Reaction Mechanisms

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Observation of Spontaneous C=C Bond Breaking in the Reaction between Atomic Boron and Ethylene in Solid Neon

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Abstract: *A ground-state boron atom inserts into the C=C bond of ethylene to spontaneously form the allene-like compound H_2CBCH_2 on annealing in solid neon. This compound can further isomerize to the propyne-like $HCBCH_3$ isomer under UV light excitation. The observation of this unique spontaneous C=C bond insertion reaction is consistent with theoretical predictions that the reaction is thermodynamically exothermic and kinetically facile. This work demonstrates that the stronger C=C bond, rather than the less inert C–H bond, can be broken to form organoboron species from the reaction of a boron atom with ethylene even at cryogenic temperatures.*

The activation of carbon–hydrogen (C–H) and carbon–carbon (C–C) bonds, the two fundamental linkages of organic molecules, are among the most important processes in organic synthetic chemistry. These processes allow potentially more useful molecules to be made from relatively inert starting materials. It has been found that many transition-metal complexes can break C–H bonds through formation of the corresponding metal–carbon and metal–hydrogen bonds.[1–4] This reaction opened the way to the development of catalytic methods for the controlled modification of molecules at the site of a C–H bond.[5] The analogous reaction for carbon–carbon bonds is much rarer because C–C bonds are usually less reactive than C–H bonds. Very few transition-metal complexes have been found to break a carbon–carbon bond, opening up fresh opportunities for organic synthesis.[6–10]

The reactions of atomic atoms with simple hydrocarbons serve as the prototypical models to understand the thermochemistry, mechanism, and periodic trends of C–H and C–C bond activations. The elementary reactions of metal atoms with simple hydrocarbons have been intensively investigated[11,12] using matrix isolation spectroscopy, a powerful method for delineating reaction mechanisms through the isolation and characterization of reactive intermediates.[13] These studies indicate that metal insertion into a C–H bond is in fact a general phenomenon in the reactions of transition-metal atoms with the simplest hydrocarbons such as acetylene and ethylene.[11,12] Metal insertion into the C–C bond is believed to be both kinetically and thermodynamically less favorable. Herein, we report a joint matrix-isolation infrared spectroscopic and theoretical study of the reaction of a boron atom with the simplest alkene, C_2H_4, in solid neon. We will show that the ground-state boron atom can react spontaneously with ethylene to form the allene-like H_2CBCH_2 molecule on annealing, which can further isomerize to the less stable propyne-like $HCBCH_3$ isomer under UV light excitation. The result demonstrates that the more inert C=C bond of ethylene can be broken rather than the less inert C–H bond in solid neon at cryogenic temperatures.

The boron atoms were produced by pulsed laser evaporation of a bulk boron target and were co-deposited with ethylene/neon mixtures onto a CsI window at 4 K. The reaction products were characterized by infrared absorption spectroscopy.[14] The infrared spectra in the 1800–500 cm^{-1} spectral region using a ^{10}B-enriched (97%) target and 0.1% C_2H_4 are shown in Figure 1. Absorption bands for new products were produced either on sample deposition, on annealing, or photolysis, which can be classified into several groups based on their annealing and photochemical behaviors (labeled as species **A**–**C** in Figure 1). Four bands for species **A** were detected at 1489.4, 1258.6, 878.3, and 640.3 cm^{-1}. These bands were detected on sample deposition, increased on subsequent sample annealing, but markedly decreased on

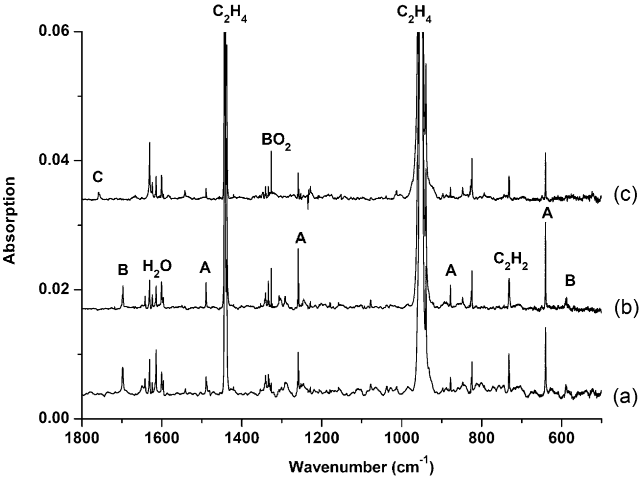

Figure 1. Infrared spectra in the 1800–500 cm^{-1} spectral region from co-deposition of laser-evaporated boron atoms (^{10}B-enriched, 97%) with 0.1% ethylene in solid neon. Spectra after a) 30 min of sample deposition at 4 K, b) after annealing to 12 K, and c) after 15 min of $280 < \lambda < 580$ nm irradiation. Species **A**: H_2CBCH_2, **B**: $H_2CBCH_2^-$, and **C**: $HCBCH_3$.

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broad-band irradiation in the wavelength range of $\lambda = 280$–580 nm using a high-pressure mercury arc lamp. Three bands were detected for species **B** at 2942.8, 1697.2, and 587.4 cm^{-1}, which were present on sample deposition, remained almost unchanged on subsequent sample annealing, but were destroyed upon $280 < \lambda < 580$ nm light irradiation. The intensities of these bands could not be recovered on subsequent sample annealing to high temperatures. Two absorptions were detected for species **C** at 3258.8 and 1758.4 cm^{-1}. Both bands were produced only under broad-band UV/visible irradiation at the expense of the group **A** and **B** absorption bands. The spectra in selected regions with different isotopic samples (natural abundance boron: ^{10}B: 19.8 %; ^{11}B: 80.2 %, $^{13}C_2H_4$, $^{12}C_2D_4$, and $^{12}C_2H_4 + {}^{13}C_2H_4$) are shown in Figures S1–S3 of the Supporting Information.

The group **A** absorption bands are assigned to different vibrational modes of the $H_2C^{10}BCH_2$ molecule (Table 1). The spectra using different isotopically labeled samples (Figure S1) clearly demonstrate that species **A** involves only one boron and one ethylene subunits. The 1489.4 cm^{-1} absorption with quite large boron and carbon isotopic shifts is due to an antisymmetric CBC stretching vibration. The remaining three absorptions have quite small boron and carbon isotopic shifts but quite large deuterium isotopic shifts. The 1258.6 cm^{-1} absorption band is attributed to the CH_2 deformation mode, while the 878.3 and 640.3 cm^{-1} absorptions are assigned to the in-plane and out-of-plane wagging modes.

The group **B** absorptions are assigned to different vibrational modes of the $H_2CBCH_2^-$ ion, which is isoelectronic with allene. The 1697.2 cm^{-1} band corresponds to the absorption reported at 1700.0 cm^{-1} that was tentatively assigned to the anion in solid argon.[15] The observed boron (37.4 cm^{-1}) and carbon (18.2 cm^{-1}) isotopic shifts imply that the 1697.2 cm^{-1} band is an antisymmetric CBC stretching vibration. The much weaker 2942.8 and 587.4 cm^{-1} bands are attributed to the CH stretching and out-of-plane wagging vibrations.

Species **C** was produced under UV/visible irradiation at the expense of the bands attributable to species **A** and **B**, suggesting that species **C** is a structural isomer of H_2CBCH_2. The band position and isotopic shifts indicate that the 1758.4 cm^{-1} absorption is an antisymmetric CBC stretching vibration. The upper absorption at 3258.8 cm^{-1} shows a very small (1.2 cm^{-1}) boron isotopic shift. The band position is indicative of a CH stretching vibration. Accordingly, species **C** is assigned to $HCBCH_3$, which is isoelectronic with the propyne cation.

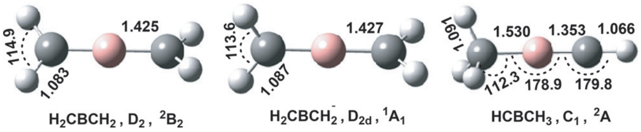

Figure 2. Optimized geometries of species **A**–**C** (from left to right) at the B3LYP/aug-cc-pVTZ level. The bond lengths and angles are in [Å] and [°], respectively.

To verify the experimental assignments, we carried out quantum chemical calculations. Figure 2 shows the optimized geometries of the experimentally observed species **A**–**C** at the B3LYP/aug-cc-pVTZ level. The H_2CBCH_2 molecule is predicted to have a $^2B_2$ ground state with D_2 symmetry. The two CH_2 planes have a dihedral angle of 29.2°. The H_2CBCH_2 molecule is isoelectronic with the allene cation, which was experimentally determined to have a D_2-symmetric structure with a dihedral angle of $49 \pm 3°$.[16] Natural population analysis indicates that the unpaired electron occupies a b_2 orbital which is located mainly at the two carbon atoms. The calculated harmonic vibrational frequencies and intensities are in quite poor agreement with the experimental values. The anharmonic calculations provide much better agreement as shown in Table 1. The four experimentally observed modes are predicted to have most intense IR intensities (Table S2). The antisymmetric CBC stretching mode observed at 1489.4 cm^{-1} is predicted at 1503.7 cm^{-1}. The CH_2 deformation mode observed at 1258.6 cm^{-1} is predicted to appear at 1283.7 cm^{-1}. The two CH_2 wagging modes observed at 878.3 and 640.3 cm^{-1} are calculated to be 871.0 and 663.3 cm^{-1}, respectively. The calculated relative IR intensities as well as the isotopic frequency shifts are also in quite good agreement with the experimental values, which leaves no doubt that the assignment is correct. The $H_2CBCH_2^-$ anion has a closed-shell $^1A_1$ ground state with D_{2d} symmetry, analogous to the

Table 1: Observed and calculated vibrational frequencies (cm^{-1}) of H_2CBCH_2, $H_2CBCH_2^-$, and $HCBCH_3$.

Species	Mode	Exptl.[a]		Calcd. Harmonic[b]		Calcd. Anharmonic[b]	
		^{10}B	^{11}B	^{10}B	^{11}B	^{10}B	^{11}B
H_2CBCH_2 (**A**)	CBC asym. str.	1489.4(0.28)	1469.7(0.1)	1509.5(54)	1473.3(32)	1503.7(28)	1477.2(15)
	CH_2 deform.	1258.6(0.78)	1249.7(1.0)	1340.3(84)	1326.7(97)	1283.7(68)	1276.9(77)
	CH_2 wag	878.3(0.17)	866.3(0.1)	892.2(19)	878.3(18)	871.0(24)	856.6(23)
	CH_2 wag	640.3(1.00)	638.8(1.0)	709.4(76)	706.2(77)	663.3(89)	662.7(73)
$HCBCH_3$ (**C**)	CH str	3258.8(0.2)	3257.7(0.2)	3389.1(45)	3388.7(44)	3253.2(36)	3253.9 (35)
	CBC asym. str.	1758.4(1.0)	1705.9(1.0)	1807.3(166)	1751.6(155)	1772.0(166)	1719.9(151)
$H_2CBCH_2^-$ (**B**)	CH str.	2942.8(0.1)	2936.8(0.2)	3072.9(95)	3072.8(96)	2938.8(105)	2929.0(106)
	CBC asym. str.	1697.2(1.0)	1659.8(1.0)	1715.3(504)	1662.7(471)	1734.9(88)	1609.2(306)
	CH_2 wag	587.4(0.2)	587.4(0.3)	616.0(218)	615.7(220)	603.4(198)	603.2(200)

[a] The values in parentheses are the integrated intensities normalized to the most intense absorption; [b] The calculated IR intensities are listed in parentheses in km mol^{-1}. str = stretch; asym = asymmetric.

isoelectronic allene neutral molecule. The experimentally observed modes are predicted to be the most intense vibrations with calculated harmonic band positions at 3072.9, 1715.3, and 616.0 cm^{-1} (Table S3).

The $HCBCH_3$ molecule is predicted to have a doublet ground state without symmetry. The CBCH moiety is close to linearity with a CBC angle of 178.9°. The two B–C bond distances are 1.530 and 1.353 Å, respectively. Natural population analysis indicates that the singly occupied orbital is mainly a bonding π orbital of the shorter C–B bond. Consistent with experimental observations, only the two experimentally observed modes are predicted to have appreciable IR intensities in the probed spectral region (Table S4). The calculated harmonic frequencies are slightly higher than the experimental values with isotopic frequency shifts very close to the experimental data (Table 1; Table S4).

The experimental observations shown in Figure 1 clearly demonstrate that only the H_2CBCH_2 molecule is formed from the $B + C_2H_4$ reaction on annealing. This indicates that the C=C bond of ethylene can be selectively broken by the ground-state boron atom at cryogenic temperatures and that this insertion reaction is exothermic and requires negligible activation energy. In addition to the neutral molecule, the $H_2CBCH_2^-$ ion is also formed after sample deposition presumably via electron capture by the neutral H_2CBCH_2 molecule during the co-condensation process. The adiabatic electron affinity of H_2CBCH_2 is predicted to be 43.9 kcal mol^{-1} at the CCSD(T)//B3LYP level. The absorption bands attributable to H_2CBCH_2 and $H_2CBCH_2^-$ decrease on broad-band irradiation, during which the $HCBCH_3$ absorption bands are produced. It is clear that the $H_2CBCH_2^-$ ion is photobleached and that the $HCBCH_3$ molecule is formed from photoinduced isomerization of the H_2CBCH_2 isomer.

The observation of the C=C bond insertion reaction is quite surprising as only insertion of the more reactive C–H bond was observed in previous investigations of similar reactions between metal atoms and ethylene.[12] The detailed potential energy profile for the reaction $B + C_2H_4$ was calculated previously at the CCSD(T)/cc-pVTZ//B3LYP/6-311G(d, p) level.[17] The profile related to the present study is recalculated at the CCSD(T)//B3LYP/aug-cc-pVTZ level, and the result is shown in Figure 3. In agreement with previous calculations, the reaction proceeds with the initial formation of a C_{2v}-symmetric $B(C_2H_4)$ borirane radical.[17,18] This addition reaction is barrierless and is exothermic by 47.0 kcal mol^{-1}. $B(C_2H_4)$ rearranges to the inserted H_2CBCH_2 isomer via a transition state (TS1) located at 15.8 kcal mol^{-1} above $B(C_2H_4)$. The overall C=C bond insertion reaction is predicted to be exothermic by 73.3 kcal mol^{-1}, and proceeds via a transition state lying 31.2 kcal mol^{-1} lower in energy than the ground-state reactants $B + C_2H_4$, implying that this insertion reaction is both thermodynamically favorable and kinetically facile. Owing to the small barrier, the $B(C_2H_4)$ intermediate cannot be frozen in the solid neon matrix. Experimentally, we do not observe any absorption bands that can be assigned to $B(C_2H_4)$. It should be pointed out that the inserted H_2CBCH_2 molecule was predicted to be the global minimum on the potential energy surface of BC_2H_4 due to strongly delocalized CBC bonding and that the reaction pathway for the formation of H_2CBCH_2 is the most energetically favorable pathway.[17] The reaction pathways to form the other isomers, including cyclic $CH(BH)CH_2$, the C–H bond insertion product vinylborane radical HBC_2H_3, and H_2BCCH_2, were predicted to be both kinetically and thermodynamically less favorable.[17]

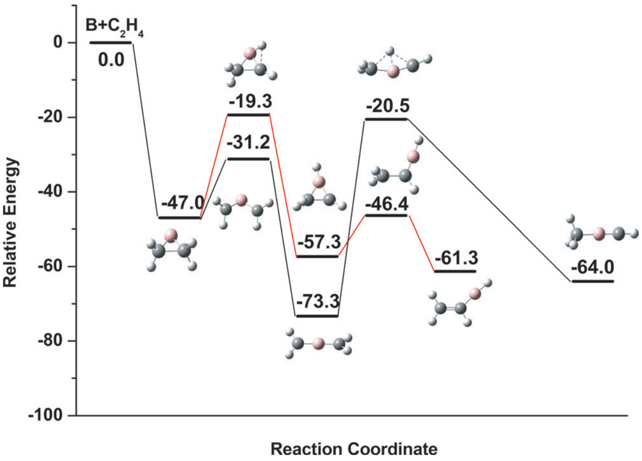

Figure 3. The potential energy profile of the $B + C_2H_4$ reaction calculated at the CCSD(T)//B3LYP/aug-cc-pVTZ level of theory. The energies are in kcal mol^{-1} and are corrected with zero-point energy.

The H_2CBCH_2 undergoes a hydrogen-atom transfer to form the less stable $HCBCH_3$ isomer via a transition state (TS2), which lies 52.8 kcal mol^{-1} above H_2CBCH_2 (Figure 3). This isomerization reaction is predicted to be endothermic by 9.3 kcal mol^{-1} and requires activation energy, in agreement with the experimental observation that the $HCBCH_3$ isomer is produced only under UV light excitation. The isomerization reaction of the isoelectronic allene cation to form a propyne cation was predicted to have a similar mechanism.[19]

The observation of this spontaneous insertion reaction is consistent with a previous gas-phase kinetic study which indicated the absence of any significant activation barrier in the entrance channel of the potential energy surface of the reaction between atomic boron and C_2H_4.[20] However, an early matrix-isolation infrared spectroscopic study on the reaction of laser-ablated boron atoms with C_2H_4 in solid argon identified three BC_2H_3 isomers, namely borirene $(CH)_2BH$, ethynylborane H_2BCCH, and borallene $HBCCH_2$, as the major reaction products.[15] In that study, the experiments were performed using quite high ablation laser energy. The major products were detected right after sample deposition,[15] suggesting that these species were formed initially in the gas phase and were subsequently trapped during the co-condensation process. A gas-phase reactivity study under single collision conditions in a crossed beam experiment with mass spectrometric detection confirmed the formation of these BC_2H_3 products via bound intermediate(s).[17,21] The initial steps of the $B + C_2H_4$ reaction are highly exothermic and the excess internal energy can barely be released in collision-free gas-phase environment, which induces a bond fission leading to the stable end products. In contrast, in this study the insertion reaction is observed to proceed in a neon matrix on annealing. The matrix environment is able to disperse the reaction energy released, thus, the most favorable intermediate is stabilized. The results from complementary experiments in solid argon with low evaporation laser energy give similar results to the neon matrix experiments. The inserted H_2CBCH_2 molecule formed on annealing is the major product. The $HCBCH_3$ isomer is also formed under UV light excitation. In contrast, the previously reported BC_2H_3 species are barely observed (see the Supporting Information).

In summary, our investigations clearly show that a ground-state boron atom reacts spontaneously with ethylene to form the molecule H_2CBCH_2 on annealing in solid neon, which can further isomerize to the less stable $HCBCH_3$ isomer under UV light excitation. The formation of this isomer indicates that the more inert C=C bond of ethylene can be selectively broken even at cryogenic temperatures. The present findings provide a new reaction route, as an alternative to selective C–C bond activation, for the synthesis of organoboron compounds. The H_2CBCH_2 and $HCBCH_3$ species are potential intermediates in combustion and interstellar chemistry,[22,23] analogous to the well-studied isoelectronic allene and propyne cations.[19,24]

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[1] a) B. A. Arndtsen, R. G. Bergman, *Science* **1995**, *270*, 1970; b) B. A. Arndtsen, R. G. Bergman, T. A. Mobley, T. H. Peterson, *Acc. Chem. Res.* **1995**, *28*, 154.
[2] a) W. D. Jones, *Science* **2000**, *287*, 1942; b) R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2001**, 2437.
[3] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507.
[4] X. C. Wang, W. Gong, L. Z. Fang, R. Y. Zhu, S. H. Li, K. M. Engle, J. Q. Yu, *Nature* **2015**, *519*, 334.
[5] a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147.
[6] a) M. Gandelman, A. Vigalok, L. Konstantinovski, D. Milstein, *J. Am. Chem. Soc.* **2000**, *122*, 9848; b) R. H. Crabtree, *Nature* **2000**, *408*, 415.
[7] a) A. Sattler, G. Parkin, *Nature* **2010**, *463*, 523; b) A. S. Goldman, *Nature* **2010**, *463*, 435.
[8] S. W. Hu, T. Shima, Z. M. Hou, *Nature* **2014**, *512*, 413.
[9] a) F. Chen, T. Wang, N. Jiao, *Chem. Rev.* **2014**, *114*, 8613; b) T. Wang, N. Jiao, *Acc. Chem. Res.* **2014**, *47*, 1137.
[10] S. K. Murphy, J. W. Park, F. A. Cruz, V. M. Dong, *Science* **2015**, *347*, 56.
[11] a) Z. G. Huang, A. H. Zeng, J. Dong, M. F. Zhou, *J. Phys. Chem. A* **2003**, *107*, 2329; b) H. G. Cho, G. P. Kushto, L. Andrews, C. W. Bauschlicher, Jr., *J. Phys. Chem. A* **2008**, *112*, 6295; c) Y. L. Teng, Q. Xu, *J. Phys. Chem. A* **2009**, *113*, 12163; d) Y. L. Teng, Q. Xu, *J. Phys. Chem. A* **2010**, *114*, 9069; e) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2010**, *114*, 10028; f) X. F. Wang, L. Andrews, *J. Phys. Chem. A* **2011**, *115*, 9447; g) Q. Wang, X. Liu, B. Xu, X. F. Wang, *J. Phys. Chem. A* **2012**, *116*, 9261; h) H. G. Cho, J. T. Lyon, L. Andrews, *J. Phys. Chem. A* **2012**, *116*, 11880; i) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2012**, *116*, 10917; j) H. G. Cho, L. Andrews, *J. Mol. Spectrosc.* **2015**, *310*, 84.
[12] a) Y. K. Lee, L. Manceron, I. Papai, *J. Phys. Chem. A* **1997**, *101*, 9650; b) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 3965; c) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 10441; d) M. G. K. Thompson, J. M. Parnis, *J. Phys. Chem. A* **2005**, *109*, 9465; e) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2007**, *111*, 5201; f) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2008**, *112*, 12071; g) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2009**, *113*, 6677; h) H. G. Cho, L. Andrews, *J. Phys. Chem. A* **2009**, *113*, 5073.
[13] a) V. E. Bondybey, A. M. Smith, J. Agreiter, *Chem. Rev.* **1996**, *96*, 2113; b) H. J. Himmel, A. J. Downs, T. M. Greene, *Chem. Rev.* **2002**, *102*, 4191; c) M. E. Jacox, *Acc. Chem. Res.* **2004**, *37*, 727; d) M. F. Zhou, L. Andrews, C. W. Bauschlicher, Jr., *Chem. Rev.* **2001**, *101*, 1931; e) Y. Gong, M. F. Zhou, L. Andrews, *Chem. Rev.* **2009**, *109*, 6765.
[14] G. J. Wang, M. F. Zhou, *Int. Rev. Phys. Chem.* **2008**, *27*, 1.
[15] a) D. V. Lanzisera, P. Hassanzadeh, Y. Hannachi, L. Andrews, *J. Am. Chem. Soc.* **1997**, *119*, 12402; b) L. Andrews, D. V. Lanzisera, P. Hassanzadeh, Y. Hannachi, *J. Phys. Chem. A* **1998**, *102*, 3259.
[16] Z. Z. Yang, L. S. Wang, Y. T. Lee, D. A. Shirley, S. Y. Huang, W. A. Lester, Jr., *Chem. Phys. Lett.* **1990**, *171*, 9.
[17] F. T. Zhang, X. B. Gu, R. I. Kaiser, N. Balucani, C. H. Huang, C. H. Kao, A. H. H. Chang, *J. Phys. Chem. A* **2008**, *112*, 3837.
[18] Y. Hannachi, P. Hassanzadeh, L. Andrews, *Chem. Phys. Lett.* **1996**, *250*, 421.
[19] a) A. M. Mebel, A. D. Bandrauk, *J. Chem. Phys.* **2008**, *129*, 224311; b) G. Frenking, H. Schwarz, *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 131; c) W. J. van der Hart, *Int. J. Mass Spectrom. Ion Processes.* **1995**, *151*, 27.
[20] A. Canosa, S. D. Le Picard, W. D. Geppert, *J. Phys. Chem. A* **2004**, *108*, 6183.
[21] N. Balucani, O. Asvany, Y. T. Lee, R. I. Kaiser, N. Galland, Y. Hannachi, *J. Am. Chem. Soc.* **2000**, *122*, 11234.
[22] N. Balucani, F. T. Zhang, R. I. Kaiser, *Chem. Rev.* **2010**, *110*, 5107.
[23] a) N. Hansen, J. A. Miller, P. R. Westmoreland, T. R. Kasper, J. Wang, T. A. Cool, *Combust. Flame* **2009**, *156*, 2153; b) R. I. Kaiser, *Chem. Rev.* **2002**, *102*, 1309; c) M. J. McEwan, G. B. I. Scott, N. G. Adams, L. M. Babcock, R. Terzieva, E. Herbst, *Astrophys. J.* **1999**, *513*, 287.
[24] a) D. Forney, M. E. Jacox, C. L. Lugez, W. E. Thompson, *J. Chem. Phys.* **2001**, *115*, 8418; b) M. C. Liu, S. C. Chen, C. H. Chin, T. P. Huang, H. F. Chen, Y. J. Wu, *J. Phys. Chem. Lett.* **2015**, *6*, 3185.

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