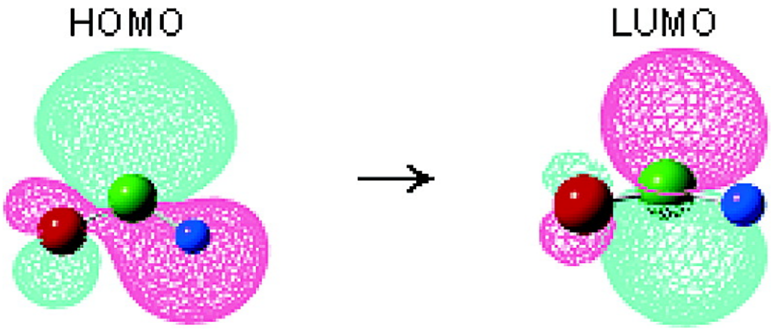
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

A Family of New Boron-Containing Free Radicals

Sheng-Gui He, Fumie X. Sunahori, and Dennis J. Clouthier

J. Am. Chem. Soc., **2005**, 127 (31), 10814-10815• DOI: 10.1021/ja053736a • Publication Date (Web): 16 July 2005



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Family of New Boron-Containing Free Radicals

Sheng-Gui He, Fumie X. Sunahori, and Dennis J. Clouthier*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received June 7, 2005; E-mail: dclaser@uky.edu

Boron halides are widely used in the semiconductor industry as feed gases in chemical vapor deposition, etching, and ion implantation processes. Despite their importance in such plasma and discharge chemistry, relatively little is known about the simplest boron halide free radicals. We have recently begun a program of spectroscopic studies of these species to establish methods of producing, detecting, and characterizing them in the gas phase, with the aim of providing the necessary spectroscopic database for quantifying boron-containing reactive intermediates in industrial environments. In this communication we report the discovery of a family of hitherto unknown HBX (X = F, Cl, Br) free radicals.

The HBX free radicals were prepared in a supersonic discharge jet source using techniques described in detail elsewhere.[1] For these experiments, a precursor mixture of 10% hydrogen in argon was seeded with a few percent of the vapor of the appropriate trihaloboron compound (BX_3). The corresponding deuterated species were prepared by substituting deuterium gas for hydrogen in the precursor mixture. A pulsed DC discharge fragmented the precursor molecules, yielding a variety of atomic, radical, and ionic species which reacted downstream prior to supersonic expansion cooling. The jet-cooled products were probed using laser-induced fluorescence (LIF) and wavelength-resolved emission spectroscopic techniques.

In the first of these experiments, a $BF_3 + H_2$ precursor mixture gave a rich, complex LIF spectrum in the 600−700 nm region, with partially resolved rotational structure at a resolution of 0.1 cm^{-1}. These bands were not present when hydrogen was omitted from the gas mixture and substitution of deuterium for hydrogen gave a different series of features in the same region. It proved difficult to find any assignable vibrational pattern to the LIF bands, suggesting that the beginning of the spectrum lies at much longer wavelengths.

Emission spectra obtained by exciting the intensity maxima of different features in the LIF spectra gave more readily interpretable information concerning the identity of the emitting species. Figure 1 shows the spectrum obtained by laser excitation of the Q-branch maximum at 15909 cm^{-1}. The spectrum consists of a series of doublets separated by an almost constant interval of 78−92 cm^{-1} and two vibrational intervals of 993 and 1311 cm^{-1}. Suspecting that this spectrum was due to the HBF free radical, we carried out a series of high level ab initio calculations of the ground-state properties of the HBX radicals using the Gaussian 03 suite of programs.[2,3] At the coupled cluster singles and doubles with triples included perturbatively [CCSD(T)] level of theory with Dunning's correlation consistent triple-ζ basis set augmented by diffuse functions[4] [aug-cc-pVTZ], we obtained HBF bending and B−F stretching mode frequencies of 1008 and 1320 cm^{-1}, respectively, in good agreement with experiment. Deuteration shifted the experimental frequencies to 771 and 1295 cm^{-1} compared to theoretical values of 778 and 1305 cm^{-1}.

Further confirmation that the spectra are due to HBF/DBF comes from the calculated molecular structures and the doublet splittings in the emission data. Theory predicts that all of the HBX radicals are bent near-prolate asymmetric top molecules in the $^2A'$ ground state, with bond angles from 121 to 124° (HBF to HBBr). The *a*-inertial axis lies almost coincident with the B−X bond so that the *A* rotational constant depends primarily on the mass of the hydrogen atom and the HBX bond angle. In the near-prolate asymmetric top approximation, the ground-state energy levels are given by the expression

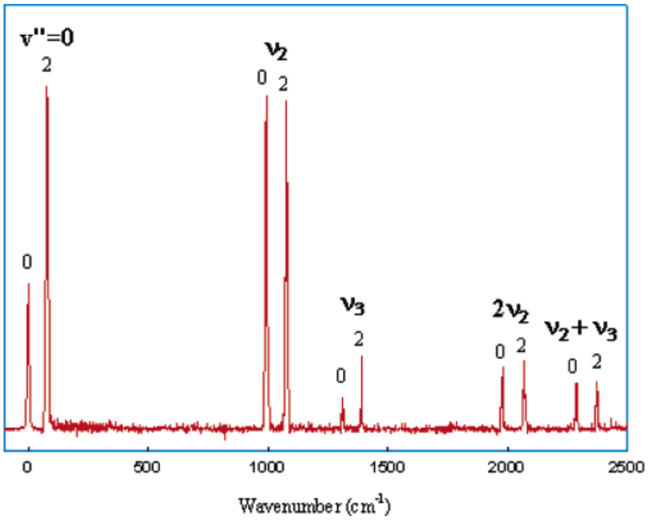


Figure 1. Single vibronic level emission spectrum of HBF excited at 15909 cm^{-1}. The wavenumber scale is displacement from the excitation laser and gives a direct measure of the ground-state energy of each band in the spectrum. Each vibronic transition consists of two features, both originating from $K_a = 1$ in the upper state and terminating at $K_a = 0$ or 2 as indicated. The left-hand feature of the $v'' = 0$ transition was attenuated as it was obscured by scattered laser light.

$$F(J,K_a) = (A - \bar{B})K_a^{\,2} + \bar{B}J(J+1) \qquad (1)$$

where A and $\bar{B} = (B + C)/2$ are the rotational constants. Neglecting the small J-dependent term in eq 1, we interpret the doublets in the spectrum as rovibronic transitions from the excited state $K_a = 1$ level down to the $K_a = 0$ (left-hand member) and $K_a = 2$ (right-hand member) stacks of rotational states in the HBF ground state. From the ab initio structure, we calculate the approximate splitting to be 72.4 cm^{-1}, in agreement with the observed 78.0 ± 2 cm^{-1} $v'' = 0$ value. Since the molecular structure cannot change appreciably on deuteration, the splitting in DBF can be readily calculated from the geometry and is predicted to be 42.4 cm^{-1}, in accord with the 47.4 ± 2 cm^{-1} observed value.

The splitting patterns in the emission spectra change, depending on which feature in the LIF spectrum is excited. In some cases no splitting is observed, whereas in others the splitting becomes larger. All of these observations are readily interpreted if we assume that the relevant rotational selection rule is $\Delta K_a = \pm 1$. Population of an upper state $K_a = 0$ level (Σ if linear) yields a single transition

10.1021/ja053736a CCC: $30.25

Table 1. Experimental and ab Initio Gound-State Parameters of the HBX/DBX (X = F, Cl, Br) Free Radicals[a]

	HBF/DBF		HBCl/DBCl		HBBr/DBBr	
	expt	theory[b]	expt	theory[b]	expt	theory[b]
ν_1	−	2541/1879	−	2641/1951	−	2653/1959
ν_2	993/771	1008/778	836/644	843/652	834/−	846/603
ν_3	1311/1295	1320/1305	894/864	909/872	−/738	726/749
$A - \bar{B}$	19.5/11.9	18.1/10.6	21.2/12.2	19.4/11.1	20.4/11.8	19.6/11.2
r(B−H) (Å)[b]		1.203		1.191		1.190
r(B−X) (Å)[b]		1.309		1.724		1.872
θ(HBX) (deg)[b]		121.1		123.3		123.8

[a] All quantities except the geometric parameters are in cm^{-1} and are for the most abundant isotopomer in each case. [b] CCSD(T)/aug-cc-pVTZ ab initio values.

with no splitting down to $K_a = 1$, whereas transitions from $K_a = 1$ (Π) or $K_a = 2$ (Δ) yield doublets with splittings of $4(A - \bar{B})$ and $8(A - \bar{B})$, respectively, as calculated from eq 1 and precisely as is observed.

Experiments with boron triiodide failed to yield any spectra, due to the low vapor pressure and limited thermal stability of BI_3, but BCl_3 and BBr_3 gave LIF spectra with both hydrogen and deuterium. In these cases, bands were also found in the 600−700 nm region, although the spectra were complicated by overlap with bands of the BCl_2 and BBr_2 radicals which are also under current investigation in our laboratory. The wavelength-resolved emission spectra of HBCl/DBCl and HBBr/DBBr were similar to those of HBF/DBF, with activity in the bending and B−X stretching modes. In HBCl the assignments are simply our best estimates as the bending and stretching modes are in Fermi resonance, and it is difficult to identify which is which without further isotopic data. It is important to note that the observed B−F and B−Cl stretching frequencies are substantially lower than the known 1633 and 1122 cm^{-1} values for the linear HBF^+ and $HBCl^+$ ions[5,6] but quite similar to the 1379 and 829 cm^{-1} vibrational fundamentals[7,8] of BF and BCl. The boron−hydrogen stretching frequency, ν_1, was not evident in the emission spectra of any of the radicals. The experimental results and the corresponding ab initio predictions are summarized in Table 1, which shows good agreement between theory and experiment in all cases, leaving no doubt that the species detected are indeed the HBX/DBX free radicals.

Although the ground-state energy levels of these radicals appear to be fairly well-behaved, the excited-state levels, as judged from the LIF spectra, are much more complex and have defied assignment to date. On the basis of the known spectrum[9] of BH_2 and Walsh diagrams,[10] one would predict that the ground and first excited states of the HBX radicals are the two components (a Renner−Teller pair) of a $^2\Pi$ state at linear geometry. In the simplest approximation, the ground-state electronic configuration is $(a'')^2\,(a')^2\,(a')^1$, which would be predicted to have a nonlinear structure, in accord with our observations, but promotion of an electron from the HOMO to the LUMO yields a $(a'')^2\,(a')^2\,(a'')^1$ excited-state configuration, which should have a linear geometry. A linear excited-state geometry would be consistent with the complexity of the LIF spectra, since the upper state K_a levels would now correspond to the vibrational angular momentum components of different vibrational levels, disrupting the usual asymmetric top K-type sub-band structure. The only difficulty is that linear−bent transitions would be expected to have long bending progressions in the emission spectra, which are not observed. It may be that the bending progression is actually much stronger beyond 850 nm, which is the practical detection limit of our apparatus, or that the barrier to linearity in the ground state is so low that it precludes extensive vibrational structure in the emission spectrum.

The data presented in this work will be helpful in attempts to find the infrared matrix isolation spectra of the HBX radicals. Our calculations indicate that the radicals have significant dipole moments (−0.5 D) so they should also be detectable by microwave spectroscopy, although the rotational constants are quite large. Finally, thorough ab initio investigations of the ground- and excited-state potentials and energy levels would be very useful as an adjunct to our ongoing investigations of the rotational and vibrational structure in the LIF spectra.

Acknowledgment. F.X.S. is grateful to the University of Kentucky Graduate School for a Kentucky Opportunity Fellowship. We thank the National Science Foundation for support of this research.

Supporting Information Available: Complete ref 2. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Harjanto, H.; Harper, W. W.; Clouthier, D. J. *J. Chem. Phys.* **1996**, *105*, 10189−10200. (b) Harper, W. W.; Clouthier, D. J. *J. Chem. Phys.* **1997**, *106*, 9461−9473.
(2) Frisch, M. J. et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford CT, 2004.
(3) Previous Hartree−Fock calculations on HBF have been reported by Brotchie, D. A.; Thomson, C. *Chem. Phys. Lett.* **1973**, *22*, 338−343.
(4) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(5) Kawaguchi, K.; Hirota, E. *Chem. Phys. Lett.* **1986**. *123*, 1−3.
(6) Hunt, N. T.; Liu, Z.; Davies, P. B. *Mol. Phys.* **1999**, *97*, 205−208.
(7) Nakanaga, T.; Takeo, H.; Kondo, S.; Matsumura, C. *Chem. Phys. Lett.* **1985**, *114*, 88−91.
(8) Maki, A. G.; Lovas, F. J.; Suenram, R. D. *J. Mol. Spectrosc.* **1982**, *91*, 424−429.
(9) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc. London, Ser. A* **1967**, *298*, 142−159.
(10) Walsh, A. D. *J. Chem. Soc.*, **1953**, 2260−2262.

JA053736A