Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Vibrational Spectrum and Photochemistry of Phosphaketene HPCO

## *Supporting Information*

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**Table of Content**

## Computational details

Local minima were confirmed by vibrational frequencies analysis, and transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations.[1] The natural population analysis (NPA), natural spin densities, and Wiberg bond indices (WBI) were computed at the CCSD(T)/cc-pVTZ level with the Natural Bond Orbital (NBO) method.[2] The structures and harmonic frequencies were performed with ORCA.[3] The electrostatic potential maps were performed with Multiwfn[4] and Gaussian 09 software,[5] respectively.

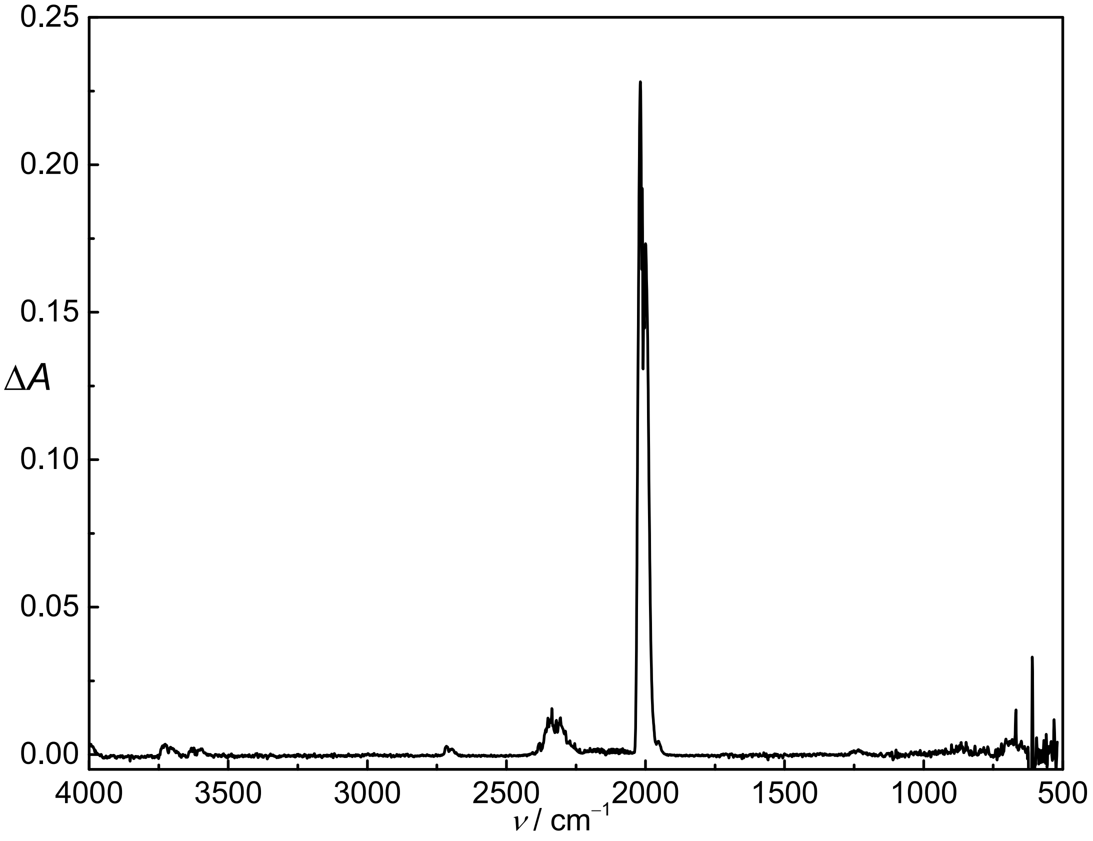

**Figure S1**. Gas phase IR spectrum of HPCO (130 Pa).

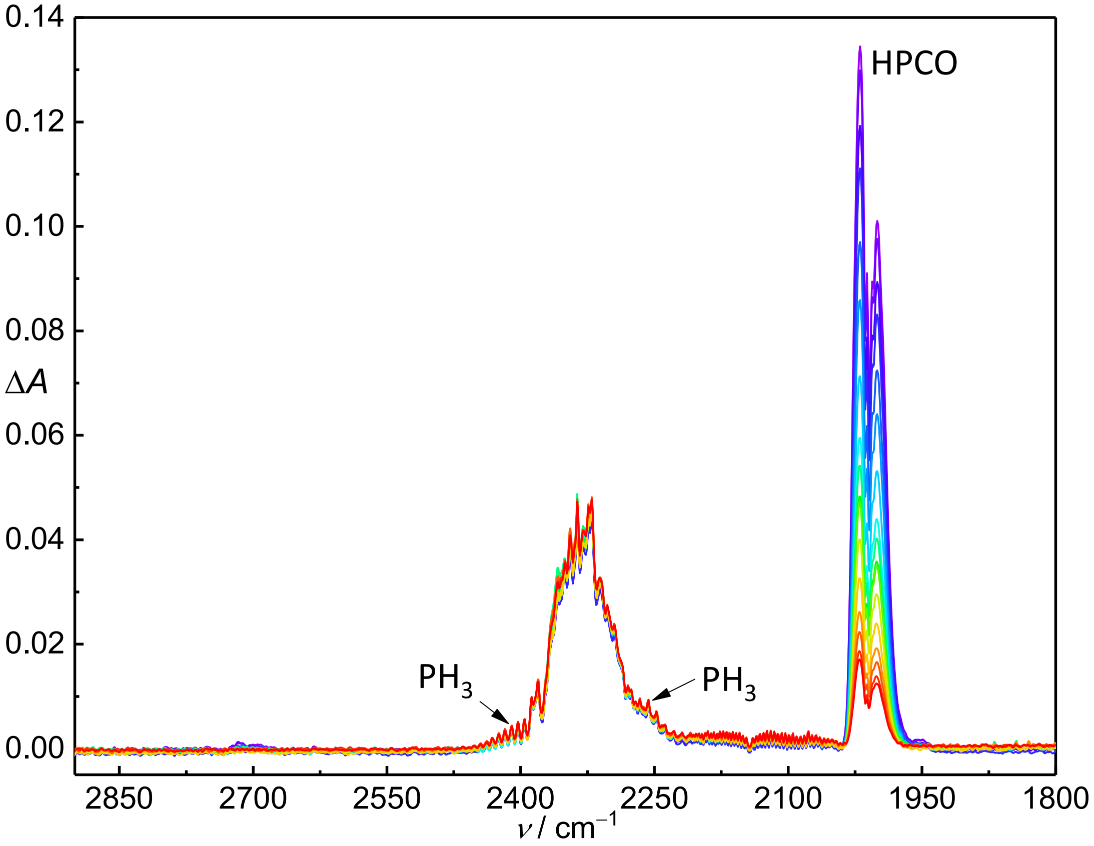

**Figure S2**. IR spectra reflecting the decomposition of HPCO (300.0 Pa) and formation of $PH_3$ in the gas phase at 26 °C over a period of 124.5 min.

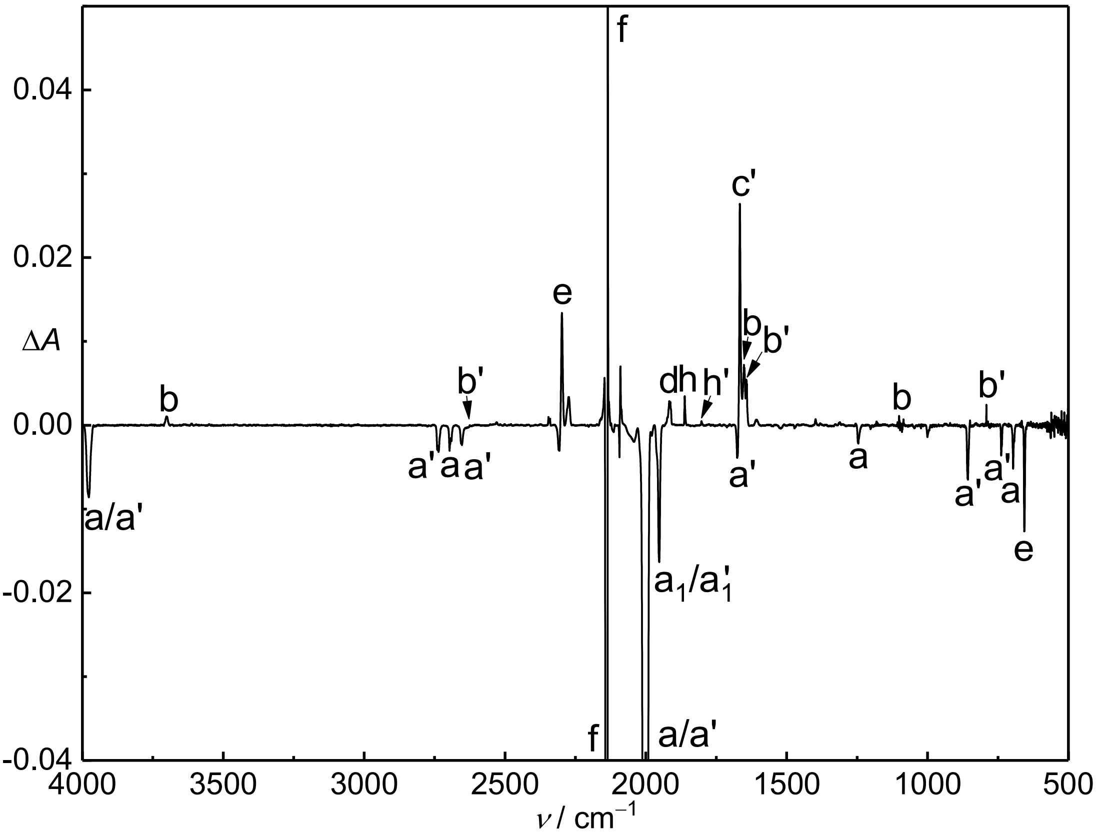

**Figure S3**. IR difference spectrum showing the changes of DPCO/CO/Ar=1:50:1000 upon 193 nm laser irradiation (5.0 min). The bands of HPCO (a), HP$^{13}$CO (a$_1$), DP$^{13}$CO (a$_1$’), DP(c’), PCO (d), CO$_2$ (e), CO (f), HCO (h), and DCO (h’) are labeled.

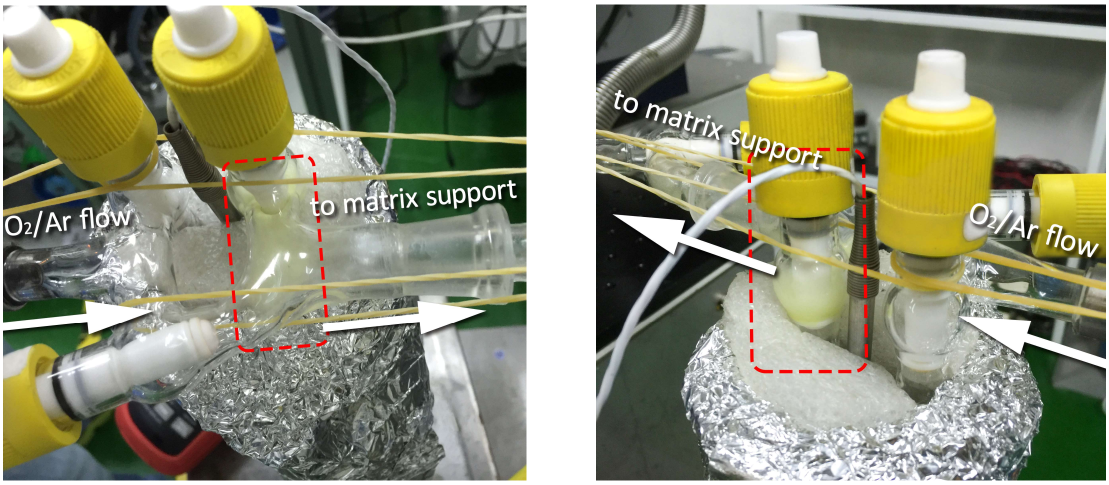

**Figure S4**. The oxidation of the HPCO vapor by passing the $O_2$/Ar mixture (3:1000) through the cold trap containing solid HPCO (ca. –139 °C).

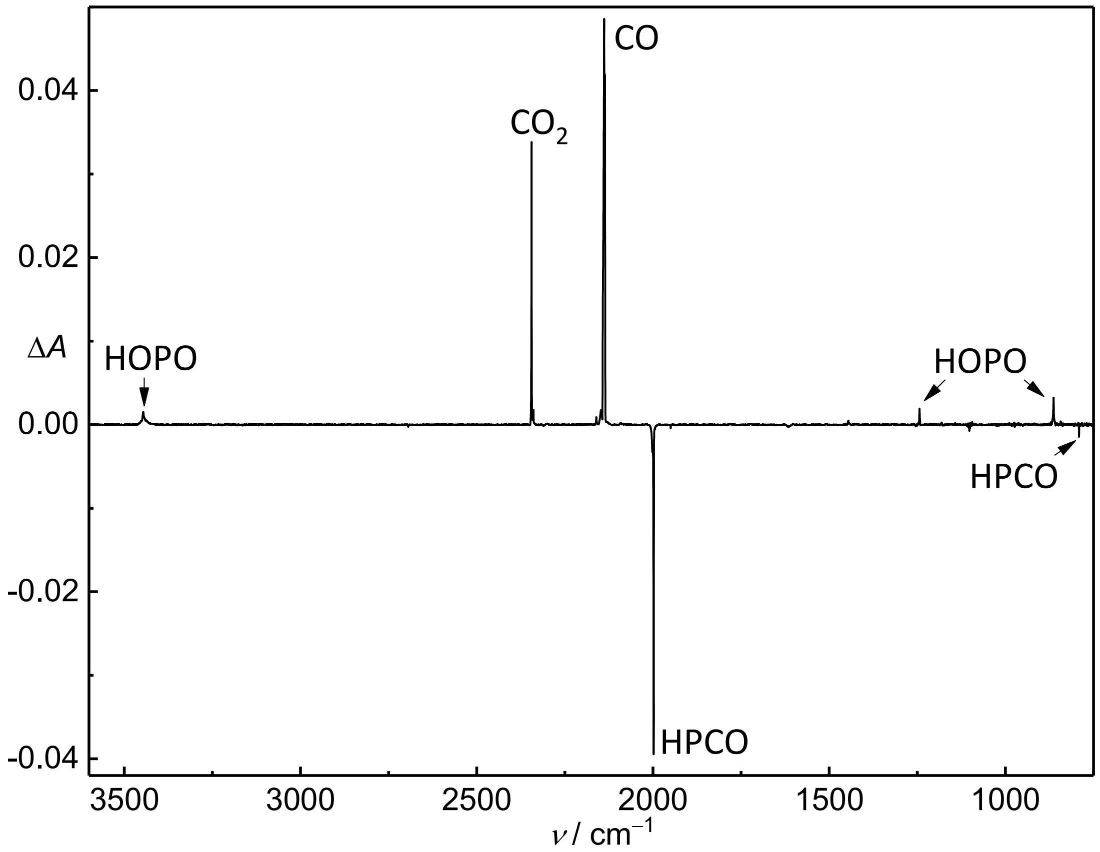

**Figure S5**. IR difference spectrum showing the changes of HPCO/$O_2$/Ar=1:3:1000 upon 365 nm LED irradiation (12.0 K, 30.0 min).

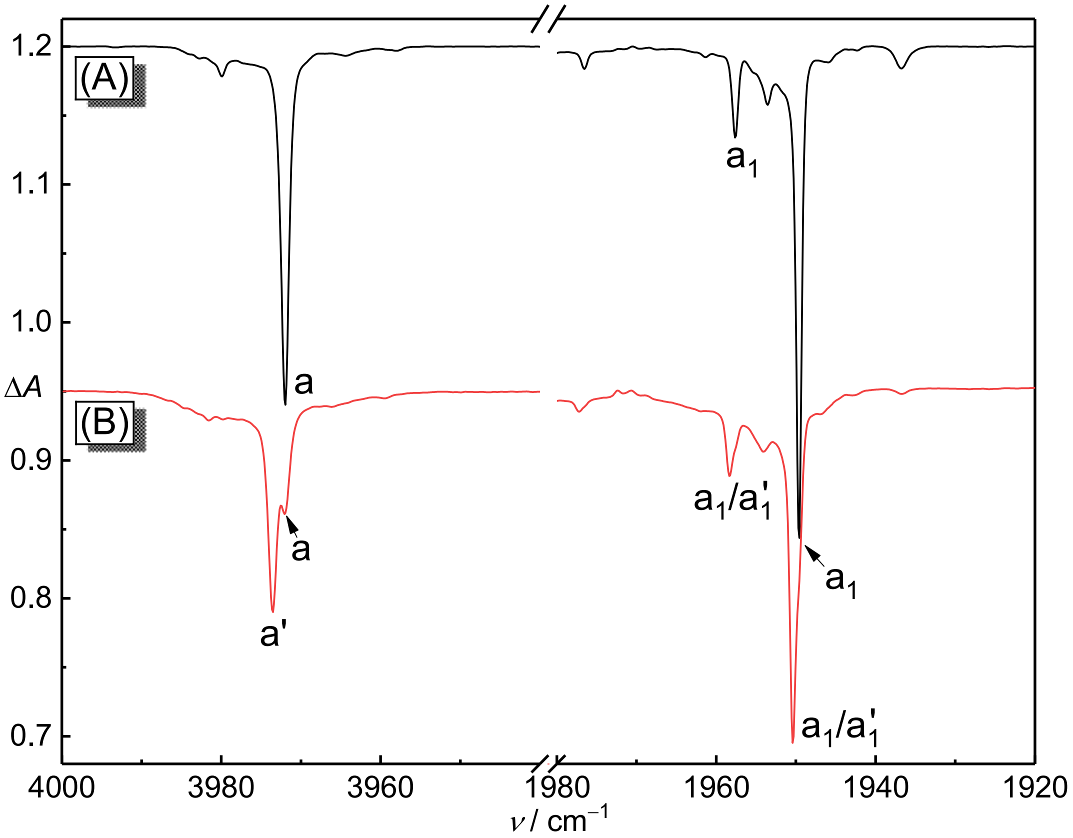

**Figure S6**. A) IR different spectrum in the ranges of 4000–3940 and 1980–1920 $cm^{-1}$ showing the depletion of HPCO (a) upon 193 nm laser irradiation (5 mJ, 7.5 min). B) IR difference spectrum in the range of 4000–3940 and 1980–1920 $cm^{-1}$ showing the depletion of DPCO (a') in Ar-matrix upon 193 nm laser irradiation (5 mJ, 5.5 min). The IR bands of $HP^{13}CO$ ($a_1$), $DP^{13}CO$ ($a_1'$) are also labeled.

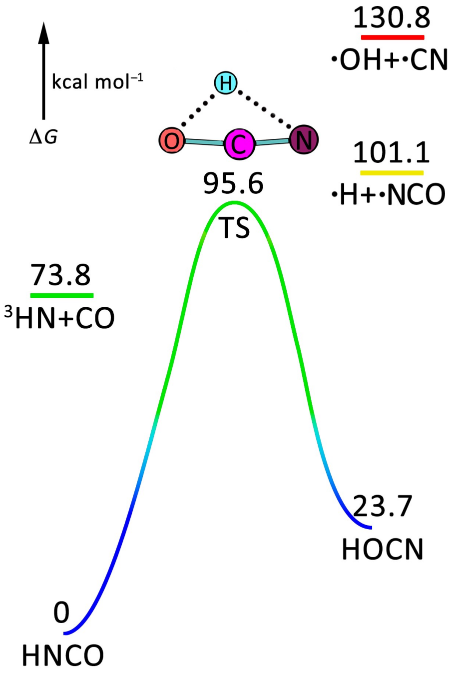

**Figure S7**. Potential energy profile for HNCO/HOCN, and relative energies with ZPE corrections (in kcal mol$^{-1}$) calculated at the CCSD(T)/cc-pVTZ level.

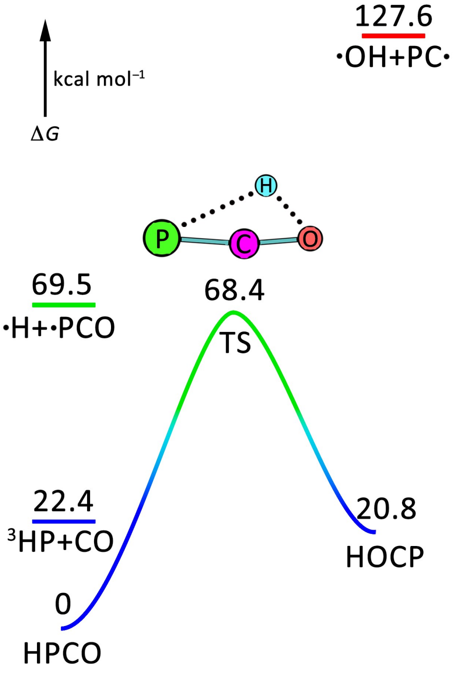

**Figure S8.** Potential energy profile for HPCO/HOCP, and relative energies with ZPE corrections (in kcal mol$^{-1}$) calculated at the CCSD(T)/cc-pVTZ level.

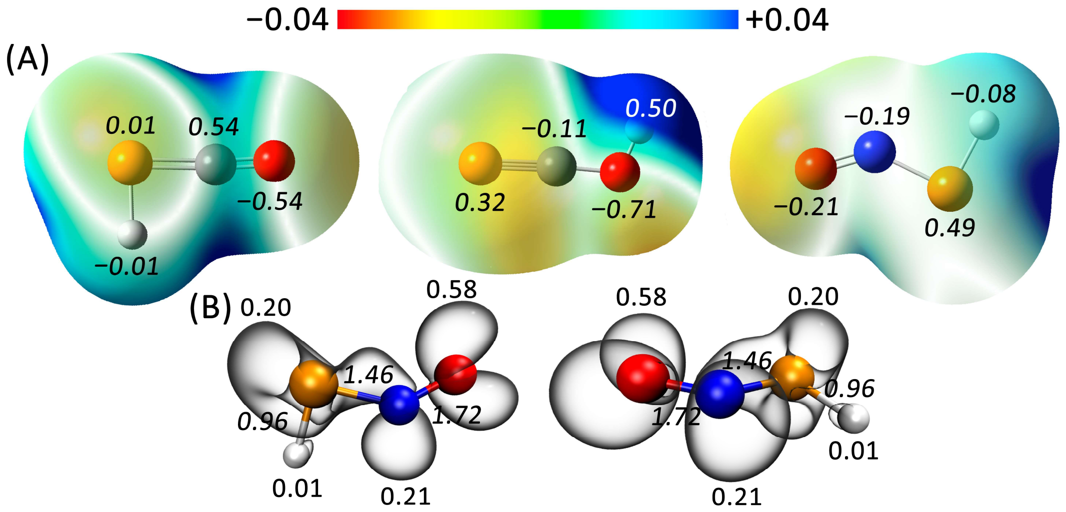

**Figure S9**. A) CCSD(T)/cc-pVTZ calculated molecular electrostatic potential (ESP) maps (isovalue = 0.001) and natural population analysis (NPA) charges (numbers in italics) for HPCO (a, left), HOCP (b, middle), and *anti*-HPNO• (g, right). B) Calculated spin densities and Wiberg bond indices (WBI, numbers in italics) for *anti*-HPNO• .

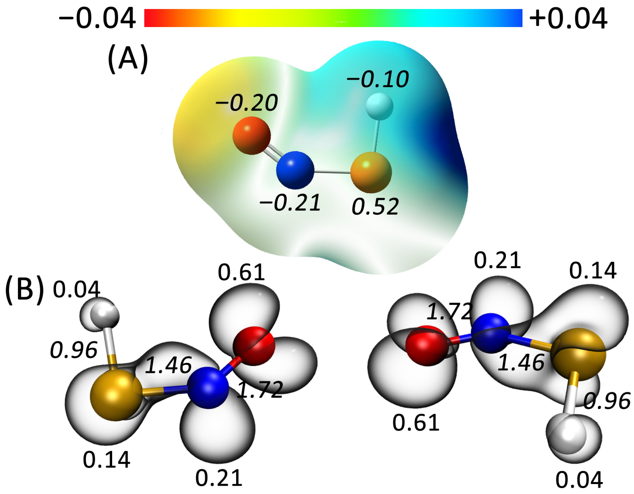

**Figure S10**. A) CCSD(T)/cc-pVTZ calculated molecular electrostatic potential (ESP) maps (isovalue = 0.001) and natural population analysis (NPA) charges (numbers in italics) for *syn*-HPNO•. B) Calculated spin densities and Wiberg bond indices (WBI, numbers in italics) for *syn*-HPNO•.

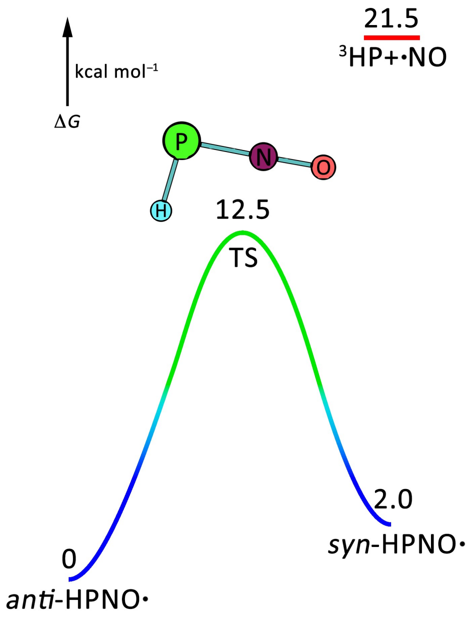

**Figure S11**. Potential energy profile for *anti*-HPNO•, and relative energies with ZPE corrections (in kcal mol$^{-1}$) calculated at the UCCSD(T)/cc-pVTZ level.

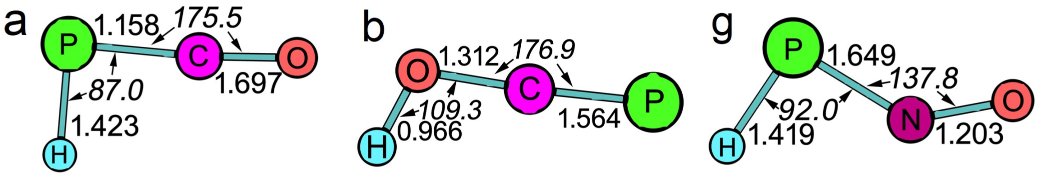

**Figure S12**. The CCSD(T)/cc-pVTZ computed bond lengths (Å) and angles (°).

**Table S1**. Observed and Calculated IR Frequencies ($cm^{-1}$) for HPCO.

| $\nu_{calc.}$[a] | | $\nu_{obs.}$[b] | $\Delta\nu$(H/D) | | assignment[c] |
|---|---|---|---|---|---|
| harmonic | VPT2 | | obs.[d] | calc.[e] | |
| 2390.9 (16) | 2292.9 (17) | 2311.9 (1.22) | 634.7 | 627.3 | $\nu_1$, $\nu$(PH) |
| 2042.1 (631) | 2011.0 (605) | 1998.5 (100) | −1.1 | −0.6 | $\nu_2$, $\nu$(CO) |
| 867.4 (11) | 851.1 (11) | 857.9 (1.67) | 118.5 | 122.8 | $\nu_3$, $\delta$(HPC) |
| 703.1 (5) | 686.2 (4) | 698.4 (0.76) | 40.7 | 36.0 | $\nu_4$, $\nu$(PC) |
| 467.0 (<1) | 470.5 (<1) | 473.4[f] | −1.6[f] | 5.6 | $\nu_5$, $\delta_{o.o.p.}$(PCO) |
| 381.3 (7) | 386.6 (7) | 392.6[f] | 47.9[f] | 43.6 | $\nu_6$, $\delta_{i.p.}$(PCO) |

[a] Calculated frequencies and intensities (km $mol^{-1}$, in parenthesis) at the CCSD(T)/cc-pVTZ level. [b] Observed frequencies and relative intensities (in parenthesis) in Ar-matrix. [c] Tentative assignment of the vibrational modes. [d] Observed isotope shifts in the Ar-matrix. [e] VPT2 computed isotope shifts. [f] Derived from overtone bands.

**Table S2**. Calculated and Observed IR Frequencies (4000–500 cm$^{-1}$) of HPCO and DPCO.

| HPCO | | DPCO | | assignment[c] |
|---|---|---|---|---|
| $\nu_{\text{calc.}}$[a] | $\nu_{\text{obs.}}$[b] | $\nu_{\text{calc.}}$[a] | $\nu_{\text{obs.}}$[b] | |
| 2292.9 (16.76) | 2311.8 (1.22) | 1665.6 (8.25) | 1677.1 (0.42) | $\nu_1$, $\nu$(PH) |
| 2011.0 (604.79) | 1998.5 (100) | 2011.6 (605.72) | 1999.6 (100) | $\nu_2$, $\nu$(CO) |
| 851.1 (10.66) | 857.9 (1.67) | 728.3 (1.96) | 739.4 (0.52) | $\nu_3$, $\delta$(HPC) |
| 686.2 (4.13) | 698.4 (0.76) | 650.2 (6.32) | 657.7 (1.61) | $\nu_4$, $\nu$(PC) |
| 470.5 (0.02) | 473.4[d] | 464.9 (0.07) | 471.8[d] | $\nu_5$, $\delta_{\text{o.o.p.}}$(PCO) |
| 386.6 (6.92) | 392.6[d] | 343.0(6.04) | 344.7[d] | $\nu_6$, $\delta_{\text{i.p.}}$(PCO) |
| 4302.6 (0.34) | n.o.[e] | 3286.3 (0.02) | n.o.[e] | $2\nu_1$ |
| 3998.9 (7.61) | 3972.0 (1.36) | 4000.1(7.60) | 3973.6 (3.83) | $2\nu_2$ |
| 1697.6 (0.87) | 1709.1 (0.27) | 1450.5 (0.31) | 1473.6 (0.06) | $2\nu_3$ |
| 1364.7 (0.37) | 1389.7 (0.05) | 1297.0 (0.06) | n.o.[e] | $2\nu_4$ |
| 941.6 (0.48) | 946.8 (0.02) | 930.6 (0.42) | 943.6 (0.08) | $2\nu_5$ |
| 779.7 (0.86) | 785.2 (0.10) | 689.5 (1.35) | 689.4 (0.00) | $2\nu_6$ |
| 4302.6 (0.34) | n.o [e] | 3676.2(0.19) | 3674.8 (0.02) | $\nu_1 + \nu_2$ |
| 3124.4 (0.05) | 3151.7 (0.02) | 2391.2 (0.07) | 2414.7 (0.01) | $\nu_1 + \nu_3$ |
| 2977.8 (0.17) | 3009.2 (0.03) | 2309.3 (0.15) | 2311.7 (0.33) | $\nu_1 + \nu_4$ |
| 2763.3 (0.01) | 2774.2 (0.03) | 2130.4 (0.00) | n.o.[e] | $\nu_1 + \nu_5$ |
| 2679.1 (0.12) | 2689.9 (0.01)[f] | 2007.2 (0.32) | 2010.9[g] | $\nu_1 + \nu_6$ |
| 2859.0 (0.11) | 2852.2 (0.03) | 2738.2 (2.71) | 2736.6 (0.82) | $\nu_2 + \nu_3$ |
| 2696.0 (4.58) | 2694.8 (0.83) | 2658.6 (2.00) | 2652.9 (0.36) | $\nu_2 + \nu_4$ |
| 2475.3 (0.04) | n.o.[e] | 2470.3 (0.03) | n.o.[e] | $\nu_2 + \nu_5$ |
| 2393.0 (0.08) | 2383.5 (0.01) | 2352.5 (0.00) | n.o.[e] | $\nu_2 + \nu_6$ |
| 1535.4 (0.26) | 1554.2 (0.07) | 1376.2 (0.17) | 1389.6 (0.07) | $\nu_3 + \nu_4$ |
| 1324.2 (0.02) | n.o.[e] | 1191.5 (0.01) | n.o.[e] | $\nu_3 + \nu_5$ |
| 1236.4 (3.01) | 1246.4 (0.60) | 1073.7 (1.08) | 1091.2 (0.27) | $\nu_3 + \nu_6$ |
| 1152.2 (0.00) | n.o.[e] | 1115.2 (0.01) | n.o.[e] | $\nu_4 + \nu_5$ |
| 1062.8 (0.02) | 1082.2 (0.01) | 984.6 (1.01) | 1001.6 (0.30) | $\nu_4 + \nu_6$ |
| 870.9 (0.00) | n.o.[e] | 813.1 (0.00) | n.o.[e] | $\nu_5 + \nu_6$ |

[a] Computed anharmonic IR frequencies (cm$^{-1}$) and intensities (km mol$^{-1}$, in parentheses) at the CCSD(T)/cc-pVTZ level using VPT2. [b] Observed band positions (cm$^{-1}$) and normalized relative intensities (in parentheses) in Ar-matrix at 12 K. [c] Tentative assignment of the vibrational modes according to the computed vibrational displacement vectors. [d] Derived from combination and overtone bands. [e] Not observed due to either out of range (4000–500 cm$^{-1}$) or low intensity. [f] Overlap with the strong band at 2694.8 cm$^{-1}$. [g] Overlap with the strong band at 1996.9 cm$^{-1}$.

**Table S3**. Experimental and Calculated IR Frequencies (cm$^{-1}$) for HP.

| $\nu_{\text{calc.}}$[a] | $\nu_{\text{obs.}}$ | | $\Delta\nu$(H/D) | | assignment[b] |
|---|---|---|---|---|---|
| | Ar-matrix | $N_2$-matrix | obs.[c] | calc.[d] | |
| 2264.4 (75) | 2300.9 | 2291.3 | 633.1 | 620.0 | $\nu_1$, $\nu$(PH) |

[a] Calculated VPT2 anharmonic frequencies and intensities (km mol$^{-1}$, in parenthesis) at the UCCSD(T)/cc-pVTZ level. [b] Tentative assignment of the vibrational modes according to the computed vibrational displacement vectors. [c] Observed isotope shift in Ar-matrix. [d] VPT2 computed isotope shift.

**Table S4**. Observed and Calculated IR Frequencies (cm$^{-1}$) for PCO•.

| $\nu_{\text{calc.}}$[a] | $\nu_{\text{obs.}}$ | | | assignment[b] |
|---|---|---|---|---|
| | ref.[c] | Ar-matrix | $N_2$-matrix | |
| 1921.2 (1189) | 1912.7 | 1912.8 | 1919.3 | $\nu_1$, $\nu$(CO) |
| 718.7 (9) | n.o. | n.o. | n.o. | $\nu_2$, $\nu$(CP) |
| 407.2 (9) | n.o. | n.o. | n.o. | $\nu_3$, $\delta$(PCO) |

[a] Calculated VCI (utilizing quartic force fields) anharmonic frequencies and intensities (km mol$^{-1}$, in parenthesis) at the UCCSD(T)-F12/cc-pVTZ-F12 level. [b] Tentative assignment of the vibrational modes according to the computed vibrational displacement vectors. [c] In Ar-matrix, see reference 6.

**Table S5**. Calculated IR Frequencies (cm$^{-1}$) for *syn*-HPNO•.

| $\nu_{\text{calc.}}$[a] | $\Delta\nu_{\text{calc.}}$(H/D) | $\Delta\nu_{\text{calc.}}$($^{14}$N/$^{15}$N) | assignment[b] |
|---|---|---|---|
| 2194.8 (74) | 594.8 | 0.1 | $\nu_1$, $\nu$(HP) |
| 1598.4 (241) | −1.4 | 29.2 | $\nu_2$, $\nu$(NO) |
| 905.9 (33) | 222.9 | 3.0 | $\nu_3$, $\delta$(HP) |
| 721.4 (2) | −5.4 | 7.2 | $\nu_4$, $\nu$(PN) |
| 503.9 (<1) | 59.9 | 6.6 | $\nu_5$, $\tau$(HPN) |
| 291.8 (4) | 12.9 | 4.7 | $\nu_6$, $\delta$(PNO) |

[a] VPT2 computed anharmonic frequencies and intensities (km mol$^{-1}$, in parenthesis) at the UCCSD(T)/cc-pVTZ level. [b] Tentative assignment of the vibrational modes according to the computed vibrational displacement vectors.

**Table S6**. Calculated and Observed IR Frequencies (4000–500 cm$^{-1}$) for HOCP.

| $\nu_{\text{calc.}}$[a] | $\nu_{\text{obs.}}$[b] | | $\Delta\nu$(H/D) | | assignment[c] |
|---|---|---|---|---|---|
| | Ar-matrix | $N_2$-matrix | obs.[d] | calc.[e] | |
| 3599.0 (138) | 3549.6 (43) | 3514.8 (49) | 924.2 | 940.6 | $\nu_1$, $\nu$(OH) |
| 1647.7 (274) | 1647.8 (100) | 1653.4 (100) | 9.3 | 10.0 | $\nu_2$, $\nu$(CP) |
| 1188.4 (173) | 1174.8 (55) | 1186.0 (44) | 254.4 | 261.9 | $\nu_3$, $\delta$(COH) |
| 793.8 (5) | n.o. | n.o. | n.o. | 15.8 | $\nu_4$, $\nu$(CO) |
| 423.6 (7) | n.o. | n.o. | n.o. | 12.2 | $\nu_5$, $\tau$(CP) |
| 376.8 (22) | n.o. | n.o. | n.o. | 28.6 | $\nu_6$, $\delta$(OCP) |

[a] VPT2 computed anharmonic frequencies and intensities (km mol$^{-1}$, in parenthesis) at the CCSD(T)/cc-pVTZ level. [b] Observed frequencies and relative intensities (in parenthesis). [c] Tentative assignment of the vibrational modes according to the computed vibrational displacement vectors. [d] Observed isotope shifts in the Ar-matrix. [e] VPT2 computed isotope shifts.

## Computed Atomic Coordinates (in Angstrom) and Energies (in Hartree) for All Optimized Structures

**HPCO**

**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| P | -1.100245047 | 0.048807065 | 0.000000000 |
| H | -1.090711152 | -1.373954481 | 0.000000000 |
| C | 0.595063156 | -0.027036592 | 0.000000000 |
| O | 1.752883159 | 0.012341826 | 0.000000000 |

Electronic energy ... -454.64156814 Eh
Total thermal energy -454.62238243 Eh
Final Gibbs free enthalpy ... -454.65076644 Eh

**HOCP**

**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| O | -1.740823680 | -0.061696019 | -0.000061935 |
| H | -2.106797437 | 0.831972640 | -0.000085531 |
| C | -0.430008729 | 0.006372289 | 0.000166622 |
| P | 1.134111968 | 0.002320421 | -0.000029787 |

Electronic energy ... -454.61202767 Eh
Total thermal energy -454.58962864 Eh
Final Gibbs free enthalpy ... -454.61761738 Eh

**HP**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| P | 0.000000000 | 0.000000000 | 0.045028872 |
| H | 0.000000000 | 0.000000000 | -1.383884561 |

Electronic energy ... -341.43243743 Eh
Total thermal energy -341.42471969 Eh
Final Gibbs free enthalpy ... -341.44603401 Eh

**CO**

**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| O | 0.000000000 | 0.000000000 | 0.057140293 |
| C | 0.000000000 | 0.000000000 | 1.192859706 |

Electronic energy ... -113.15557882 Eh
Total thermal energy -113.14831307 Eh
Final Gibbs free enthalpy ... -113.16980983 Eh

**•OH**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| O | 0.695488760 | -1.228722864 | 0.000000000 |
| H | 0.371339909 | -0.313354755 | 0.000000000 |

Electronic energy ... -75.63772341 Eh

Total thermal energy -75.62683265 Eh

Final Gibbs free enthalpy ... -75.64611268 Eh

**CP•**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| C | -0.653083910 | 0.857418100 | 0.000000000 |
| P | 0.916614530 | 0.857418100 | 0.000000000 |

Electronic energy ... -378.78325596 Eh

Total thermal energy -378.77800658 Eh

Final Gibbs free enthalpy ... -378.80160969 Eh

***anti*-HPNO•**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| 15 | -1.038126422 | 0.111786535 | 0.000000000 |
| 1 | -1.484825179 | -1.235056968 | 0.000000000 |
| 7 | 0.544302781 | -0.353112824 | 0.000000000 |
| 8 | 1.627343016 | 0.170487738 | 0.000000000 |

Electronic energy ... -471.19848650 Eh

Total thermal energy -471.17969340 Eh

Final Gibbs free enthalpy ... -471.20880834 Eh

***syn*-HPNO•**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| P | -1.063708608 | -0.017849466 | 0.000000000 |
| H | -0.889245425 | -1.440578177 | 0.000000000 |
| N | 0.546334228 | 0.337811611 | 0.000000000 |
| O | 1.637576881 | -0.170409484 | 0.000000000 |

Electronic energy ... -471.19466453 Eh

Total thermal energy -471.17627530 Eh

Final Gibbs free enthalpy ... -471.20566272 Eh

**Transition State between *anti*-HPNO• and *syn*-HPNO•**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| P | 1.079466172 | -0.092598085 | 0.000580892 |
| H | 1.317499597 | 1.331149001 | 0.000008963 |
| N | -0.523003292 | -0.015719276 | -0.001379523 |
| O | -1.722561477 | 0.022807360 | 0.000789667 |

Electronic energy ... -471.17680516 Eh

Total thermal energy -471.15998894 Eh

Final Gibbs free enthalpy ... -471.18884990 Eh

**•NO**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| N | -0.444719623 | 0.857418100 | 0.000000000 |

| | | | |
|---|---|---|---|
| O | 0.708250243 | 0.857418100 | 0.000000000 |

Electronic energy ... -129.71683452 Eh
Total thermal energy -129.70965925 Eh
Final Gibbs free enthalpy ... -129.73201664 Eh

**HNCO**
**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| N | -1.171115912 | -0.142141094 | 0.000024010 |
| H | -1.813621773 | 0.631516391 | 0.000075577 |
| C | 0.039215417 | 0.023101154 | -0.000083948 |
| O | 1.208968268 | 0.021270548 | 0.000026360 |

Electronic energy ... -168.43278174 Eh
Total thermal energy -168.40832301 Eh
Final Gibbs free enthalpy ... -168.43450920 Eh

**HCPO**
**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| C | 1.518133822 | -0.284235130 | 0.000000000 |
| H | 2.445485779 | 0.267824417 | 0.000000000 |
| P | 0.000913866 | 0.195934792 | 0.000000000 |
| O | -1.436662468 | -0.182136079 | 0.000000000 |

Electronic energy ... -454.56033210 Eh
Total thermal energy -454.54067364 Eh
Final Gibbs free enthalpy ... -454.56915187 Eh

**HC(O)P**
**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| C | 0.000457206 | 0.781580643 | -0.000000010 |
| H | -0.782662110 | 1.563931260 | 0.000000003 |
| O | 1.178350141 | 1.074180219 | 0.000000003 |
| P | -0.579361237 | -0.994681123 | 0.000000002 |

Electronic energy ... -454.57934304 Eh
Total thermal energy -454.55818747 Eh
Final Gibbs free enthalpy ... -454.58797734 Eh

**HNCO**
**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| N | -1.171115912 | -0.142141094 | 0.000024010 |
| H | -1.813621773 | 0.631516391 | 0.000075577 |
| C | 0.039215417 | 0.023101154 | -0.000083948 |
| O | 1.208968268 | 0.021270548 | 0.000026360 |

Electronic energy ... -168.43278174 Eh
Total thermal energy -168.40832301 Eh
Final Gibbs free enthalpy ... -168.43450920 Eh

**HOCN**

**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| O | -0.143197172 | -1.124264726 | -0.000000000 |
| H | 0.732552710 | -1.530925334 | -0.000000000 |
| C | -0.003116049 | 0.175951619 | 0.000000000 |
| N | 0.057698510 | 1.339341442 | -0.000000000 |

Electronic energy ... -168.39491798 Eh

Total thermal energy -168.37014483 Eh

Total Enthalpy ... -168.36920062 Eh

**HONC**

**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| O | -0.025775253 | -1.103505582 | -0.000000000 |
| H | -0.969430144 | -1.317130319 | -0.000000000 |
| C | 0.189909632 | 1.401261104 | -0.000000000 |
| N | 0.008377765 | 0.234011796 | 0.000000000 |

Electronic energy ... -168.30115974 Eh

Total thermal energy -168.27714809 Eh

Total Enthalpy ... -168.27620388 Eh

**HCNO**

**CCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| C | -0.049835343 | -1.181202165 | -0.000000023 |
| H | -0.073360528 | -2.241518724 | 0.000000015 |
| O | 0.046590201 | 1.188114095 | 0.000000007 |
| N | 0.000231671 | -0.016294204 | -0.000000000 |

Electronic energy ... -168.32119851 Eh

Total thermal energy -168.29954789 Eh

Final Gibbs free enthalpy ... -168.32224866 Eh

**HC(O)N**

**UCCSD(T)/cc-pVTZ**

| | | | |
|---|---|---|---|
| C | -0.008730904 | 0.384329647 | -0.000000006 |
| H | 0.031804281 | 1.484125745 | 0.000000002 |
| O | -1.058648635 | -0.244859578 | 0.000000002 |
| N | 1.217379258 | -0.261461814 | 0.000000001 |

Electronic energy ... -168.29852456 Eh

Total thermal energy -168.27635840 Eh

Total Enthalpy ... -168.27541419 Eh

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