The Identification of the Classical Donor–Acceptor Complex $H_3N–BF_3$ in the Gas Phase

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The $J = 1 \leftarrow 0$ rotational transitions of the four isotopomers $H_3{}^{14}N^{11}BF_3$, $H_3{}^{14}N^{10}BF_3$, $H_3{}^{15}N^{11}BF_3$ and $H_3{}^{15}N^{10}BF_3$ of the archetypal donor–acceptor complex formed between ammonia and boron trifluoride have been detected with a pulsed-nozzle, Fourier-transform microwave spectrometer; by using a fast-mixing nozzle, H_3NBF_3 has been isolated in collisionless expansion before condensation can occur, thereby allowing the first detection of this elusive species in the gas phase.

By virtue of its preparation in 1809 by Gay-Lussac[1] and in 1812 by Davy[2] as a solid adduct, H_3NBF_3 has been referred to as the first known coordination compound of any element.[3] H_3NBF_3 is also the simplest of the class of compounds R_3BNH_3 used by G. N. Lewis to illustrate the dative bond.[4] All of this allows H_3NBF_3 to be described as the archetypal donor–acceptor complex. Curiously, it has so far eluded detection in the vapour phase. On mixing NH_3 and BF_3 gases at room temperature in a fast flow system, Lovas and Johnson[5] were able to detect only the microwave spectrum of the planar molecule $H_2N{=}BF_2$ weakly and found that heating to 140 °C the white solid formed on mixing the gases also gave the same spectrum. An earlier attempt by Prokhorov and Shipulo[6] to observe the rotational spectrum of H_3NBF_3 in the vapour above the heated crystalline solid was unsuccessful. More recently, Kroto and McNaughton[7] examined the photoelectron spectrum of the vapour produced from the solid adduct at 140 °C but again only H_2NBF_2 was detected. This evidence demonstrates that although NH_3 and BF_3 react rapidly on mixing to produce a solid condensate, it is difficult to generate H_3NBF_3 in spectroscopically detectable concentrations in the vapour by heating the solid and only $H_2N{=}BF_2$ appears to be observable. In fact, it has been suggested[8] that solid H_3NBF_3 undergoes irreversible decomposition when heated above 125 °C. On the other hand, H_3NBF_3 has been detected by matrix isolation methods.[9] One possible way to observe H_3NBF_3 in the gas phase is to probe spectroscopically a nascent mixture of NH_3 and BF_3 in the short period before the solid is precipitated.

We report the first identification of the classical donor–acceptor complex H_3NBF_3 in the gas phase. It was detected through its rotational spectrum with a pulsed-nozzle, Fourier-transform microwave spectrometer[10] employing a fast-mixing nozzle.[11,12] The fast-mixing nozzle consisted of a pair of concentric tubes venting into the Fabry–Pérot cavity at the same point. A continuous stream of a gas mixture composed of 70% BF_3 (Matheson Inc.) in argon at a stagnation pressure of 1 atm issued into the vacuum chamber from the 0.3 mm diameter central tube while the other component, 2% NH_3 (Argo International) in argon at a stagnation pressure of 3 atm, was pulsed into the 0.7 mm diameter outer tube from a General Valve Corp. Series Nine solenoid valve. Molecules of H_3NBF_3 formed at the point of mixing travel at supersonic speeds and within 10 nozzle diameters (*i.e.* a few millimetres) are in collisionless expansion. Consequently, species that survive clustering and condensation in the first *ca.* 10

microseconds will persist and can be characterized spectroscopically in effective isolation in the usual way.[10]

We first established that the $J = 1 \leftarrow 0$ transition of H_2NBF_2 centred at 14 483 MHz[5] was not present in the supersonically expanded gas emerging from the nozzle. Apparently, H_2NBF_2 is not formed in the gas-phase reaction of NH_3 and BF_3 on the timescale of *ca.* 10 microseconds before collisionless expansion sets in. Then, an extensive search revealed a highly congested group of approximately 20 weak transitions falling within a range of 2 MHz centred on 9 297 MHz which required both NH_3 and BF_3.

This set of lines was eventually assigned as the $J = 1 \leftarrow 0$ transitions of the two isotopomers $H_3{}^{14}N^{11}BF_3$ and $H_3{}^{14}N^{10}BF_3$, accidentally coincident in frequency because the B atom lies virtually on the molecular centre of mass. The large number of components arises not only because each $J = 1 \leftarrow 0$ transition has associated with it a complicated hyperfine structure generated by quadrupole coupling of the ^{14}N ($I = 1$) and ^{11}B ($I = 3/2$) or ^{10}B ($I = 3$) nuclear spins to the rotational angular momentum but also because each hyperfine component is in turn split into a doublet of separation approximately 60 kHz. There is also evidence of the partially resolved effects of spin–spin splitting arising from the H and F nuclei but these were ignored in the analysis given below.

We shall show that H_3NBF_3 has an N–B bond only slightly longer than the C–C bond in the isoelectronic molecule CH_3CF_3. In symmetric-top molecules, like CH_3CF_3, rotational transitions in the ground torsional state can exhibit small A,E splittings but only by virtue of high order vibration–torsion–rotation interactions.[13] The threefold barrier $V_3 = 14.6$ kJ mol^{-1} in CH_3CF_3 is sufficiently high[14] that no A,E splitting can be resolved in the $J = 1 \leftarrow 0$ transition even in a molecular beam.[15] A reduced barrier is expected in H_3NBF_3 and would lead to an increased A,E splitting. The doubling of approximately 60 kHz is assigned to this effect and is similar in magnitude to that observed[13] in CH_3SiH_3, for which $V_3 = 7.09$ kJ mol^{-1}. Presumably, a similar barrier height for H_3NBF_3 is thereby implied.

The nuclear quadrupole hyperfine structure for each state A and E of each isotopomer was fitted separately in a conventional iterative least-squares analysis in which only diagonal matrix elements of the two-quadrupole Hamiltonian $H = H_{Q(\mathrm{N})} + H_{Q(\mathrm{B})}$ in the coupled basis $\mathbf{I}_\mathrm{N} + \mathbf{J} = \mathbf{F}_1$, $\mathbf{F}_1 + \mathbf{I}_\mathrm{B} = \mathbf{F}$ were retained.[16] Unperturbed line-centre frequencies υ_0 and the various nuclear quadrupole coupling constants $\chi(^{14}N)$,$\chi(^{11}B)$ and $\chi(^{10}B)$ so obtained are collected in Table 1. To confirm the spectral assignment, the isotopomers $H_3{}^{15}N^{11}BF_3$ and $H_3{}^{15}N^{10}BF_3$ were also investigated, with the aim of simplifying the spectrum by removing ^{14}N coupling effects. A group of transitions observed in a 1 MHz range of frequencies centred on 9098 MHz was assigned to the interpenetrating B-nuclear quadrupole hyperfine components of the $J = 1 \leftarrow 0$ A,E pair of torsional ground-state transitions of $H_3{}^{15}N^{11}BF_3$ and $H_3{}^{15}N^{10}BF_3$. Values of υ_0 and $\chi(B)$ obtained for the ^{15}N species are included in Table 1.

The spectral congestion and consequent overlap of transitions result in errors in the coupling constants that are larger than usual, especially for the weaker ^{10}B species, but nevertheless the $\chi(B)$ of $H_3{}^{14}NBF_3$ and $H_3{}^{15}NBF_3$ agree within experimental error (Table 1). Moreover, the ratios $\chi(^{10}B) : \chi(^{11}B) = 2.04(9)$ (A) and 2.07(5) (E) for the $H_3{}^{14}NBF_3$ isotopomers are in satisfactory agreement with the value 2.084(2) accepted for the ratio of the B nuclear electric quadrupole moments.[17] The corresponding ratios for the ^{15}N isotopomers are 2.01(7) (A) and 2.11(4) (E), respectively.

The observed nuclear quadrupole hyperfine patterns in the $J = 1 \leftarrow 0$ transitions of the isotopomers $H_3{}^{14}N^{11}BF_3$, $H_3{}^{14}N^{10}BF_3$, $H_3{}^{15}N^{11}BF_3$ and $H_3{}^{15}N^{10}BF_3$ together with the small A,E splittings attributed to internal rotation are consistent with a symmetric-top C_{3v} arrangement of the nuclei of the type H_3NBF_3. Unfortunately, the $J = 2 \leftarrow 1$ transitions were outside the high-sensitivity range of our spectrometer and were not available to confirm the symmetric-top nature of the complex. Nevertheless, the proposed arrangement seems likely in view of the established geometries of H_3NBH_3,[18] Me_3NBH_3[19] and Me_3NBF_3.[20]

Table 1 Unperturbed frequencies of $J = 1 \leftarrow 0$ transitions and nuclear quadrupole coupling constants for the ground state of four isotopomers of H_3NBF_3

Isotopomer	Torsional state[a]	υ_0/MHz	$\chi(^{14}N)$/MHz	$\chi(B)$/MHz
$H_3{}^{14}N^{11}BF_3$	A	9297.269(1)	−2.301(6)	1.21(2)
	E	9297.330(1)	−2.324(3)	1.128(7)
$H_3{}^{14}N^{10}BF_3$[b]	A	9297.139(4)	−2.31(2)	2.47(7)
	E	9297.204(3)	−2.36(1)	2.33(5)
$H_3{}^{15}N^{11}BF_3$	A	9097.934(2)	—	1.187(10)
	E	9098.001(1)	—	1.148(3)
$H_3{}^{15}N^{10}BF_3$[b]	A	9098.172(7)	—	2.39(6)
	E	9098.237(3)	—	2.42(3)

[a] Each ground state transition is split into a doublet by high order vibrational–rotational–torsional effects. The assignment of the A label to the lower frequency component follows ref. 13. [b] The congestion of the spectra coupled with the lower abundance of ^{10}B led to a poorer determination of the spectroscopic constants for the ^{10}B isotopomers.

Given that the B and N nuclei lie on the C_3 (z) axis, the distance r(N–B) is available as follows. The r_s-coordinate z_N of ^{14}N in $H_3{}^{14}N^{11}BF_3$ is straightforwardly available from the change in B_0 on ^{15}N substitution through Kraitchman's equation[21] for substitution on the axis of a symmetric top molecule. Ignoring the effects of centrifugal distortion, we have $B_0 = \frac{1}{2}\upsilon_0$ ($J = 1 \leftarrow 0$) and obtain $z_\mathrm{N} = 1.555$ Å for both A and E states of $H_3{}^{14}N^{11}BF_3$ using Kraitchman's equation. The tiny changes in υ_0 on substitution of ^{10}B by ^{11}B (125 kHz for $H_3{}^{14}NBF_3$ and −237 kHz for $H_3{}^{15}NBF_3$) reveal that the B atom lies very close to the centre of mass in $H_3{}^{14}NBF_3$ but on the opposite side from N. Detailed arguments† allow the estimate $z_\mathrm{B} = -0.03(3)$ Å. The implication of this analysis is that r(N–B) = 1.59(3) Å.

The distance r(N–B) in H_3NBF_3 can be compared with 1.60(2) Å from the X-ray diffraction study of the solid condensate[22] and with 1.68 Å obtained in *ab initio* calculations.[23] The molecules H_3NBF_3 and H_2NBF_2 are isoelectronic with H_3CCF_3 and H_2CCF_2, respectively. The N–B single and N=B double bond lengths of 1.59(3) and 1.402(24) Å[5] are consistently longer than the corresponding C–C bond lengths of 1.492[24] and 1.315 Å,[25] respectively, of the carbon analogues. If H_3NBF_3 is isostructural, as well as isoelectronic, with H_3CCF_3, the N and B nuclei would sit at the centre of an approximately tetrahedral environment, with only a small electric field gradient at each along the symmetry axis z. The

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† Usually, the effect on the rotational constant of an isotopic substitution can be described on the sum of two parts. An increase of mass will decrease the *equilibrium* rotational constant but usually decreases the magnitude of the zero-point contribution to B_0, which is negative in sign. If B is very close to the centre of mass, the latter contribution will dominate and lead to an increase in υ_0 (and presumably B_0), as observed in the $J = 1 \leftarrow 0$ transitions of $H_3{}^{14}NBF_3$ when ^{11}B replaces ^{10}B. For the isotopomers containing ^{15}N, on the other hand, $\Delta\upsilon_0$ is now negative, presumably because the first contribution is larger. These facts suggest that the B atom lies very close to the centre of mass in $H_3{}^{14}N^{11}BF_3$ but probably on the opposite side from N. Substitution of ^{15}N moves the centre of mass towards N, increases the magnitude of z_B and hence of the equilibrium value of ΔB so that it exceeds the contribution due to zero-point changes. Experience shows that changes of the magnitude observed mean that B lies within 0.05 Å of the centre of mass and hence we choose $z_\mathrm{B} = -0.03$ (3) Å.

relatively small magnitudes of $\chi(^{14}N)$ and $\chi(B)$ (Table 1) are consistent with such an assumption. Certainly, $\chi(^{14}N)$ is small compared with $\chi_0(^{14}N) = -4.09$ MHz in free $^{14}NH_3$.[26] A more quantitative interpretation of $\chi(^{14}N)$ and $\chi(B)$ to give the N–B bond order must await a detailed knowledge of the geometry at N and B. Further work is in progress.

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References

1 J. L. Gay-Lussac and J. L. Thénard, *Mem. de Phys. et de Chim de la Soc. d'Arcueil*, 1809, **2**, 210.
2 J. Davy, *Phil. Trans.*, 1812, **102**, 365.
3 N. N. Greenwood, in *Comprehensive Inorganic Chemistry*, Pergamon, Oxford, 1973, vol. 1, p. 666.
4 G. N. Lewis, *Valence and the Structures of Atoms and Molecules*, The Chemical Catalog Company Inc., New York, 1923, p. 98.
5 F. J. Lovas and D. R. Johnson, *J. Chem. Phys.*, 1973, **59**, 2347.
6 A. M. Prokhorov and G. P. Shipulo, *Opt. Spectrosc.*, 1960, **8**, 218.
7 H. W. Kroto and D. McNaughton, *J. Chem. Soc., Dalton Trans.*, 1985, 1767.
8 A. W. Laubengayer and G. K. Condike, *J. Am. Chem. Soc.*, 1948, **70**, 2274.
9 R. L. Hunt and B. S. Ault, *Spectros. Int. J.*, 1982, **1**, 31.
10 A. C. Legon, *Annu. Rev. Phys. Chem.*, 1983, **34**, 275.
11 A. C. Legon and C. A. Rego, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1915.
12 T. Emilsson, T. D. Klots, R. S. Ruoff and H. S. Gutowsky, *J. Chem. Phys.*, 1990, **93**, 6971.
13 W. L. Meerts and I. Ozier, *J. Mol. Spectrosc.*, 1982, **94**, 38.
14 H. T. Minden and B. P. Dailey, *Phys. Rev.*, 1951, **82**, 338.
15 W. L. Meerts and I. Ozier, *Chem. Phys.*, 1991, **152**, 241.
16 P. Thaddeus, L. C. Krisher and J. H. N. Loubser, *J. Chem. Phys.*, 1964, **40**, 257.
17 W. Gordy and R. L. Cook, *Techniques of Organic Chemistry*, Microwave Molecular Spectra, ed. A. Weissberger, Interscience, New York, vol. IX, 1970.
18 C. R. Thorne, R. D. Suenram and F. J. Lovas, *J. Chem. Phys.*, 1983, **78**, 167.
19 P. Cassoux, R. L. Kuczkowski, P. S. Bryan and R. C. Taylor, *Inorg. Chem.*, 1975, **14**, 126.
20 P. Cassoux, R. L. Kuczkowski and A. Serafini, *Inorg. Chem.*, 1977, **16**, 3005.
21 J. Kraitchman, *Am. J. Phys.*, 1953, **21**, 17.
22 J. L. Hoard, S. Geller and W. M. Cashin, *Acta Crystallogr.*, 1951, **4**, 396.
23 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley Interscience, New York, 1986, p. 217.
24 L. F. Thomas, J. S. Heeks and J. Sheridan, *Z. Elecktrochem.*, 1957, **61**, 935.
25 V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, 1963, **38**, 2693.
26 M. D. Marshall and J. S. Muenter, *J. Mol. Spectrosc.*, 1981, **85**, 322.