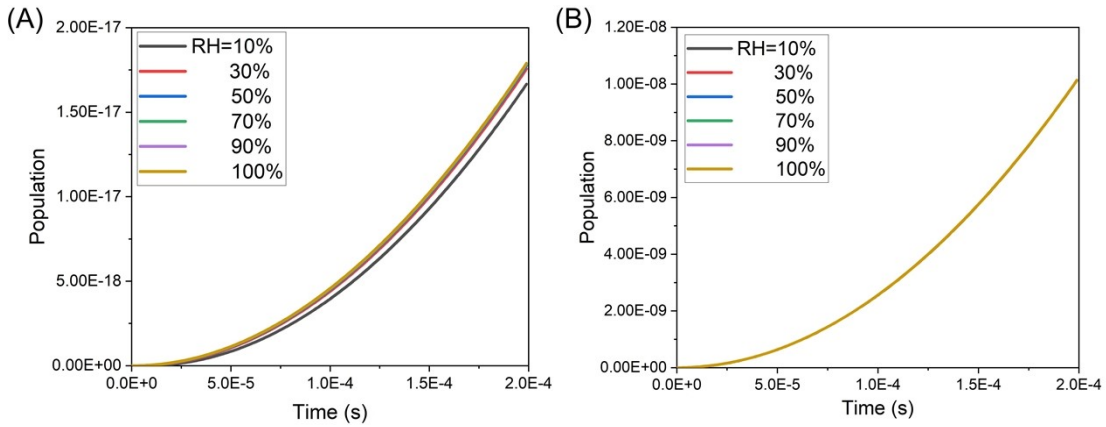


Figure S18. Micro-kinetics for HONO formation from B1 radical intermediate with NO_2 in the presence of water with various relative humidity at (A) 250K and (B) 300K. The initial concentration of B1 and NO_2 are taken from the results of the photolysis under the 80 kcal/mol irradiation.

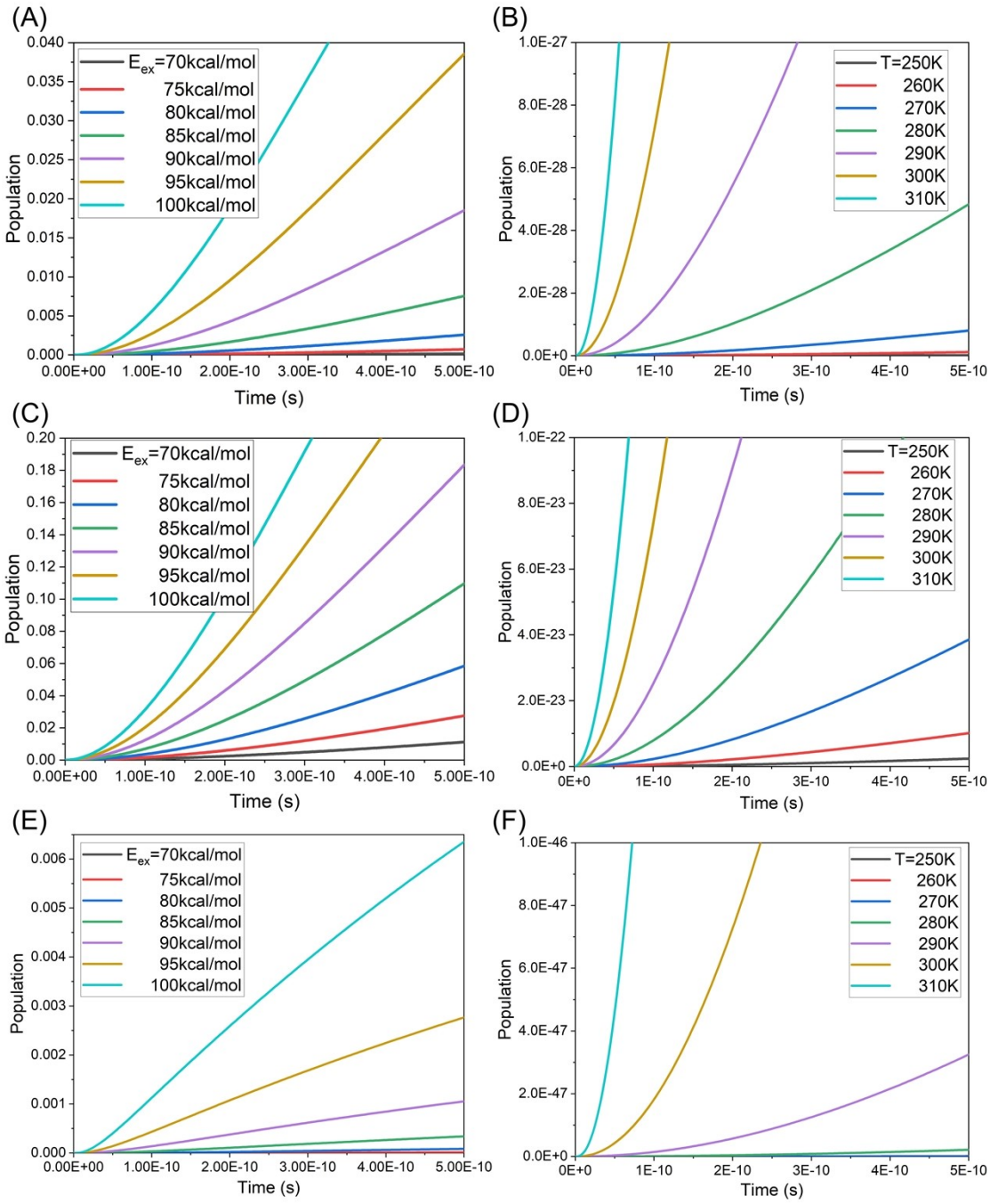


Figure S19. Micro-kinetics for photolysis of 4-NP in aqueous phase based on the microcanonical rate constants for (A) NO_2, (B) NO and (C) HONO formation as the function of excitation energy of 70 ~ 100 kcal/mol; temperature-dependent micro-kinetics for photolysis pathways of (D) NO_2, (E) NO and (F) HONO formation based on the canonical rate constant.

S3. Supplementary Tables

Table S1. Functional test for linear response time-dependent density functional theory (LR-TDDFT) calculation to predict the wavelength of light absorption for $S_0 \rightarrow S_1$ transition of 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) at the Franck-Condon point. The molecular geometry is optimized by the B3LYP/6-311++G(d,p) level of theory.

Functional	**Wavelength (nm)**	
	2-NP	**4-NP**
Exp.	~ 350	~ 320
M06-2X	302.75	320.08
B3LYP	358.08	325.62
PBE0	362.44	319.33
ωB97X-D	313.76	314.46
cam-B3LYP	315.28	314.59

Table S2. Computed excitation properties (TD-B3LYP/6-311++G(d,p)) for the first four singlet and triplet states for 2-NP and 4-NP.

	2-NP				4-NP			
	VEE / eV	λ / nm	f	Electronic Transition	VEE / eV	λ / nm	f	Electronic Transition
T_1	2.74	452.82	N/A	(π, π*)	2.94	422.17	N/A	(π, π*)
T_2	3.07	404.27	N/A	(π, π*)	3.10	399.49	N/A	(π, π*)
T_3	3.36	368.40	N/A	(π, π*)	3.27	378.76	N/A	(n, π*)
T_4	3.40	364.04	N/A	(n, π*)	3.85	321.76	N/A	(n, π*)
S_1	3.46	358.08	0.0583	(π, π*)	3.81	325.62	0.0000	(n, π*)
S_2	3.94	316.30	0.0000	(n, π*)	4.24	292.04	0.2622	(π, π*)

Table S3. Binding free energies (B3LYP/6-311++G(d,p) level) and vertical excitation energies ((TD)-B3LYP/6-311++G(d,p) level) to the S_1 and T_1 States of water-NP hydrated complex at the FC Points.

	Binding Energy	**Binding Free Energy**	**VEE(T_1)**	**VEE(S_1)**
2-NP	N/A	N/A	2.74	3.46
2-NP·1W_1	-2.59	4.77	2.73	3.45
2-NP·1W_2	-2.68	3.55	2.60	3.33
2-NP·2W	-8.12	9.01	2.65	3.20
4-NP	N/A	N/A	2.94	3.81
4-NP·1W_1	-3.23	3.15	2.98	3.85
4-NP·1W_2	-3.55	3.84	2.96	3.83
4-NP·2W	-8.37	7.08	2.92	3.85

* The unit for all the data in this table is kcal/mol.

* All the geometries in this Table are listed in the Figure S2.

* The binding energies are included with zero-point energy correction.

Table S4. Computed spin-orbit coupling (SOC) integral values (TD-B3LYP/6-311++G(d,p)) for 2-NP and 4-NP at Franck-Condon points.

Structure	SOC (cm^{-1})								
	$S_0 \rightarrow T_1$	$S_1 \rightarrow T_n$				$S_2 \rightarrow T_n$			
		T_1	T_2	T_3	T_4	T_1	T_2	T_3	T_4
2-NP	0.51	0.19	0.08	0.52	10.59	14.96	54.58	18.32	2.15
4-NP	0.06	58.45	13.37	0.11	39.07	0.22	0.07	13.47	18.84

Table S5. Computed parameters for intersystem crossing (ISC) of NP isomers and their complexes.

Geometry	Electronic Transition	SOC/cm^{-1}	ΔE/eV	ISC rate / s^{-1}
2-NP(S_0)	$S_1 \rightarrow T_4$	10.59	0.06	3.92E+10
	$S_1 \rightarrow T_3$	0.52	0.10	4.13E+07
	$S_1 \rightarrow T_2$	0.08	0.39	7.26E+04
	$S_1 \rightarrow T_1$	0.19	0.72	1.21E+05
	$T_1 \rightarrow S_0$	0.51	2.91	5.39E+04
2-NP-HT1(T_1)	$T_1 \rightarrow S_0$	0.71	0.81	1.34E+06
2-NP-HT2(T_1)	$T_1 \rightarrow S_0$	1.83	0.11	4.57E+08
2-NP-HT3(T_1)	$T_1 \rightarrow S_0$	8.01	-0.05	2.80E+10
2-NP·1W(S_0)	$S_1 \rightarrow T_4$	7.90	0.07	1.66E+10
	$S_1 \rightarrow T_3$	5.93	0.08	7.41E+09
	$S_1 \rightarrow T_2$	0.29	0.37	1.07E+06
	$S_1 \rightarrow T_1$	0.20	0.72	1.39E+05
	$T_1 \rightarrow S_0$	0.68	2.91	9.50E+04
2-NP-HT1·1W(T_1)	$T_1 \rightarrow S_0$	3.71	0.06	4.68E+09
2-NP-HT2·1W(T_1)	$T_1 \rightarrow S_0$	3.00	0.09	1.81E+09
2-NP-HT3·1W(T_1)	$T_1 \rightarrow S_0$	7.02	0.00	6.17E+10
4-NP (S_0, gas)	$S_1 \rightarrow T_4$	39.07	-0.04	8.90E+11
	$S_1 \rightarrow T_3$	0.11	0.54	7.19E+04
	$S_1 \rightarrow T_2$	13.37	0.61	8.33E+08
	$S_1 \rightarrow T_1$	58.45	0.87	7.84E+09
	$T_1 \rightarrow S_0$	0.07	2.94	8.60E+02
4-NP (T_1, gas)	$T_1 \rightarrow S_0$	21.90	1.32	4.76E+08

	$S_1 \rightarrow T_4$	21.62	-0.07	1.17E+11
	$S_1 \rightarrow T_3$	2.31	0.53	3.34E+07
4-NP·1W (S_0, gas)	$S_1 \rightarrow T_2$	46.82	0.81	5.85E+09
	$S_1 \rightarrow T_1$	41.18	0.97	3.16E+09
	$T_1 \rightarrow S_0$	2.50	2.96	1.24E+06
4-NP·1W (T_1, gas)	$T_1 \rightarrow S_0$	30.94	1.36	8.94E+08
	$S_1 \rightarrow T_4$	0.28	0.17	4.51E+06
	$S_1 \rightarrow T_3$	16.59	0.37	3.46E+09
4-NP (S_0, aq)	$S_1 \rightarrow T_2$	0.28	0.58	4.04E+05
	$S_1 \rightarrow T_1$	0.02	1.08	5.96E+02
	$T_1 \rightarrow S_0$	0.01	2.62	4.32E+01
4-NP (T_1, aq)	$T_1 \rightarrow S_0$	1.65	2.09	1.08E+06
	$S_1 \rightarrow T_4$	0.23	0.17	2.99E+06
	$S_1 \rightarrow T_3$	17.01	0.29	5.99E+09
4-NP·1W (S_0, aq)	$S_1 \rightarrow T_2$	0.31	0.52	6.20E+05
	$S_1 \rightarrow T_1$	0.03	1.10	1.22E+03
	$T_1 \rightarrow S_0$	0.01	2.56	2.01E+01
4-NP·1W (T_1, aq)	$T_1 \rightarrow S_0$	0.02	2.05	2.06E+02
	$S_1 \rightarrow T_4$	16.61	-0.09	4.93E+10
	$S_1 \rightarrow T_3$	14.99	0.02	2.34E+11
4-NP·3W (S_0, aq)	$S_1 \rightarrow T_2$	22.54	0.22	1.81E+10
	$S_1 \rightarrow T_1$	3.06	0.96	1.76E+07
	$T_1 \rightarrow S_0$	10.59	2.52	3.07E+07
4-NP·3W (T_1, aq)	$T_1 \rightarrow S_0$	21.23	1.03	7.45E+08
Aci-4-NP·3W (T_1, aq)	$T_1 \rightarrow S_0$	8.52	0.51	4.74E+08

Table S6. Computed RRKM unimolecular microcanonical rate constant k(E) (in s^{-1}) as the function of excitation energy of 70 ~ 100 kcal·mol^{-1} (corresponding to wavelength of 280 ~ 410 nm) for each elementary reaction of photolysis channels of NPs and their hydrated complexes.

	Excitation Energy (kcal/mol)						
	70	75	80	85	90	95	100
k_1	1.82E+12	2.14E+12	2.46E+12	2.79E+12	3.12E+12	3.44E+12	3.76E+12
k_{-1}	1.41E+13	1.38E+13	1.36E+13	1.35E+13	1.33E+13	1.32E+13	1.31E+13
k_2	3.10E+04	1.87E+05	8.45E+05	3.04E+06	9.18E+06	2.40E+07	5.59E+07
k_{-2}	1.65E+04	9.53E+04	4.14E+05	1.45E+06	4.26E+06	1.09E+07	2.49E+07
k_{3a}	1.07E+05	6.47E+05	2.91E+06	1.05E+07	3.15E+07	8.22E+07	1.91E+08
k_{3b}	5.33E+08	1.61E+09	4.12E+09	9.29E+09	1.88E+10	3.51E+10	6.09E+10
k_{4a}	1.36E+05	1.18E+06	7.11E+06	3.24E+07	1.19E+08	3.67E+08	9.85E+08
k_{5a}	1.20E+05	9.47E+05	5.29E+06	2.27E+07	7.90E+07	2.34E+08	6.04E+08
k_{5b}	3.45E+10	6.59E+10	1.15E+11	1.88E+11	2.87E+11	4.20E+11	5.88E+11
k_{1w}	4.83E+12	5.48E+12	6.12E+12	6.74E+12	7.34E+12	7.93E+12	8.49E+12
k_{-1w}	5.35E+12	5.42E+12	5.48E+12	5.53E+12	5.58E+12	5.62E+12	5.66E+12
k_{2w}	1.30E+08	2.37E+08	3.99E+08	6.29E+08	9.39E+08	1.34E+09	1.84E+09
k_{-2w}	1.64E+08	2.93E+08	4.85E+08	7.53E+08	1.11E+09	1.56E+09	2.13E+09
k_{3aw}	3.22E+03	2.35E+04	1.25E+05	5.24E+05	1.80E+06	5.29E+06	1.37E+07
k_{3bw}	2.50E+07	8.98E+07	2.67E+08	6.86E+08	1.56E+09	3.21E+09	6.11E+09

k_{4aw}	1.36E+02	2.58E+03	2.93E+04	2.27E+05	1.30E+06	5.88E+06	2.20E+07
k_{5aw}	3.44E+02	5.67E+03	5.78E+04	4.10E+05	2.18E+06	9.31E+06	3.30E+07
k_{5bw}	4.55E+08	1.40E+09	3.65E+09	8.39E+09	1.74E+10	3.30E+10	5.83E+10
k_{6}	1.81E+06	7.85E+06	2.72E+07	7.86E+07	1.97E+08	4.41E+08	8.97E+08
k_{7}	1.47E+08	3.54E+08	7.55E+08	1.45E+09	2.58E+09	4.27E+09	6.69E+09
k_{6w}	2.35E+04	1.35E+05	5.94E+05	2.11E+06	6.32E+06	1.65E+07	3.86E+07
k_{7w}	1.14E+07	3.09E+07	7.25E+07	1.52E+08	2.91E+08	5.15E+08	8.58E+08
k_{15}	5.87E+05	2.79E+06	1.03E+07	3.17E+07	8.37E+07	1.95E+08	4.12E+08
k_{16}	4.30E+07	1.07E+08	2.33E+08	4.57E+08	8.23E+08	1.38E+09	2.20E+09
k_{17}	1.55E+03	2.89E+03	4.88E+03	7.63E+03	1.12E+04	1.58E+04	2.13E+04
k_{18}	3.44E+06	6.91E+06	1.27E+07	2.15E+07	3.43E+07	5.19E+07	7.52E+07
k_{19}	4.31E+05	2.36E+06	9.97E+06	3.43E+07	1.00E+08	2.56E+08	5.85E+08
k_{20}	1.58E+09	3.28E+09	6.15E+09	1.06E+10	1.72E+10	2.64E+10	3.87E+10

Table S7. Computed RRKM unimolecular canonical rate constant k(T) (in s^{-1}) as the function of temperature of 250 ~ 310 K for each elementary reaction of photolysis channels of NPs and their hydrated complexes.

	Temperature (K)						
	250	260	270	280	290	300	310
k_1	3.88E+09	5.39E+09	7.30E+09	9.67E+09	1.26E+10	1.61E+10	2.02E+10
k_{-1}	2.80E+13	2.70E+13	2.61E+13	2.53E+13	2.46E+13	2.39E+13	2.33E+13
k_2	5.53E-13	5.42E-12	4.48E-11	3.19E-10	1.98E-09	1.09E-08	5.37E-08
k_{-2}	4.86E-13	4.60E-12	3.68E-11	2.54E-10	1.53E-09	8.21E-09	3.94E-08
k_{3a}	2.00E-12	1.96E-11	1.61E-10	1.15E-09	7.10E-09	3.90E-08	1.92E-07
k_{3b}	9.89E-05	5.22E-04	2.43E-03	1.02E-02	3.85E-02	1.33E-01	4.27E-01
k_{4a}	8.22E-14	1.04E-12	1.08E-11	9.58E-11	7.29E-10	4.85E-09	2.85E-08
k_{5a}	1.66E-13	1.96E-12	1.94E-11	1.62E-10	1.17E-09	7.43E-09	4.18E-08
k_{5b}	5.83E+01	1.77E+02	4.97E+02	1.29E+03	3.15E+03	7.24E+03	1.57E+04
k_{1w}	4.41E+00	5.44E+00	6.61E+00	7.91E+00	9.36E+00	1.09E+01	1.27E+01
k_{-1w}	1.24E+02	1.27E+02	1.29E+02	1.31E+02	1.34E+02	1.36E+02	1.38E+02
k_{2w}	2.09E-09	5.04E-09	1.14E-08	2.42E-08	4.90E-08	9.44E-08	1.75E-07
k_{-2w}	3.97E-09	9.33E-09	2.06E-08	4.28E-08	8.48E-08	1.60E-07	2.91E-07
k_{3aw}	1.44E-21	1.21E-20	8.74E-20	5.47E-19	3.01E-18	1.48E-17	6.58E-17
k_{3bw}	1.20E-14	5.85E-14	2.54E-13	9.94E-13	3.54E-12	1.16E-11	3.50E-11

k_{4aw}	2.34E-25	3.37E-24	3.98E-23	3.94E-22	3.34E-21	2.45E-20	1.58E-19
k_{5aw}	1.10E-24	1.48E-23	1.64E-22	1.53E-21	1.23E-20	8.56E-20	5.26E-19
k_{5bw}	1.62E-12	6.87E-12	2.61E-11	9.03E-11	2.86E-10	8.41E-10	2.30E-09
k_6	5.03E-20	3.77E-19	2.43E-18	1.38E-17	6.90E-17	3.11E-16	1.27E-15
k_7	5.23E-14	2.15E-13	7.95E-13	2.68E-12	8.31E-12	2.39E-11	6.41E-11
k_{6w}	7.93E-20	5.66E-19	3.49E-18	1.89E-17	9.11E-17	3.95E-16	1.56E-15
k_{7w}	2.50E-13	9.31E-13	3.15E-12	9.77E-12	2.80E-11	7.49E-11	1.88E-10
k_{15}	5.45E-21	4.40E-20	3.05E-19	1.84E-18	9.78E-18	4.66E-17	2.01E-16
k_{16}	9.10E-15	3.86E-14	1.47E-13	5.09E-13	1.62E-12	4.76E-12	1.31E-11
k_{17}	8.93E-17	3.63E-16	1.33E-15	4.44E-15	1.36E-14	3.89E-14	1.04E-13
k_{18}	5.80E-09	1.24E-08	2.49E-08	4.77E-08	8.73E-08	1.54E-07	2.60E-07
k_{19}	1.91E-26	2.69E-25	3.11E-24	3.03E-23	2.51E-22	1.81E-21	1.15E-20
k_{20}	2.46E-09	6.88E-09	1.79E-08	4.33E-08	9.89E-08	2.14E-07	4.39E-07

Table S8. Bimolecular rate constants (in molecules·cm^{-1}·s^{-1}) for elementary steps used for the kinetics analysis at 250 K and 300 K involved in eq. (S20) ~ (S32).

	250 K	300 K
k_8	8.41E-11	3.48E-10
k_9	3.71E-05	1.81E-05
k_{10}	5.47E-02	1.91E+08
k_{11}	3.17E+02	1.07E+01
k_{12}	6.76E-09	2.05E+02
k_{13}	1.36E+04	2.48E+02

k_{14}	1.27E-02	4.10E+07

Table S9. Calculated concentrations (in molecules·cm^{-3}) of H_2O under the different values of Relative Humidity (RH, %) at 250 K and 300 K.

RH / %	**Concentration of H_2O / molecules·cm^{-3}**	
	250 K	**300 K**
0	0	0
10	2.24E+15	8.61E+16
20	4.47E+15	1.72E+17
30	6.71E+15	2.58E+17
40	8.94E+15	3.45E+17
50	1.12E+16	4.31E+17
60	1.34E+16	5.17E+17
70	1.56E+16	6.03E+17
80	1.79E+16	6.89E+17
90	2.01E+16	7.75E+17
100	2.24E+16	8.61E+17

Table S10. Calculated initial relative population of water-NP complex in the atmosphere under the different values of Relative Humidity (RH, %) at 250 K and 300 K.

RH / %	Initial Relative Population							
	water-2-NP		water-4-NP (gas)		4-NP·1W (aq)		4-NP·3W (aq)	
	250 K	300 K	250 K	300 K	250 K	300 K	250 K	300 K
0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
10	3.73E-06	1.43E-04	3.72E-06	1.43E-04	1.86E-09	2.08E-06	1.99E-09	1.47E-02
20	7.44E-06	2.86E-04	7.43E-06	2.86E-04	3.71E-09	4.16E-06	1.58E-08	1.17E-01
30	1.12E-05	4.30E-04	1.12E-05	4.29E-04	5.56E-09	6.24E-06	5.34E-08	3.96E-01
40	1.49E-05	5.74E-04	1.49E-05	5.74E-04	7.41E-09	8.35E-06	1.26E-07	9.48E-01
50	1.86E-05	7.18E-04	1.86E-05	7.17E-04	9.29E-09	1.04E-05	2.48E-07	1.85E+00
60	2.23E-05	8.61E-04	2.23E-05	8.60E-04	1.11E-08	1.25E-05	4.25E-07	3.19E+00
70	2.60E-05	1.00E-03	2.59E-05	1.00E-03	1.29E-08	1.46E-05	6.71E-07	5.06E+00
80	2.98E-05	1.15E-03	2.98E-05	1.15E-03	1.48E-08	1.67E-05	1.01E-06	7.55E+00
90	3.34E-05	1.29E-03	3.34E-05	1.29E-03	1.67E-08	1.87E-05	1.43E-06	1.07E+01
100	3.73E-05	1.43E-03	3.72E-05	1.43E-03	1.86E-08	2.08E-05*	1.99E-06	1.47E+01*

* The data are selected as the initial concentration of 4-NP hydrated complexes in micro-kinetics studies.

Table S11. Final relative populations, total first-order microcanonical rate constant (in s^{-1}) and quantum yields of HONO and OH· formation as the function of excitation energy of 70 ~ 100 kcal·mol^{-1} (corresponding to wavelength of 280 ~ 410 nm) from unimolecular and water-assisted reaction of 2-NP.

	Excitation Energy (kcal·mol^{-1})						
	70	75	80	85	90	95	100
Final Relative Populations							
HONO[a]	2.10E-04	4.90E-04	1.00E-03	1.80E-04	3.10E-04	5.00E-04	7.70E-04
HONO[b]	7.10E-10	5.50E-09	3.00E-08	1.40E-07	5.10E-07	1.60E-06	4.20E-06
OH·[a]	0.89	0.96	0.98	0.99	0.99	0.99	0.99
OH·[b]	5.50E-06	2.00E-05	5.60E-05	1.30E-04	2.60E-04	4.50E-04	6.50E-04
Total microcanonical rate constants (s^{-1})							
HONO[a]	2.10E+04	4.91E+04	1.78E+05	8.01E+04	2.59E+05	6.61E+05	1.49E+06
HONO[b]	4.97E+02	7.26E+02	3.09E+03	2.18E+04	8.29E+04	3.11E+05	1.01E+06
OH·[a]	8.90E+07	9.62E+07	1.75E+08	4.11E+08	7.96E+08	1.30E+09	1.92E+09
OH·[b]	3.85E+06	2.45E+06	7.25E+06	2.02E+07	4.23E+07	8.51E+07	1.30E+08
Quantum Yields							
HONO[a]	2.36E-04	5.10E-04	1.02E-03	1.95E-04	3.26E-04	5.06E-04	7.77E-04
HONO[b]	1.29E-04	2.96E-04	4.25E-04	1.08E-03	1.96E-03	3.64E-03	7.74E-03
OH·[a]	1.00E+00	9.99E-01	9.99E-01	1.00E+00	1.00E+00	9.99E-01	9.99E-01
OH·[b]	1.00E+00	1.00E+00	1.00E+00	9.99E-01	9.98E-01	9.96E-01	9.92E-01

[a] HONO and OH· formation from unimolecular reactions;

[b] HONO and OH· formation from water-assisted reactions with the relative humidity of 100%.

Table S12. Final relative population, total first-order microcanonical rate constants (in s^{-1}) and quantum yields of NO_2 and NO formation as the function of excitation energy of 70 ~ 100 kcal·mol^{-1} (corresponding to wavelength of 280 ~ 410 nm) from unimolecular and water-assisted reaction of 4-NP.

	Excitation Energy (kcal·mol^{-1})						
	70	75	80	85	90	95	100
Final relative populations							
NO_2[a]	2.89E-03	9.37E-03	2.16E-02	3.92E-02	6.06E-02	8.50E-02	1.11E-01
NO_2[b]	3.71E-08	2.09E-07	8.78E-07	2.88E-06	7.59E-06	1.66E-05	3.08E-05
NO[a]	2.35E-01	4.22E-01	6.00E-01	7.23E-01	7.93E-01	8.23E-01	8.30E-01
NO[b]	1.80E-05	4.78E-05	1.07E-04	2.07E-04	3.49E-04	5.17E-04	6.85E-04
Total microcanonical rate constants (s^{-1})							
NO_2[a]	2.89E+05	9.37E+05	2.16E+06	4.41E+06	9.24E+06	2.20E+07	4.81E+07
NO_2[b]	2.60E+03	1.46E+04	6.14E+04	2.01E+05	5.30E+05	1.16E+06	2.22E+06
NO[a]	2.35E+07	4.22E+07	6.00E+07	8.13E+07	1.21E+08	2.13E+08	3.59E+08
NO[b]	1.26E+06	3.34E+06	7.50E+06	1.45E+07	2.44E+07	3.63E+07	4.94E+07
Quantum yields							
NO_2[a]	1.22E-02	2.17E-02	3.48E-02	5.14E-02	7.09E-02	9.36E-02	1.18E-01
NO_2[b]	2.06E-03	4.35E-03	8.13E-03	1.37E-02	2.13E-02	3.10E-02	4.31E-02
NO[a]	9.88E-01	9.78E-01	9.65E-01	9.49E-01	9.29E-01	9.06E-01	8.82E-01
NO[b]	9.98E-01	9.96E-01	9.92E-01	9.86E-01	9.79E-01	9.69E-01	9.57E-01

[a] NO_2 and NO formation from unimolecular reactions;

[b] NO_2 and NO formation from water-assisted reactions with the relative humidity of 100%.

Table S13. Final population of HONO formation as the function of relative humidity of 10% ~ 100% at 250 K and 300 K with initial population of B1 intermediate and NO_2 of 2.16×10^{-2} (generate under the 80 kcal/mol irradiation). The simulation timescale is 2×10^{-4} s.

Temperatur	Relative Humidity					
e	10%	30%	50%	70%	90%	100%
250K	0.17E-16	0.18E-16	0.18E-16	0.18E-16	0.18E-16	0.18E-16

300K	0.10E-07	0.10E-07	0.10E-07	0.10E-07	0.10E-07	0.10E-07

Table S14. Final relative population, total microcanonical rate constants (in s^{-1}) and quantum yields of NO_2, NO and HONO formation as the function of excitation energy of 70 ~ 100 kcal·mol^{-1} (corresponding to wavelength of 280 ~ 410 nm) from the photolysis of 4-NP in aqueous phase. The simulation timescale is 5×10^{-10} s.

	Excitation Energy (kcal·mol^{-1})						
	70	75	80	85	90	95	100
Final relative populations							
NO_2	1.53E-04	7.18E-04	2.59E-03	7.61E-03	1.87E-02	3.88E-02	6.96E-02
NO	1.12E-02	2.75E-02	5.85E-02	1.10E-01	1.83E-01	2.75E-01	3.72E-01
HONO[a]	9.90E-12	1.85E-11	3.12E-11	4.87E-11	7.15E-11	1.01E-10	1.36E-10
HONO[b]	1.70E-06	1.50E-05	8.50E-05	3.40E-04	1.00E-03	2.80E-03	6.40E-03
HONO[c]	1.70E-06	1.50E-05	8.50E-05	3.40E-04	1.00E-03	2.80E-03	6.40E-03
Total microcanonical rate constants (in s^{-1})							
NO_2	3.06E+05	1.44E+06	5.17E+06	1.52E+07	3.73E+07	7.76E+07	1.39E+08
NO	2.24E+07	5.51E+07	1.17E+08	2.19E+08	3.67E+08	5.49E+08	7.43E+08
HONO	2.31E+02	2.04E+03	1.16E+04	4.63E+04	1.36E+05	3.81E+05	8.71E+05
Quantum yields							
NO_2	1.35E-02	2.54E-02	4.23E-02	6.49E-02	9.23E-02	1.24E-01	1.58E-01
NO	9.87E-01	9.75E-01	9.58E-01	9.35E-01	9.07E-01	8.76E-01	8.41E-01
HONO	1.02E-05	3.61E-05	9.47E-05	1.97E-04	3.37E-04	6.07E-04	9.85E-04

[a] HONO formation from bimolecular reactions, where 4-NP reacts with water molecules;

[b] HONO formation from unimolecular dissociation of aci-4-NP, which is initiated from the intermolecular excited hydrogen transfer;

[c] total quantum yields for HONO formation.

Table S15. Total canonical rate constants (in s^{-1}) as the function of temperature of 250 ~ 310 K from the photolysis of NP in gas and aqueous phase. The simulation timescale is 5×10^{-10} s.

	Temperature (K)						
	250	260	270	280	290	300	310
2-Nitrophenol							
HONO (gas)	1.98×10^{-12}	1.94×10^{-11}	1.60×10^{-10}	1.14×10^{-9}	6.37×10^{-9}	3.86×10^{-8}	1.90×10^{-7}
OH· (gas)	9.80×10^{-5}	5.17×10^{-4}	2.41×10^{-3}	1.01×10^{-2}	3.44×10^{-2}	1.32×10^{-1}	4.23×10^{-1}
4-Nitrophenol							
NO_2 (gas)	1.05E-20	7.85E-20	5.06E-19	2.87E-18	1.44E-17	6.47E-17	2.64E-16
NO (gas)	1.04E-02	4.48E-14	1.66E-13	5.58E-13	1.73E-12	4.98E-12	1.33E-11
NO_2 (aq)	2.86E-21	2.31E-20	7.72E-14	2.67E-13	8.51E-13	2.50E-12	6.88E-12
NO (aq)	4.78E-15	2.03E-14	1.60E-19	9.66E-19	5.14E-18	2.45E-17	1.06E-16
HONO (aq)[a]	2.23E-44	6.73E-43	1.56E-41	2.92E-40	4.42E-39	5.62E-38	6.03E-37

[a] HONO formation from unimolecular dissociation of aci-4-NP, which is initiated from the intermolecular excited hydrogen transfer.

S4. Cartesian Coordinates

All the atomic cartesian coordinates of intermediates and transition states in the manuscript are shown below (in Å):

4.1 Photolysis of 2-Nitrophenol in Gas-Phase

2-NP (S_0, gas)

C	-1.90323800	-1.41426400	0.00002000
C	-0.52388600	-1.45798000	0.00001700
C	0.21518100	-0.26631700	0.00007600
C	-0.42790600	0.99442000	0.00001300
C	-1.83194600	1.01008900	-0.00000500
C	-2.55257600	-0.16961400	-0.00001200
H	-2.47595400	-2.33276900	0.00002100
H	0.01553900	-2.39509100	0.00003700
H	-2.32231300	1.97551600	-0.00007700
H	-3.63587100	-0.12801700	-0.00002700
O	0.20735900	2.17042000	-0.00004300
H	1.17105000	1.98336800	-0.00021400
N	1.66463300	-0.36228600	-0.00001500
O	2.32028300	0.69903100	0.00010900
O	2.19002500	-1.46257600	-0.00010200

TS1 (S_0, gas)

C	1.79606054	-1.52652711	0.46631310
C	0.63909681	-1.44204109	-0.23523735
C	-0.12821234	-0.22817671	-0.20981344
C	0.23739208	0.89471043	0.71342982
C	1.53812510	0.72699779	1.36746809
C	2.25596439	-0.41559056	1.26281138
H	2.39561162	-2.42711898	0.41577371
H	0.28838136	-2.25359733	-0.85861592
H	1.86302585	1.55818701	1.98138941
H	3.19827017	-0.51157644	1.79192721
O	-0.49850785	1.84016688	0.97355552
H	-2.56880205	1.15397557	-0.70809755
N	-1.23057747	-0.18596855	-0.97729058
O	-1.75449746	1.09148121	-1.23212241

O	-1.75115763	-1.11912227	-1.57560882

2-NP-HT1 (S_0, gas)

C	-1.86925000	-1.44426100	0.00002800
C	-0.51425900	-1.46756900	0.00001800
C	0.22924500	-0.23762000	0.00000500
C	-0.46327300	1.08990000	-0.00000500
C	-1.92714800	0.99296600	-0.00004800
C	-2.58133000	-0.19149800	-0.00001500
H	-2.42621500	-2.37309200	0.00004400
H	0.03866100	-2.39681800	0.00000200
H	-2.45135100	1.94093800	-0.00005500
H	-3.66619800	-0.20974400	0.00002800
O	0.10846100	2.17298500	0.00002200
H	3.21608500	0.45989200	-0.00020600
N	1.56810800	-0.35587000	0.00000300
O	2.30729400	0.81025300	0.00004400
O	2.21778800	-1.40593600	-0.00003200

TS2 (S_0, gas)

C	1.87616657	-1.50458151	-0.00017482
C	0.52246897	-1.49412467	0.00022548
C	-0.17467360	-0.23510871	0.00012648
C	0.55714733	1.07465801	-0.00012385
C	2.01688061	0.93745266	-0.00068940
C	2.62679874	-0.27015802	-0.00068898
H	2.40995673	-2.44691192	-0.00010369
H	-0.05984782	-2.40572589	0.00063234
H	2.57443925	1.86608927	-0.00103616
H	3.71027306	-0.32630054	-0.00110154
O	-0.00622737	2.15833860	0.00007871
H	-3.05850995	-0.32906341	0.00045768
N	-1.49671213	-0.25201285	0.00029153
O	-2.34298567	0.73919439	0.00029858
O	-2.26218005	-1.32817719	0.00043415

2-NP-HT2 (S_0, gas)

C	-1.74724000	-1.53949500	0.00001300

C	-0.39307400	-1.45939400	0.00004300
C	0.24451900	-0.17302900	0.00007900
C	-0.55165400	1.09544600	0.00025500
C	-2.00185100	0.88650400	-0.00001900
C	-2.55672900	-0.34841600	-0.00005800
H	-2.22968600	-2.50910100	-0.00003900
H	0.21883200	-2.34928300	0.00000700
H	-2.60153800	1.78859900	-0.00013100
H	-3.63650200	-0.45495800	-0.00017300
O	-0.05195300	2.21306700	-0.00012900
H	3.18973800	-1.04100200	-0.00010400
N	1.58190100	-0.07809900	0.00000200
O	2.29304300	0.90924400	0.00003200
O	2.26166300	-1.32946800	-0.00008400

TS3 (S_0, gas)

C	2.49017491	-1.56824508	-0.01332329
C	1.10112446	-1.59920030	0.07052348
C	0.53444544	-0.36938872	0.26781337
C	0.56696229	0.90597987	-0.14453993
C	2.09395266	0.79527813	0.09014743
C	2.98886164	-0.25757592	0.00524344
H	3.09261022	-2.45212357	-0.16914541
H	0.47975893	-2.46864079	-0.10437920
H	2.40825660	1.79045873	0.39407373
H	4.05144778	-0.04367742	0.01093817
O	-0.06628941	1.93630571	-0.32158294
H	-1.76472957	1.49847126	-0.19953060
N	-2.25936416	-0.29834705	0.04180521
O	-2.62983232	1.02185980	-0.09550464
O	-3.18076176	-1.02103590	0.17781155

TS4 (S_0, gas)

C	2.10156500	-1.58033400	-0.04770700
C	0.72650900	-1.38483500	-0.09088200
C	0.32435000	-0.09128400	0.09692700
C	0.66728600	1.20436600	-0.10479000
C	2.15229400	0.81338800	0.17259000

C	2.82415600	-0.38311700	0.09975000
H	2.55304900	-2.55439900	-0.17211700
H	-0.00143200	-2.16102900	-0.28933800
H	2.64352000	1.74854500	0.42365500
H	3.90534100	-0.37994500	0.18349200
O	0.27787200	2.34487700	-0.23297900
H	-3.84742900	0.42114400	0.33176000
N	-2.15140600	-0.33374600	-0.07032200
O	-2.93941100	0.75558400	0.16805900
O	-2.70973300	-1.37636100	-0.02764700

TS5 (S_0, gas)

C	-2.08392872	-1.66242474	-0.02632768
C	-0.71347453	-1.42328750	-0.02564286
C	-0.36631179	-0.10697971	-0.12310429
C	-0.75182806	1.16233969	0.15776781
C	-2.23361381	0.73955249	-0.05529168
C	-2.85397117	-0.48669039	-0.04767002
H	-2.49538675	-2.65978193	0.03801146
H	0.04766848	-2.18532728	0.07791036
H	-2.77437914	1.67039544	-0.19733947
H	-3.93734226	-0.52144844	-0.07982999
O	-0.38711613	2.30621129	0.33469434
H	3.63989960	-1.28462131	-0.01213694
N	2.14712946	-0.06793430	-0.04452276
O	2.93388750	0.74849048	-0.34331171
O	2.67575445	-1.34785119	0.14875075

2-NP·1W_1 (S_0, gas)

C	2.57813500	-1.35772800	0.01494700
C	1.20386300	-1.45251500	-0.00038700
C	0.42050600	-0.28462900	-0.00892200
C	1.02486500	0.99813500	-0.00198500
C	2.42415300	1.06483900	0.01392500
C	3.18466400	-0.08990400	0.02210700
H	3.18366900	-2.25470400	0.02141400
H	0.70881600	-2.41338900	-0.00587900
H	2.88601300	2.04438800	0.01903500

H	4.26543500	-0.01101400	0.03413000
O	0.34716100	2.16034400	-0.00988300
H	-3.65423600	0.25672600	0.01864700
N	-1.00672200	-0.43080400	-0.02373300
O	-1.50988500	-1.54997100	-0.02580000
O	-1.71540200	0.60348000	-0.03397300
O	-4.62037200	0.15691300	0.04570200
H	-0.61127500	1.95605500	-0.02160300
H	-4.76049400	-0.79774800	0.05390800

2-NP·1W_2 (S_0, gas)

C	-2.98602900	0.31109000	0.01076600
C	-1.84070300	1.07771600	0.00814300
C	-0.58004900	0.45623600	-0.00051900
C	-0.46447100	-0.95667200	-0.00843200
C	-1.64473900	-1.71138800	-0.00881100
C	-2.88018200	-1.08937300	0.00164300
H	-3.95759100	0.78805600	0.02032100
H	-1.89074500	2.15744600	0.01473100
H	-1.55835900	-2.79095300	-0.01658600
H	-3.77756600	-1.69708700	0.00250000
O	0.70094200	-1.62846700	-0.01729100
H	3.78968100	-0.27870600	-0.01964000
N	0.58605400	1.29426300	-0.00158600
O	0.45941100	2.51662900	-0.01453500
O	1.71442300	0.75723800	0.01308700
O	4.50441300	-0.91960700	0.08228200
H	1.43237300	-0.97460500	-0.01562400
H	5.20334800	-0.59598700	-0.49968300

2-NP·2W (S_0, gas)

C	2.90897600	-1.15830800	-0.40346100
C	1.57923900	-1.45641600	-0.17407200
C	0.67868000	-0.43380500	0.14717600
C	1.07210700	0.92309300	0.18058200
C	2.43173900	1.19245300	-0.05415800
C	3.32998400	0.17660100	-0.33006200
H	3.61326700	-1.94851800	-0.62993700

H	1.21097600	-2.47299400	-0.21135400
H	2.74262200	2.22957100	-0.02933600
H	4.37110000	0.42370200	-0.50453400
O	0.27406600	1.97314500	0.38347100
H	-4.40975200	-0.67893900	0.14474800
N	-0.68030700	-0.82536300	0.48615900
O	-1.16178100	-1.81788000	-0.07506500
O	-1.28461600	-0.16734000	1.32447300
O	-3.77939100	-0.60183200	-0.57877000
H	-3.08678800	-1.25472800	-0.38317300
H	-0.68170700	1.78229500	0.24072800
O	-2.26129300	1.74261700	-0.58465800
H	-2.87522800	0.97845800	-0.58291800
H	-2.42256700	2.22730300	-1.39897500

2-NP-HT1·1W (S_0, gas)

C	2.51099300	-1.39432000	0.01962600
C	1.15434900	-1.44916900	0.00294000
C	0.37839900	-0.24348500	-0.00974200
C	1.03045200	1.08550700	-0.00317000
C	2.48226200	1.04047600	0.01395700
C	3.17933700	-0.12590500	0.02462300
H	3.09310900	-2.30705300	0.02848200
H	0.63371900	-2.39627600	-0.00168000
H	2.98563700	2.00019900	0.01773200
H	4.26367500	-0.10479300	0.03713700
O	0.42729300	2.17797100	-0.01023700
H	-2.71822800	0.38855300	-0.03506800
N	-0.97142800	-0.40118300	-0.02584300
O	-1.73700800	0.70235500	-0.04848700
O	-1.54864400	-1.49552600	-0.02322300
O	-4.24138000	0.11768400	-0.03788100
H	-4.68248600	0.55695600	0.70234600
H	-4.39226300	-0.82780600	0.10117700

2-NP-HT2·1W (S_0, gas)

C	2.14734400	-1.71404000	0.00470100
C	0.81297100	-1.45755600	-0.00813600

C	0.34338300	-0.10345800	-0.00748500
C	1.28645500	1.03695600	0.00551400
C	2.68718000	0.66202900	0.01800200
C	3.09157300	-0.63597100	0.01791400
H	2.50332800	-2.73642400	0.00510500
H	0.09488400	-2.26398200	-0.01817100
H	3.39994100	1.47831400	0.02794400
H	4.15081100	-0.86886800	0.02811900
O	0.93696800	2.23567000	0.00568400
H	-2.76077900	-0.62961800	-0.03263700
N	-0.99032400	0.13799000	-0.02115000
O	-1.54060800	1.23762200	-0.01850400
O	-1.79073700	-0.96283300	-0.04139000
O	-4.29254500	-0.32878300	-0.04791700
H	-4.42595900	0.62130600	0.07646700
H	-4.74802900	-0.74783000	0.69517900

TS3·1W (S_0, gas)

C	-3.06979500	-0.87022700	0.24549500
C	-1.75800300	-1.33654300	0.21665000
C	-0.84122700	-0.39256700	-0.13271400
C	-0.52630100	0.91757800	-0.09578600
C	-2.02912800	1.24151300	-0.24249100
C	-3.16974500	0.50587000	-0.00721700
H	-3.90395900	-1.50504900	0.50882800
H	-1.44049000	-2.33037400	0.50299000
H	-2.05847900	2.25757800	-0.62586500
H	-4.12896200	1.00863400	-0.05274500
O	0.36235900	1.75627700	-0.16953700
H	2.63081600	-0.21181600	0.75094400
N	1.54251700	-1.50974500	-0.19577200
O	2.19213700	-1.25362400	-1.15783100
O	1.96704600	-0.94225600	0.96426200
O	3.06416000	1.39804300	0.42861700
H	2.16514500	1.70773500	0.19570500
H	3.61789200	1.58025000	-0.33716200

TS4·1W (S_0, gas)

C	2.69665100	-1.65231200	0.02127500
C	1.33859600	-1.36403700	0.02553700
C	1.02766700	-0.04350200	-0.17299200
C	1.42340500	1.21733000	0.11243300
C	2.88751300	0.73124100	-0.17512700
C	3.49459400	-0.50028700	-0.09704900
H	3.08302800	-2.65251500	0.15804700
H	0.55120800	-2.08261900	0.21400700
H	3.42830200	1.63602000	-0.43506900
H	4.57558400	-0.55767100	-0.16299300
O	1.11318600	2.37468100	0.28196000
H	-3.23145800	0.50273000	-0.18414700
N	-1.47951000	-0.23276200	0.06138000
O	-2.28112300	0.81409100	-0.19428200
O	-2.03059200	-1.27781100	0.23019100
O	-4.88288100	-0.04140300	-0.14996200
H	-5.64507600	0.44354000	0.18361400
H	-4.96429900	-0.94722500	0.16915100

TS5·1W (S_0, gas)

C	2.52169300	-1.78877600	0.00010200
C	1.19635700	-1.37694100	-0.06520800
C	1.02201800	-0.02695800	-0.21386700
C	1.51780300	1.18103400	0.13739600
C	2.94645700	0.57369400	-0.06258000
C	3.42766100	-0.71371300	-0.00920300
H	2.80512000	-2.82603900	0.11029500
H	0.33692100	-2.02581900	0.03994900
H	3.58797000	1.43220200	-0.23657000
H	4.50056500	-0.87188200	-0.00723600
O	1.29700400	2.35669200	0.32928900
H	-3.11705700	-0.81107300	0.20001100
N	-1.50524900	0.20328200	-0.13336200
O	-2.22385900	1.09063000	-0.44637500
O	-2.12978600	-0.95237200	0.24985000
O	-4.81238800	-0.41029900	0.06539200
H	-4.88135700	0.52843100	-0.14549500
H	-5.53512700	-0.61603100	0.66749300

2-NP-HT1 (T_1, gas)

C	-1.93413700	-1.38109700	0.05665900
C	-0.51987900	-1.44074600	0.03425300
C	0.22215200	-0.27907600	-0.00510200
C	-0.45208000	1.02192800	-0.04620700
C	-1.89091800	1.02055600	-0.01299400
C	-2.61664600	-0.15847100	0.03792500
H	-2.49241600	-2.31229600	0.08662700
H	-0.00115300	-2.39158500	0.04152200
H	-2.36910200	1.99464200	-0.03270700
H	-3.70155700	-0.13775800	0.05729900
O	0.19476500	2.11080800	-0.11496300
H	1.79356800	1.51809600	0.07075400
N	1.62982400	-0.36149500	-0.10860900
O	2.39431800	0.74746900	0.26306700
O	2.22478500	-1.46317700	-0.12940700

TS1 (T_1, gas)

C	-1.86814700	-1.43304200	0.15419500
C	-0.45661200	-1.42480500	0.07552700
C	0.21505100	-0.23283200	-0.05097600
C	-0.49649300	1.04142000	-0.14204600
C	-1.93896100	0.97093800	-0.02663800
C	-2.59937300	-0.23604900	0.11435900
H	-2.38579200	-2.38318100	0.24683600
H	0.10906800	-2.34986200	0.10332300
H	-2.47080700	1.91562000	-0.08181000
H	-3.68309100	-0.26355000	0.18176800
O	0.09491800	2.12934600	-0.34168500
H	3.06645900	0.87099200	0.41641800
N	1.63951600	-0.22847500	-0.17777200
O	2.23138600	0.58797300	0.83292100
O	2.26804000	-1.25537800	-0.53731800

2-NP-HT2 (T_1, gas)

C	-1.86814700	-1.43304200	0.15419500
C	-0.45661200	-1.42480500	0.07552700

C	0.21505100	-0.23283200	-0.05097600
C	-0.49649300	1.04142000	-0.14204600
C	-1.93896100	0.97093800	-0.02663800
C	-2.59937300	-0.23604900	0.11435900
H	-2.38579200	-2.38318100	0.24683600
H	0.10906800	-2.34986200	0.10332300
H	-2.47080700	1.91562000	-0.08181000
H	-3.68309100	-0.26355000	0.18176800
O	0.09491800	2.12934600	-0.34168500
H	3.06645900	0.87099200	0.41641800
N	1.63951600	-0.22847500	-0.17777200
O	2.23138600	0.58797300	0.83292100
O	2.26804000	-1.25537800	-0.53731800

TS2 (T_1, gas)

C	-1.83136500	-1.49293700	-0.09448500
C	-0.41699000	-1.41678200	-0.02062700
C	0.19572500	-0.18991600	0.05846200
C	-0.57217400	1.05486200	0.09234500
C	-2.00697400	0.90921800	-0.01582900
C	-2.61473500	-0.33468200	-0.10136200
H	-2.30138800	-2.47047100	-0.14360400
H	0.18960600	-2.31520400	-0.01970900
H	-2.58110500	1.83033300	-0.00713500
H	-3.69611600	-0.41240000	-0.16391300
O	-0.03033100	2.17779300	0.22595700
H	3.08032100	-0.35370200	-0.33244000
N	1.60728000	-0.11762900	0.17556200
O	2.36545600	0.70712900	-0.54033300
O	2.35697600	-1.21413800	0.30523100

2-NP-HT3 (T_1, gas)

C	1.74956200	-1.53357400	0.13026800
C	0.34261800	-1.40766600	0.07559500
C	-0.22872200	-0.16117200	-0.03146100
C	0.59015800	1.05173900	-0.11753300
C	2.02246100	0.85509200	-0.02444500
C	2.58072900	-0.40399000	0.08910800

H	2.18473400	-2.52572100	0.20563400
H	-0.28864100	-2.28713500	0.11159400
H	2.62977400	1.75342300	-0.07309000
H	3.65904800	-0.52459300	0.13808500
O	0.09408400	2.18889900	-0.29011200
H	-3.21169800	-1.01550600	-0.11375400
N	-1.64672700	0.01531800	-0.09372400
O	-2.24886700	0.76546700	0.71487600
O	-2.31858800	-1.19315100	-0.46746300

TS3a (T_1, gas)

C	2.26617300	-1.34977600	0.05819000
C	0.86820300	-1.52026700	0.12929700
C	0.09083800	-0.40207100	0.09475100
C	0.59208300	0.94362000	-0.01566300
C	2.04150800	1.06236500	-0.08089600
C	2.83403900	-0.05702000	-0.04391500
H	2.91395100	-2.21960800	0.07385600
H	0.43643300	-2.51353700	0.19867200
H	2.45393300	2.06257900	-0.15045400
H	3.91238800	0.04135600	-0.09356800
O	-0.15726600	1.95214700	-0.05118300
H	-1.83947100	1.42158300	0.14199600
N	-2.16564500	-0.35777500	-0.31514000
O	-2.58993300	0.79574100	0.31820400
O	-2.86214900	-1.29151900	-0.11891000

TS4a (T_1, gas)

C	-1.95210900	-1.57629600	0.06553100
C	-0.55221200	-1.40373600	-0.01975200
C	-0.07474900	-0.12817600	-0.07202900
C	-0.86496300	1.08136400	-0.05674600
C	-2.30549900	0.82586000	0.03271200
C	-2.81128600	-0.45309500	0.09101600
H	-2.36923600	-2.57911300	0.10659400
H	0.11745700	-2.26036000	-0.04658800
H	-2.94708200	1.70253400	0.05394900
H	-3.88458800	-0.60970600	0.15634300

O	-0.40395600	2.24175600	-0.10812000
H	3.42207600	0.48148200	0.95309400
N	2.29278400	-0.21798900	-0.39883600
O	2.82224500	0.86980000	0.27317000
O	2.70381000	-1.27211000	0.00045800

TS5a (T_1, gas)

C	1.92490400	-1.58905000	0.04598800
C	0.52648400	-1.40183700	-0.00292300
C	0.06392300	-0.12391100	-0.03253700
C	0.86745400	1.07485700	-0.03317700
C	2.30616600	0.80463200	0.02026500
C	2.79630800	-0.47751500	0.05772700
H	2.33008200	-2.59480000	0.06810400
H	-0.15160900	-2.24805000	-0.02220900
H	2.95707400	1.67200600	0.03152800
H	3.86664300	-0.64662000	0.09521000
O	0.41740000	2.23450500	-0.07107700
H	-3.35622100	-1.20671600	0.60731400
N	-2.26398300	0.07779500	-0.33798900
O	-2.84016000	0.87639500	0.30931800
O	-2.66592900	-1.26633000	-0.08150100

TS3a·1W (T_1, gas)

C	2.58097400	-1.18141600	0.12956300
C	1.18885000	-1.39294700	0.09054200
C	0.36148300	-0.31416400	-0.00116300
C	0.82811200	1.05176400	-0.06722100
C	2.27880300	1.21194500	-0.02920200
C	3.11139100	0.12786400	0.06900500
H	3.25101800	-2.03154300	0.19705300
H	0.78133100	-2.39912400	0.11417200
H	2.65380700	2.22825700	-0.07347400
H	4.18587200	0.26806600	0.09855400
O	0.08796600	2.06155400	-0.14631900
H	-2.65700100	0.33577000	0.31632600
N	-1.67234700	-1.15598700	-0.32394400
O	-2.62974200	-0.64810400	0.51078000

O	-1.59449400	-2.34295700	-0.28705300
O	-2.61023100	1.92523500	-0.06591800
H	-2.98898500	2.60031400	0.50457200
H	-1.64528500	2.10607000	-0.13067500

TS4a·1W (T_1, gas)

C	-2.49971373	-1.53209221	-0.17051415
C	-1.10062014	-1.34900483	-0.23265123
C	-0.62864013	-0.07088132	-0.29382399
C	-1.43112298	1.13080219	-0.31030782
C	-2.87106647	0.86599565	-0.24240370
C	-3.36839450	-0.41568641	-0.17536546
H	-2.91018393	-2.53753715	-0.12376884
H	-0.42343787	-2.20011768	-0.23678478
H	-3.51958157	1.73787003	-0.24461381
H	-4.44152583	-0.57996708	-0.12675971
O	-0.98005077	2.29503356	-0.37240844
H	2.91931407	0.51775942	0.79140186
N	1.75237072	-0.18360302	-0.56430771
O	2.29341578	0.87396624	0.08448087
O	2.13572954	-1.27084422	-0.18388425
O	3.94048540	-0.41472038	1.84323029
H	3.57092321	-1.22004025	1.43622418
H	4.86444068	-0.38743821	1.54760485

TS5a·1W (T_1, gas)

C	0.74700491	-2.80708068	0.26208856
C	0.25662643	-1.65759434	-0.39246303
C	0.45739115	-0.45289441	0.20739202
C	1.14051993	-0.23387954	1.45978977
C	1.62180409	-1.46871547	2.08341941
C	1.42483921	-2.69421779	1.49662903
H	0.60683174	-3.78282814	-0.19036451
H	-0.25714438	-1.73164616	-1.34485990
H	2.13578413	-1.35945615	3.03219390
H	1.79294744	-3.59190381	1.98087348
O	1.31769387	0.87932713	1.98923558
H	-1.83718362	1.18194141	-2.15363298

N	-0.21395214	1.37869404	-1.11428270
O	-0.77980480	2.27562274	-0.57366038
O	-0.95001159	0.73871978	-2.10415636
O	-3.35502256	2.13249397	-2.00480697
H	-3.07974520	2.78245060	-1.34599201
H	-3.85341744	2.61054785	-2.67548469

A2 (T_1, gas)

C	-1.77566100	0.04463800	-0.00005000
C	-1.15235500	-1.22224000	0.00002300
C	0.20751500	-1.25215700	0.00010900
C	1.08916800	-0.10967700	-0.00002800
C	0.37337800	1.16855600	0.00006400
C	-0.99857400	1.22446900	0.00000200
H	-2.85820900	0.10911000	-0.00019000
H	-1.74800800	-2.12920000	-0.00009300
H	0.98721000	2.06268600	0.00012200
H	-1.50051000	2.18551700	-0.00000400
O	2.33233500	-0.16870500	-0.00006900

A3 (Doublet, gas)

C	1.29126900	-1.62591700	0.00037100
C	-0.04855400	-1.43847100	0.00061900
C	-0.56964800	-0.08963400	0.00014400
C	0.33133300	1.10689700	0.00030700
C	1.76176800	0.78233700	-0.00072900
C	2.19959800	-0.49839100	-0.00045100
H	1.70025900	-2.62929900	0.00076000
H	-0.74719800	-2.26646700	0.00111800
H	2.44364700	1.62408100	-0.00137400
H	3.26538600	-0.70179900	-0.00091500
O	-0.09670200	2.25215800	0.00072400
N	-1.85912900	0.14708600	-0.00035500
O	-2.83364700	-0.56178800	-0.00055900

4.2 Photolysis of 4-Nitrophenol in Gas-Phase

4-NP (S_0, gas)

C	-1.38377700	-1.20499900	-0.00020900
C	-0.00027800	-1.21515000	-0.00015800
C	0.69007200	0.00016000	0.00003700
C	0.01357400	1.22487000	0.00021400
C	-1.36837300	1.23177300	0.00018800
C	-2.06995200	0.01789100	-0.00002700
H	-1.94311200	-2.13337200	-0.00037600
H	0.54000800	-2.15123400	-0.00031700
H	-1.91848700	2.16425100	0.00032400
N	2.13673300	-0.00833300	-0.00008900
O	2.73928700	1.07099200	-0.00008300
H	0.56590800	2.15379100	0.00037500
O	2.72747700	-1.09421700	0.00019900
O	-3.42654600	0.08580300	-0.00005300
H	-3.81079200	-0.80299200	-0.00016700

4-NP·1W_1 (S_0, gas)

C	1.96472700	-1.26308900	-0.00001200
C	0.58605400	-1.16068200	-0.00036900
C	-0.00345200	0.10770100	-0.00039900
C	0.77109100	1.27363800	-0.00007600
C	2.14812100	1.16771000	0.00027800
C	2.74852100	-0.10001200	0.00030800
H	2.44361400	-2.23540200	0.00002700
H	-0.02925500	-2.04936800	-0.00061500
H	2.77215700	2.05245800	0.00052400
N	-1.44161100	0.21845100	-0.00078700
O	-1.95961000	1.33807100	-0.00068700
H	0.29593400	2.24451500	-0.00011400
O	-2.11859100	-0.82139600	-0.00119100
O	4.10433700	-0.14530300	0.00067700
H	4.41138900	-1.06357400	0.00060400
O	-5.01093700	-0.44744700	0.00171800
H	-4.04113500	-0.52448000	0.00067900
H	-5.17339900	0.50368700	0.00188800

4-NP·1W_2 (S_0, gas)

C	-1.37956800	1.19818500	0.48396600

C	-0.07617300	0.74310700	0.55898700
C	0.21877500	-0.55381900	0.12747300
C	-0.77584300	-1.40017800	-0.37686000
C	-2.07592400	-0.94028800	-0.45597500
C	-2.38117500	0.35935400	-0.02559000
H	-1.63384800	2.19756800	0.81784400
H	0.70309800	1.37909600	0.95462600
H	-2.86433900	-1.57101600	-0.84683900
N	1.57715700	-1.03264600	0.20560500
O	1.81346700	-2.21331100	-0.06434400
H	-0.52641200	-2.39901500	-0.70624100
O	2.47276500	-0.24493700	0.54612000
O	-3.67413900	0.75986100	-0.12277200
H	-3.77267700	1.66738200	0.20097800
O	3.03156100	2.40843600	-0.66970500
H	2.78263600	1.55515900	-0.28089100
H	3.94166300	2.28078700	-0.96512200

4-NP·2W (S_0, gas)

C	-0.22249800	-0.53457700	0.08038700
C	-2.25629000	0.13487100	1.15323500
C	-2.87826800	0.19956400	-0.09953400
C	-2.16113300	-0.10351800	-1.26314100
C	-0.82882400	-0.46673200	-1.17436300
H	-2.81373200	0.37898800	2.05173300
H	-2.66274600	-0.04322900	-2.22049800
O	-4.18033600	0.55324000	-0.25077200
H	-4.57634100	0.75097300	0.60523900
C	-0.92304000	-0.23269900	1.24507500
H	-0.25127400	-0.69657800	-2.05867400
H	-0.41841000	-0.27894300	2.19983300
N	1.18131200	-0.91127200	0.17874700
O	1.68110100	-1.02994000	1.28956400
O	1.80497600	-1.09607900	-0.87266700
O	4.22691000	0.39783000	-0.40812500
H	4.69773100	0.08462500	0.37068500
H	3.61394200	-0.32045800	-0.63639900
O	2.06511500	2.16139200	0.14748500

H	2.90461000	1.69883800	-0.03000000
H	2.07521900	2.93168600	-0.42698100

4-NP* (T_1, gas)

C	-1.40229500	1.20119500	0.00242200
C	-0.01542700	1.21481600	0.03681700
C	0.67882600	-0.00057800	0.04964300
C	-0.00853700	-1.22343600	0.04036200
C	-1.39185900	-1.22420100	0.00553700
C	-2.09547200	-0.01405500	-0.01214300
H	-1.94785900	2.13931500	-0.01606400
H	0.53094200	2.14908700	0.04357400
H	-1.94676000	-2.15375200	-0.01067400
N	2.07202600	0.00493000	0.13730600
O	2.83043500	-1.03273300	-0.09050400
H	0.54674700	-2.15252500	0.05032500
O	2.82091600	1.05228200	-0.07854700
O	-3.45647200	-0.08666100	-0.04431700
H	-3.83771000	0.79780900	-0.05718600

4-NP*·1W (T_1, gas)

C	-1.33009500	1.24443300	-0.20597300
C	-0.01976800	0.79414600	-0.27040800
C	0.23288800	-0.57440700	-0.10827900
C	-0.81416500	-1.48481000	0.10697400
C	-2.11517800	-1.02022000	0.16991900
C	-2.38001200	0.34582100	0.01175400
H	-1.53424600	2.30473900	-0.31592100
H	0.79353200	1.49417900	-0.41749700
H	-2.94074600	-1.69923400	0.34167400
H	-0.59666800	-2.53833100	0.22845000
O	-3.68268700	0.73811600	0.08278400
H	-3.74989500	1.69198000	-0.03443500
N	1.53651100	-1.05950700	-0.22031600
O	1.93082600	-2.22941600	0.21482500
O	2.61487600	-0.32576200	-0.26947600
O	2.79145100	2.53978400	0.35470500
H	2.99163700	1.59497700	0.40267300

H	3.60305600	2.95669000	0.05064700

TS(4-NP*-B2) (T_1, gas)

C	-1.37548400	1.18691000	-0.18625800
C	-0.02811300	1.34996600	-0.04539600
C	0.85845000	0.20180800	0.26002400
C	0.18903100	-1.11736200	0.35002500
C	-1.15576600	-1.23369200	0.20568900
C	-1.96117200	-0.09468200	-0.07386800
H	-2.00899800	2.04867700	-0.37794000
H	0.44199200	2.32277500	-0.10707700
H	-1.64955100	-2.19219800	0.31632000
H	0.81472900	-1.96857600	0.58565700
O	-3.29431400	-0.30793600	-0.20166300
H	-3.75325600	0.52171200	-0.37767000
N	2.15876400	0.25193500	-0.50672600
O	2.84693400	-0.66255200	-0.88141800
O	1.93263600	0.43878400	1.13889300

TS(4-NP*·1W-B2) (T_1, gas)

C	2.01369500	0.92348700	-0.51229900
C	0.72514900	1.35857200	-0.62855300
C	-0.40644900	0.52512600	-0.16927600
C	-0.05240200	-0.78041400	0.42963600
C	1.24388100	-1.17425700	0.51807400
C	2.29874800	-0.33345800	0.06664100
H	2.82903700	1.54295300	-0.87543700
H	0.47879800	2.30850800	-1.08453300
H	1.50251800	-2.14839300	0.91643400
H	-0.87003100	-1.42499100	0.72825800
O	3.55954400	-0.81139400	0.20217100
H	4.20020800	-0.17993300	-0.14544800
N	-1.48510000	1.31716200	0.50491300
O	-2.24443000	0.99617800	1.38152500
O	-1.59252600	0.57351600	-0.97251000
O	-2.98250900	-1.94736100	-0.60470600
H	-3.93004100	-1.85141000	-0.47314100
H	-2.67116500	-1.06872100	-0.87769400

TS(4-NP*-B1) (T_1, gas)

C	1.40501400	-1.19517300	0.18548500
C	0.01168400	-1.13845000	0.23540400
C	-0.55717300	0.09720900	0.04889400
C	0.11736800	1.28834900	-0.10623100
C	1.50798700	1.21684000	-0.15728400
C	2.14623400	-0.02074800	-0.00903600
H	1.91250100	-2.14986300	0.28941700
H	-0.59391400	-2.02744800	0.36975300
H	2.10948900	2.10581900	-0.30350200
H	-0.40438800	2.23234700	-0.19727400
O	3.50726000	-0.02146800	-0.06425700
H	3.84662800	-0.91489000	0.05718200
N	-2.47661300	0.07157000	-0.29909000
O	-2.80270600	0.95067600	0.54259000
O	-2.86964200	-1.08359800	-0.39150100

TS(4-NP*·1W-B1) (T_1, gas)

C	1.44597100	1.23112000	-0.08460800
C	0.11712700	0.82354500	-0.19245200
C	-0.10779300	-0.53403900	-0.12277400
C	0.85894300	-1.51811000	-0.07297500
C	2.18050200	-1.09546100	0.03323600
C	2.46896400	0.27631300	0.02904100
H	1.68748000	2.29023200	-0.08916000
H	-0.69012600	1.54359700	-0.28981800
H	2.99427400	-1.80557300	0.11660600
H	0.60238300	-2.57031000	-0.08501000
O	3.77854500	0.62825200	0.13090300
H	3.86934000	1.58752600	0.11303700
N	-1.93311900	-1.16704800	0.33079600
O	-2.18176600	-1.72126000	-0.76221400
O	-2.59672200	-0.31985000	0.91824100
O	-2.77430800	2.39510300	-0.17445400
H	-3.01190200	1.55232200	0.23881800
H	-3.50789700	2.61339000	-0.75665700

B2 (Double, gas)

C	0.64439400	1.21447400	-0.00002100
C	-1.50342300	0.00800400	-0.00026000
C	-0.74795600	-1.23315500	-0.00006000
C	0.62168300	-1.23944000	-0.00004700
C	1.33014300	-0.01834300	-0.00002700
H	1.21188300	2.14133500	0.00009000
H	1.18848300	-2.16308700	0.00004800
H	-1.31615800	-2.15577400	0.00003300
O	2.68260800	-0.09435400	0.00011700
H	3.06952500	0.78886700	-0.00005700
O	-2.75461000	0.02163900	0.00022400
C	-0.72806400	1.23541700	-0.00003700
H	-1.27838200	2.16863300	-0.00012900

TS(B2-B6) (Doublet, gas)

C	-0.78324565	0.99622810	0.50633860
C	1.11927306	-0.51341527	0.20904216
C	0.24565481	-1.53859664	-0.15783489
C	-1.11690769	-1.29602463	-0.21019492
C	-1.63016311	-0.01586080	0.10170149
H	-1.17538987	1.96312140	0.80354840
H	-1.81108347	-2.07171799	-0.50940087
H	0.65302148	-2.50449610	-0.42910124
O	-2.98572619	0.12518737	0.01010662
H	-3.23747846	1.02988248	0.22509716
O	2.45137491	-0.72437107	0.18161803
H	2.84375744	0.13029978	-0.07612086
C	0.61202769	0.77313266	0.55926686
H	1.22074569	1.42663306	1.16683634
O	1.71816977	1.70341380	-0.91467429
H	1.21397049	1.48721839	-1.71300865

B6 (Doublet, gas)

C	0.71772600	-1.06088300	0.25349700
C	-1.13268200	0.61190400	0.11111200
C	-0.21091800	1.60466100	-0.10351600
C	1.15815400	1.30566800	-0.13641400

C	1.59394800	-0.04335300	0.02527100
H	1.06169900	-2.07874800	0.40944800
H	1.89863300	2.07326700	-0.31688000
H	-0.55861100	2.61627900	-0.27736800
O	2.94986100	-0.22220800	-0.06870200
H	3.16301200	-1.15239200	0.06233800
O	-2.46124700	0.88021200	0.10385900
H	-2.93091100	0.03786100	0.01177100
C	-0.74832500	-0.81556200	0.38851500
H	-1.09401900	-1.07794400	1.40125600
O	-1.56412600	-1.70272500	-0.43406700
H	-1.20311800	-1.67516400	-1.33007800

B1 (Doublet, gas)

C	-0.95714500	-1.20358400	0.01451500
C	0.44286400	-1.14005000	0.05254100
C	1.00519200	0.11225900	0.06076800
C	0.31378700	1.30147100	0.03814300
C	-1.08175800	1.22384200	0.00055200
C	-1.70876300	-0.02567300	-0.01115800
H	-1.45373500	-2.16981300	0.00393400
H	1.03586000	-2.04706300	0.07131800
H	-1.69059500	2.12000400	-0.02118500
H	0.81063000	2.26474600	0.04538500
O	-3.07749300	-0.03015000	-0.04802900
H	-3.40364300	-0.93596800	-0.05615300

TS(B1-B4) (Doublet, gas)

C	0.90434500	1.20173600	-0.00625800
C	-0.49223700	1.21127200	-0.04770100
C	-1.16074200	0.00078200	-0.08180900
C	-0.50045900	-1.21779100	-0.04813100
C	0.89273100	-1.22452200	-0.00653100
C	1.59131200	-0.01456500	0.01414200
H	1.45278100	2.13922800	0.00907200
H	-1.03180600	2.15074400	-0.06387600
H	1.44846300	-2.15439300	0.00875800
H	-1.04987700	-2.15158400	-0.06615500

O	2.95680500	-0.08567400	0.05714200
H	3.33212600	0.80102800	0.06341900
H	-2.40922800	0.00903900	-0.18816100
H	-3.69256000	-0.02016000	0.95321400
O	-3.63925400	0.02125300	-0.01446100

B4 (Singlet, gas)

C	-0.26279900	1.19768700	-0.00000400
C	1.13132300	1.21727000	-0.00004300
C	1.85511600	0.02725800	0.00006900
C	1.16984100	-1.18882900	-0.00008000
C	-0.22083300	-1.22161700	0.00009700
C	-0.93810500	-0.02405100	0.00016200
H	-0.82305900	2.12836500	-0.00016200
H	1.64899800	2.16998400	0.00002900
H	-0.76393900	-2.15892200	0.00015600
H	1.72227300	-2.12188700	0.00005100
O	-2.30532900	-0.11037000	-0.00028300
H	-2.68724700	0.77341000	0.00127400
H	2.93834700	0.04569500	-0.00028300

TS(B4-B5a) (Doublet, gas)

C	-0.65918813	-1.20346412	-0.23460171
C	0.67915895	-1.17998872	-0.58243186
C	1.39656504	0.04250044	-0.62547260
C	0.67573329	1.24869582	-0.41908379
C	-0.66023615	1.22821949	-0.07301027
C	-1.33327732	0.00006465	0.02397682
H	-1.19369157	-2.14680765	-0.17128957
H	1.20178642	-2.10561601	-0.78869250
H	-1.21129448	2.14127821	0.11628400
H	1.19852534	2.19343367	-0.50290015
O	-2.64902103	0.03963621	0.36870988
H	-3.01023984	-0.85320258	0.40143117
H	2.36037346	0.07565846	-1.11109573
H	1.78692203	-0.07423552	1.73743385
O	2.50358041	-0.09320436	1.08480240

TS(B4-B5b) (Doublet, gas)

C	1.04173000	1.11706900	0.29787200
C	-0.19798100	1.73910300	0.10821400
C	-1.26795500	1.02859400	-0.40594500
C	-1.12288800	-0.35853600	-0.69603900
C	0.15399200	-0.96115300	-0.56370200
C	1.21152500	-0.23522200	-0.04216600
H	1.87647400	1.68106400	0.70369100
H	-0.30991600	2.78686500	0.36192500
H	0.29904400	-1.99950200	-0.83240200
H	-1.85828300	-0.84324800	-1.32235200
O	2.41052300	-0.87789300	0.11113600
H	3.07446500	-0.26295600	0.43957100
H	-2.23061800	1.50039700	-0.55283800
H	-1.63077800	-0.83822200	1.56877500
O	-2.17688900	-1.12254800	0.81939300

TS(B4-B5c) (Doublet, gas)

C	0.49142229	1.38056781	-0.34073028
C	-0.80515728	1.55993446	-0.81991400
C	-1.66578757	0.46522987	-0.98996895
C	-1.22770168	-0.80692938	-0.66455555
C	0.05574132	-1.00948893	-0.10167384
C	0.93824477	0.10054944	-0.02110798
H	1.15897958	2.23055067	-0.23661858
H	-1.14371592	2.55803950	-1.07340300
H	0.47643237	-2.00186626	-0.03205994
H	-1.87545481	-1.66519562	-0.79552630
O	2.20206794	-0.16428593	0.38544229
H	2.69421515	0.65637829	0.49990731
H	-2.66270621	0.61685741	-1.38579953
H	-1.10071494	-0.56632906	1.96184367
O	-0.38705249	-1.21872250	1.88561522

B5a (Doublet, gas)

C	0.69557800	-1.21680900	-0.07872900
C	-0.64980500	-1.24610200	-0.30642300
C	-1.48273000	0.00059500	-0.37725200

C	-0.66315100	1.25083100	-0.29688800
C	0.67900100	1.23715800	-0.08227900
C	1.38149300	0.01278400	0.04118400
H	1.25356900	-2.14667300	0.00302800
H	-1.16242100	-2.19671400	-0.41147300
H	1.24212500	2.16014200	-0.00212900
H	-1.19981300	2.18857400	-0.37832800
O	2.72690000	0.08649700	0.25957600
H	3.09561800	-0.79982000	0.34117400
H	-2.06643500	0.00600600	-1.31278000
H	-3.14251100	-0.59012900	0.54178100
O	-2.44970600	0.05698700	0.71805500

B5b (Doublet, gas)

C	1.16553500	1.11090900	0.13850100
C	-0.07774400	1.78222000	0.05544600
C	-1.23624500	1.10708700	-0.18340000
C	-1.25909300	-0.37427500	-0.39279200
C	0.08830600	-1.01938500	-0.27515800
C	1.21790800	-0.29700000	-0.02303800
H	2.07448700	1.66897400	0.33797900
H	-0.09964700	2.85722400	0.19804100
H	0.16010000	-2.09402400	-0.40351400
H	-1.65653600	-0.56989400	-1.40641400
O	2.41270000	-0.96910100	0.06775000
H	3.11724400	-0.35104900	0.28588700
H	-2.19128900	1.61724700	-0.21708000
H	-2.33561500	-1.85800100	0.35106100
O	-2.22029300	-0.92187600	0.54933500

B5c (Doublet, gas)

C	0.46681000	1.46826400	-0.14866400
C	1.76524800	0.91448000	-0.20024400
C	1.95067000	-0.47274200	0.02345100
C	0.89936000	-1.29743500	0.29035700
C	-0.51246500	-0.80572100	0.36072400
C	-0.61123300	0.67312300	0.11911000
H	0.32500300	2.53167900	-0.32368100

H	2.61295200	1.55147800	-0.41804600
H	-0.93182800	-1.01779500	1.36059600
H	1.04108800	-2.36034100	0.44573500
O	-1.90053400	1.11609100	0.20062600
H	-1.94503100	2.05717000	-0.00440700
H	2.95346700	-0.88344400	-0.02349200
H	-2.21707900	-1.27534700	-0.50217700
O	-1.29808000	-1.55149200	-0.60099300

P1 (Singlet, gas)

C	0.65378900	1.40047100	0.00005100
C	1.87966000	0.73181400	0.00001900
C	1.90867100	-0.66036300	-0.00006200
C	0.71917400	-1.38900100	-0.00009200
C	-0.50374200	-0.72787400	0.00003400
C	-0.52965700	0.67375300	0.00009900
H	0.61861500	2.48604300	0.00017700
H	2.80108600	1.30133600	0.00000800
H	0.72080600	-2.47242100	-0.00025300
O	-1.78926500	1.23526000	0.00010900
H	-1.73058200	2.19548900	-0.00114900
H	2.85662500	-1.18507300	-0.00015300
H	-2.40533200	-0.82483300	-0.00207600
O	-1.66430800	-1.44442600	0.00028600

P4 (Singlet, gas)

C	0.64357700	1.06876000	-0.00000100
C	-0.70999000	0.74220300	0.00000400
C	-1.12481900	-0.59278700	0.00000600
C	-0.16172800	-1.59482600	0.00000000
C	1.19567900	-1.28284600	-0.00000900
C	1.59921500	0.04975700	-0.00001000
H	0.94834000	2.11234100	0.00000000
H	1.94636300	-2.06261300	-0.00001500
H	-0.49082200	-2.62693700	0.00000200
O	2.94859300	0.30802900	-0.00001600
H	3.10212300	1.25774800	-0.00004500
O	-2.45399800	-0.91997200	0.00000800

O	-1.72263800	1.67607700	0.00001300
H	-1.36416000	2.56847400	0.00003000
H	-2.96910500	-0.10365100	0.00005000

P5 (Singlet, gas)

C	-0.69826600	-1.19420200	-0.00002700
C	0.69826600	-1.19420900	0.00011700
C	1.39800800	0.00944100	0.00003400
C	0.69425600	1.21531700	-0.00012700
C	-0.69425200	1.21531700	-0.00002200
C	-1.39801400	0.00945600	-0.00002600
H	-1.23370700	-2.13892200	-0.00013700
H	1.23367100	-2.13894900	0.00041300
H	-1.24777100	2.14643400	-0.00011200
H	1.24776700	2.14643300	-0.00029900
O	-2.77076500	0.07752800	-0.00001900
H	-3.14009800	-0.81110500	0.00029500
H	3.14013700	-0.81108200	-0.00385900
O	2.77076600	0.07753000	0.00052000

P6 (Singlet, gas)

C	-1.22502100	1.07471200	0.00013500
C	-0.01975900	1.77749400	-0.00002100
C	1.20219700	1.11662300	0.00006000
C	1.21351900	-0.28071000	0.00000300
C	0.02226100	-1.00338700	-0.00025700
C	-1.19381900	-0.31990400	0.00001600
H	-2.17312100	1.60261200	0.00043400
H	-0.03846500	2.86142700	0.00009500
H	0.01796000	-2.08823100	-0.00075100
O	-2.32961900	-1.08454500	0.00022100
H	-3.10381200	-0.51223900	-0.00164500
H	2.14097900	1.65512800	0.00010200
H	2.31816600	-1.85303800	0.00401800
O	2.43487200	-0.89728300	-0.00045500

4.3 Photolysis of 4-Nitrophenol in Aqueous-Phase

4-NP (Singlet, aq)

C	1.38379000	1.20524900	0.00007600
C	0.00075400	1.21546000	0.00008100
C	-0.69060000	-0.00016100	0.00001300
C	-0.01355800	-1.22506700	-0.00005300
C	1.36795100	-1.23212100	-0.00007600
C	2.07020400	-0.01797000	-0.00001500
H	1.94270600	2.13395300	0.00015000
H	-0.54037300	2.15119300	0.00016200
H	1.91807800	-2.16461400	-0.00013800
H	-0.56686100	-2.15360300	-0.00009100
O	3.42590700	-0.08588800	-0.00004000
H	3.81117200	0.80235300	-0.00000500
N	-2.13634100	0.00838400	0.00000600
O	-2.73901300	-1.07070700	0.00022700
O	-2.72709100	1.09405600	-0.00022200

4-NP* (Triplet, aq)

C	-1.37426700	-1.23123300	0.00010000
C	-0.00999200	-1.24106100	0.00011300
C	0.70456400	0.00161100	0.00002400
C	0.00725700	1.24971200	-0.00005200
C	-1.35671200	1.25298100	-0.00006700
C	-2.07470400	0.01447000	-0.00001100
H	-1.94460200	-2.15305500	0.00020500
H	0.54429900	-2.16697600	0.00022900
H	-1.92100700	2.17711000	-0.00008600
H	0.57091800	2.16991800	0.00000400
O	-3.39827000	0.09125300	-0.00004900
H	-3.81627000	-0.78731900	-0.00007100
N	2.10234600	-0.00752000	0.00001100
O	2.73698100	1.11837000	0.00016000
O	2.72046000	-1.14286300	-0.00023500

4-NP*·1W (Triplet, aq)

C	-1.93457300	-1.29014000	-0.00003200
C	-0.57413900	-1.18351500	-0.00018000
C	0.02918500	0.11473800	-0.00014800

C	-0.76948600	1.29886700	0.00002200
C	-2.12916600	1.18673200	0.00015600
C	-2.73772200	-0.10867100	0.00012900
H	-2.42195700	-2.25827700	-0.00003400
H	0.05752100	-2.05860100	-0.00030000
H	-2.76954800	2.05990400	0.00027800
H	-0.28566400	2.26349200	0.00003000
O	-4.06199000	-0.14945000	0.00027200
H	-4.39659200	-1.06319300	0.00027600
N	1.42339700	0.22590800	-0.00030000
O	1.96352500	1.39695600	-0.00031800
O	2.13631100	-0.85901000	-0.00043900
O	4.90604300	-0.46123000	0.00066000
H	3.92836100	-0.54050400	0.00026900
H	5.06839600	0.48963000	0.00050400

TS(4-NP*-B2) (Triplet,aq)

C	-1.38705000	1.18337000	-0.19003600
C	-0.03825400	1.34571800	-0.07200800
C	0.83959900	0.20049200	0.21778300
C	0.19324700	-1.11820200	0.30804300
C	-1.15591600	-1.23851900	0.19015000
C	-1.96855300	-0.10035600	-0.06663000
H	-2.02837300	2.03800700	-0.37828700
H	0.42593100	2.31990600	-0.15849200
H	-1.63656000	-2.20364400	0.30224200
H	0.82472100	-1.97359100	0.51271900
O	-3.30450700	-0.30788600	-0.17069000
H	-3.76770900	0.52800000	-0.33245400
N	2.17332000	0.25357600	-0.47029900
O	2.88014500	-0.65620600	-0.84150600
O	1.93314900	0.44925200	1.14001400

B2 (Triplet,aq)

C	-1.64205700	0.99412400	-0.65886000
C	-0.42675600	1.40914700	-0.18382900
C	0.34172500	0.58996800	0.72961500
C	-0.23069200	-0.68217100	1.11744900

C	-1.44516800	-1.08910500	0.63751000
C	-2.16274400	-0.25703800	-0.25369100
H	-2.21832000	1.60781500	-1.34358400
H	-0.00857900	2.36374100	-0.48150900
H	-1.87812000	-2.04040600	0.92377500
H	0.33561200	-1.30414200	1.80091100
O	-3.35379900	-0.71108400	-0.69309500
H	-3.76183700	-0.07331700	-1.29803100
N	3.65158800	0.03384400	-0.90167500
O	3.80740800	-1.08149100	-0.67931900
O	1.46692600	0.97005700	1.17003900

TS(4-NP*·1W-B2) (Triplet,aq)

C	2.24634900	1.01587900	-0.01853400
C	0.94726500	1.42407600	-0.08894900
C	-0.14891600	0.44555500	-0.16571300
C	0.22610000	-0.97401600	-0.09312200
C	1.53300600	-1.34247000	-0.02795800
C	2.56341500	-0.36302100	0.01282000
H	3.05286100	1.74147600	0.00598100
H	0.68264800	2.47315400	-0.12622700
H	1.81304000	-2.38956100	-0.02093000
H	-0.57027900	-1.70626100	-0.13734300
O	3.84004600	-0.81449400	0.06617000
H	4.46366300	-0.07236500	0.06920300
N	-1.39619700	0.85392000	0.60102400
O	-2.23114300	0.14487900	1.11999900
O	-1.24915000	0.78049900	-1.03397600
O	-4.76348200	-0.74692800	-0.33341700
H	-4.68168100	-1.70731700	-0.38680700
H	-3.96035200	-0.46423200	0.12749900

B2·NO·H_2O (Triplet, aq)

C	2.34934400	-0.58934300	-0.80065300
C	1.20630100	-1.31667300	-0.99434300
C	0.03472500	-1.10064800	-0.17453200
C	0.12087800	-0.08860300	0.85577600
C	1.26791800	0.63185100	1.04369700

C	2.39236700	0.39095400	0.21885100
H	3.23006000	-0.74871900	-1.41401200
H	1.15036100	-2.07316300	-1.76834200
H	1.34051100	1.39038600	1.81415600
H	-0.75118900	0.08080100	1.47575900
O	3.49293800	1.13183900	0.45021300
H	4.20465500	0.89311800	-0.16325500
N	-2.73429200	2.60025600	-0.79748500
O	-2.51821900	1.49200300	-0.59417400
O	-1.02463300	-1.77590900	-0.35780500
O	-3.45443900	-1.28943000	0.93263000
H	-2.57863600	-1.42157400	0.51094300
H	-3.65009100	-0.35589900	0.78746100

TS(4-NP*-B1) (Triplet, aq)

C	1.43230100	-1.22507800	0.11373900
C	0.14951400	-1.23092400	0.61175200
C	-0.51845700	0.00260700	0.72377900
C	0.13467800	1.24380500	0.60713700
C	1.41720500	1.25086300	0.11164800
C	2.06721500	0.01625600	-0.14848400
H	1.97380100	-2.14683700	-0.07117400
H	-0.35105500	-2.16315700	0.84655600
H	1.95219900	2.17416800	-0.07667000
H	-0.37823800	2.17076700	0.83584000
O	3.31757200	0.08225100	-0.61937000
H	3.69393800	-0.80384500	-0.74607100
N	-2.26598800	-0.01057100	-0.35640700
O	-2.85323700	1.07364900	-0.35565900
O	-2.85476700	-1.09368400	-0.32635300

B1·NO_2 (Triplet, aq)

C	0.96928800	-0.16229500	1.24276900
C	0.13438900	0.96380800	1.28149700
C	0.09983700	1.75356400	0.15630400
C	0.81401300	1.53007800	-0.99856000
C	1.64584300	0.40350500	-1.02578600
C	1.71477600	-0.43205200	0.09215000

H	1.03733100	-0.82524900	2.09987500
H	-0.44678000	1.18259100	2.17026900
H	2.23436200	0.17216800	-1.90661600
H	0.75173600	2.18471900	-1.86082200
O	2.55007600	-1.52968200	0.00733600
H	2.51666100	-2.03096400	0.83353500
N	-2.81871300	-0.67212500	-0.40696100
O	-1.79785500	-1.01109100	-0.92327000
O	-3.08111900	0.00101800	0.54371500

TS(4-NP*·1W-B1) (Triplet, aq)

C	2.03496900	-1.28598700	0.12448600
C	0.76985300	-1.17909600	0.65472000
C	0.21247500	0.10730600	0.76793800
C	0.95818000	1.28936100	0.60922800
C	2.22302000	1.18392600	0.08096100
C	2.76153200	-0.10442300	-0.17583300
H	2.49558100	-2.25098300	-0.05859800
H	0.20059800	-2.06326400	0.91702100
H	2.82597000	2.05706500	-0.13833500
H	0.52780400	2.25840200	0.83365600
O	3.99691400	-0.15004900	-0.68384300
H	4.29154800	-1.06650300	-0.81219900
N	-1.57589100	0.22721900	-0.30340100
O	-2.08195800	1.34726600	-0.31207400
O	-2.25011100	-0.80943700	-0.25272500
O	-5.12079800	-0.45590400	-0.09528900
H	-4.15132500	-0.54400200	-0.14748100
H	-5.27149300	0.49721600	-0.08780600

B1·NO_2·H_2O (Triplet, aq)

C	1.86787600	-0.87080700	-0.97186200
C	1.21632300	-1.88820400	-0.25929900
C	0.86989300	-1.61560300	1.04275600
C	1.10957400	-0.43164900	1.70182900
C	1.75951500	0.57849100	0.98044500
C	2.13079300	0.35067400	-0.34728100
H	2.16322800	-1.02666500	-2.00461200

H	1.00494200	-2.83920300	-0.73568400
H	1.97549100	1.53565700	1.44194800
H	0.81691000	-0.26538000	2.73261700
O	2.76153100	1.38542700	-1.01047300
H	2.94698900	1.12170200	-1.92179900
N	-1.55600000	1.13057800	0.13558000
O	-2.30950200	1.07557900	1.06057600
O	-1.45228800	0.52012400	-0.88367900
O	-4.47407300	-0.75867900	-0.69843000
H	-3.65433200	-0.68037900	-1.20347000
H	-4.29042100	-0.27681000	0.11844500

TS(4-NP*·1W-IM1) (Triplet, aq)

C	-0.50633400	0.16341600	-0.22740200
C	1.55864100	-0.99474700	-0.70516000
C	2.25891000	0.04801900	-0.05453500
C	1.56709400	1.15605000	0.48965900
C	0.20066500	1.22178200	0.39416900
H	2.11193600	-1.82592200	-1.12689800
H	2.13368400	1.94172700	0.97346400
O	3.59189700	0.04114200	0.07222000
H	3.97841100	-0.75811000	-0.32010100
C	0.19463800	-0.93654200	-0.80030000
H	-0.34660700	2.06618700	0.78954800
H	-0.36202400	-1.71644300	-1.30236100
N	-1.90139000	0.32831500	-0.51940900
O	-2.68243900	-0.77573000	-0.28916800
O	-2.43884100	1.47533300	-0.46044700
O	-1.25555500	-1.27000000	1.57445700
H	-2.17751400	-1.14814800	0.63436800
H	-1.39033900	-0.57132800	2.23275600

IM1 (Triplet, aq)

C	-0.51914500	0.11575500	-0.22312700
C	1.55081800	-1.08383800	-0.55594300
C	2.25465600	0.03927100	-0.07900900
C	1.56816400	1.20836900	0.29824000
C	0.19634000	1.25806500	0.20977000

H	2.09921000	-1.96931500	-0.85703200
H	2.13260500	2.06219100	0.65196600
O	3.60168100	0.04825000	0.03162900
H	3.97457000	-0.80106500	-0.24986000
C	0.18092000	-1.04590600	-0.64518400
H	-0.34540700	2.15397300	0.48018900
H	-0.37186100	-1.89592100	-1.02160800
N	-1.90750800	0.24974600	-0.53090800
O	-2.68427500	-0.89570500	-0.32425000
O	-2.50081200	1.35804800	-0.50014000
O	-1.15008400	-0.88884400	1.77428000
H	-2.38287500	-1.17371300	0.58609600
H	-1.27629000	-0.04866600	2.24597600

TS(IM1-IM2) (Triplet, aq)

C	-0.51662244	0.03339695	-0.07188305
C	1.56837075	-1.17438427	-0.38880029
C	2.27788904	-0.01091031	-0.02040544
C	1.59225180	1.18916482	0.25808664
C	0.22397171	1.22889253	0.19807947
H	2.11804338	-2.07519343	-0.63861261
H	2.16219452	2.07522325	0.50933485
O	3.62652388	0.01078689	0.05932852
H	3.99631344	-0.85876048	-0.15702864
C	0.20077246	-1.15026737	-0.45798524
H	-0.31640278	2.14473530	0.39260991
H	-0.35543415	-2.02484459	-0.76749908
N	-1.86057610	0.18884880	-0.58232420
O	-2.69602438	-0.91321730	-0.34231133
O	-2.41541340	1.31061890	-0.67110809
O	-1.19301163	-0.47493259	1.70490345
H	-2.44241415	-1.15528321	0.58528641
H	-0.47162971	-1.05044138	2.00088726

IM2 (Triplet, aq)

C	-0.61044700	-0.08756900	0.39140100
C	1.50138800	-1.19427100	-0.34633500
C	2.21349600	0.00931400	-0.13586400

C	1.54540200	1.16138800	0.34510600
C	0.20778800	1.14158200	0.58869500
H	2.03880600	-2.06884400	-0.69914600
H	2.12416300	2.05922800	0.53050400
O	3.55336500	0.11048600	-0.36440700
H	3.90278200	-0.73506600	-0.68089400
C	0.16227200	-1.26354500	-0.10372600
H	-0.30565100	2.01188600	0.97587000
H	-0.39079800	-2.18134700	-0.26267200
N	-1.73856300	0.22538900	-0.63175800
O	-2.77627700	-0.74822400	-0.61950300
O	-2.10172200	1.39923800	-0.87285700
O	-1.36575400	-0.39801100	1.58073400
H	-2.84661500	-1.01541700	0.31865300
H	-0.94904100	-1.15746700	2.01260200

P5·HONO (Singlet, aq)

C	-0.15921900	1.53782900	0.01509400
C	1.23653700	-0.00910100	1.23445200
C	1.88963700	-0.35275100	0.05153400
C	1.51716800	0.24858100	-1.15023100
C	0.49292400	1.19115600	-1.16846800
H	1.52588500	-0.48019100	2.16808200
H	2.02807100	-0.02314500	-2.06667500
O	2.91535500	-1.28459100	0.01438100
H	3.08529300	-1.61740500	0.90595400
C	0.21370900	0.93915000	1.21694700
H	0.19721500	1.66069300	-2.09951100
H	-0.29684500	1.20508900	2.13653200
N	-2.00367000	-1.40198100	-0.61486000
O	-2.86104900	-0.88570600	0.36423300
O	-1.21257000	-2.13516700	-0.14199900
O	-1.17262700	2.48070800	-0.06474600
H	-3.45968100	-0.29181600	-0.12312500
H	-1.55165500	2.62949400	0.81185400

TS(4-NP*·2W-IM1·1W) (Triplet, aq)

C	-0.17565500	0.43389000	-0.23532500

C	2.04408500	0.96463600	0.57552600
C	2.54235600	-0.17520700	-0.09230500
C	1.67791400	-0.99761900	-0.84881200
C	0.34397500	-0.69665000	-0.93720400
H	2.72547500	1.58743300	1.14430200
H	2.08758300	-1.85810800	-1.36315400
O	3.84409100	-0.52653800	-0.04962900
H	4.35652300	0.09726500	0.48748100
C	0.71163900	1.27849300	0.49872900
H	-0.32434400	-1.30624600	-1.52716600
H	0.31645800	2.15269100	0.99496700
N	-1.48254200	0.88978900	-0.50997700
O	-1.92094000	1.97189000	-0.00232500
O	-2.31942400	0.08412500	-1.18564900
O	-2.84712600	-1.61933500	0.43740900
H	-3.66412700	-1.41658600	0.91570600
H	-2.68930000	-0.82229800	-0.39385700
O	-0.89836800	-0.75916300	1.65752300
H	-2.00680800	-1.33528800	1.06302500
H	-0.15542300	-1.38047400	1.62625100

IM1·1W (Triplet, aq)

C	-0.13076700	0.44390200	-0.24070300
C	2.09519000	0.93898000	0.56602900
C	2.57202400	-0.21506000	-0.08241800
C	1.69675300	-1.02643600	-0.82726500
C	0.36441800	-0.69836300	-0.92560200
H	2.78391500	1.55893200	1.12903900
H	2.08621200	-1.90401600	-1.32827000
O	3.87441800	-0.59051300	-0.02943700
H	4.39061800	0.03628500	0.49900500
C	0.76517500	1.27907300	0.47951800
H	-0.31003100	-1.30712800	-1.50961300
H	0.38872200	2.16944600	0.96247200
N	-1.43688100	0.91328000	-0.48522200
O	-1.91237000	1.95582100	0.03508900
O	-2.26688100	0.14010100	-1.27721100
O	-3.11283200	-1.64729400	0.46024300

H	-3.89422700	-1.36027500	0.95027200
H	-2.69066300	-0.54095400	-0.66213700
O	-0.88330500	-0.69000000	1.66668100
H	-2.33828800	-1.42321600	1.03409800
H	-0.12709500	-1.29953100	1.66141400

TS(IM1·1W-IM2·1W) (Triplet, aq)

C	-0.15318655	0.31438965	-0.07776415
C	2.08387482	0.92882842	0.65861973
C	2.61366737	-0.12831973	-0.11148447
C	1.76696450	-0.91981914	-0.91557571
C	0.41732867	-0.68551766	-0.93870583
H	2.75358272	1.54889535	1.24401601
H	2.20130121	-1.70294413	-1.52481063
O	3.93586693	-0.41844597	-0.13464145
H	4.43366665	0.18431389	0.43789187
C	0.73667743	1.17657852	0.65263982
H	-0.23627554	-1.27362738	-1.56598633
H	0.31791442	1.99319581	1.22331714
N	-1.43309454	0.86266309	-0.42131951
O	-1.97973783	1.75766672	0.27046762
O	-2.24160388	0.09716550	-1.25159421
O	-3.22154434	-1.67391467	0.46558632
H	-3.93962066	-1.33519921	1.01572199
H	-2.73298867	-0.54905055	-0.65468836
O	-0.85634291	-0.77765772	1.40338246
H	-2.38846559	-1.48775666	0.96682183
H	-0.13583566	-1.42198165	1.47685557

IM2·1W (Triplet, aq)

C	-0.19300400	0.07324700	0.25393600
C	2.09712600	1.06598400	0.39412200
C	2.66589400	-0.16121900	-0.02106300
C	1.83908300	-1.28239100	-0.26819300
C	0.48603100	-1.19467100	-0.14678700
H	2.75417700	1.89981200	0.62105700
H	2.30431900	-2.22177900	-0.54519500
O	4.01189000	-0.32539100	-0.17226000

H	4.47352900	0.50175400	0.02849500
C	0.74846100	1.20118500	0.52655800
H	-0.14656000	-2.05510300	-0.31866300
H	0.31008500	2.13105500	0.86374000
N	-1.16414700	0.51382000	-0.84981800
O	-1.67365300	1.66194300	-0.80308500
O	-1.98781200	-0.51974400	-1.33741500
O	-3.82674800	-0.72290400	0.63265400
H	-4.43619900	0.02356600	0.70210500
H	-2.76290700	-0.57137200	-0.70969900
O	-1.08516600	-0.13340900	1.38078800
H	-3.10050300	-0.51727900	1.24555300
H	-0.61656200	-0.68417400	2.02443700

P6·HONO·1W (Singlet, aq)

C	-0.06168000	1.59167900	0.10069200
C	1.85657500	0.66351600	-1.02933200
C	2.18167800	-0.05726600	0.11856000
C	1.38529900	0.04907800	1.25875900
C	0.26350700	0.87327000	1.25035200
H	2.47781200	0.58098000	-1.91503400
H	1.64376900	-0.51526100	2.14711700
O	3.28596700	-0.89211100	0.18065200
H	3.74631300	-0.88403000	-0.66931600
C	0.73207700	1.48825600	-1.03860200
H	-0.36010800	0.95999200	2.13235400
H	0.47318700	2.04655900	-1.93209500
N	-0.86704200	-2.38020400	-0.65353300
O	-1.40663500	-1.44728700	-1.14862200
O	-1.12188800	-2.53958400	0.68611400
O	-3.46838800	0.57937500	0.20977400
H	-3.04388100	-0.20174000	-0.16999600
H	-1.71040500	-1.80958600	0.98280600
O	-1.19733200	2.38922500	0.13645000
H	-2.75725900	1.24435600	0.21939800
H	-1.27866700	2.87201200	-0.69802400

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