

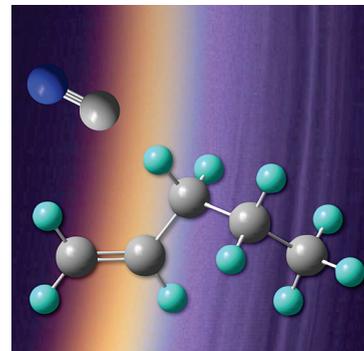
Crossed-Beam Imaging of the H Abstraction Channel in the Reaction of CN with 1-Pentene

Armando D. Estillore,[†] Laura M. Visger,[†] Ralf I. Kaiser,[‡] and Arthur G. Suits*^{·†}

[†]Department of Chemistry, Wayne State University, Detroit, Michigan 48202, and [‡]Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822

ABSTRACT The reaction of the cyano radical with 1-pentene has been studied in crossed molecular beams experiments at a range of collision energies from 5 to 9 kcal/mol. In these studies, the pentenyl radical product is probed using single-photon ionization at 157 nm, and the product flux contour map is obtained directly using DC slice imaging. The results clearly demonstrate the presence of the hydrogen abstraction channel in this reaction, which has largely been neglected in studies of analogous systems. The reaction likely gives rise to the resonantly stabilized C₅H₅ radical. The yield of this channel is estimated by comparison to the reaction of the cyano radical with *n*-pentane. The results have implications for hydrocarbon growth and nitrile incorporation in formation of haze particles on Saturn's moon, Titan.

SECTION Dynamics, Clusters, Excited States



The cyano radical (CN(X²Σ⁺)) is an extremely reactive species that can abstract hydrogen from saturated hydrocarbons without a barrier and add to π bonds of unsaturated hydrocarbons to form strongly bound intermediates also without a barrier. These may then be stabilized by collision or decay through a variety of pathways, predominantly via atomic hydrogen or alkyl radical elimination, forming nitriles. Owing to its ability to react without barriers and its relative abundance in the atmosphere of Titan, the cyano radical plays a key role in the low-temperature chemistry on Titan, including hydrocarbon growth processes and nitrogen incorporation into the haze particles that are a dominant feature of its atmosphere.^{1–3}

Cyano radical reactions with unsaturated hydrocarbons have been examined in a variety of kinetics studies, including some using supersonic flows at temperatures down to 20 K.^{4–6} The reaction rates are found to be extremely fast and show a negative temperature dependence, with rates of $2.5 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported for the reaction of cyano with ethylene at 298 K.⁷ Two recent kinetics studies are particularly noteworthy in that products were detected for reaction with propene. The Seakins group⁸ at Leeds detected H atom elimination following CN addition and determined absolute yields for this channel; then, they compared these to a master equation calculation using a model potential surface. Trevitt et al.⁹ also studied the CN + propene reaction in a flow reactor using tunable synchrotron radiation to obtain isomer-specific detection of products. They detected H and CH₃ elimination and identified distinct product isomers but saw no evidence for formation of the allyl radical when the ionization energy was tuned above the threshold for detection of allyl but below that for ionization of other products. In addition to these kinetic studies, a number of

crossed-beam studies for cyano radical plus unsaturated hydrocarbons have been reported, notably from the Kaiser laboratory.^{10,11} Also, Huang et al.¹² used ab initio theory at the CBS-CCSD(T) level to examine the possible product channels for crossed beam results at a detailed level for this reaction. They found slight barriers to H abstraction but acknowledged that these may disappear at higher levels of theory. Gannon et al.⁸ used an IRC search at the UMP2/6-311+G(d,p) level and concluded there was no barrier. In any case, the traditional crossed-beam approach has little sensitivity to the abstraction reaction, owing to unfavorable kinematics and background at the product masses; therefore, this pathway has often been omitted in the analysis.

We have been using crossed-beam slice imaging^{13–15} with single-photon ionization at 157 nm as a sensitive and direct probe of crossed-beam reactive scattering for a variety of reactions.^{16–18} We earlier reported cyano radical reaction with *n*-alkanes¹⁹ and have recently embarked on systematic studies of chlorine atoms with alkanes²⁰ and alkenes.²¹

In the present study, we investigate the reaction between the cyano radical and 1-pentene at four collision energies from 5 to 9 kcal/mol. The sliced images of the C₅H₅ radical, corrected for the density-to-flux effects,²⁰ are shown in Figure 1 with the most probable Newton diagrams superimposed. As discussed in the Experimental Section, the photochemistry background interferes in the vicinity of the pentene beam, so that portion of the image is suppressed. From these images, we extract the center-of-mass translational energy and angular distributions shown in Figure 2. The translational energy

Received Date: June 24, 2010

Accepted Date: July 22, 2010

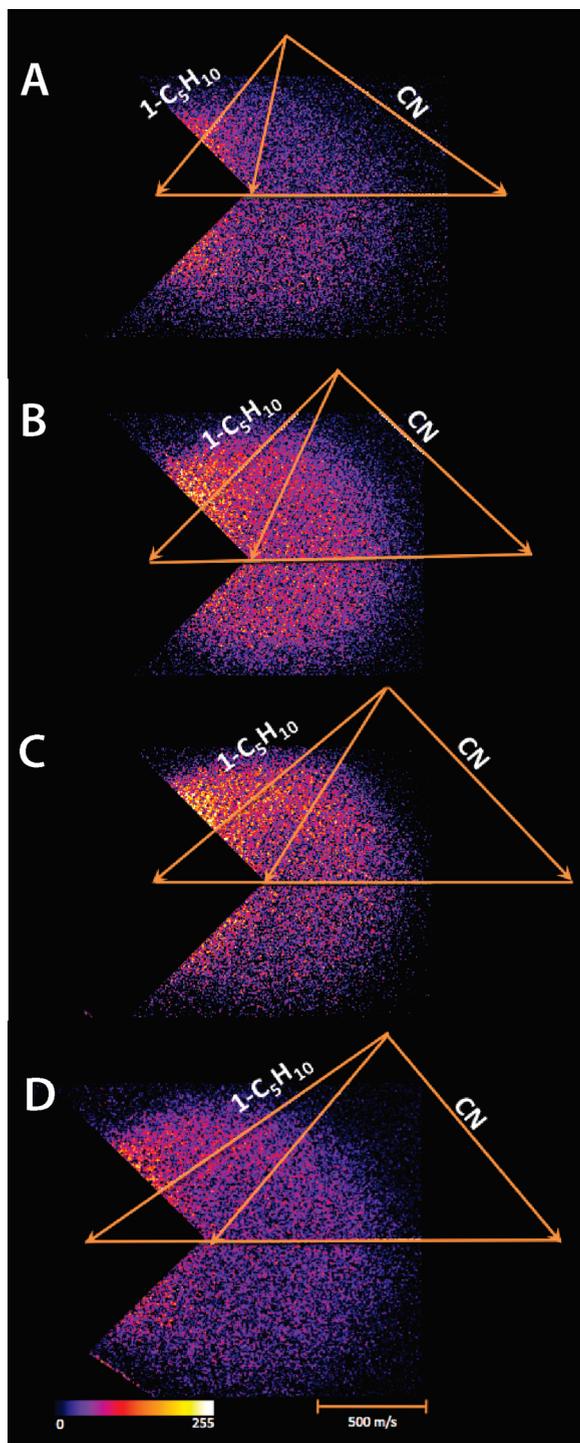


Figure 1. DC sliced images of pentenyl radical product from reactions of $\text{CN}(X^2\Sigma^+)$ with 1-pentene at different collision energies and superimposed Newton diagrams. (A) 5.1, (B) 6.0, (C) 7.3, and (D) 9.2 kcal/mol.

distributions are given separately for the sideways ($60\text{--}120^\circ$) and backwards ($120\text{--}180^\circ$) portions of the scattering distributions. Neglecting the undetected forward-scattered part of the distribution, the angular distributions are isotropic at all

collision energies studied. The translational energy distributions peak near zero, despite very large exoergicity for some of the HCN-forming channels, as shown in Figure 3. This figure gives 0 K reaction enthalpies for H abstraction by CN based on CBS-QB3^{22,23} calculations of the bond dissociation energies given in ref 21. The average translational energy release is given in Figure 2, but the fraction of available energy is not shown because, as shown in Figure 3, this depends very strongly on the particular H atom that is abstracted. It is, in any case, likely that the products are highly vibrationally excited, in particular, the HCN product, as has been seen in CN + alkane reactions.²⁴

The present results unambiguously show the occurrence of hydrogen abstraction in the CN + 1-pentene reaction. The isotropic angular distributions and relatively low kinetic energy release are consistent with complex formation, as is the similarity between the sideways- and backwards-scattered translational energy distributions. This is the generally assumed entrance path for these reactions given the very high reaction rates, negative temperature dependence, and relatively stable addition complex. We have roughly estimated the yield of the product radical in this reaction relative to that of the C_5H_{11} radical in reaction of CN with *n*-pentane. On the basis of total integrated image intensities for a comparable acquisition time, we find the yields to be roughly the same, within experimental uncertainties of at least $\pm 25\%$, owing to possible differences in beam intensities, ionization cross sections, and so forth. The room-temperature rate for the reaction of CN with *n*-pentane is $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²⁵ This reaction only gives rise to H abstraction. We do not find a literature rate determination for CN + 1-pentene, but Gannon et al. give the rate for 2-butene at room temperature as $2.93 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and we suspect that for 1-pentene will be similar. At 5 kcal/mol, much above room temperature, the pentane rate will likely increase, and the pentene rate will likely decrease. By using the room-temperature rates to estimate the branching for HCN production, we will thus find a lower bound. On this basis, we estimate the branching to H abstraction in reaction of CN with 1-pentene to be 1.6/2.93, or about 50%. Although there are many approximations and uncertainties in this determination, we conclude that HCN production is probably not a minor channel.

A key question is whether this may occur in smaller systems such as propene or propyne that possess similar strongly exoergic channels giving rise to the resonantly stabilized allyl and propargyl radicals, respectively. Gannon et al. examined this question indirectly in the kinetic study of CN + propene mentioned previously. They calculated barriers for isomerization of the addition complex and its dissociation giving H or CH_3 . The surface included a barrierless abstraction channel forming HCN and the allyl radical, the most exoergic reaction pathway, but this was not included in the master equation modeling, owing to the difficulty of treating the barrierless process. They found that methyl loss branching slightly exceeds H loss under all conditions. They obtained satisfactory agreement with the experimental results for H atom yield and concluded that the calculations “support but cannot confirm the absence of a direct channel”. Trevitt and

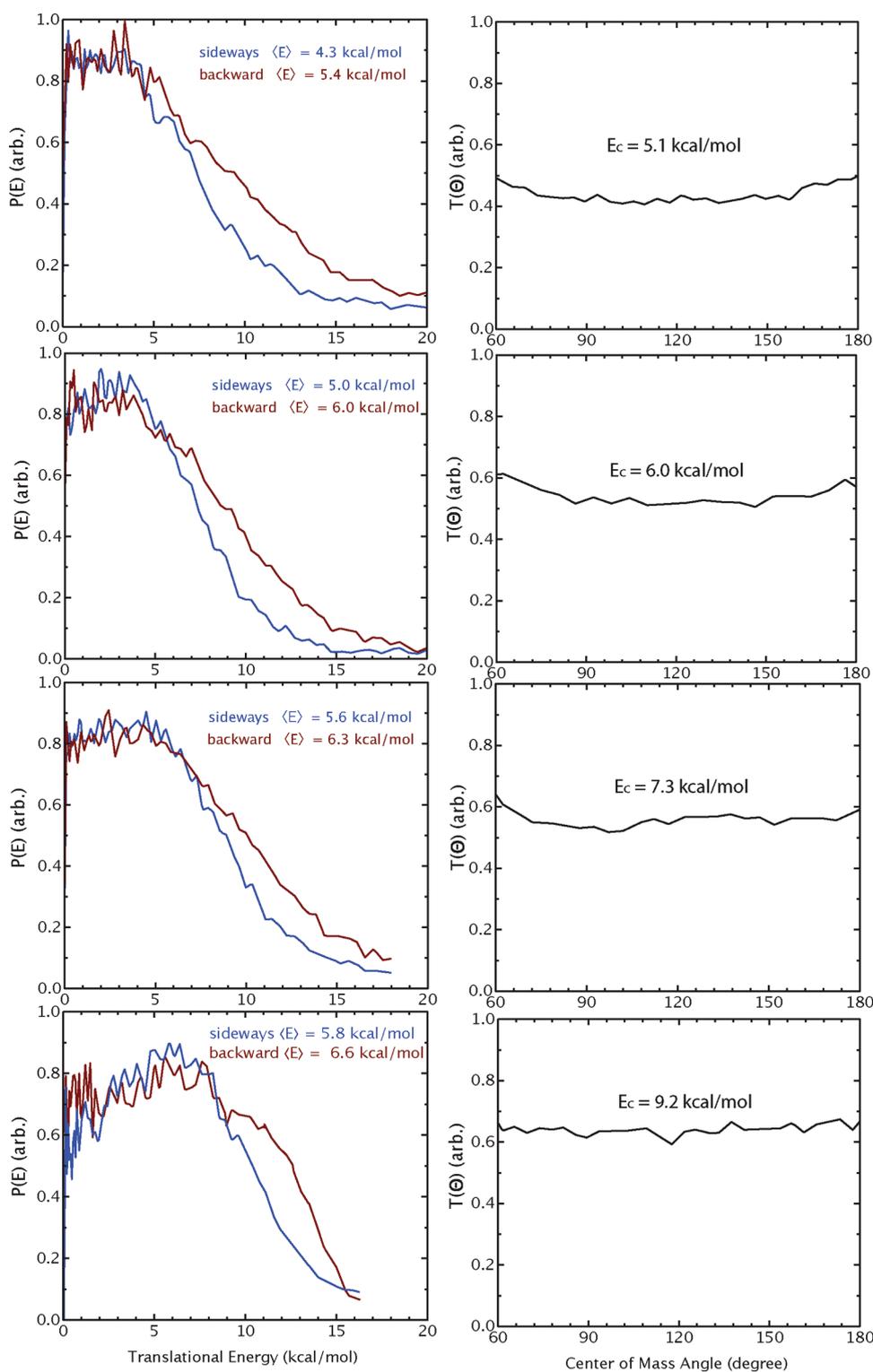


Figure 2. Left side: Center-of-mass translational energy distributions at the sideways ($60\text{--}120^\circ$) and backwards ($120\text{--}180^\circ$) regions and the average translational energy release at each region. Right side: Center-of-mass angular distributions at indicated collision energies.

co-workers also studied the CN + propene reaction with direct vacuum ultraviolet probe of the products using a time-resolved multiplexed mass spectrometer coupled to a flow reactor at

5 Torr. Most relevant to our results was their failure to detect the allyl radical, despite attempts to probe this species directly at a photoionization energy of 9.68 eV. This energy was chosen,

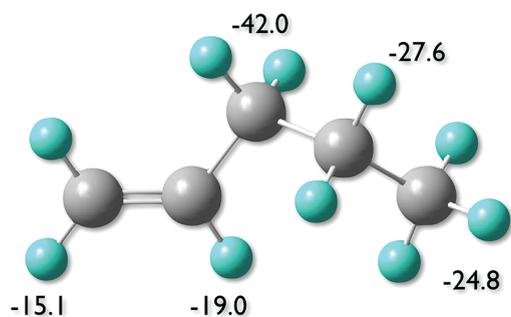


Figure 3. Structure of 1-pentene with 0 K reaction enthalpies (kcal/mol) for H abstraction by CN at indicated carbon atoms.

just below the ionization onset for propene, to eliminate interference from propene itself. They concluded that the branching must be less than 2%. The obvious explanation for the absence of the H abstraction channel in the propene study despite what we see in pentene is that these are two different systems with different dynamics and reaction pathways. Given the similar energetics for these two systems, the present results suggest that it may be worthwhile to attempt more theoretical and experimental investigations to unravel the origin of this distinct behavior.

This similarities between the cyano radical plus alkene reactions and those for chlorine atoms with alkenes, which we have studied in some detail recently,²¹ warrant some discussion. The angular distribution that we observe here is consistent, over the detected angular range, with our results for the analogous chlorine plus alkene reactions. In the latter reactions, however, we saw a sharp forward-scattered peak that rose with collision energy, accounting for 3% of the scattered flux at 4 kcal/mol and 11% at 7 kcal/mol. Furthermore, for the Cl reaction, this collision-energy-dependent forward-scattered flux has a distinct translational energy distribution. As it strongly resembles the translational energy distribution for the forward scattering in Cl + alkane reactions, we associated it with abstraction of the alkyl H atoms in pentene and hexene, rather than the allylic H atoms. Unfortunately, we are blind to this portion of the angular distribution in the CN + pentene experiments; therefore, we cannot determine whether a similar direct component is present. On the other hand, this feature in the Cl reactions only became significant at high collision energy; therefore, it is unlikely to be relevant to Titan.

Nitrogen chemistry on Titan is an area of active investigation with a number of puzzling aspects. The HCN vertical distribution is not well-reproduced by photochemical models, and an extra sink term has been incorporated in several of them to account for this.²⁶ A significant additional source of HCN would increase this discrepancy. There is also uncertainty about the contribution of nitrogen-containing radicals in the lower stratosphere produced by cosmic rays.²⁷ The branching in the subject reactions between nitrogen incorporation and chain lengthening versus HCN production along with resonantly stabilized radicals can have a significant impact on models, and further investigation is clearly warranted.

EXPERIMENTAL SECTION

In the crossed-beam DC slice imaging approach,^{15,20,28} we cross a beam of photolytically prepared radicals with a beam of the target reactant in a vacuum chamber and detect the radical products by single-photon ionization using a compact 157 nm excimer laser. Owing to the limited photon energy of the probe (7.9 eV), our detection is largely confined to C4 and larger radical products. We directly image the relevant “slice” of the detected product, which is then readily converted into the velocity–flux contour map that embodies the reaction dynamics. Cyano radicals are prepared by 193 nm photolysis of cyanogen (Apogee Technology, 98.5%),^{7,29} after which it is entrained in the helium carrier gas. The target reactant, 1-pentene (Sigma-Aldrich, 98%) is seeded in various carrier gases (He, H₂) chosen to give the collision energy of interest. As we have seen in some cases in the past, 157 nm photolysis of the 1-pentene also gives the product radical, which is then also detected. This gives an interfering signal centered at the pentene beam velocity that, for these reactions, precludes determination of the reactive scattering within 60° of the beam direction.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: asuits@chem.wayne.edu.

ACKNOWLEDGMENT A.G.S. acknowledges valuable discussions with S. Klippenstein. This work was supported by the Cooperative Research in Chemistry (CRC) program of the NSF under Award Number CHE-0627854.

REFERENCES

- (1) Suits, A. G. Titan: A Strangely Familiar World. *J. Phys. Chem. A* **2009**, *113*, 11097.
- (2) McCord, T. B.; Hansen, G. B.; Buratti, B. J.; Clark, R. N.; Cruikshank, D. P.; D'Aversa, E.; Griffith, C. A.; Baines, E. H.; Brown, R. H.; Ore, C. M. D.; et al. Composition of Titan's Surface from Cassini VIMS. *Planet. Space Sci.* **2006**, *54*, 1524.
- (3) Kunde, V. G.; Aikin, A. C.; Hanel, R. A.; Jennings, D. E.; Maguire, W. C.; Samuelson, R. E. C₄H₂, HC₃N and C₂N₂ in Titan's Atmosphere. *Nature* **1981**, *292*, 686.
- (4) Sims, I. R.; Queffelec, J. L.; Travers, D.; Rowe, B. R.; Herbert, L. B.; Karthaus, J.; Smith, I. W. M. Rate Constants for the Reactions of CN with Hydrocarbons at Low and Ultra-Low Temperatures. *Chem. Phys. Lett.* **1993**, *211*, 461.
- (5) Carty, D.; Le Page, V.; Sims, I. R.; Smith, I. W. M. Low Temperature Rate Coefficients for the Reactions of CN and C₂H radicals with allene (CH₂=C=CH₂) and Methyl Acetylene. *Chem. Phys. Lett.* **2001**, *344*, 310.
- (6) Morales, S. B.; Le Picard, S. D.; Canosa, A.; Sims, I. R. Experimental Measurements of Low Temperature Rate Coefficients for Neutral–Neutral Reactions of Interest for Atmospheric Chemistry of Titan, Pluto and Triton: Reactions of the CN Radical. *Faraday Discuss.* **2010**, in press.
- (7) North, S. W.; Hall, G. E. Vector and Scalar Correlations in Statistical Dissociation: The Photodissociation of NCCN at 193 nm. *J. Chem. Phys.* **1997**, *106*, 60.

- (8) Gannon, K. L.; Glowacki, D. R.; Blitz, M. A.; Hughes, K. J.; Pilling, M. J.; Seakins, P. W. H. Atom Yields from the Reactions of CN Radicals with C₂H₂, C₂H₄, C₃H₆, *trans*-2-C₄H₈, and *iso*-C₄H₈. *J. Phys. Chem. A* **2007**, *111*, 6679.
- (9) Trevitt, A. J.; Goulay, F.; Meloni, G.; Osborn, D. L.; Taatjes, C. A.; Leone, S. R. Isomer-Specific Product Detection of CN Radical Reactions with Ethene and Propene by Tunable VUV Photoionization Mass Spectrometry. *Int. J. Mass Spectrom.* **2009**, *280*, 113.
- (10) Balucani, N.; Asvany, O.; Chang, A. H. H.; Lin, S. H.; Lee, Y. T.; Kaiser, R. I.; Osamura, Y. Crossed Beam Reaction of Cyano Radicals with Hydrocarbon Molecules. III. Chemical Dynamics of Vinylcyanide (C₂H₃CN;X¹A') Formation from Reaction of CN(X²Σ⁺) with Ethylene, C₂H₄(X¹A_g). *J. Chem. Phys.* **2000**, *113*, 8643.
- (11) Gu, X. B.; Zhang, F. T.; Kaiser, R. I. Reaction Dynamics on the Formation of 1- and 3-Cyanopropylene in the Crossed Beams Reaction of Ground-State Cyano Radicals (CN) with Propylene (C₃H₆) and Its Deuterated Isotopologues. *J. Phys. Chem. A* **2008**, *112*, 9607.
- (12) Huang, C. H.; Kaiser, R. I.; Chang, A. H. H. Theoretical Study on the Reaction of Ground State Cyano Radical with Propylene in Titan's Atmosphere. *J. Phys. Chem. A* **2009**, *113*, 12675.
- (13) Chandler, D. W.; Houston, P. L. Two-Dimensional Imaging of State-selected Photodissociation Products Detected by Multiphoton Ionization. *J. Chem. Phys.* **1987**, *87*, 1445.
- (14) Eppink, A.; Parker, D. H. Velocity Map Imaging of Ions and Electrons using Electrostatic Lenses: Application in Photoelectron and Photofragment Ion Imaging of Molecular Oxygen. *Rev. Sci. Instrum.* **1997**, *68*, 3477.
- (15) Townsend, D.; Minitti, M. P.; Suits, A. G. Direct Current Slice Imaging. *Rev. Sci. Instrum.* **2003**, *74*, 2530.
- (16) Ahmed, M.; Peterka, D. S.; Suits, A. G. H. Abstraction Dynamics by Crossed-Beam Velocity Map Imaging: Cl+CH₃OH → CH₂OH+HCl. *Chem. Phys. Lett.* **2000**, *317*, 264.
- (17) Ahmed, M.; Peterka, D. S.; Suits, A. G. Imaging H Abstraction Dynamics in Crossed Molecular Beams: Cl+ROH Reactions. *Phys. Chem. Chem. Phys.* **2000**, *2*, 861.
- (18) Liu, X. H.; Gross, R. L.; Hall, G. E.; Muckerman, J. T.; Suits, A. G. Imaging O(³P) + Alkane Reactions in Crossed Molecular Beams: Vertical Versus Adiabatic H Abstraction Dynamics. *J. Chem. Phys.* **2002**, *117*, 7947.
- (19) Huang, C.; Li, W.; Estillore, A. D.; Suits, A. G. Dynamics of CN+Alkane Reactions by Crossed-Beam DC Slice Imaging. *J. Chem. Phys.* **2008**, *129*, 074301.
- (20) Estillore, A. D.; Visger, L. M.; Suits, A. G. Crossed-Beam DC Slice Imaging of Chlorine Atom Reactions with Pentane Isomers. *J. Chem. Phys.* **2010**, *132*, 164313.
- (21) Estillore, A. D.; Visger, L. M.; Suits, A. G. Imaging the Dynamics of Chlorine Atom Reactions with Alkenes. *J. Chem. Phys.* **2010**, in press.
- (22) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A Complete Basis Set Model Chemistry. VI. Use of Density Functional Geometries and Frequencies. *J. Chem. Phys.* **1999**, *110*, 2822.
- (23) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A Complete Basis Set Model Chemistry. VII. Use of the Minimum Population Localization Method. *J. Chem. Phys.* **2000**, *112*, 6532.
- (24) Copeland, L. R.; Mohammad, F.; Zahedi, M.; Volman, D. H.; Jackson, W. M. Rate Constants for CN Reactions with Hydrocarbons and the Product HCN Vibrational Populations: Examples of Heavy–Light–Heavy Abstraction Reactions. *J. Chem. Phys.* **1992**, *96*, 5817.
- (25) Sayah, N.; Li, X. C.; Caballero, J. F.; Jackson, W. M. Laser-Induced Fluorescence Studies of CN Reactions with Alkanes, Alkenes and Substituted Aliphatic Species. *J. Photochem. Photobiol., A* **1988**, *45*, 177.
- (26) Lara, L. M.; Lellouch, E.; Shematovich, V. Titan's Atmospheric Haze: The Case for HCN Incorporation. *Astron. Astrophys.* **1999**, *341*, 312.
- (27) Capone, L. A.; Duback, J.; Prasad, S. S.; Whitten, R. C. Galactic Cosmic Rays and N₂ Dissociation on Titan. *Icarus* **1983**, *55*, 73.
- (28) Huang, C. S.; Li, W.; Suits, A. G. Rotationally Resolved Reactive Scattering: Imaging Detailed Cl+C₂H₆ Reaction Dynamics. *J. Chem. Phys.* **2006**, *125*, 133107.
- (29) Eres, D.; Gurnick, M.; McDonald, J. D. Photodissociation of Cyanogen — Angle and Velocity Distributions of State Resolved Fragments. *J. Chem. Phys.* **1984**, *81*, 5552.