

## Synthesis of a New Structure $B_2H_4$ from $B_2H_6$

Diborane molecules are composed of two boron atomic centers and multiple hydrogen atoms, hence represented as  $B_2H_x$ . The structures of diborane species are still controversial. The normally existing  $B_2H_6$  contains two bridging B-H-B bonds and four terminal B-H bonds in the calculated most stable conformation; gaseous samples show also a central B-B bond. Other  $B_2H_x$  might be synthesized in collisions of  $H_2$  and boron atoms but no neutral diboron hydride species with less than six H atoms and a bridging B-H-B bond has been experimentally observed.

Bing-Ming Cheng and his co-workers dispersed  $B_2H_6$  in neon on a KBr

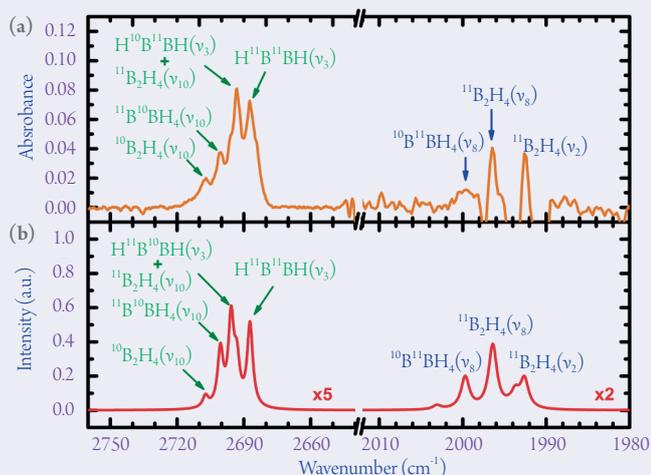


Fig. 1: Infrared absorption of  $B_2H_4$  in modes  $\nu_3$ ,  $\nu_8$  and  $\nu_{10}$  (a) from photolysis of  $B_2H_6/Ne = 1/1000$  at 3 K upon excitation at 122.6 nm and (b) from simulations. Some assignments are indicated.

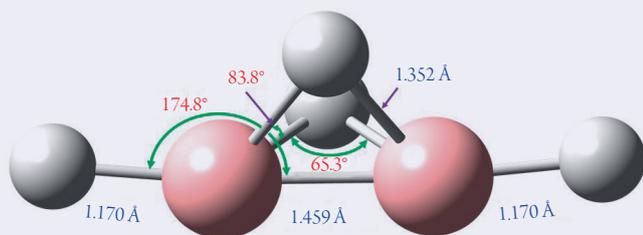


Fig. 2: Calculated structure of  $B_2H_4$ .

window at 3 K. They utilized the advantages of synchrotron radiation at BL21A2 to direct the vacuum-ultraviolet light onto the neon surface with wavelengths varied from 115 nm to 220 nm.<sup>1</sup> With excitation energies at light wavelengths 200 nm and 220 nm, a product was identified with infrared absorption spectra to be  $B_2H_2$ , previously detected elsewhere. On decreasing the wavelength of VUV light to 180 nm, many IR absorption features of other products appeared, as partly shown in Fig. 1. The structures observed by others failed to fit these new absorption signals, so diborane molecules of an entirely new structure should have been synthesized.

Cheng and his co-workers carefully undertook new quantum-chemical calculations of the harmonic and anharmonic vibrational motions to calculate the wavenumbers and intensities of each vibrational mode for various conformers. They eventually recognized the vibrational characteristics of neutral  $B_2H_4$  with two bridging B-H-B bonds and two terminal B-H bonds that satisfactorily fit the newly observed absorption features of the synthesized diborane species. The calculated structure of  $B_2H_4$  is shown in Fig. 2.

There are two major boron isotopes in nature,  $^{11}B$  and  $^{10}B$ ; the boron atoms in  $B_2H_4$  could hence be  $^{10}B^{10}B$  or  $^{10}B^{11}B$  or  $^{11}B^{11}B$ . As the atomic masses differ, the vibrational frequencies also vary. In Fig. 1, some vibrational modes for all  $^{10}B^{10}BH_4$ ,  $^{10}B^{11}BH_4$  and  $^{11}B^{11}BH_4$  were observed. To confirm the structure of the new species, neutral  $B_2H_4$ , Cheng replaced the hydrogen atoms with deuterium atoms. Both the absorption spectra and the calculated vibrational energies of  $B_2D_4$  conform to the calculated structure shown in Fig. 2. On that basis they assigned this new species as diborane(4). Because the infrared absorption features appear with vacuum-ultraviolet photons of wavelength 180 nm, the photolysis threshold to synthesize diborane(4) is about 6.6 eV. Although the detailed process of the dissociation and synthesis is still unrevealed, the new species is definitely formed from the precursor with vacuum-ultraviolet light as confirmed with infrared spectra. (Reported by Chen-Lin Liu)

This report features the work of Bing-Ming Cheng and his co-workers published in *Chem. Sci.* **6**, 6872 (2015).

### Reference

1. S.-L. Chou, J.-I. Lo, Y.-C. Peng, M.-Y. Lin, H.-C. Lu, B.-M. Cheng, and J. F. Ogilvie, *Chem. Sci.* **6**, 6872 (2015).

## Highly Selective Dissociation of Peptide Bonds

Molecules are composed of atoms and chemical bonds. To control a chemical reaction, breaking and forming specific chemical bonds is a key aspect. The use of photons to control the cleavage of a selected chemical bond in a complicated molecule remains a challenge in chemistry. Photochemists traditionally vary the ratios of cleavages of chemical bonds on tuning monochromatic radiation, typically in the ultraviolet region, to the energies of excited states of precursor molecules, but the selectivity is limited. This

method has been extended on combining infrared and ultraviolet photons and using vibrationally mediated photodissociation to control further the breakage of a chemical bond for small polyatomic molecules. An optimally shaped, strong-field laser pulse provides another method to control the cleavage of a specific chemical bond; shaping the pulse is a complicated process that has so far been applied to only few molecules.

A third method utilizes the near-edge X-ray

absorption of core electrons, in which the energy of a photon to excite a particular atom is sensitive to that atomic chemical environment. On tuning the X-ray wavelength to the K-edge absorption of atoms of a particular element, one might excite selectively that specific atomic entity. Such selective excitation can be specific to either an element or a site of the same element. An X-ray absorption corresponds to an excitation from the 1s orbital of this particular atom to an empty valence orbital or to direct ionization. One major channel after