

Gas-Phase Study of the Elementary Reaction of the D1-Ethynyl Radical (C_2D ; $\text{X}^2\Sigma^+$) with Propylene (C_3H_6 ; $\text{X}^1\text{A}'$) Under Single Collision Conditions

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ABSTRACT

The bimolecular gas-phase reactions of the D1-ethynyl radical (C_2D ; $X^2\Sigma^+$) with propylene (C_3H_6 ; $X^1\text{A}'$) and partially substituted D3-3,3,3-propylene ($\text{C}_2\text{H}_3\text{CD}_3$; $X^1\text{A}'$) were studied under single collision conditions utilizing the crossed molecular beams technique. Combining our laboratory data with electronic structure and statistical calculations, the D1-ethynyl radical is found to add without barrier to the C1 and C2 carbons of the propylene reactant, resulting in doublet $\text{C}_5\text{H}_6\text{D}$ intermediate(s) with lifetime(s) longer than their rotational period(s). These intermediates undergo isomerization and unimolecular decomposition via atomic hydrogen loss through tight exit transition states forming predominantly *cis/trans*-3-penten-1-yne ($(\text{HCC})\text{CH}=\text{CH}(\text{CH}_3)$) and to a minor amount 3-methyl-3-buten-1-yne ($(\text{HCC})\text{C}(\text{CH}_3)=\text{CH}_2$) via overall exoergic reactions. Although the title reaction does not lead to the cyclopentadiene molecule ($\text{c-C}_5\text{H}_6$, $X^1\text{A}_1$), high temperature environments can convert the identified acyclic C_5H_6 isomers through hydrogen atom assisted isomerization to cyclopentadiene ($\text{c-C}_5\text{H}_6$, $X^1\text{A}_1$). Since both the ethynyl radical and propylene reactants have been observed in cold interstellar environments such as TMC-1 and the reaction is exoergic and all barriers lie below the energy of the separated reactants, the these C_5H_6 product isomers are predicted to form in those low temperature regions.

1. INTRODUCTION

The ethynyl radical (C_2H , $X^2\Sigma^+$) has been recognized by the astrochemistry and planetary science community¹⁻³ as a fundamental building block involved in low-temperature molecular mass growth processes leading to highly unsaturated hydrocarbons – among them aromatic structures like o-benzyne (o- C_6H_4 , $X^1\text{A}_1$),^{4,5} benzene (C_6H_6 , $X^1\text{A}_{1g}$),⁶ and toluene ($\text{C}_6\text{H}_5\text{CH}_3$, $X^1\text{A}'$)⁷ (Scheme 1) along with polyacetylenes such as diacetylene (C_4H_2 , $X^1\Sigma_g^+$)⁸ and triacetylene (C_6H_2 , $X^1\Sigma_g^+$)⁹ in cold molecular clouds like the Taurus Molecular Cloud (TMC-1)⁶ and in hydrocarbon rich atmospheres of planets and their moons such as Titan and Triton.¹⁰ In the interstellar medium (ISM), the ethynyl radical was detected in 1974 by Thaddeus and coworkers¹¹ toward the Orion Molecular Cloud (OMC-1) possibly formed via photodissociation of acetylene (C_2H_2 , $X^1\Sigma_g^+$)¹² or via the barrierless and exoergic bimolecular reactions of ground state carbon (C , ^3P) with triplet carbene (CH_2 , $X^3\text{B}_1$) or the methyldiyne (CH , $X^2\Pi$) radical self-reaction. In hydrocarbon rich atmospheres, solar Lyman- α photons photodissociate acetylene (C_2H_2 , $X^1\Sigma_g^+$) to ethynyl (C_2H , $X^2\Sigma^+$) followed by rapid, barrierless reactions with unsaturated hydrocarbons through stepwise two-carbon molecular mass growth processes holding rate constants of a few $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ even at temperatures as low as 15 K.¹³ Crossed molecular beam studies merged with electronic structure calculations provided knowledge of a rich hydrocarbon chemistry of elementary reactions of ethynyl radicals with unsaturated C_2 to C_8 hydrocarbons with reaction mechanisms ranging from simple ethynyl addition–hydrogen atom elimination pathways along with a conservation of the carbon moieties to unprecedented addition–cyclization pathways leading to aromatic structures like o-benzyne (o- C_6H_4 , $X^1\text{A}_1$),^{4,5} benzene (C_6H_6 , $X^1\text{A}_{1g}$),⁶ and toluene ($\text{C}_6\text{H}_5\text{CH}_3$, $X^1\text{A}'$)⁷ (Scheme 1).

Surprisingly, the elementary reaction of the ethynyl radical with propylene (C_3H_6) as detected in the cold molecular cloud TMC-1¹⁴ and in Titan's atmosphere¹⁵ has not been explored to date under single collision conditions. This system accesses the doublet C_5H_7 potential energy surface (PES) and hence may lead to C_5H_6 isomers, among them the cyclopentadiene molecule (c- C_5H_6 , $X^1\text{A}_1$), which was recently observed toward the molecular cloud TMC-1.¹⁶ Here we reveal the chemical dynamics of the elementary reaction of the D1-ethynyl radical (C_2D , $X^2\Sigma^+$) with propylene (C_3H_6 , $X^1\text{A}'$) along with its partially D3-deuterated counterpart ($\text{C}_2\text{H}_3\text{CD}_3$; $X^1\text{A}'$). Combined with electronic structure calculations, the results propose the formation of partially deuterated *cis/trans*-3-penten-1-yne ((HCC)CH=CH(CH₃)) and 3-methyl-3-buten-1-yne

((HCC)C(CH₃)=CH₂) products through long-lived intermediates initiated by D1-ethynyl radical addition to the α -carbon of propylene; these dynamics are also compared to the isoelectronic cyano (CN, $X^2\Sigma^+$) – propylene (C₃H₆, X^1A') system studied earlier in our group.¹⁷ Although the title reaction does not lead to the cyclopentadiene molecule (c-C₅H₆, X^1A_1), in high temperature environments such as circumstellar envelopes of carbon stars like IRC+10216 close to the central star and planetary nebulae as their descendants along with combustion systems, hydrogen atom assisted isomerization processes could convert the identified acyclic C₅H₆ isomers *cis/trans*-3-penten-1-yne and 3-methyl-3-buten-1-yne to cyclopentadiene (c-C₅H₆, X^1A_1), but not in cold molecular clouds, where the addition of atomic hydrogen to double and triple bonds is hindered by barriers of up to 30 kJ mol⁻¹ due to the low temperatures of 10 K.

2. METHODS

2.1. Experimental Methods. Reactions of the D1-ethynyl radical (C₂D, $X^2\Sigma^+$) with propylene (C₃H₆, $\geq 99\%$, Sigma-Aldrich) and of D3-3,3,3-propylene (C₂H₃CD₃, 99.8% D atom, CDN Isotopes) were performed under single collision conditions utilizing a crossed molecular beams apparatus.¹⁸⁻²⁸ Briefly, a pulsed supersonic beam of D1-ethynyl radicals was generated by laser ablation of a rotating carbon rod with 5–7 mJ of the 266 nm output of a Nd:YAG laser (Quanta-Ray Pro 270, Spectra-Physics); the ablated species subsequently reacted with neat deuterium gas (D₂, 99.999%, Linde), which passed through a Proch-Trickl²⁹ pulsed valve with an open time of 80 μ s at an amplitude of –400 V. Deuterium also acted as a carrier gas with a backing pressure of 4 atm.^{4,6,7,30,31} The pulsed beam passed through a skimmer and was velocity selected by a chopper wheel resulting in a peak velocity (v_p) and speed ratio (S) of 2136 ± 19 m s⁻¹ and 5.5 ± 0.3 , respectively. Since the travel time of D1-ethynyl radicals from the ablation center to the interaction region was about 30 μ s, any species in the A²Π excited state, which has a lifetime of less than 1 μ s, relaxed back to the $X^2\Sigma^+$ ground state. The D1-ethynyl beam crossed then perpendicularly with a pulsed propylene beam ($v_p = 840 \pm 10$, $S = 11.0 \pm 0.2$) resulting in a collision energy (E_c) and center-of-mass (CM) angle (θ_{CM}) of 42.3 ± 0.8 kJ mol⁻¹ and $33.2 \pm 0.5^\circ$, respectively; experiments carried out with D3-3,3,3-propylene ($v_p = 830 \pm 10$ m s⁻¹, $S = 11.0 \pm 0.2$) gave an E_c of 43.3 ± 0.8 kJ mol⁻¹ and θ_{CM} of $34.7 \pm 0.6^\circ$. It is important to note that the primary beam also contains carbon atoms, as well as dicarbon and tricarbon molecules. Previous experiments involving tricarbon reactions with acetylene, ethylene,³² and methylacetylene³³

suggest a high entrance barrier for the reaction of tricarbon with propylene, thus insinuating it was not observed in our experimental conditions. In addition, carbon and dicarbon are lighter by 14 and 2 amu than D1-ethynyl, respectively, indicating that the products of their reactions with propylene do not interfere with the products of the title reaction.

Reactively scattered products were collected by a triply differentially pumped universal detector which is rotatable within the plane of the reactant beams. Neutral products are ionized by electron impact ionization at 80 eV and an emission current of 2 mA. Ionized products are filtered by a quadrupole mass spectrometer (QMS) operating in the time-of-flight (TOF) mode at a constant mass-to-charge ratio (m/z). Up to 2.5×10^6 TOF spectra were taken in 2.5° steps at angles between $19 \leq \theta \leq 49^\circ$ with respect to the D1-ethynyl beam ($\theta = 0^\circ$). A laboratory angular distribution was created by integrating the TOF spectra and normalizing to the CM angle. To gain information on the reaction dynamics, the laboratory angular distribution and TOF spectra were fit utilizing a forward convolution routine; this created user-defined CM translational energy ($P(E_T)$) and angular ($T(\theta)$) flux distributions which were refined iteratively until a satisfactory fit of the laboratory data was achieved.^{34,35} These functions were used to develop a flux contour map, shown as $I(u, \theta) \sim P(u) \times T(\theta)$,³⁶ which portrays an overall image of the outcome of the reaction.

2.2. Computational Methods. Geometries of the reactants, products, reaction intermediates, and transition states on the section of the C_5H_7 PES accessed by the $C_2H + C_3H_6$ reaction were optimized applying the long-range corrected hybrid density functional ω B97X-D³⁷ with the 6-311G(d,p) basis set. Vibrational frequencies for each optimized structure were calculated at the same ω B97X-D/6-311G(d,p) level of theory to assess zero-point vibrational energy corrections (ZPE); the frequencies were also utilized in rate constant computations. Single-point energies for all stationary structures were rectified using the explicitly correlated coupled clusters method with single and double excitations and perturbative treatment of triple excitations, CCSD(T)-F12,^{38,39} with Dunning’s correlation-consistent cc-pVTZ-f12 basis set.⁴⁰ The CCSD(T)-F12/cc-pVTZ-f12// ω B97X-D/6-311G(d,p) + ZPE(ω B97X-D/6-311G(d,p)) dual-level approach is normally capable of achieving accuracy in relative energies within 4 kJ mol⁻¹ or better.⁴¹ The PES calculations were carried out with the GAUSSIAN 09⁴² and MOLPRO 2010⁴³ quantum chemistry software packages.

The Rice–Ramsperger–Kassel–Marcus (RRKM) approach^{44–46} was employed to evaluate energy-dependent rate constants of all unimolecular reaction steps following the initial ethynyl

radical addition to propylene. In these calculations, the internal energy for all the C_5H_7 isomers and transition states was taken as the sum of the collision and chemical activation energy, with the latter being a negative of the relative energy of each species with regard to the separated $C_2H + C_3H_6$ reactants. The internal energy dependent rate constants were computed using our own Unimol code.⁴⁷ The calculations were carried out at the zero-pressure limit emulating the conditions of the crossed molecular beams experiment and those in cold molecular clouds. The computed RRKM rate constants were used to obtain reaction product branching ratios employing the steady-state approximation.⁴⁸

3. RESULTS

3.1. Laboratory Frame. Reactive scattering signal for the reaction of the D1-ethynyl radical (C_2D , $X^2\Sigma^+$, 26 amu) with propylene (C_3H_6 , X^1A' , 42 amu) was observed at $m/z = 67$ ($C_5H_5D^+$) and 66 ($C_5H_4D^+$, $C_5H_6^+$). The TOF spectra obtained at both m/z ratios overlap after scaling suggesting that signal at $m/z = 67$ and 66 originate from the same reaction channel forming the heavy product (C_5H_5D , 67 amu) and atomic hydrogen (H, 1 amu). Signal at $m/z = 66$ is attributed to dissociative ionization of the C_5H_5D product in the electron impact ionizer. The TOF spectra (Figure 1B) for the C_5H_5D product were collected at $m/z = 67$ and are very broad ranging typically from 480 to 820 μs . The laboratory angular distribution (Figure 1A) is nearly symmetric around the center of mass angle Θ_{CM} thus indicating indirect scattering dynamics via C_5H_6D reaction intermediate(s) leading to C_5H_5D plus atomic hydrogen. Therefore, the hydrogen atom is emitted from the propylene reactant.

The reaction of the D1-ethynyl radical (26 amu) with D3-3,3,3-propylene ($C_2H_3CD_3$, X^1A' , 45 amu) was also conducted in order to gain information on the position(s) of atomic hydrogen loss(es), i.e. the methyl group versus the vinyl moiety. Reactive scattering signal for this system was detected at the CM angle of 34° at $m/z = 70$ ($C_5H_2D_4^+$) and 69 ($C_5HD_4^+$, $C_5H_3D_3^+$). The TOF spectra for both $m/z = 70$ and 69 overlap after scaling revealing the likely existence of only one reaction channel, i.e. the atomic hydrogen loss from the vinyl (C_2H_3) moiety; signal at $m/z = 69$ is attributed to dissociative electron impact ionization of $C_5H_2D_4$. This finding reveals that the atomic hydrogen loss occurs at least from the C_1 and/or C_2 carbons of propylene. A comparison of the intensity of the reactive scattering signal at $m/z = 70$ for the D1-ethynyl – D3-3,3,3-propylene system with that at $m/z = 67$ for the D1-ethynyl – propylene system results in a ratio of $(0.8 \pm$

0.5):(1.0 \pm 0.4), respectively. This indicates that the hydrogen atom loss from the methyl group of propylene is only a minor contributor within the error limits.

3.2. Center of Mass Frame. To elucidate the reaction dynamics of the D1-ethynyl radical with propylene, the laboratory data were transformed from the laboratory reference frame to the CM reference frame. The TOF spectra and laboratory angular distribution were fit with a single channel corresponding to the product C₅H₅D plus atomic hydrogen; the best-fit CM functions are shown in Figure 2. The red lines shown in Figure 1B correspond to the best fits of the data within the error limits specified by Figures 1A and 2, which are represented by grey envelopes. The uniqueness of the TOF fits (Figure 1B) is defined by the range of acceptable fits within these error limits. In addition, any reaction channel other than H loss would have a different mass-to-charge ratio and therefore a different flight time, giving a TOF peak in a different position, which also attests to the uniqueness of the fits for the TOF spectra. The CM translational energy distribution, $P(E_T)$ (Figure 2A), provides a maximum translational energy release, E_{\max} , of 150 \pm 17 kJ mol⁻¹. The reaction energy can be recovered using the maximum translational energy and the reaction collision energy, given by $\Delta_r G = E_c - E_{\max}$, for those reaction products born without internal excitation. Hence, this reaction is exoergic by 108 \pm 18 kJ mol⁻¹. Further, the distribution has a maximum at 45 kJ mol⁻¹ which indicates a tight exit transition state from the decomposing C₅H₆D intermediate(s) to C₅H₅D plus atomic hydrogen.⁴⁹ Finally, the CM angular flux distribution, $I(\theta)$ (Figure 2B), provides additional information on the scattering dynamics. This distribution shows a forward-backward symmetry and equal scattering probability in all directions. These findings suggest indirect scattering dynamics through C₅H₆D intermediate(s) with lifetimes longer than the rotational period(s). The flux contour map as shown in Figure 2C reflects these findings. The isotropic scattering signal is the effect of the light hydrogen atom carrying away an insignificant fraction of the total angular momentum.⁵⁰

4. DISCUSSION

The experimental results were combined with electronic structure and statistical calculations to unveil the underlying dynamics of the ethynyl-propylene system (Figures 3–5, Table 1, Tables S1–S3). The doublet PES was studied systematically through ethynyl radical addition to either the central or terminal carbon atoms of the carbon-carbon double bond of the propylene molecule followed by isomerization via 19 C₅H₇ intermediates (**i1–i19**) and 48 transition states eventually

leading to atomic hydrogen loss products (C_5H_6 ; **p2**, **p3**, **p4**, **p5**, **p6**, **p7**, **p9**), CH_3 loss product (C_4H_4 ; **p1**), C_2H_3 loss product (C_3H_4 ; **p10**), and C_3H_3 loss product (C_2H_4 ; **p8**). For simplicity, the PES has been split into three figures (Figures 3–5).

4.1. Formation of products p1–p3 through intermediates i1–i8 (Figure 3). The radical center of the ethynyl radical can add without barrier to the C1 or C2 carbon atoms of the carbon-carbon double bond of propylene to form three possible intermediates. First, the addition to the central carbon leads to intermediate **i1**; second, addition to the sterically more accessible terminal (C1) carbon leads to *cis* and *trans* conformers **i4** and **i3**, respectively. **i1** can cyclize to **i2** which then undergoes ring opening forming **i4** via barriers of 16 and 14 kJ mol^{-1} with respect to **i2**. Essentially, this reaction sequence portrays an ethynyl migration from C2 to C1 via the cyclic intermediate **i2**. Alternatively, **i1** can isomerize to **i4** in one step through ethynyl migration without a formation of the three-membered ring intermediate **i2** through a much higher barrier of 209 kJ mol^{-1} above **i1**. Intermediate **i1** can also experience a methyl group shift from CH to CH_2 through a significant barrier 223 kJ mol^{-1} above **i1** producing **i8**. Product **p1** can be formed by methyl loss from **i1** through an exit transition state located 47 kJ mol^{-1} above **p1**. Intermediate **i3** can form **i4** by rotation around the central $CH-CH_2$ bond through a small barrier of only 2 kJ mol^{-1} above **i4**. Alternately, **i3** may undergo two distinct hydrogen atom migrations to form **i5** or **i8** through barriers of 194 or 145 kJ mol^{-1} above **i3**, respectively. Product **p3** can be formed by hydrogen atom emission from intermediate **i3** through an exit barrier 22 kJ mol^{-1} above **p3**. **i4** can undergo hydrogen shift to **i6** through a 143 kJ mol^{-1} barrier above **i4**; both **i4** and **i6** can decompose to **p2** through exit barriers of 23 and 14 kJ mol^{-1} above **p2**. Intermediate **i6** can also isomerize through a small barrier of only 1 kJ mol^{-1} by the $CH-CH_2$ bond rotation to **i8**, which then decomposes to **p1** through an exit transition state 27 kJ mol^{-1} above **p1**. **i5** may form **i7** by a central $C=C$ bond rotation through a high barrier of 196 kJ mol^{-1} above **i7**; both **i5** and **i7** can decompose by hydrogen loss, forming **p3** and **p2**, respectively, through barriers 24 kJ mol^{-1} above their respective products.

4.2. Formation of products p4–p6 through intermediates i1–i4 and i9–i13 (Figure 4). The reactions portraying the section of the PES, which compiles the pathways to products **p4–p6**, are initiated by the same entrance channels as those shown in Figure 3 and discussed in 5.1. Intermediate **i3** can isomerize by hydrogen atom migration from the methyl group to form **i9** through a barrier located 163 kJ mol^{-1} above **i9**. Additionally, **i3** may decompose by atomic hydrogen loss from the methyl group to produce **p4** or **p5**. From **i4**, intermediates **i10–i12** can be

formed via distinct hydrogen atom migrations, as well as product **p6** by atomic hydrogen loss, through barriers 170, 151, 196, and 154 kJ mol⁻¹ above **i4**, respectively. Intermediate **i9** may undergo bond rotation to **i10** through a 13 kJ mol⁻¹ barrier or decomposes to form **p5** by hydrogen atom loss over an exit barrier of 22 kJ mol⁻¹ above the products. The decomposition of **i10** leads to **p6** + H through an exit transition state positioned 20 kJ mol⁻¹ above **p6**. Both **i10** and **i11** can undergo hydrogen shifts to **i12** through significant barriers located 197 and 186 kJ mol⁻¹, respectively, above **i12**. Alternately, **i11** may decompose by hydrogen loss to **p4** via a small exit barrier 13 kJ mol⁻¹ above the product. Finally, **i12** can form **i13** by bond rotation through a 1 kJ mol⁻¹ barrier; both **i12** and **i13** can form **p6** by hydrogen loss decomposition through exit transition states 21 and 20 kJ mol⁻¹ above **p6**. All three products in this section of the surface lie within the limits of the experimentally derived reaction energy; **p4** and **p5** can be formed through loose exit barriers immediately from **i3**, while **p6** can be produced from decomposition of **i4**, where both intermediates are created from barrierless addition of the reactants. Essentially, **p4** to **p6** represent distinct conformers formed via hydrogen atom elimination de-facto from the methyl group of the propylene moiety.

4.3. Formation of products p7–p10 through intermediates i1–i5, i7, and i9–i19 (Figure 5). Products **p8** to **p10** are formed from **i10**, **i1**, and **i11** by C₃H₃, H atom, and C₂H₃ loss through exit transition states located 54, 32, and 23 kJ mol⁻¹ above the products, respectively. The formation of cyclopentadiene (**p7**) involves multiple steps. Intermediate **i10** can undergo ring closure to form **i16** passing a barrier located 78 kJ mol⁻¹ above **i10**. This is followed by hydrogen atom migration to **i19** through a transition state located 198 kJ mol⁻¹ above **i16**. **i11** can form **i14** via a hydrogen migration barrier of 158 kJ mol⁻¹ above **i11** prior to conformational isomerization through barriers of 43 and 34 kJ mol⁻¹ to **i15** and then to **i17**. Intermediate **i17** can also be formed by 1,5-hydrogen migration from **i7** through a low 36 kJ mol⁻¹ barrier above **i7**. **i13** can undergo ring closure to form **i18** through a barrier 45 kJ mol⁻¹. Intermediate **i18** can decompose to **p7** via hydrogen loss through a loose transition state residing 15 kJ mol⁻¹ above **p7**. Both **i17** and **i18** can isomerize to **i19** via ring closure and hydrogen migration, respectively, through barriers located 129 kJ mol⁻¹ above **i17** and 151 kJ mol⁻¹ above **i18**. Intermediate **i19** can decompose to **p7** through an exit transition state lying 10 kJ mol⁻¹ above **p7**. In the **p7–p10** group, products **p9** and **p10** match the experimentally derived reaction energy with only the former decomposing via hydrogen

atom loss. Product **p9** is formed from a single reaction pathway that involves an ethynyl addition – hydrogen loss and a fairly low exit barrier of only 32 kJ mol⁻¹.

4.4. Reaction Pathways. The experimental results are now linked with the computations to propose the most likely reaction pathways. *First*, the laboratory data of the D1-ethynyl (C₂D) – propylene (C₃H₆) system reveals the formation of C₅H₅D products via atomic hydrogen loss at a collision energy of 42.3 ± 0.8 kJ mol⁻¹. The nearly symmetric laboratory angular distribution indicates an indirect reaction through C₅H₆D reaction intermediate(s) with the hydrogen atom leaving from the propylene molecule. *Second*, the D1-ethynyl reaction with D3-3,3,3-propylene provides evidence that hydrogen atom loss occurs dominantly from the C1 and/or C2 carbons of the vinyl moiety. *Third*, from the $P(E_T)$, the reaction energy is derived to be -108 ± 18 kJ mol⁻¹; the distribution maximum of 45 kJ mol⁻¹ indicates a tight exit transition state(s). The isotropic $T(\theta)$ denotes an indirect reaction with long-lived intermediate(s).

The computations predict three barrierless additions of the ethynyl radical with its radical center located at the carbon atom to the C1 and/or C2 carbon of propylene forming intermediates **i1**, **i3**, and/or **i4** (Figures 3-5). Overall, 19 intermediates are accessible through isomerization; these were found to undergo unimolecular decomposition to 10 possible products **p1–p10** with reaction energies ranging from 97 to 238 kJ mol⁻¹. In principle, all reaction intermediates are energetically accessible since their energies and the transition states connecting them lie below the collision energy of 42.3 ± 0.8 kJ mol⁻¹. These possible pathways are narrowed down by comparing the experimental reaction energy of -108 ± 18 kJ mol⁻¹ with the computed reaction energies. This comparison suggests that based on the energetics, **p2–p6** and **p9** ($\Delta_R G = -120, -119, -97, -97, -99$, and -119 kJ mol⁻¹) can account within the error limits for the experimental reaction energy. Only accounting for the hydrogen loss products, **p10** (-104 kJ mol⁻¹), which involves the formation of allene (H₂CCCH₂) through loss of a vinyl radical (C₂H₃), can be eliminated. Since the position of the hydrogen atom loss in the unimolecular decomposition of the C₅H₇ intermediates was found to predominantly stem from the vinyl moiety (i.e. no hydrogen loss from the methyl group), the 4-penten-1-yne isomers (**p4–p6**) cannot form since they would involve a hydrogen atom elimination in intermediate **i3** and/or **i4** from the methyl group. However, the remaining products **p2**, **p3**, and **p9** are accessible via unimolecular decomposition from collision complexes **i1**, **i3**, and/or **i4**. Also, the PES reveals that pathways to **p4–p6** have slightly higher energy exit transition states than those leading to **p2**, **p3**, and **p9**, with the lowest values of -84, -75, and -70 kJ mol⁻¹ with respect to the

separated reactants for **p4**, **p5**, and **p6**, respectively, as compared to -97 , -97 , and -87 kJ mol^{-1} for **p2**, **p3**, and **p9**. Therefore, due to the higher energy barriers, 4-penten-1-yne isomers (**p4–p6**) are deemed less likely to form; consequently, these considerations propose that 3-penten-1-yne isomers (**p2/p3**) and 3-methyl-3-buten-1-yne (**p9**) likely represent the major reaction products. The most probable reaction pathways to form **p2** and **p3** involve barrierless ethynyl addition to the C1 carbon of propylene to form **i4** and **i3**, which undergo hydrogen atom loss through tight exit transition states of 23 and 22 kJ mol^{-1} above the separated products, respectively. **p9** is formed by barrierless ethynyl addition to the more sterically hindered C2 carbon of propylene to form **i1** prior to a hydrogen atom loss also through a tight exit transition state of 32 kJ mol^{-1} above the separated products. In all three cases, unimolecular decomposition occurs in one step after the formation of the collision complex.

RRKM calculations provide statistical branching ratios for the reaction of ethynyl radicals with propylene within a limit of a complete energy randomization. Three distinct sets of calculations are formed starting with intermediates **i1**, **i3**, and **i4**, respectively, for the experimental collision energy and for zero collision energy resembling the low temperature (10 K) conditions of molecular clouds such as TMC-1 and OMC-1 (Table 1). The most likely reaction pathway involves methyl loss leading to vinylacetylene (**p1**) at 35–46 % of the reaction products formed; however, this pathway could not be explored experimentally because the D1-ethynyl (C_2D , $X^2\Sigma^+$) beam contains atomic carbon (C ; $^3\text{P}_j$), which reacts with propylene (C_3H_6 ; $X^1\text{A}'$) to form the methylpropargyl radical (C_4H_5) via hydrogen atom loss.⁵¹ This product can fragment within the ionizer to C_4H_4^+ ions at $m/z = 52$, cloaking any signal from the much weaker methyl loss channel of the D1-ethynyl–propylene reaction. Since the major goal is to explore molecular mass growth processes, we therefore focus on the atomic hydrogen loss of the ethynyl–propylene reaction. The next major hydrogen loss products predicted are *cis*- and *trans*-3-penten-1-yne (**p2** and **p3**) at overall levels of typically 26 to 33 % of all products; this corresponds to levels of up to 51 % of all hydrogen loss products. This is followed by the 4-penten-1-yne product isomers (**p4–p6**) at 7–9 %, 7–9 %, and 6–8 %, respectively. Recall that within our signal-to-noise, which for the present system limits the detection of hydrogen versus deuterium losses to fractions above typically 10 %, **p4–p6** were predicted to be minor products. Finally, the 3-methyl-3-buten-1-yne (**p9**) product is predicted to form in lower amounts than **p4–p6**, at levels of 3–5%. The hydrogen loss channel

leading to the thermodynamically most stable isomer, cyclopentadiene (**p7**), is predicted to contribute only 0.1% and has a reaction energy that lies outside our experimentally derived values.

Note that previous crossed beam experiments on the reactions of propylene with small molecules/radicals have been conducted, namely propylene with atomic carbon (C; 3P_j),⁵¹ dicarbon (C₂; $X^1\Sigma_g^+ / a^3\Pi_u$),⁵² cyano (CN; $X^2\Sigma^+$),¹⁷ and methylidyne (CH; $X^2\Pi$);⁵³ a comparison of these reaction products with the current study is presented in Scheme 2. In all five cases, the reaction is initiated by a barrierless addition; the carbon, dicarbon, and methylidyne reactants add to the double bond of propylene to form a cyclic three-member ring collision complex, while the cyano and ethynyl radicals add to the C1 and/or C2 carbon leading to an acyclic intermediate. In the methylidyne study, the ring structure remains intact upon atomic hydrogen loss decomposition, yielding 1- and 3-methylcyclopropene. Conversely, the initial intermediate in the reactions involving carbon and dicarbon undergoes ring opening before hydrogen atom loss to methylpropargyl (carbon–propylene) and 1- and 3-vinylpropargyl radicals (dicarbon–propylene). The cyano radical is isoelectronic to the ethynyl radical and therefore should have similar reaction dynamics.⁵⁴ The cyano radical adds to the C1 carbon of propylene forming the CH₃CHCH₂CN intermediate before H loss decomposition to *cis/trans*-2-butenenitrile (75%) and 3-butenenitrile (25%) at experimental reaction energies of $-103 \pm 8 \text{ kJ mol}^{-1}$. The ethynyl–propylene reaction follows the equivalent pathway at experimental reaction energies of $-108 \pm 18 \text{ kJ mol}^{-1}$ through CH₃CHCH₂CCH intermediates (**i3/i4**) before hydrogen loss to the major product *cis/trans*-3-penten-1-yne (**p2/p3**) with only a minor contribution to 4-penten-1-yne (**p4–p6**); these are isoelectronic to the *cis/trans*-2-butenenitrile and 3-butenenitrile products, respectively, formed from the cyano–propylene system. Notably, the five reactions are exoergic and all barriers have relative energies below that of the separated reactants, which indicates that these reactions can occur in cold interstellar environments such as molecular clouds.

5. CONCLUSION

Crossed molecular beams experiments were conducted to explore the chemical dynamics of the reaction of D1-ethynyl radicals (C₂D; $X^2\Sigma^+$) with propylene (C₃H₆; X^1A') and partially deuterated D3-3,3,3-propylene (C₂H₃CD₃; X^1A'). The reaction dynamics were inferred to be indirect and initiated by addition of the D1-ethynyl radical center to the C1 and/or C2 carbon of propylene yielding C₅H₅D intermediate(s) before atomic hydrogen loss decomposition through a tight exit

transition state. The combination of experimental results with the computed PES narrowed down the possible products to *cis/trans*-3-penten-1-yne (**p2/p3**) and 3-methyl-3-buten-1-yne (**p9**); out of these, RRKM calculations predict **p2** and **p3** as the major hydrogen loss products formed. Experiments utilizing D3-3,3,3-propylene are in agreement and help to eliminate non-dominant reaction pathways to 4-penten-1-yne isomers (**p4–p6**). Although the ethynyl–propylene reaction does not lead to the cyclopentadiene molecule (c-C₅H₆, X¹A₁), high temperature environments such as circumstellar envelopes of carbon stars close to the central star, planetary nebulae as their descendants, as well as combustion systems may exhibit hydrogen atom assisted isomerization processes that could convert *cis/trans*-3-penten-1-yne and 3-methyl-3-buten-1-yne to cyclopentadiene (c-C₅H₆, X¹A₁), similar to trans-1-phenylvinylacetylene and 4-phenylvinylacetylene isomerization to naphthalene.⁵⁵ The ethynyl radical and propylene have both been detected in the interstellar medium in cold molecular clouds like in TMC-1.^{11,14} Hence, based on the chemical dynamics derived, the title reaction should lead to *cis/trans*-3-penten-1-yne in cold interstellar environments such as TMC-1.

SUPPORTING INFORMATION

Cartesian coordinates and vibrational frequencies (Table S1) as well as RRKM rate constants at 41.1 kJ mol^{−1} (Table S2) and 0 kJ mol^{−1} (Table S3) for all species on the potential energy surface.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Basic Energy Sciences grants DE-FG02-03ER15411 and DE-FG02-04ER15570 to the University of Hawaii and Florida International University, respectively. The work at Lebedev Physical Institute was supported by the Ministry of Higher Education and Science of the Russian Federation under grant no. 075-15-2021-597.

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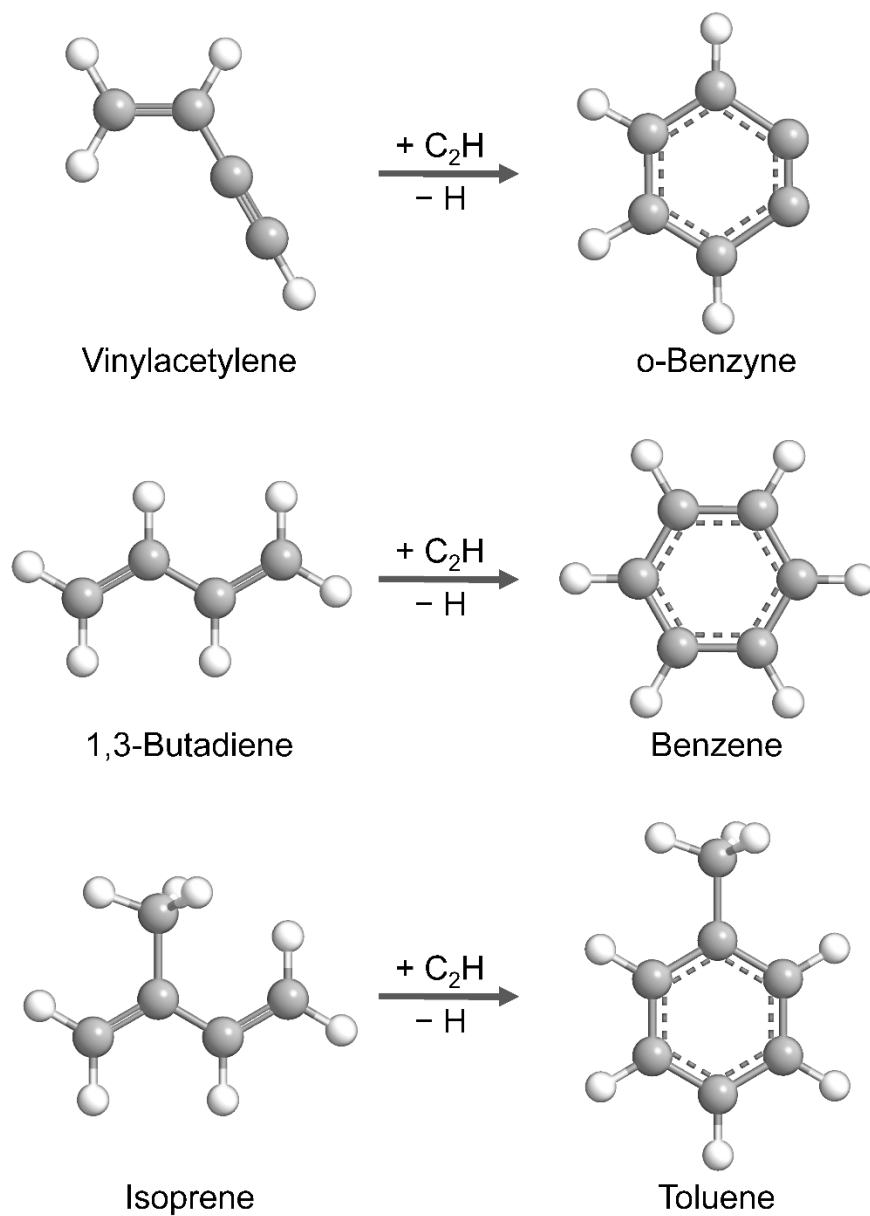
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Scheme 1. Addition–cyclization reaction pathways involving key reactions of the ethynyl radical with vinylacetylene, 1,3-butadiene, and isoprene leading to o-benzyne, benzene, and toluene, respectively.

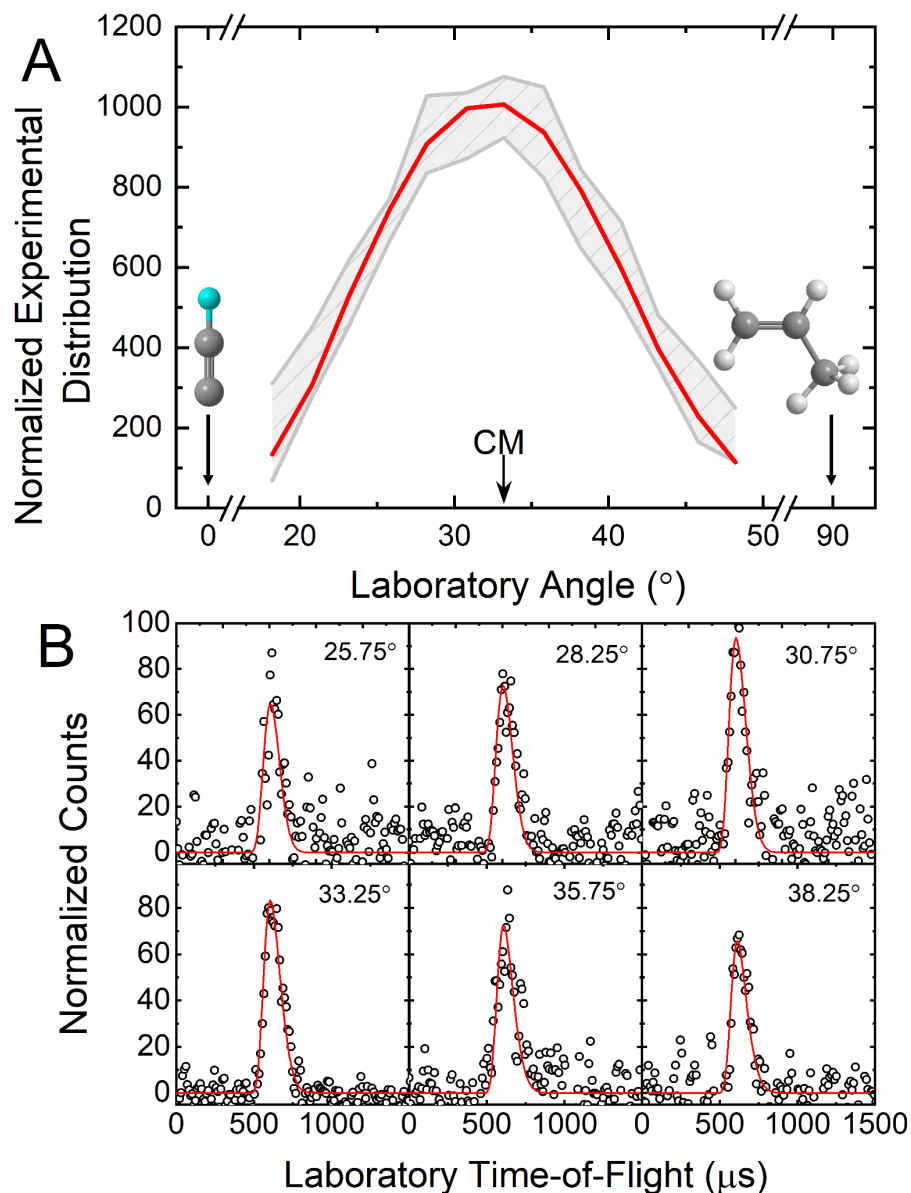


Figure 1. Laboratory angular distribution (A) and time-of-flight (TOF) spectra (B) recorded at mass-to-charge (m/z) = 67 for the reaction of propylene (C_3H_6) with the D1-ethynyl radical (C_2D). CM represents the center-of-mass angle, and 0° and 90° define the directions of the D1-ethynyl and propylene beams, respectively. The black circles depict the data, red lines the fits, and shaded areas the experimental error limits. Atoms are colored as follows: carbon (grey), hydrogen (white), deuterium (light blue).

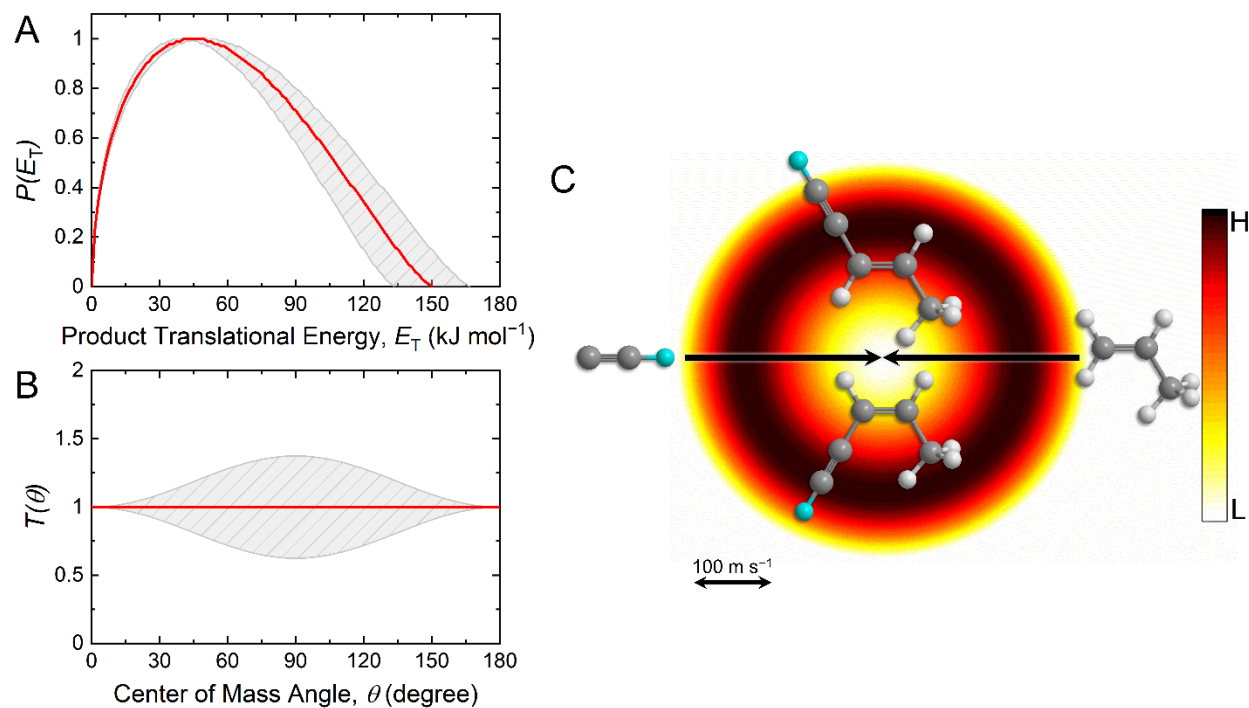


Figure 2. CM translational energy (A) and angular (B) flux distributions, as well as the associated flux contour map (C) leading to the formation of C₅H₅D isomers plus atomic hydrogen in the reaction of the D1-ethynyl radical (C₂D) with propylene (C₃H₆). Red lines define the best-fit functions while shaded areas provide the error limits. The flux contour map represents the intensity of the reactively scattered products as a function of product velocity (u) and scattering angle (θ), and the color bar indicates flux gradient from high (H) to low (L) intensity. Atoms are colored as follows: carbon (grey), hydrogen (white), and deuterium (light blue).

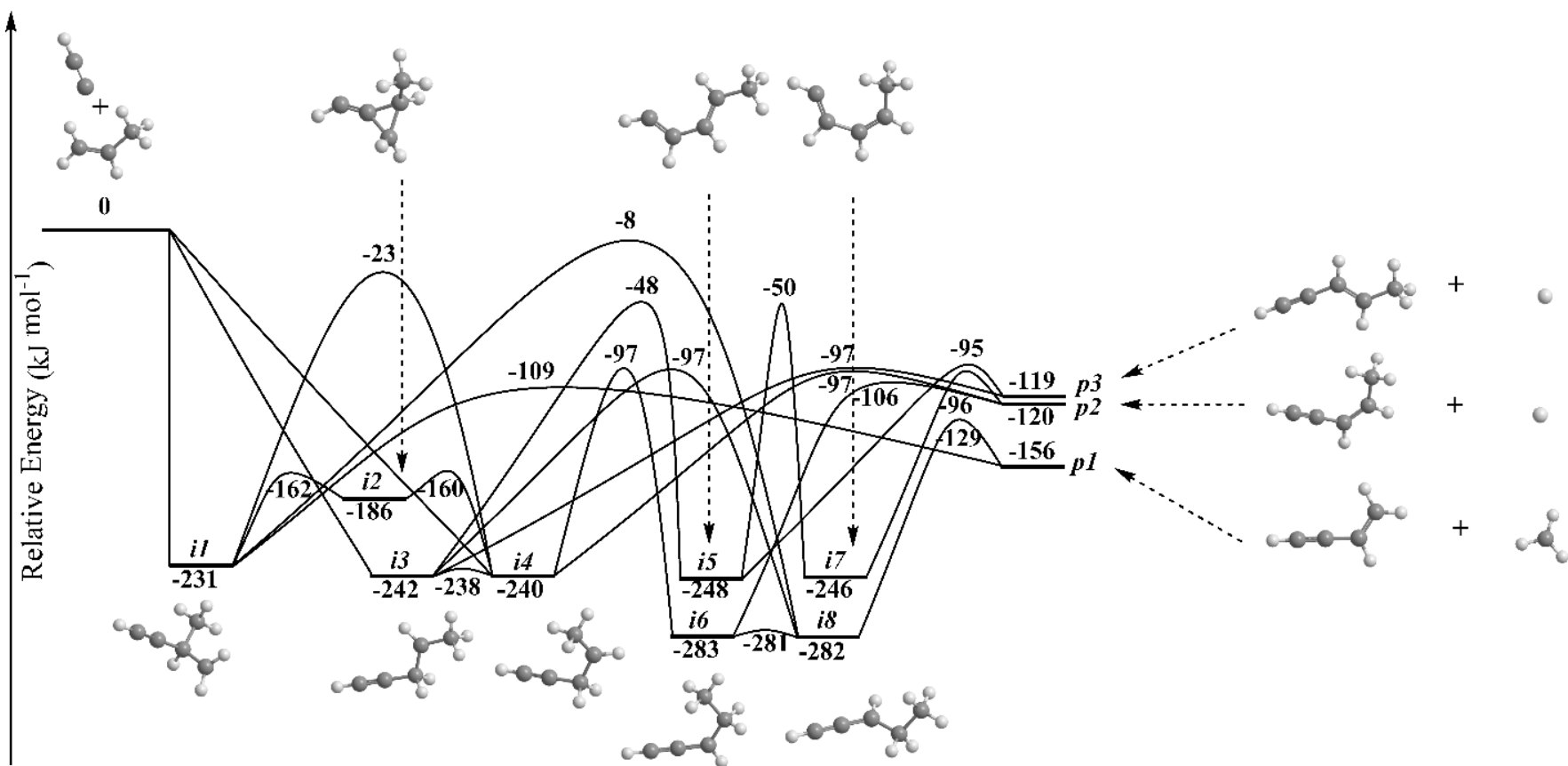


Figure 3. Portion of the C_5H_7 PES leading to products **p1–p3** through intermediates **i1–i8**.

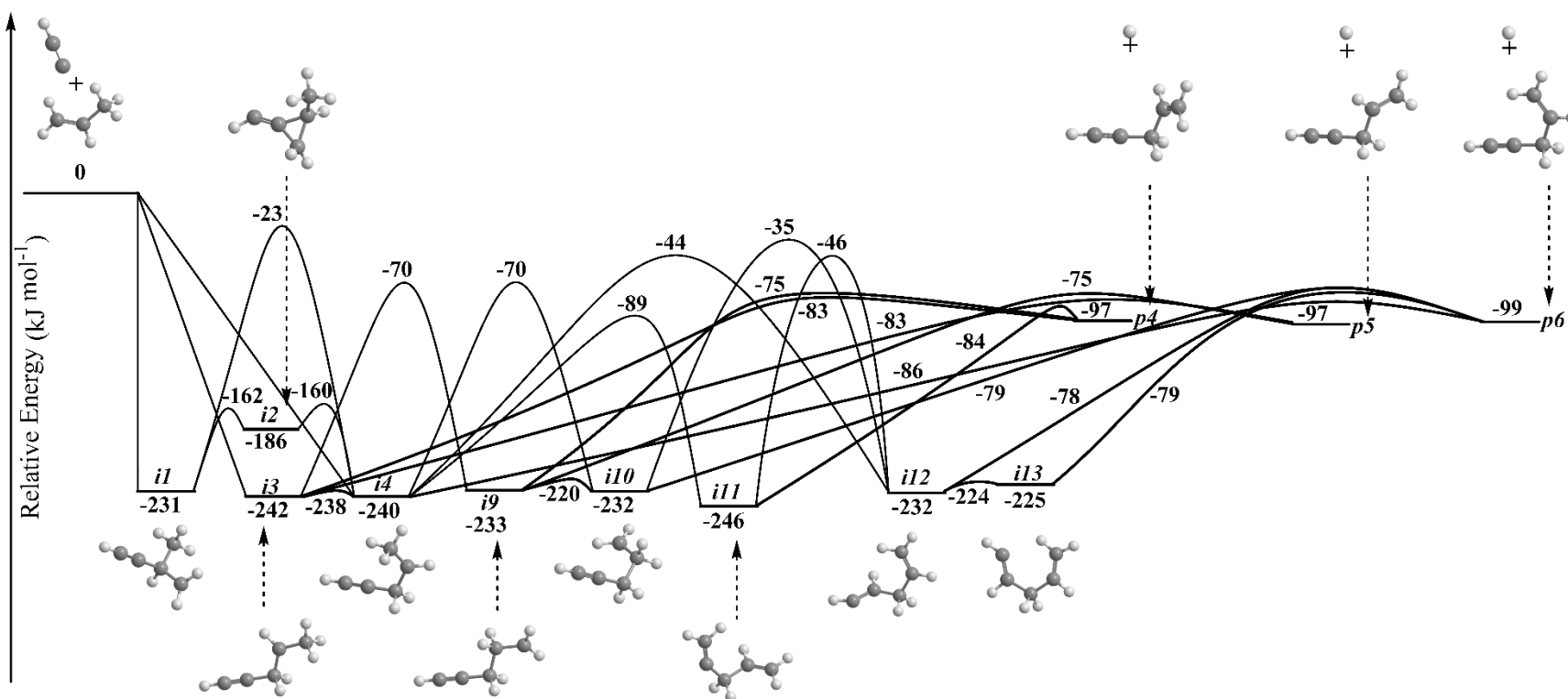


Figure 4. Portion of the C₅H₇ PES leading to products **p4**–**p6** through intermediates **i1**–**i4** and **i9**–**i11**.

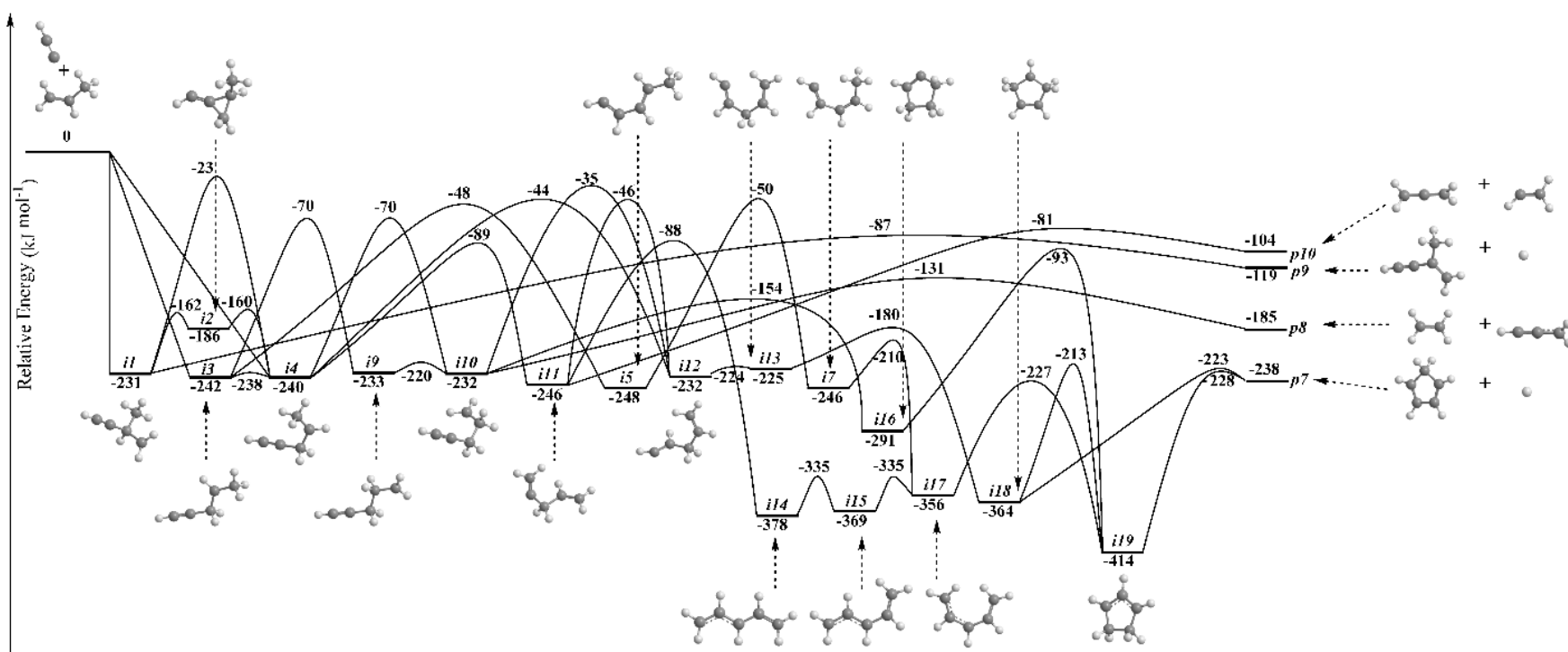
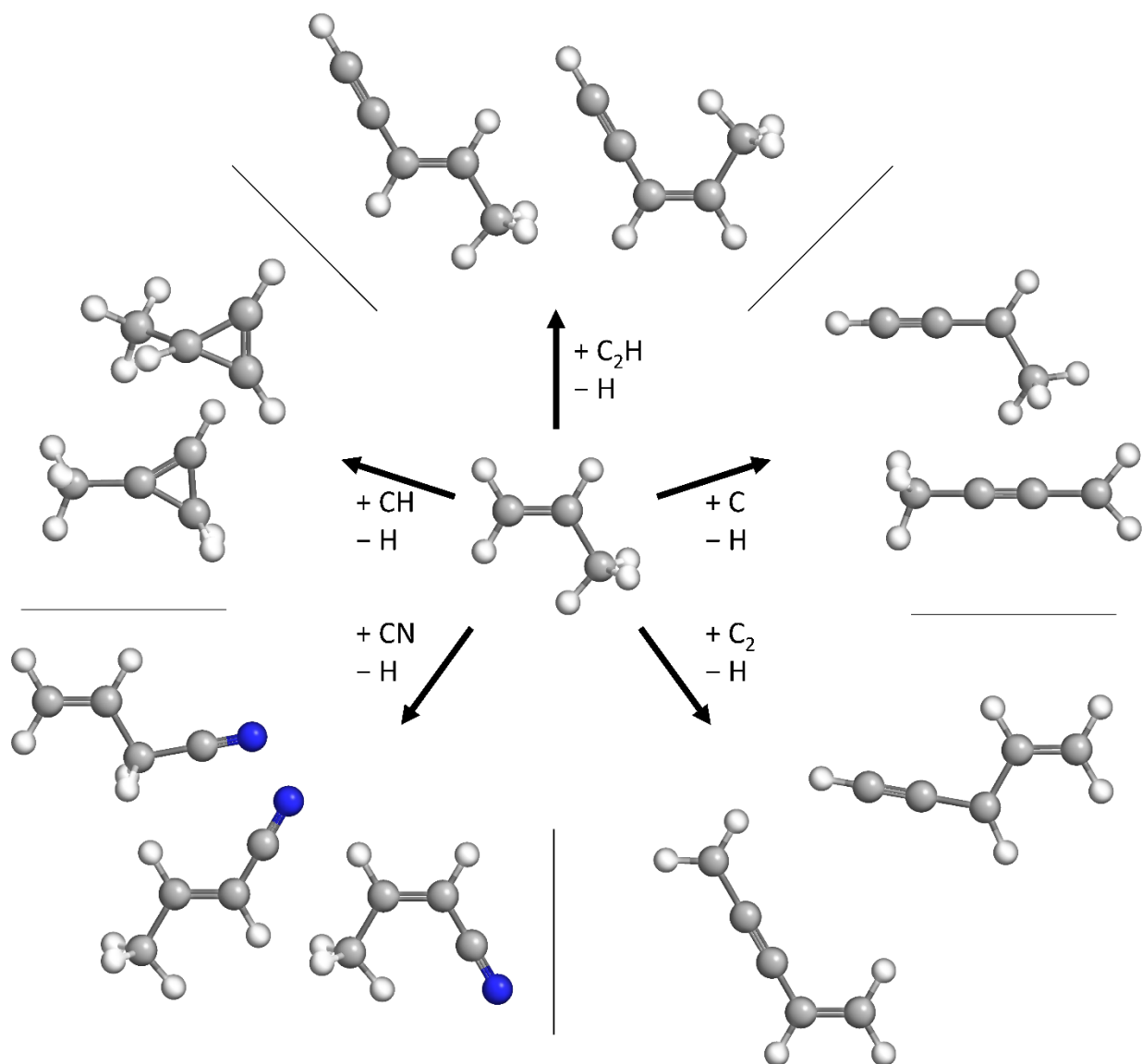


Figure 5. Portion of the C₅H₇ PES leading to products **p7–p10** through intermediates **i1–i5**, **i7**, and **i9–i19**.

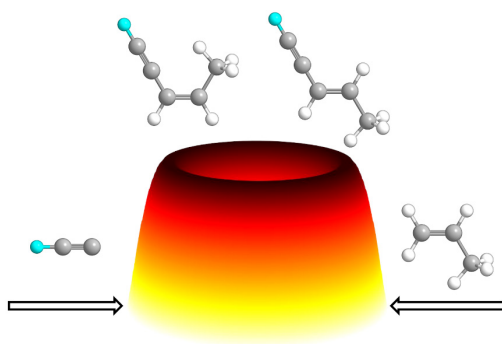
Table 1. Statistical branching ratios (%) for the C₂H + propylene reaction at collision energies of 41.1 and 0 kJ mol⁻¹.

<i>E_c</i> = 41.1 kJ mol ⁻¹			
Initial intermediate	i1 100%	i3 100%	i4 100%
p1	46.3	34.6	34.7
p2	11.8	15.1	15.1
p3	14.0	17.9	17.9
p4	7.2	9.2	9.2
p5	7.2	9.2	9.2
p6	6.2	7.9	7.9
p7	0.9	1.1	1.1
p8	1.2	1.6	1.6
p9	5.1	3.3	3.2
p10	0.1	0.1	0.1
<i>E_c</i> = 0 kJ mol ⁻¹			
Initial intermediate	i1 100%	i3 100%	i4 100%
p1	50.6	46.3	46.3
p2	12.6	14.0	14.0
p3	14.8	16.4	16.4
p4	5.4	6.0	6.0
p5	5.4	6.0	6.0
p6	5.0	5.6	5.6
p7	0.7	0.7	0.7
p8	0.8	0.9	0.9
p9	4.6	4.0	4.0
p10	0.1	0.1	0.1



Scheme 2. Products formed in the bimolecular reactions of propylene with small carbon-containing reactants such as atomic carbon ($\text{C}; {}^3\text{P}_j$), dicarbon ($\text{C}_2; \text{X}^1\Sigma_g^+ / \text{a}^3\Pi_u$), cyano ($\text{CN}; \text{X}^2\Sigma^+$), methylidyne ($\text{CH}; \text{X}^2\Pi$), and ethynyl ($\text{C}_2\text{H}; \text{X}^2\Sigma^+$) under single collision conditions in crossed molecular beam experiments.

TOC GRAPHIC



**Gas-Phase Study of the Elementary Reaction of the D1-Ethynyl Radical
(C₂D; X²Σ⁺) with Propylene (C₃H₆; X¹A') Under Single Collision Conditions**

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Table S1. Optimized Cartesian coordinates (Å) and vibrational frequencies (cm⁻¹) for all intermediates, transition states, reactants, and products involved in the C₂H + propylene reaction at the ωB97X-D/6-311G(d,p) level.

Reactants

Propene (C₃H₆)

C	-1.276382	-0.221005	0.000011
C	-0.134665	0.454315	0.000065
C	1.230687	-0.162110	-0.000007
H	-2.235678	0.284449	-0.000197
H	-1.291429	-1.307503	0.000032
H	-0.168945	1.542398	-0.000050
H	1.801146	0.152652	-0.879851
H	1.175233	-1.253094	0.000755
H	1.801836	0.153898	0.878900

Frequencies

182.1163	433.1263	584.8533
935.9604	946.6639	949.9836
1028.6410	1072.0141	1195.7134
1328.2163	1407.9847	1453.7621
1479.9109	1496.4393	1741.6224
3037.0035	3096.8485	3127.1754
3147.8492	3161.1146	3240.4151

Ethynyl (C₂H)

C	0.000000	0.000000	0.728763
C	0.000000	0.000000	-0.472485
H	0.000000	0.000000	-1.537669

Frequencies

479.6131	479.6132	2105.5192
3467.3577		

Intermediate states

il

C	0.435423	0.067251	0.402465
C	1.178918	-1.163326	-0.136946
C	-1.006460	-0.025483	0.117877
C	-2.177429	-0.091750	-0.136275
C	0.976854	1.347526	-0.160654
H	0.544560	0.090481	1.494038
H	1.068302	-1.227461	-1.222314
H	0.780721	-2.080446	0.301116
H	2.242696	-1.090710	0.100655
H	-3.215860	-0.152781	-0.356018
H	1.350879	1.368244	-1.178146
H	0.784862	2.287362	0.341861

Frequencies

52.2843	177.0370	226.4886
274.9168	355.8492	485.1906
534.7233	593.8586	688.3975
706.3797	805.2265	921.9487
961.0979	1061.8229	1143.5687
1186.6983	1317.1732	1332.6596
1412.9761	1457.3451	1499.4403
1506.2048	2237.0780	3039.6257
3054.2257	3135.3316	3143.2789
3155.7671	3271.0887	3484.6795

i2

C	0.580527	0.136687	0.499874
C	1.688996	-0.609415	-0.204384
C	-0.825050	-0.058759	0.076467
C	-1.846234	-0.830484	-0.020805
C	-0.164209	1.255171	-0.206396
H	0.094430	1.463738	-1.240192
H	0.722560	0.279555	1.568454
H	1.812261	-1.608824	0.219666
H	2.638715	-0.075672	-0.107655
H	1.464176	-0.722547	-1.267981
H	-2.850531	-0.808804	-0.414969
H	-0.485789	2.113347	0.374138

Frequencies

180.8270	217.7740	320.1807
367.7494	449.3210	672.5861
739.5636	748.7619	856.5489
885.6046	931.5259	946.5295
1041.9071	1081.4755	1140.3249
1166.6831	1182.6140	1378.0281
1428.3132	1464.5717	1496.6867
1508.1727	1809.3341	3047.4418
3121.6670	3123.6991	3127.0002
3149.9132	3216.8646	3271.0181

i3

C	0.104673	0.626723	-0.032823
C	-0.926799	-0.457292	-0.013950
C	-2.368634	-0.100800	0.036229
C	2.604446	-0.280534	0.029200
C	1.480743	0.136163	0.002665
H	-0.053398	1.309524	0.814885
H	-0.020050	1.256222	-0.929576
H	-0.615677	-1.476724	-0.204747
H	-2.709389	0.360405	-0.904428
H	-2.575112	0.630581	0.828002
H	-2.994546	-0.977220	0.213227
H	3.601603	-0.648349	0.054706

Frequencies

61.5528	103.9672	156.9744
307.0908	337.5207	363.1863
514.1601	678.6571	693.3724
870.3411	891.2006	987.8227
992.5555	1114.3100	1150.8599
1202.5265	1289.1941	1392.9748
1417.5927	1452.9181	1475.6706
1490.4551	2254.9661	2970.7348
2980.5482	3015.1755	3043.2463
3130.3393	3217.7392	3484.2336

i4

C	-1.226956	0.463469	-0.265802
C	-1.601690	-0.930641	0.085679
C	1.224592	0.142746	0.019982
C	2.147923	-0.615179	-0.084061
C	0.087212	1.056033	0.150035
H	0.038896	1.385703	1.202081
H	-1.990808	1.156663	-0.599803
H	-0.809117	-1.636784	-0.183846
H	-2.522985	-1.234662	-0.414739
H	-1.763037	-1.046798	1.169686
H	2.969772	-1.283332	-0.176273
H	0.290792	1.960643	-0.432105

Frequencies

77.2630	145.1035	166.0933
328.1326	348.5903	398.9994
598.5643	691.5675	694.7446
857.9759	876.8576	952.0553
1000.5952	1101.7089	1159.5219
1228.1579	1339.3264	1378.6410
1427.5919	1452.2304	1480.7913
1491.8445	2250.0157	2960.6237
2977.2249	3070.5731	3074.7685
3132.1998	3198.2973	3484.5331

i5

C	-0.850749	-0.343592	-0.042172
C	-2.331890	-0.134598	0.016506
C	1.522085	0.450244	-0.029372
C	2.202317	-0.673077	0.046772
C	0.062885	0.631650	0.016703
H	-0.507384	-1.371696	-0.141823
H	-2.770821	-0.666663	0.868637
H	-2.822802	-0.528300	-0.881030
H	-2.587934	0.923613	0.108787
H	2.100270	1.376576	-0.133971
H	3.236942	-0.979235	0.030159
H	-0.276152	1.661940	0.098620

Frequencies

44.5428	193.4510	203.7967
249.1474	382.6177	581.2466
613.6789	781.2283	849.6687
861.9355	900.9192	1001.3408
1048.9201	1066.3437	1126.9943
1269.2228	1326.8148	1343.6494
1413.6469	1478.6082	1490.2469
1637.4804	1707.4298	3008.0451
3011.0249	3048.5295	3090.2716
3127.1937	3136.5485	3245.5932

i6

C	-1.303426	0.508757	0.000093
C	-1.437781	-1.009821	-0.000026
C	1.219710	0.214243	-0.000001
C	2.203808	-0.504767	-0.000041
C	0.106633	1.019118	-0.000019
H	-1.822469	0.929826	0.871868
H	-1.822664	0.929990	-0.871481
H	-0.961928	-1.445683	-0.881711
H	-2.490424	-1.301297	0.000053
H	-0.961759	-1.445835	0.881491
H	3.066328	-1.126207	-0.000038
H	0.259251	2.094024	-0.000221

Frequencies

57.9174	156.1498	257.9616
365.2581	384.6332	495.0886
565.5971	628.2811	663.1821
788.1300	859.3335	997.0678
1075.3162	1103.8947	1162.9934
1284.3523	1366.9661	1401.6846
1435.2845	1480.5151	1501.3198
1511.3022	2026.7060	3017.6102
3040.1461	3056.2531	3132.5336
3135.6487	3183.6786	3474.4880

i7

C	1.146570	0.582552	0.033202
C	1.540784	-0.859226	-0.043539
H	1.960483	1.300334	0.101531
H	1.684542	-1.280898	0.959258
H	2.485446	-0.979948	-0.581317
H	0.771026	-1.461959	-0.533686
C	-1.360207	0.326936	-0.062985
C	-1.564356	-0.966584	0.080962
C	-0.101055	1.076043	0.026421
H	-2.243075	0.945176	-0.268967
H	-2.411149	-1.635836	0.045636
H	-0.217680	2.154806	0.073173

Frequencies

86.9692	127.9951	221.1698
375.2709	417.3283	611.1505
671.9381	715.8242	850.1903
860.2409	904.4331	993.7330
1017.3344	1054.4650	1102.8729
1274.1613	1279.9476	1399.7284
1440.2382	1476.0818	1481.2348
1627.8176	1691.0090	3005.5056
3006.5915	3052.8281	3084.4790
3131.1913	3157.1139	3236.4052

i8

C	-1.006349	0.045971	0.603440
C	-2.144116	-0.348885	-0.345966
C	1.424551	0.120173	-0.089267
C	2.542631	-0.362965	-0.052130
C	0.158358	0.651018	-0.118553
H	-0.671292	-0.825131	1.171320
H	-1.388996	0.772580	1.332336
H	-2.500359	0.516153	-0.912383
H	-2.990282	-0.757447	0.211993
H	-1.808279	-1.103791	-1.060837
H	3.518782	-0.782874	-0.020470
H	-0.010028	1.548638	-0.707106

Frequencies

29.7020	182.6515	261.5818
337.0403	384.5115	483.4008
542.6707	620.8612	673.8804
784.2518	889.2375	1008.9730
1067.5716	1120.1009	1168.0270
1284.0152	1330.2978	1414.9843
1426.4876	1488.0011	1503.1664
1510.0957	2031.3926	3022.0314
3049.1228	3100.1501	3127.5664
3132.3573	3176.9394	3474.5984

i9

C	-0.049913	0.638499	-0.063472
C	-1.429892	0.163915	-0.013532
C	-2.553063	-0.254545	0.027397
H	0.105664	1.199134	-0.990483
H	0.117795	1.340857	0.760203
H	-3.550966	-0.619476	0.064779
C	0.974642	-0.506569	0.022260
C	2.379510	-0.023042	0.006207
H	0.800817	-1.211196	-0.797816
H	0.774297	-1.075815	0.944145
H	3.186165	-0.675276	-0.303985
H	2.638519	0.932221	0.449997

Frequencies

104.3449	157.6864	176.3147
350.7517	356.6233	498.0631
516.7562	685.6384	691.4793
743.9763	869.0743	977.2493
1001.9598	1093.5373	1113.0756
1193.2963	1294.1928	1315.4238
1388.5475	1463.1446	1473.4176
1484.7173	2251.0268	2981.4418
3055.0790	3072.1104	3100.1060
3156.9619	3265.4476	3483.8907

i10

C	-0.027383	-0.962277	-0.272092
C	1.237182	-0.358308	0.367105
C	-1.219180	-0.143920	-0.060600
C	-2.185258	0.541846	0.126783
C	1.614103	0.967241	-0.188670
H	-0.205541	-1.958879	0.143100
H	0.131712	-1.088737	-1.347688
H	2.627791	1.335207	-0.089330
H	2.062190	-1.069291	0.246616
H	1.066114	-0.280909	1.452985
H	-3.047378	1.141911	0.291390
H	0.848327	1.653207	-0.532235

Frequencies

121.9389	164.0553	198.4734
353.4607	362.7020	497.2786
556.8645	684.3415	692.6719
769.2920	876.3469	945.8313
1000.4529	1080.1863	1122.0596
1195.6295	1287.2731	1362.3074
1379.1157	1466.6771	1472.4938
1483.8222	2251.1900	2978.9688
3054.7024	3069.6567	3098.9043
3157.5049	3266.3789	3486.8210

i11

C	1.026521	-0.035543	0.463444
C	2.030546	-0.498737	-0.273518
H	0.877515	-0.411542	1.472976
H	2.200369	-0.152675	-1.288666
H	2.723234	-1.238221	0.112688
C	-1.352976	0.430107	-0.109597
C	-1.985230	-0.714366	-0.060771
C	0.015133	0.987507	-0.006644
H	-3.063887	-0.781788	-0.177315
H	-1.457692	-1.660377	0.090671
H	0.316720	1.394911	-0.978336
H	-0.000226	1.835882	0.690496

Frequencies

75.5130	155.7144	202.0040
404.4071	433.5156	474.8439
659.2508	886.8853	890.8017
910.9392	929.3940	949.1514
1016.1076	1030.9095	1116.0611
1237.4975	1302.1301	1323.1444
1409.7826	1445.7365	1461.7327
1698.4543	1736.6489	3000.0899
3038.4101	3040.6318	3124.7854
3139.2680	3143.2712	3209.2360

i12

C	-1.111490	-0.048219	0.379400
C	-0.048599	0.950234	-0.013156
C	-2.140848	-0.395618	-0.347669
H	-0.985285	-0.502962	1.369743
H	-0.059468	1.775670	0.712019
H	-0.307062	1.399688	-0.978547
H	-2.996474	-1.049703	-0.269904
C	1.698679	-0.886840	-0.039884
C	1.354944	0.396513	-0.078546
H	2.737138	-1.191629	-0.100969
H	0.959427	-1.676223	0.043248
H	2.135609	1.148741	-0.176466

Frequencies

94.8587	149.5862	261.2462
397.3912	512.4101	573.0960
670.2748	780.0799	828.2312
907.6220	938.5341	953.0874
1031.0532	1045.8603	1109.2076
1207.1294	1275.4922	1326.1066
1348.6986	1444.8478	1467.7263
1678.2893	1706.4365	2996.7222
3011.8479	3040.4544	3122.0202
3137.3159	3216.2996	3239.1734

i13

C	1.333055	-0.307040	0.000129
C	1.530823	0.985185	-0.000008
C	0.041024	-1.089405	-0.000177
H	2.222998	-0.951380	0.000486
H	2.381982	1.649875	0.000002
H	0.063616	-1.768771	0.864873
H	0.063589	-1.767935	-0.865905
C	-1.515654	0.935037	-0.000051
C	-1.281653	-0.372530	0.000140
H	-2.530866	1.317033	0.000193
H	-0.712131	1.663640	-0.000372
H	-2.134760	-1.049948	0.000526

Frequencies

67.3766	166.4240	226.4881
369.8941	516.8935	616.8735
630.2011	808.9787	821.0974
854.2551	943.9462	967.0059
1017.5074	1028.9874	1084.5895
1245.6107	1258.1739	1334.2598
1387.3866	1442.0943	1453.7389
1685.3034	1713.5386	2979.8521
2991.5512	2993.7626	3111.4752
3122.4734	3206.9262	3235.0516

i14

C	-1.247024	0.391393	-0.000118
C	-0.000038	-0.271576	-0.000085
C	2.460638	-0.227013	0.000079
C	1.246943	0.391212	0.000097
C	-2.460578	-0.227030	0.000058
H	-1.223363	1.479937	-0.000192
H	-2.541681	-1.308868	0.000196
H	-0.000216	-1.359604	-0.000161
H	3.384036	0.338074	-0.000014
H	2.542215	-1.308836	-0.000267
H	1.223518	1.479793	-0.000012
H	-3.384157	0.337591	0.000271

Frequencies

157.1994	203.8249	255.7876
454.5763	492.6832	586.2926
627.0054	834.6782	854.7655
873.5676	921.8113	984.7204
1011.0370	1030.4246	1168.0496
1255.0541	1279.8851	1301.6895
1303.0369	1443.5366	1487.9647
1521.9903	1589.8185	3121.0417
3122.1092	3136.3543	3136.6552
3139.3291	3229.3588	3229.9683

i15

C	1.005914	-0.354273	-0.000157
C	0.047131	0.690515	-0.000119
C	-2.074819	-0.623449	0.000073
C	-1.361544	0.539533	0.000030
C	2.349610	-0.158664	0.000123
H	0.640397	-1.378079	-0.000450
H	0.433395	1.706226	-0.000118
H	-3.157338	-0.608923	0.000101
H	-1.601364	-1.598232	0.000157
H	-1.930321	1.466511	0.000087
H	2.773650	0.840159	0.000401
H	3.043818	-0.989641	0.000121

Frequencies

141.4443	219.4607	236.5522
395.5770	577.3508	611.4989
623.1879	817.2661	847.8632
877.3821	919.7505	1000.0811
1011.8468	1038.5197	1096.2510
1195.0101	1270.3874	1312.2925
1379.8274	1444.8444	1479.5751
1545.7774	1591.4766	3128.2620
3134.3882	3139.9179	3148.3089
3152.7473	3227.4932	3232.3218

i16

C	0.924445	0.813963	0.100282
C	1.121523	-0.692477	-0.051689
C	-1.259491	-0.401937	0.088694
C	-0.058512	-1.279671	-0.056460
C	-0.606656	1.005526	-0.118024
H	1.236459	1.136438	1.101396
H	1.515848	1.390020	-0.617806
H	2.093096	-1.167495	-0.102557
H	-2.044673	-0.608500	-0.642720
H	-1.706404	-0.511217	1.083562
H	-1.034561	1.758524	0.546483
H	-0.787627	1.329806	-1.145176

Frequencies

137.8487	372.4520	616.0320
749.2827	761.8559	808.4100
875.2964	889.0067	925.7360
969.8328	1011.5062	1049.2511
1134.5725	1190.1821	1212.2763
1230.9241	1291.4342	1301.7532
1332.2806	1481.3545	1489.4207
1505.0061	1673.9001	3007.3907
3020.8662	3045.6754	3056.6234
3067.9338	3099.5600	3193.5100

i17

C	-1.284170	0.436808	0.102503
C	-1.642337	-0.858283	-0.111563
H	-2.087675	1.128344	0.349229
H	-0.941946	-1.610939	-0.447292
H	-2.674727	-1.166436	0.000497
C	0.000024	1.038614	0.000035
C	1.642236	-0.858304	0.111604
C	1.284268	0.436790	-0.102496
H	0.000051	2.124816	0.000013
H	2.674541	-1.166740	-0.000716
H	0.941847	-1.610968	0.447297
H	2.087780	1.128179	-0.349528

Frequencies

133.3319	243.5107	277.4382
376.8691	572.8968	590.7022
697.0076	806.5978	871.0013
877.1310	901.3722	989.1513
1004.7381	1009.0864	1122.1980
1179.3454	1269.0199	1314.8904
1416.2983	1448.8253	1471.7295
1556.7040	1599.7454	3117.7415
3122.3881	3149.4651	3151.3626
3158.6275	3235.6491	3246.0282

i18

C	0.666058	1.033790	-0.000266
C	-0.666259	1.033670	0.000464
C	1.235890	-0.368801	-0.000036
C	-1.235878	-0.368968	-0.000346
C	0.000105	-1.218883	0.000066
H	1.290483	1.919476	-0.000374
H	-1.290603	1.919432	0.000635
H	1.881997	-0.550442	0.874899
H	1.882178	-0.550803	-0.874560
H	-1.881734	-0.550894	-0.875242
H	-1.882221	-0.551164	0.874252
H	0.000401	-2.300454	0.001099

Frequencies

205.8843	331.1613	390.0321
681.6008	742.8666	791.9530
896.0363	913.6082	924.0704
944.1522	961.7924	969.4016
1033.8085	1128.6138	1128.6583
1132.3383	1274.4514	1299.3070
1324.5548	1386.7380	1456.4985
1462.4737	1675.4155	2942.8478
2943.1634	2944.2467	2947.7481
3172.7613	3197.0995	3206.3454

i19

C	0.490839	1.145867	0.000023
C	-0.971546	0.779126	-0.000127
C	1.273704	0.000770	-0.000020
C	-0.970585	-0.780285	0.000131
C	0.492293	-1.145294	-0.000041
H	0.858065	2.163533	0.000594
H	-1.491679	1.186472	-0.875740
H	-1.492080	1.186978	0.875002
H	2.357468	0.001438	-0.000101
H	-1.490527	-1.188659	-0.875080
H	-1.490191	-1.188336	0.875703
H	0.860723	-2.162533	-0.000175

Frequencies

124.1706	449.7200	597.3540
641.9963	727.0993	804.5544
810.3011	905.6072	911.5470
948.8191	992.3520	1026.8690
1072.8327	1105.5569	1141.8848
1221.9749	1274.2185	1300.4541
1317.9040	1400.3031	1469.5809
1478.6199	1493.4128	2997.5239
3008.7137	3010.3043	3030.6200
3179.9963	3201.9144	3213.6407

Transition states

i1 – i4

C	-1.053960	0.234157	-0.405692
C	-1.406432	-1.102893	0.154786
C	1.384282	0.153452	-0.403495
C	2.336454	-0.368391	0.136757
C	-0.679631	1.302803	0.325253
H	-1.162549	0.357067	-1.479995
H	-1.201063	-1.156623	1.224966
H	-0.837029	-1.886717	-0.349428
H	-2.468989	-1.306951	-0.013589
H	3.228400	-0.814223	0.511987
H	-0.566734	1.234161	1.401803
H	-0.476321	2.258517	-0.141396

Frequencies

-230.2626	44.5316	75.0690
171.2677	212.9421	270.2581
431.9510	617.5610	655.4169
682.0503	932.0187	959.4662
973.4057	1010.2083	1068.7275
1206.4643	1332.1459	1408.9985
1453.3384	1485.2350	1497.4575
1670.3154	2023.4371	3050.4629
3120.8220	3148.8531	3164.4163
3181.2579	3265.9176	3456.7649

i1 – i2

C	-0.540531	-0.109148	0.476045
C	-1.625705	0.707491	-0.202373
C	0.838126	0.193333	0.139451
C	1.963918	0.656157	-0.076966
C	-0.073065	-1.361991	-0.192491
H	-0.249978	-1.496885	-1.251330
H	-0.700853	-0.217743	1.549555
H	-1.675727	1.711876	0.223092
H	-2.596079	0.221263	-0.073825
H	-1.422499	0.800235	-1.271840
H	2.970909	0.657358	-0.430733
H	0.297769	-2.191151	0.393084

Frequencies

-715.2085	193.3926	226.5889
308.1422	368.9198	440.7574
493.5076	639.8831	706.1671
714.8351	838.0965	900.7783
930.3171	1083.5133	1165.7075
1170.9410	1228.4812	1364.8059
1417.5132	1451.5766	1496.4182
1501.4962	1964.5541	3049.1846
3100.5388	3131.2427	3136.7978
3167.3446	3288.1660	3416.6089

i4 – i2

C	0.710050	0.185232	0.527149
C	1.693236	-0.675860	-0.194981
C	-1.023147	0.098466	-0.049150
C	-1.945432	-0.726263	-0.056132
C	-0.107864	1.213335	-0.188038
H	0.748261	0.247202	1.607742
H	1.812403	-1.646047	0.293278
H	2.682763	-0.200306	-0.234323
H	1.373398	-0.855779	-1.225259
H	-2.401632	-1.666574	0.163483
H	0.195087	1.442548	-1.209803
H	-0.371338	2.109498	0.371789

Frequencies

-711.9133	151.8863	168.5758
313.4035	367.4242	396.0944
511.2245	669.5866	718.8939
858.7633	919.5504	952.3033
1033.3051	1059.5540	1163.5471
1187.2179	1206.2619	1376.6112
1424.6575	1470.0399	1488.1939
1501.5807	1972.9726	3012.6328
3085.4848	3087.5893	3123.7747
3157.6930	3209.1574	3409.6758

i4 – i3

C	0.118997	0.789767	0.010648
C	2.467513	-0.467206	0.098824
C	1.416248	0.109207	0.067947
H	-0.139963	1.144514	1.014239
H	0.232174	1.690204	-0.610802
H	3.400894	-0.975116	0.130964
C	-0.972774	-0.089189	-0.523315
C	-2.209310	-0.345870	0.259428
H	-0.794747	-0.603278	-1.460346
H	-2.702628	0.589614	0.556960
H	-1.990434	-0.885791	1.193018
H	-2.929332	-0.940409	-0.305221

Frequencies

-74.9989	101.2664	188.6175
324.4199	351.1258	387.2232
520.3430	690.6866	708.8621
856.9647	903.8081	968.9531
982.3896	1117.6125	1155.3746
1232.8035	1297.2686	1396.3077
1432.7001	1456.7154	1478.5519
1488.2920	2246.8691	2991.3156
3002.4047	3036.1848	3076.4140
3132.9112	3207.7067	3484.7609

il – p1

C	0.323554	0.459250	0.454563
C	1.226495	-1.523030	-0.148914
C	-1.028475	0.106924	0.136352
C	-2.161730	-0.188237	-0.117769
C	0.987384	1.428355	-0.233781
H	0.644802	0.216581	1.459488
H	0.963901	-1.530843	-1.196470
H	0.659388	-2.177710	0.498061
H	2.269658	-1.373046	0.090888
H	-3.169645	-0.437546	-0.339527
H	0.603137	1.814248	-1.166893
H	1.945390	1.788743	0.111752

Frequencies

-537.9091	141.7631	150.2263
233.8153	243.5659	398.2040
544.2863	573.0534	577.1719
601.6090	675.1779	726.3108
837.9359	867.6707	905.7770
980.5340	1109.7311	1277.3224
1421.4244	1428.0737	1428.5578
1552.3892	2241.8578	3106.2021
3167.9653	3188.0073	3268.8136
3271.6299	3274.8814	3486.2214

i1 – i8

C	0.182794	0.326511	0.565741
C	-1.147668	0.125437	0.163510
C	-2.266756	-0.128039	-0.209333
C	1.213155	0.876785	-0.326264
H	0.365170	0.389659	1.629957
H	-3.264854	-0.309007	-0.521686
H	0.939545	1.133618	-1.338355
H	2.059041	1.381708	0.115153
C	1.291883	-0.969064	-0.096474
H	0.987941	-1.268905	-1.092501
H	0.896037	-1.717598	0.608919
H	2.376669	-0.999257	0.015429

Frequencies

-1348.0386	124.2767	164.7858
215.1843	447.5530	542.6494
549.8578	561.2217	637.2207
673.1659	768.3627	813.3008
867.7284	990.8106	1038.2680
1109.3737	1213.5903	1337.6476
1395.2101	1430.8647	1469.5301
1497.6626	2160.4577	2894.0422
3046.6121	3157.5300	3193.2729
3195.4368	3277.3192	3481.4486

i5 – i3

C	-0.070781	-0.471215	-0.071684
C	0.972171	0.432172	-0.007714
C	2.406628	0.018548	-0.005774
C	-2.633851	0.236786	-0.119596
C	-1.465636	-0.134338	0.014734
H	-0.871838	-0.631751	1.124108
H	0.134619	-1.516676	-0.290359
H	0.739956	1.484137	0.122712
H	2.978021	0.565986	-0.762767
H	2.517680	-1.049924	-0.208212
H	2.885193	0.225635	0.959934
H	-3.634817	0.430875	0.194787

Frequencies

-1859.1632	139.9078	159.2214
172.9508	360.5305	380.6251
494.7765	553.2996	630.4409
747.9513	787.5142	909.4547
1020.0927	1036.7801	1058.7067
1133.4569	1265.4053	1311.8950
1423.7004	1481.5887	1484.4944
1498.1040	1588.0710	2052.8143
3019.9116	3076.3583	3119.4043
3159.7434	3193.6657	3426.7581

i4 – i6

C	-1.287030	0.499273	0.000145
C	-1.566561	-0.966333	-0.014172
C	1.241531	0.172337	-0.023202
C	2.202016	-0.557943	0.000036
C	0.113177	1.021146	-0.023154
H	-0.571801	0.991314	1.037707
H	-2.051774	1.210248	-0.286814
H	-1.427712	-1.382805	-1.021773
H	-2.588814	-1.178518	0.304317
H	-0.880504	-1.508697	0.642394
H	3.052334	-1.195422	0.012059
H	0.249466	2.053001	-0.325806

Frequencies

-1903.9331	141.5482	170.3721
228.9574	349.5593	401.2262
567.9529	596.7305	622.6735
703.0445	805.2899	862.2672
984.0051	1040.1524	1109.9744
1202.4985	1256.1771	1370.1537
1382.2963	1429.0850	1479.6171
1499.5028	2177.9552	2220.5722
3005.8569	3088.3827	3135.7029
3197.1372	3216.9779	3483.4782

i8 – i3

C	0.146249	0.536854	0.117294
C	-0.973287	-0.448106	0.179278
C	-2.360198	-0.026565	-0.181304
C	2.644491	-0.209093	-0.122759
C	1.494850	0.143042	-0.029702
H	-0.118378	1.566545	-0.098975
H	-0.692127	-1.494063	0.175125
H	-2.495133	-0.001233	-1.271776
H	-2.577470	0.980290	0.189734
H	-3.107507	-0.705431	0.234003
H	3.658775	-0.512311	-0.217331
H	-0.380792	0.189416	1.212378

Frequencies

-1912.5594	130.1267	158.8549
184.1308	349.0476	401.8859
519.7030	571.1697	662.5475
698.8488	769.9204	891.9372
1030.6656	1055.6540	1113.2631
1197.5537	1230.1668	1308.6612
1411.4711	1438.7858	1483.3918
1495.7469	2187.8396	2221.7212
3005.9444	3078.5395	3126.4108
3182.7464	3207.0630	3483.3676

i7 – i5

C	-1.005400	0.351305	0.504811
C	-1.908134	-0.541473	-0.285968
H	-1.171723	0.447014	1.575936
H	-2.115040	-0.130884	-1.281092
H	-2.859792	-0.707399	0.224594
H	-1.444769	-1.527501	-0.449147
C	1.431749	0.301856	-0.194073
C	1.734415	-0.951301	0.227704
C	0.196120	0.956143	-0.065528
H	2.241387	0.878343	-0.658898
H	2.523419	-1.630487	-0.073414
H	0.134013	1.971732	-0.459650

Frequencies

-746.2991	87.9199	127.7117
239.9593	264.5242	334.4937
416.4157	555.4742	657.1212
766.8098	873.5584	916.0154
979.9605	1051.9568	1087.7924
1170.8324	1196.1614	1321.9529
1384.2518	1396.6545	1448.6241
1472.5084	1483.5306	2957.5085
3011.6887	3026.0026	3082.7408
3086.9616	3118.8556	3192.9223

i8 – i6

C	-1.180683	0.497452	0.354831
C	-1.677767	-0.855860	-0.170479
H	-1.085861	0.438501	1.446468
H	-1.922364	1.272168	0.145429
H	-1.827215	-0.823286	-1.252520
H	-2.626559	-1.126768	0.299404
H	-0.950897	-1.642440	0.045488
C	1.281362	0.159901	-0.064218
C	2.280090	-0.517449	0.095960
C	0.138275	0.909904	-0.232187
H	3.158338	-1.100937	0.231731
H	0.206892	1.819076	-0.819446

Frequencies

-50.7322	167.8761	254.0236
335.7985	376.6715	511.7778
555.1366	620.7428	675.4784
785.9946	881.2145	991.9979
1070.7983	1121.3823	1150.9653
1289.2963	1355.4230	1386.2630
1417.4168	1489.7429	1501.6013
1509.7410	2036.2540	3028.7772
3046.8278	3096.3501	3125.7003
3132.3927	3188.5227	3476.4472

i3 – p3

C	-0.087374	0.452467	-0.148724
C	0.922253	-0.410910	0.107057
C	2.364501	-0.075517	-0.059999
C	-2.625845	-0.227719	-0.012490
C	-1.466330	0.079248	-0.061797
H	0.125112	1.393282	-0.649674
H	-0.035872	1.577352	1.438825
H	0.677372	-1.387467	0.515071
H	2.874755	-0.086496	0.909658
H	2.500833	0.911541	-0.506603
H	2.867274	-0.815237	-0.690754
H	-3.652708	-0.498391	0.039193

Frequencies

-862.4702	150.9339	167.6982
174.9903	314.4362	388.0097
427.1593	494.9497	547.0636
665.1093	711.7054	827.6708
916.8089	1007.9818	1047.5087
1060.1589	1140.7694	1310.8412
1313.0179	1420.6399	1481.3472
1490.3980	1648.2761	2245.2967
3038.5643	3100.4465	3129.6414
3170.2860	3189.2189	3487.0519

i4 – p2

C	-1.213176	0.486500	0.145981
C	-1.616123	-0.931083	-0.068876
C	1.210822	0.115977	0.047246
C	2.186445	-0.583367	0.019029
C	0.055433	0.960701	0.105650
H	-2.009079	1.212528	0.285031
H	-2.160166	-1.029613	-1.015569
H	-2.294664	-1.264383	0.722110
H	-0.753212	-1.597809	-0.097854
H	3.052432	-1.199499	-0.011810
H	0.239461	2.001257	0.351886
H	0.184816	1.585154	-1.727977

Frequencies

-864.5164	137.2677	162.5756
249.4072	299.5092	384.8594
416.8230	562.2459	661.5597
683.0046	703.0599	772.1900
907.5086	975.8409	1006.6747
1058.3335	1127.9923	1263.3439
1400.5555	1438.9236	1483.9274
1488.4462	1631.3346	2240.5266
3038.3741	3098.2182	3145.6556
3175.7536	3194.1978	3485.2313

i6 – p2

C	1.177922	0.485266	0.095049
C	1.542480	-0.966042	0.048606
C	-1.247108	0.166442	0.023949
C	-2.245161	-0.498357	-0.070079
C	-0.080695	0.969500	0.138958
H	1.565120	0.933866	-1.919815
H	1.987421	1.190866	0.258011
H	1.827030	-1.305333	1.050589
H	2.396963	-1.136072	-0.609196
H	0.705970	-1.577903	-0.291874
H	-3.128829	-1.084001	-0.152871
H	-0.238307	2.037723	0.246264

Frequencies

-602.2680	101.2723	164.2499
200.0612	343.1166	355.7068
387.1659	509.1748	663.5490
666.9537	700.7308	781.3561
911.3865	976.6861	998.3205
1058.1260	1126.9191	1264.1491
1396.9781	1437.2396	1480.7999
1490.7029	1649.9260	2221.6879
3050.6210	3119.6347	3151.8873
3179.1616	3197.7294	3484.2281

i5 – p3

C	-0.944115	-0.387109	-0.063246
C	-2.402001	-0.059141	0.008763
C	1.430568	0.162487	0.007460
C	2.490843	-0.434876	0.042408
C	0.042129	0.509818	0.069583
H	-0.681453	-1.427672	-0.236475
H	-2.888753	-0.620137	0.814454
H	-2.911905	-0.341093	-0.919266
H	-2.569780	1.005842	0.182517
H	2.060709	1.897318	-0.486550
H	3.482206	-0.817783	0.024210
H	-0.195566	1.556450	0.231300

Frequencies

-719.0065	41.6863	180.4338
198.9055	201.9972	398.5663
471.5628	512.4073	567.1619
627.8711	675.7954	816.4455
911.3163	990.6399	1037.1508
1066.0649	1128.7328	1314.2575
1330.8111	1413.8803	1478.2393
1488.4813	1688.1625	2103.8228
3013.7968	3056.3151	3099.5586
3146.1875	3158.7715	3464.3577

i7 – p2

C	1.213708	0.562787	0.028461
C	1.672324	-0.857612	-0.046604
C	-1.205493	0.150839	0.000041
C	-1.957710	-0.805932	0.051407
C	-0.054131	1.002926	0.044975
H	1.994052	1.318435	0.074618
H	2.267506	-1.115391	0.836874
H	2.324003	-1.005317	-0.915004
H	0.837118	-1.554632	-0.115643
H	-2.457223	1.501894	-0.493889
H	-2.734434	-1.531744	0.049273
H	-0.243207	2.068710	0.094088

Frequencies

-728.1593	22.9335	122.4887
188.9943	296.8966	410.6077
507.2691	524.8836	624.7440
653.3201	695.1906	746.7775
899.9434	968.3253	993.5846
1062.9889	1121.2010	1272.5740
1397.7895	1428.3015	1480.7644
1485.1735	1675.4422	2098.3421
3016.1894	3056.5604	3119.0148
3143.2158	3178.4430	3463.0839

i8 – p1

C	-0.796511	0.906765	0.455765
C	-2.260091	-0.918168	-0.133316
C	1.405237	0.018447	-0.098540
C	2.367550	-0.671897	0.117513
C	0.272897	0.827778	-0.370253
H	-0.763743	0.468969	1.445597
H	-1.599388	1.601636	0.244619
H	-2.493103	-0.647104	-1.154888
H	-3.027487	-0.772357	0.617564
H	-1.538654	-1.709393	0.023290
H	3.219458	-1.276638	0.314767
H	0.268420	1.357339	-1.317966

Frequencies

-365.1698	79.7931	106.6010
216.1581	229.2923	386.4837
458.7615	488.2364	565.7888
641.2470	698.6775	733.5616
766.9352	897.2827	930.5398
980.5763	1116.3466	1293.6265
1417.0813	1419.0864	1428.6152
1587.4944	2207.8607	3102.4858
3172.7510	3186.9840	3271.9748
3272.5651	3282.2149	3484.4529

i3 – i9

C	-0.089718	0.651872	-0.134251
C	-1.451182	0.137239	0.006608
C	-2.563503	-0.297495	0.110754
C	0.956754	-0.428136	-0.159667
C	2.373000	-0.081750	0.133297
H	-0.030204	1.254168	-1.053597
H	0.116335	1.347197	0.688515
H	-3.549169	-0.683660	0.208555
H	0.765484	-1.319891	-0.744575
H	1.568456	-0.697279	0.951427
H	3.164620	-0.716544	-0.241114
H	2.612373	0.925628	0.450343

Frequencies

-1917.4962	84.7542	161.6858
346.3319	347.0284	358.1815
519.4655	690.5439	699.2422
705.8327	734.6995	880.9623
930.4716	990.5415	1114.8316
1175.2094	1223.5894	1288.5040
1301.4880	1401.8458	1434.9528
1467.8089	2249.7812	2254.8603
2991.6497	3054.5242	3161.3307
3201.8020	3280.6792	3484.8423

i10 – i4

C	0.060922	1.041839	-0.174748
C	-1.246153	0.417949	0.245066
C	1.214552	0.153451	-0.027012
C	2.149633	-0.587564	0.092632
C	-1.589462	-0.974754	-0.144276
H	0.242182	1.953099	0.402693
H	0.002255	1.345552	-1.231623
H	-2.071412	1.089016	0.452491
H	-1.232356	-0.599357	1.050754
H	2.982893	-1.239375	0.198935
H	-2.629425	-1.264472	-0.212566
H	-0.831086	-1.589985	-0.610651

Frequencies

-1927.2184	110.7474	167.1374
337.7716	353.3847	365.0174
578.8928	686.6370	694.0266
698.7305	734.8841	872.7826
935.7533	949.1792	1080.1376
1173.8330	1255.6909	1272.2190
1348.4718	1369.6071	1435.7981
1465.0780	2247.5502	2250.8878
2985.5512	3086.8802	3164.9363
3198.0758	3285.8256	3484.8221

i10 – i9

C	0.074538	0.756655	-0.196517
C	1.372703	0.096494	-0.092011
C	2.431670	-0.458163	0.005118
H	0.173719	1.778514	0.180158
H	-0.185940	0.850933	-1.255225
H	3.372905	-0.944959	0.090006
C	-1.062979	0.018349	0.562213
C	-2.173815	-0.433425	-0.315569
H	-1.456141	0.664740	1.353686
H	-0.627467	-0.844628	1.087957
H	-3.152390	-0.640894	0.100122
H	-1.977383	-0.743168	-1.336108

Frequencies

-121.4795	85.3605	202.1936
320.9953	383.2383	476.1153
533.3683	695.3035	725.2461
764.7964	894.3636	959.2661
974.5648	1090.2302	1118.5629
1218.0939	1258.2185	1341.3166
1378.0489	1466.3499	1474.6523
1485.7710	2251.3825	2992.6306
3062.5732	3071.1980	3103.3279
3153.9706	3261.9916	3486.5005

i12 – i4

C	-1.352793	0.445651	-0.209928
C	-1.467540	-0.908129	0.098135
C	0.984473	-0.113336	-0.020956
C	2.202954	-0.341645	-0.103376
C	-0.035681	1.018346	0.202110
H	-1.913770	0.897923	-1.018878
H	-0.004567	-1.075380	-0.183019
H	-2.209335	-1.520898	-0.407312
H	-1.244704	-1.244679	1.112273
H	3.137386	-0.842834	-0.218598
H	-0.000174	1.264101	1.270311
H	0.246688	1.916451	-0.350681

Frequencies

-2318.7568	107.4054	298.0507
342.2198	488.0320	496.2866
550.1756	676.4174	692.5587
740.2021	866.0974	893.2091
966.2420	981.4830	1068.1492
1168.3011	1210.7337	1238.5291
1287.7358	1417.7460	1469.5594
1487.0228	1533.2509	1920.5202
3044.3699	3096.3473	3114.4288
3191.6485	3214.2115	3432.0445

i11 – i4

C	-1.142192	0.370209	-0.264336
C	-1.222513	-0.948483	0.182286
C	1.252524	0.399357	-0.003365
C	1.466553	-0.830960	-0.127340
C	0.025198	1.228935	0.172021
H	-1.622825	0.645768	-1.198191
H	0.107803	-1.272495	-0.133814
H	-1.934168	-1.613440	-0.297598
H	-1.073261	-1.145887	1.245152
H	2.227715	-1.585494	-0.193058
H	-0.052911	1.505638	1.230914
H	0.070226	2.151565	-0.409003

Frequencies

-2151.7227	243.5174	348.1233
454.1456	473.2543	579.6057
650.1262	693.0854	802.6969
868.5227	905.0034	925.3801
945.6702	1041.3530	1099.8775
1201.9923	1240.5035	1254.4923
1289.9082	1408.2107	1434.5513
1470.8196	1538.1854	1899.2289
3039.3863	3099.3476	3117.8665
3183.4362	3209.5041	3343.5454

i12 – i10

C	-0.047361	0.887737	-0.032750
C	1.024058	-0.120761	-0.431643
C	-1.214406	-0.020505	0.047755
C	-2.399253	-0.354422	0.123809
C	2.168704	-0.331446	0.288826
H	-0.180870	1.706160	-0.745664
H	0.164700	1.319502	0.949319
H	1.003804	-0.412280	-1.480213
H	-0.136059	-1.084147	-0.087830
H	-3.267429	-0.971494	0.171159
H	2.929540	-1.019046	-0.059734
H	2.295863	0.097690	1.276975

Frequencies

-2164.7852	98.2960	200.8795
363.4914	408.9417	447.0347
492.2515	606.7895	658.5880
739.8006	814.7851	832.9982
917.6005	939.0958	1073.7020
1108.6503	1221.0986	1258.7009
1289.5835	1305.0336	1438.6660
1473.7158	1587.2237	2017.8455
3065.1454	3114.7887	3147.0424
3153.9381	3251.0186	3437.2899

i9 – p4

C	0.048878	0.728942	-0.049293
C	1.390535	0.154750	0.021100
C	2.491525	-0.317564	0.061430
C	-1.044452	-0.288418	-0.299295
C	-2.301384	-0.133300	0.141820
H	-0.161751	1.281637	0.870981
H	0.030383	1.460635	-0.866041
H	3.464664	-0.743157	0.108267
H	-0.370941	-1.650853	0.984863
H	-0.823459	-1.047385	-1.044418
H	-3.083968	-0.825364	-0.144562
H	-2.565531	0.658025	0.836339

Frequencies

-782.7375	93.9926	172.9436
338.3710	363.4468	415.2081
426.8943	514.0214	613.8413
688.9684	720.7043	900.5893
919.2044	939.7612	1005.1624
1051.6249	1138.0766	1255.5393
1307.2193	1332.8923	1453.4611
1467.6848	1655.9317	2256.0514
3047.6138	3096.4602	3158.8319
3181.2781	3255.5801	3486.5372

i12 – i11

C	1.216017	-0.307256	-0.315619
C	2.236755	0.496726	-0.040982
C	-1.285276	-0.193753	-0.152347
C	-2.401058	0.458037	-0.156134
C	0.001008	-0.481070	0.560068
H	1.223167	-0.897193	-1.229319
H	2.257530	1.106988	0.856862
H	3.090336	0.574908	-0.704673
H	-3.026983	1.168443	0.386701
H	-2.177715	-0.445568	-1.047290
H	0.068191	0.171430	1.441723
H	-0.039201	-1.515112	0.926083

Frequencies

-2104.4208	69.4566	123.0677
179.5453	290.2638	397.9880
419.3193	609.6745	636.0357
826.6905	892.7463	915.9859
948.9339	955.3099	1030.6987
1119.1497	1221.8712	1287.6507
1323.6738	1445.4776	1457.1408
1709.8645	1844.4594	2350.9335
2983.1789	3025.4946	3052.7533
3125.5190	3137.2847	3210.9770

i3 – p4

C	-0.100834	0.748151	0.019137
C	0.972784	-0.237816	0.395437
C	2.090644	-0.430384	-0.310616
C	-2.506310	-0.386859	-0.087171
C	-1.426830	0.132465	-0.044222
H	0.133742	1.212529	-0.943312
H	-0.126715	1.555112	0.762044
H	0.814385	-0.782233	1.322189
H	3.399708	1.024072	0.435870
H	2.243382	0.053344	-1.270344
H	2.823104	-1.170287	-0.010656
H	-3.464329	-0.845883	-0.131188

Frequencies

-525.0145	74.5948	161.1767
234.3298	324.3423	346.4109
422.0076	503.5401	692.5659
695.2758	726.2101	912.0308
939.0268	990.6040	994.8629
1029.3956	1139.8341	1253.9397
1317.9994	1333.2281	1457.9100
1474.2420	1682.1020	2255.2514
3041.4900	3096.2691	3153.6790
3184.0945	3250.5367	3486.5653

i3 – p5

C	0.100835	0.748139	0.019156
C	2.506324	-0.386842	-0.087171
C	1.426836	0.132467	-0.044227
H	0.126711	1.555041	0.762127
H	-0.133739	1.212595	-0.943255
H	3.464348	-0.845861	-0.131170
C	-0.972775	-0.237863	0.395387
C	-2.090675	-0.430339	-0.310627
H	-0.814328	-0.782396	1.322061
H	-2.243473	0.053517	-1.270280
H	-2.823121	-1.170275	-0.010713
H	-3.399673	1.024007	0.436120

Frequencies

-525.0629	74.5804	161.1737
234.3370	324.3507	346.4143
422.0044	503.5394	692.5617
695.2598	726.2125	912.0314
939.0263	990.5963	994.8619
1029.3692	1139.8355	1253.9362
1317.9935	1333.2254	1457.9071
1474.2474	1682.1003	2255.2492
3041.4827	3096.2736	3153.6957
3184.1017	3250.5496	3486.5608

i10 – p6

C	-0.013874	-1.020601	-0.149434
C	1.306972	-0.291932	-0.009335
C	-1.195384	-0.174087	-0.022504
C	-2.164056	0.524589	0.079312
C	1.467776	1.035129	-0.112852
H	-0.068384	-1.824354	0.590589
H	-0.031441	-1.508528	-1.131430
H	2.180081	-0.938403	-0.033106
H	1.468738	-0.483241	1.948316
H	-3.028876	1.135985	0.173828
H	2.456656	1.477054	-0.095365
H	0.614625	1.702896	-0.163954

Frequencies

-770.9930	119.4693	166.7775
340.5720	373.7158	394.5233
450.3408	579.6915	626.9950
689.3885	700.7436	876.5953
932.4916	958.1227	975.8944
1045.4702	1096.5138	1242.7093
1310.1461	1362.9881	1436.5038
1475.3286	1654.8529	2257.6209
3050.1749	3092.7474	3161.1091
3173.3816	3260.6996	3486.7150

i12 – p6

C	-1.137246	0.138884	0.061810
C	0.031788	1.023073	-0.032492
C	-2.135961	-0.503559	-0.183310
C	1.592165	-0.976230	-0.030902
C	1.377316	0.333270	-0.049709
H	-0.892434	-0.301469	1.936658
H	0.010157	1.740678	0.795982
H	-0.072954	1.621197	-0.947280
H	-3.009485	-1.105888	-0.248960
H	2.599132	-1.376404	-0.049422
H	0.775328	-1.688173	0.005941
H	2.221876	1.017429	-0.085310

Frequencies

-674.3154	116.0700	153.4362
201.2634	389.1813	419.7650
475.5023	565.9675	614.9878
653.4663	683.6950	865.5704
947.9714	964.8534	965.6240
1029.4692	1094.0168	1237.2615
1325.9674	1353.5860	1444.0817
1462.5840	1712.7708	2133.1050
3008.4867	3035.3334	3133.0898
3145.3028	3224.5539	3464.1375

i13 – p6

C	1.151044	-0.135361	0.000004
C	1.879669	0.833540	0.000097
C	-0.005793	-1.038201	0.000052
C	-1.601660	0.943506	-0.000050
C	-1.359663	-0.360906	0.000004
H	2.472515	-1.565020	-0.000550
H	2.633096	1.583535	-0.000160
H	0.061510	-1.703399	0.869827
H	0.061519	-1.703514	-0.869630
H	-2.617816	1.320435	-0.000074

Frequencies

-641.9023	95.4826	166.0544
195.5698	351.5908	406.4738
468.5982	570.2041	617.3488
667.4709	674.7484	865.0490
946.2147	960.4500	964.1813
1027.5171	1090.6280	1245.1257
1324.6265	1352.2614	1441.2156
1461.8595	1713.1330	2137.2279
3014.1824	3030.4734	3130.4028
3143.6608	3223.5929	3465.5415

i9 – p5

C	-0.048892	0.728848	-0.049224
C	-1.390582	0.154724	0.021091
C	-2.491630	-0.317467	0.061350
C	1.044481	-0.288501	-0.299114
C	2.301493	-0.133147	0.141637
H	-0.030322	1.460462	-0.866022
H	0.161569	1.281607	0.871045
H	-3.464859	-0.742886	0.107992
H	0.823353	-1.047903	-1.043750
H	0.371215	-1.651207	0.985236
H	3.084019	-0.825331	-0.144629
H	2.565800	0.658518	0.835691

Frequencies

-781.8517	93.7958	172.9211
338.3126	363.2911	415.0759
426.4806	514.0173	613.7746
688.9152	720.6609	900.5789
919.1921	939.7074	1005.1842
1051.6346	1138.0793	1255.5167
1307.2367	1332.8783	1453.4647
1467.6500	1655.9968	2256.0340
3047.7267	3096.5212	3158.8735
3181.3181	3255.6007	3486.4960

i11 – p4

C	1.196913	0.151774	-0.424330
C	2.246533	0.338583	0.366514
C	-1.252168	-0.101501	-0.116298
C	-2.330997	0.435964	-0.029039
C	0.044168	-0.775034	-0.104902
H	1.127498	0.678444	-1.372514
H	2.337328	-0.165402	1.323872
H	3.054195	1.004713	0.085941
H	-2.913423	0.060258	1.919438
H	-3.250290	0.956310	-0.147006
H	0.199928	-1.239859	0.875597
H	0.018068	-1.593180	-0.837004

Frequencies

-478.0087	41.3272	87.3294
177.8809	252.2285	390.9784
409.5842	486.0012	645.3983
660.3918	763.2465	895.0065
924.7482	954.9388	981.4982
1028.9433	1124.6331	1241.8229
1313.1821	1328.9423	1449.8453
1459.6135	1709.7480	2170.4386
3001.1478	3039.6286	3128.9094
3146.8465	3214.7246	3462.9564

i4 – p6

C	-1.280804	0.424333	0.085713
C	-1.507540	-0.887502	0.194558
C	1.206401	0.161509	-0.013596
C	2.136311	-0.592985	0.038275
C	0.069069	1.073842	-0.076158
H	-2.118920	1.115853	0.070162
H	-0.689422	-1.596529	0.263796
H	-1.665732	-1.523525	-1.786259
H	-2.511802	-1.266021	0.342897
H	2.965119	-1.257722	0.080878
H	0.187920	1.847592	0.691735
H	0.092214	1.605173	-1.035969

Frequencies

-529.4447	123.3922	165.5474
225.9914	331.9774	347.6882
388.4494	619.2805	641.3324
702.5690	704.4940	880.8639
964.2226	973.4739	993.1060
1031.2867	1098.3659	1240.3596
1322.9273	1362.3317	1435.0728
1471.0937	1679.1156	2256.2066
3037.4890	3066.7160	3160.4040
3180.8404	3256.0861	3484.4495

i13 – i12

C	-1.279274	-0.279755	-0.239402
C	-1.643621	0.862994	0.281311
H	-1.955248	-0.745544	-0.966999
H	-2.475127	1.546375	0.193372
C	-0.027175	-1.075950	0.076418
C	1.516476	0.946592	-0.130602
C	1.293635	-0.343018	0.094481
H	0.052618	-1.902038	-0.640027
H	-0.159773	-1.564599	1.051687
H	2.521812	1.350733	-0.091701
H	0.712844	1.637671	-0.356506
H	2.142628	-0.987776	0.316936

Frequencies

-111.8208	128.2582	223.1372
386.5574	533.8016	578.8678
655.5355	792.1702	836.3145
857.0331	944.7111	962.0470
1020.4479	1034.0929	1090.5951
1240.4556	1259.9804	1329.9726
1369.3455	1440.6318	1473.3350
1673.1192	1711.4109	2995.9901
3004.0111	3031.2607	3116.2311
3138.5439	3219.4603	3237.4768

i14 – i11

C	1.244896	-0.408971	-0.048780
C	2.453422	0.162794	-0.146695
C	-1.282353	-0.261710	0.112274
C	-2.519899	0.071588	-0.227925
C	0.019252	0.311032	0.269354
H	1.136075	-1.475965	-0.228310
H	2.595286	1.227268	0.009182
H	3.331786	-0.418986	-0.396516
H	-2.705364	0.874854	-0.944406
H	-3.388120	-0.470874	0.130061
H	0.101886	1.386248	0.450501
H	-0.563455	-0.370940	1.230122

Frequencies

-1861.5061	134.9403	179.9150
257.5103	378.6433	468.3024
581.8199	686.4474	845.1498
867.6243	897.9569	910.9718
1000.0660	1012.8424	1077.8644
1117.9487	1185.3595	1267.8542
1315.1788	1431.7012	1460.7424
1652.9565	1669.4671	2095.8594
3051.6456	3057.8660	3134.5607
3141.8800	3174.0744	3224.2916

i16 – i10

C	-0.368701	-1.195486	0.139437
C	-1.215726	0.062733	-0.222089
C	1.023885	-0.745643	-0.030168
C	1.581078	0.352811	-0.096648
C	-0.480375	1.311631	0.172362
H	-0.631249	-2.050479	-0.486917
H	-0.529121	-1.494015	1.180559
H	-2.198074	0.002168	0.260231
H	-1.382159	0.066495	-1.302254
H	2.383864	1.054130	-0.165811
H	-0.498891	2.167265	-0.493175
H	-0.385334	1.538163	1.230008

Frequencies

-584.1382	180.1101	331.7358
464.2893	510.5064	591.4287
678.0056	697.1304	800.5799
823.1210	878.8069	911.7923
1000.0391	1056.4549	1107.9323
1201.1535	1234.8076	1324.1634
1342.8054	1464.5693	1479.6200
1500.2683	1963.7546	3047.7970
3065.7076	3102.0802	3119.4048
3143.3002	3244.5452	3416.3076

i13 – i18

C	-1.290607	0.068300	-0.000148
C	-0.868071	-1.166239	-0.170515
C	-0.253600	1.180725	0.152977
C	1.326502	-0.695719	0.224507
C	1.050738	0.549784	-0.260185
H	-2.349719	0.325062	0.044756
H	-1.349504	-2.128870	-0.276159
H	-0.242822	1.539252	1.192102
H	-0.504689	2.045205	-0.468443
H	2.095241	-1.311945	-0.230653
H	1.025731	-0.991621	1.223272
H	1.535997	0.901817	-1.164689

Frequencies

-518.3952	235.2388	315.8765
465.9473	603.2208	637.9660
695.1974	815.9137	871.6497
894.0825	907.1708	927.6301
945.9227	984.1812	1087.4920
1193.5268	1212.3706	1270.6601
1311.2295	1421.4046	1479.4873
1561.9783	1644.2632	2988.8245
3057.5818	3093.1520	3125.2523
3159.0753	3204.3096	3217.7943

i17 – i7

C	1.150176	0.570553	-0.026656
C	1.298534	-0.898904	0.026205
C	-1.295398	0.360266	0.024687
C	-1.273656	-0.968180	-0.044491
C	-0.062009	1.153456	0.025368
H	2.037320	1.186776	-0.158314
H	1.438685	-1.308471	1.030702
H	2.013222	-1.331520	-0.676145
H	0.081629	-1.303061	-0.194877
H	-2.240589	0.904876	0.031475
H	-2.084671	-1.685691	-0.061465
H	-0.151473	2.233943	-0.002057

Frequencies

-1581.2797	172.5470	352.3467
427.5580	520.5550	562.1910
614.9997	704.1404	763.2665
919.4956	932.0295	957.4266
968.7686	1033.2694	1045.4491
1112.1690	1212.7823	1274.0459
1328.0545	1412.1068	1443.9725
1530.9774	1586.1968	1670.4772
3044.6852	3086.8612	3109.2559
3122.2868	3174.4393	3194.6932

i14 – i15

C	1.121039	-0.310577	0.233124
C	0.048767	0.519301	-0.069556
C	-2.278054	-0.338251	-0.330591
C	-1.337231	0.277237	0.382286
C	2.427196	-0.091610	-0.156662
H	0.907471	-1.203990	0.816958
H	0.240063	1.424628	-0.643776
H	-3.280227	-0.477691	0.060002
H	-2.077648	-0.723611	-1.325039
H	-1.597123	0.647211	1.376390
H	2.699650	0.779581	-0.742458
H	3.217504	-0.782728	0.106318

Frequencies

-215.5315	152.7076	242.3701
403.1961	485.9003	541.6318
664.3832	736.3868	802.1330
908.8416	958.5548	994.8227
1013.1578	1024.6439	1116.8707
1201.7816	1275.0303	1310.9043
1318.2832	1441.1722	1485.3075
1516.4523	1688.6661	3076.2654
3115.0551	3128.8164	3130.1695
3138.0784	3212.4288	3234.1540

i15 – i17

C	-1.108108	0.148733	0.460526
C	-1.983087	-0.461918	-0.335500
H	-1.252715	0.084189	1.540928
H	-1.886691	-0.431055	-1.415888
H	-2.825072	-1.012948	0.069249
C	0.054765	0.937196	0.001442
C	1.726847	-0.879583	0.053348
C	1.341961	0.430494	-0.149671
H	-0.105966	1.996635	-0.181277
H	2.755998	-1.186129	-0.083249
H	1.011415	-1.638404	0.346316
H	2.108760	1.138187	-0.456944

Frequencies

-168.8161	209.4259	242.2804
438.2514	502.2537	522.7862
678.4002	723.0430	810.1290
913.8033	958.2159	993.6987
1013.2995	1030.8765	1078.6176
1165.0680	1232.8215	1314.8892
1405.4693	1439.7497	1461.3403
1520.6434	1688.8658	3078.9838
3125.7685	3129.2176	3142.5224
3149.4894	3212.7053	3240.0962

i17 – i19

C	-1.167622	0.481019	0.169240
C	-1.183028	-0.837252	-0.229641
C	0.064421	1.202773	-0.084161
C	1.060133	-1.007791	0.197523
C	1.179266	0.438662	-0.086275
H	-1.895098	0.870746	0.875350
H	-0.777404	-1.121089	-1.192265
H	-1.894266	-1.541685	0.193136
H	0.102930	2.283397	-0.174876
H	1.504767	-1.722064	-0.489823
H	1.080877	-1.316618	1.241709
H	2.159169	0.882847	-0.253347

Frequencies

-664.8297	211.4786	406.5081
451.7594	511.2242	642.6582
715.5318	736.0026	771.6530
862.3547	938.2213	963.8755
985.2993	1008.9120	1041.0700
1066.9963	1162.3060	1241.3689
1371.3908	1421.8352	1444.0492
1531.5551	1591.7899	3086.7849
3115.9201	3123.3195	3147.3168
3171.0700	3173.0264	3204.0590

i19 – i18

C	0.441477	1.146362	-0.004430
C	-0.886014	0.889392	-0.019736
C	1.262304	-0.128955	-0.013311
C	-1.138293	-0.538598	-0.020134
C	0.202511	-1.209030	-0.004442
H	0.888385	2.130920	0.045933
H	-1.669877	1.635373	0.001899
H	1.955355	-0.187370	0.841336
H	1.911154	-0.198870	-0.905991
H	-2.045711	-1.025311	-0.352008
H	-0.678718	-1.067679	1.026481
H	0.347506	-2.242083	-0.285326

Frequencies

-1913.1968	271.2348	489.8277
557.9211	682.7480	729.0915
800.3762	826.8239	905.6700
923.7509	930.6590	946.3861
1006.3674	1054.8270	1121.8295
1132.0939	1239.0837	1268.2900
1291.6132	1318.5104	1389.2401
1465.2804	1566.9432	2162.2918
2884.2925	2936.8821	3186.7835
3194.3595	3210.1078	3217.1003

i19 – i16

C	1.212542	0.275436	-0.101696
C	0.602816	-1.104640	0.058299
C	-1.192572	0.263512	-0.057997
C	-0.789793	-1.093123	-0.140405
C	-0.009311	1.219058	0.107525
H	2.011834	0.439876	0.627846
H	1.666660	0.430938	-1.090295
H	1.181349	-1.970147	0.359060
H	-2.166821	0.608408	-0.396559
H	-1.575998	-0.590252	0.841934
H	0.008668	1.694843	1.093136
H	-0.067788	2.024866	-0.629468

Frequencies

-1516.1606	143.5922	464.5835
555.8428	607.4803	710.2109
787.2740	824.4365	891.3462
909.4491	971.3288	1008.3211
1066.0199	1125.2844	1176.2052
1221.3591	1240.1472	1261.6980
1305.8774	1325.3017	1385.0737
1463.7448	1482.5262	2025.7793
2985.5999	3034.2023	3049.6289
3074.5505	3140.0833	3182.1346

i10 – p8

C	0.351380	1.100772	-0.269619
C	-1.481960	0.215985	0.517474
C	1.370774	0.151185	-0.083330
C	2.197014	-0.709152	0.104209
C	-1.841348	-0.837910	-0.269415
H	0.360463	1.969364	0.381459
H	0.025850	1.286726	-1.286583
H	-2.014656	1.157708	0.430794
H	-0.992830	0.036028	1.468463
H	2.946283	-1.447684	0.256027
H	-2.477334	-0.702798	-1.137164
H	-1.422939	-1.824627	-0.108904

Frequencies

-628.4135	75.1420	127.2291
257.6510	354.8707	384.6389
471.9757	595.5308	635.4415
692.4277	779.4467	832.2936
856.7216	985.4235	1027.4327
1057.8173	1071.0137	1248.9297
1290.1937	1457.7301	1467.5501
1573.4791	2155.1124	3141.0378
3144.2314	3159.4417	3228.4142
3235.1854	3258.2662	3481.7977

i11 – p10

C	1.559101	0.020745	0.564551
C	2.349405	-0.477747	-0.354772
H	1.601972	0.009783	1.646482
H	2.134859	-0.388540	-1.417836
H	3.268894	-1.010564	-0.101070
C	-1.418040	0.210915	-0.076135
C	-2.302612	-0.737205	0.023132
C	-0.421905	1.081313	-0.130734
H	-3.345078	-0.580921	-0.241979
H	-2.028857	-1.729786	0.376097
H	0.067337	1.295613	-1.074773
H	-0.294819	1.816287	0.656829

Frequencies

-327.9283	22.9875	107.8199
169.6419	250.3638	339.2289
367.4767	379.4073	794.5197
850.1649	872.0135	872.8810
881.0343	934.8126	999.3580
1031.5405	1060.3622	1091.2476
1397.7565	1420.2789	1466.4312
1640.5715	1970.8349	3050.8367
3091.1607	3122.8526	3134.2764
3159.8259	3197.6003	3199.2879

i18 – p7

C	0.936518	0.823015	0.029571
C	-0.357120	1.165408	-0.087956
C	1.058869	-0.677608	0.054114
C	-1.181745	-0.054768	-0.141811
C	-0.361747	-1.139357	-0.100231
H	1.778498	1.497116	0.108247
H	-0.755321	2.170919	-0.120346
H	1.506022	-1.035708	0.992942
H	1.704159	-1.057373	-0.749677
H	-2.241007	-0.069603	-0.359233
H	-1.897564	-0.029093	1.752107
H	-0.663434	-2.176402	-0.146159

Frequencies

-554.6787	263.1678	295.1440
377.0117	547.6056	691.7145
709.0503	811.0909	817.7765
919.7062	925.1422	955.3196
966.1770	970.5989	1006.5221
1106.3207	1124.5800	1128.7552
1271.0188	1313.1121	1393.2486
1414.6786	1516.4608	1620.5193
3001.3791	3024.8371	3195.7479
3204.1742	3219.1359	3226.2726

i19 – p7

C	-0.404699	1.140896	-0.107060
C	-1.157814	0.018479	-0.144619
C	0.999725	0.773475	0.041140
C	-0.251133	-1.178523	-0.089469
C	1.108447	-0.565776	0.061649
H	-0.775708	2.155720	-0.165819
H	-2.221139	-0.036776	-0.330408
H	-1.783971	0.028188	1.928027
H	1.813958	1.481812	0.121433
H	-0.322855	-1.760574	-1.017829
H	-0.498232	-1.862741	0.728921
H	2.020792	-1.136934	0.165832

Frequencies

-510.9544	227.5863	295.3875
372.6181	527.7159	697.0797
771.0298	818.3538	821.0934
916.7738	937.7575	969.1519
975.5928	983.5410	1030.0797
1110.1445	1132.4776	1135.5312
1278.0666	1327.1608	1406.0964
1423.3075	1546.1322	1648.7277
3048.7226	3097.1466	3220.7962
3231.2664	3248.9549	3255.6982

il – p9

C	0.416225	0.114368	0.058280
C	1.157571	-1.194457	-0.089941
C	-1.018785	0.029488	0.010474
C	-2.209319	-0.081527	-0.059138
C	1.025100	1.310647	-0.106457
H	0.460396	0.069966	1.943573
H	1.004781	-1.584311	-1.097668
H	0.790079	-1.937548	0.614237
H	2.223971	-1.050581	0.072223
H	-3.265618	-0.172553	-0.119008
H	2.102647	1.373742	-0.169202
H	0.458993	2.230167	-0.123456

Frequencies

-990.6462	188.2601	242.2548
281.6569	387.3344	438.5722
498.6596	561.9958	584.0203
677.3083	686.9491	715.1876
781.3488	911.1495	965.9395
1048.3650	1076.2847	1294.2218
1419.3474	1434.7844	1496.7368
1508.3428	1608.2952	2243.0734
3061.4031	3133.8342	3158.1089
3171.2249	3270.7050	3484.1733

Products

p1 including the methyl radical (CH₃)

C	0.735469	0.110223	0.000086
C	-1.659547	-0.371443	-0.000057
C	-0.635848	0.488624	-0.000043
C	1.906556	-0.171716	-0.000032
H	-2.682927	-0.016566	0.000061
H	-1.500620	-1.443220	0.000192
H	-0.832585	1.557992	0.000100
H	2.936361	-0.432338	-0.000074

Frequencies

224.2867	316.4180	557.7143
647.7405	680.3845	703.4961
892.2675	954.7839	1009.9860
1111.4766	1320.9319	1443.5005
1668.4638	2205.6653	3136.5876
3147.5830	3236.4066	3476.2183

p2 including H

C	-1.202292	0.542763	-0.000079
C	-1.645730	-0.885237	-0.000019
C	1.219844	0.145766	0.000002
C	2.221543	-0.524619	0.000053
C	0.066812	0.978728	0.000028
H	-1.987388	1.294487	-0.000082
H	-2.268509	-1.096578	-0.876600
H	-0.798957	-1.572565	-0.002829
H	-2.263492	-1.097953	0.879832
H	3.100856	-1.120378	-0.000332
H	0.256429	2.048577	0.000096

Frequencies

136.6859	157.8647	274.8248
374.7152	502.7787	630.2292
661.7995	679.5908	749.8505
901.1060	973.5395	987.8983
1063.3332	1120.7954	1265.7218
1398.6581	1430.3399	1482.6620
1483.8772	1683.1863	2199.3013
3015.0403	3055.6654	3113.9473
3136.8641	3156.1774	3476.3682

p3 including H

C	0.925056	-0.394350	0.000012
C	2.371246	-0.011169	-0.000008
C	-1.466238	0.109466	0.000001
C	-2.639574	-0.165085	0.000016
C	-0.093017	0.477133	-0.000018
H	0.697974	-1.457539	0.000054
H	2.884328	-0.419494	-0.878030
H	2.884334	-0.419427	0.878041
H	2.502368	1.073139	-0.000050
H	-3.671109	-0.417575	0.000030
H	0.117264	1.544925	-0.000060

Frequencies

167.0357	170.9676	199.8552
390.5346	450.1885	544.8979
626.0470	681.2255	816.2460
912.4616	986.8754	1046.6087
1065.7194	1128.4006	1314.4868
1328.7208	1414.4391	1477.7085
1489.6826	1695.6858	2203.1267
3012.8784	3054.9688	3097.4517
3125.2985	3147.4522	3477.9955

p4 including H

C	-1.338270	0.111976	-0.043656
C	-0.039083	0.772602	0.091737
C	2.193061	-0.313669	-0.301312
C	1.081494	-0.191272	0.414143
C	-2.399348	-0.441833	-0.144895
H	-0.113034	1.524078	0.889181
H	0.194377	1.317986	-0.828708
H	2.973102	-1.011742	-0.020010
H	2.364542	0.278153	-1.195387
H	0.931740	-0.805140	1.298553
H	-3.337848	-0.930163	-0.239728

Frequencies

89.3954	187.7194	337.6049
408.6864	475.0917	644.9942
664.4057	680.2830	898.3696
925.9499	953.1208	982.0640
1030.8713	1127.9109	1245.4688
1314.0050	1330.0467	1450.5476
1464.4171	1709.5795	2223.6181
3001.9565	3049.7914	3127.8671
3146.0430	3213.3811	3477.6481

p5 including H

C	1.338364	0.111812	-0.043717
C	2.399674	-0.441361	-0.145081
C	-1.081490	-0.191863	0.413768
C	-2.193393	-0.313113	-0.301327
C	0.039087	0.772259	0.092273
H	3.338310	-0.929368	-0.240259
H	-0.931447	-0.806970	1.297257
H	-2.365269	0.279877	-1.194540
H	-2.973410	-1.011459	-0.020609
H	0.112779	1.523095	0.890368
H	-0.194414	1.318421	-0.827713

Frequencies

89.1871	187.4077	337.4265
408.6538	475.0295	644.9127
664.5444	680.3927	898.3509
925.9920	953.1322	982.0512
1030.8683	1127.9541	1245.4893
1314.0216	1330.0750	1450.5950
1464.4220	1709.6609	2223.9987
3001.8282	3049.6767	3127.9373
3146.1104	3213.3494	3477.6527

p6 including H

C	-1.163693	0.167288	0.000096
C	-2.133665	-0.541117	-0.000019
C	0.012695	1.031130	0.000113
C	1.538108	-0.994979	-0.000148
C	1.348571	0.318440	-0.000019
H	-2.995522	-1.162115	-0.000082
H	-0.032561	1.697068	0.872207
H	-0.032649	1.697226	-0.871856
H	2.537300	-1.414736	-0.000236
H	0.705184	-1.689370	-0.000169
H	2.206159	0.987355	-0.000002

Frequencies

147.5206	162.0456	332.3985
378.7846	568.0392	614.7230
663.9413	681.5658	866.6468
947.0140	965.1155	966.7503
1030.0920	1093.1564	1237.7560
1325.0798	1353.6219	1441.0304
1463.1201	1712.5303	2226.1384
3000.4644	3016.9398	3131.0362
3143.4622	3223.0748	3476.4354

p7 including H

C	0.736623	0.987585	0.000000
C	1.178765	-0.283674	0.000003
C	-0.732076	0.990950	-0.000042
C	-0.002784	-1.215526	0.000012
C	-1.180063	-0.278271	-0.000012
H	1.351623	1.878553	0.000008
H	2.208871	-0.612750	0.000074
H	-1.342974	1.884740	0.000182
H	-0.004416	-1.877171	0.877009
H	-0.004230	-1.877090	-0.877061
H	-2.211661	-0.602668	0.000024

Frequencies

348.6040	524.0849	681.4372
712.6337	816.8658	818.7255
917.4930	924.4380	954.1554
955.7283	970.8450	1012.4461
1111.9798	1125.8854	1129.9476
1266.1830	1314.9867	1397.1448
1414.9789	1552.2415	1638.8444
3010.5306	3032.0452	3186.7348
3196.8341	3215.4703	3222.0692

p8 including the propargyl radical (C₃H₃)

C	0.663422	0.000006	0.000021
C	-0.663514	-0.000020	-0.000122
H	1.234985	-0.922431	0.000012
H	1.234746	0.922528	0.000061
H	-1.234596	0.922630	0.000243
H	-1.234582	-0.922640	0.000292

Frequencies

834.9037	973.0542	973.9308
1066.6751	1238.6866	1379.6577
1472.3233	1691.9537	3120.9179
3136.0676	3192.0523	3220.5232

p9 including H

C	-1.004075	0.039682	-0.000023
C	-2.202667	-0.079851	-0.000040
C	0.424308	0.121973	0.000002
C	1.167364	-1.194836	0.000087
C	1.046741	1.308301	-0.000048
H	-3.261115	-0.169603	-0.000056
H	0.901453	-1.788033	0.879923
H	2.246492	-1.032930	0.000101
H	0.901489	-1.788125	-0.879698
H	2.129017	1.368606	-0.000029
H	0.492638	2.238473	-0.000109

Frequencies

176.0542	186.9003	268.6311
396.9905	546.3948	571.1248
650.0507	677.8309	743.9201
775.5743	931.9078	964.8473
1031.9442	1071.4830	1284.5910
1410.5281	1435.3005	1478.0144
1495.8336	1675.6068	2201.3420
3028.1446	3080.9802	3112.9291
3143.5745	3233.6641	3476.5419

p10 including the vinyl radical (C₂H₃)

C	1.302452	0.000002	-0.000016
C	-0.000002	-0.000073	0.000117
C	-1.302448	0.000028	-0.000019
H	1.866971	0.663127	0.648052
H	1.866901	-0.663016	-0.648258
H	-1.867110	-0.648184	0.662825
H	-1.866772	0.648328	-0.663111

Frequencies

371.7987	371.8106	866.2426
866.2584	885.0895	1017.1692
1017.1764	1109.3233	1422.4951
1479.5973	2052.4143	3117.2859
3121.3263	3192.2676	3192.2929

Radicals

Methyl

C	-0.000035	-0.000090	0.000016
H	-0.998670	-0.412387	-0.000033
H	0.856880	-0.658119	-0.000033
H	0.142001	1.071048	-0.000033

Frequencies

505.2897	1402.6327	1403.3797
3104.1952	3282.8105	3283.7762

Vinyl

C	0.586665	0.029432	-0.000348
C	-0.706546	-0.142672	-0.000013
H	1.282549	-0.806960	0.001029
H	1.038849	1.025354	0.000631
H	-1.602110	0.461046	0.000505

Frequencies

710.0974	818.1174	921.1459
1045.3942	1390.9565	1649.7997
3038.3302	3135.2321	3236.1642

Propargyl

C	-1.337790	-0.000036	-0.000137
C	1.251310	0.000077	-0.000077
C	-0.115777	0.000017	0.000412
H	-2.399972	0.000257	-0.000456
H	1.806292	-0.930175	-0.000367
H	1.807221	0.929569	-0.000368

Frequencies

351.7867	402.9866	468.4694
637.7994	681.7457	1031.4004
1089.4462	1455.3690	2011.5641
3139.3202	3229.8787	3468.0096

Table S2. Rate constants k (s^{-1}) for all unimolecular reactions in the $\text{C}_2\text{H} + \text{propylene}$ system calculated using RRKM theory at $E_c = 41.1 \text{ kJ mol}^{-1}$.

Reaction	k	Reaction	k	Reaction	k
i14 – i15	4.19E+12	i5 – i7	4.63E+06	i11 – i4	1.19E+07
i15 – i14	2.79E+12	i6 – p2	3.56E+08	i4 – i11	1.71E+07
i15 – i17	1.96E+12	i4 – i6	2.97E+08	i12 – i4	1.88E+06
i17 – i15	4.48E+12	i6 – i4	4.10E+07	i4 – i12	6.78E+05
i17 – i19	7.76E+09	i1 – i4	3.09E+05	i1 – i8	2.60E+03
i19 – i17	6.48E+09	i4 – i1	2.63E+05	i8 – i1	1.76E+02
i19 – p7	2.20E+10	i8 – p1	2.04E+09	i4 – i2	1.15E+10
i15 – p2	1.39E+07	i4 – p6	3.41E+08	i2 – i4	6.20E+12
i19 – i18	1.89E+09	i4 – p2	6.17E+08	i12 – i10	1.28E+06
i18 – i19	1.53E+10	i1 – i2	1.26E+10	i10 – i12	1.06E+06
i15 – p3	1.19E+07	i2 – i1	5.81E+12	i4 – i3	5.39E+12
i13 – i18	4.45E+10	i10 – p8	3.31E+10	i3 – i4	1.95E+12
i18 – i13	9.21E+08	i10 – p6	2.24E+08	i5 – i3	1.06E+06
i18 – p7	1.40E+11	i10 – i4	6.65E+07	i3 – i5	8.85E+05
i13 – i21	2.23E+12	i4 – i10	2.91E+07	i3 – p4	1.45E+08
i12 – i13	2.17E+12	i10 – i8	1.04E+08	i3 – p3	2.85E+08
i19 – i16	1.57E+05	i8 – i10	7.26E+06	i8 – i3	1.74E+07
i16 – i19	8.74E+07	i7 – i4	5.26E+07	i3 – i8	7.94E+07
i13 – p6	5.92E+08	i4 – i7	5.05E+07	i3 – p5	1.45E+08
i12 – p6	3.78E+08	i16 – i10	1.47E+10	i10 – i9	6.06E+12
i17 – i7	2.90E+09	i10 – i16	4.15E+09	i9 – i10	3.97E+12
i7 – i17	6.91E+11	i1 – p1	1.60E+09	i3 – i9	1.45E+07
i7 – p2	5.07E+09	i1 – p9	5.79E+07	i9 – i3	6.00E+07
i5 – p3	1.13E+09	i8 – i6	9.26E+11	i9 – p4	1.23E+08
i7 – i5	1.11E+07	i6 – i8	1.61E+12	i9 – p5	1.23E+08

Table S3. Rate constants k (s^{-1}) for all unimolecular reactions in the $\text{C}_2\text{H} + \text{propylene}$ system calculated using RRKM theory at $E_c = 0 \text{ kJ mol}^{-1}$.

Reaction	k	Reaction	k	Reaction	k
i14 – i15	3.53E+12	i5 – i7	1.55E+05	i11 – i4	1.98E+06
i15 – i14	2.42E+12	i6 – p2	5.06E+07	i4 – i11	3.00E+06
i15 – i17	1.70E+12	i4 – i6	5.56E+07	i12 – i4	9.06E+04
i17 – i15	4.09E+12	i6 – i4	5.93E+06	i4 – i12	3.14E+04
i17 – i19	3.93E+09	i1 – i4	1.55E+03	i1 – i8	4.78E+00
i19 – i17	2.65E+09	i4 – i1	1.23E+03	i8 – i1	2.32E-01
i19 – p7	8.68E+09	i8 – p1	4.37E+08	i4 – i2	5.63E+09
i15 – p2	1.35E+06	i4 – p6	3.95E+07	i2 – i4	4.47E+12
i19 – i18	7.15E+08	i4 – p2	9.54E+07	i12 – i10	3.52E+04
i18 – i19	6.87E+09	i1 – i2	6.77E+09	i10 – i12	2.92E+04
i15 – p3	9.69E+05	i2 – i1	4.25E+12	i4 – i3	5.27E+12
i13 – i18	3.09E+10	i10 – p8	1.07E+10	i3 – i4	1.90E+12
i18 – i13	3.06E+08	i10 – p6	2.31E+07	i5 – i3	4.18E+04
i18 – p7	6.27E+10	i10 – i4	6.68E+06	i3 – i5	3.66E+04
i13 – i21	2.20E+12	i4 – i10	2.78E+06	i3 – p4	1.54E+07
i12 – i13	2.02E+12	i10 – i8	1.62E+07	i3 – p3	4.28E+07
i19 – i16	1.37E+04	i8 – i10	8.29E+05	i8 – i3	2.50E+06
i16 – i19	1.19E+07	i7 – i4	5.00E+06	i3 – i8	1.46E+07
i13 – p6	6.12E+07	i4 – i7	5.05E+06	i3 – p5	1.54E+07
i12 – p6	3.55E+07	i16 – i10	4.92E+09	i10 – i9	5.46E+12
i17 – i7	1.26E+09	i10 – i16	2.10E+09	i9 – i10	3.59E+12
i7 – i17	5.18E+11	i1 – p1	3.45E+08	i3 – i9	1.37E+06
i7 – p2	6.94E+08	i1 – p9	7.79E+06	i9 – i3	5.99E+06
i5 – p3	1.49E+08	i8 – i6	9.21E+11	i9 – p4	1.11E+07
i7 – i5	3.72E+05	i6 – i8	1.60E+12	i9 – p5	1.11E+07