

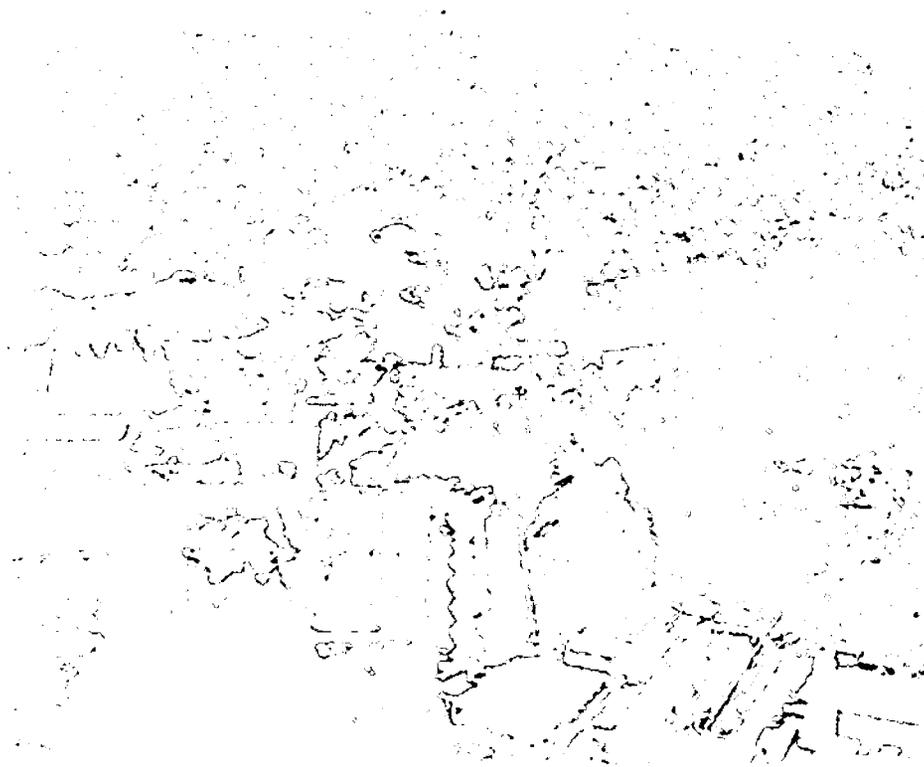


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**A Coupled-Cluster *ab initio* Study of Triplet C₃H₂
and the Neutral-Neutral Reaction to Interstellar C₃H**

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Abstract

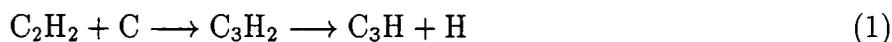
For the initially formed C_3H_2 collision complexes of molecular beam experiments ab initio calculations are presented. Resolving energetics and properties of these intermediates is essential for the understanding of the reaction of $C(^3P)$ with C_2H_2 to form interstellar cyclic and linear isomers of C_3H . Computed reaction energies agree with results from molecular beam experiments. The combination of crossed molecular beam experiments and ab initio calculations allows to identify two reaction channels for the carbon-hydrogen exchange and to explain astronomical observations of a higher $c\text{-}C_3H$ to $l\text{-}C_3H$ ratio in dark clouds as compared to hotter envelopes of carbon stars.

1 Introduction

Reactions involving atomic carbon in its electronic 3P ground state have received great interest both theoretically and experimentally due to the importance in hydrocarbon syntheses, combustion processes, and interstellar chemistry. Isomers of C_3H_2 and C_3H were detected in interstellar clouds and envelopes of evolved carbon stars. Cyclopropenylidene, $c-C_3H_2$, was discovered in 1985 in a cold dark cloud TMC-1 (Taurus Molecular Cloud 1) by Matthews et al. [1] and Thaddeus et al. [2]. Another isomer of C_3H_2 , vinylidenecarbene (H_2CCC), was first observed in interstellar space by Cernicharo et al. [3]. At the same time the hydrocarbon radical C_3H was first detected in its linear form (propynylidyne) by Thaddeus et al. [2] via microwave spectroscopy towards TMC-1 and the carbon star IRC+10216. A corresponding cyclic isomer, $c-C_3H$ (cyclopropynylidyne), was found only two years later in TMC-1 by Yamamoto et al. [4].

Although interstellar fractional abundances of such hydrocarbons relative to atomic hydrogen of up to 10^{-8} are relatively large compared to other hydrocarbon species, their formation mechanisms in space have not yet been fully understood. Due to very small average kinetic energies of interstellar molecules of typically 0.8 kJ/mol in diffuse clouds and only 0.08 kJ/mol in dark clouds, reactions to these interstellar species must have little or no barriers. Further, only two-body collisions provide reasonable reaction probabilities. Reaction models for interstellar chemistry were focusing on radiative association, dissociative recombination, and exothermic ion-molecule processes (e.g. Ref. [5, 6]). However, these mechanisms were not able to reproduce observed number densities and isomer ratios such as for the linear and cyclic form of C_3H . Recent kinetic studies by Clary et al. [7], showed no barriers in fast neutral-neutral reactions of atomic $C(^3P)$ with unsaturated hydrocarbons and initiated the interest for such reaction paths. However, the formation of C_3H remained unclear.

To investigate this unresolved problem in interstellar chemistry, the formation process of C_3H via neutral-neutral reactions has been studied using crossed molecular beam experiments by three of us, R. I. K., Y. T. L., and A. G. S. [8, 9]. In the present theoretical *ab initio* investigation our main interest is to elucidate energetics and properties of the initially formed triplet C_3H_2 collision complexes [10]



and to compute accurate reaction energies using high level electronic structure theory methods. We restrict ourselves to the triplet surface, as the C_3H_2 intermediates do not fulfill requirements of intersystem crossing [11, 12]. Although this molecule has been subject of a multitude

of theoretical [13–23] and experimental [1, 2, 8, 9, 24] studies, a complete investigation of the different possible structures using high level ab initio methods and sufficiently large basis sets for structures, energetics, and vibrational frequencies was still lacking.

Similar interest has been attributed to the C_3H molecule both theoretically [4, 19, 22, 25–28] and experimentally [4, 29–32]. The main difficulty of this system is the occurrence of symmetry breaking in theoretical treatments. Such problems for the cyclic C_3H structure have been solved by a state of the art theoretical study of Stanton [26] using the EOMIP-CCSD (equation of motion coupled cluster singles and doubles approximation for ionized states) method (e.g. Ref. [33]), where C_{2v} symmetry is found in agreement with experiments. However, symmetry determination — by accurate calculation of vibrational frequencies — remains an open issue for the linear structure, although attempts have been made to solve these problems [22, 27, 31]. Due to both methodological difficulties and basis set deficiencies, theoretical studies so far do not yet provide conclusive theoretical estimates concerning the symmetry of the linear equilibrium structure of C_3H . However, this is an issue which we will not address in this study, as our main interest here in C_3H are relative energies and reaction energies which are shown to be only very little influenced by stability problems. Relative energies of the cyclic and the linear form of this radical are as well an important issue, as previous results of theoretical calculations reside in a wide range between 1 kJ/mol [27] and 75 kJ/mol [4].

2 Details of Computation

All ab initio calculations have been carried out with the program system ACES II [34]. Unrestricted Hartree-Fock (UHF) wavefunctions are used and only pure spherical harmonic components of d, f, and g functions are included. Throughout this study the CCSD(T) (single- and double-excitation coupled cluster with a perturbational estimate of triple excitations) method [35] has been employed. Some SCF (self-consistent field), MP2 [36] (Møller-Plesset second order perturbation theory), and CCSD [37] relative energies are given for comparison to show the inadequacy of simple approaches like SCF and MP2 for C_3H_2 and C_3H .

Further, Brueckner CC methods [38–43] have been used for the treatment of C_3H , where symmetry-breaking problems play an important role. As the single excitation (T_1) amplitudes account for most of the orbital relaxation effects in CC methods, in Brueckner methods the so called Brueckner determinant is used as a reference functions, which is defined as the one

for which single excitations do not mix with the exact wavefunction (FCI, full configuration interaction). In approximate methods such as the CCSD method, the reference function for which the T_1 amplitudes vanish leads to the B-CCD method [39–43]. This approach has proven its usefulness for the treatment of symmetry breaking problems such as encountered for example in case of NO_3 [43] or O_4^+ [44].

Stability of the zeroth-order SCF wavefunctions (e.g. Ref. [45]) has been checked throughout this study. Spin contamination occurring in the SCF wavefunction (typically 2.40 for $\langle S^2 \rangle$ in triplet states of C_3H_2) is mostly eliminated within the CC scheme (to typically about 2.05 for $\langle S^2 \rangle$ for the projected spin multiplicities using T_1 and T_2 [46]). Such a behavior is well known for CC methods and reflects the insensitivity with respect to the choice of orbitals [47].

All structures were fully optimized at the CCSD(T) level imposing proper symmetries of D_{2h} and subgroups. To characterize stationary points (local minima or saddle points, IR data, and zero-point vibrational energies, ZPE), vibrational frequencies have been calculated numerically within the harmonic approximation using analytic CCSD(T) gradients [48]. To recognize possible problems in numerical calculations of frequencies due to unstable or differing zeroth-order wavefunctions, frequencies have been computed as a check both analytically and numerically at the SCF level using the same structure.

The following basis sets have been used:

DZP:	H:	(4s1p)/[2s1p]	[49]
	C:	(8s4p1d)/[4s2p1d]	
TZP:	H:	(5s1p)/[3s1p]	[49]
	C:	(10s6p1d)/[6s3p1d]	
TZPP:	H:	(5s2p1d)/[3s2p1d]	[49]
	C:	(10s6p2d1f)/[6s3p2d1f]	
QZ2P:	H:	(7s2p1d)/[4s2p1d]	[49]
	C:	(11s7p2d1f)/[6s4p2d1f]	
cc-pVQZ:	H:	(6s3p2d1f)/[4s3p2d1f]	[50]
	C:	(12s6p3d2f1g)/[5s4p3d2f1g]	

The double and triple zeta polarization basis sets [49], DZP and TZP, respectively, were used for geometry optimizations and the calculation of vibrational frequencies. The triple zeta double polarization basis (TZPP) [49] was used partly for geometry optimizations and the calculation of frequencies to check the accuracy of the smaller basis sets. The quadruple zeta

double polarization basis denoted QZ2P [49] and the correlation consistent polarized valence quadruple zeta (cc-pVQZ) basis [50] (which contains up to g functions on C and up to f on H) were used only for single-point energy calculations and can be considered to be complete enough to yield reliable relative energies and reaction energies at the CCSD(T) level.

3 Discussion of Results

In the following, we will discuss first, aspects of methodology and results for the different C_3H_2 structures. The accuracy of the CCSD(T) calculations using different basis sets will be assessed and the necessity to use such high-level methods is shown. Further, a comparison to results in the literature is made. Finally, selected reaction energies are presented.

3.1 C_3H_2 minima

Table 1 shows relative energies of four minima (Fig. 1) and five saddle points (Fig. 2) of C_3H_2 on the triplet surface. The most stable isomer is the so called propargylene, denoted C_2^{lin} , which is energetically favored by more than 134.9 kJ/mol (CCSD(T)/QZ2P/ZPE) versus other isomers of C_3H_2 . Its C_2 symmetry (Fig. 1 (a)) agrees with results of a recent FTIR (Fourier transform IR) experiment, in which the assignment was made by ^{13}C -labeling studies in argon matrices [51]. The CCC angle is almost linear, 171.9° , and the torsion angle of the two H atoms is 88.0° (CCSD(T)/TZP, Table 5). The C–C bond length of 127.9 pm has to be compared to bond lengths of 120.9 pm for a typical triple bond (C_2H_2) and 132.8 pm for a double bond (C_2H_4) within the same approach. The lowest vibrational frequency of 215 cm^{-1} (CCSD(T)/TZP; Table 2) indicates the floppiness of the structure.

Similarly the second-most stable isomer, vinylidenecarbene (denoted C_{2v} ; Fig. 1 (b)), with C_{2v} symmetry is also floppy with a vibrational frequency of 222 cm^{-1} (CCSD(T)/TZP). The C–C bond length to the carbon holding the two hydrogen atoms is 136.9 pm whereas the other C–C bond is much shorter with 123.8 pm. C–H bond distances of 108.1 pm compare to 108.4 pm found in C_2H_4 (CCSD(T)/TZP).

Cyclopropenylidene c - C_3H_2 , denoted C_1^{cyclic} , shows no symmetry (Fig. 1 (c)) and is 172.4 kJ/mol (CCSD(T)/QZ2P/ZPE) higher in energy compared to the most stable isomer, C_2^{lin} . In contrast to all other structures its lowest vibrational frequency is much higher, 599.1 cm^{-1} (CCSD(T)/TZP). One hydrogen is placed almost in the plane of the carbon cycle (out of

plane angle only 0.2°), whereas the other H atom is distorted by 46.1° out of the CCC plane (CCSD(T)/TZP). C–C distances range between 130.4 and 155.1 pm (Table 5).

Another isomer (C_s^{trans}), trans-propenediylidene (Fig. 1 (d); trans with respect to the H atoms) shows C_s symmetry and is 250.8 kJ/mol (CCSD(T)/QZ2P/ZPE) less stable than the most stable C_3H_2 structure. C–C bond lengths of 134.9 and 139.2 pm (CCSD(T)/TZP) have to be compared to the bond length of 132.8 pm found in C_2H_4 . For the C_s^{trans} structure the lowest frequency of all C_3H_2 isomers is observed: 187.2 cm^{-1} (CCSD(T)/TZP).

3.2 Aspects of methodology and connection to literature data

Before discussing the different saddle points found for C_3H_2 (Fig. 2 and Tables 1, 3, and 4) it is important to assess the accuracy which might be expected for relative energies, structural properties, and vibrational frequencies of this molecule. For this purpose we use the linear structure with $D_{\infty h}$ symmetry of C_3H_2 , as it allows us to investigate basis set effects not only on structural parameters and vibrational frequencies, but — as it is a saddle point on the hypersurface — effects on imaginary frequencies can be observed as well. The high point group symmetry of the $D_{\infty h}$ structure permits the use of quite large basis sets.

The already mentioned typical spin contamination of C_3H_2 SCF wavefunctions suggests the necessity of using high-level ab initio methods like the CC scheme. This is supported by analyzing relative energies of C_3H_2 structures shown in Table 1: the most drastic example represents the cyclic isomer C_1^{cyclic} for which energy differences relative to the most stable isomer C_2^{lin} change from 229.6 kJ/mol (SCF), over 104.3 kJ/mol (MP2), to 169.3 kJ/mol (CCSD) and finally to our most accurate result 160.9 kJ/mol (CCSD(T) using the QZ2P basis. This trend reflects the well known overestimation of correlation effects at the MP2 level and shows the inappropriateness of the SCF and MP2 method for C_3H_2 . The largest T_1^{max} and T_2^{max} CC amplitudes range typically around 0.08 and 0.06, respectively.

A recent study of C_3H_2 by Takahashi and Yamashita [22] using the SCF and MP2 approximations for the computation of energetics and vibrational frequencies of C_3H_2 also shows inadequacies of these methods for the treatment of this molecule. For example, their MP2/6-31G(d,p) calculations on a cyclic triplet C_1 isomer of C_3H_2 lead to an unphysical vibrational frequency of 5714 cm^{-1} [22]. The occurrence of completely unreasonable force constants is a well known problem at lower levels of theory like SCF and MP2, especially in case of open-shell systems with low-lying excited states [26, 52]. Such defects within the optimized SCF

wavefunction are only very slowly compensated in a simple perturbation expansion like in many-body perturbation theory (MBPT(n)) [53] with higher order n . This is further support for using CC methods.

Using SCF and MP2 Takahashi and Yamashita [22] find a different most stable isomer of C_3H_2 on the triplet surface compared to our CCSD(T) study. Instead of the almost linear structure with C_2 symmetry we calculated (C_2^{lin} ; Fig. 1), whose symmetry agrees with results of recent FTIR experiments [51], they find another almost linear structure, C_s^{lin} (Fig. 2), as the most stable isomer of the C_3H_2 triplet surface. Our CCSD(T)/QZ2P results characterize this structure to be virtually isoenergetic with the most stable isomer of our study (C_2^{lin}), but it is a saddle point at the CCSD(T) level (Table 3). Our calculation supports the C_2 symmetry found for the linear isomer at the QCISD(T)/6-31G* level by Herges et. al [21]. The second most stable isomer of C_3H_2 (triplet), vinylidencarbene (C_{2v}), was not considered in the study of Takahashi and Yamashita [22]. Further, trans-propenediylidene (C_s^{trans}), found as a saddle point by Takahashi and Yamashita [22] at the MP2 level (structure **2a** in Ref. [22]), is a minimum on the CCSD(T) hypersurface (Table 2).

Another serious problem of ab initio studies are instabilities and symmetry-breaking in the zeroth-order SCF wavefunction, which we will discuss extensively for the C_3H molecule. Related to this often underestimated difficulty, the published cis-propenediylidene (cis with respect to the H atoms; structure **2b** in Ref. [22]) structure of C_3H_2 found as a local minimum by Takahashi and Yamashita [22] is based on an unstable HF wavefunction (for which the energy was listed as -114.55617 Hartree, Table III in Ref. [22]), although in this case a stable HF solution within the same symmetry can be found by running along the mode of the negative eigenvalue describing the corresponding orbital rotations. In such a case MP2 enhances the error introduced in the zeroth-order wavefunction as reflected by even bigger energy differences between using unstable and stable wavefunctions (whereas CC methods tend to largely overcome such errors). This will be discussed more extensively for symmetry-broken HF wavefunctions in context of the C_3H molecule. The cis-propenediylidene structure of C_3H_2 found using the unstable SCF wavefunction by Takahashi and Yamashita [22], was not located using the CCSD(T) method (using of course a stable zeroth-order wavefunction), which lead on several optimizations from different starting points to a linear structure. However, this does not safely exclude the existence of this structure as a stationary point, it can be only concluded that if existent its surrounding hypersurface is probably very flat.

After we have shown the problematic nature of low level methods for the computational

treatment of C_3H_2 , it is important to continue the evaluation of accuracies which might be expected at the CCSD(T) level for different properties and aspects of this system. The CCSD(T)/QZ2P relative energies are expected to be highly accurate and basis set effects to be small, as indicated by a change of less than 4 kJ/mol in increasing the basis from TZPP to QZ2P. Due to its high point group symmetry the linear structure $D_{\infty h}$ allows us to investigate basis set effects on both structural properties and vibrational frequencies. The data listed in Table 4 shows the excellent agreement of structural constants computed at the CCSD(T)/TZP level as compared to data obtained using the bigger basis sets TZPP and QZ2P, with deviations of less than 0.4 pm. Vibrational frequencies (CCSD(T)/TZP) differ by less than 30 cm^{-1} using basis sets up to QZ2P, whereas imaginary frequencies are more sensitive to basis set effects (Table 4). However, no change in the number of imaginary frequencies was observed. The good accuracy achieved for vibrational frequencies leads to only small changes in zero-point vibrational energies (ZPE) with deviations of less than 1 kJ/mol (Table 4).

The examination of relative energies including zero-point vibrational energies for the C_3H_2 triplet structures, C_2^{lin} (which is almost isoenergetic with the saddle point C_s^{lin} found in Ref. [22] as a minimum) and structure C_1^{cyclic} , which we might compare to the ab initio study of Takahashi and Yamashita [22], reveals a surprisingly good coincidence of their MP4/6-311G(d,p)//MP2/6-31G(d,p) value (MP4 single-point at MP2 structure) with our CCSD(T)/QZ2P/ZPE data. However, the unexpected small deviation of only slightly more than 10 kJ/mol is a result of a fortuitous cancellation of errors in their study [22]: they used the zero-point energy which includes the unreasonable vibrational frequency of 5714 cm^{-1} , mentioned earlier, for the calculation of relative energies (the ZPE effect on the relative energy of these two structures is 38 kJ/mol [22]).

3.3 Saddle points of C_3H_2

Three almost linear structures, C_s^{lin} , C_{2v}^{lin} , and the exactly linear one $D_{\infty h}$ (Fig. 2 (a)-(c)), are saddle points (CCSD(T)/TZP) with one and two imaginary frequencies, respectively (Table 3 and 4; for $D_{\infty h}$ the two imaginary modes are degenerate). The first one, C_s^{lin} , has been previously found to be a minimum at lower levels of theory (e.g. Ref. [22]). However, all these structures are virtually isoenergetic (within 1 kJ/mol, CCSD(T)/QZ2P) with the most stable minimum of C_3H_2 , C_2^{lin} . For example, the energy difference between the most stable

isomer C_2^{lin} and the saddle point C_s^{lin} is extremely small (see Table 1). The reason for occurring negative values (-0.3 to $+0.5$ kJ/mol) within the CCSD(T)/TZPP and CCSD(T)/QZ2P approach is attributed to the non-optimized structures used in the single-point approach (at the CCSD(T)/TZP structures), a fact which has been checked using the TZPP basis (non-optimized vs. optimized). These small energy differences reflect again the flatness of the hypersurface in the vicinity of the most stable C_3H_2 isomer, C_2^{lin} , which is indicated as well by its lowest vibrational frequency of 215.2 cm^{-1} (CCSD(T)/TZP).

A cyclic C_3H_2 structure with both hydrogen atoms attached to the same carbon has not been investigated in this study, as it is considered to be unimportant for the reaction of $C(^3P)$ with C_2H_2 [10], where the two H atoms are bound to different carbons and hydrogen migration can not take place within the lifetime of this collision complex, see Ref. [9]. Its energy difference with respect to the the most stable linear triplet isomer of C_3H_2 was found by Jonas et al. [20] to be 256 kJ/mol, as obtained by using a spin-projected MP4 method at MP2 geometries (PMP4/6-311G(2df)//MP2/6-31G(d)).

The cyclic isomer of C_3H_2 , C_1^{cyclic} , which is a minimum on the CCSD(T)/TZP hypersurface has been derived by distortion from higher symmetry analogues, C_2^{cyclic} and C_{2v}^{cyclic} , showing one and two imaginary frequencies, respectively (Fig. 2 (d) and (e), and Table 3). The energy gain by the distortion from the C_{2v}^{cyclic} structure with the highest symmetry is 26.4 kJ/mol (CCSD(T)/QZ2P, Table 1).

3.4 C_3H

Before we discuss computed reaction energies of the neutral-neutral reaction (1) presented in the introduction of this paper, we need to investigate the product of the reaction, C_3H . This study focus on its energetics, and, as mentioned before, it is not our intention to treat the still open issue of what symmetry has to be assigned to the equilibrium geometry of the linear isomer using ab initio methods. This question has only negligible influence on reaction energies, which are our only concern about C_3H in the present study.

Table 6 lists relative energies of three C_3H structures: a cyclic c - C_3H (C_{2v} symmetry), a linear l - C_3H ($C_{\infty v}$), and a bent b - C_3H (trans) form with C_s symmetry (see Fig. 3). The c - C_3H isomer is 13.0 kJ/mol more stable than the linear form l - C_3H at the CCSD(T)/cc-pVQZ level. The change in increasing the basis from QZ2P to cc-pVQZ is less than 1 kJ/mol, indicating the sufficient size of the employed basis sets. The two linear structures l - C_3H and b - C_3H are

virtually isoenergetic with an energetic difference of less than 1 kJ/mol (CCSD(T)/cc-pVQZ).

Comparison of our most reliable CCSD(T) data with results at lower levels of theory like SCF and MP2 reveals, as expected, an even much more pronounced deficiency of these methods for the treatment of C_3H than for C_3H_2 . SCF favors the linear structures by more than 30 kJ/mol, whereas for MP2 a strong overestimation of correlation effects can be observed, preferring the linear structure by more than 80 kJ/mol (Table 6). The problem is reflected by high maximal amplitudes T_1^{max} and T_2^{max} : although reasonable values of 0.04–0.05 and 0.06–0.07, respectively, occur for $c-C_3H$, much higher values of $T_1^{max} = 0.17$ –0.22 and $T_2^{max} = 0.08$ –0.10. are observed for linear structures of C_3H . This is closely related to the problem that for $c-C_3H$ stable HF solutions can be found using basis sets like TZP and larger, whereas for the linear structures no stable SCF wavefunction within the true symmetry (always D_{2h} and subgroups) can be found. However, energy differences between using the true symmetry wavefunction and the stable C_1 zeroth-order wavefunction are very small (negative sign if C_1 solution is lower in energy; basis TZP):

$$\begin{array}{l} l-C_3H \quad -0.4 / +5.0 / +0.3 / +0.2 \quad (\text{SCF} / \text{MP2} / \text{CCSD} / \text{CCSD(T)}) \\ b-C_3H \quad -0.3 / +4.4 / +0.2 / +0.1 \quad (\text{SCF} / \text{MP2} / \text{CCSD} / \text{CCSD(T)}) \end{array}$$

As mentioned before such energy differences between a true symmetry and a symmetry-broken solution are increased by the MP2 method, whereas the CCSD(T) method compensates the already small energy difference within the SCF approach to 0.2 and 0.1 kJ/mol, respectively. This shows that energetics are only slightly influenced by such effects.

In addition we performed Brueckner CC calculations B-CCD, known for their ability to be often efficient for the treatment of symmetry-breaking problems and the occurrence of larger T_1^{max} amplitudes [43, 44]. The change in relative energies as compared to the CCSD data (basis QZ2P) is less than 2 kJ/mol, confirming the validity of the conventional CCSD approach for this molecule.

Our relative energies are in excellent agreement with MRCI data including the Davidson correction published by Takahashi and Yamashita [22] using a valence triple zeta basis. They found the $c-C_3H$ isomer to be favored by 8.6 kJ/mol versus $l-C_3H$, and the slightly bent one, $b-C_3H$, to be separated by less than 2 kJ/mol from the exactly linear $l-C_3H$ structure.

Structural data for $c-C_3H$ (CCSD(T)/TZP) shows excellent agreement with both theoretical and experimental results. Bond lengths differ by less than 0.3 pm from data obtained by microwave experiments [30]. For the cyclic isomer of C_3H we use the most accurate zero-point

vibrational energy (49.94 kJ/mol) of Stanton [26], obtained by applying the EOMIP-CCSD method.

Problems are more difficult for linear structures of C_3H considered in this study, as no stable wavefunction within the correct symmetry restrictions can be found. However, as mentioned above, energetic differences in using symmetry-restricted and stable C_1 zeroth-order wavefunctions are negligible. It shows that the influence of optimizing the structures of l - C_3H ($C_{\infty v}$ point group) and b - C_3H (C_s symmetry) using these different zeroth-order wavefunctions is extremely small.

In Table 7 vibrational frequencies for the b - C_3H structure at the CCSD(T)/TZP level are listed. These results were obtained using the symmetry-constrained C_s wavefunction, as one would expect in general, that the use of an optimized wavefunction which does not belong to any irreducible representation at a point of high symmetry leads to an artifactual cusp in the energy and to a non-differentiable function (see Refs. [43, 54]). The use of the symmetry-constrained C_s wavefunction is further supported by the agreement of the corresponding numerical and analytical frequencies at the SCF level. Our zero-point vibrational energy for b - C_3H , which is our main interest in this study, of 44.0 kJ/mol is in good agreement with CASSCF studies [22, 27, 31] with a deviation of less than 2.7 kJ/mol.

An experimental study of ^{13}C isotopomers for C_3H in a solid Ar matrix using FTIR spectroscopy [32] assigned absorptions at 1159.8 and 1824.7 cm^{-1} to the linear form of this radical. The agreement of these observed frequencies with our corresponding CCSD(T)/TZP data for the almost linear isomer b - C_3H of 1170.1 and 1876.1 cm^{-1} (Table 7) is excellent, considering theoretical difficulties encountered for C_3H and the slightly distorted linear conformation.

We use the zero-point vibrational energy of b - C_3H as computed at the CCSD(T)/TZP level for the correction of reaction energies of both l - C_3H and b - C_3H , as these structures are very similar. The calculation of vibrational frequencies for l - C_3H remains an open issue, which we do not address in this publication. The difficulties encountered for the l - C_3H structure are reflected by three CASSCF studies: one by Takahashi et al. [22] leading to a minimum with a lowest vibrational frequency of 325 cm^{-1} , the other by Aoki et al. [27] finding l - C_3H as a transition state (355i cm^{-1}), and a third CASSCF study of Kanada et al. [31] which yields as well an imaginary frequency of 247i cm^{-1} . However, the influence of basis set effects has not yet been investigated, so that no final conclusion concerning vibrational frequencies of the exactly linear structure can be drawn.

A better understanding of the linear C_3H structure can be gained by comparing experi-

mental to theoretical structure data. A recent microwave study of Kanada et al. [31] finds in combination with theoretical data a quasi-linear structure. This is strongly supported by an exceptionally short C–H bond of 101.7 pm found experimentally [31], whereas the corresponding bond length of the exactly linear l -C₃H structure has been computed to be significantly larger (106.5 pm at CCSD(T)/TZP). The short distance may be interpreted as due to the very low lying vibronic state corresponding to the CCH bending mode as a result from a large Renner-Teller effect (e.g. Ref. [55]). Further, it is possible that the bent isomer, b -C₃H, represents the equilibrium structure. Projection of the C–H bond length on to the z -axis (for simplicity we just take the C1–C3 axis) leads to a bond length of 100.8 pm (CCSD(T)/TZP) compared to 101.7 pm found in the experiment [31], which is within error bars for the angle and bond length used for projection. As for the other computed bond lengths (here without projection, as the CCC bond angle is with 174.0° quite close to a linear form), they compare well to experimental values. The computed C–C distance to the terminal CH group is 125.3 pm, which is much shorter and closer to a typical triple bond than the second carbon-carbon bond length of 133.6 pm at the CCSD(T)/TZP level (Table 7). This data is in good agreement with experimental values of 125.4 and 132.6 pm, respectively [31]. For comparison the corresponding C–C bond lengths of the exactly linear structure l -C₃H are 124.3 and 134.7 pm, respectively, differing by less than 1 pm from those in b -C₃H.

3.5 Reaction energies

In Table 8 reaction energies for the neutral-neutral reaction of C(³P) with C₂H₂ (1) are displayed. In addition to our most reliable CCSD(T) data, we also list in this table data computed at lower levels of theory, which confirms the already discussed deficiencies of the SCF and MP2 method for the treatment of C₃H₂ and C₃H.

The initial formation of C₃H₂ collision complexes is exothermic by 385.4 kJ/mol (CCSD(T)/QZ2P/ZPE). The whole reaction to the cyclic isomer, c -C₃H, is computed to be exothermic by 8.6 kJ/mol (CCSD(T)/cc-pVQZ/ZPE). The change of 18 kJ/mol for this energy in increasing the basis from TZP to cc-pVQZ shows the importance of using an adequate basis set. The cc-pVQZ basis is expected to yield reaction energies for this reaction that are accurate to a few kJ/mol at the CCSD(T) level. As mentioned before, the linear form of C₃H is only slightly higher in energy compared to c -C₃H leading to a still slightly exothermic reaction energy (Table 8).

4 Experimental implications

In this section, we briefly discuss the experimental implications of our ab initio calculations for the reaction of ground state carbon, $C(^3P)$, with acetylene, C_2H_2 , as studied via the crossed molecular beams technique described elsewhere [8, 9]. This approach allows insight into chemical dynamics of the reaction and reveals information on reaction intermediates as well as C_3H isomers, when the experimental data is compared to what is expected based on our ab initio structures and energetics. For more complete discussions, see Refs. [9, 10].

Reaction dynamics inferred from the experimental data together with our ab initio calculations suggest two microchannels on the triplet ground state surface initiated by addition of $C(^3P)$ either to one acetylenic carbon to form trans-propenediylidene, C_s^{trans} , or to two carbon atoms to yield *c*- C_3H_2 , cyclopropenylidene (C_1^{cyclic}). Propenediylidene itself undergoes [2,3]-H-migration to propargylene, followed by the final C–H bond rupture to *l*- C_3H and H. Direct stripping dynamics contribute to the second microchannel to form *c*- C_3H via a short lived triplet *c*- C_3H_2 intermediate.

The high energy cut-offs of the translational energy distributions, $P(E_T)$ s, suggest a reaction exothermicity of about 10–15 kJ/mol to C_3H , which stands in excellent agreement with our ab initio value of 8.6 kJ/mol. The difference falls within error limits of the experimental peak collision energies and the accuracy of the calculations. Further, the peaks of all $P(E_T)$ s range between 5 and 10 kJ/mol, indicating an almost simple bond-rupture via a loose exit transition state from decomposing C_3H_2 reaction intermediates to the products. This framework correlates with minor geometry changes from triplet C_3H_2 complexes to *l*/*c*- C_3H isomers, c.f. C_3H description and Tables 5 and 7. Compared to triplet propargylene, the C–C and C–H distances alter by less than 7 pm in *l*- C_3H , i.e. the C–C-bond distance changes from 127.9 pm to 124.3 pm and 134.7 pm, respectively. The bending angle of the three propargylene carbon atoms deviates by only of 8.1° from the linear geometry, and the HCC bond angle widens from 156.5° to 180.0° or even remains unchanged (156.5°), if the bent structure is adopted (Table 7). Larger geometry changes up to about 17 pm are found in the cyclic C_3H isomer as compared to triplet *c*- C_3H_2 . Finally, the experimental center-of-mass angular distributions support the C_2 rotation axis of the propargyl isomer. This geometry and a rotation around the symmetry axis lead to a symmetric transition state to *l*- C_3H , since both hydrogen atoms can be interconverted and depart with equal probability in the center-of-mass angles Θ and $\Pi - \Theta$ to yield a symmetric, collision energy invariant isotropic shape.

With rising collision energies from 8.8 kJ/mol, over 28.0 kJ/mol, to 45.0 kJ/mol, the shape of the observed center-of-mass angular distributions changes significantly, showing a decrease of the forward-backward intensity ratio at 0° and 180° (see Refs. [9,10]). This indicates the occurrence of two microchannels. We show elsewhere [9,10], that the combination of ab initio information characterizing the C_3H_2 surface and molecular beam experiments allows us to attribute the strong forward peaking microchannel to the formation of *c*- C_3H , a channel which becomes quenched with rising collision energy. The second microchannel leads to *l*- C_3H through the propargylene C_3H_2 complex. This explains a higher *c*- C_3H to *l*- C_3H number density ratio observed in dark clouds versus hotter envelopes of carbon stars.

5 Conclusion

High level ab initio calculations (CCSD(T)) have been performed to investigate energetics of the initially formed triplet C_3H_2 collision complexes. Resolving energetics and properties of these isomers is crucial for the neutral-neutral reaction of $C(^3P)$ with C_2H_2 to the interstellar isomers of C_3H , studied by crossed molecular beam experiments. The most stable almost linear isomer of C_3H_2 shows C_2 symmetry in agreement with results of a recent FTIR experiment [51]. Similar almost linear structures of C_3H_2 are found to be virtually isoenergetic, although they are characterized to be saddle points on the CCSD(T) hypersurface. Other isomers are energetically unfavored relative to the most stable C_2^{lin} isomer by more than 134 kJ/mol.

The exothermicity for the reaction of $C(^3P)$ with C_2H_2 to *c*- C_3H is computed as -8.6 kJ/mol at the present highest level of theory. This value is consistent with experimental data inferred from the molecular beam experiments. The reaction energy to linear (or quasi-linear) C_3H is calculated to be slightly less exothermic.

The combination of ab initio calculations and crossed molecular beam experiments, described extensively elsewhere [9,10], allows for the explicit identification of both isomers of C_3H : the cyclic and the linear form. This reaction under single collision conditions avoids the need for successive binary encounters as in ion-molecule processes. Reaction dynamics in the molecular beam experiment show that the microchannel leading to *c*- C_3H is quenched with rising collision energy [9,10]. This explains hitherto unresolved astronomical observations of number density ratios *c*- C_3H versus *l*- C_3H of 1 in cold molecular clouds (e.g. TMC-1) compared to 0.2 ± 0.1 found in the hotter envelope surrounding IRC+10216.

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References

- [1] H. Matthews and W. M. Irvine; *Astrophys. J. Lett.* **298**, L61 (1985).
- [2] P. Thaddeus, J. M. Vrtilik, and C. A. Gottlieb; *Astrophys. J. Lett.* **299**, L63 (1985).
- [3] J. Cernicharo, C. Kahane, M. Guelin, and J. Gomez-Gonzalez; *Astron. Astrophys.* **189**, L1 (1988).
- [4] S. Yamamoto, S. Saito, M. Ohishi, H. Suzuki, S. Ishikawa, N. Kaifu, and A. Murakami; *Astrophys. J. Lett.* **322**, L55 (1987).
- [5] T. J. Millar, C. M. Leung, and E. Herbst; *Astron. Astrophys.* **183**, 109 (1987).
- [6] D. Smith; *Chem. Rev.* **92**, 1580 (1992).
- [7] D. C. Clary, N. Haider, D. Husain, and M. Kabir; *Astrophys. J. Lett.* **422**, 416 (1994).
- [8] R. I. Kaiser, Y. T. Lee, and A. G. Suits; *J. Chem. Phys.* **103**, 10395 (1995).
- [9] R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee, and A. G. Suits; *J. Chem. Phys.* submitted.
- [10] R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee, and A. G. Suits; *Science* in press.
- [11] N. J. Turro;
'Modern Molecular Photochemistry'
(University Science Books, Mill Valley, CA (1991)).
- [12] R. I. Kaiser, Y. T. Lee, and A. G. Suits; *J. Chem. Phys.* in press (October 1996).
- [13] W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman, and Z. R. Wasserman; *J. Am. Chem. Soc.* **98**, 4378 (1976).
- [14] J. W. Kenney III, J. Simons, G. D. Purvis, and R. J. Bartlett;
J. Am. Chem. Soc. **100**, 6930 (1978).
- [15] C. E. Dykstra, C. A. Parsons, and C. L. Oates; *J. Am. Chem. Soc.* **101**, 1962 (1979).
- [16] R. Shepard, A. Banerjee, and J. Simons; *J. Am. Chem. Soc.* **101**, 6174 (1979).
- [17] T. J. Lee, A. Bunge, H. F. Schaefer; *J. Am. Chem. Soc.* **107**, 137 (1985).
- [18] J. M. Bofill, J. Farras, S. Olivella, A. Sole, and J. Vilarrasa;
J. Am. Chem. Soc. **110**, 1694 (1988).

- [19] D. L. Cooper and S. C. Murphy; *Astrophys. J. Lett.* **333**, 482 (1988).
- [20] V. Jonas, M. Böhme, and G. Frenking; *J. Phys. Chem.* **96**, 1640 (1992).
- [21] R. Herges and A. Mebel; *J. Am. Chem. Soc.* **116**, 8229 (1994).
- [22] J. Takahashi and K. Yamashita; *J. Chem. Phys.* **104**, 6613 (1996).
- [23] C. D. Sherrill, C. G. Brandow, W. D. Allen, and H. F. Schaefer; *J. Am. Chem. Soc.* **118**, 7158 (1996).
- [24] G. Maier, H. P. Reisenauer, W. Schwab, P. Carsky, V. Spirko, B. A. Hess, Jr., and L. J. Schaad; *J. Chem. Phys.* **91**, 4763 (1989).
- [25] F. Pauzat, Y. Ellinger, and A. D. McLean; *Astrophys. J. Lett.* **369**, L13 (1991).
- [26] J. F. Stanton; *Chem. Phys. Lett.* **237**, 20 (1995).
- [27] K. Aoki, K. Hashimoto, and S. Ikuta; *Astrophys. J.* submitted.
- [28] D. E. Woon; *Chem. Phys. Lett.* **244**, 45 (1995).
- [29] S. Yamamoto and S. Saito; *Astrophys. J. Lett.* **363**, L13 (1990).
- [30] S. Yamamoto and S. Saito; *J. Chem. Phys.* **101**, 5484 (1994).
- [31] M. Kanada, S. Yamamoto, S. Saito, Y. Osamura; *J. Chem. Phys.* **104**, 2192 (1996).
- [32] Q. Jiang, C. M. L. Rittby, and W. R. M. Graham; *J. Chem. Phys.* **99**, 3194 (1993).
- [33] R. J. Bartlett und J. F. Stanton, in;
'Reviews of Computational Chemistry'
(Vol. 5, eds. K. B. Lipkowitz und D. B. Boyd, VCH Publishers, New York (1990), pp. 65).
- [34] ACES II, an ab initio program system written by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett;
'Quantum Theory Project', University of Florida, Gainesville (1992);
for a detailed description, see J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett; *Int. J. Quantum Chem. Symp.* **26**, 879 (1992).
- [35] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon; *Chem. Phys. Lett.* **157**, 479 (1989).

- [36] C. Møller and M. S. Plesset; *Phys. Rev.* **46**, 618 (1934).
- [37] G. D. Purvis and R. J. Bartlett; *J. Chem. Phys.* **76**, 1910 (1982).
- [38] K. A. Brueckner, A. M. Lockett, and B. Rotenberg;
Phys. Rev. **121**, 255 (1961) and references therein.
- [39] R. A. Chiles and C. E. Dykstra; *J. Chem. Phys.* **74**, 4544 (1981).
- [40] L. Z. Stolarczyk and H. J. Monkhorst;
Int. J. Quantum Chem. Symp. **18**, 267 (1984).
- [41] N. C. Handy, J. A. Pople, M. Head-Gordon, K. Raghavachari, and G. W. Trucks;
Chem. Phys. Lett. **164**, 185 (1989).
- [42] K. Raghavachari, J. A. Pople, E. S. Replogle, M. Head-Gordon, and N. C. Handy;
Chem. Phys. Lett. **167**, 115 (1990).
- [43] J. F. Stanton, J. Gauss, and R. J. Bartlett; *J. Chem. Phys.* **97**, 5554 (1992).
- [44] L. A. Barnes and R. Lindh; *Chem. Phys. Lett.* **223**, 207 (1994).
- [45] J. Čížek and J. Paldus; *J. Chem. Phys.* **47**, 3976 (1967).
- [46] G. D. Purvis, H. Sekino, and R. J. Bartlett;
Collection Czech. Chem. Commun. **53**, 2203 (1988).
- [47] J. F. Stanton; *J. Chem. Phys.* **101**, 371 (1994).
- [48] J. D. Watts, J. Gauss, and R. J. Bartlett; *Chem. Phys. Lett.* **200**, 1 (1992).
- [49] A. Schäfer, H. Horn, and R. Ahlrichs; *J. Chem. Phys.* **97**, 2571 (1992).
- [50] T. H. Dunning; *J. Chem. Phys.* **90**, 1007 (1989).
- [51] R. A. Seburg and R. J. McMahon; *Angew. Chem.* **107**, 2198 (1995).
- [52] N. A. Burton, Y. Yamaguchi, I. L. Alberts, and H. F. Schaefer;
J. Chem. Phys. **95**, 7466 (1991).
- [53] R. J. Bartlett; *Ann. Rev. Phys. Chem.* **32**, 359 (1981).
- [54] E. R. Davidson and W. T. Borden; *J. Phys. Chem.* **87**, 4783 (1983).
- [55] G. Herzberg;
'Molecular Spectra and Molecular Structure'
(Vol. III, reprint edition, Krieger Publishing Company, Malabar, Florida (1991)).

Table 1: Relative energies of C_3H_2 isomers depicted in Figs. 1 and 2 with respect to the most stable C_2^{lin} isomer for which total energies are listed.

Method/Basis	C_2^{lin} [Hartree]	Minima			Saddlepoints ^a				
		C_{2v}	C_1^{cyclic}	C_s^{trans}	C_s^{lin}	C_{2v}^{lin}	$D_{\infty h}$	C_2^{cyclic}	C_{2v}^{cyclic}
		[kJ/mol]			[kJ/mol]				
CCSD(T)/DZP	-115.042385	114.3	161.1	238.9	0.5	0.8	3.7	175.5	194.4
CCSD(T)/TZP	-115.106431	118.8	164.6	240.9	0.5	0.7	2.9	177.4	195.7
CCSD(T)/TZPP ^b	-115.173001	122.2	160.5	243.1	-0.1	0.1	0.4	173.2	187.7
CCSD(T)/QZ2P ^b	-115.199261	124.4	160.9	247.1	-0.3	0.0	-0.4	173.6	187.3
CCSD(T)/QZ2P/ZPE ^{b,c}	-115.173119	134.9	172.4	250.8	—	—	—	—	—
SCF/QZ2P ^b	-114.677750	104.0	229.6	202.9	0.7	1.0	4.1	238.7	256.6
MP2/QZ2P ^b	-115.129589	124.5	104.3	256.3	-2.6	-0.8	-5.2	141.5	149.4
CCSD/QZ2P ^b	-115.176692	122.1	169.3	241.9	-0.5	-0.1	-0.9	182.0	195.1

^aSecond derivatives with respect to nuclear displacement as computed at the CCSD(T)/TZP level. Imaginary frequencies described in text and Tables 3 and 4.

^bSingle-point calculations at the CCSD(T)/TZP geometry.

^cZero-point vibrational energies included as computed at the CCSD(T)/TZP level (only included for minima).

Table 2: Harmonic vibrational frequencies computed at the CCSD(T) level using DZP and TZP bases, respectively, of C_3H_2 isomers depicted in Fig. 1. Symmetry of modes, wavenumbers (cm^{-1}), and IR intensities (km/mol; in parentheses) are listed.

C_2^{lin}	DZP	TZP	C_{2v}	DZP	TZP
b	221.1 (95.3)	215.2 (98.6)	b_1	210.6 (0.4)	221.8 (0.4)
a	332.0 (1.3)	324.5 (3.2)	b_2	391.7 (1.9)	374.9 (2.7)
b	396.5 (10.2)	391.8 (14.2)	b_2	661.5 (50.4)	649.5 (61.2)
a	401.1 (21.3)	398.8 (27.0)	b_1	992.1 (5.5)	996.9 (7.0)
a	469.3 (38.4)	450.3 (47.1)	a_1	1107.3 (5.7)	1094.1 (5.6)
a	1261.7 (0.0)	1257.4 (0.1)	a_1	1475.5 (0.0)	1484.6 (0.0)
b	1622.6 (16.2)	1610.5 (12.8)	a_1	1962.9 (1.0)	1953.5 (0.6)
b	3410.8 (57.6)	3409.8 (60.4)	a_1	3186.9 (2.1)	3170.5 (3.3)
a	3416.7 (6.0)	3416.4 (4.4)	b_1	3297.8 (0.2)	3272.1 (0.4)
C_1^{cyclic}	DZP	TZP	C_s^{trans}	DZP	TZP
a	591.0 (46.1)	599.1 (55.3)	a'	178.6 (10.6)	187.2 (11.9)
a	786.1 (22.3)	720.1 (6.5)	a''	469.7 (23.2)	412.8 (27.3)
a	934.1 (12.1)	919.6 (72.4)	a''	690.3 (32.5)	674.3 (38.9)
a	959.9 (29.3)	934.6 (1.4)	a'	840.0 (26.0)	834.7 (32.2)
a	1015.2 (37.9)	995.4 (18.6)	a'	1052.4 (1.9)	1063.1 (1.4)
a	1153.2 (16.3)	1089.1 (28.3)	a'	1193.9 (0.1)	1171.8 (2.3)
a	1686.5 (2.8)	1672.9 (4.9)	a'	1383.1 (50.9)	1355.4 (47.5)
a	3136.2 (25.5)	3125.0 (22.3)	a'	3120.2 (14.3)	3115.2 (13.1)
a	3347.3 (13.6)	3343.8 (15.6)	a'	3279.6 (1.2)	3268.5 (1.1)

Table 3: Harmonic vibrational frequencies computed at the CCSD(T)/TZP level of C_3H_2 saddle points depicted in Fig. 2. Symmetry of modes, wavenumbers (cm^{-1}), and IR intensities (km/mol ; in parentheses) are listed.

C_s^{lin}			C_{2v}^{lin}			C_2^{cyclic}			C_{2v}^{cyclic}		
a''	212.0i	(24.9)	a_2	258.8i	(0.0)	b	701.5i	(320.2)	a_2	761.7i	(0.0)
a'	232.2	(27.1)	b_2	177.2i	(57.3)	a	732.8	(9.2)	b_1	620.1i	(155.8)
a''	388.5	(25.4)	b_1	394.2	(25.4)	a	785.8	(3.8)	a_1	722.7	(1.7)
a'	395.0	(40.4)	a_1	400.0	(15.7)	b	809.6	(3.0)	b_2	782.7	(95.4)
a'	471.0	(52.8)	a_1	453.5	(60.6)	a	873.3	(116.2)	a_1	816.7	(135.5)
a'	1241.1	(0.6)	a_1	1262.9	(0.1)	b	1071.7	(24.8)	b_2	840.0	(51.1)
a'	1645.0	(10.9)	b_2	1608.9	(8.7)	a	1556.1	(0.3)	a_1	1574.5	(0.3)
a'	3388.9	(25.3)	b_2	3421.8	(74.8)	b	3264.8	(4.7)	b_2	3365.2	(69.2)
a'	3456.7	(51.8)	a_1	3430.5	(5.6)	a	3272.0	(0.8)	a_1	3395.5	(8.9)

Table 4: Comparison of equilibrium geometries (bond length, r , in pm), harmonic vibrational frequencies (cm^{-1}), IR intensities (km/mol ; in parentheses), and zero-point vibrational energies, ZPE, (kJ/mol) as computed at the CCSD(T) level using various basis sets for the linear structure ($D_{\infty h}$) of C_3H_2 shown in Fig. 2 (c).

Parameter	DZP	TZP	TZPP	QZ2P
$r(\text{CC})$	128.2	127.4	127.2	127.0
$r(\text{CH})$	107.3	106.3	106.1	106.1
$\omega(\pi_u)$	398.1i (71.1)	374.9i (94.3)	247.8i (89.0)	196.2i (93.3)
$\omega(\pi_g)$	302.2i (0.0)	308.8i (0.0)	198.2i (0.0)	149.3i (0.0)
$\omega(\pi_u)$	397.1 (21.6)	390.6 (26.3)	408.7 (20.0)	414.1 (21.0)
$\omega(\sigma_g^+)$	1282.6 (0.0)	1274.5 (0.0)	1275.8 (0.0)	1283.6 (0.0)
$\omega(\sigma_u^-)$	1626.7 (6.5)	1617.5 (4.4)	1633.1 (3.7)	1647.1 (3.5)
$\omega(\sigma_u^-)$	3457.4 (126.9)	3449.6 (114.9)	3437.6 (122.4)	3469.3 (121.3)
$\omega(\sigma_g^+)$	3470.0 (0.0)	3463.1 (0.0)	3448.8 (0.0)	3481.8 (0.0)
ZPE	63.59	63.32	63.48	64.06

Table 5: Structural data of C_3H_2 isomers (Figs. 1 and 2) as computed at the CCSD(T)/TZP level.

Isomer ^a	Structural data ^b		
C_2^{lin}	(C*-C) = 127.9 (C*,C,H) = 156.5°	(C-H) = 106.7 (H-C'-C-H') = 88.0°	(C,C*,C') = 171.9°
C_{2v}	(C1-C2) = 136.9 (H,C1,C2) = 120.5°	(C2-C3) = 123.8	(C1-H) = 108.1
C_1^{cyclic}	(C1-C2) = 144.8 (C1-H1) = 108.8 (H2,C3,C1) = 141.1°	(C2-C3) = 130.4 (C3-H2) = 107.3 (H1,C2,C3,C1) = 46.1°	(C1-C3) = 155.1 (H1,C1,C3) = 125.9° (H2,C1,C2,C3) = 0.2°
C_s^{trans}	(C1-C2) = 134.9 (C3-H2) = 107.9 (C2,C3,H2) = 134.1°	(C2-C3) = 139.2 (C1,C2,C3) = 121.2°	(C2-H1) = 109.2 (C1,C2,H1) = 117.1°
C_s^{lin}	(C1-C2) = 129.6 (C3-H2) = 106.4 (C2,C3,H2) = 173.4°	(C2-C3) = 126.2 (C1,C2,C3) = 172.6°	(C1-H1) = 106.9 (H1,C1,C2) = 150.9°
C_{2v}^{lin}	(C*-C) = 127.8 (H,C,C*) = 160.1°	(C-H) = 106.6	(C,C*,C') = 171.0°
C_2^{cyclic}	(C*-C) = 135.5 (H,C,C') = 133.1°	(C-C') = 159.3 (H,C,C*) = 146.4°	(C-H) = 107.7
C_{2v}^{cyclic}	(C*-C) = 134.9 (H,C,C') = 144.8°	(C-C') = 159.2	(H-C) = 106.9

^aFor structures with a C_2 -symmetry axis (and not all C atoms situated on this axis, as in the C_{2v} structure, Fig. 1) the symmetry-unique C atom is labeled C*. C' is the symmetry-corresponding atom of C. If no such symmetry is found, C and H atoms, respectively, are numbered from left to the right in Figs. 1 and 2 (for the cyclic isomer C_1^{cyclic} , atom C2 is characterized by holding no H atoms).

^bNotation: (C*-C) = 127.9 denotes bond length in pm, (C,C*,C') = 171.9° denotes bond angle with apical atom C*, (H1,C2,C3,C1) = 46.1° stands for the out of plane angle between the bond H1-C1 and the plane C2-C3-C1, and (H-C'-C-H') = 88.0° stands for the torsion angle H-C-C'-H'.

Table 6: Relative energies of C_3H isomers depicted in Fig. 3 with respect to the most stable $c-C_3H$ isomer for which total energies are listed. The problem of symmetry-broken SCF solutions is discussed in text.

Method/Basis	$c-C_3H$ [Hartree]	$l-C_3H$ [kJ/mol]	$b-C_3H$ [kJ/mol]
CCSD(T)/TZP	-114.456072	9.0	8.0
CCSD(T)/TZPP ^a	-114.520676	10.5	11.0
CCSD(T)/QZ2P ^a	-114.547545	13.8	14.5
CCSD(T)/cc-pVQZ ^a	-114.575798	13.0	13.8
CCSD(T)/cc-pVQZ/ZPE ^{ab}	-114.556777	7.1	7.8
B-CCD/TZP ^{ac}	-114.432541	5.1	5.6
B-CCD/TZPP ^{ac}	-114.493095	7.3	9.0
B-CCD/QZ2P ^{ac}	-114.519135	10.1	12.0
SCF/QZ2P ^a	-114.011204	-32.5	-32.3
SCF/cc-pVQZ ^a	-114.013119	-31.1	-30.8
MP2/QZ2P ^a	-114.504602	86.8	94.7
MP2/cc-pVQZ ^a	-114.534580	87.0	95.2
CCSD/QZ2P ^a	-114.520326	8.9	10.5
CCSD/cc-pVQZ ^a	-114.546944	8.8	10.5

^aSingle-point calculations at the CCSD(T)/TZP structures using for all wavefunctions the full symmetry (D_{2h} and subgroups) of the corresponding structure.

^bZPE: for $c-C_3H$ the value of 49.94 kJ/mol [26] is used (discussion in text); for both $l-C_3H$ and $b-C_3H$ the value as computed within the CCSD(T)/TZP approach for the $b-C_3H$ isomer (Table 7) is taken.

^cInitial values of T_1^{max} : for $c-C_3H$ 0.04–0.05, for $l-C_3H$ 0.17–0.18, and for $b-C_3H$ 0.19.

Table 7: Equilibrium geometry, harmonic vibrational frequencies (cm^{-1}), IR intensities (km/mol , in parentheses), and zero-point vibrational energies, ZPE, (kJ/mol) of $b\text{-C}_3\text{H}$ (C_s point group; Fig. 3). Stability difficulties in the zeroth-order wavefunction are discussed in text. Labelling used for internal coordinates as described in Table 5.

Parameter	CCSD(T)/TZP
$r(\text{H-C1})$	107.2 pm
$r(\text{C1-C2})$	125.3 pm
$r(\text{C2-C3})$	133.6 pm
$\angle(\text{H,C1,C2})$	156.5°
$\angle(\text{C1,C2,C3})$	174.0°
$\omega(a'')$	207.8 (0.1)
$\omega(a')$	351.2 (15.9)
$\omega(a')$	368.6 (58.4)
$\omega(a')$	1170.1 (52.0)
$\omega(a')$	1876.1 (170.3)
$\omega(a')$	3379.9 (28.9)
ZPE	43.98

Table 8: Selected reaction energies in kJ/mol computed at CCSD(T)/TZP geometries^a.

Method/Basis	ΔE_{R1}^b	ΔE_{R2}^c	ΔE_{R3}^d	ΔE_{R4}^e
CCSD(T)/TZP	27.7	36.7	-367.5	395.3
CCSD(T)/TZPP	19.9	30.4	-380.5	400.4
CCSD(T)/QZ2P	12.7	26.5	-385.7	398.4
CCSD(T)/cc-pVQZ	9.8	22.9	—	—
CCSD(T)/QZ2P/ZPE	-5.7	2.2	-385.4	379.7
CCSD(T)/cc-pVQZ/ZPE	-8.6	-1.5	—	—
SCF/QZ2P	90.9	58.3	-346.4	437.3
SCF/cc-pVQZ	89.0	57.9	—	—
MP2/QZ2P	-13.8	72.9	-342.0	328.2
MP2/cc-pVQZ	-16.3	70.7	—	—
CCSD/QZ2P	33.1	42.0	-377.4	410.6
CCSD/cc-pVQZ	30.0	38.8	—	—

^aFull point-group symmetries (D_{2h} and subgroups) are used for the wavefunctions (see discussion in text).

^b $C_2H_2 + C \rightarrow c-C_3H + H$.

^c $C_2H_2 + C \rightarrow l-C_3H + H$.

^d $C_2H_2 + C \rightarrow C_3H_2$.

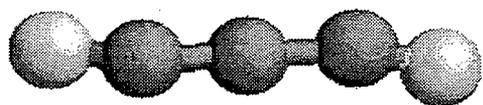
^e $C_3H_2 \rightarrow c-C_3H + H$.

Legend of Figures

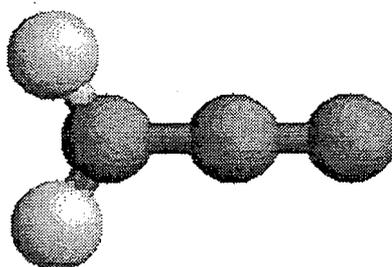
Figure 1: Computed minima of C_3H_2 . Relative energies with respect to the most stable isomer C_2^{lin} are listed in kJ/mol (CCSD(T)/QZ2P/ZPE). Large grey circles denote carbon atoms and smaller white circles hydrogen.

Figure 2: Saddle points of C_3H_2 . Relative energies with respect to the most stable C_3H_2 isomer, C_2^{lin} (Fig. 1 (a)), are given in kJ/mol (CCSD(T)/TZP).

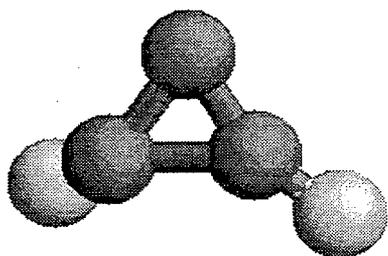
Figure 3: Considered C_3H structures and energy differences with respect to the most stable isomer $c-C_3H$ (C_{2v} symmetry) in kJ/mol (CCSD(T)/cc-pVQZ).



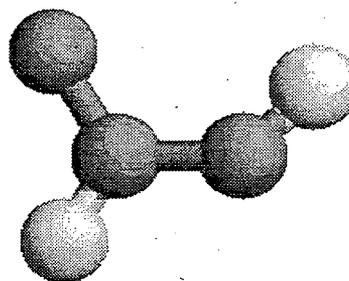
(a) C_2^{lin} (0.0)



(b) C_{2v} (134.9)

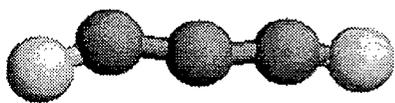


(c) C_1^{cyclic} (172.4)

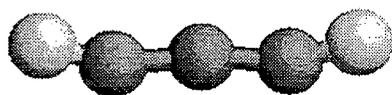


(d) C_s^{trans} (250.8)

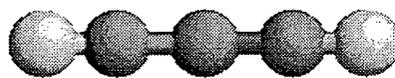
Fig. 1



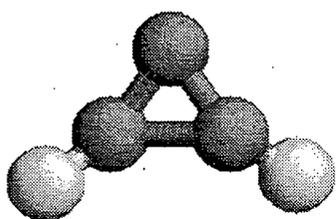
(a) C_s^{lin} (0.5)



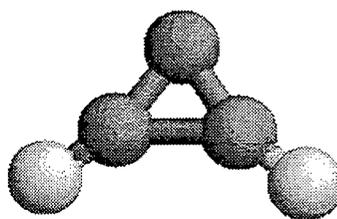
(b) C_{2v}^{lin} (0.7)



(c) $D_{\infty h}$ (2.9)

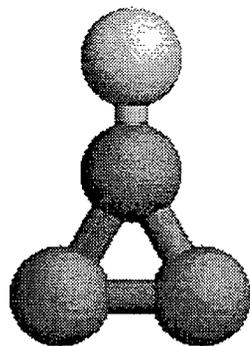


(d) C_2^{cyclic} (177.4)

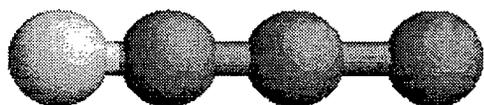


(e) C_{2v}^{cyclic} (195.7)

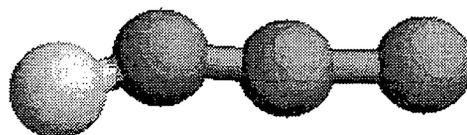
Fig. 2



(a) *c*-C₃H (0.0)



(b) *l*-C₃H (13.0)



(c) *b*-C₃H (13.8)

Fig. 3

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