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Diborene: Generation and Photoelectron Spectroscopy of an Inorganic Biradical

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ABSTRACT: Diborenes, R-BB-R' are of current interest in inorganic chemistry, because they offer the opportunity to tune the properties of a biradical by modifying the substituents of the diborene parent, HBBH. Here we synthesize the elusive diborene by H-atom abstraction from diborane, B₂H₆ using fluorine atoms and report a vibrationally resolved photoelectron spectrum of the HBBH biradical. The spectrum is interpreted by comparison with high-level *ab initio* computations, taking into account the Renner-Teller splitting in the X⁺ ²Π ionic ground state, which show an excellent agreement with the experimental spectrum. An adiabatic ionization energy of 9.080±0.015 eV was determined and a vibrational progression in the boron-boron stretching vibration of 0.14 eV is visible. This is due to the reduction of bond order upon ionization, accompanied by an increase of the computed boron-boron bond length R_{BB} from 1.514 Å to 1.606 Å.

TOC GRAPHICS

KEYWORDS ionization energy, ab initio calculations, gas phase reaction, synchrotron radiation

Inorganic biradicals receive increasing attention due to their unusual binding properties that are still a challenge for theory,¹ but also due to the difficulties to prepare them. Diborenes R-BB-R' constitute particularly interesting candidates, because varying the ligands provides the opportunity to tune the properties of the biradicalic HBBH parent, which has the same number of electrons as C₂. Only recently the synthesis and characterization of double-bond-containing species based on boron, as well as their fully twisted diradical congeners was reported.² Such biradicals expand the wealth of binding motives³ in boron chemistry that range from stabilized diborenes with B=B double⁴⁻⁶ and diborynes with triple bonds⁷⁻¹¹ to singlet borylenes¹² and larger boron clusters including fullerene-type structures.¹³ However, in contrast to their organic counterparts,¹⁴ accurate spectroscopic studies of inorganic reactive intermediates that yield structural and thermochemical information are scarce and in particular the diborene parent compound HBBH (**1** in scheme 1) has remained almost elusive so far. The molecule has only been observed in rare gas matrices, where EPR (electron paramagnetic resonance) spectra indicated a triplet ground state¹⁵ and an IR-spectrum revealed the ν_3 antisymmetric stretch at 2679.9 cm⁻¹.¹⁶ Previous photoion yield spectra gave approximate ionization and appearance energies for B₂H₄¹⁷ and B₂H₅,¹⁸ but no data on smaller B_xH_y species were reported. Here we present a vibrationally resolved photoelectron spectrum of diborene **1**, obtained by photoionization with synchrotron radiation (SR). The experiments are complemented by high-level *ab initio* computations. A large number of theoretical studies are available for the neutral ground state of **1**,¹⁹⁻²² also focusing on the EPR properties²³ and most recently on the competition between multicenter and classical bonding.²⁴ However, no computations of the Renner-Teller-split cation have yet been reported.

Scheme 1. Diborene **1** was produced from diborane **2** by the reaction with fluorine atoms.

Diborene **1** is a linear molecule of $D_{\infty h}$ symmetry with a $^3\Sigma_g^-$ ground state.²³ The highest singly occupied molecular orbitals (SOMO) are the $[1\pi_u(p_x)]^1[1\pi_u(p_y)]^1$ binding orbitals, so the formal bond order is 2. However, since the unpaired electrons are situated in orthogonal MOs, the double bond used in a Lewis-description is questionable in MO theory and therefore omitted from Scheme 1.

Diborene **1** was produced from diborane **2** according to Scheme 1 by reaction with fluorine atoms, generated in a microwave discharge from F_2 . The driving force for this reaction is the large binding energy of HF ($D_e=592$ kJ/mol).²⁵ H-abstraction by F-atoms has been utilized before to record photoelectron spectra of reactive intermediates,^{26,27} but application has been limited by the unselectivity of the approach. In fact, the reaction with fluorine atoms produces a range of B_xH_y species, with the maximum of the distribution depending on the F-concentration, as demonstrated in Figure 1. We therefore applied photoelectron-photoion coincidence spectroscopy (PEPICO),²⁸ a method that permits to record mass-selected photoelectron spectra (ms-PES) for each composition by correlating ions and electrons. Several reactive molecules generated by fluorine discharges,^{29,30} pyrolysis³¹⁻³⁵ or photolysis³⁶ have been studied using PEPICO, which is evolving into an analytical tool to probe elusive intermediates for example in model flames,^{37,38} catalytic reactors³⁹ and kinetics experiments.^{36,40}

Figure 1. The mass spectrum of B_2H_6 in a fluorine discharge.

Figure 1 depicts a mass spectrum, integrated over all photon energies from 8.5 to 11.4 eV to show all species present in the reactor. The presence of a large number of different molecules demonstrates the need for mass-selection, i.e. coincidence detection of electrons and ions. The spectrum is dominated by BF, which is efficiently formed due to the strong boron-fluorine bond. The molecule has been investigated by Dyke and coworkers, who reported an IE of 11.12 ± 0.01 eV for the transition into the $X^+ \ ^2\Sigma^+$ ground state of the cation.⁴¹ Beside BF a number of B_2H_y compounds are visible. The experimental conditions were chosen to maximize B_2H_2 . As visible, BH_2 is present as well, but the intensity was not sufficient to record a photoelectron spectrum. In addition we observed peaks corresponding to B_4H_y , which originate from boron-clusters that have formed in the sample.

Figure 2. Full photoelectron spectrum matrix of the $m/z=24$ mass channel. Note that around 9.65 eV the amount of sample started to decrease.

The photoelectron signal in the $m/z=24$ mass channel, corresponding to **1** as a function of electron kinetic energy (eKE) and photon energy is shown as a two-dimensional color (intensity) maps representing the PES- (Photoelectron Spectrum) matrix in Figure 2. From the matrix the slow photoelectron spectrum (SPES) can be obtained by integrating the photoelectron signal along diagonal lines of constant slope $eKE = h\nu - IE$, following the procedure outlined previously.^{30,42} This yields the mass-selected slow photoelectron spectrum (ms-SPES), given as a white line in Figure 2, which is associated with a resolution comparable to the more common threshold PES, but with a higher signal-to-noise ratio.

The ms-SPES of **1** is shown in more detail in the upper trace of Figure 3. Note that contributions from $^{10}\text{B}^{11}\text{BH}_3$ will appear in the $m/z=24$ mass channel, but can be identified by comparison with

the $^{11}\text{B}_2\text{H}_3$ spectrum recorded in the $m/z=25$ channel. In addition small contributions from $^{10}\text{B}_2\text{H}_4$ might appear. We computed the IE for three isomers of B_2H_4 using the CBS-QB3 composite method and arrived at values of 10.38 eV ($\text{H}_2\text{B}-\text{BH}_2$), 9.57 eV (bridged structure I, $\text{HB}(\text{H})_2\text{BH}$) and 8.43 eV (bridged structure II, $\text{B}(\text{H})_3\text{BH}$). The FC simulation of bridged structure 1 shows a long progression with a weak origin band, maximizing at the second overtone. Thus contributions from $^{10}\text{B}_2\text{H}_4$ to the spectrum can be excluded. A contribution of the higher energy isomer BBH_2 to $m/z=24$ has also to be considered. The IE was calculated to be 8.97 eV, but again a different vibrational progression is expected from a Franck-Condon simulation.

The first band in Figure 3 at 9.08 ± 0.015 eV corresponds to the adiabatic ionization energy IE_{ad} of HBBH . The error bars are taken from the full width at half maximum of the first band and reflect the underlying rotational distribution. No significant hot band activity is apparent, indicating that the molecules are approximately at room temperature. A rotational temperature of 200 K is deduced from the molecular beam velocity, which is extracted from the ion image. The vibrational temperature might be slightly higher, but the small hot band intensity shows that the exothermicity of the H atom abstraction is mostly taken up by the HF vibration. At higher energies a vibrational progression with a spacing of 0.14 eV appears that can be qualitatively explained within molecular orbital theory: Upon photoionization an electron is removed from the $1\pi_u$ binding orbital, the bond order is reduced from 2 to 1.5, and the boron-boron-bond length R_{BB} will increase. Consequently, activity in the BB-stretching vibration is expected.

Figure 3. Experimental (upper trace) and computed photoelectron spectrum of HBBH. The computed spectrum was shifted by 0.195 eV to achieve the best match with the experiment.

However, analysis is impeded by the fact that the ionic ground state is a doubly degenerate $^2\Pi$ state, which exhibits Renner-Teller splitting. Complete active space multireference configuration interaction (CAS-MRCI) computations show that the two components (called D_0 and D_1 below for simplicity) are isoenergetic at the linear geometry. The degeneracy is lifted by excitation of a bending motion, but the minimum energy geometry remains linear. While for the totally symmetric vibrational mode ν_1 a wavenumber of 1108 cm^{-1} (0.137 eV) was computed for both D_0 and D_1 , the bending mode energies are slightly higher in D_1 . Therefore the latter state has a higher zero point energy (4801 cm^{-1} compared to 4518 cm^{-1}), which should lead to the appearance of two progressions in the PES. This is evident from the Franck-Condon simulation based on the computations depicted in the lower trace of Figure 3. The two progressions cannot be fully resolved in the experimental spectrum, but the bands show a shoulder at the high-energy

side, which is assigned to the $T_0 \rightarrow D_1$ transition. Nevertheless, the agreement between experiment and simulation is excellent and both the ν_1 vibrational spacing and the intensities are well reproduced, indicating that the computations accurately reflect both the geometry change upon photoionization and the shape of the cationic potential energy surfaces. IE_{ad} was computed to be 8.865 eV, i.e. roughly 0.2 eV lower than the experimental value. A bond length R_{BB} of 1.514 Å was computed for the $X^3\Sigma_g^-$ state, comparable to B=B double bonds.⁶ For the $X^+2\Pi$ state $R_{BB}=1.606$ Å was found, thus the bond length increases by almost 0.1 Å upon ionization. Note that previous MRCI computations found slightly shorter R_{BB} for the neutral ground state.¹⁹⁻

²¹ The most important parameters are summarized in table 1.

Table 1. Important parameters for diborene 1.

	$X^3\Sigma_g^-$ [a]	$X^+2\Pi(D_0)$ [a]	$X^+2\Pi(D_1)$ [a]	Experiment
$R_{BB}/\text{\AA}$	1.514	1.606	1.606	
ν_1/eV	0.156	0.137	0.137	0.14
ZPE /eV	0.576	0.560	0.595	
IE_{ad}/eV	8.865			9.08 ± 0.015

[a] CAS-MRCI computations

In conclusion we report the gas phase synthesis and the first photoelectron spectrum of diborene, a prototype inorganic biradical, yielding an $IE_{ad}=9.08$ eV. Excellent agreement with high-level computations is observed. Despite the tendency of boron to form strong B-F bonds, HBBH was formed in sufficient concentration to record a vibrationally resolved photoelectron spectrum. The work represents a cornerstone for systematic studies of the effects that changes in the substitution pattern have on the electronic stability of diborenes.

Methods

Experiments were conducted at the DESIRS undulator beamline⁴³ of the SOLEIL storage ring in St. Aubin/F, using the DELICIOUS 3 double imaging photoelectron/photoion coincidence (i2PEPICO) spectrometer.⁴⁴ HBBH was generated from B_2H_6 (0.5% in Ar) via H-abstraction by fluorine according to Scheme 1 in a fast flow tube at low pressure that is described in detail elsewhere.⁴⁵ Fluorine atoms were produced in a microwave discharge of a mixture of around 5%

F₂ diluted in He, introduced into the flow tube 50 cm before the reaction zone. The amount of F₂ was adjusted to maximize the signal of **1**, the Fluorine atom density being typically around 10¹³ atoms·cm⁻³. After passage through the flow tube, the mixture is adiabatically expanded through a first skimmer into a differentially pumped chamber (few 10⁻⁴ mbar), and through a second skimmer (*f* = 1 mm, Beam Dynamics Inc.) into the ionization chamber (few 10⁻⁸ mbar). The VUV radiation was provided by a variable polarization undulator, which feeds the DESIRS beamline. Radiation with a narrow bandwidth was selected by a 6.65 m normal incidence monochromator with a 200 g/mm SiC grating and focused onto a 200/200 μm (H/V) spot at the ionization region. The entrance and exit slits were set to yield a resolution of around 5 meV at 9 eV for a flux of 2×10¹² photons/s. A gas filter filled with 0.25 mbar Ar cut off the higher order radiation from the undulator.⁴⁶ The photon energy was scanned in 5 meV steps and data were averaged for 300 s at each energy. Photoelectron spectra were obtained via the slow PES (SPES) technique described in Ref.⁴² The spectral resolution is around 20 meV.

Electronic structure calculations were performed at the CAS-MRCI level with the ANO-RCC basis set using the software package MOLPRO.⁴⁷ The orbitals of an active space consisting of 10 electrons in 10 orbitals were optimized by minimizing the energy of one triplet and two ionic doublet states. This was followed by multireference CI calculations with the same active space to find the lowest triplet and the lowest two ionic doublet states. Geometry optimizations in the T₀, D₀ and D₁ states at the same level of theory were followed by a frequency calculation. All 7 vibrational frequencies were positive and the remaining 5 frequencies were 0 within numerical precision. The Franck-Condon factors were computed using the pGopher program,⁴⁸ including Duschinsky rotation.

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REFERENCES

- (1) Miliordos, E.; Ruedenberg, K.; Xantheas, S. S. Unusual Inorganic Biradicals: A Theoretical Analysis. *Angew. Chem. Int. Ed.* **2013**, *52*, 5736-5729.
- (2) Böhnke, J.; Dellermann, T.; Celik, M. A.; Krummenacher, I.; Dewhurst, R. D.; Demeshko, S.; Ewing, W. C.; Hammond, K.; Heß, M.; Bill, E.; Welz, E.; Röhr, M. I. S.; Mitrić, R.; Engels, B.; Meyer, F.; Braunschweig, H. Isolation of Diborenes and their 90°-Twisted Diradical Congeners. *Nature Comm.* **2018**, *9*, 1197.
- (3) Braunschweig, H.; Dewhurst, R. D. Single, Double, Triple Bonds and Chains: The Formation of Electron-Precise BB Bonds. *Angew. Chem. Int. Ed.* **2013**, *52*, 3574-3583.
- (4) Auerhammer, D.; Arrowsmith, M.; Bissinger, P.; Braunschweig, H.; Dellermann, T.; Kupfer, T.; Lenczyk, C.; Roy, D. K.; Schafer, M.; Schneider, C. Increasing the Reactivity of Diborenes: Derivatization of NHC-Supported Dithienyldiborenes with Electron-Donor Groups. *Chem. Eur. J.* **2018**, *24*, 266-273.
- (5) Braunschweig, H.; Constantinidis, P.; Dellermann, T.; Ewing, W. C.; Fischer, I.; Hess, M.; Knight, F. R.; Rempel, A.; Schneider, C.; Ullrich, S.; Vargas, A.; Woollins, J. D. Highly Strained Heterocycles Constructed from Boron-Boron Multiple Bonds and Heavy Chalcogens. *Angew. Chem. Int. Ed.* **2016**, *55*, 5606-5609.
- (6) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F.; Schleyer, P. V.; Robinson, G. H. A Stable Neutral Diborene Containing a B = B Double Bond. *J. Am. Chem. Soc.* **2007**, *129*, 12412-12413.
- (7) Zhou, M.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L.; Xu, Q. OCBBCO: A Neutral Molecule with Some Boron-Boron Triple Bond Character. *J. Am. Chem. Soc.* **2002**, *124*, 12936-12937.
- (8) Braunschweig, H.; Dewhurst, R.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond. *Science* **2012**, *336*, 120-1422.

- (9) Frenking, G.; Holzmann, N. A Boron-Boron Triple Bond. *Science* **2012**, *336*, 1394-1395.
- (10) Bohnke, J.; Braunschweig, H.; Constantinidis, P.; Dellermann, T.; Ewing, W. C.; Fischer, I.; Hammond, K.; Hupp, F.; Mies, J.; Schmitt, H. C.; Vargas, A. Experimental Assessment of the Strengths of B-B Triple Bonds. *J. Am. Chem. Soc.* **2015**, *137*, 1766-1769.
- (11) Li, S. D.; Zhai, H. J.; Wang, L. S. $B_2(BO)_2^{2-}$ Diboronyl Diborene: A Linear Molecule with a Triple Boron-Boron Bond. *J. Am. Chem. Soc.* **2008**, *130*, 2573-2579.
- (12) Bettinger, H. F. Phenylborylene: Direct Spectroscopic Characterization in Inert Gas Matrices. *J. Am. Chem. Soc.* **2006**, *128*, 2534-2535.
- (13) Zhai, H.-J.; Zhao, Y.-F.; Li, W.-L.; Chen, Q.; Bai, H.; Hu, H.-S.; Piazza, Z. A.; Tian, W.-J.; Lu, H.-G.; Wu, Y.-B.; Mu, Y.-W.; Wei, G.-F.; Liu, Z.-P.; Li, J.; Li, S.-D.; Wang, L.-S. Observation of an All-Boron Fullerene. *Nature Chem.* **2014**, *6*, 727-731.
- (14) Abe, M. Diradicals. *Chem. Rev.* **2013**, *113*, 7011-7088.
- (15) Knight Jr., L. B.; Kerr, K.; Miller, P. K.; Arrington, C. A. ESR Investigation of the HBBH ($X^3\Sigma$) Radical in Neon and Argon Matrices at 4 K. Comparison with ab Initio SCF and CI Calculations. *J. Phys. Chem.* **1995**, *99*, 16842-16848.
- (16) Tague Jr., T. J.; Andrews, L. Reactions of Pulsed-Laser Evaporated Boron Atoms with Hydrogen. Infrared Spectra of Boron Hydride Intermediate Species in Solid Argon. *J. Am. Chem. Soc.* **1994**, *116*, 4970-4976.
- (17) Ruscic, B.; Schwarz, M.; Berkowitz, J. Molecular Structure and Thermal Stability of B_2H_4 and $B_2H_4^+$ Species. *J. Chem. Phys.* **1989**, *91*, 4576-4582.
- (18) Ruscic, B.; Schwarz, M.; Berkowitz, J. Structure and Bonding in the B_2H_5 Radical and Cation. *J. Chem. Phys.* **1989**, *91*, 4183-4188.
- (19) Miliordos, E.; Mavridis, A. Ab Initio Investigation of the Electronic Structure and Bonding of BH, BH-, and HBBH Molecules. *J. Chem. Phys.* **2008**, *128*, 144308.
- (20) Peric, M.; Ostojic, B.; Engels, B. Ab Initio Study of the Electronic Spectrum of B_2H_2 . 1. Vertical Spectrum and trans- and cis-Bending Potential Curves. *J. Mol. Spec.* **1997**, *182*, 280-294.
- (21) Peric, M.; Ostojic, B.; Engels, B. Ab Initio Study of the Electronic Spectrum of B_2H_2 . 2. Potential Curves for Torsional Motion, Symmetric B-H Stretching, and B-B Separation. *J. Mol. Spec.* **1997**, *182*, 295-308.
- (22) Brites, V.; Leonard, C. Rovibrational energies of B_2H_2 ($X^3\Sigma^-g$) from an explicitly correlated potential energy surface. *Comput. Theor. Chem.* **2013**, *1025*, 24-29.
- (23) Engels, B.; Suter, H. U.; Peric, M. Ab Initio Investigation of Vibrational Effects on Magnetic Hyperfine Coupling Constants in the $X^3\Sigma_g^-$ State of B_2H_2 . *J. Phys. Chem.* **1996**, *100*, 10121-10122.
- (24) Lundell, K. A.; Boldyrev, A. I. Tug-of-War Between Classical and Multicenter Bonds in H-(Be) $_n$ -H Species. *Chem. Phys. Lett.* **2018**, *699*, 85-87.
- (25) Peterson, K. A.; Dunning, T. H. Benchmark Calculations with Correlated Molecular Wave Functions. VII. Binding Energy and Structure of the HF Dimer. *J. Chem. Phys.* **1995**, *102*, 2032-20141.
- (26) Baker, J.; Barnes, M.; Cockett, M. C. R.; Dyke, J. M.; Ellis, A. M.; Feher, M.; Lee, E. P. F.; Morris, A.; Zamanpour, H. Photoelectron Spectroscopy of Unstable Molecules. *J. Electron Spectrosc.* **1990**, *51*, 487-511.

(27) West, J. B.; Dyke, J. M.; Morris, A.; Wright, T. G.; Gamblin, S. D. Photoelectron Spectroscopy of Short-Lived Molecules Using Synchrotron Radiation. *J. Phys. B -At. Mol. Opt. Phys.* **1999**, *32*, 2763-2782.

(28) Baer, T.; Tuckett, R. P. Advances in Threshold Photoelectron Spectroscopy (TPEA) and Threshold Photoelectron Photoion Coincidence (TPEPICO). *Phys. Chem. Chem. Phys.* **2017**, *19*, 9698-9723.

(29) Gans, B.; Holzmeier, F.; Kruger, J.; Falvo, C.; Roder, A.; Lopes, A.; Garcia, G. A.; Fittschen, C.; Loison, J. C.; Alcaraz, C. Synchrotron-Based Valence Shell Photoionization of CH Radical. *J. Chem. Phys.* **2016**, *144*, 204307.

(30) Garcia, G. A.; Gans, B.; Krüger, J.; Holzmeier, F.; Röder, A.; Lopes, A.; Fittschen, C.; Alcaraz, C.; Loison, J. C. Valence Shell Threshold Photoelectron Spectroscopy of C₃H_x (x = 0–3). *Phys. Chem. Chem. Phys.* **2018**, *20*, 8707-8718.

(31) Holzmeier, F.; Lang, M.; Hader, K.; Hemberger, P.; Fischer, I. H₂CN⁺ and H₂CNH⁺: New Insight into the Structure and Dynamics from Mass-Selected Threshold Photoelectron Spectra. *J. Chem. Phys.* **2013**, *138*, 214310.

(32) Holzmeier, F.; Lang, M.; Hemberger, P.; Bodi, A.; Schäfer, M.; Dewhurst, R.; Braunschweig, H.; Fischer, I. Photoionization and Pyrolysis of a 1,4-Azaborinine: Retro-Hydroboration in the Cation and Identification of Novel Organoboron Ring Systems. *Chem. Eur. J.* **2014**, *20*, 9683-9692.

(33) Reusch, E.; Holzmeier, F.; Constantinidis, P.; Hemberger, P.; Fischer, I. Isomer-Selective Generation and Spectroscopic Characterization of Picolyl Radicals. *Angew. Chem. Int. Ed.* **2017**, *56*, 8000-8003.

(34) Steinbauer, M.; Hemberger, P.; Fischer, I.; Bodi, A. Photoionization of C₇H₆ and C₇H₅: Observation of the Fulvenallenyl Radical. *ChemPhysChem* **2011**, *12*, 1795-1797.

(35) Cunha de Miranda, B. K.; Alcaraz, C.; Elhanine, M.; Noller, B.; Hemberger, P.; Fischer, I.; Garcia, G.; Soldi-Lose, H.; Gans, B.; Viera Mendez, L. A.; Boye-Peronne, S.; Douin, S.; Zabka, J.; Botschwina, P. Threshold Photoelectron Spectroscopy of the Methyl Radical Isotopomers, CH₃, CH₂D, CHD₂ and CD₃: Synergy between VUV Synchrotron Radiation Experiments and Explicitly Correlated Coupled Cluster Calculations. *J. Phys. Chem. A* **2010**, *114*, 4818-4830.

(36) Schleier, D.; Constantinidis, P.; Faßheber, N.; Fischer, I.; Friedrichs, G.; Hemberger, P.; Reusch, E.; Sztaray, B.; Voronova, K. Kinetics of the a-C₃H₅+O₂ Reaction, Investigated by Photoionization Using Synchrotron Radiation. *Phys. Chem. Chem. Phys.* **2018**, *20*, 10721-10731.

(37) Oßwald, P.; Hemberger, P.; Bierkandt, T.; Akyildiz, E.; Köhler, M.; Bodi, A.; Gerber, T.; Kasper, T. In Situ Flame Chemistry Tracing by Imaging Photoelectron Photoion Coincidence Spectroscopy. *Rev. Sci. Instrum.* **2014**, *85*, 025101.

(38) Krüger, J.; Garcia, G. A.; Felsmann, D.; Moshhammer, K.; Lackner, A.; Brockhinke, A.; Nahon, L.; Kohse-Höinghaus, K. Photoelectron-photoion coincidence spectroscopy for multiplexed detection of intermediate species in a flame. *Phys. Chem. Chem. Phys.* **2014**, *16*, 22791-22804.

(39) Hemberger, P.; Custodis, V. B. F.; Bodi, A.; Gerber, T.; van Bokhoven, J. A. Understanding the Mechanism of Catalytic Fast Pyrolysis by Unveiling Reactive Intermediates in Heterogeneous Catalysis. *Nature Comm.* **2017**, *8*, 15946.

- (40) Sztaray, B.; Voronova, K.; Torma, K. G.; Covert, K. J.; Bodi, A.; Hemberger, P.; Gerber, T.; Osborn, D. L. CRF-PEPICO: Double Velocity Map Imaging Photoelectron Photoion Coincidence Spectroscopy for Reaction Kinetics Studies. *J. Chem. Phys.* **2017**, *147*, 013944.
- (41) Dyke, J. M.; Kirby, C.; Morris, A. Study of the Ionization Process $\text{BF}(X^2X^+) + \text{BF}(X^1X^+)$ by High-temperature Photoelectron Spectroscopy. *J. Chem. Soc. Faraday Trans.* **1983**, *79*, 483-490.
- (42) Pouilly, J. C.; Schermann, J. P.; Nieuwjaer, N.; Lecomte, F.; Grégoire, G.; Desfrancois, C.; Garcia, G. A.; Nahon, L.; Nandi, D.; Poisson, L.; Hochlaf, M. Photoionization of 2-Pyridone and 2-Hydroxypyridine. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3566-3572.
- (43) Nahon, L.; de Oliveira, N.; Garcia, G. A.; Gil, J., -F.; Pilette, B.; Marcouille, O.; Lagarde, B.; Polack, F. DESIRS: A State-of-the-Art VUV Beamline Featuring High resolution and Variable Polarization for Spectroscopy and Dichroism at SOLEIL. *J. Synchrotron Rad.* **2012**, *19*, 508-520.
- (44) Garcia, G. A.; Cunha de Miranda, B. K.; Tia, M.; Daly, S.; Nahon, L. DELICIOUS III: A Multipurpose Double Imaging Particle Coincidence Spectrometer for Gas Phase Vacuum Ultraviolet Photodynamics Studies. *Rev. Sci. Instrum.* **2013**, *84*, 053112.
- (45) Garcia, G. A.; Tang, X.; Gil, J.-F.; Nahon, L.; Ward, M.; Batut, S.; Fittschen, C.; Taatjes, C. A.; Osborn, D. L.; Loison, J.-C. Synchrotron-Based Double Imaging Photoelectron/Photoion Coincidence Spectroscopy of Radicals Produced in a Flow Tube: OH and OD. *J. Chem. Phys.* **2015**, *142*, 164201.
- (46) Mercier, B.; Compin, M.; Prevost, C.; Bellec, G.; Thissen, R.; Dutuit, O.; Nahon, L. Experimental and Theoretical Study of a Differentially Pumped Absorption Gas Cell Used as a Low Energy-Pass Filter in the Vacuum Ultraviolet Photon Energy Range. *J. Vac. Sci. Tech. A* **2000**, *18*, 2533-2541.
- (47) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. *MOLPRO, Version 2012.1, a Package of Ab Initio Programs*, Cardiff University: Cardiff, UK, 2012.
- (48) Western, C. M.; Billingham, B. E. Automatic Assignment and Fitting of Spectra with PGOPHER. *Phys. Chem. Chem. Phys.* **2017**, *19*, 10222-10226.

Scheme 1

71x13mm (300 x 300 DPI)

Figure_1

272x208mm (300 x 300 DPI)

Figure_3

272x208mm (300 x 300 DPI)

toc figure

338x190mm (96 x 96 DPI)