# NON-THRESHOLD, THRESHOLD, AND NONADIABATIC BEHAVIOR OF THE KEY INTERSTELLAR C + C\_2H\_2 REACTION

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#### ABSTRACT

The C + C<sub>2</sub>H<sub>2</sub> reaction is a key process in interstellar cloud chemistry. In a crossed-beam scattering experiment approaching the low-collision energies that characterize these environments, we determined relative differential cross sections by detecting the H-atom product. High-level ab initio calculations of the reaction energies of two competing pathways, leading to *cyclic* and *linear* C<sub>3</sub>H, were also performed. Both channels are clearly distinguishable: the integral cross section of the *c*-C<sub>3</sub>H + H channel monotonically decreases with increasing relative translational energy whilst the *l*-C<sub>3</sub>H + H channel exhibits a translational energy threshold. Moreover, a comparison of the H-atom yields from the C + C<sub>2</sub>H<sub>2</sub> and C + C<sub>2</sub>H<sub>4</sub> reactions shows that the C<sub>3</sub> + H<sub>2</sub> nonadiabatic channel dominates. These results are consistent with the calculated enthalpies and corroborate earlier low-temperature kinetic experiments. Branching ratios of the three reaction pathways are given in the T = 15-300 K temperature domain for inclusion in astrochemical databases.

Key words: astrochemistry – ISM: abundances – ISM: molecules – molecular processes

### 1. INTRODUCTION

The primary goal of astrophysical chemists is to understand the evolution of interstellar matter through the comparison between observations and models (Smith et al. 2004; Woodall et al. 2007). Considering that many of the 150 molecules currently identified in the interstellar medium are exotic by terrestrial standards and the reactions which govern their synthesis and their fate take place under extreme conditions, this represents a significant challenge. In dense interstellar clouds, temperatures between 10 and 30 K are prevalent, photons from neighboring stars are unable to penetrate, and reactions between neutral atomic carbon and carbon-bearing molecules are important. The  $C + C_2H_2$  reaction is considered to be a key process in the synthesis of unsaturated carbon chains (Clary et al. 1994; Herbst 1995a, 1995b) since it has a marked non-Arrhenius behavior with a rate increasing with decreasing temperature from 300 K to 15 K (Clary et al. 1994; Chastaing et al. 2001).

Numerous theoretical and experimental studies have aimed at elucidating the dynamics of the  $C + C_2H_2$  reaction: determinations of the potential energy surfaces (Takahashi & Yamashita 1996; Ochsenfeld et al. 1997; Guadagnini et al. 1998; Buonomo & Clary 2001; Clary et al. 2002; Takayanagi 2005; Mebel et al. 2007) including calculations in the full nine dimensions (Park et al. 2006), quantum (Buonomo & Clary 2001; Clary et al. 2002; Takayanagi 2006), quasi-classical trajectory (Park et al. 2006), and statistical calculations (Mebel et al. 2007); measurements of differential cross sections and integral cross sections in crossed molecular beam experiments employing electron-impact ionization mass spectrometric time-of-flight analysis for C<sub>3</sub>H and C<sub>3</sub> detection with pulsed (Kaiser et al. 1997; Gu et al. 2007) or continuous beams (Clary et al. 2002; Cartechini et al. 2002; Costes et al. 2006; Leonori et al. 2008) and spectroscopic probing of the H-atom product (Clary et al. 2002; Cartechini et al. 2002; Costes et al. 2006). Three channels have been identified: two H-elimination channels leading to cyclic and linear forms of the C<sub>3</sub>H radical, the former being slightly exoergic and the latter being almost thermoneutral (Ochsenfeld et al. 1997; Mebel et al.

2007), and one strongly excergic  $H_2$ -elimination channel which is forbidden in the Born-Oppenheimer approximation, since it requires a nonadiabatic transition from the ground-state triplet potential energy surface to a singlet one:

$$C({}^{3}P_{J}) + C_{2}H_{2}(X^{1}\Sigma_{g}^{+}) \rightarrow c - C_{3}H(X^{2}B_{2}) + H({}^{2}S_{1/2})$$
$$\Delta H_{0}^{\circ} = [-14.1, -8.6] \text{ kJ mol}^{-1}, \qquad (1a)$$

$$C({}^{3}P_{J}) + C_{2}H_{2}(X^{1}\Sigma_{g}^{+}) \rightarrow l - C_{3}H(X^{2}\Pi_{1/2}) + H({}^{2}S_{1/2})$$
$$\Delta H_{0}^{\circ} = [-3.1, -1.5] \text{ kJ mol}^{-1}, \qquad (1b)$$

$$C({}^{3}P_{J}) + C_{2}H_{2}(X^{1}\Sigma_{g}^{+}) \to C_{3}(X^{1}\Sigma_{g}^{+}) + H_{2}(X^{1}\Sigma_{g}^{+})$$
$$\Delta H_{0}^{\circ} = -106 \pm 16 \text{ kJ mol}^{-1}.$$
(1c)

Two crucial points are still unresolved as far as astrochemistry is concerned. First, even accurate ab initio calculations (Ochsenfeld et al. 1997; Mebel et al. 2007) are prone to some uncertainty, and thus it cannot be stated with assurance that channel (1b) leading to *l*-C<sub>3</sub>H is actually exoergic. Any slight potential barrier would be of paramount importance in low-temperature environments. Second, in cold interstellar clouds, typical temperatures of 10–30 K correspond to mean translational energies for collisions,  $\langle E_T \rangle = 3/2$  **R***T*, of 0.12–0.4 kJ mol<sup>-1</sup>, respectively, and branching ratios of the integral cross sections  $R1 = \sigma(1b)/\sigma(1a+1b)$  and  $R2 = \sigma(1c)/\sigma(1)$  have only been determined above a relative translational energy (collision energy) of  $E_T = 3.5$  kJ mol<sup>-1</sup> except for a preliminary measurement of *R*1 at  $E_T = 0.8$  kJ mol<sup>-1</sup> (Costes et al. 2006).

In this paper, we report high-level ab initio electronic structure calculations of c-C<sub>3</sub>H and l-C<sub>3</sub>H performed with the coupledcluster method and high-resolution, differential cross-section measurements in crossed-beam experiments at low energies that allow, with the aid of previous low-temperature kinetic results, determination of the branching ratios *R*1 and *R*2 as a function of collision energy.

## 2. AB INITIO CALCULATIONS

The c-C<sub>3</sub>H radical in its ground state is prone to symmetry breaking due to a peculiar structure that requires distributing three electrons on two centers which are equivalent by symmetry. A pseudo Jahn-Teller effect is also observed due to the nonadiabatic interaction with the first excited state. However, the investigation of these difficulties by two different highly correlated calculations has shown that the c-C<sub>3</sub>H radical is planar and belongs to the  $C_{2v}$  symmetry point group (Stanton 1995; Halvick 2007). The l-C<sub>3</sub>H radical in its electronic ground state <sup>2</sup>Π is doubly degenerate and characterized by a large Renner– Teller (R–T) effect (Yamamoto et al. 1990; Kanada et al. 1996; Gottlieb et al. 1986). The R-T coupling generates an extremely flat bending potential for one electronic component. Depending on the ab initio method and basis set used, the equilibrium geometry has been found to be linear (Ding et al. 2001; Perić et al. 2003) or slightly bent (Kanada et al. 1996; Aoki et al. 1996; Takahashi & Yamashita 1996; Ochsenfeld et al. 1997), with a barrier to linearity in the range of  $10-200 \text{ cm}^{-1}$ . The second component of the degenerate electronic state is more rigid and its linear equilibrium geometry is not ambiguous.

Coupled-cluster calculations were performed with all single and double excitations and a perturbative estimate of triple excitations (CCSD(T)). These calculations employed standard correlation consistent basis sets cc-pVXZ (X = D, T, Q, 5), which constitute a hierarchical sequence with systematic improvement from level to level (Dunning 1989). At each level, the upper level is obtained by adding an entire "shell" of functions which is expected to bring approximately the same contribution to the correlation energy. Such basis sets provide a well-defined path to the complete basis set (CBS) limit. The CCSD(T) calculations have been carried out with restricted open shell Hartree-Fock molecular orbitals. This choice of reference function avoids problems caused by spin contamination. The core electrons have not been correlated. For each basis set, the geometries have been optimized at the CCSD(T) level, with the energy derivatives calculated by finite differences. All these calculations have been carried out with the program Molpro (Werner & Knowles 2003).

The extrapolation of electronic energies toward the CBS limit uses two different models: the model of Feller (Feller 1992) for the Hartree–Fock energy, given by

$$E_X^{\rm HF} = E_{\rm CBS}^{\rm HF} + a \exp(-bx)$$

and the model proposed by Helgaker et al. 1997 for the correlation energy, given by

$$E_{\rm CBS}^{C} = \left(E_{\rm X}^{C} x^3 - E_{\rm Y}^{C} y^3\right) / (x^3 - y^3)$$

The extrapolation of Hartree–Fock energy has been done with the X = T, Q, 5 basis sets, and x is the cardinal number of the basis set, namely 3, 4, and 5. The extrapolation of the correlation energy used X = 5 and Y = Q basis sets, and consequently x = 5 and y = 4. The anharmonic correction to the vibrational frequencies of the c-C<sub>3</sub>H radical has been computed at the B3LYP/6–311G\*\* level with the Gaussian program package (Frisch et al. 2004).

Table 1 displays the geometries calculated with the CCSD(T) method. The l-C<sub>3</sub>H radical has been found to be non-linear with the double and triple zeta basis sets. At the cc-pVTZ level, the l-C<sub>3</sub>H radical is slightly bent and the barrier to linearity is 7.5 cm<sup>-1</sup>, which is close to the 8 cm<sup>-1</sup> reported previously at the

Table 1 Calculated and Experimental Equilibrium Geometries for Linear and Cyclic  $C_{3}H$ 

Species	Parameter	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	Exp.
<i>l</i> -C <sub>3</sub> H	R <sub>CC</sub>	1.3578	1.3450	1.3442	1.3431	1.326 <sup>a</sup>
	$R_{\rm CC^*}$	1.2762	1.2508	1.2442	1.2436	1.254 <sup>a</sup>
	$R_{C^*H}$	1.0862	1.0668	1.0653	1.0651	1.017 <sup>a</sup>
	$\theta_{\rm CCC^*}$	173.4	176.4	180.0	180.0	
	$\theta_{\rm CC^*H}$	154.6	165.7	180.0	180.0	
c-C <sub>3</sub> H	R <sub>CC*</sub>	1.4004	1.3811	1.3761	1.3751	1.374 <sup>b</sup>
	$R_{\rm CC}$	1.4080	1.3832	1.3770	1.3756	1.377 <sup>b</sup>
	$R_{C^*H}$	1.0956	1.0794	1.0790	1.0787	1.076 <sup>b</sup>

**Notes.** Distances are in angstrom and angles are in degree. C\* denotes the carbon atom bonded to the hydrogen atom.

<sup>a</sup> Kanada et al. 1996.

<sup>b</sup> Yamamoto & Saito 1994.

UHF/CCSD(T)/TZP level (Ochsenfeld et al. 1997). Attempts to optimize the dihedral angle have shown that the molecule remains planar. Considering the geometries calculated from the double zeta up to the quadruple zeta basis set, we observe a clear progression toward linear geometry. At the cc-pV5Z level, only the bond lengths have been optimized, the molecule being assumed to be linear. While these results do not bring a definitive answer to the question of the linearity because the effect of more correlation (for example, with CCSDT or CCSDTQ method) is known to be important for highly accurate prediction of geometries (Heckert et al. 2005), at least we are confident that l-C<sub>3</sub>H is either linear or very close to linear with a tiny barrier to linearity. Therefore, even in the last case, the calculations of vibrational frequencies have to be done with the theory for a linear molecule, because the energy of the vibrational bending ground state is expected to be significantly larger than the barrier to linearity. Moreover, in the quasi-linear case, owing to the strong anharmonicity, the harmonic frequencies calculated at the equilibrium bent geometry are inadequate for the calculation of a valid approximation of the zero-point energy (ZPE). The comparison of the calculated equilibrium geometry of l-C<sub>3</sub>H with the experimental data shows a large discrepancy for this level of theory (see Table 1). Indeed, a statistical analysis (Bak et al. 2001) has shown that CCSD(T) calculations with large basis sets such as cc-pVQZ or cc-pV5Z provide an accuracy of about 0.001–0.003 Å for the calculated bond length. Therefore, in the case of l-C<sub>3</sub>H, the calculated CH bond length is much too long in comparison with the experimental value. The same discrepancy has been consistently observed in all other calculations (see, for example, Table 1 of Perić et al. 2003). It has been suggested that, due to the large amplitude of the CCH bending motion, the CH distance derived from the experimental rotational constants is close to the effective bond length of a bent structure rather than those for the linear structure (Kanada et al. 1996).

The  $T_1$  diagnostic (Lee & Taylor 1989) is about 0.03 with all basis sets for *l*-C<sub>3</sub>H. This value, which is slightly larger than the recommended value of 0.02, indicates some non-dynamical correlation effects. However, Ochsenfeld et al. (1997) have confirmed the reliability of the CCSD(T) approach for this species by performing CC calculations with Brueckner orbitals.

Previous calculations with methods free from symmetry breaking have shown that the ground state of c-C<sub>3</sub>H belongs to the  $C_{2v}$  symmetry point group (Stanton 1995; Halvick 2007). Therefore, optimization of the geometry has been performed under this constraint. The T<sub>1</sub> diagnostic is about 0.015 for all

Species	cc-pVTZ	cc-pVQZ	cc-pV5Z	CBS	ZPE	$\Delta H^{\circ}_{0}$
$H + l-C_3H$	-114.955992 32.0	-114.985538 26 5	-114.994270 24.9	22.9	45.5	+0.7
$H + c-C_3H$	-114.959136 23.7	-114.990430 13.6	-114.999992 9 9	5.9	50.1	-11.7
$C + C_2H_2$	-114.968166 0	-114.995618 0	-115.003769 0	0	67.7	

 Table 2

 CCSD(T) Energies Calculated with the Geometries Optimized at the cc-pV5Z Level

Note. First entry: total energies in Hartree; second entry: energies relative to the reactants' energy in kJ mol<sup>-1</sup>.

basis sets, indicating a good reliability of the CC approach. This is confirmed by the excellent agreement of the calculated geometry with the experimental one.

In order to calculate the CBS limit of the reaction energy, the geometries optimized at the cc-pV5Z level have been used to compute single-point energies of the reactants and products of the reactions (1a) and (1b). Table 2 displays the total energies and the CBS reaction energies. Both reactions are endoergic for all basis sets. Increasing the size of the basis set tends to stabilize the products more than the reactants, and the cyclic structure of  $C_3H$  more than the linear one.

The ZPEs for reactants and products have been calculated with a selection of the most reliable vibrational frequencies available in the literature, both from experiments and theory. For acetylene, the ZPE is 67.7 kJ mol<sup>-1</sup>, calculated with the experimental fundamental frequencies (Shimanouchi 1972). No experimental frequencies are known for c-C<sub>3</sub>H. However, accurate ab initio calculations of the harmonic frequencies are available, calculated at the CASSCF/MRCI+Q/cc-pVQZ level (Halvick 2007). These give a ZPE of 50.9 kJ mol<sup>-1</sup>. We have taken into account the vibrational anharmonicity by multiplying this last value by the ratio ZPE(fundamental)/ZPE(harmonic) calculated at the B3LYP/6-311G\*\* level, yielding the final value of 50.1 kJ mol<sup>-1</sup> for the ZPE of c-C<sub>3</sub>H. The experimental fundamental frequencies of  $l-C_3H$  are known only for the stretching motions (Jacox 2003). We have combined these experimental frequencies with the RT ground state energy calculated by a variational quantum method that allows us to treat properly the vibronic coupling (Perić et al. 2003). This yields a value of 45.5 kJ mol<sup>-1</sup>. The reaction enthalpies are therefore calculated to be  $\Delta H_0^{\circ}(1a) = -11.7 \text{ kJ mol}^{-1}$  and  $\Delta H_0^{\circ}(1b) = 0.7 \text{ kJ mol}^{-1}$ . The calculations performed on the c-C<sub>3</sub>H radical are well founded and the accuracy of the enthalpy for reaction (1a) is expected to be good. An estimate of the error can be extracted from the statistical analysis (Bak et al. 2000) performed on the enthalpies of 13 reactions for which experimental data are available. With the CCSD(T) method with all electrons correlated and extrapolations based on cc-pCVXZ (X = Q,5), a mean absolute error of 1.2 kJ mol<sup>-1</sup> is reported. Because we used the smaller basis sets cc-pVXZ and did not include core-correlation, the error for the enthalpy of reaction (1a) is expected to be slightly larger, around  $2 \text{ kJ mol}^{-1}$ , than the latter value. The error on the enthalpy of reaction (1b) should be significantly larger, due to a  $T_1$  diagnostic slightly too large, the unsolved question of linearity, and the discrepancy between calculated and experimental equilibrium bond lengths for the *l*-C<sub>3</sub>H radical.

## 3. EXPERIMENTAL DETAILS

Experiments were performed with an all pulsed and variable beam intersection angle crossed-beam machine, the main features of which have been previously described (Naulin & Costes 1999). Briefly, the atom beam was produced by ablating C-atoms from a graphite rod in a slow helical motion. A fraction of the output, ca 0.15 mJ, from a quadrupled Nd:YAG laser was focused on a 0.05 mm waist on the graphite rod and the ablated atoms were subsequently entrained and cooled into the supersonic expansion of Ne or Ar carrier gas emitted by a first fast-pulsed valve. This skimmed, pulsed  $C({}^{3}P_{J})$  beam of velocity  $v_{\rm C}$  was collided at a given intersection angle in the range 22°.5  $\leq \chi \leq 60^{\circ}$  with a skimmed, pulsed acetylene beam of velocity  $v_{C2H2}$  produced by a second fast-pulsed valve. The background pressure remained at  $<10^{-4}$  Pa with both beams in operation and the attenuation of one beam by another was <4%. Experiments were performed at selected relative translational energies under beam conditions satisfying the relationship  $v_{\rm C} = v_{\rm C2H2} \cos \chi$ , hence providing a relative velocity vector of reagents,  $v_r$ , perpendicular to the C beam and along the axis of one of the laser beams (Costes et al. 2006).

Note that  $H(^{2}S_{1/2})$  atoms produced by the reaction were detected by resonance-enhanced 2-color ionization with sequential absorption of a VUV photon tuned to the Lyman- $\alpha$  $({}^{2}S_{1/2} \rightarrow {}^{2}P_{J}^{\circ})$  transition at 121.567 nm and a UV photon at 364.7 nm for threshold ionization. The laser system consisted of a Nd:YAG laser locked to a single longitudinal mode and a dye laser pumped by the Nd: YAG second harmonic. A UV beam (ca. 24 mJ, 8 ns) at 364.7 nm was obtained by sum-frequency mixing tunable 554 nm radiation from the dye laser with residual 1064 nm radiation in a beta-barium borate crystal cut at 36° and was separated into two components with a beam splitter. In the *parallel* configuration, the first beam with ca. 7 mJ energy propagated in the molecular beam scattering plane parallel to  $v_r$ and was focused with a movable lens (f = 92 mm at 364.7 nm) into a cell filled with ca. 12 kPa of Kr set at the entrance of a light baffle arm, 1 m away from the collision center. Tunable VUV radiation produced by frequency tripling was collimated by a fixed MgF<sub>2</sub> lens (f = 130 mm at 120 nm) that also acted as the exit window of the cell. The large difference in refractive index of MgF<sub>2</sub> between the VUV and the UV eliminated most of the divergent incident UV radiation before reaching the scattering center. The intensity of the VUV beam pulses was monitored by a fast-time-response detector with a Ni photo-emissive cathode (Dyer et al. 2002) mounted on the exit light baffle arm, the output of which was fed into a first boxcar integrator. The second beam with ca. 17 mJ energy was steered at the collision center perpendicular to the first one and the scattering plane, along the main axis of the collision chamber. In the *perpendic*ular configuration, the beam paths of the VUV and UV lasers were interchanged. Both laser beams crossed between specially cut acceleration plates-which allowed the molecular beams to pass through-of a linear two-stage Wiley-MacLaren TOF MS (Wiley & McLaren 1955), positioned in the beam scattering plane at 135° to the C-atom beam. The H<sup>+</sup> signal collected on



**Figure 1.** Spectrum of "cold" H atoms seeded within the C beam. Left:  ${}^{2}S_{1/2} \rightarrow {}^{2}P_{3/2}^{\circ}$ ; right:  ${}^{2}S_{1/2} \rightarrow {}^{2}P_{1/2}^{\circ}$ . Experimental (o); Voigt fitting function (solid line), used as the apparatus function in the fitting procedure with relative intensities taken as the ratio of statistical weights.

the micro channel plates was gated by a second boxcar integrator. The H<sup>+</sup> and VUV signals were acquired for each individual laser shot allowing for subsequent normalization ( $I_{H+}/I_{VUV}$ ) as the VUV absorption process was maintained in the linear regime while the UV ionization step was in the high-saturation regime under our operating conditions.

A strong source of background in H-atom detection had to be treated in the present experiments. Indeed, cold H atoms originating from the ablation process and highly cooled within the supersonic expansion of the carrier gas gave rise to a very narrow Doppler-Fizeau spectrum. By firing the lasers and the carbon beam at 10 Hz and the  $C_2H_2$  beam at 5 Hz, both the total signal including the reactive signal with background and the signal from background alone were alternatively recorded. Wavelength scans were conducted with 10 laser shots separately recorded at each fundamental wavelength of the dye laser incremented by 2.5 pm steps and lasted <450 s, thus avoiding any drift in the experimental conditions. The wavelength of the UV was tracked on a shot-to-shot basis with a highresolution wave meter. Because the collimated atom beam was perpendicular to the Lyman- $\alpha$  laser, the projection of its velocity along the laser axis was zero, hence the cold H atoms encountered no Doppler-Fizeau shift at all. In other words, the background revealed  $\lambda_0$  for absolute calibration at each scan and the bandwidth of the VUV laser. Shot-to-shot acquisition rather than averaging several shots at each wavelength increment led to a sharp laser line width ( $\Delta\lambda/\lambda > 10^6$ ) allowing complete separation of the two doublet peaks  $({}^{2}S_{1/2} \rightarrow {}^{2}P_{3/2}^{\circ})$  and  $({}^{2}S_{1/2}$  $\rightarrow {}^{2}P_{1/2}^{\circ}$ ) of the Lyman- $\alpha$  transition (see Figure 1). Indeed, each individual laser shot was assigned with its measured UV wavelength, thus avoiding any blurring effect due to instabilities in the oscillator of the dye laser, and shots exhibiting too complex a multimode structure-ca. 30% of the shots were single longitudinal mode-were rejected by the wave meter. Doppler-Fizeau spectra consisting of ca. 4000-7000 reactive events were generated by averaging over 6-10 experimental scans after subtraction of background from the total signal.

#### 4. EXPERIMENTAL RESULTS

Doppler–Fizeau spectra of recoiling H-atoms at  $E_{\rm T} = 0.70$ and 3.5 kJ mol<sup>-1</sup> are shown in Figures 2 and 3 for *parallel* 



**Figure 2.** Doppler–Fizeau spectra of the H-product at 0.7 kJ mol<sup>-1</sup>. *Perpendicular* configuration (a); *parallel* configuration (b). Experimental (o); fitting functions with both contributions ( $R1 = 1.5 \pm 1\%$ ) and  $\Delta H_0^{\circ}$  (c-C<sub>3</sub>H/l-C<sub>3</sub>H) = -12/0 (solid line), -8.6/-1.5 (Ochsenfeld et al. 1997; short-dashed line) and -14.1/-3.1 kJ mol<sup>-1</sup> (Mebel et al. 2007; dashed line); Lyman- $\alpha$  ( ${}^2S_{1/2} \rightarrow {}^2P_{3/2}^{\circ}$  and  ${}^2S_{1/2} \rightarrow {}^2P_{1/2}^{\circ}$ ) line positions in the center-of-mass frame are indicated (\*). Intensities are given in arbitrary units (a.u.).

and *perpendicular* configurations. Spectra at all energies are displayed in Figure 4. The spectra are fitted using a forwardconvolution procedure accounting for the density-to-flux transformation (Naulin et al. 2009) and including seven parameters: the scattering angle  $T(\theta)$  and the relative translational energy  $P(E_{\rm T}')$  center-of-mass functions (see Figure 5 and Table 3), the total energy available to reaction products,  $E_{\text{tot}} = -\Delta H^{\circ}_0 +$  $E_{\rm T}$ , for channel (1a) and (1b) and the branching ratio, R1. The requirement to fit spectra in perpendicular and parallel configurations with the same center-of-mass distributions at each  $E_{\rm T}$ , however, introduces stringent parametric constraints (Che & Liu 1996). Moreover, at  $E_{\rm T} = 0.70$  kJ mol<sup>-1</sup>, the analysis is greatly simplified because channel (1a) appears to be overwhelmingly dominant and its center-of-mass distributions can be modeled by simple functions characteristic of indirect reaction dynamics  $T(\theta) \sim 1$  and  $P(E'_{\rm T}) = (1 - E'_{\rm T}/E_{\rm tot})^m (E'_{\rm T}/E_{\rm tot})^n$  with m and n values close to 1/2. A single contribution from channel (1a) gives a reasonable agreement and the best fit is obtained with a mere 1.5% from channel (1b). At  $E_{\rm T} = 3.5$  kJ mol<sup>-1</sup>, the situation is radically different. It now becomes impossible to fit the experimental spectra with a single contribution from reaction (1a). We introduce center-of-mass functions very similar to those obtained by Leonori et al. (2008) at  $E_{\rm T}$  = 3.5 kJ mol<sup>-1</sup> for the scattered C<sub>3</sub>H product. The values  $\Delta H_0^{\circ}(1a)$  $= -12 \text{ kJ mol}^{-1}$  and  $\Delta H_0^{\circ}(1b) = 0$  give the best fits at all  $E_{\rm T}$ s, in excellent agreement with our ab initio results. In Figure 2, it is



**Figure 3.** Doppler–Fizeau spectra of the H-product at 3.5 kJ mol<sup>-1</sup>. *Perpendicular* configuration (a); *parallel* configuration (b). Experimental (o); fitting functions: major (*c*-C<sub>3</sub>H) contribution (dashed line), minor (*l*-C<sub>3</sub>H) contribution,  $R1 = 20 \pm 5\%$  (short-dashed line), total (solid line);\* same as in Figure 1.

clear that using the  $\Delta H_0^{\circ}$  values of Ochsenfeld et al. (1997) and Mebel et al. (2007) for reactions (1a) and (1b) yields an unsatisfactory agreement, demonstrating the high-energy resolution achieved in our experiment.

We plot the respective integral cross sections at the eight energies sampled in Figure 6 with the aid of our previous determination of  $\sigma(1a+1b)$  found to scale as  $[E_T]^{-0.8}$  between 0.38 and 10 kJ mol<sup>-1</sup> (Cartechini et al. 2002). Whereas the c-C<sub>3</sub>H channel displays a decreasing cross section with increasing collision energy, characteristic of a barrierless reaction, the l-C<sub>3</sub>H channel exhibits a translational energy threshold, resulting from the thermoneutral character of this pathway.

We now focus on reaction (1c), performing a comparison between the H-atom flux given by reactions (1a) and (1b) and the one given by the  $C({}^{3}P_{J}) + C_{2}H_{4}$  reaction. Although this reaction has eight possible excergic pathways, it yields exclusively the propargyl radical at low collision energy (Kaiser et al. 1996; Geppert et al. 2003):

C(<sup>3</sup>*P<sub>J</sub>*) + C<sub>2</sub>H<sub>4</sub>(X<sup>1</sup>A<sub>1</sub>) → H<sub>2</sub>CCCH(X<sup>2</sup>B<sub>2</sub>) + H(<sup>2</sup>S<sub>1/2</sub>)  

$$\Delta H_0^\circ = -190 \text{ kJ mol}^{-1}.$$
 (2a)

We performed experiments in the *perpendicular* configuration at two beam intersection angles with an equimolar  $C_2H_2/C_2H_4$ beam. Since velocities of  $C_2H_2$  and  $C_2H_4$  are the same and the

 Table 3

 Fitting Parameters

$E_{\rm T}$ (kJ mol <sup>-1</sup> )	$A_0$	$A_2$	т	n	<i>R</i> 1 (%)
0.44	1	0	0.5	0.5	$0.5 \pm 0.5$
0.70	0.98	0.02	0.5	0.55	$1.5 \pm 1.0$
1.2	0.94	0.06	0.5	0.6	$2.5~\pm~1.0$
1.8	0.9	0.10	0.5	0.7	$5.0~\pm~2.0$
2.4	0.85	0.15	0.5	0.9	$12.5 \pm 2.5$
3.0	0.825	0.175	0.5	1	$15.0 \pm 2.5$
3.5	0.8	0.20	0.5	1.3	$20.0\pm5.0$
4.5	0.75	0.25	0.5	1.45	$23.0\pm5.0$

reduced masses of the two reactive systems are almost identical, the Doppler–Fizeau spectra shown in Figures 7(a) and (b) are recorded at almost identical  $E_{\rm T}$ s. The C(<sup>3</sup> $P_J$ ) + C<sub>2</sub>H<sub>4</sub> Doppler– Fizeau spectra extend over a wide range as expected from the large reaction exoergicity and are thus strikingly different from the much sharper  $C({}^{3}P_{J}) + C_{2}H_{2}$  ones. Deconvoluting the contributions of reaction (1a), (1b), and (2a) yields the ratio  $\sigma(1a+1b)/\sigma(2a) = 0.18$  and 0.13 at  $E_{\rm T} = 0.8$  and 4.8 kJ mol<sup>-1</sup>, respectively. As the total rate coefficients of the two reactions are equivalent between 15 K and 298 K (Chastaing et al. 2001), we assume that the total integral cross sections are also the same:  $\sigma(1) \approx \sigma(2) \approx \sigma(2a)$ . It follows that  $\sigma(1)$  exhibits the same energy dependence as  $\sigma(2a)$ , i.e., in  $[E_T]^{-0.6}$  as determined between  $E_{\rm T} = 0.49$  and 8 kJ mol<sup>-1</sup> in previous work (Geppert et al. 2003). Calculating a rate coefficient  $k_1(T)$  when averaging the product  $\sigma(E_{\rm T}) \times v_{\rm r}$  over a Maxwell distribution of relative velocities at temperature T results in a  $[T]^{-0.1}$  dependence of the rate coefficient, in agreement with low-temperature kinetic experiments which give  $k_1(T) = (2.9 \pm 0.7) \times 10^{-10} (T/298)^{-(0.12 \pm 0.10)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Chastaing et al. 2001), thus justifying the assumption. This also allows us to calibrate the integral cross sections on an absolute scale. Fits of all data on the whole energy domain assessed are plotted in Figure 6.

### 5. DISCUSSION

Our best estimate of reaction energies is  $\Delta H_0^{\circ}(1a) = -11.7 \text{ kJ mol}^{-1}$  and  $\Delta H_0^{\circ}(1b) = +0.7 \text{ kJ mol}^{-1}$ . Ochsenfeld et al. (1997) determined  $\Delta H_0^{\circ}(1a) = -8.6 \text{ kJ mol}^{-1}$  and  $\Delta H_0^{\circ}(1b) = -1.5 \text{ kJ mol}^{-1}$  from electronic energy calculations performed at the cc-pVQZ level. More recently, Mebel et al. (2007) found  $\Delta H_0^{\circ}(1a) = -14.1 \text{ kJ mol}^{-1}$  and  $\Delta H_0^{\circ}(1b) = -3.1 \text{ kJ mol}^{-1}$  from the electronic energy converged at the complete basis set limit. In our own work, the geometries were optimized at the highest level of theory, cc-pV5Z, and we included separate complete basis set calculations of the Hartree–Fock and correlation energies by taking into account the slower convergence of the correlation energy. Hence, a greater accuracy can be expected from the present calculations. Our values are indeed nicely correlated with the experimental results:  $\Delta H_0^{\circ}(1a) = -12 \text{ kJ mol}^{-1}$  and  $\Delta H_0^{\circ}(1b) = 0$ .

Figure 6 emphasizes that the spin-forbidden nonadiabatic  $C_3$  +  $H_2$  channel (1c) is the dominant one. The branching ratio  $R2 = \sigma(1c)/\sigma(1)$  takes values 0.82 and 0.87 at  $E_T = 0.8$  and 4.8 kJ mol<sup>-1</sup>, respectively, which are higher than those given in the crossed-beam experiments of Leonori et al. (2008) at  $E_T \ge$  3.5 kJ mol<sup>-1</sup>, the bulk study at 300 K of Bergeat & Loison (2001) and the calculations of Mebel et al. (2007), and Park et al. (2006). It is in line with the crossed-beam study of Gu et al. (2007) since extrapolation of their curve based on data



**Figure 4.** Doppler–Fizeau spectra of the H-product from C + C<sub>2</sub>H<sub>2</sub> reaction at all relative translational energies ( $E_{\rm T}$ ). Left: *perpendicular configuration* ( $\perp$ ); right: *parallel configuration* (//). Experimental data (o); fitting functions (solid lines); R1 = ( $\sigma(1b)/\sigma(1a+1b)$ . Beam conditions ( $v_{\rm C}$ /m s<sup>-1</sup>,  $v_{\rm C2H2}$ /m s<sup>-1</sup>,  $\chi/^{\circ}$ ): 0.44 kJ mol<sup>-1</sup> (794, 855, 22.5)  $\perp$  and //; 0.7 kJ mol<sup>-1</sup> (1000, 1082, 22.5)  $\perp$  and //; 1.2 kJ mol<sup>-1</sup> (1000, 1082, 30)  $\perp$  and (1000, 1147, 28.6) //; 1.8 kJ mol<sup>-1</sup> (1000, 1082, 37)  $\perp$  and (1000, 1203, 33.6) //; 2.4 kJ mol<sup>-1</sup> (1000, 1082, 42.7)  $\perp$  and (1000, 1251, 37.4 //; 3.0 kJ mol<sup>-1</sup> (1000, 1082, 48)  $\perp$  and (1000, 1301, 40.6); 3.5 kJ mol<sup>-1</sup> (1000, 1082, 52.6)  $\perp$  and (1000, 1366, 43.1) //; 4.5 kJ mol<sup>-1</sup> (1000, 1082, 60)  $\perp$  and (1000, 1433, 46.2) //. Intensities are given in arbitrary units (a.u.).



**Figure 5.** Angular  $T(\theta)$  (a) and recoil energy (b)  $P(E'_{\rm T})$  center-of-mass functions used to fit the Doppler–Fizeau spectra. The first plot (solid line) in each panel refers to H + l-C<sub>3</sub>H (at all energies) and H + c-C<sub>3</sub>H at  $E_{\rm T} = 0.44$  kJ mol<sup>-1</sup>; other plots refer to H + c-C<sub>3</sub>H at increasing energies (in the order 0.7, 1.2, 1.8, 2.4, 3.0, 3.5, and 4.5 kJ mol<sup>-1</sup>).

at  $E_T \ge 8.8$  kJ mol<sup>-1</sup> would result in *R*2 around 0.9 at low  $E_T$ . Clearly, the title reaction is governed by indirect dynamics



**Figure 6.** Collision energy dependence of the integral cross section of various channels. Total (solid line),  $H_2 + C_3$  (dashed line),  $H + C_3H(c+l)$  (short-dashed line),  $H + c-C_3H$  (o),  $H + l-C_3H$  ( $\Delta$ ).

below  $E_{\rm T} \leq 4.8$  kJ mol<sup>-1</sup> and the collision complex finds ample time to sample the whole phase space before dissociating into products.

Our finding that the *R*2 branching ratio increases slightly from 0.82 to 0.87 with increasing  $E_{\rm T}$  from 0.8 to 4.8 kJ mol<sup>-1</sup> is in agreement with our previous integral cross section determinations (Cartechini et al. 2002; Geppert et al. 2003) since  $\sigma$ (1a+1b)  $\propto$  [ $E_{\rm T}$ ]<sup>-0.8</sup> declines faster than  $\sigma$ (1c)  $\propto$  [ $E_{\rm T}$ ]<sup>-0.6</sup>. This is at odds with previous experimental and theoretical work supported by lifetime considerations. Indeed, the lifetime of the complex is expected to decrease with increasing energy and hence the importance of the nonadiabatic channel. However, when increasing the total energy, the density of states may increase faster for C<sub>3</sub> than for *c*-C<sub>3</sub>H since the former possesses a very low energy bending mode. Linear C<sub>3</sub>H also possesses a very low energy bending mode, but the *R*1 branching ratio remains low in the



**Figure 7.** Doppler–Fizeau spectra of the H-product from  $C + C_2H_2/C_2H_4$ . *Perpendicular* configuration at 0.8 kJ mol<sup>-1</sup> (a) and at 4.8 kJ mol<sup>-1</sup> (b). Experimental (o); fitting functions: H + C<sub>3</sub>H<sub>3</sub> contribution (dashed line), H + C<sub>3</sub>H contribution (short-dashed line), total (solid line); beam conditions  $(v_C/m \text{ s}^{-1}, v_{C2H2}/m \text{ s}^{-1}, \chi/^{\circ})$ : 0.8 kJ mol<sup>-1</sup> (1000, 1132, 22.5); 4.8 kJ mol<sup>-1</sup> (1000, 1132, 60). Intensities are given in arbitrary units (a.u.).

energy range sampled in this study. This increase in the density of states in favor of channel (1c) may compensate the decrease of the complex lifetime in the low-energy regime.

From these microcanonical branching ratios *R*1 and *R*2 determined in the present work, it is possible to derive their thermal counterparts by integration over a Boltzmann distribution of collision energies: this is described in the Appendix, along with an analysis of uncertainties.

#### 6. ASTROPHYSICAL IMPLICATIONS

In conclusion, our results, combined with earlier kinetic data (Chastaing et al. 2001), allow us to recommend the following detailed low-temperature branching ratios fitted in the temperature range of 15–300 K for inclusion in current astrochemical databases (Smith et al. 2004; Woodall et al. 2007):  $\frac{k_{\rm 1b}}{k_{\rm 1}}(T) = \{0.020 \pm 0.006\} \{\frac{T}{298}\}^{1.20\pm0.09}, \frac{k_{\rm 1c}}{k_{\rm 1}}(T) = \{0.87 \pm 0.02\} \{\frac{T}{298}\}^{0.035\pm0.015}, \text{ and } k_{\rm 1a}/k_{\rm 1} = 1 - k_{\rm 1b}/k_{\rm 1} - k_{\rm 1c}/k_{\rm 1}, \text{ instead of the temperature independent values currently used <math>(k_{\rm 1a} + k_{\rm 1b})/k_{\rm 1}$  and  $k_{\rm 1c}/k_{\rm 1} = 0.5$ . The c/l ratios given by the title reaction are ca. [250–550] at T = 15 K and ca. [19–35] at T = 100 K. Turner et al. (2000) have observed c-C<sub>3</sub>H and l-C<sub>3</sub>H in dense cloud TMC-1 with c/l abundance ratio of ca. 5 whereas

Fossé et al. 2001 have reported c/l ratios between 5 and 13 at different positions in same astronomical object. Clearly, consideration of the  $C({}^{3}P_{J}) + C_{2}H_{2}$  reaction alone cannot explain the observations. Sequences of processes including charged species which are much less abundant in dense clouds than in warmer interstellar environments have to be considered. The importance of the H<sub>2</sub>-elimination channel demonstrates that although undetected for spectroscopic reasons, C<sub>3</sub> is also abundant in dense interstellar clouds. Detection through its well-known electronic transition at 405.2 nm was indeed possible at diffuse clouds (Maier et al. 2001), where photons of neighboring stars can penetrate.

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#### APPENDIX

# DETERMINATION OF INTEGRAL CROSS SECTIONS AND BRANCHING RATIOS

A Doppler–Fizeau spectrum can be related to the differential cross sections through a forward convolution-based model detailed elsewhere (Naulin et al. 2009). Briefly, the signal intensity can be expressed as  $I(\lambda) = C\sigma_R v_r F(\lambda)$ , where *C* is a constant for a given set of experiments performed under same conditions (beam densities and velocities, transition probed and detection transfer function);  $\sigma_R$  stands for the integral cross section, and  $v_r$  represents the relative velocity of the reagents. The term  $F(\lambda)$  is computed from the angular distribution functions of the recoiling product, which gives the differential cross section when a good fit is obtained. In particular, when the spectrum consists of several contributions, the total intensity at the maximum is given by  $I(\lambda_{max}) = \sum_k I_k(\lambda_{max}) = C \sum_k v_r \sigma_R^k F_{max}^k$ , where the

terms  $F_{\max}^k$  are the calculated intensities at the maximum for each contribution. The integral cross sections for each path can be expressed as  $\sigma_R^k = I_k(\lambda_{\max})/\{Cv_r F_{\max}^k\}$  and hence determined from the intensity contributions  $I_k(\lambda_{\max})$  introduced to fit the experimental spectrum and the terms  $F_{\max}^k$  calculated for each path.

This allowed the following branching ratios to be evaluated at all collision energies sampled: (1)  $R1 = \sigma(1b)/\sigma(1a+1b)$ , from the H-atom DF spectra for the reactions (1a) and (1b); (2)  $\sigma(1a+1b)/\sigma(2a)$  from the DF spectra of H-atoms from the reactions C + {C<sub>2</sub>H<sub>2</sub> / C<sub>2</sub>H<sub>4</sub>} (1a+1b and 2a); and (3) from the latter ratio,  $R2 = \sigma(1c)/\sigma(1)$ , with the assumption that  $\sigma(1) \approx$  $\sigma(2)$  (see Section 4).

The excitation functions  $\sigma(1a+1b) = \sigma_{(1a+b)}^{\circ}(E_T/E_0)^{-0.80\pm0.03}$ and  $\sigma(2a) = \sigma_{(2a)}^{\circ}(E_T/E_0)^{-0.60\pm0.03}$  have been previously determined (Cartechini et al. 2002; Geppert et al. 2003); here,  $E_0$ is a reference energy chosen as the thermal mean translational energy (3/2 k<sub>B</sub>T<sub>0</sub>) at  $T_0 = 298$  K. It is thus possible to deduce the temperature dependence of the rate coefficient since

$$k(T) = \int_0^\infty \sigma(v) v P(v) dv, \qquad (A1)$$

where P(v) is the Maxwell–Boltzmann distribution of the reactant relative velocity. For an excitation function of the form  $\sigma = \sigma^{\circ}(E_{\rm T}/E_0)^{-\alpha}$ , integration yields

$$k(T) = A \left\{ T/298 \right\}^{1/2-\alpha}$$
(A2)

Cross Sections	$\sigma_{(i)}^{o} (10^{-16} \text{ cm}^2) \text{ or } \sigma_{(i)}^{o} / \sigma_{(i)}^{o}$	$\alpha_{(i)}$ or $\alpha_{(i)} - \alpha_{(j)}$	Notes
$\sigma(1a+1b)$	$3.55 \pm 0.60$	$0.80 \pm 0.03$	а
σ(1c)	$26.8 \pm 0.6$	$0.59 \pm 0.04$	b, c
$\sigma(1) = \sigma(1a+1b) + \sigma(1c)$	$30.4 \pm 0.4$	$0.62 \pm 0.04$	с
$R1 = \sigma(1b) / \sigma(1a+1b)$	$0.19 \pm 0.05$	$-1.35 \pm 0.14$	d
$R2 = \sigma(1c) / \sigma(1)$	$0.88 \pm 0.02$	$-0.03 \pm 0.01$	e

### Notes.

Integral cross sections are in the form of  $\sigma(i) = \sigma_{(i)}^{0} (E_{T}/E_{0})^{-\alpha_{(i)}}$ . (a) Exponent from excitation function (Cartechini et al. 2002); (b) from analysis of C + {C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>} results (present work); (c) by comparison of rate coefficients for both reactions: this is consistent with the exponent value,  $\alpha_{(2)} = 0.60 \pm 0.03$ , derived from the excitation function of the C + C<sub>2</sub>H<sub>4</sub>  $\rightarrow$  C<sub>3</sub>H<sub>3</sub> + H reaction (Geppert et al. 2003); (d) from the fit of the branching ratio,  $R1 = f(E_T/E_0)$ , with values determined at the 8 energies sampled in the present work (see Figures 2–4); (e) from the tabulated integral cross sections.

Table A2 Kinetic Branching Ratios

Ratios	$A_i/A_j$	$n_{(i)} - n_{(j)}$	Notes
<i>k</i> (1b)/ <i>k</i> (1a+1b)	$0.17 \pm 0.04$	$1.38 \pm 0.06$	а
<i>k</i> (1b)/ <i>k</i> (1)	$0.020\pm0.006$	$1.20 \pm 0.08$	a, b
k(1c)/k(1)	$0.87~\pm~0.03$	$0.034 \pm 0.011$	

#### Notes.

Rate coefficients are given as  $k(i) = A_{(i)}(T/298)^{n(i)}$  and are computed by integration of Equation (A1); (a) calculated with  $\sigma(1b) = \sigma(1a+1b) \times R1$ ; (b) derived from the fit of the ratio k(1a+1b)/k(1).

with  $A = \sigma^{\circ} \langle v_r \rangle_{T_0} \{3/2\}^{\alpha} \Gamma(2 - \alpha); \langle v_r \rangle_{T_0} = \{\frac{8RT_0}{\pi\mu}\}^{1/2}$  is the mean value of the modulus of the relative velocity at  $T_0 = 298$  K,  $\mu$  is the molar reduced mass of the reagents, and  $\Gamma$  is the Gamma function. A comparison with kinetic data allowed us to estimate the absolute integral cross sections given in Table A1 from this integration.

The kinetic branching ratios can be evaluated thus:

$$\frac{k_{1c}}{k_1}(T) = \frac{A_{1c}}{A_1} \left\{ \frac{T}{298} \right\}^{\alpha_1 - \alpha_{1c}} \\ = \frac{\sigma_{1c}^0}{\sigma_1^0} \frac{\Gamma(2 - \alpha_{1c})}{\Gamma(2 - \alpha_1)} \left\{ \frac{2}{3} \times \frac{T}{298} \right\}^{\alpha_1 - \alpha_1}$$

and

$$\begin{aligned} \frac{k_{1b}}{k_{(1a+b)}}(T) &= \frac{A_{1b}}{A_{(1a+b)}} \left\{ \frac{T}{298} \right\}^{\alpha_{1a+b}-\alpha_{1b}} \\ &= \frac{\sigma_{1b}^{o}}{\sigma_{(1a+b)}^{o}} \frac{\Gamma(2-\alpha_{1b})}{\Gamma(2-\alpha_{(1a+b)})} \left\{ \frac{2}{3} \times \frac{T}{298} \right\}^{\alpha_{1a+b}-\alpha_{1b}}. \end{aligned}$$

The uncertainties in determination of these branching ratios have been estimated as follows.

- 1. From the differential cross sections for reaction (1a+1b): extreme values of R1 and  $F_{max}^k$  terms were calculated with distribution functions allowing for a reasonable fit of the DF spectra at all energies.
- 2. From the C +  $\{C_2H_2+C_2H_4\}$  reaction: a similar procedure as described in (1) was used, yielding the extreme values of *R*2 compatible with a reasonable fit of DF spectra.

The results are reported in Tables A1 (cross sections) and A2 (thermal branching ratios).

#### REFERENCES

- Aoki, K., Ikuta, S., & Murakami, A. 1996, J. Mol. Struct. (TheoChem), 365, 103
- Bak, K. L., Gauss, J., Jørgensen, P., Olsen, J., Helgaker, T., & Stanton, J. F. 2001, J. Chem. Phys., 114, 6548
- Bak, K. L., Jørgensen, P., Olsen, J., Helgaker, T., & Klopper, W. 2000, J. Chem. Phys., 112, 9229
- Bergeat, A., & Loison, J.-C. 2001, Phys. Chem. Chem. Phys., 3, 2038
- Buonomo, E., & Clary, D. C. 2001, J. Phys. Chem. A, 105, 2694
- Cartechini, L., Bergeat, A., Capozza, G., Casavecchia, P., Volpi, G. G., Geppert, W. D., Naulin, C., & Costes, M. 2002, J. Chem. Phys., 116, 5603
- Chastaing, D., Le Picard, S. D., Sims, I. R., & Smith, I. W. M. 2001, A&A, 365, 241
- Che, D.-C., & Liu, K. 1996, Chem. Phys., 207, 367
- Clary, D. C., Haider, N., Husain, D., & Kabir, M. 1994, ApJ, 422, 416
- Clary, D. C., et al. 2002, J. Phys. Chem. A, 106, 5541
- Costes, M., Daugey, N., Naulin, C., Bergeat, A., Leonori, F., Segoloni, E., Petrucci, R., Balucani, N., & Casavecchia, P. 2006, Faraday Discuss., 133, 157
- Ding, H., Pino, T., Güthe, F., & Maier, J. P. 2001, J. Chem. Phys., 115, 6913
- Dyer, F. P., Snelling, H. V., & Walton, C. D. 2002, Meas. Sci. Technol., 13, 92 Dunning, T. H. 1989, J. Chem. Phys., 90, 1007
- Feller, D. 1992, J. Chem. Phys., 96, 6104
- Fossé, D., Cernicharo, J., Gerin, M., & Cox, P. 2001, ApJ, 552, 168
- Frisch, M. J., et al. 2004, Gaussian 03, Revision D.02 (Wallingford, CT: Gaussian, Inc.)
- Geppert, W. D., Naulin, C., Costes, M., Capozza, G., Cartechini, L., Casavecchia, P., & Volpi, G. G. 2003, J. Chem. Phys., 119, 10607
- Gottlieb, C. A., Gottlieb, E. W., Thaddeus, P., & Vrtilek, J. M. 1986, ApJ, 303, 446
- Gu, X., Guo, Y., Zhang, F., & Kaiser, R. I. 2007, J. Phys. Chem. A, 111, 2980
- Guadagnini, R., Schatz, G. C., & Walch, S. P. 1998, J. Phys. Chem. A, 102, 5857
- Halvick, Ph 2007, Chem. Phys., 340, 79
- Heckert, M., Kállay, M., & Gauss, J. 2005, Mol. Phys., 103, 2109
- Helgaker, T., Klopper, W., Koch, H., & Noga, J. 1997, J. Chem. Phys., 106, 9639
- Herbst, E. 1995a, ApJ, 444, 694
- Herbst, E. 1995b, Annu. Rev. Phys. Chem., 46, 27
- Jacox, M. E. 2003, J. Phys. Chem. Ref. Data, 32
- Kaiser, R. I., Lee, Y. T., & Suits, A. G. 1996, J. Chem. Phys., 105, 8705
- Kaiser, R. I., Ochsenfeld, C., Head-Gordon, M., Lee, Y. T., & Suits, A. G. 1997, J. Chem. Phys., 106, 1729
- Kanada, M., Yamamoto, S., Saito, S., & Osamura, Y. 1996, J. Chem. Phys., 104, 2192
- Lee, T. J., & Taylor, P. R. 1989, Int. J. Quantum Chem., 23, 199
- Leonori, F., Petrucci, R., Segoloni, E., Bergeat, A., Hickson, K. M., Balucani, N., & Casavecchia, P. 2008, J. Phys. Chem. A, 112, 1363
- Maier, J. P., Lakin, N. M., Walker, G. A. H., & Bohlender, D. A. 2001, ApJ, 553, 267

Mebel, A. M., Kislov, V. V., & Hayashi, M. 2007, J. Chem. Phys., 126, 204310-1 Naulin, C., & Costes, M. 1999, Chem. Phys. Lett., 310, 231

- Naulin, C., Daugey, N., Hickson, K. M., & Costes, M. 2009, J. Phys. Chem. A, doi:10.1021/jp9038545
- Ochsenfeld, C., Kaiser, R. I., Lee, Y. T., Suits, A. G., & Head-Gordon, M. A. 1997, J. Chem. Phys., 106, 4141

- Park, W. K., Park, J., Park, S. C., Braams, B. J., Chen, C., & Bowman, J. M. 2006, J. Chem. Phys., 125, 081101-1
- Perić, M., Mladenović, M., Tomić, K., & Marian, C. J. 2003, J. Chem. Phys., 118, 4444
- Shimanouchi, T. 1972, Tables of Molecular Vibrational Frequencies Consolidated Vol. I (Washington, DC: National Bureau of Standards)
- Smith, I. W. M., Herbst, E., & Chang, Q. 2004, MNRAS, 350, 323
- Stanton, J. F. 1995, Chem. Phys. Lett., 237, 20 Takahashi, J., & Yamashita, K. 1996, J. Chem. Phys., 104, 6613
- Takayanagi, T. 2005, Chem. Phys., 312, 61

- Takayanagi, T. 2006, J. Phys. Chem. A, 110, 361
- Turner, B. E., Herbst, E., & Terzevia, R. 2000, ApJS, 126, 427
- Werner, H. J., & Knowles, P. J. 2003, MOLPRO (ver. 2002.6; Birmingham: Univ. Birmingham)
- Wiley, W. C., & McLaren, I. H. 1955, Rev. Sci. Instr., 26, 1150
- Woodall, J., Agúndez, M., Markwick-Kemper, A. J., & Millar, T. J. 2007, A&A, 466, 1197
- Yamamoto, S., Saito, S., Suzuki, H., Deguchi, S., Kaifu, N., Ishikawa, S.-I., & Ohishi, M. 1990, ApJ, 348, 363
- Yamamoto, S., & Saito, S. 1994, J. Chem. Phys., 101, 5484