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A Combined Experimental and Theoretical Study
on the Formation of Interstellar C₃H Isomers

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Abstract

The reaction ground state carbon atoms with acetylene was studied under single collision conditions in crossed beam experiments to investigate the chemical dynamics of forming c- and l-C_3H isomers in interstellar environments via an atom-neutral reaction. Combined state-of-the-art *ab initio* calculations and explicit experimental identification of the carbon-hydrogen exchange channel classify this reaction as an important alternative to ion-molecule encounters to synthesize C_3H radicals in the interstellar medium. Our findings strongly correlate with actual astronomical observations and explain a higher [c-C_3H]/[l-C_3H] ratio in the dark cloud TMC-1 as compared to the carbon star IRC+10216.

For over two decades, networks of radiative association, dissociative recombination, and exothermic ion-molecule reactions have been postulated to account for chemistry in the interstellar medium (ISM) (1). This framework, however, cannot reproduce number densities and isomer ratios of ubiquitous reactive radicals such as linear and cyclic C_3H (l-C_3H, propynylidyne and c-C_3H, cyclopropynylidene) (2) via the postulated addition of C^+ to C_2H_2 yielding l/c-C_3H^+ + H, subsequent radiative association of l/c-C_3H^+ and molecular hydrogen to c-$C_3H_3^+$, and a final dissociative electron-ion recombination forming l/c-C_3H and two hydrogen atoms or H_2. Fueled by recent kinetic studies of barrier less, fast neutral-neutral reactions of atomic carbon $C(^3P_j)$ with unsaturated hydrocarbons (3), Herbst et al. implemented this reaction class into generic models of the dark molecular cloud TMC-1 and the circumstellar envelope surrounding the carbon star IRC+10216 to improve the fit to astronomical surveys (4). These models, however, suffer from sparse laboratory data on reaction products and cannot elucitate the contribution to distinct structural isomers such as l/c-C_3H. Therefore, even this refined network does not explain the interstellar c-C_3H to l-C_3H ratio of unity in cold molecular clouds versus 0.2 ± 0.1 around IRC+10216. Hence the formation of interstellar C_3H isomers remains to be resolved.

In this report, we present combined high level *ab initio* calculations and crossed beam experiments on the atom-neutral reaction (1) to interstellar C_3H isomers via C_3H_2 intermediates:

(1a) $C(^3P_j) + C_2H_2(X^1\Sigma^+_g) \rightarrow C_3H_2 \rightarrow$ l-$C_3H(X^2\Pi_j) + H(^2S_{1/2})$,

(1b) $\rightarrow C_3H_2 \rightarrow$ c-$C_3H(X^2B_2) + H(^2S_{1/2})$.
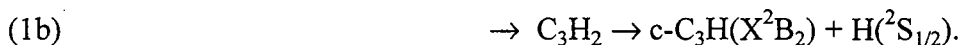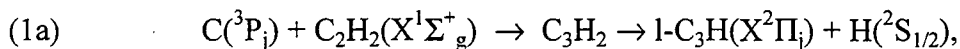
This system represents the prototype reaction of ubiquitous interstellar carbon atoms with the simplest unsaturated hydrocarbon molecule, acetylene, to synthesize hydrocarbon radicals via a

single atom-neutral collision in interstellar environments. The circumstellar shell of IRC+10216, for example, contains C_2H_2 as well as $C(^3P_j)$ reservoirs at distances of 10^{14} - 10^{15}m from the central star (5), and formation of C_3H via reaction (1) is feasible. Our investigations elucidate dynamical information on the elementary steps to C_3H isomers: since the laboratory data strongly depend on the structure(s) of the initially formed C_3H_2 collision complex(es), we first calculate the *ab initio* geometries of energetically accessible C_3H_2 isomers. We, then, compare our crossed beam data and experimental dynamics with those arising from distinct C_3H_2 adducts. Once the isomer(s) is (are) identified, we ultimately reveal the exit channel(s) from C_3H_2 via a carbon-hydrogen bond rupture to c- and/or l-C_3H.

Ab initio electronic structure calculations were performed at a level of theory high enough to predict relative energies to a precision of a few $kJmol^{-1}$. Specifically, our calculations employed the CCSD(T) (single- and double-excitation coupled cluster with a perturbational estimate of triple excitations) level (6) based on unrestricted Hartree-Fock (UHF) wavefunctions (7). The ACES II program package (8) was used. Structures were fully optimized using a triple zeta polarization (TZP) basis set (9) and stationary points characterized by vibrational frequencies within the harmonic approximation (10). Energy differences and reaction energies were obtained by single-point calculations with a quadruple zeta double polarization (QZ2P) (9) and a correlation consistent polarized valence quadruple zeta (cc-pVQZ) (11) basis; zero point energies were included as computed at the CCSD(T)/TZP level (12). Since no triplet C_3H_2 minimum fulfills requirements of intersystem crossing (13), the discussion is limited to the triplet potential energy surface (PES).

Our *ab initio* calculations are summarized in Fig. 1 and Tab. 1. They show that propargylene, HCCCH, is the global minimum on the triplet C_3H_2 PES and is bound by 385.4kJmol^{-1} with respect to the reactants (QZ2P). Its C_2 symmetry agrees with recent experimental FTIR assignments based on isotope substitution studies in argon matrices (14) and shows an almost linear CCC angle of 171.9^0 and a torsion angle of the two H atoms of 88.0^0, c.f. Tab. 1 and Fig. 1. A second isomer, vinylidenecarbene, H_2CCC, possesses C_{2v} symmetry and lies 134.9kJmol^{-1} above propargylene. Its enthalpy of formation ΔH_f° (0K)=678.6kJmol^{-1} stands in excellent agreement with recent experimental data of 668±30kJmol^{-1} (15). Triplet cyclopropenylidene, c-C_3H_2, is situated 172.4kJmol^{-1} above propargylene and shows no symmetry. One hydrogen is placed almost in the plane of the carbon tricycle, whereas the second H atom is distorted out of the CCC plane. Another isomer, s-trans propenediylidene, CCHCH, (C_s symmetry) lies an additional 78.4kJmol^{-1} higher. The most stable isomer on the doublet C_3H PES is a cyclic structure with C_{2v} symmetry in agreement with ref. (12). A linear geometry ($C_{\infty v}$) and a slightly distorted linear structure (C_s) (CCC bond angle of 174.0^0; HCC bond angle 156.5^0) are virtually isoenergetic. The CCCH bending mode of only 212cm^{-1} indicates the extreme floppiness of the bent isomer. Both structures are about 7kJmol^{-1} higher in energy than the cyclic one, and the reaction exothermicity to c-$C_3H(X^2B_2)$ + H is calculated to be 8.6kJmol^{-1} (cc-pVQZ).

The experiments are performed under single collision conditions at three different collision energies of 8.8, 28.0, and 45.0kJmol^{-1} using a universal crossed molecular beam apparatus (16). The 266nm output of a Nd:YAG laser is focused on a rotating carbon rod, and ablated carbon atoms were seeded into neon or helium carrier gas (17). The carbon beam crosses a continu-

ous acetylene beam at 90° in the interaction region, and time-of-flight (TOF) spectra and product angular distributions (LAB) of reactively scattered products were monitored using a quadrupole mass spectrometer with an electron-impact ionizer. Information on the reaction dynamics is gained by fitting our data using a forward-convolution routine (18) yielding the angular flux distribution $T(\theta)$ and the translational energy flux distribution $P(E_T)$ in the center-of-mass system.

The laboratory angular distributions and TOF spectra of the reactive scattering signal at $m/e = 37$, i.e. C_3H, are shown for a selected collision energy at $28.0 kJmol^{-1}$ in Figures 2 and 3, respectively. No radiative association to C_3H_2 was detected. The identification of this carbon-hydrogen exchange under single collision conditions alone underlines the potential importance of this reaction to build up C_3H radicals in interstellar environments. In addition, this result strongly demonstrates that the highly internally excited C_3H_2 adduct does not survive under single collision conditions in our experiments as well as in the interstellar medium; however denser planetary or cometary atmospheres can supply a third body reaction to stabilize the reaction intermediate. The crossed beam method further allows insight into the chemical dynamics of the reaction and reveals information on reaction intermediates as well as C_3H isomers, when the observed dynamics are compared to what is expected based on our *ab initio* structures and energetics. Fig. 4 presents the translational energy $P(E_T)$ and angular distributions $T(\theta)$ of reaction (1) inferred from the experimental results. All $P(E_T)$s peak between 5 and $10 kJmol^{-1}$ suggesting a nearly simple bond-rupture process via a loose exit transition state from the decomposing C_3H_2 reaction intermediate to the products. The high energy cut-offs of the translational energy distributions stand in excellent agreement with our *ab initio* reaction exothermicities plus the relative collision energy. The discrepancies of about $4-7kJmol^{-1}$ fall

within the error limits of the peak collision energies and the accuracy of the *ab initio* calculations. Since our calculations indicate l- and c-C_3H differ only by 7kJmol[-1], the isomer(s) cannot be assigned based solely on the translational energy distributions, and the center-of-mass angular distributions have to be analyzed in detail.

As the collision energy rises, the form of center-of-mass the angular distributions (Fig. 4) changes significantly and show a decreasing forward-backward intensity ratio at the poles from 2.6 (8.8kJmol[-1]) via 1.2 (28.0kJmol[-1]) to 1.0 (45.0kJmol[-1]). These data show the disappearance of forward peaked products with respect to the carbon beam at higher collision energy and suggest decomposing the single angular distribution into two distinct micromechanisms. The first microchannel involves a collision energy invariant forward-backward symmetric $T(\theta)$. This is due to a C_3H_2 collision complex with a lifetime longer than its rotational period or, alternatively, a symmetric exit transition state in which both hydrogen atoms can be interconverted via a rotation around a principal axis and hence depart with equal probability into the center-of-mass angles θ and $\pi-\theta$ (19). Microchannel two shows a strong forward peaking with respect to the carbon beam. This contribution is quenched as the collision energy rises. If we integrate the product of the center of mass distributions, $T(\theta)*P(E_T)$, we obtain a relative cross section ratio of $[\sigma(8.8kJmol^{-1})/\sigma(28.0kJmol^{-1})] = 3.5\pm1.4$. This finding correlates qualitatively with bulk experiments (3). The deviation of our experimental ratio from the theoretical prediction of 1.3 calculated within the capture theory (20) indicates that the structure of the acetylene molecule plays a significant role when the orbiting radii fall below the van der Waals dimension of the C_2H_2 molecule.

We now resolve the chemical dynamics of the isotropic microchannel. An interpretation

of a long-lived C_3H_2 collision complex contributing to an isotropic $T(\theta)$ can be dismissed. From

the potential energy well depth of all C_3H_2 isomers relative to the reactants and products,

propargylene is expected to have the longest lifetime at the collision energy of $45kJmol^{-1}$. Even

with a well depth of $385.4kJmol^{-1}$, the lifetime of the reaction intermediate is expected to be less

than the rotation period of the reaction intermediate. This evidence is even stronger if we

compare the dynamics with those of the reaction $C(^3P_j) + CH_3CCH$ (X^1A_1) (21). Since the

fragmenting methylpropargylene has a lifetime equivalent to its rotational period at $33.2kJmol^{-1}$

collision energy in this experiment, a HCCCH complex with a lifetime less than its rotational

period is expected due to the reduced number of 7 (propargylene) versus 15 (methylpropar-

gylene) vibrational. Therefore, microchannel one originates in a symmetric exit transition state.

This restricts possible C_3H_2 complexes to H_2CCC or HCCCH. Based on our *ab initio* geome-

tries, c-C_3H_2 and CCHCH can be excluded, since no symmetry operation interconverts both

hydrogen atoms. If H_2CCC were formed, the fragmenting complex would rotate around the C_2

symmetry axis to yield exclusively l-$C_3H(X^2\Pi_j)$. The linear isomer would be excited to rotations

around its internuclear axis, but due to the vanishing moment of inertia this rotation is not

energetically accessible, and this pathway cannot account for rotational excitation in l-C_3H.

Although the slightly bent C_3H structure is a local minimum, this isomer behaves like a

quasilinear molecule (22), since its bending mode can be easily excited. These arguments reveal

that the symmetric exit transition state originates in the rotation of HCCCH around the C_2 axis.

What dynamics account for the formation of HCCCH itself? Direct insertion of $C(^3P_j)$

into the acetylenic C-H-bond can be ruled out, since this symmetry forbidden pathway is

expected to involve a significant entrance barrier, much larger than our lowest collision energy of 8.8 kJmol^{-1}. In strong support, C(^{3}P$_j$) reaction with methylacetylene exhibits no evidence of insertion into the acetylenic C-H-bond (21). On the other hand, the initial addition to yield CCHCH involves maximum orbital overlap and opens a large range of impact parameters for reactive encounters. A subsequent [2,3]-H-migration yields propargylene, followed by a final C-H bond rupture to 1-C$_3$H(X^{2}Π$_j$) and H(^{2}S$_{1/2}$). The loose exit transition state inferred from the P(E$_T$)s goes hand in hand with only minor geometry changes from the decomposing HCCCH to 1-C$_3$H: C-C and C-H distances alter by less than 0.07Å, and the bending angle of three propargylene carbon atoms opens only 8.1° (Tab. 1).

The second, forward-scattered microchannel follows direct reaction dynamics. Large impact parameters and reaction intermediates with shallow potential energy wells contribute to the reactive scattering signal. Therefore, C(^{3}P$_j$) insertion to form HCCCH can be excluded. The large deviation of the relative cross sections from the classical capture theory (20) resolves the underlying dynamics for this microchannel. Although the detailed structure of the molecule does not play a role within the simple capture framework, this approximation breaks down as the orbiting radius decreases with rising collision energy: reactive encounters from radii exceeding the symmetric π-cloud to form c-C$_3$H$_2$ become more and more unlikely and are preferentially shifted toward orbits in which the π-cloud can be attacked sideways to yield the CCHCH isomer. This model explains both the decreasing cross section and less polarized center-of-mass angular distribution as the collision energy rises. The final C-H bond rupture forms the cyclic C$_3$H isomer and a hydrogen atom.

Our crossed beam studies combined with presented *ab initio* calculations explicitly identify both isomers, the l-C_3H and c-C_3H, under single collision conditions. This reaction represents a one-step encounter to build up C_3H isomers in the ISM and eliminates the need for successive binary encounters as required in ion-molecule networks. The chemical dynamics that cause an increasing ratio of l-C_3H to c-C_3H with rising collision energy explain previously unresolved astronomical observations. Dark molecular clouds hold typical averaged translational temperatures of 10K, whereas circumstellar shells around carbon stars are heated up to about 4000K giving mean translational energies of about 0.1 and 40kJmol^{-1}, respectively. Therefore, both isomers are anticipated to exist in dark clouds, but less c-C_3H in the hotter envelope surrounding IRC+10216. This expected pattern is reflected in observed number density ratios of c-C_3H versus l-C_3H of unity in cold molecular clouds, e.g. TMC-1, versus 0.2±0.1 around IRC+10216. Therefore a common acetylene reactant to interstellar l/c-C_3H radicals via atom-neutral reaction with $C(^3P_j)$ and distinct structural isomers must be included into interstellar reaction networks.

This work is just the beginning toward a better understanding of reactions of neutral atoms with neutral reactants in the interstellar medium. The direct observation of the carbon-hydrogen exchange channel represents a versatile synthetic route to reactive hydrocarbon radicals in the ISM. Interstellar environments of unsaturated hydrocarbons methylacetylene (CH_3CCH), ethinyl (C_2H), vinyl (C_2H_3), ethylene (C_2H_4), or propylene (C_3H_6) overlapping with large concentrations of atomic carbon should be sought. Once these regions have been charted, the search for hitherto unobserved interstellar radicals as reaction products of these atom-neutral reactions is open.

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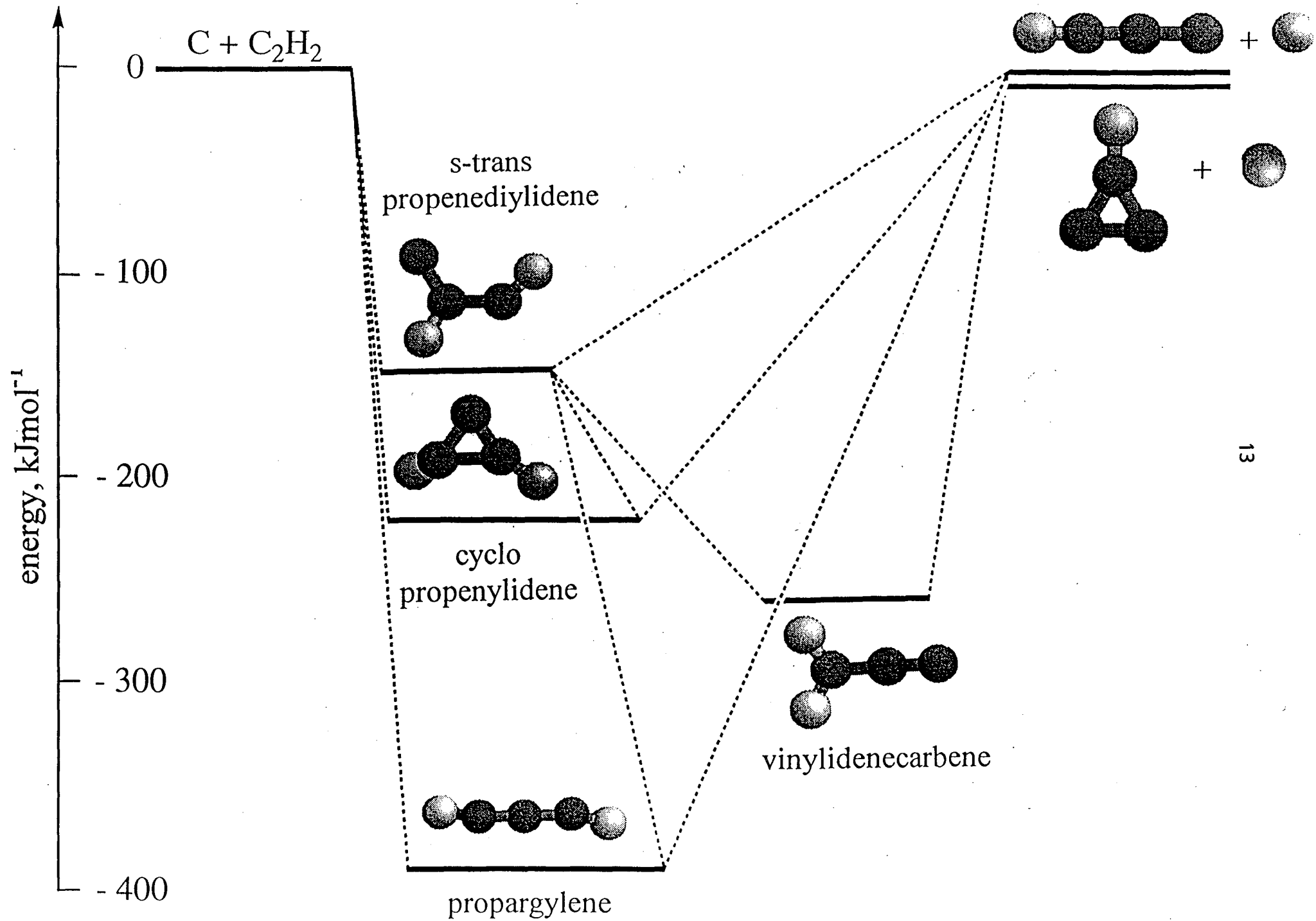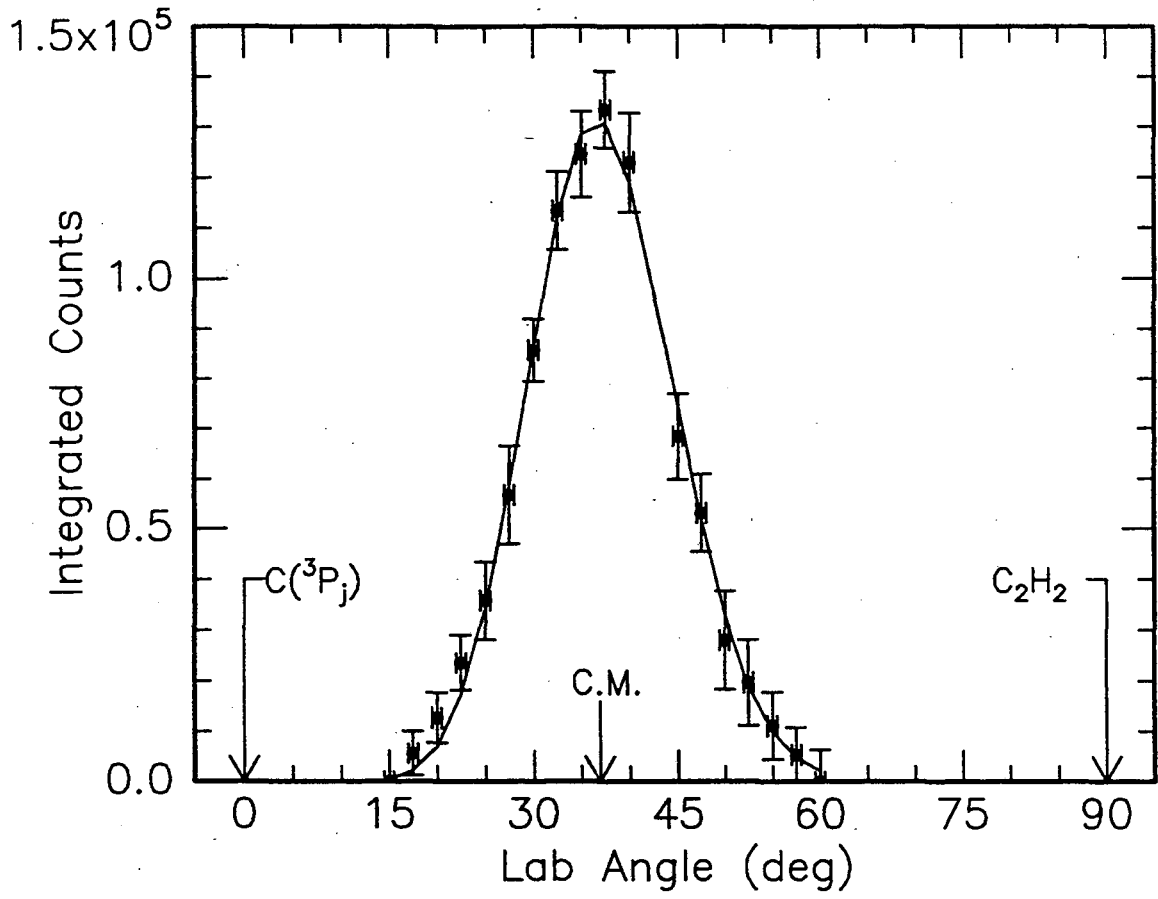
Figure 1. Schematic reaction pathways of $C(^3P_j)$ with $C_2H_2(X^1\Sigma_g^+)$ and *ab initio* structures of triplet C_3H_2 and doublet C_3H isomers. Black balls denote carbon atoms, grey balls hydrogen atoms.
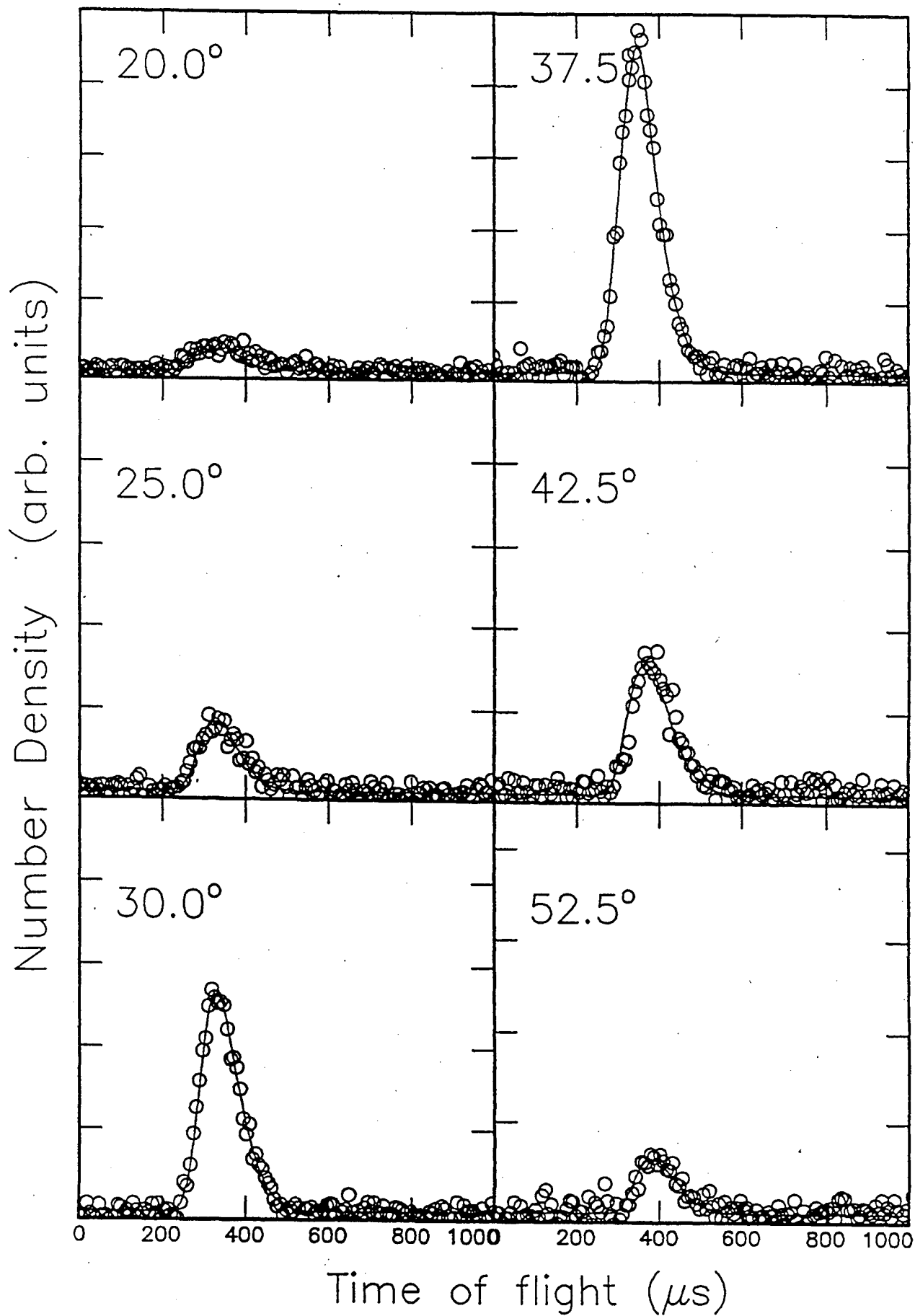
Figure 2. Laboratory angular distribution of C_3H at m/e = 37 at a selected collision energy of 28.0 kJmol^{-1}. Circles and 1σ error bars indicate experimental data, the solid lines the calculated distribution .

Figure 3. Time-of-flight data at m/e = 37 at a selected collision energy of 28.0kJmol^{-1}. Open circles represent experimental data, the solid line the fit. TOF spectra have been normalized to the relative intensity at each angle.

Figure 4. Lower: Center-of-mass angular flux distributions for the reaction $C(^3P_j)$ + $C_2H_2(X^1\Sigma_g^+)$ at peak collision energies of 8.8 (solid li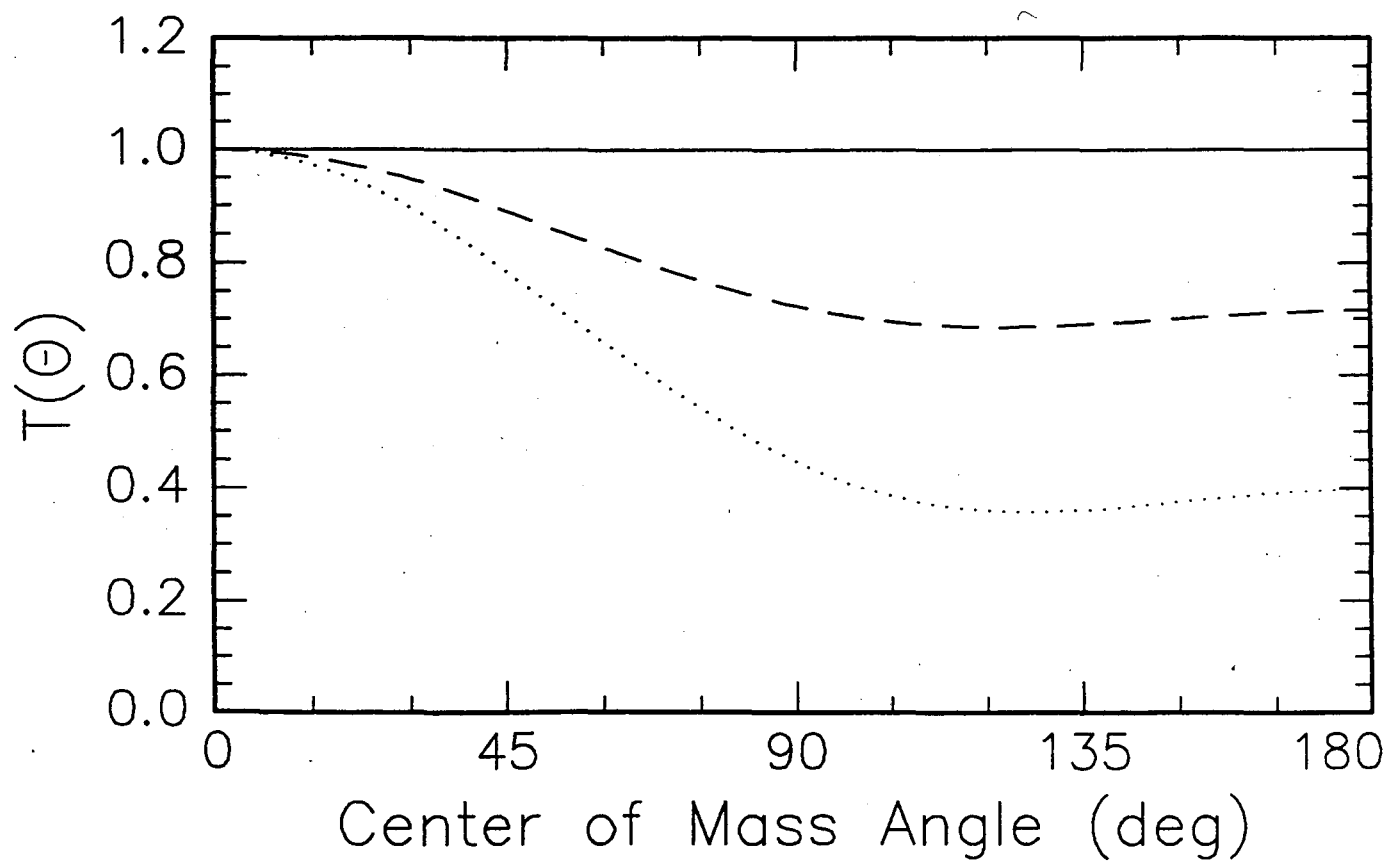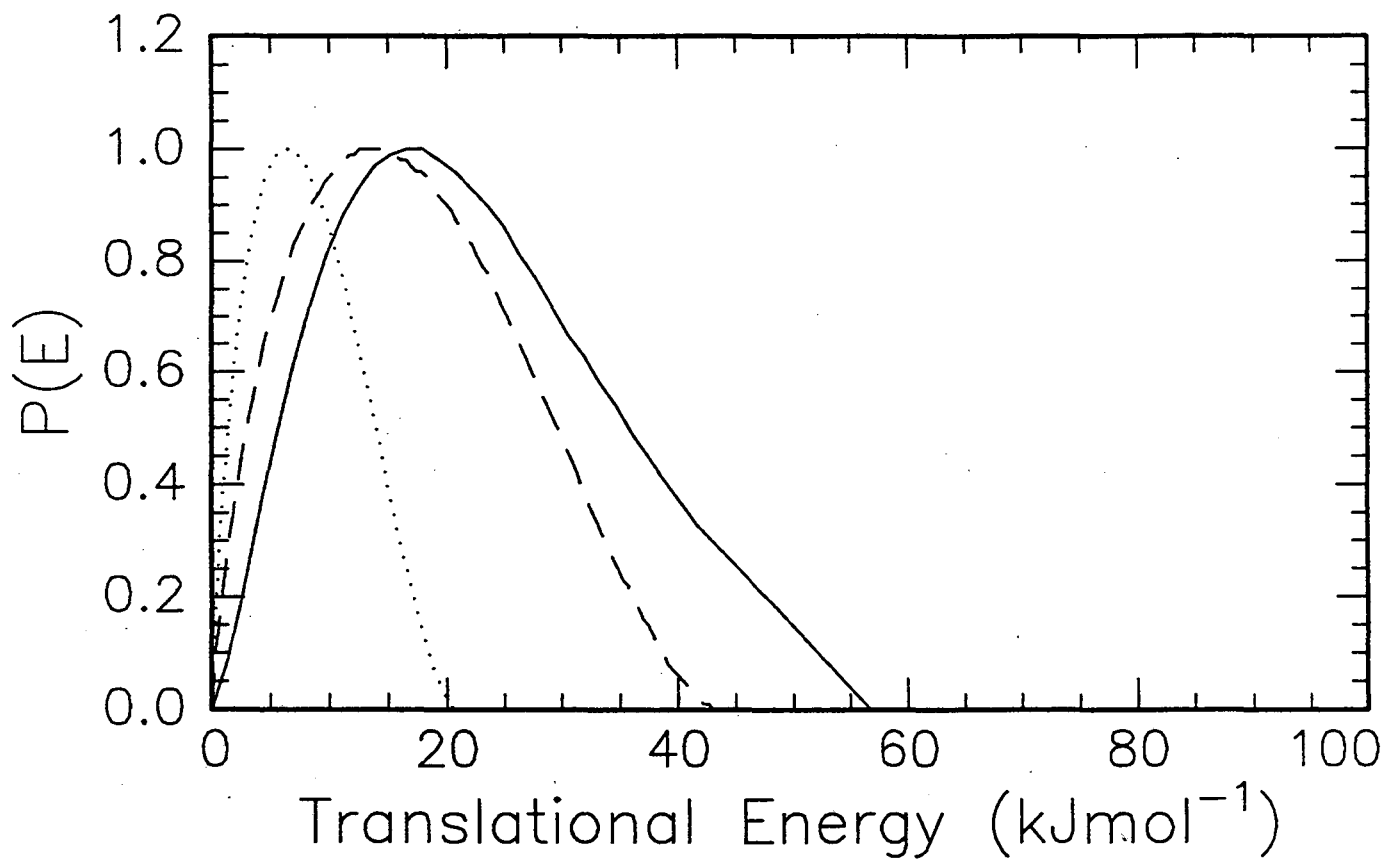ne), 28.0 (dashed line), and 45.0kJmol^{-1} (dotted line). Upper: Center-of-mass translational energy flux distributions for the reaction $C(^3P_j)$ + $C_2H_2(X^1\Sigma_g^+)$ at peak collision energies of 8.8 (solid line), 28.0 (dashed line), and 45.0kJmol^{-1} (dotted line).

energy, kJmol^{-1}

$C + C_2H_2$

s-trans
propenediylidene

cyclo
propenylidene

propargylene

vinylidenecarbene

0

− 100

− 200

− 300

− 400

13

Time of flight (μs)

Table 1. Structural data of C_3H_2 and C_3H isomers as depicted in Fig. 4.

Isomer[a]	Structural data[b]		
HCCCH	(C*-C) = 127.9	(C-H) = 106.7	(C,C*,C') = 171.9°
	(C*,C,H) = 156.5°	(H-C'-C-H') = 88.0°	
H_2CCC	(C1-C2) = 136.9	(C2-C3) = 123.8	(C1-H) = 108.1
	(H,C1,C2) = 120.5°		
c-C_3H_2	(C1-C2) = 144.8	(C2-C3) = 130.4	(C1-C3) = 155.1
	(C1-H1) = 108.8	(C3-H2) = 107.3	(H1,C1,C3) = 125.9°
	(H2,C3,C1) = 141.1°	(H1,C2,C3,C1) = 46.1°	(H2,C1,C2,C3) = 0.2°
CHCCH	(C1-C2) = 134.9	(C2-C3) = 139.2	(C2-H1) = 109.2
	(C3-H2) = 107.9	(C1,C2,C3) = 121.2°	(C1,C2,H1) = 117.1°
	(C2,C3,H2) = 134.1°		
c-C_3H	(C-C*) = 137.7	(C,C') = 137.8	(C*-H) = 107.8
l-C_3H	(H-C1) = 106.5	(C1-C2) = 124.3	(C2-C3) = 134.7
b-C_3H	(H-C1) = 106.9	(C1-C2) = 125.2	(C2-C3) = 133.8
	(H,C1,C2) = 156.9°	(C1,C2,C3) = 174.0°	

[a]For structures with a C_2-symmetry axis (and not all C atoms situated on this axis, as in the H_2CCC structure, Fig. 4 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 Fig. 4 (for the cyclic isomer c-C_3H_2 atom C2 is characterized by holding no H atoms).

[b]Notation: (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'.