Crossed beams study of the reaction $^1CH_2+C_2H_2\rightarrow C_3H_3+H$

H. Floyd Davis
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301

Jinian Shu, Darcy S. Peterka, and Musahid Ahmed
Chemical Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, California 94720

The reaction of electronically excited singlet methylene ($^1CH_2$) with acetylene (C_2H_2) was studied using the method of crossed molecular beams at a mean collision energy of 3.0 kcal/mol. The angular and velocity distributions of the propargyl radical (C_3H_3) products were measured using single photon ionization (9.6 eV) at the advanced light source. The measured distributions indicate that the mechanism involves formation of a long-lived C_3H_4 complex followed by simple C-H bond fission producing C_3H_3+H. This work, which is the first crossed beams study of a reaction involving an electronically excited polyatomic molecule, demonstrates the feasibility of crossed molecular beam studies of reactions involving $^1CH_2$. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1785152]

I. INTRODUCTION

Methylene is the simplest building block of hydrocarbon molecules. The singlet electronically excited state ($^1CH_2$) lies just 9.0 kcal/mol above the triplet ground state,[1] and is readily quenched by collisions with inert gases.[2,3] Like $O(^1D)$, $^1CH_2$ has a very long radiative lifetime and can insert into the covalent bonds of stable small molecules[4] or can add across double or triple bonds of unsaturated species.[2,5,6] In the absence of stabilization by collisions in the gas phase, the activated reaction intermediates will undergo unimolecular decomposition.[7] The ground triplet state of methylene ($^3CH_2$), on the other hand, is only reactive with open-shell species like O_2 and NO.[8] Both electronic states of methylene are known to be formed in combustion, and $^1CH_2$ has been directly detected in methane/oxygen[9] and methane/oxygen/nitrogen flames.[10] While there have been a number of kinetic studies of reactions involving both singlet[11–13] and triplet methylene,[14–16] to date there have been no studies in which the product angular and velocity distributions have been measured.

Reactions of a number of atomic and diatomic radicals have been studied in crossed molecular beams.[17,18] It is notable, however, that few studies of reactions involving open-shell species more complex than diatomics have been carried out. A review paper[19] summarizing such work reveals that reactions of only two polyatomic radicals, NH_2[20] and CH_3,[21] have been studied under crossed beam conditions. The lack of information on polyatomic radical reaction dynamics largely results from difficulties associated with production of such species at densities sufficiently high to permit studies of their chemical reactivity.

In an effort to overcome limitations in the sensitivity of mass spectrometric detection of polyatomic products from crossed beam reactions, several technical advances have been introduced. One approach involves the use of synchrotron radiation for single photon nonresonant ionization of products at energies just above threshold.[22] One advantage of this approach is that by tuning the photon energy of the ionization light source just above threshold, it is possible to minimize dissociative ionization, so a larger fraction of the species of interest can be detected at the parent mass to charge ratio. As a side benefit, it is possible to avoid contributions from dissociative ionization processes involving precursor molecules used for production of radical reactants that may contribute to the background signal at the mass to charge ratio of interest.

The only molecular beam source of singlet methylene was reported in a spectroscopic study by Smalley and co-workers.[23] Although it was clear that $^1CH_2$ beams could be prepared at intensities sufficient for spectroscopic studies, whether or not a beam of intensity sufficient for bimolecular reactions could be produced remained an open question. Here, we report the experimental study of the reaction of singlet methylene in crossed beams. As far as we know, this is the *first* report of the reaction of an electronically excited polyatomic molecule under single collision conditions.

II. EXPERIMENT

The $^1CH_2$ source employed photolysis of ketene (CH_2CO) at 308 nm at the orifice of a supersonic nozzle. At this wavelength, most of the singlet methylene is produced in its vibrational ground state, with about 20% produced with one quantum of bending excitation.[24,25] The ketene was synthesized by pyrolysis of acetic anhydride and trapped at 77 K.[26] The ketene beam was produced by bubbling helium through a liquid sample of CH_2CO held at $-30\,°C$, producing a 5% beam. In all experiments, a piezoelectrically actuated pulsed valve with a 1 mm diameter orifice was employed.

The initial development of the source was carried out at Cornell using laser induced fluorescence (LIF) to monitor the $^1CH_2$ beam directly. Figure 1 shows $CH_2\,(b\,^1B_1\leftarrow a\,^1A_1)$ fluorescence excitation spectra[11,27] recorded under two different conditions. Although this apparatus was not optimized
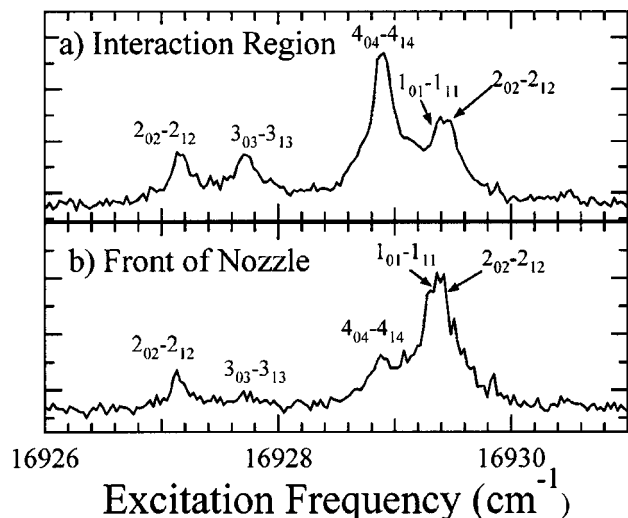
6254

FIG. 1. Singlet methylene fluorescence excitation spectra: (a) copropagating pump and probe lasers at interaction region; (b) same but photolysis laser realigned to be 3 mm from nozzle.

for LIF studies, it provided sufficient detection sensitivity for the purpose of evaluating the $^1CH_2$ beam. In the upper portion of Fig. 1, the skimmed ketene beam was photolyzed at 320 nm using the frequency doubled radiation from a tunable dye laser, and the $^1CH_2$ was probed by LIF near 590 nm, using a copropagating laser beam triggered ≈ 50 ns following the photolysis laser. This spectrum thus corresponds to the nascent collision-free CH_2 produced from CH_2CO photodissociation at 320 nm. The lower spectrum was recorded under similar conditions, except the 320 nm photolysis laser was relocated to be ≈ 3 mm in front of the orifice of the pulsed valve. Following dissociation of CH_2CO in the collisional region of the expansion, the CH_2 radicals passed through the skimmer and were probed by LIF, as before. As evidenced by the spectra, rotational excitation has been relaxed considerably due to collisions with He carrier gas in the supersonic expansion. The signal intensity remained comparable to that for "collision free" CH_2, indicating that only a modest fraction of the $^1CH_2$ was consumed by collisional quenching or bimolecular reaction in dilute beams seeded in He.

It was found that the $^1CH_2$ intensity decreased sharply if the distance between the nozzle and photolysis laser was decreased to be less than 3 mm. This behavior results from collisional quenching of $^1CH_2$ to $^3CH_2$ in the supersonic expansion, which becomes more complete if photolysis is carried out in higher density regions closer to the orifice. Since rotational cooling of $^1CH_2$ is nearly an order of magnitude more efficient than quenching,[11] it is possible to prepare an intense $^1CH_2$ beam with some rotational cooling through careful control of the location of the laser position relative to the nozzle.

At the advanced light source (ALS), the CH_2 beam was produced by photodissociation of CH_2CO at 308 nm, using a Lambda-Physik LPX 210i excimer laser. The laser produced ≈ 300 mJ/pulse, and was operated at 100 Hz. Since LIF experiments were not possible using this apparatus, we instead reoptimized the source conditions by monitoring the reactive

signal from reaction of $^1CH_2$ with H_2, which is known to proceed with no potential energy barrier:[28]

$$^1CH_2 + H_2 \rightarrow CH_4 \rightarrow CH_3 + H. \tag{1}$$

The raw undulator radiation near 10.5 eV was used to ionize the CH_3 products (IP=9.84 eV) in the UHV detector of the apparatus. It should be noted that $^3CH_2$, which is also inevitably present in the beam due to collision induced quenching, is not reactive with H_2[29] or C_2H_2 (Ref. 30) under our experimental conditions. Therefore, the CH_3 signal intensity from reaction (1) was a direct measure of the $^1CH_2$ beam intensity. In the experiments at the ALS, the 308 nm excimer laser was aligned along the axis of rotation of the source assembly, focused gently using a 50 cm focal length lens, and then periscoped into the source chamber using a pair of quartz prisms. Because the excimer beam was aligned to be exactly coaxial with the axis of source rotation, the laser remained aligned with respect to the nozzle as the source assembly was rotated to different angles.

It was found that the source conditions yielding the maximum CH_3 signal from reaction (1) were essentially identical to those used in the LIF experiments. The H_2 beam was then replaced with a beam of neat C_2H_2, in order to study reaction (2):

$$^1CH_2 + C_2H_2 \rightarrow C_3H_3 + H. \tag{2}$$

From the measured beam velocity distributions, the mean collision energy employed in our study of reaction (2) was 3.0 kcal/mol. The C_3H_3 products from bimolecular reactions were ionized using a photon energy of 9.6 eV, somewhat above the IP of the propargyl radical, measured to be 8.67 ± 0.02 eV.[31] For these experiments, a MgF_2 window was placed into the VUV beam to remove shorter wavelength radiation passing through a Ne gas filter employed to suppress higher order harmonics. It was found that without this MgF_2 window, dissociative ionization of ketene led to substantial background signal at $m/e = 39$, likely due to mass spillover from CCO^+, nominally observed at $m/e = 40$.

III. RESULTS

Time-of-flight spectra were recorded at various laboratory angles at $m/e = 39$, $C_3H_3^+$. The time-of-flight spectra of the propargyl radical products, C_3H_3, from the reaction with acetylene, are shown in Fig. 2. Each time-of-flight (TOF) spectrum corresponds to $\approx 120\,000$ laser shots, involving 20 min of data acquisition. These spectra were integrated to obtain the laboratory angular distribution shown as solid points in the upper portion of Fig. 3. At laboratory angles smaller than or equal to 28°, some time dependent background signal was present, and this was subtracted from the TOF spectra using data recorded with the excimer laser turned off. The solid-line fits to the laboratory time of flight and angular distributions were simulations of the experimental data, calculated using a computer program that takes as input trial CM translational energy, $P(E)$, and angular $T(\theta)$ distributions, as well as the measured beam velocity distributions and known apparatus functions. The two input functions were iteratively adjusted until satisfactory agreement
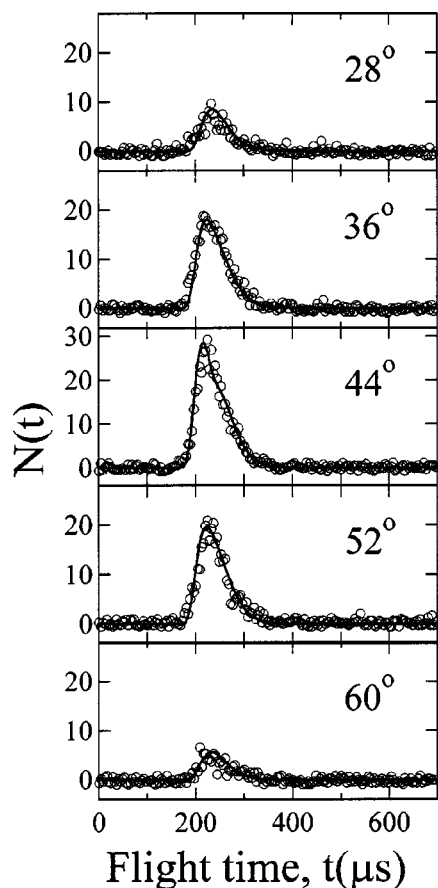
FIG. 2. TOF distributions at indicated laboratory angles for C_3H_3 products from $^1CH_2 + C_2H_2 \rightarrow C_3H_3 + H$ reaction. Open circles are experimental data and solid line are theoretical fits based on $P(E)$ and $T(\theta)$ shown in Fig. 3.
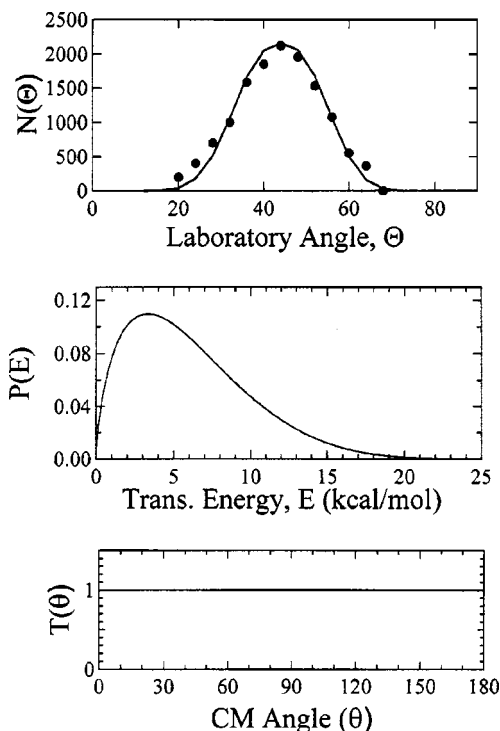

FIG. 3. Laboratory angular distribution, and CM distributions, $P(E)$ and $T(\theta)$, for $^1CH_2 + C_2H_2 \rightarrow C_3H_3 + H$ reaction at $E_{coll} = 3.0$ kcal/mol.

between the experimental data and theoretical simulations were obtained. The optimized $P(E)$ and $T(\theta)$ are shown in Fig. 3.

IV. DISCUSSION

The reaction of singlet methylene with acetylene is initiated either by addition across the triple-bond forming cyclopropene (c-C_3H_4), or by C-H insertion forming propyne (Fig. 4).[32–34] The potential energy barrier to isomerization between cyclopropene and propyne is small relative to the available energy. In the absence of collisions, both isomeric forms, as well as allene, are likely to be accessed by the initially-formed highly vibrationally excited C_3H_4 adduct. Fission of a C-H bond in the propyne isomer leads to formation of propargyl radicals, CH_2CCH, the most thermodynamically stable isomer of C_3H_3.[33,34] The enthalpy of formation of the propynyl radical CH_3CC is 39.9 kcal/mol higher than propargyl,[35] and is energetically closed at this collision energy. Reaction (2) is thought to be the dominant source of propargyl radicals in combustion environments.[36,37] These radicals are believed to be important in soot formation,[38] as they may subsequently dimerize to form benzene,[32–39] or undergo further reaction, leading to production of other aromatic molecules.[40]

In studies of the reaction of singlet methylene with acetylene in a static gas cell by Adamson and co-workers, the formation of propargyl radicals was monitored directly by IR absorption spectroscopy.[5] In that work, $^1CH_2$ was produced by photolysis of ketene at 308 nm, as in our experiment. The rate constant for formation of propargyl radicals was measured to be $(3.5 \pm 0.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, indicating that reaction occurs on nearly every collision, which is typical of reactions involving $^1CH_2$. Blitz and co-workers have studied the dependence of the reaction rate constant on temperature, and have used a master equation model employing a three-well mechanism to model the temperature and pressure dependence of the branching ratios for formation of propargyl radicals and collisionally-stabilized reaction intermediates.[6] These studies, as well as more detailed theoretical modeling by Frankcombe and Smith,[34] predict that under collision-free conditions, the C_3H_4 intermediates decay primarily to $C_3H_3 + H$, with negligible decay back to reactants. Since the rate for this decay process is of the order of 10^6 s^{-1}, the energized C_3H_4 intermediates decay on a time scale of a few microseconds or less. Although this lifetime for the C_3H_4 intermediates is extremely long, due to the geometry of the apparatus essentially all $C_3H_3 + H$ products are formed within the viewing range of the detector, and a negligible error in the measured $P(E)$ and $T(\theta)$ should arise due to bulk transport of the reaction intermediates out of the detector viewing region prior to their decay.

From the thermodynamics shown in Fig. 4, the reaction is exothermic by 18 kcal/mol. At a collision energy of 3 kcal/mol, the total energy available to be partitioned into C_3H_3 rovibrational excitation and $C_3H_3 + H$ relative product translational energy is 21 kcal/mol. The $P(E)$ shown in Fig. 3 is broad and structureless, with the most probable translational energy release near 3 kcal/mol, extending to the maxi-
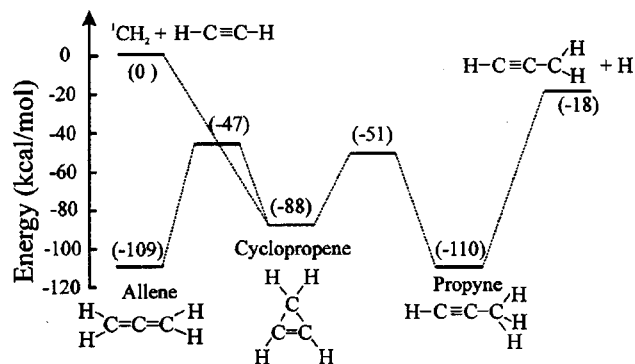
FIG. 4. Energetics of ^{1}CH$_2$ + C$_2$H$_2$ reaction, taken from Ref. 34.

mum available energy. This distribution is quite typical for the unimolecular decomposition of a polyatomic species forming two radicals by simple bond fission with negligible reverse potential energy barrier.

The center of mass angular distribution, $T(\theta)$, is isotropic (Fig. 3). For a reaction involving formation of long-lived complexes with lifetimes exceeding several rotational periods, a forward-backward symmetric angular distribution (symmetric about $\theta=90°$) is anticipated.[41,42] In the present case, the microsecond lifetimes of the C$_3$H$_4$ intermediates facilitate $\sim 10^6$ rotations before unimolecular decomposition or decay back to reactants. Decay of a long-lived prolate collision complex leads to a $T(\theta)$ with maximum product intensities at 0° and 180°.[41,42] However, for reactions leading to elimination of a very light atom such as H, conservation of total angular momentum often dictates that the initial and final orbital angular momenta during the reactive encounter are only weakly coupled.[41–43] This leads to a totally isotropic CM angular distribution, as observed in this study and discussed recently in detail elsewhere.[43]

V. CONCLUSIONS

We have developed a photolytic source of ^{1}CH$_2$ providing intensities sufficient for studies of chemical reactions in crossed molecular beams, and the reaction with acetylene leading to formation of propargyl radical was studied. The reaction involved formation of long-lived C$_3$H$_4$ complexes which subsequently decayed via simple bond fission forming propargyl+H. The signal to noise ratios obtained in this experiment are comparable to those observed previously in photodissociation experiments using this apparatus, demonstrating the feasibility of future studies of reactions involving ^{1}CH$_2$ in crossed molecular beams.

[1] P. Jensen and P. R. Bunker, J. Chem. Phys. **89**, 1327 (1988).
[2] A. H. Laufer, Rev. Chem. Intermed. **4**, 225 (1981).
[3] U. Bley and F. Temps, J. Chem. Phys. **98**, 1058 (1993).
[4] M. A. Blitz, M. J. Pilling, and P. W. Seakins, Phys. Chem. Chem. Phys. **3**, 2241 (2001).
[5] J. D. Adamson, C. L. Morter, J. D. DeSain, G. P. Glass, and R. F. Curl, J. Phys. Chem. **100**, 2125 (1996).
[6] M. A. Blitz, M. S. Beasley, M. J. Pilling, and S. H. Robertson, Phys. Chem. Chem. Phys. **2**, 805 (2000).
[7] I. Oref and B. S. Rabinovitch, Acc. Chem. Res. **12**, 166 (1979).
[8] D. C. Darwin, A. T. Young, H. S. Johnston, and C. B. Moore, J. Phys. Chem. **93**, 1074 (1989).
[9] A. McIlroy, Chem. Phys. Lett. **296**, 151 (1998).
[10] S. Cheskis, I. Derzy, V. A. Lozovsky, A. Kachanov, and F. Stoeckel, Chem. Phys. Lett. **277**, 423 (1997).
[11] A. O. Langford, H. Petek, and C. B. Moore, J. Chem. Phys. **78**, 6650 (1983).
[12] W. Hack, M. Koch, H. G. Wagner, and A. Wilms, Ber. Bunsenges. Phys. Chem. **92**, 674 (1988).
[13] G. Hancock and M. R. Heal, J. Phys. Chem. **96**, 10316 (1992); P. Biggs, G. Hancock, M. R. Heal, D. J. McGarvey, and A. D. Parr, Chem. Phys. Lett. **180**, 533 (1991); M. N. R. Ashfold, M. A. Fullstone, G. Hancock, and G. W. Ketley, Chem. Phys. **55**, 245 (1981).
[14] U. Bley, F. Temps, H. G. Wagner, and M. Wolf, Ber. Bunsenges. Phys. Chem. **96**, 1043 (1992).
[15] V. Seidler, F. Temps, H. F. Wagner, and M. Wolf, J. Phys. Chem. **93**, 1070 (1989).
[16] S. Bauerle, M. Klatt, and H. G. Wagner, Ber. Bunsenges. Phys. Chem. **99**, 97 (1995).
[17] K. Liu, Annu. Rev. Phys. Chem. **52**, 139 (2001).
[18] P. Casavecchia, Rep. Prog. Phys. **63**, 355 (2000).
[19] J. C. Whitehead, Rep. Prog. Phys. **59**, 993 (1996).
[20] D. Patel-Misra and P. J. Dagdigian, Chem. Phys. Lett. **185**, 387 (1991); D. Patel-Misra, D. G. Sauder, and P. J. Dagdigian, J. Chem. Phys. **95**, 955 (1991).
[21] S. M. A. Hoffmann, D. J. Smith, N. Bradshaw, and R. Grice, Mol. Phys. **57**, 1219 (1986); G. N. Robinson, G. M. Nathanson, R. E. Continetti, and Y. T. Lee, J. Chem. Phys. **89**, 6744 (1988).
[22] X. Yang, J. Lin, Y. T. Lee, D. A. Blank, A. G. Suits, and A. Wodtke, Rev. Sci. Instrum. **68**, 3317 (1997); D. A. Blank, M. Hemmi, A. G. Suits, and Y. T. Lee, Chem. Phys. **231**, 261 (1998).
[23] D. L. Monts, T. G. Dietz, M. A. Duncan, and R. E. Smalley, Chem. Phys. **45**, 133 (1980).
[24] I. Garcia-Moreno, E. R. Lovejoy, and C. B. Moore, J. Chem. Phys. **100**, 8902 (1994).
[25] C. G. Morgan, M. Drabbles, and A. M. Wodtke, J. Chem. Phys. **104**, 7460 (1996).
[26] J. Vogt, A. D. Williamson, and J. L. Beauchamp, J. Am. Chem. Soc. **100**, 3478 (1978); S. Andreades and H. D. Carlson, Org. Synth. **45**, 50 (1965).
[27] H. Petek, D. J. Nesbitt, D. C. Darwin, and C. B. Moore, J. Chem. Phys. **86**, 1172 (1987).
[28] M. Sironi, D. L. Cooper, J. Gerratt, and M. Raimondi, J. Am. Chem. Soc. **112**, 5054 (1990); R. D. Bach, M.-D. Su, E. Aldabbagh, J. L. Andres, and H. B. Schlegel, *ibid.* **115**, 10237 (1993); B. S. Jursic, J. Mol. Struct.: THEOCHEM **467**, 103 (1999).
[29] C. P. Baskin, C. F. Bender, C. W. Bauschlicher, Jr., and H. F. Schaefer III, J. Am. Chem. Soc. **96**, 2709 (1974).
[30] D. C. Darwin, A. T. Young, H. S. Johnston, and C. B. Moore, J. Phys. Chem. **93**, 1074 (1989).
[31] D. W. Minsek and P. Chem, J. Phys. Chem. **94**, 8399 (1990).
[32] S. P. Walch, J. Chem. Phys. **103**, 7064 (1995).
[33] R. Guadagnini, G. Schatz, and S. P. Walch, J. Phys. Chem. A **102**, 5857 (1998).
[34] J. Frankcombe and S. C. Smith, Faraday Discuss. **119**, 159 (2001).
[35] M. S. Robinson, M. L. Polak, V. M. Bierbaum, C. H. DePuy, and W. C. Lineberger, J. Am. Chem. Soc. **117**, 6766 (1995).
[36] J. A. Miller and S. J. Klippenstein, J. Phys. Chem. A **105**, 7254 (2001).
[37] C. L. Morter, S. K. Farhat, J. D. Adamson, G. P. Glass, and R. F. Curl, J. Phys. Chem. **98**, 7029 (1994).
[38] J. A. Miller, 26th Symposium on Combustion/The Combustion Institute (1996).
[39] J. D. DeSain and C. A. Taatjes, J. Phys. Chem. A **107**, 4843 (2003).
[40] E. V. Shafir, I. R. Slagle, and V. D. Knyazev, J. Phys. Chem. A **107**, 8893 (2003).
[41] W. B. Miller, S. A. Safron, and D. R. Herschbach, J. Chem. Phys. **56**, 3581 (1972).
[42] R. D. Jarvis and R. Grice, Mol. Phys. **66**, 675 (1989).
[43] J. J. Schroden, M. Teo, and H. Floyd Davis, J. Chem. Phys. **117**, 9258 (2002).