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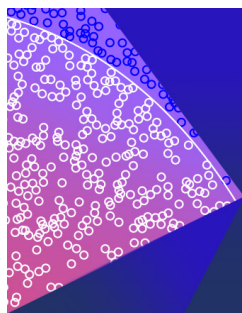


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## ABSTRACT

Phosphorus is of particular interest in astrochemistry because it is a biogenic element together with hydrogen, carbon, nitrogen, oxygen, and sulfur. However, the chemical evolution of such element in the interstellar medium (ISM) is still far from an accurate characterization, with the chemistry of P-bearing molecules being poorly understood. To provide a contribution in this direction, we have carried out an accurate investigation of the potential energy surface for the reaction between the CP radical and methanimine ( $\text{CH}_2\text{NH}$ ), two species already detected in the ISM. In analogy to similar systems, i.e.,  $\text{CH}_2\text{NH} + \text{X}$ , with  $\text{X} = \text{OH}$ ,  $\text{CN}$ , and  $\text{CCH}$ , this reaction can occur—from an energetic point of view—under the harsh conditions of the ISM. Furthermore, since the major products of the aforementioned reaction, namely, *E*- and *Z*-2-phosphanylidineethan-1-imine ( $\text{HN}=\text{CHCP}$ ) and *N*-(phosphanylidinemethyl)methanimine ( $\text{H}_2\text{C}=\text{NCP}$ ), have not been spectroscopically characterized yet, some effort has been made for filling this gap by means of accurate computational approaches.

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## I. INTRODUCTION

Phosphorus is an essential constituent of life on Earth due to the important roles played by its compounds in living systems. Therefore, it is considered a biogenic element together with hydrogen, carbon, nitrogen, oxygen, and sulfur.<sup>1</sup> While phosphorus is ubiquitous on our planet, the elemental abundance of gaseous P in the interstellar medium (ISM), i.e., due to P-bearing molecules, is still unclear, the reasons being its low cosmic abundance ( $\sim 2.8 \times 10^{-7}$  with respect to hydrogen<sup>1–3</sup>) and the poor comprehension of its chemistry.<sup>1,4,5</sup> Concerning the former issue, phosphorus can only be formed by stars having a mass 15 times greater than the solar mass, thus a small subgroup of astronomical objects.<sup>1</sup> Furthermore, the nuclear processes involved in the production of atomic phosphorus lead to a yield of only 2.5%.<sup>1,3</sup> Another important consideration is related to the high condensation temperature of atomic

phosphorus, which results in what is, probably, a high depletion of such an element onto dust grains, thus reducing the possibility of gas-phase reactions involving atomic phosphorus to form P-containing species.<sup>4</sup>

Nonetheless, some small P-bearing molecules have been detected in the ISM, and this apparent lack might be due to phosphorus molecules not yet discovered.<sup>6</sup> In chronological order, the first molecule observed in molecular clouds was PN,<sup>7,8</sup> followed a few years later by the CP radical ( $X^2\Sigma^+$ ).<sup>9</sup> The latter is probably formed from photodissociation processes of the HCP molecule, also detected in the ISM, in 2007.<sup>10</sup> Indeed, the latter species is considered the “ferry” carrying phosphorus from the condensed state to the gas phase, via photodesorption. More recently, searches for  $\text{PH}_3$ , CCP, and the PO molecules have been proven successful,<sup>11–13</sup> with the latter being also the only species identified in space containing the P–O bond, whose relevance is

correlated with its role in biochemistry. Tentative detections of other P-bearing species, such as, e.g.,  $\text{PH}_2\text{CN}$  and  $\text{CH}_3\text{PH}_2$ , turned out to be unsuccessful.<sup>14</sup>

The CP and CCP radicals have been detected, up to date, only in the carbon-rich circumstellar shell IRC+10216.<sup>9,12</sup> Circumstellar envelopes of evolved stars are among the most remarkable chemical laboratories in the universe. Therefore, they are excellent bench tests to understand chemical synthesis in space. Among the molecules that might react with these radicals, a plausible and interesting species is methanimine ( $\text{CH}_2\text{NH}$ ) whose presence in IRC+10216 was confirmed by Tenenbaum *et al.*<sup>15</sup> In this respect, this work aims at investigating the reaction between the CP radical and methanimine, which is particularly promising in view of the fact that the reaction involving the isoelectronic CN radical is the only formation route available so far for the production of *E*- and *Z*-cyanomethanimine ( $\text{HNCHCN}$ ) in the gas phase.<sup>16,17</sup> Furthermore, it has been recently demonstrated that the reaction between methanimine and the CCH radical leads to the formation of propargylimine,<sup>18</sup> a newly detected species in the ISM,<sup>19</sup> and it has been suggested that the reaction of  $\text{CH}_2\text{NH}$  with small radicals is a general mechanism for the production of complex imines.<sup>18</sup> Among the successful reaction of methanimine, that with the OH radical<sup>20</sup> should also be mentioned.

In analogy with the works previously cited, the expected products of the CP+ $\text{CH}_2\text{NH}$  reaction are *E*- and *Z*-2-phosphanylideneethan-1-imine ( $\text{HN} = \text{CHCP}$ ) and *N*-(phosphanylidinemethyl) methanimine ( $\text{H}_2\text{C} = \text{NCP}$ ). In the present study, an accurate rotational spectroscopic characterization of these species has also been carried out, with our spectral simulations providing a useful support to experimental measurements. The accurate knowledge of the experimental rotational spectra is, indeed, the mandatory requirement for astronomical searches.<sup>3,21</sup>

This paper is organized as follows. In Sec. II, the computational methodologies employed for the accurate investigation of the potential energy surface (PES) of the reactive system as well as those used for the computational spectroscopic investigations are outlined. In Sec. III, the reactive PES is discussed in view of drawing the most important energetic considerations. Subsequently, the results of the spectroscopic characterization for the products will be reported, together with the corresponding spectral simulations. In the last section, the conclusions are drawn.

## II. COMPUTATIONAL METHODS

The reactive PES of the CP +  $\text{CH}_2\text{NH}$  system has been explored employing the double-hybrid B2PLYP functional,<sup>22</sup> including the D3 dispersion correction,<sup>23,24</sup> and using the partially augmented jun-cc-pVTZ basis set with an additional *d* function on second-row atoms, namely, the jun-cc-pV(T+d)Z basis set<sup>25–28</sup> (available on the basis set exchange website<sup>29–31</sup>). The nature of the stationary points located on the reactive PES has been confirmed by Hessian evaluations at the same level of theory, which also provide the corresponding harmonic zero-point vibrational energy (ZPE) corrections. To ensure the correct linking of the reaction pathways, each transition state (TS) has been connected to the corresponding minima by means of the intrinsic reaction coordinate (IRC) analysis.<sup>32</sup>

To improve the quality of the CP+ $\text{CH}_2\text{NH}$  reactive PES, the next step was the refinement of the electronic energies, which have been computed using the junChS composite scheme.<sup>33</sup> This approach starts from a single-point energy calculation employing the CCSD(T) method (coupled cluster singles and doubles with a perturbative treatment of triples)<sup>34</sup> in conjunction with the jun-cc-pV(T+d)Z basis set and within the frozen-core approximation (fc). This leading term [ $E(\text{CC}/\text{junTZ})$ ] is then corrected by incorporating two terms, thus relying on the additivity approximation:

1. The extrapolation to the complete basis set (CBS) limit. This contribution ( $\Delta E_{\text{MP2}}^\infty$ ) is obtained as described in Eq. (1), with second-order Møller–Plesset perturbation theory<sup>35</sup> (MP2) being used in fc energy calculations in conjunction with the jun-cc-pV(T+d)Z and jun-cc-pV(Q+d)Z basis sets. The total fc-MP2 energies are then extrapolated to the CBS limit by employing the  $n^{-3}$  formula by Helgaker *et al.*<sup>36</sup> The effective contribution is obtained by subtracting the fc-MP2/jun-cc-pV(T+d)Z energy from the extrapolated value,

$$\Delta E_{\text{MP2}}^\infty = \frac{4^3 E_{\text{MP2}}^{\text{jun}(Q+d)Z} - 3^3 E_{\text{MP2}}^{\text{jun}(T+d)Z}}{4^3 - 3^3} - E_{\text{MP2}}^{\text{jun}(T+d)Z}. \quad (1)$$

2. The core-valence (CV) correlation contribution. This term, denoted as  $\Delta E_{\text{MP2}}^{\text{CV}}$ , accounts for the correlation of core electrons. It is computed as the energy difference between all-electron (ae) and fc-MP2 computations, both performed with the polarized-weighted core valence triple- $\zeta$  basis set (cc-pwCVTZ).<sup>37</sup>

Overall, the total junChS electronic energy is given by:

$$E(\text{junChS}) = E(\text{CC}/\text{junTZ}) + \Delta E_{\text{MP2}}^\infty + \Delta E_{\text{MP2}}^{\text{CV}}. \quad (2)$$

To avoid spin-contamination of higher electronic spin-states, the junChS approach was evaluated using the restricted open-shell Hartree–Fock wave function (ROHF) for both the CCSD(T)<sup>38,39</sup> and MP2<sup>40,41</sup> methods, as pointed out in Ref. 42. In contrast, B2PLYP-D3 energies have been computed using the unrestricted version of the reference wave function (UHF) in view of the fact that density functional theory (DFT) is less affected by spin-contamination.<sup>43</sup> While the accuracy of the junChS model has been demonstrated for the interaction energy of noncovalent complexes, this is its first application to reaction energies. For this reason, its accuracy has been checked by evaluating a small portion of the PES using an HEAT-like protocol, which is described in detail in Refs. 42 and 44–48. According to Ref. 42, the cc-pVnZ basis sets<sup>25,27</sup> have been employed to compute the extrapolation to the CBS limit of the Hartree–Fock self-consistent field (HF-SCF; with  $n = \text{T, Q, and 5}$ ) and fc-CCSD(T) correlation ( $n = \text{T and Q}$ ) energies. The contribution due to the correlation of inner electrons has been included at the CCSD(T)/cc-pCVTZ<sup>37,49</sup> level. However, to reach the “sub-kJ accuracy,” other additive terms have also been considered: (i) the full account of triple excitations at the CCSDT/cc-pVTZ level of theory;<sup>50,51</sup> (ii) the contribution of quadruple excitations by means of the CCSDT(Q)

method<sup>52–54</sup> in conjunction with the cc-pVDZ basis set; (iii) the scalar relativistic correction (the mass–velocity and Darwin terms) using perturbative techniques,<sup>55,56</sup> computed at the CCSD(T)/aug-cc-pCVDZ level; (iv) the diagonal Born–Oppenheimer correction (DBOC) computed at the HF-SCF level<sup>57</sup> in conjunction with the aug-cc-pVDZ basis set.<sup>27,58</sup>

The energetic investigation of the CP+CH<sub>2</sub>NH reactive PES has been complemented by the spectroscopic characterization of the three major products, namely, *E*- and *Z*-HN=CHCP and H<sub>2</sub>C=NCP. To accurately simulate their rotational spectra, the rotational and centrifugal distortion constants should be computed at the highest possible level of theory.<sup>59</sup> Since equilibrium rotational constants (*B<sub>e</sub>*) are straightforwardly derived from the equilibrium structure, an accurate geometry optimization has been carried out. In detail, the fc-CCSD(T)/CBS(Q,5)+CV/(wCVTZ) “gradient” composite scheme<sup>60,61</sup> has been exploited, with the following energy gradient thus being minimized:

$$\frac{dE_{\text{CBS+CV}}}{dx} = \frac{dE_{\text{HF}}^{\text{CBS}}}{dx} + \frac{d\Delta E_{\text{CCSD(T)}}^{\text{CBS}}}{dx} + \frac{d\Delta E_{\text{CV}}}{dx}, \quad (3)$$

where the first term on the right-hand side is the extrapolation of the HF-SCF energy to the CBS limit using the three-point expression by Feller<sup>62</sup> in combination with the cc-pV(*n*+*d*)Z basis sets, with *n* = T, Q, and 5. The second term is the extrapolation to the CBS limit of the CCSD(T) correlation energy obtained with the *n*<sup>−3</sup> formula, previously introduced for the junChS model, and

employing the cc-pV(*Q*+*d*)Z and cc-pV(*5*+*d*)Z sets. The last term is the CV contribution, which is computed at the CCSD(T)/cc-pwCVTZ level. Further details can be found in Refs. 60, 61, and 63. To move from equilibrium to the vibrational ground state, vibrational corrections to the equilibrium rotational constants have to be included.<sup>59,64</sup> Within second-order vibrational perturbation theory (VPT2),<sup>65,66</sup> these corrections require the knowledge of the vibration–rotation interaction constants, which, in turn, involve anharmonic force field computations (full cubic and semi-diagonal quartic force constants). These have been carried out at the B2PLYP-D3/jun-cc-pV(*T*+*d*)Z level.

The other parameters needed for a reliable simulation of the rotational spectrum are as follows:

1. the quartic centrifugal-distortion constants, which have been obtained from a harmonic force field computed at the ae-CCSD(T)/cc-pwCVQZ level of theory.
2. the electric dipole moment components, which have been obtained by combining the equilibrium values at the ae-CCSD(T)/pwCVQZ level with the vibrational corrections at the B2PLYP-D3/jun-cc-pV(*T*+*d*)Z level.

All DFT computations together with the single-point energy calculations within the junChS scheme have been carried out using the Gaussian suite of program,<sup>67</sup> while geometry optimizations and force-field evaluations involving the CCSD(T) method have

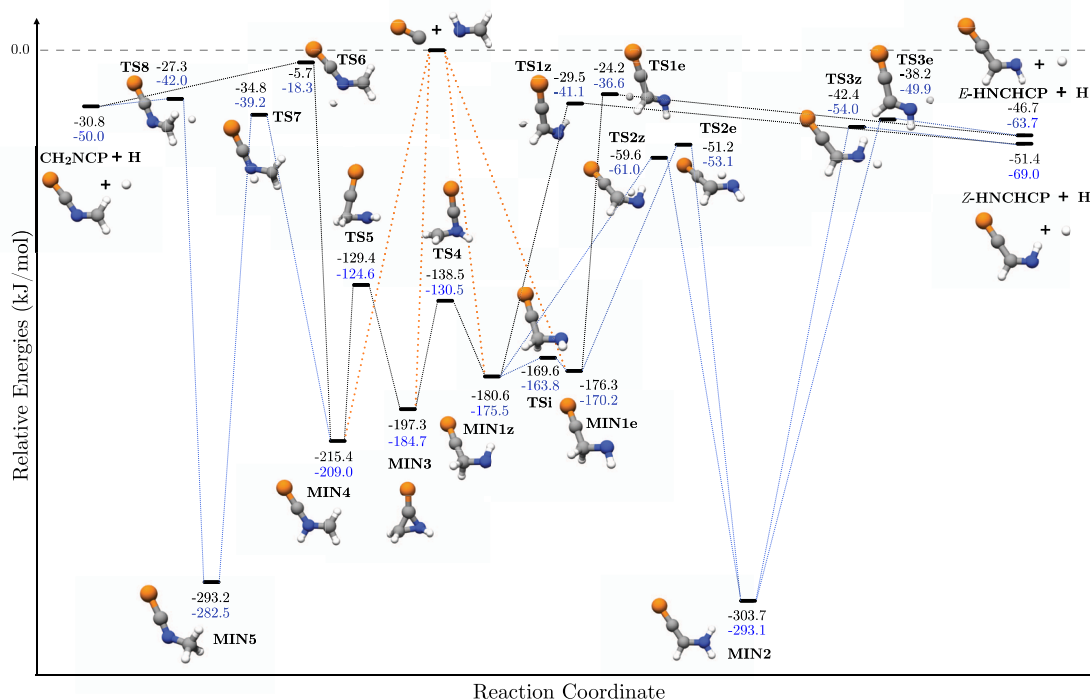


FIG. 1. CP + CH<sub>2</sub>NH reaction pathways: junChS relative energies (black) and their harmonic ZPE-corrected (blue) counterparts.

been performed employing the CFOUR quantum chemical program package.<sup>68,69</sup>

### III. RESULTS

#### A. The reactive PES of the CP + CH<sub>2</sub>NH system

The severe conditions of the interstellar clouds, namely, low temperatures (10 K–100 K) and low number density (10 cm<sup>-3</sup>–10<sup>7</sup> cm<sup>-3</sup>), pose tight constraints on reactivity, thus allowing only reactions that can occur without overcoming activation barriers, with the only exception due to tunneling effects. For this reason, we focused on reaction pathways presenting only submerged barriers. Based on previous studies,<sup>17,18</sup> the nucleophilic attacks of the C-end of the CP radical on both the carbon and nitrogen sides of methanimine have been considered. The resulting reaction paths are depicted in Fig. 1, which also shows the structures of all the stationary points identified.

The strong nucleophilicity of the CP radical leads to three barrierless entrance channels:

1. The CP attack to the methanimine C-end. This forms two isomers of pre-reactive complexes **MIN1**, **MIN1e**, and **MIN1z**, which can be easily interconverted through **TSi** because of the low isomerization barrier (~10 kJ mol<sup>-1</sup>).
2. The CP attack to the methanimine N-end. This leads to the formation of a planar pre-reactive complex, **MIN4**.
3. The CP attack to the  $\pi$ -system of the imine double bond. This leads to the formation of a stable cyclic adduct (**MIN3**), which links the left (N-end) and right (C-end) portions of the reactive PES through barriers of the order of 50 kJ mol<sup>-1</sup>–60 kJ mol<sup>-1</sup>.

Despite the weaker electrophilic character of nitrogen compared to the carbon atom of methanimine, the **MIN4** intermediate is the most stable pre-reactive complex from an energetic point of view, analogously to what occurs in the reactions of methanimine with CN or CCH.<sup>17,18</sup> This might be attributed to the stabilizing effect of electronic delocalization. However, the crucial interconversion barriers between the first intermediates, i.e., **MIN4**, **MIN3**, and **MIN1e/z**, are slightly different from those obtained for the CCH radical.<sup>18</sup> The intermediates **MIN4** and **MIN1** (both the *E* and *Z* isomers) evolve into the products CH<sub>2</sub>NCP and HNCHCP (both the *E* and *Z* isomers), respectively, by elimination of a hydrogen atom. The elimination mechanism can occur in two different ways: either through a path (depicted in black in Fig. 1), involving only one transition state at high energy (**TS6**, **TS1e**, and **TS1z**), but still submerged with respect to reactants, or through a two-step path (depicted in blue in Fig. 1), which involves the formation of the most stable intermediates (**MIN5** and **MIN2**) of the entire PES.

Table I shows the B2PLYP-D3/jun-cc-pV(T+d)Z and junChS relative energies, together with the ZPE-corrected counterparts, for

**TABLE I.** Relative electronic energies (kJ mol<sup>-1</sup>) of the stationary points for the CP + CH<sub>2</sub>NH reaction.

	B2PLYP-D3/jun-cc-pV(T+d)Z		junChS	
	Energy	ZPE corrected <sup>a</sup>	Energy	ZPE corrected <sup>a</sup>
Reactants	0.00	0.00	0.00	0.00
MIN1z	-201.48	-196.38	-180.59	-175.49
TSi	-189.85	-184.06	-169.57	-163.79
MIN1e	-196.65	-190.57	-176.29	-170.22
TS1e	-42.40	-54.73	-24.24	-36.58
TS1z	-47.15	-58.82	-29.46	-41.12
TS2z	-79.03	-80.38	-59.62	-60.98
TS2e	-69.92	-71.80	-51.19	-53.08
MIN2	-326.45	-315.89	-303.66	-293.10
TS3e	-60.41	-72.16	-38.18	-49.92
TS3z	-64.43	-75.96	-42.45	-54.00
<i>E</i> -HNCHCP + H	-73.10	-90.17	-46.67	-63.74
<i>Z</i> -HNCHCP + H	-68.14	-85.71	-51.41	-68.97
TS5	-147.84	-143.05	-129.44	-124.62
MIN3	-214.53	-201.92	-197.30	-184.75
TS4	-152.28	-144.29	-138.47	-130.48
MIN4	-241.05	-234.78	-215.36	-209.02
TS6	-36.00	-48.47	-5.68	-18.26
TS7	-58.84	-63.19	-34.76	-39.19
MIN5	-321.65	-311.06	-293.22	-282.53
TS8	-50.70	-65.57	-27.29	-42.04
CH <sub>2</sub> NCP + H	-58.87	-78.08	-30.77	-49.96

<sup>a</sup>Harmonic ZPE corrections at the B2PLYP-D3/jun-cc-pV(T+d)Z level.

all stationary points of the reactive PES. While the junChS model does not change the trends resulting from DFT calculations, it reduces the relative energies by about  $14 \text{ kJ mol}^{-1}$ – $30 \text{ kJ mol}^{-1}$ . In particular, the largest change occurs for **TS6**, which increases the relative energy by about  $30 \text{ kJ mol}^{-1}$ , thus approaching the energy of the reactants (albeit being still submerged). Overall, we can note that the reaction barriers are approximately left unchanged.

As mentioned in Sec. II, to validate the accuracy of the junChS approach, the path Reactants  $\rightarrow$  **MIN1** (both the *E* and *Z* isomers)  $\rightarrow$  **TS1** (both the *E* and *Z* isomers)  $\rightarrow$  HNCHCP (both the *E* and *Z* isomers) has been re-investigated employing the HEAT-like protocol<sup>42,44–48</sup> on top of B2PLYP-D3/jun-cc-pV(T+d)Z geometries. The comparison between junChS and HEAT-like energies is reported in Table II and shows a maximum absolute deviation of  $\sim 0.8 \text{ kJ mol}^{-1}$  and an average absolute deviation of  $\sim 0.6 \text{ kJ mol}^{-1}$ . Therefore, it has been confirmed that the approach adopted for this investigation has the required accuracy for reactive PES investigation.

## B. Spectroscopic characterization of *E/Z*-HNCHCP and CH<sub>2</sub>NCP

As mentioned in the Introduction, the identification of new molecules in astronomical environments is driven by the observation of their rotational transitions,<sup>70</sup> which are unambiguous fingerprints. With only few exceptions,<sup>71–73</sup> experimental rotational transition frequencies are required for the assignment of the spectra collected by using radio-telescopes and/or interferometers. However, whenever there is a complete lack of information, computed spectra are the mandatory starting point for experiment in the laboratory, especially if the species of interest is unstable and produced inside the spectrometer cell via, e.g., electric discharge or pyrolysis.

The laboratory synthesis of species-like HNCHCP and CH<sub>2</sub>NCP is not feasible, and their production *in situ* is challenging. Indeed, a suitable precursor for pyrolysis needs to be envisaged, which, according to the works on propargylimine<sup>19</sup> and cyanomethanimine,<sup>74</sup> should be a substituted N-containing phosphine or a P-bearing amine. In view of the complexity of the experimental investigation, the accurate computational characterization of rotational spectra of HNCHCP and CH<sub>2</sub>NCP is particularly important.

**TABLE II.** Relative electronic energies ( $\text{kJ mol}^{-1}$ ) for the  $\text{CH}_2\text{NH} + \text{CP} \rightarrow \text{MIN1e/z} \rightarrow \text{TS1e/z} \rightarrow \text{E/Z-HNCHCP} + \text{H}$  path.

	junChS	HEAT-like	$ \Delta E ^a$
MIN1z	−180.59	−179.86	0.73
MIN1e	−176.29	−175.50	0.79
TS1e	−24.24	−24.67	0.43
TS1z	−29.46	−29.90	0.44
Z-HNCHCP + H	−51.41	−51.12	0.29
E-HNCHCP + H	−46.67	−45.86	0.81

<sup>a</sup> Absolute junChS-HEAT-like energy difference.

Table III collects the spectroscopic parameters computed with the protocol described in Sec. II. According to Ref. 63, the expected accuracy of the vibrational ground-state rotational constants is  $\sim 0.06\%$ , while the uncertainty affecting the quartic centrifugal-distortion constants is about one order of magnitude greater.<sup>75,76</sup> Figure 2 depicts the simulation of the rotational spectra of the *Z* and *E* isomers of HNCHCP, at a temperature of 100 K, based on the spectroscopic parameters of Table III. Figure 2 shows that, while the maximum of intensity is around 180 GHz for both species, the larger dipole moment components of the *E* isomer result in a more intense spectrum. Since the uncertainties on the computed parameters propagate by increasing the rotational quantum number *J* (denoting the lowest rotational level involved in the transition), the most accurate estimates are obtained for rotational transitions with low *J* values, which usually lie at low frequencies. For this reason, Fig. 2 also shows a zoomed-in view of the rotational spectra in the 30 GHz–100 GHz frequency range, with the different *K<sub>a</sub>*-components of each transition being evident. It has to be noted that, for both isomers, *a*- and *b*-type transitions are observable; however, the  $\mu_b$  component of the dipole moment is rather small, in particular for the *Z*-HNCHCP species. As a consequence, the *b*-type spectrum of *Z*-HNCHCP is not discernible in Fig. 2; for the *E* isomer, instead, this type of transitions becomes well visible at frequencies greater than 250 GHz (darker red lines). In Fig. 3, the rotational spectrum for CH<sub>2</sub>NCP, simulated at *T* = 100 K, is shown in the 0 GHz–500 GHz frequency range. Both *a*- and *b*-type transitions are evident, and the maximum of intensity is above 500 GHz. However, at such frequencies, the predictions are less accurate, and higher frequencies have thus not been considered.

**TABLE III.** Rotational spectroscopic parameters (MHz, if not otherwise stated) of *E/Z*-HNCHCP and CH<sub>2</sub>NCP (Watson's *S* reduction and *I'* representation).

Parameter <sup>a</sup>	<i>Z</i> -HNCHCP	<i>E</i> -HNCHCP	CH <sub>2</sub> NCP
<i>A<sub>e</sub></i>	50 319.38	58 098.90	61 454.73
<i>B<sub>e</sub></i>	2 846.04	2 796.71	2 997.13
<i>C<sub>e</sub></i>	2 693.69	2 668.27	2 857.76
$\Delta A_{\text{vib}}$	272.77	52.49	1 372.17
$\Delta B_{\text{vib}}$	−11.55	−6.82	−17.25
$\Delta C_{\text{vib}}$	−12.34	−8.66	−16.54
<i>A<sub>0</sub></i>	50 592.15	58 151.39	62 826.90
<i>B<sub>0</sub></i>	2 834.49	2 789.89	2 979.88
<i>C<sub>0</sub></i>	2 681.35	2 659.61	2 841.22
<i>D<sub>J</sub></i>	$0.65 \times 10^{-3}$	$0.54 \times 10^{-3}$	$0.63 \times 10^{-3}$
<i>D<sub>JK</sub></i>	−0.056	−0.066	−0.080
<i>D<sub>K</sub></i>	3.9	6.2	7.7
<i>d<sub>1</sub></i>	$−0.90 \times 10^{-4}$	$−0.70 \times 10^{-4}$	$−0.88 \times 10^{-4}$
<i>d<sub>2</sub></i>	$−0.47 \times 10^{-5}$	$−0.32 \times 10^{-5}$	$−0.45 \times 10^{-5}$
$ \mu_a /D$	1.58	1.90	1.68
$ \mu_b /D$	0.06	0.37	1.39
$ \mu_c /D$	0.00	0.00	0.00

<sup>a</sup> Equilibrium rotational constants at the fc-CCSD(T)/CBS(Q,5)+CV/(wCVTZ) level. Anharmonic corrections ( $\Delta B_{\text{vib}}$ 's) at the B2PLYP-D3/jun-cc-pV(T+d)Z level. Quartic centrifugal distortion constants at the ae-CCSD(T)/cc-pwCVQZ level. Equilibrium dipole moment components (in debye) at the ae-CCSD(T)/cc-pwCVQZ level corrected for vibrational contributions at the B2PLYP-D3/jun-cc-pV(T+d)Z level.

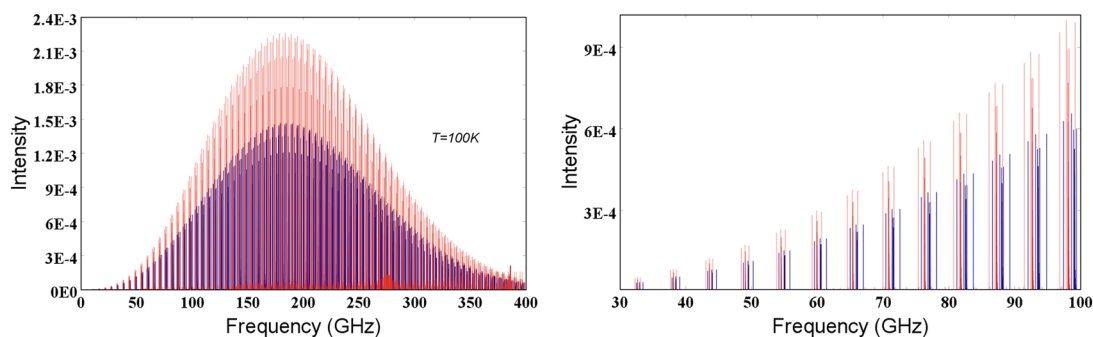


FIG. 2. Left panel: Simulated rotational spectra of Z- and E-HNCHCP, blue and red lines, respectively, up to 400 GHz. Right panel: A zoomed-in view of the rotational spectra between 30 GHz and 100 GHz. Intensity in  $\text{nm}^2 \text{ MHz}$ .

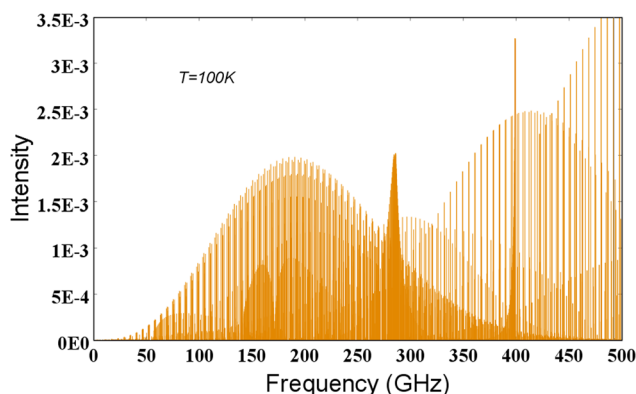


FIG. 3. Simulated rotational spectrum of  $\text{CH}_2\text{NCP}$  in the 0 GHz–500 GHz frequency range. Intensity in  $\text{nm}^2 \text{ MHz}$ .

A good candidate for the observation in the case of  $\text{CH}_2\text{NCP}$  is the transition  $J_{K_a, K_c} = 2_{1,2} \leftarrow 1_{1,1}$ , which is predicted at 11 503.8 MHz with an error, according to estimates addressed above, of only 5.4 MHz.

#### IV. CONCLUSIONS

In analogy to the addition of the CN and CCH radicals to methanimine, the CP radical is expected to lead to reaction paths that are “open” (i.e., energetically accessible) under the harsh conditions of the ISM. Interestingly, the reactive CP +  $\text{CH}_2\text{NH}$  PES is, in any detail, analogous to that of the CN +  $\text{CH}_2\text{NH}$  and CCH +  $\text{CH}_2\text{NH}$  systems, thus supporting the idea of a general mechanism for the formation of complex imines in interstellar clouds. Furthermore, the present work is the first application of the new junChS model for energetic studies of reactive PESs. The comparison with the results issuing from an extremely accurate HEAT-like approach pointed out to a great accuracy and suitability for energy evaluations of reactive systems, despite its limited computational cost. Finally, this work has been complemented by the spectroscopic characterization of the major reaction products, namely,

E-/Z-HNCHCP and  $\text{CH}_2\text{NCP}$ , with a methodology at the state of the art, able to predict rotational transitions with accuracy better than 0.2%.

#### DEDICATION

This work is dedicated to Laura Bassi-Veratti (Bologna, 1711–1778) as the symbol of all women who pursued or are pursuing a scientific academic career. She was the second woman to achieve a university degree, the very first to obtain a Ph.D. in a scientific subject, and a teaching position at the University of Bologna. She fought for equal rights for women and men in academics.

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#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### REFERENCES

- 1 E. Maciá, “The role of phosphorus in chemical evolution,” *Chem. Soc. Rev.* **34**, 691–701 (2005).
- 2 N. Grevesse and A. J. Sauval, “Standard solar composition,” *Space Sci. Rev.* **85**, 161–174 (1998).
- 3 S. Yamamoto, *Introduction to Astrochemistry: Chemical Evolution From Interstellar Clouds to Star and Planet Formation* (Springer, Japan, 2017).
- 4 V. Leboutellier, Kuassivi, and R. Ferlet, “Phosphorus in the diffuse interstellar medium,” *Astron. Astrophys.* **443**, 509–517 (2005).
- 5 J. Chantzos, V. M. Rivilla, A. Vasyunin, E. Redaelli, L. Bizzocchi, F. Fontani, and P. Caselli, “The first steps of interstellar phosphorus chemistry,” *Astron. Astrophys.* **633**, A54 (2020).
- 6 S. N. Milam, D. T. Halfen, E. D. Tenenbaum, A. J. Apponi, N. J. Woolf, and L. M. Ziurys, “Constraining phosphorus chemistry in carbon- and oxygen-rich

- circumstellar envelopes: Observations of PN, HCP, and CP," *Astrophys. J.* **684**, 618–625 (2008).
- <sup>7</sup>L. M. Ziurys, "Detection of interstellar PN: The first phosphorus-bearing species observed in molecular clouds," *Astrophys. J.* **321**, L81–L85 (1987).
- <sup>8</sup>B. E. Turner and J. Bally, "Detection of interstellar PN: The first identified phosphorus compound in the interstellar medium," *Astrophys. J.* **321**, L75–L79 (1987).
- <sup>9</sup>M. Guélin, J. Cernicharo, G. Paubert, and B. E. Turner, "Free CP in IRC+10216," *Astron. Astrophys.* **230**, L9–L11 (1990).
- <sup>10</sup>M. Agúndez, J. Cernicharo, and M. Guélin, "Discovery of phosphacetyne (HCP) in space: Phosphorus chemistry in circumstellar envelopes," *Astrophys. J.* **662**, L91–L94 (2007).
- <sup>11</sup>M. Agúndez, J. Cernicharo, L. Decin, P. Encrenaz, and D. Teyssier, "Confirmation of circumstellar phosphine," *Astrophys. J.* **790**, L27 (2014).
- <sup>12</sup>D. T. Halfen, D. J. Clouthier, and L. M. Ziurys, "Detection of the CCP radical ( $X^2\Pi_r$ ) in IRC+10216: A new interstellar phosphorus-containing species," *Astrophys. J.* **677**, L101–L104 (2008).
- <sup>13</sup>E. D. Tenenbaum, N. J. Woolf, and L. M. Ziurys, "Identification of phosphorus monoxide ( $X^2\Pi_r$ ) in VY Canis Majoris: Detection of the first P–O bond in space," *Astrophys. J.* **666**, L29–L32 (2007).
- <sup>14</sup>D. T. Halfen, D. J. Clouthier, and L. M. Ziurys, "Millimeter/submillimeter spectroscopy of  $\text{PH}_2\text{CN}$  ( $X^1A'$ ) and  $\text{CH}_3\text{PH}_2$  ( $X^1A'$ ): Probing the complexity of interstellar phosphorus in chemistry," *Astrophys. J.* **796**, 36 (2014).
- <sup>15</sup>E. D. Tenenbaum, J. L. Dodd, S. N. Milam, N. J. Woolf, and L. M. Ziurys, "Comparative spectra of oxygen-rich vs carbon-rich circumstellar shells: VY Canis Majoris and IRC+10216 at 215–285 GHz," *Astrophys. J.* **720**, L102–L107 (2010).
- <sup>16</sup>V. A. Basiuk and V. I. Bogillo, "Theoretical study of amino acid precursor formation in the interstellar medium. 2. Reaction of methylenimine with CN radical," *Adv. Space Res.* **30**, 1445–1450 (2002).
- <sup>17</sup>F. Vazart, C. Latouche, D. Skouteris, N. Balucani, and V. Barone, "Cyanomethanimine isomers in cold interstellar clouds: Insights from electronic structure and kinetic calculations," *Astrophys. J.* **810**, 111 (2015).
- <sup>18</sup>J. Lupi, C. Puzzarini, and V. Barone, "Methanimine as a key precursor of imines in the interstellar medium: The case of propargylimine," *Astrophys. J. Lett.* **903**, L35 (2020).
- <sup>19</sup>L. Bizzocchi, D. Prudenzano, V. M. Rivilla, A. Pietropoli-Charmet, B. M. Giuliano, P. Caselli, J. Martín-Pintado, I. Jiménez-Serra, S. Martín, M. A. Requena-Torres, F. Rico-Villas, S. Zeng, and J.-C. Guillemin, "Propargylimine in the laboratory and in space: Millimetre-wave spectroscopy and its first detection in the ISM," *Astron. Astrophys.* **640**, A98 (2020).
- <sup>20</sup>F. Vazart, D. Calderini, C. Puzzarini, D. Skouteris, and V. Barone, "State-of-the-art thermochemical and kinetic computations for astrochemical complex organic molecules: Formamide formation in cold interstellar clouds as a case study," *J. Chem. Theory Comput.* **12**, 5385–5397 (2016).
- <sup>21</sup>M. Melosso, L. Dore, F. Tamassia, C. L. Brogan, T. R. Hunter, and B. A. McGuire, "The submillimeter rotational spectrum of ethylene glycol up to 890 GHz and application to ALMA band 10 spectral line data of NGC 6334I," *J. Phys. Chem. A* **124**, 240–246 (2020).
- <sup>22</sup>S. Grimme, "Semiempirical hybrid density functional with perturbative second-order correlation," *J. Phys. Chem.* **124**, 034108 (2006).
- <sup>23</sup>S. Grimme, S. Ehrlich, and L. Goerigk, "Effect of the damping function in dispersion corrected density functional theory," *J. Comput. Chem.* **32**, 1456–1465 (2011).
- <sup>24</sup>S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, "A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu," *J. Chem. Phys.* **132**, 154104 (2010).
- <sup>25</sup>T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," *J. Chem. Phys.* **90**, 1007–1023 (1989).
- <sup>26</sup>T. H. Dunning, K. A. Peterson, and A. K. Wilson, "Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited," *J. Chem. Phys.* **114**, 9244–9253 (2001).
- <sup>27</sup>D. E. Woon and T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon," *J. Chem. Phys.* **98**, 1358–1371 (1993).
- <sup>28</sup>E. Papajak and D. G. Truhlar, "Convergent partially augmented basis sets for post-Hartree-Fock calculations of molecular properties and reaction barrier heights," *J. Chem. Theory Comput.* **7**, 10–18 (2011).
- <sup>29</sup>B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, and T. L. Windus, "A new basis set exchange: An open, up-to-date resource for the molecular sciences community," *J. Chem. Inf. Model.* **59**, 4814–4820 (2019).
- <sup>30</sup>K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, "Basis set exchange: A community database for computational sciences," *J. Chem. Inf. Model.* **47**, 1045–1052 (2007).
- <sup>31</sup>D. Feller, "The role of databases in support of computational chemistry calculations," *J. Comput. Chem.* **17**, 1571–1586 (1996).
- <sup>32</sup>K. Fukui, "The path of chemical reactions—The IRC approach," *Acc. Chem. Res.* **14**, 363–368 (1981).
- <sup>33</sup>S. Alessandrini, V. Barone, and C. Puzzarini, "Extension of the "Cheap" composite approach to noncovalent interactions: The jun-ChS scheme," *J. Chem. Theory Comput.* **16**, 988–1006 (2019).
- <sup>34</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, "A fifth-order perturbation comparison of electron correlation theories," *Chem. Phys. Lett.* **157**, 479–483 (1989).
- <sup>35</sup>C. Møller and M. S. Plesset, "Note on an approximation treatment for many-electron systems," *Phys. Rev.* **46**, 618–622 (1934).
- <sup>36</sup>T. Helgaker, W. Klopper, H. Koch, and J. Noga, "Basis-set convergence of correlated calculations on water," *J. Chem. Phys.* **106**, 9639 (1997).
- <sup>37</sup>K. A. Peterson and T. H. Dunning, Jr., "Accurate correlation consistent basis sets for molecular core-valence correlation effects: The second row atoms Al–Ar, and the first row atoms B–Ne revisited," *J. Chem. Phys.* **117**, 10548–10560 (2002).
- <sup>38</sup>J. Gauss, W. J. Lauderdale, J. F. Stanton, J. D. Watts, and R. J. Bartlett, "Analytic energy gradients for open-shell coupled-cluster singles and doubles (CCSD) calculations using restricted open-shell Hartree–Fock (ROHF) reference functions," *Chem. Phys. Lett.* **182**, 207–215 (1991).
- <sup>39</sup>J. D. Watts, J. Gauss, and R. J. Bartlett, "Coupled-cluster methods with non-iterative triple excitations for restricted open-shell Hartree–Fock and other general single determinant reference functions. Energies and analytical gradients," *J. Chem. Phys.* **98**, 8718–8733 (1993).
- <sup>40</sup>W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, "Many-body perturbation theory with a restricted open-shell Hartree–Fock reference," *Chem. Phys. Lett.* **187**, 21–28 (1991).
- <sup>41</sup>W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, "Restricted open-shell Hartree–Fock-based many-body perturbation theory: Theory and application of energy and gradient calculations," *J. Chem. Phys.* **97**, 6606–6620 (1992).
- <sup>42</sup>C. Puzzarini and V. Barone, "The challenging playground of astrochemistry: An integrated rotational spectroscopy—Quantum chemistry strategy," *Phys. Chem. Chem. Phys.* **22**, 6507–6523 (2020).
- <sup>43</sup>A. S. Menon and L. Radom, "Consequences of spin contamination in unrestricted calculations on open-shell species: Effect of Hartree–Fock and Møller–Plesset contributions in hybrid and double-hybrid density functional theory approaches," *J. Phys. Chem. A* **112**, 13225–13230 (2008).
- <sup>44</sup>A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, "HEAT: High accuracy extrapolated *ab initio* thermochemistry," *J. Comput. Phys.* **121**, 11599–11613 (2004).
- <sup>45</sup>Y. J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P. G. Szalay, A. G. Császár, J. Gauss, and J. F. Stanton, "High-accuracy extrapolated *ab initio* thermochemistry. II. Minor improvements to the protocol and a vital simplification," *J. Chem. Phys.* **125**, 064108 (2006).
- <sup>46</sup>M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, "High-accuracy extrapolated *ab initio* thermochemistry. III. Additional improvements and overview," *J. Chem. Phys.* **128**, 114111 (2008).
- <sup>47</sup>C. Puzzarini, Z. Salta, N. Tasinato, J. Lupi, C. Cavallotti, and V. Barone, "A twist on the reaction of the CN radical with methylamine in the interstellar medium:



- New hints from a state-of-the-art quantum-chemical study," *Mon. Not. R. Astron. Soc.* **496**, 4298–4310 (2020).
- <sup>48</sup>J. Lupi, C. Puzzarini, C. Cavallotti, and V. Barone, "State-of-the-art quantum chemistry meets variable reaction coordinate transition state theory to solve the puzzling case of the  $\text{H}_2\text{S} + \text{Cl}$  system," *J. Chem. Theory Comput.* **16**, 5090–5104 (2020).
- <sup>49</sup>D. E. Woon and T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon," *J. Chem. Phys.* **103**, 4572–4585 (1995).
- <sup>50</sup>J. Noga and R. J. Bartlett, "The full CCSDT model for molecular electronic structure," *J. Chem. Phys.* **86**, 7041–7050 (1987).
- <sup>51</sup>G. E. Scuseria and H. F. Schaefer III, "A new implementation of the full CCSDT model for molecular electronic structure," *Chem. Phys. Lett.* **152**, 382–386 (1988).
- <sup>52</sup>Y. J. Bomble, J. F. Stanton, M. Kállay, and J. Gauss, "Coupled-cluster methods including noniterative corrections for quadruple excitations," *J. Chem. Phys.* **123**, 054101 (2005).
- <sup>53</sup>M. Kállay and J. Gauss, "Approximate treatment of higher excitations in coupled-cluster theory," *J. Chem. Phys.* **123**, 214105 (2005).
- <sup>54</sup>M. Kállay and J. Gauss, "Approximate treatment of higher excitations in coupled-cluster theory. II. Extension to general single-determinant reference functions and improved approaches for the canonical Hartree–Fock case," *J. Chem. Phys.* **129**, 144101 (2008).
- <sup>55</sup>R. D. Cowan and D. C. Griffin, "Approximate relativistic corrections to atomic radial wave functions," *J. Opt. Soc. Am.* **66**, 1010–1014 (1976).
- <sup>56</sup>W. Klopper, "Simple recipe for implementing computation of first-order relativistic corrections to electron correlation energies in framework of direct perturbation theory," *J. Comput. Chem.* **18**, 20–27 (1997).
- <sup>57</sup>N. C. Handy, Y. Yamaguchi, and H. F. Schaefer III, "The diagonal correction to the Born–Oppenheimer approximation: Its effect on the singlet–triplet splitting of  $\text{CH}_2$  and other molecular effects," *J. Chem. Phys.* **84**, 4481–4484 (1986).
- <sup>58</sup>R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, "Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions," *J. Chem. Phys.* **96**, 6796–6806 (1992).
- <sup>59</sup>C. Puzzarini, J. F. Stanton, and J. Gauss, "Quantum-chemical calculation of spectroscopic parameters for rotational spectroscopy," *Int. Rev. Phys. Chem.* **29**, 273–367 (2010).
- <sup>60</sup>M. Heckert, M. Kállay, and J. Gauss, "Molecular equilibrium geometries based on coupled-cluster calculations including quadruple excitations," *Mol. Phys.* **103**, 2109–2115 (2005).
- <sup>61</sup>M. Heckert, M. Kállay, D. P. Tew, W. Klopper, and J. Gauss, "Basis-set extrapolation techniques for the accurate calculation of molecular equilibrium geometries using coupled-cluster theory," *J. Chem. Phys.* **125**, 044108 (2006).
- <sup>62</sup>D. Feller, "The use of systematic sequences of wave functions for estimating the complete basis set, full configuration interaction limit in water," *J. Phys. Chem.* **98**, 7059–7071 (1993).
- <sup>63</sup>S. Alessandrini, J. Gauss, and C. Puzzarini, "Accuracy of rotational parameters predicted by high-level quantum-chemical calculations: Case study of sulfur-containing molecules of astrochemical interest," *J. Chem. Theory Comput.* **14**, 5360–5371 (2018).
- <sup>64</sup>C. Puzzarini, M. Heckert, and J. Gauss, "The accuracy of rotational constants predicted by high-level quantum-chemical calculations. I. Molecules containing first-row atoms," *J. Chem. Phys.* **128**, 194108 (2008).
- <sup>65</sup>I. M. Mills, "Vibration-rotation structure in asymmetric-and symmetric-top molecules," *Mol. Spectrosc.* **1**, 115 (1972).
- <sup>66</sup>V. Barone, "Anharmonic vibrational properties by a fully automated second-order perturbative approach," *J. Chem. Phys.* **122**, 014108 (2005).
- <sup>67</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian16 Revision C.01, Gaussian, Inc., Wallingford, CT, 2016.
- <sup>68</sup>J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, and P. G. Szalay, "CFOUR, coupled-cluster techniques for computational chemistry, a quantum-chemical program package," with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, O. Christiansen, F. Engel, R. Faber, M. Heckert, O. Heun, M. Hilgenberg, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, T. Kirsch, K. Klein, W. J. Lauderdale, F. Lipparini, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, and J. D. Watts, and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version see <http://www.cfour.de>.
- <sup>69</sup>D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowitz, T.-C. Jagau, P. G. Szalay, J. Gauss, and J. F. Stanton, "Coupled-cluster techniques for computational chemistry: The CFOUR program package," *J. Chem. Phys.* **152**, 214108 (2020).
- <sup>70</sup>B. A. McGuire, "2018 census of interstellar, circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules," *Astrophys. J., Suppl. Ser.* **239**, 17 (2018).
- <sup>71</sup>A. H. Saleck, R. Simon, N. Schneider, and G. Winnewisser, "Detection of interstellar  $^{12}\text{C}^{15}\text{N}$ ," *Astrophys. J. Lett.* **414**, L133 (1993).
- <sup>72</sup>J. Cernicharo, M. Guélin, M. Agúndez, M. C. McCarthy, and P. Thaddeus, "Detection of  $\text{C}_5\text{N}^-$  and vibrationally excited  $\text{C}_6\text{H}$  in IRC+10216," *Astrophys. J. Lett.* **688**, L83 (2008).
- <sup>73</sup>N. Marcelino, M. Agúndez, B. Tercero, C. Cabezas, C. Bermúdez, J. D. Gallego, P. deVicente, and J. Cernicharo, "Tentative detection of  $\text{HC}_5\text{NH}^+$  in TMC-1," *Astron. Astrophys.* **643**, L6 (2020).
- <sup>74</sup>M. Melosso, A. Melli, C. Puzzarini, C. Codella, L. Spada, L. Dore, C. Degli Esposti, B. Lefloch, R. Bachiller, C. Ceccarelli, J. Cernicharo, and V. Barone, "Laboratory measurements and astronomical search for cyanomethanimine," *Astron. Astrophys.* **609**, A121 (2018).
- <sup>75</sup>C. Puzzarini, G. Cazzoli, and J. Gauss, "The rotational spectra of  $\text{HD}^{17}\text{O}$  and  $\text{D}_2^{17}\text{O}$ : Experiment and quantum-chemical calculations," *J. Chem. Phys.* **137**, 154311 (2012).
- <sup>76</sup>C. Puzzarini, J. Bloino, N. Tasinato, and V. Barone, "Accuracy and interpretability: The devil and the holy grail. New routes across old boundaries in computational spectroscopy," *Chem. Rev.* **119**, 8131–8191 (2019).