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Communication

Interstellar Formation of the Elusive Phosphanyloxyphosphane (H_2POPH_2) and Phosphanylphosphinous Acid (H_2PPHOH) via Nonequilibrium Chemistry: Precursors to the Phosphate Backbone of Nucleotides

Jia Wang, Bing-Jian Sun, Alexandre Bergantini, Zesen Wang, Andrew M. Turner, Agnes H. H. Chang,* and Ralf I. Kaiser*

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ABSTRACT: The P−O−P moiety plays a central role in inorganic and biological systems and is considered to be a critical precursor to the phosphate backbone of nucleotides. However, the isolation of the simplest prototype, phosphanyloxyphosphane (H_2POPH_2), has remained elusive due to its high susceptibility to hydrolysis. Here, we report the first preparation of phosphanyloxyphosphane and its isomer phosphanylphosphinous acid (H_2PPHOH) in low-temperature phosphine (PH_3)−carbon dioxide (CO_2) ices upon exposure to galactic cosmic ray proxies in the form of energetic electrons. These isomers were isolated and identified in the gas phase using tunable vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry combined with isotopic labeling studies. Our findings not only suggest that the hitherto undetected phosphanyloxyphosphane and phosphanylphosphinous acid can be synthesized in phosphine-rich extraterrestrial ices but also advance our fundamental understanding of the formation of P−O−P and P−P−O linkages via nonequilibrium chemistry under astrophysical conditions.

Since the first detection of phosphorus monoxide (PO) in the interstellar medium (ISM) nearly two decades ago,[1] phosphorus- and oxygen-containing molecules have attracted particular attention from the astronomy,[2,3] astrobiology,[4] astrochemistry,[5] physical organic chemistry,[6] and theoretical chemistry communities.[7−9] This broad interest is mainly due to their crucial roles as molecular precursors in the synthesis of nucleotides, phospholipids, and sugar phosphates, which are essential to nucleic acid metabolism and glycolysis (Figure 1).[4,10,11] Although only eight simple phosphorus-bearing molecules have been identified in the ISM,[12,13] more complex phosphorus molecules such as alkylphosphonic acids (RP(O)-$(OH)_2$) with R being an alkyl group (C_nH_{2n+1}) and phosphates (PO_4^{3-}) have been detected in the Murchison meteorite at abundances as high as 9 nmol g^{-1} and 25 μmol g^{-1}, respectively,[14] suggesting potential exogenous delivery of phosphorus to early Earth via meteorites.[15] Laboratory experiments have provided compelling evidence that alkylphosphonic acids and phosphorus oxoacids can be synthesized abiotically through energetic processing of low-temperature interstellar ice analogs composed of water (H_2O), carbon dioxide (CO_2), methane (CH_4), and phosphine (PH_3) by galactic cosmic ray (GCR) proxies.[5,16] However, despite the astrobiological significance of phosphorus- and oxygen-bearing molecules, the formation mechanisms of the P−O−P linkage, which can play a crucial role in prebiotic phosphorus chemistry, under astrophysical conditions have remained unanswered.

Analogous to the C−C bond in organic chemistry, the P−O−P linkage is of fundamental importance in inorganic and biological systems; however, due to its high susceptibility to hydrolysis, it is naturally present solely as a product of synthesis by living organisms.[17] Enzymes facilitate rapid hydrolysis by transiently forming P−O−P bridges; for example, the aspartyl phosphate intermediate in sarcoplasmic reticulum Ca^{2+}-ATPase (SERCA) relies on a more labile bridging P−O bond to achieve a hydrolysis rate enhancement of 10^{11}−10^{15} times.[18] Remarkably, molecules bearing a P−O−P linkage serve as key precursors to the phosphate backbone of nucleotides such as ADP and ATP (Figure 1). In ATP, the high-energy P−O−P bonds store energy due to repulsion between negatively charged phosphates, and breaking one, such as the conversion of ATP to ADP and inorganic phosphate, releases energy because the newly formed P−O and O−H bonds are stronger and more stable than those that are broken.[19] Therefore, elucidating the fundamental formation pathways of such species is essential to advancing our understanding of the molecular mass growth processes leading to phosphorus-bearing biomolecules that are necessary for the origins of life. However, even the isolation of their simplest prototype, phosphanyloxyphosphane (H_2POPH_2, **1**), has remained elusive as of now.

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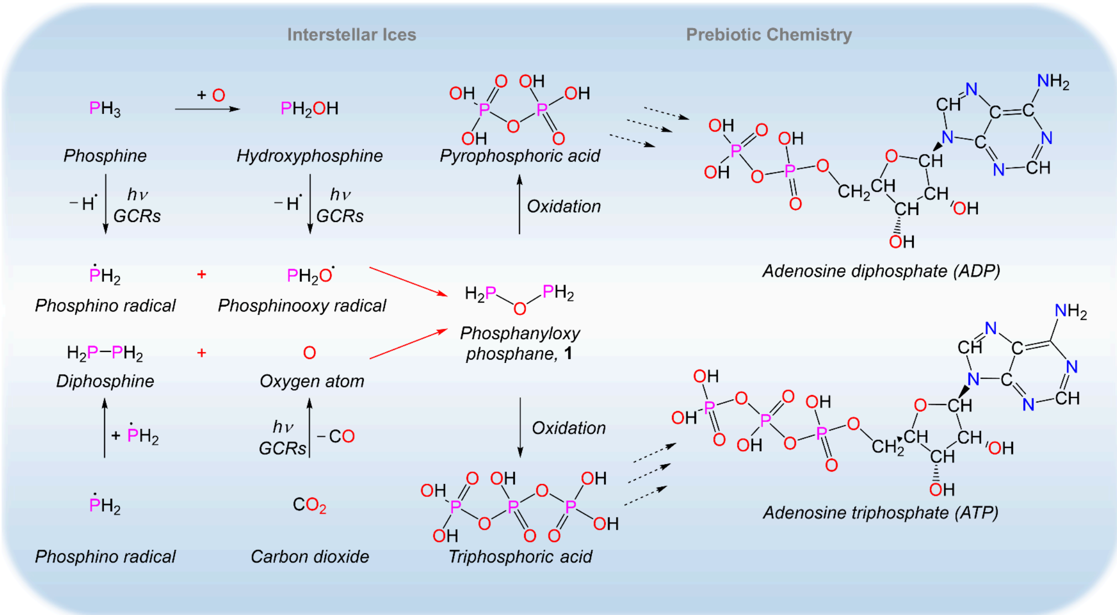

Figure 1. Proposed formation pathways of phosphanyloxyphosphane (H_2POPH_2, **1**) in phosphine-rich and carbon dioxide-rich interstellar ices and its potential role as a molecular building block of the phosphate backbone of ADP and ATP.

Here, we report the first preparation of phosphanyloxyphosphane (H_2POPH_2, **1**) and its isomer phosphanylphosphinous acid (H_2PPHOH, **2**). This is accomplished in low-temperature (5 K) interstellar model ices containing phosphine (PH_3) and carbon dioxide (CO_2) exposed to GCR proxies in the form of energetic electrons.[20] The irradiation doses are equivalent to $(8 \pm 2) \times 10^6$ years of GCR exposure in interstellar ices within cold molecular clouds (Supporting Information).[21] Utilizing tunable vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) combined with isotopic labeling studies, **1** and **2** were identified in the gas phase during the temperature-programmed desorption (TPD) of irradiated phosphine−carbon dioxide ices based on their desorption profiles and computed adiabatic ionization energies (IEs). These findings provide direct evidence for the facile synthesis of P−O−P and P−P−O bond linkages via nonequilibrium chemistry in phosphine-rich extraterrestrial ices, shedding light on the potential formation pathways of prebiotic phosphorus species. PH_3 has been detected in the circumstellar envelope of the carbon-rich star IRC+10216 at an abundance of 10^{-8} relative to hydrogen (H_2)[22] and is believed to be a primary phosphorus carrier in comet 67P/Churyumov−Gerasimenko.[23] On interstellar grain surfaces, PH_3 forms via successive hydrogenation of atomic phosphorus, analogous to the formation of water from atomic oxygen and hydrogen.[24] CO_2 is one of the most abundant constituents of interstellar ices with an abundance of up to 40% relative to water.[25] Therefore, our results suggest that the hitherto elusive isomers **1** and **2** can be synthesized in phosphine- and carbon dioxide-rich interstellar ices. Once formed, isomers **1** and **2** may serve as key precursors to hypophosphoric acid ($P_2H_4O_6$) and polyphosphates such as pyrophosphoric acid ($P_2H_4O_7$) and triphosphoric acid ($P_3H_5O_{10}$) (Figure 1). These compounds could have been incorporated into planetesimals during the gravitational collapse of molecular clouds into star-forming regions. As these objects collided with the early Earth, they may survive the entrance of the meteorite into the Earth's atmosphere,[15] contributing to a critical exogenous source of phosphate-containing precursors to biomolecules such as nucleotides.

The photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS) technique was utilized to identify individual H_4P_2O isomers based on isomer selective photoionization in the temperature-programmed desorption (TPD) phase and their computed adiabatic ionization energies. The three isomers of H_4P_2O are phosphanyloxyphosphane (H_2POPH_2, **1**), phosphanylphosphinous acid (H_2PPHOH, **2**), and diphosphine monoxide ($H_2PP(O)H_2$, **3**) (Figure 2). In

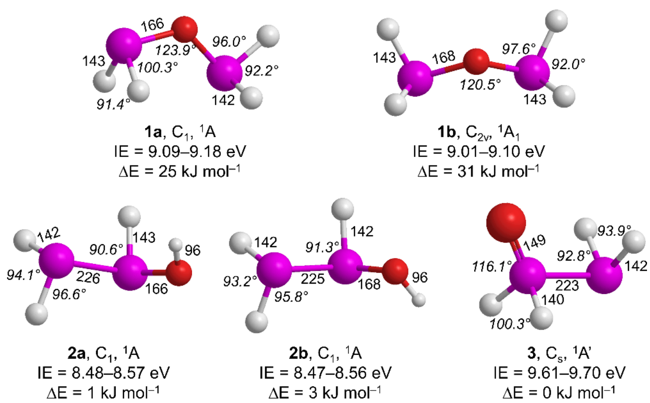

Figure 2. Molecular structures of H_4P_2O isomers **1**−**3**. Bond length (millimeters), angles (italic), point groups, electronic ground states, and relative energies (ΔE) are shown. The adiabatic ionization energies (IEs) are calculated at the CCSD(T)/CBS//B3LYP/cc-pVTZ level.

the experiments, VUV photons with energies of 10.86, 9.60, 8.77, and 8.11 eV were utilized to selectively photoionize distinct H_4P_2O isomers in the gas phase during TPD. At a photon energy of 10.86 eV, the TPD profile of mass-to-charge ratio (m/z) of 82 exhibits a broad sublimation event spanning 180−265 K (Figure 3). Given the molecular weights of the reactants of PH_3 and CO_2, the ion signal of m/z = 82 can

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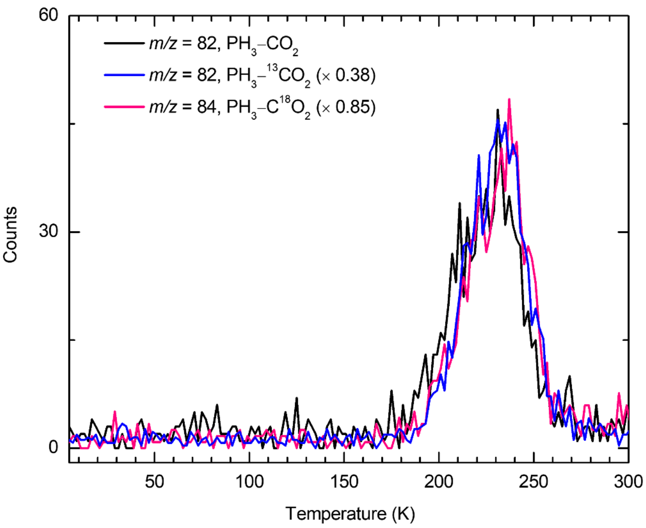

Figure 3. Temperature-programmed desorption (TPD) profiles of irradiated phosphine−carbon dioxide ($PH_3{-}CO_2$) ice and its isotopically labeled ($PH_3{-}^{13}CO_2$ and $PH_3{-}C^{18}O_2$) ices recorded at 10.86 eV.

correspond to compounds with molecular formulas C_6H_{10}, C_5H_6O, $C_4H_2O_2$, C_4H_3P, H_4P_2O, H_3PO_3, and/or H_2O_5. To confirm the molecular formula, experiments were conducted using isotopically labeled $PH_3{-}^{13}CO_2$ ice and $PH_3{-}C^{18}O_2$ ice (Figure 3) to eventually assign the ion signal of m/z = 82 to the H_4P_2O isomers. In particular, the TPD profile of m/z = 82 from irradiated $PH_3{-}^{13}CO_2$ ice closely matches that of m/z = 82 from irradiated $PH_3{-}CO_2$ ice, indicating the absence of the carbon atom in the molecular formula. In contrast, replacing $PH_3{-}CO_2$ ice with $PH_3{-}C^{18}O_2$ ice leads to a 2 amu mass shift, from m/z = 82 to 84, confirming the incorporation of only one oxygen atom. Therefore, the sublimation event of m/z = 82 from irradiated $PH_3{-}CO_2$ ice can be clearly attributed to a molecular species with the formula H_4P_2O.

At a photon energy of 10.86 eV, the TPD profile of m/z = 82 ($H_4P_2O^+$) from irradiated $PH_3{-}CO_2$ ice can be deconvoluted into two Gaussian components peaking at 210 (peak I) and 234 K (peak II) (Figure 4a). A blank experiment using $PH_3{-}CO_2$ ice was carried out at 10.86 eV under identical conditions but without electron irradiation; no sublimation event at m/z = 82 was detected, confirming that peaks I and II result from electron-induced processing of the ices. At 10.86 eV, all three H_4P_2O isomers **1** (IE = 9.01−9.18 eV), **2** (IE = 8.47−8.57 eV), and **3** (IE = 9.61−9.70 eV) can be photoionized (Figure 2, Table S1). Therefore, both peaks can be linked to **1**, **2**, and/or **3**. Thereafter, the photon energy was reduced to 9.60 eV, at which **3** (IE = 9.61−9.70 eV) cannot be ionized. At 9.60 eV, ion signals of peaks I and II remain (Figure 4b), indicating that no evidence of the formation of **3** can be provided. The computed IEs were compared with experimental measurements, yielding combined error bounds of −0.03/+0.06 eV (Table S2). For isomer **3**, the calculated IE is 9.67 eV, corresponding to an effective experimental range of 9.61−9.70 eV after applying a −0.03 eV correction for thermal and Stark effects; this range remains above the 9.60 eV photon energy used in the experiments. Moreover, since the photoionization cross section is expected to be very small when the photon energy closely matches the IE, only a weak ion signal would typically be observed. However, comparable ion counts were observed for the lower sublimation event

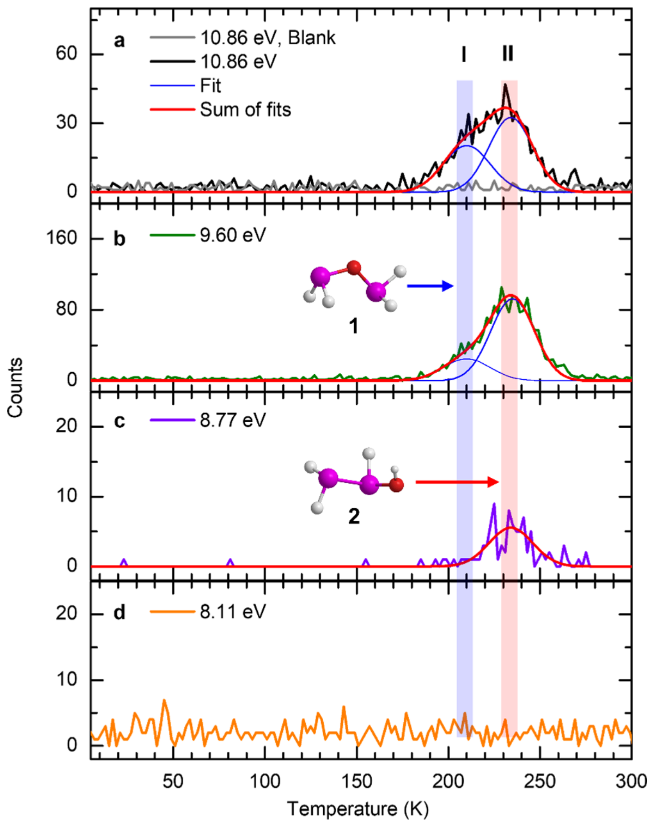

Figure 4. TPD profiles of the ion signal at m/z = 82 from irradiated $PH_3{-}CO_2$ ice, recorded at photon energies of 10.86 eV (a), 9.60 eV (b), 8.77 eV (c), and 8.11 eV (d).

(peak 1) at 10.86 eV (358 ± 27) and 9.60 eV (398 ± 23), further indicating the lack of detection of **3**. Lowering the photon energy to 8.77 eV, sufficient to ionize **2** (IE = 8.47−8.57 eV) but not **1** (IE = 9.01−9.18 eV), results in the disappearance of peak I, while peak II remains (Figure 4c). This result suggests that peak I corresponds to **1**, whereas peak II is attributed to **2**. When the photon energy was further reduced to 8.11 eV, at which none of the H_4P_2O isomers can be ionized, no sublimation event was detected at m/z = 82 (Figure 4d), confirming that the ion signal of peak II arises from **2**. Overall, the PI-ReToF-MS experiments demonstrated the gas-phase detection of isomers **1** and **2**.

Having provided compelling evidence for the formation of phosphanyloxyphosphane (**1**) and its isomer phosphanylphosphinous acid (**2**) in phosphine−carbon dioxide ices under astrophysical conditions, we now turn to their potential formation mechanisms. The initial step involves phosphorus−hydrogen bond rupture in phosphine to generate the phosphino ($\dot{P}H_2$) radical and atomic hydrogen ($\dot{H}$) via reaction 1,[26] which is endoergic by 340 ± 4 kJ mol^{-1}.[27,28] This energy is supplied by the GCR proxies in the form of energetic electrons. Diphosphine (H_2PPH_2) can subsequently form via a barrierless radical−radical recombination of two phosphino radicals through reaction 2,[29] which is exoergic by 236 ± 4 kJ mol^{-1}.[27] Simultaneously, electron irradiation leads to the radiolysis of carbon dioxide, forming electronically excited oxygen atoms ($O(^1D)$) via reaction 3 with an endoergicity of 732 kJ mol^{-1}.[30] As demonstrated in previous laboratory experiments, the oxygen atom can undergo barrierless insertion into the phosphorus−hydrogen bond of phosphine, yielding hydroxyphosphine (PH_2OH) with a reaction exoergicity of 798 kJ mol^{-1} (reaction 4).[5] Note that the diphosphine (H_2PPH_2) and/or hydroxyphosphine (PH_2OH) were also tentatively detected via FTIR spectroscopy at 2283 cm^{-1} in irradiated PH_3−CO_2 ice (Supporting Information).[31,32]

$$PH_3(X^1A_1) \rightarrow \dot{P}H_2(X^2B_1) + \dot{H}(^2S) \quad (1)$$

$$\dot{P}H_2(X^2B_1) + \dot{P}H_2(X^2B_1) \rightarrow H_2PPH_2(X^1A) \quad (2)$$

$$CO_2(X^1\Sigma_g^+) \rightarrow CO(X^1\Sigma^+) + O(^1D) \quad (3)$$

$$PH_3(X^1A_1) + O(^1D) \rightarrow PH_2OH(X^1A') \quad (4)$$

The unimolecular decomposition of hydroxyphosphine (PH_2OH) can yield atomic hydrogen plus either a phosphinooxy ($PH_2\dot{O}$) radical or a hydroxyphosphino ($\dot{P}HOH$) radical via reactions 5 and 6, respectively. Reaction 6 is endoergic by 321 kJ mol^{-1}.[28,33] Once formed through ionizing radiation, these species can remain trapped within the ice matrix due to limited molecular mobility at 5 K,[20] thereby serving as precursors to the formation of H_4P_2O isomers.

$$PH_2OH \rightarrow PH_2\dot{O} + \dot{H} \quad (5)$$

$$PH_2OH \rightarrow \dot{P}HOH + \dot{H} \quad (6)$$

Finally, isomers **1** and **2** can be formed through barrierless radical−radical recombination of the phosphino ($\dot{P}H_2$) radical with either the phosphinooxy ($PH_2\dot{O}$) radical (reaction 7) or the hydroxyphosphino ($\dot{P}HOH$) radical (reaction 8). The radical−radical recombination can occur either during irradiation at 5 K or during TPD at higher temperatures. Alternatively, the insertion of an electronically excited oxygen atom into the phosphorus−phosphorus and phosphorus−hydrogen bond of diphosphine also leads to the formation of **1** and **2** via reactions 9 and 10, respectively. It is worth noting that isomer **3** may form via the addition of an oxygen atom to diphosphine. However, no evidence for its formation could be provided under our experimental conditions, which may result from competing reaction pathways of oxygen atoms in the ice and/or a small production yield below our detection limit.

$$\dot{P}H_2 + PH_2\dot{O} \rightarrow H_2POPH_2(\mathbf{1}) \quad (7)$$

$$\dot{P}H_2 + \dot{P}HOH \rightarrow H_2PPHOH(\mathbf{2}) \quad (8)$$

$$H_2PPH_2 + O \rightarrow H_2POPH_2(\mathbf{1}) \quad (9)$$

$$H_2PPH_2 + O \rightarrow H_2PPHOH(\mathbf{2}) \quad (10)$$

In conclusion, the hitherto elusive phosphanyloxyphosphane (H_2POPH_2, **1**) and its isomer phosphanylphosphinous acid (H_2PPHOH, **2**) have been synthesized and detected for the first time. These molecules were formed in phosphine−carbon dioxide ices irradiated at low temperatures of 5 K by energetic electrons, which simulate secondary electrons generated by the interaction of GCRs with interstellar ices in cold molecular clouds. Utilizing tunable VUV PI-ReToF-MS and isotopic labeling experiments, **1** and **2** were isolated and identified in the gas phase during TPD. Assuming Maxwell−Boltzmann velocity distribution for the thermal sublimation of molecules from the ices,[34] an average molecular velocity of 240 m s^{-1} was determined for these isomers subliming at around 220 K. Given the 2.0 ± 0.5 mm distance between the photoionization region and ice surface, the lifetimes of neutral **1** and **2** in the gas phase exceed 8 ± 2 μs. The formation of isomers **1** and **2** is initiated by endoergic bond-cleavage of phosphine and carbon dioxide via nonequilibrium chemistry, followed by either radical−radical recombination via reactions 7 and 8 or oxygen-atom insertion through reactions 9 and 10. These pathways underscore the pivotal role of GCR-induced nonequilibrium chemistry in facilitating the formation of novel P−O−P and P−P−O bond linkages within phosphine-rich extraterrestrial ices. These findings advance our fundamental understanding of the plausible abiotic routes toward complex phosphorus oxoacids, shedding light on the formation of biorelevant phosphorus-containing molecules in deep space.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.5c12481.

Experimental and computational methods, IEs and relative energies of H_4P_2O isomers, error analysis of computed IEs, infrared spectra results, VUV generation parameters, Cartesian coordinates, harmonic frequencies, infrared intensities of calculated structures (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Agnes H. H. Chang − *Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan*; Email: hhchang@gms.ndhu.edu.tw

Ralf I. Kaiser − *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*; orcid.org/0000-0002-7233-7206; Email: ralfk@hawaii.edu

Authors

Jia Wang − *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

Bing-Jian Sun − *Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan*

Alexandre Bergantini − *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

Zesen Wang − *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

Andrew M. Turner − *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States; Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.5c12481

Notes

The authors declare no competing financial interest.

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