

# Unraveling the Formation of HCPH( $X^2A'$ ) Molecules in Extraterrestrial Environments: Crossed Molecular Beam Study of the Reaction of Carbon Atoms, $C(^3P_j)$ , with Phosphine, $PH_3(X^1A_1)$

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The reaction between ground state carbon atoms,  $C(^3P_j)$ , and phosphine,  $PH_3(X^1A_1)$ , was investigated at two collision energies of 21.1 and 42.5 kJ mol<sup>-1</sup> using the crossed molecular beam technique. The chemical dynamics extracted from the time-of-flight spectra and laboratory angular distributions combined with ab initio calculations propose that the reaction proceeds on the triplet surface via an addition of atomic carbon to the phosphorus atom. This leads to a triplet CPH<sub>3</sub> complex. A successive hydrogen shift forms an HCPH<sub>2</sub> intermediate. The latter was found to decompose through atomic hydrogen emission leading to the *cis/trans*-HCPH( $X^2A'$ ) reaction products. The identification of *cis/trans*-HCPH( $X^2A'$ ) molecules under single collision conditions presents a potential pathway to form the very first carbon–phosphorus bond in extraterrestrial environments like molecular clouds and circumstellar envelopes, and even in the postplume chemistry of the collision of comet Shoemaker–Levy 9 with Jupiter.

## 1. Introduction

Despite the large cosmic abundance of phosphorus in the galaxy of  $3 \times 10^{-7}$  relative to atomic hydrogen<sup>1</sup> and the strong implications of organophosphorus chemistry in astrobiology,<sup>2</sup> only two phosphorus-bearing molecules have been detected in the interstellar medium to date. These are phosphorus nitride (PN)<sup>3</sup> and phosphorus carbide (PC).<sup>4</sup> Both diatomic molecules were observed in the circumstellar envelope of the carbon star IRC+10216;<sup>5</sup> phosphorus nitride is also present in cold molecular clouds such as in the Taurus Molecular Cloud-1 (TMC-1).<sup>6,7</sup> Charnley et al. also indicated that the simplest closed shell hydride–phosphine (PH<sub>3</sub>)—should be present at early stages of the life span of cold molecular clouds; the subsequent chemical processing of phosphine is suggested to be dominated by atomic hydrogen, oxygen, and nitrogen; these processes are expected to lead to phosphorus oxide (PO) and phosphorus nitride (PN).<sup>8</sup> However, these conclusions were drawn from chemical reaction models holding various limitations. First, the majority of the reactions of phosphorus-bearing molecules included in these kinetic models have not been investigated in the laboratory: the rate constants of these processes were only guessed. Second, it is very surprising that the chemistry of carbon—despite the astrobiological relevance—is not included in these models. Note, for instance, that the only bimolecular reaction between a molecule containing phosphorus and carbon considered was the reaction of the phosphorus cation (P<sup>+</sup>) with methane (CH<sub>4</sub>).<sup>9</sup> Due to these limited studies to date, the mechanisms leading to the formation of the very first carbon–phosphorus bond in the interstellar medium still remain to be ascertained.

During the last years, various laboratory experiments and computations have been conducted to shed light on the formation pathways and spectroscopic properties of potential organophosphorus molecules in extraterrestrial environments. These in-

cluded, for instance, an investigation of the reaction of P<sup>+</sup> with C<sub>3</sub>H<sub>2</sub> isomers,<sup>10</sup> the microwave spectrum of the CH<sub>2</sub>P isomer,<sup>11</sup> the thermodynamic stabilities of the CH<sub>2</sub>P isomer with respect to the *cis/trans*-HCPH conformers, and theoretical studies on carbon–phosphorus clusters of the generic formula C<sub>*n*</sub>P (*n* = 1–3)<sup>12</sup> together with H<sub>2</sub>CCP,<sup>13</sup> HCP,<sup>14</sup> and C<sub>3</sub>P.<sup>15</sup> Despite these investigations, the basic reaction route to form the fundamental carbon–phosphorus bond in extraterrestrial environments still remains elusive.

In this paper, we investigate to what extent the neutral–neutral reaction of carbon atoms,  $C(^3P_j)$ , with phosphine,  $PH_3(X^1A_1)$ , can lead to the formation of a carbon–phosphorus bond in extraterrestrial environments. Utilizing a crossed molecular beams machine, we unravel the energy-dependent chemical dynamics of the reaction of atomic carbon,  $C(^3P_j)$ , with phosphine,  $PH_3(X^1A_1)$ , under single collision conditions. The measured product velocity and angular distributions identify the primary reaction channel(s) and obtain dynamics information on the elementary steps of this reaction. Electronic structure calculations on the triplet CPH<sub>3</sub> and doublet CPH<sub>2</sub> surfaces supplement our experimental data.

## 2. Experimental Section

The experiments were carried out under single collision conditions in a crossed molecular beams machine at The University of Hawai'i.<sup>16</sup> Pulsed beams of ground state carbon atoms,  $C(^3P_j)$ , were produced in the primary source chamber by laser ablation of graphite at 266 nm by tightly focusing 8–11 mJ per pulse at a repetition rate of 30 Hz onto a rotating graphite rod. The ablated species were seeded in helium carrier gas (99.9999%; 3040 Torr) released by a Proch-Trickl pulsed valve. After passing a skimmer, a four-slot chopper wheel selected a part of the carbon beam at peak velocities  $v_p$  of  $2024 \pm 9$  ms<sup>-1</sup> and  $2988 \pm 18$  ms<sup>-1</sup> (Table 1). The ablation beam also contained dicarbon and tricarbon molecules. However, optimiz-

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**TABLE 1: Peak Velocities ( $v_p$ ), Speed Ratios ( $S$ ), Center-of-Mass Angles ( $\Theta_{CM}$ ), Together with the Nominal Collision Energies of the Carbon and the Phosphine Reactants ( $E_c$ )**

beam	$v_p$ (ms $^{-1}$ )	$S$	$E_c$ (kJ mol $^{-1}$ )	$\Theta_{CM}$
PH $_3$ (X $^1$ A $_1$ )	809 $\pm$ 17	13.7 $\pm$ 0.9		
C( $^3$ P)/He	2024 $\pm$ 9	5.1 $\pm$ 0.1	21.1 $\pm$ 0.1	48.6 $\pm$ 0.8
C( $^3$ P)/He	2988 $\pm$ 18	2.5 $\pm$ 0.1	42.5 $\pm$ 0.4	37.5 $\pm$ 0.8

ing the pulsed valve–laser delay time and focusing the laser tightly reduced the dicarbon concentrations to less than 2% compared to the atomic carbon beam; also, we could not detect any signal from the reaction of dicarbon and tricarbon with phosphine at larger masses. The atomic carbon beam crossed a pulsed phosphine (99.9995+%, electronic grade, Aldrich) beam released by a second pulsed valve at a pressure of 550 Torr perpendicularly under well-defined collision energies of 21.1  $\pm$  0.1 kJ mol $^{-1}$  and 42.5  $\pm$  0.4 kJ mol $^{-1}$  in the interaction region. The reactively scattered species were monitored using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron impact ionization of the molecules. The detector can be rotated within the plane defined by the primary and the secondary reactant beams to take angularly resolved TOF spectra. By integrating the TOF spectra at distinct laboratory angles, we obtained the laboratory angular distribution, i.e., the integrated signal intensity of an ion of distinct  $m/z$  versus the laboratory angle. Information on the chemical dynamics were extracted by fitting these TOF spectra and the angular distribution in the laboratory frame (LAB) using a forward-convolution routine.<sup>17</sup> This approach initially presumes the angular flux distribution  $T(\theta)$  and the translational energy flux distribution  $P(E_T)$  in the center-of-mass system (CM) assuming mutual independence. TOF spectra and the laboratory angular distributions are then calculated from these  $T(\theta)$  and  $P(E_T)$  convoluted over the apparatus functions to obtain simulations of the experimental data.

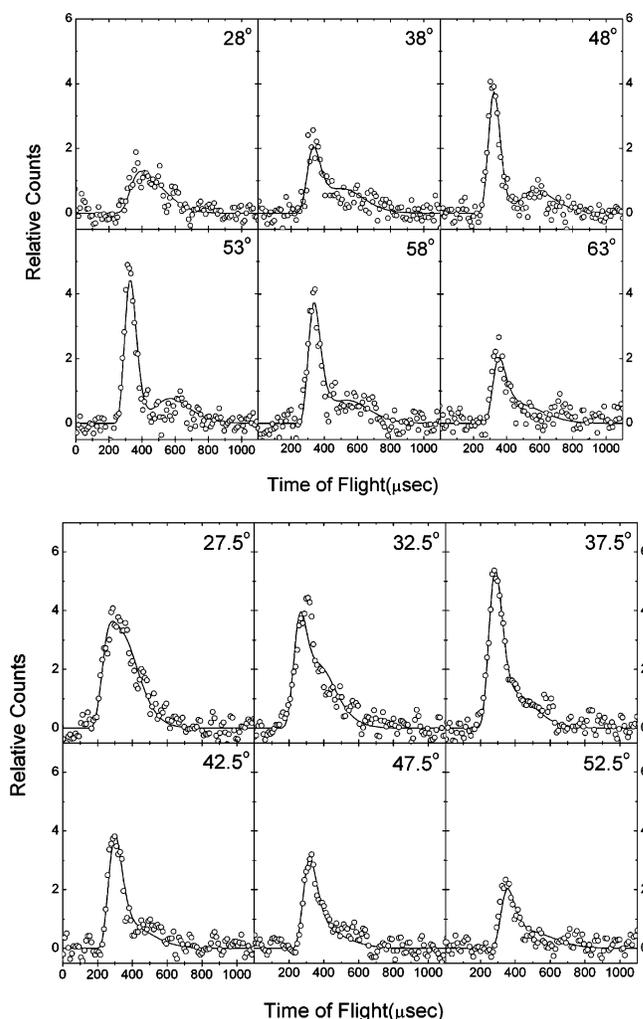
### 3. Electronic Structure Calculations

The triplet potential energy surface (PES) of the reaction of ground state carbon with phosphine was examined in terms of ab initio molecular orbital methods. We have employed the hybrid density functional B3LYP method, i.e., Becke's three-parameter nonlocal exchange functional<sup>18</sup> with the nonlocal correlation functional of Lee, Yang, and Parr<sup>19</sup> and the 6-311G-(d,p) basis set.<sup>20</sup> The structures of the intermediates and transition states have been confirmed with the vibrational analysis; all relative energies are the corrected values of the zero-point vibrational energies with the B3LYP/6-311G(d,p) level of calculation. The coupled cluster CCSD(T)<sup>21,22</sup> calculations with the ccPVTZ basis set<sup>23</sup> have also been performed for selected reaction products at the optimized structures obtained with the B3LYP method in order to refine the energetics. All computations have been carried out using the Gaussian 98 program package.<sup>24</sup>

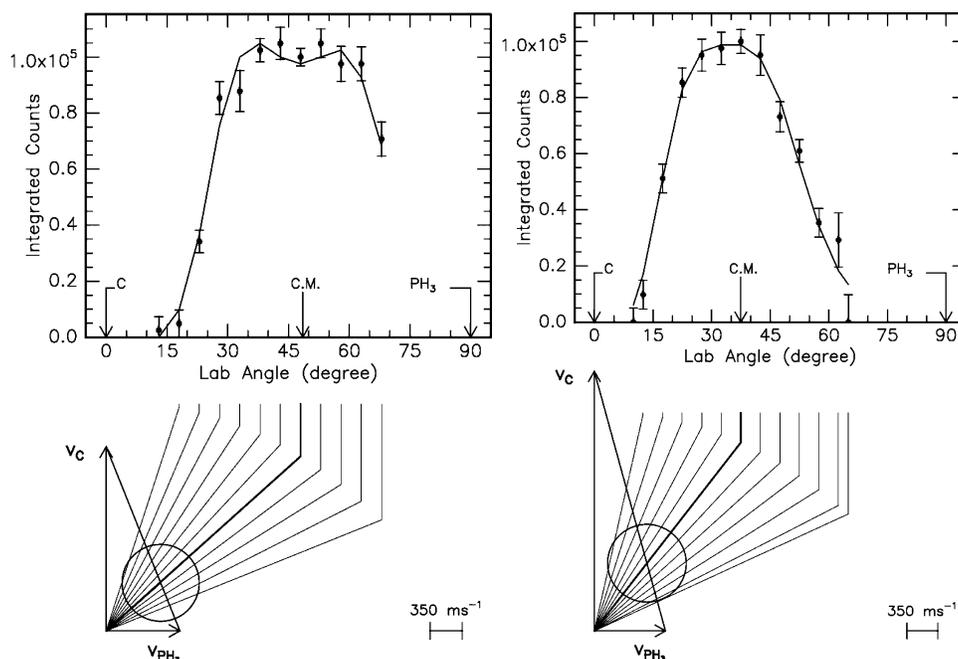
### 4. Results

**4.1. Laboratory Data.** Reactive scattering signal was observed at mass-to-charge ratios,  $m/z$ , of 45 (CPH $_2^+$ ), 44 (CPH $^+$ ), and 43 (CP $^+$ ). Figure 1 depicts selected time-of-flight spectra (TOF) at the most intense mass-to-charge value,  $m/z = 45$  (CPH $_2^+$ ), for various scattering angles at both collision energies. At each collision energy investigated, the TOF spectra taken at mass-to-charge ratios from 45 to 43 are superimposable. This finding indicates that  $m/z = 44$  and 43 result from dissociative ionization of the CPH $_2$  parent molecule in the electron impact

ionizer. Also, we can conclude that only the atomic carbon versus atomic hydrogen exchange pathway is open in the  $m/z$  range of 45–43, resulting in the synthesis of molecules of the generic formula CPH $_2$  plus atomic hydrogen. It should be noted that, based on our signal-to-noise ratio at  $m/z = 44$ , upper limits of about 5% can be derived of the molecular hydrogen elimination channel. Also, a signal at higher masses was not detected, suggesting that the dicarbon and tricarbon molecules do not contribute to the reactive scattering signal (section 2). Further, we can integrate the recorded time-of-flight spectra to obtain the laboratory angular distribution (LAB). Figure 2 depicts the most probable Newton diagrams of the reactions of carbon atoms with phosphine together with the derived laboratory angular distributions of the CPH $_2$  isomer(s) recorded at the most intense mass-to-charge ratio of  $m/z = 45$  (CPH $_2^+$ ). Both distributions are very broad and extend about 55 $^\circ$  in the scattering plane defined by both beams. In summary, the analysis



**Figure 1.** Selected time-of-flight data for  $m/z = 45$  (CPH $_2^+$ ) recorded at collision energies of 21.1 (top) and 42.5 kJ mol $^{-1}$  (bottom) at various laboratory angles. The circles indicate the experimental data; the solid lines indicate the calculated fit.

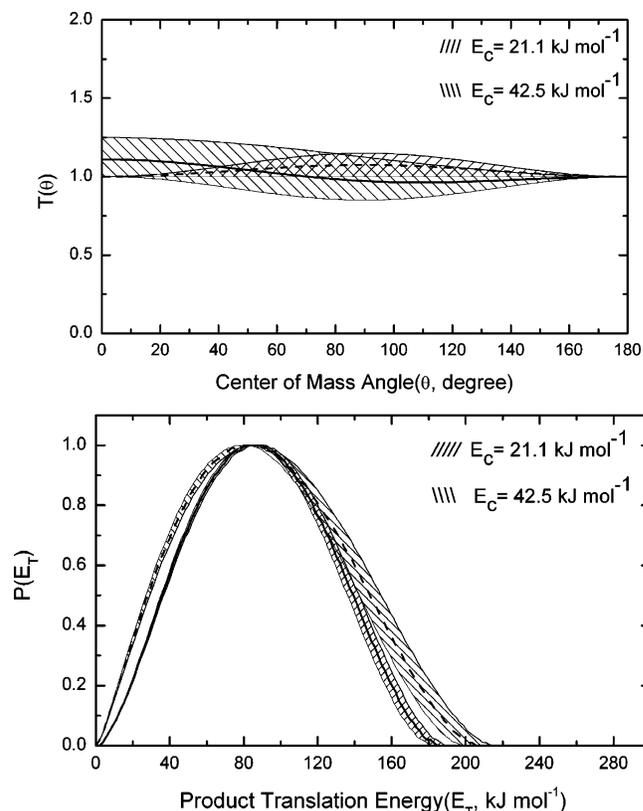


**Figure 2.** Newton diagrams for the reaction of carbon atoms with phosphine at two collision energies of 21.1 (left) and 42.5 kJ mol<sup>-1</sup> (right) together with the corresponding laboratory angular distribution of the CPH<sub>2</sub> radical(s) recorded at  $m/z = 45$  (CPH<sub>2</sub><sup>+</sup>). Circles and error bars indicate experimental data; the solid lines indicate the calculated distribution with the best-fit center-of-mass functions.

of the laboratory data alone entails the presence of a carbon versus atomic hydrogen replacement channel leading to CPH<sub>2</sub> isomer(s) under single collision conditions.

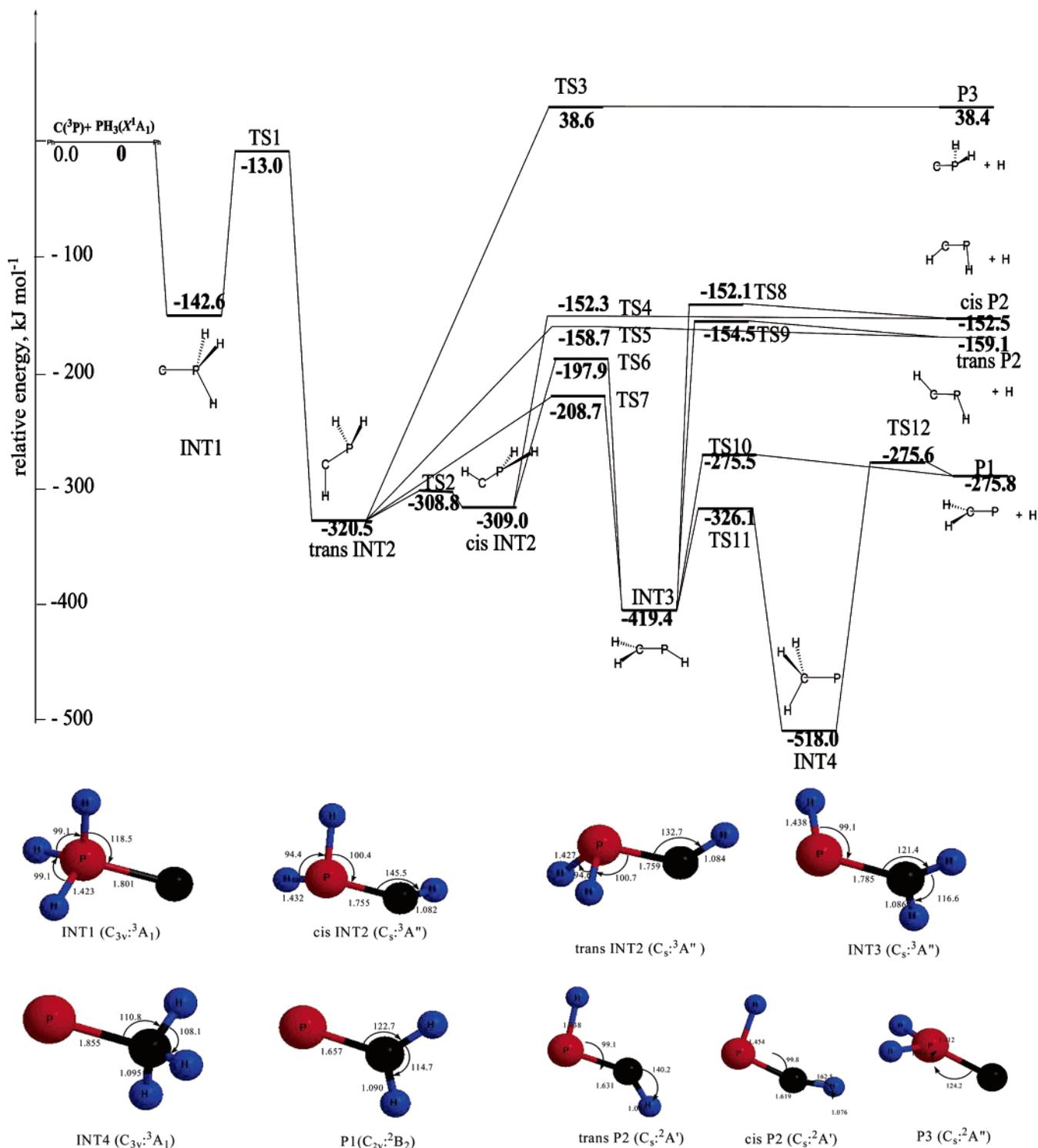
**4.2. Center-of-Mass Translational Energy,  $P(E_T)$ , and Angular Distribution,  $T(\theta)$ .** For two collision energies of 21.1 and 42.5 kJ mol<sup>-1</sup>, the translational energy distributions in the center-of-mass frame,  $P(E_T)$ , are shown in Figure 3. We obtained best fits of the TOF spectra and of the LAB distributions with a single channel fit, i.e., one center-of-mass translational energy distribution at each collision energy. Both  $P(E_T)$ 's extended to a maximum translational energy,  $E_{\max}$ , of 185 and 205 kJ mol<sup>-1</sup> at collision energies of 21.1 and 42.5 kJ mol<sup>-1</sup>, respectively. Since the coreaction product is a light hydrogen atom, the high-energy tails are relatively insensitive: cutting or adding up to 10 kJ mol<sup>-1</sup> has no influence on the fit. It should be stressed that the maximum translational energy released depicts the sum of the collision energy and the reaction exoergicity. Therefore,  $E_{\max}$  can be employed to estimate the energetics of the carbon plus phosphine reaction. Averaging over both collision energies, the reaction to form the CPH<sub>2</sub> isomer(s) plus atomic hydrogen under single collision conditions was found to be exoergic by  $165 \pm 10$  kJ mol<sup>-1</sup>. Also, the translational energy distributions were found to peak well away from zero translational energy. As a matter of fact, the distributions almost show a symmetric, Gaussian-like shape. Comparing this finding with previous reactions of carbon atoms studied under single collision conditions,<sup>25</sup> we find that a relatively short lifetime of the decomposing intermediate is expected.

The center-of-mass angular flux distribution,  $T(\theta)$ , of the atomic hydrogen loss pathway(s) (Figure 3) assists in extracting additional information on the scattering dynamics. Most importantly, both distributions illustrate intensity over the complete angular range from 0° to 180°. This finding suggests that the chemical dynamics are indirect and that the reaction of atomic carbon with phosphine proceeds via formation of CPH<sub>3</sub> complex(es). Also, as the collision energy rises, the distribution becomes slightly more forward peaked with respect to the carbon beam; intensity ratio at the poles of  $T(0^\circ)/T(180^\circ) = 1.13 \pm 0.13$  were



**Figure 3.** Center-of-mass translational energy flux (bottom) and angular distributions (top) for the reaction of carbon atoms with phosphine. The hatched areas indicate the error limits of the distributions; the lines within the hatched areas indicate the best fit functions.

derived. This may suggest that the lifetime of the decomposing intermediate(s) is—at the higher collision energy—comparable to its rotational period. The observed collision-energy dependence of the center-of-mass angular flux distributions could indicate the existence of an osculating complex.<sup>26</sup> By identifying



**Figure 4.** Relevant stationary points on the triplet  $\text{CPH}_3$  and doublet  $\text{CPH}_2$  potential energy surfaces of the reaction of ground state atomic carbon with phosphine. Angles are given in degrees and bond distances in angstroms. The point groups and symmetries of the electronic wave functions are also included.

the decomposing complex(es) and taking into account the intensity ratio at the poles, we can estimate its lifetime (section 5.2).

## 5. Discussion

**5.1. Energetic Considerations.** The center-of-mass translational energy distributions suggest that the reaction to form the  $\text{CPH}_2$  radical(s) plus atomic hydrogen is exoergic by  $165 \pm 10 \text{ kJ mol}^{-1}$ . Considering the energetics to form various  $\text{CPH}_2$

isomers plus atomic hydrogen (Figure 4), the experimental reaction energy correlates nicely with the formation of the *trans*-HCPH ( $\text{C}_s$ ,  $X^2\text{A}'$ ,  $\Delta_r G = -159 \text{ kJ mol}^{-1}$  [ $-144 \text{ kJ mol}^{-1}$ ]) and/or *cis*-HCPH ( $\text{C}_s$ ,  $X^2\text{A}'$ ,  $\Delta_r G = -153 \text{ kJ mol}^{-1}$  [ $-136 \text{ kJ mol}^{-1}$ ]) isomer calculated at the B3LYP/6-311G(d,p) level of theory; the numbers in square brackets depict the energetics calculated at the CCSD(T)/cc-pVTZ level of theory at B3LYP/6-311g(d,p) optimized geometry. Since the reaction energies of both conformers differ by only  $6 \text{ kJ mol}^{-1}$ , it is not possible

to decide to what extent the *trans* versus the *cis* structure is formed. This energy difference is in line with an earlier study by Schaefer et al. suggesting that the *trans* structure is favored by 8 kJ mol<sup>-1</sup> on the CCSD(T)/cc-pVTZ level of theory.<sup>27</sup> Note that the formation of the thermodynamically most stable isomer, H<sub>2</sub>CP (*C*<sub>2v</sub>, X<sup>2</sup>B<sub>2</sub>, Δ<sub>r</sub>G = -276 kJ mol<sup>-1</sup> [-264 kJ mol<sup>-1</sup>]), does not correlate with our experimentally derived data. Our computational study at the B3LYP/6-311G(d,p) level of theory suggested an energy difference between the H<sub>2</sub>CP(X<sup>2</sup>B<sub>2</sub>) and the *trans*-HCPH (*C*<sub>s</sub>, X<sup>2</sup>A') structure of 116 kJ mol<sup>-1</sup>—in excellent agreement with a previous data of 117 kJ mol<sup>-1</sup> on the CCSD(T)/cc-pVTZ level of theory.<sup>27</sup> Finally, the fourth isomer, CPH<sub>2</sub> (*C*<sub>s</sub>, X<sup>2</sup>A', Δ<sub>r</sub>G = +38 kJ mol<sup>-1</sup> [+47 kJ mol<sup>-1</sup>]), which was not investigated by Schaefer et al., was found to be the least stable structure. At our lower collision energy, this isomer is energetically not accessible. However, at the higher collision energy of 42.5 kJ mol<sup>-1</sup>, minor contributions of this isomer to the reactive scattering signal at *m/z* = 45 cannot be ruled out. Having established the *trans/cis*-HCPH(X<sup>2</sup>A') isomer as the sole (*E*<sub>c</sub> = 21.1 kJ mol<sup>-1</sup>) and dominant (*E*<sub>c</sub> = 42.5 kJ mol<sup>-1</sup>) reaction product, we can utilize the center-of-mass translational energy distributions to derive the fraction of the energy channeling into the translational modes of the products. The averaged fraction of the translational energy was computed to be 48 ± 2% almost invariant on the collision energy.

**5.2. Reaction Dynamics.** What reaction dynamics can be proposed to associate the structures of the *trans/cis*-HCPH(X<sup>2</sup>A') products with the carbon atom and phosphine reactants? First, the shapes of the *T*(θ)s (section 4.2) demonstrate that the reaction is indirect and involves the formation of CPH<sub>3</sub> intermediate(s). Based on this information we now attempt to unravel the underlying mechanism for the formation of HCPH(X<sup>2</sup>A'). For this, we compare first the structure of the phosphine reactant with the reaction product. The HCPH(X<sup>2</sup>A') isomer carries a hydrogen atom at both the carbon and the phosphorus atom. To connect HCPH(X<sup>2</sup>A') to the phosphine reactant via a reaction intermediate, it is necessary that in the reversed reaction a hydrogen atom adds to the carbon–phosphorus double bond either at the carbon or at the phosphorus atom, forming intermediate **INT3** and/or *trans/cis*-**INT2**, respectively (Figure 4). These structures are stabilized by 419 and 321 kJ mol<sup>-1</sup> (*trans*) as well as 309 kJ mol<sup>-1</sup> (*cis*) compared to the separated reactants. However, neither **INT2** nor **INT3** correlates with the reactants: both intermediates carry only two and one hydrogen atoms, respectively, at the phosphorus atom, whereas three hydrogen atoms are connected to the phosphorus atom of the phosphine molecule. Therefore, we have to recommend that at least one additional reaction step connects the reactants with the proposed intermediate **INT2**.

As a matter of fact, our electronic structure calculations agree nicely with this proposed reaction sequence (Figure 4). Here, atomic carbon was found to add without entrance barrier to the phosphorus atom of the phosphine molecule, forming a weakly bound (-143 kJ mol<sup>-1</sup>) CPH<sub>3</sub>(*C*<sub>3v</sub>, <sup>3</sup>A<sub>1</sub>) collision complex **INT1**. The latter can undergo a hydrogen shift via **TS1** to the proposed *trans*-**INT2**. Here, *cis*- and *trans*-**INT2** can be easily interconverted via a barrier of less than 1 kJ mol<sup>-1</sup> through **TS2**. Both *cis*- and *trans*-**INT2** can undergo hydrogen migration via **TS6** and **TS7**, respectively, to **INT3**. We should mention that our computations also located the energetically most stable PCH<sub>3</sub> isomer (**INT4**) on the triplet surface. However, since all hydrogen atoms are connected to the carbon atom, this **INT4** can only fragment via atomic hydrogen loss to form H<sub>2</sub>CP(X<sup>2</sup>B<sub>2</sub>). This structure, however, was not identified as the

reaction product (section 4.1). Therefore, we conclude that **INT4** is not the decomposing intermediate.

How can we discriminate to what extent **INT2** or **INT3** or even both intermediates are responsible for the formation of the *trans/cis*-HCPH(X<sup>2</sup>A') reaction products? First of all, we should recall that at the higher collision energy of 42.5 kJ mol<sup>-1</sup>, the experimental data could be fit with a forward-scattered—with respect to the carbon beam—center-of-mass angular distribution (Figure 3; section 4.3). This finding indicates that, in the decomposing complex, the incorporated carbon atom and the leaving hydrogen atom must be located on different sides of the rotation axis.<sup>28</sup> Therefore, we will investigate the location of the principal rotational axes of *cis/trans*-**INT2** and **INT3** to see which rotation would fulfill the above requirement. A detailed inspection of the principal axes (Figure 5) suggests that in **INT3** neither rotations around the *A*, nor *B*, nor the *C* axis can result in a forward scattering of the *cis/trans*-HCPH(X<sup>2</sup>A') product with respect to the carbon beam. However, a look at the *B/C* rotation axis of *cis/trans*-**INT2** shows that the carbon atom and the ejected hydrogen atom reside on opposite sides of the rotational axis. Therefore, *B/C*-like rotations of *cis/trans*-**INT2** can explain the experimentally observed forward peaking of the center-of-mass angular distribution.

Having inferred *cis/trans*-**INT2** as the decomposing intermediates and *B* and *C* as the rotational axes, we attempt now to estimate the lifetime of the intermediates at a collision energy of 42.5 kJ mol<sup>-1</sup>. Recall that the rotational period of *cis/trans*-**INT2** acts as a clock in the molecular beam experiment and can be utilized to estimate the lifetime  $\tau$  of the decomposing complex. Here, the osculating model relates the intensity ratio of *T*(θ) at both poles to  $\tau$  via eq 1

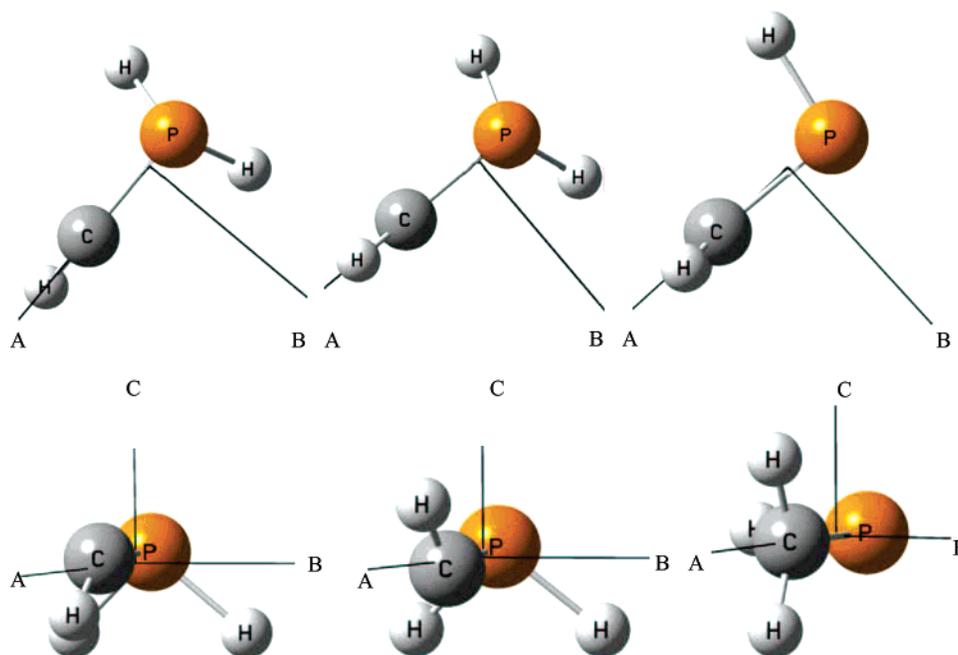
$$I(180^\circ)/I(0^\circ) = \exp\left(-\frac{t_{\text{rot}}}{2\tau}\right) \quad (1)$$

where  $t_{\text{rot}}$  represents the rotational period with

$$t_{\text{rot}} = 2\pi I_i/L_{\text{max}} \quad (2)$$

$I_i$  stands for the moment of inertia of the complex rotating around the *i*-axis (*i* = *A*, *B*, *C*), and  $L_{\text{max}}$  is the maximum orbital angular momentum. Using the ab initio geometries of the *cis/trans*-**INT2** intermediates (Figure 4), we can compute the moments of inertia (Table 2). Taking the maximum impact parameter to be on the order of 3.2 Å estimated from the hard sphere model of a reaction having no entrance barrier,<sup>29</sup> the reduced mass of the reactants of 8.7 × 10<sup>-3</sup> kg, and the relative velocity of the reactants as computed from Table 1, a maximum orbital angular momentum of 1.4 × 10<sup>-32</sup> kg m<sup>2</sup> s<sup>-1</sup> is obtained. Employing the rotational constants from our ab initio calculations, we calculate  $\tau(A) = 0.04$  ps and  $\tau(B/C) = 0.37$  ps. Recalling that reactions with collision times ≪ 0.1 ps follow direct scattering dynamics without complex formation,<sup>29</sup> the *T*(θ)s should be strongly forward scattered and are expected to show less intensity at backward angles as found experimentally. Therefore, *cis/trans*-**INT2** molecules rotating around the *A* axis can be safely excluded. This finding correlates well with our investigation of the accessible rotational axis (see above) which suggested that the *cis/trans*-HCPH(X<sup>2</sup>A') products should be excited to *B/C*-like rotations; also, the lifetime of the decomposing complex is estimated to be about 0.37 ps.

To compare our experimental results with the theoretical predictions, we conducted a brief RRKM study of this system. The methods applied are described in refs 30 and 31.<sup>30,31</sup> This approach computes individual rate constants and product branching ratios within the limit that the energy of the



**Figure 5.** Two (upper row) and three-dimensional structures (lower row) of the *cis*-INT2 (left), *trans*-INT2 (center), and INT3 (right) intermediates together with their A and B principal rotational axes; projections parallel to the C axes are shown.

**TABLE 2: Moments of Inertia,  $I$ , and Estimated Lifetimes,  $\tau$ , of Various Reaction Intermediates<sup>a</sup>**

	$I_A$ (kg m <sup>2</sup> )	$I_B$ (kg m <sup>2</sup> )	$I_C$ (kg m <sup>2</sup> )
<i>cis</i> -INT2	$7.05 \times 10^{-47}$	$5.72 \times 10^{-46}$	$5.76 \times 10^{-46}$
<i>trans</i> -INT2	$7.09 \times 10^{-47}$	$5.70 \times 10^{-46}$	$5.72 \times 10^{-46}$
	$\tau(A)$ (ps)	$\tau(B)$ (ps)	$\tau(C)$ (ps)
<i>cis</i> -INT2	0.04	0.37	0.37
<i>trans</i> -INT2	0.04	0.37	0.37

<sup>a</sup> The principal axes of the rotating intermediates are shown in Figure 5.

decomposing intermediate is completely randomized. Our calculations indicate that *trans*- and *cis*-INT2 isomerize rapidly; these intermediates are expected to be formed in a 1:1 ratio. Most importantly, the rate constants of the decomposition of *trans/cis*-INT2 to form *cis/trans*-P2 (HCPH) + H are at our collision energies up to 3 orders of magnitude larger than the competing rearrangement to INT3. Therefore, both the experiments and statistical calculations support the formation of the *cis/trans*-HCPH( $X^2A'$ ) product.

## 6. Conclusions

We investigated the reaction of ground state carbon atoms, C(<sup>3</sup>P<sub>2</sub>), with phosphine, PH<sub>3</sub>(<sup>1</sup>A<sub>1</sub>), at two collision energies of 21.1 and 42.5 kJ mol<sup>-1</sup> using the crossed molecular beams technique. The chemical dynamics were found to be indirect and proceed without entrance barrier via the addition of the carbon atom to the phosphorus atom of the phosphine molecule on the triplet surface. A successive hydrogen shift formed a HCPH<sub>2</sub> intermediate which fragmented via an atomic hydrogen loss to the *cis/trans*-HCPH reaction products. The identification of *cis/trans*-HCPH molecules under single collision conditions presents a potential pathway to form the very first carbon–phosphorus bond in molecular clouds and in circumstellar envelopes.

These examinations also hold strong implications to the postplume chemistry of the collision of comet Shoemaker–Levy

9 with Jupiter<sup>32</sup> and to astrobiology.<sup>33</sup> On July 16–22, 1994, about 20 fragments of the split nucleus of the comet impacted Jupiter, causing enormous atmospheric disturbances and chemical reactions. Prior to the impact, phosphine was detected in the atmosphere in Jupiter in 1976 via its 943 cm<sup>-1</sup> band;<sup>34</sup> the identification was confirmed by the Infrared Space Observatory (ISO)<sup>35,36</sup> and during the recent 2000 flyby of the Cassini Space Probe.<sup>37</sup> In the troposphere of the planet, phosphine abundances of a few 10<sup>-6</sup> with respect to molecular hydrogen were derived.<sup>38</sup> The impact itself led to temperatures in the Jovian atmosphere of up to a few 1000 K.<sup>32</sup> Under these conditions, chemical models predict carbon to be present only in its atomic form. In the postimpact plume chemistry, these carbon atoms could also react with phosphine to form the *cis/trans*-HPCH molecules. From the astrobiological viewpoint, it should be noted that orthophosphoric acids (H<sub>x</sub>PO<sub>4</sub><sup>3-x</sup> (x = 1–3)) are the key phosphorus-bearing moieties in contemporary biochemistry.<sup>39</sup> As of today, it is still unclear how these molecules and the first phosphorus–oxygen bonds in general are formed. Recent laboratory experiments suggested that the formation process could involve an anaerobic hydrolysis of phosphorus alkynes and their derivatives under thermal and photochemical conditions.<sup>40</sup> Therefore, a hydrolysis of *cis/trans*-HCPH or their partially dehydrogenated form—HCP—may have contributed to the formation of alkylphosphonic acids (methyl, ethyl) as extracted from the Murchison meteorite.<sup>41</sup>

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## References and Notes

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