[11] H. Schroeder, R. Leventis, S. Rex, M. Schelhaas, E. Nagele, H. Waldmann, J. R. Silvius, *Biochemistry* **1997**, *36*, 13102 – 13109.
[12] F. Kotzyba-Hibert, I. Kapfer, M. Goeldner, *Angew. Chem.* **1995**, *107*, 1391 – 1408; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1296 – 1312.
[13] T. A. Kale, C. Raab, N. Yu, D. E. Dean, M. D. Distefano, *J. Am. Chem. Soc.* **2001**, *123*, 4373 – 4381.
[14] G. Dorman, G. D. Prestwich, *Trends Biotechnol.* **2000**, *18*, 64 – 77.
[15] B. Bader, K. Kuhn, D. J. Owen, H. Waldmann, A. Wittinghofer, J. Kuhlmann, *Nature* **2000**, *403*, 223 – 226.
[16] K. Kuhn, D. J. Owen, B. Bader, A. Wittinghofer, J. Kuhlmann, H. Waldmann, *J. Am. Chem. Soc.* **2001**, *123*, 1023 – 1035.
[17] D. M. Marecak, Y. Horiuchi, H. Arai, M. Shimonaga, Y. Maki, T. Koyama, K. Ogura, G. D. Prestwich, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 1973 – 1978.
[18] D. Bar-Sagi, J. R. Feramisco, *Cell* **1985**, *42*, 841 – 848.
[19] R. H. Cool, G. Schmidt, C. U. Lenzen, H. Prinz, D. Vogt, A. Wittinghofer, *Mol. Cell. Biol.* **1999**, *19*, 6297 – 6305.
[20] E. Choy, V. K. Chiu, J. Silletti, M. Feoktistov, T. Morimoto, D. Michaelson, I. E. Ivanov, M. R. Philips, *Cell* **1999**, *98*, 69 – 80.
[21] A. M. de Vos, L. Tong, M. V. Milburn, P. M. Matias, J. Jancarik, S. Noguchi, S. Nishimura, K. Miura, E. Ohtsuka, S. H. Kim, *Science* **1988**, *239*, 888 – 893.
[22] E. F. Pai, W. Kabsch, U. Krengel, K. C. Holmes, J. John, A. Wittinghofer, *Nature* **1989**, *341*, 209 – 214.
[23] K. Scheffzek, M. R. Ahmadian, W. Kabsch, L. Wiesmuller, A. Lautwein, F. Schmitz, A. Wittinghofer, *Science* **1997**, *277*, 333 – 338.
[24] K. Yamasaki, G. Kawai, Y. Ito, Y. Muto, J. Fujita, T. Miyazawa, S. Nishimura, S. Yokoyama, *Biochem. Biophys. Res. Commun.* **1989**, *162*, 1054 – 1062.

Bismuthine BiH_3: Fact or Fiction? High-Resolution Infrared, Millimeter-Wave, and Ab Initio Studies**

Wolfgang Jerzembeck, Hans Bürger,*
Lucian Constantin, Laurent Margulès, Jean Demaison,
Jürgen Breidung, and Walter Thiel

Standard Inorganic Chemistry textbooks[1] report that bismuthine, BiH_3, is a common although unstable Group 15 hydride. Typically only the boiling point[2] of +16.8 °C is mentioned for characterization. Apart from the early observation of a "volatile bismuth hydride" by Paneth in 1918,[3] its relevance in analytical chemistry,[4] and a mass spectrometric study,[5] all experimental information on BiH_3 (synthesis, isolation, and vapor pressure) originates from the report by Amberger in 1961.[2] To the best of our knowledge nobody has to date been able to repeat Amberger's (admittedly presumptuous) synthesis of BiH_3 by decomposition of CH_3BiH_2 at −55 to −45 °C, or to develop an alternative route to this compound. Hence, unlike the case of the short-lived monohydride BiH,[6] neither the structure nor the vibrational spectrum of BiH_3 have been determined experimentally.

We report herein the successful repetition of Amberger's synthesis of BiH_3 and its unambiguous characterization by independent, modern spectroscopic methods, which are supported by ab initio caclulations. Our particular interest in BiH_3 concerns those structural and spectroscopic properties that are expected to be unique for BiH_3. First, BiH_3 should have the smallest H-X-H bond angle (ca. 90.0°) of any of the hydrides of the composition XH_2 and XH_3 (Figure 1). In the vibrational ground state, BiH_3 should thus be an oblate symmetric top ($I_a = I_b < I_c$) extremely close to the spherical top ($I_a = I_b = I_c$) limit, even more so than SbH_3.[7] In vibrationally excited states it may switch to a prolate symmetric top with $I_a < I_b = I_c$. Therefore it should reveal, with unprecedented distinction, particular ground and excited state rotational energy patterns that require appropriate reductions of the rotational – vibrational Hamiltonian.[8] Owing to the near-rectangular H-Bi-H angle, the heavy central atom, the expected small HBi/BiH′ coupling, and the large anharmonicity of the BiH stretching motion, BiH_3 would also be a prototype molecule for local mode behavior.[9]

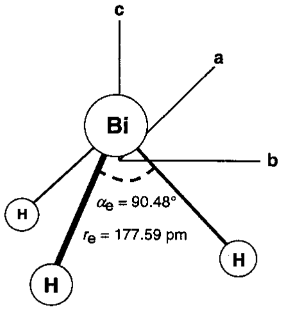

Figure 1. Molecular structure of BiH_3 with principal axes of inertia indicated; α_e, r_e = bond angle and length in the equilibrium structure.

After numerous failures we were able to repeat the reported synthesis[2] and eventually obtained apparently pure BiH_3 in quantities sufficient to enable us to carry out gas-phase infrared (IR) and millimeter-wave (MMW) measurements over periods of minutes to hours. In brief, we first prepared $Bi(CH_3)_3$ from $BiCl_3$ and CH_3MgI, and then reacted this with $BiCl_3$ to give CH_3BiCl_2 by using standard procedures.[10] CH_3BiCl_2 was then reduced with $LiAlH_4$ in di-*n*-butyl ether at −78 °C to give CH_3BiH_2 whose disproportionation at −55 to −45° C yielded BiH_3 along with methylbismuthanes. Some hydrogen, which formed by decomposition of the hydrides, was pumped off while the reaction mixture was cooled by using liquid nitrogen. Thereafter this mixture was allowed to warm to about −50° C and volatile material expanded into cooled absorption cells until a total vapor pressure of between 10 and 100 Pa was reached.

IR spectra were recorded in the region for stretching fundamentals $\nu_1(A_1)/\nu_3(E)$ at about 1700 cm^{-1} with a resolution of 4.4×10^{-3} cm^{-1} (Figure 2), and in the region for bending modes $\nu_2(A_1)/\nu_4(E)$ at about 750 cm^{-1} with a resolution of 6.6×10^{-3} cm^{-1} (Figure 3).[11] An external dou-

---

[*] Prof. Dr. H. Bürger, Dr. W. Jerzembeck
Anorganische Chemie
Bergische Universität Wuppertal
42097 Wuppertal (Germany)
Fax: (+49) 202-439-2901
E-mail: buerger1@uni-wuppertal.de

Dr. L. Constantin, Dr. L. Margulès, Dr. J. Demaison
Laboratoire de Physique des Lasers, Atomes et Molécules
Université de Lille 1
59655 Villeneuve d'Ascq (France)

Dr. J. Breidung, Prof. Dr. W. Thiel
Max-Planck-Institut für Kohlenforschung
45470 Mülheim (Germany)

[**] We thank the German – French PROCOPE program and the PICS 599 project for support. We also thank Prof. H. Stoll, Stuttgart, for helpful discussions.

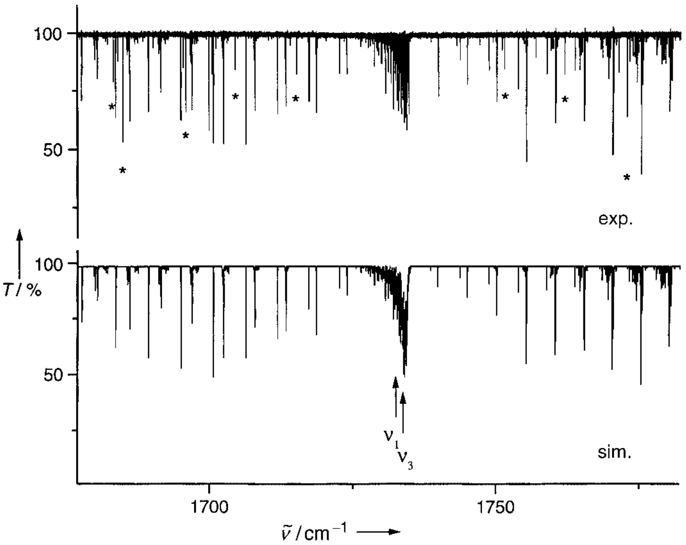

Figure 2. The ν_1 and ν_3 bands of BiH_3. Lines denoted by an asterisk in the experimental spectrum (top) are attributed to residual H_2O in the interferometer. In the simulated spectrum (bottom) the band centers are indicated by arrows.

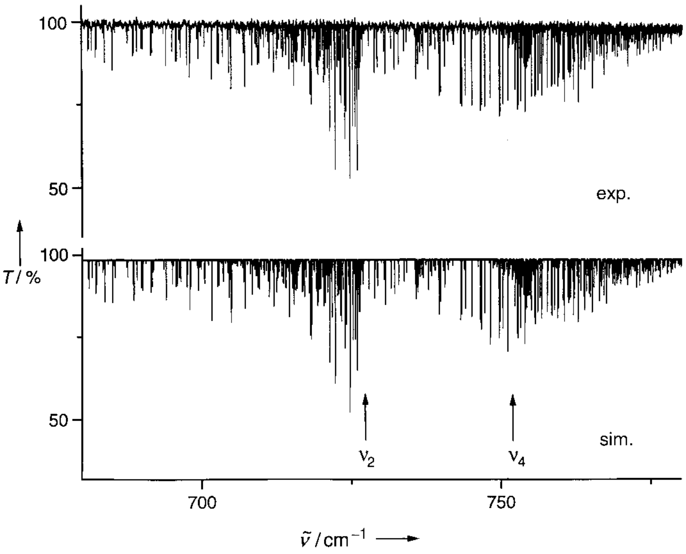

Figure 3. The ν_2 and ν_4 bands of BiH_3: Experimental (top) and simulated spectrum (bottom; band centers are indicated by arrows).

ble-jacketed glass cell (inner diameter 70 mm, 120 cm long) equipped with NaCl windows and cooled to −40 °C was used. At a total pressure of about 100 Pa data were collected for periods of 10–30 min before absorptions assignable to BiH_3 disappeared and it was necessary to recharge the cell. We confirm Amberger's observation[2] that deposited metallic Bi accelerates the decomposition of BiH_3 significantly. Altogether 30 and 76 scans were collected in the ν_1/ν_3 and ν_2/ν_4 spectral regions, respectively. The analysis of the spectra established that essentially all observed absorption lines could be assigned to the ν_1, ν_2, ν_3, and ν_4 bands of $^{209}BiH_3$ (Bi is a monoisotopic element).

Since the analysis of the spectra required highly accurate constants of the ground vibrational state we also measured rotational $J = 1 \leftarrow 0$, $2 \leftarrow 1$, $4 \leftarrow 3$, and $8 \leftarrow 7$ transitions in the 158, 317, 633, and 1260 GHz ranges, respectively.[12] The $J = 8 \leftarrow 7$, $K = 3^+$ transition is illustrated in Figure 4. The observed nuclear quadrupole hyperfine structure is in agreement with a spin $I = 9/2$ for ^{209}Bi. Rotational and vibrational (ground-state combination difference) data, including 210 combinations with $\Delta K \neq 0$ providing C_0, were merged and fitted.[13]

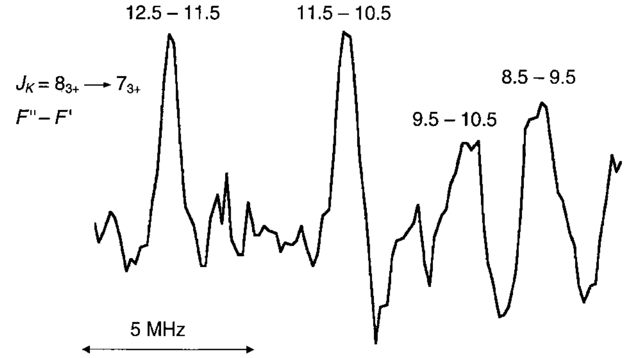

Figure 4. Part of the $J_K = 8_{3+} \leftarrow 7_{3+}$ transition of BiH_3, split by quadrupole hyperfine structure, between the upper components 3+ of the split $K = 3$ sublevels. (F″ − F′) components are labeled.

The rotational–vibrational analyses of the ν_1/ν_3[14] and ν_2/ν_4 bands,[15] which will be reported in detail elsewhere, yield the vibrational wavenumbers and, among other constants, the vibrational corrections to the ground state rotational constants ($B_0 - B_e$, $C_0 - C_e$) which can be used to calculate the equilibrium rotational constants (B_e, C_e) and to derive the equilibrium geometry (r_e), Table 1.

Since the experimental data differ from published ab initio results[16, 17] by more than is nowadays tolerable, we have performed novel ab initio calculations[18–28] at highly correlated levels by using several large basis sets and different relativistic pseudopotentials for the Bi atom (small-core pseudopotentials with and without counterpoise corrections, large-core pseudopotentials with and without core polarization potential). We will provide a full account of the results of these calculations elsewhere, here we only present the geometries, rotational constants, and fundamental wavenumbers at the highest theoretical level applied[18] and compare them with their experimental counterparts (Table 1).

Table 1. Molecular parameters of BiH_3 (all derived from this work).

	Experiment	Ab initio calculation
ν_1 [cm⁻¹]	1733.2547	1746[a]
ν_2 [cm⁻¹]	726.6990	737[a]
ν_3 [cm⁻¹]	1734.4669	1758[a]
ν_4 [cm⁻¹]	751.2386	761[a]
B_0 [cm⁻¹]	2.6416	2.6257[b]
C_0 [cm⁻¹]	2.6010	2.6024[b]
B_e [cm⁻¹]	2.6709	2.6517[c]
C_e [cm⁻¹]	2.6297	2.6274[c]
r_0(BiH) [pm]	178.52	179.16
α_0(HBiH) [°]	90.50	90.07
r_e(BiH) [pm]	177.59	178.29[c]
α_e(HBiH) [°]	90.48	90.08[c]

[a] Harmonic wavenumbers from CCSD(T), anharmonicity corrections from MP2.[18] [b] Equilibrium values from CCSD(T), vibrational corrections from MP2.[18] [c] From CCSD(T).[18]

The agreement of experimental (Figure 2, top and Figure 3, top) and simulated spectra (Figure 2, bottom and Figure 3, bottom) proves unambiguously that the observed spectra originate from BiH_3, and moreover that the rotational–vibrational analyses are correct and the determined molecular constants reliable and meaningful. The results of our ab initio calculations are consistent with the experimental data (Table 1) and thus offer further support for the experimental assignments.

In conclusion, we have confirmed that Amberger obtained BiH_3 in his demanding (and thus presumably to date unrepeated) synthesis. We have determined for the first time accurate molecular constants for BiH_3 from IR and MMW spectra as well as accurate r_0 and r_e structures, vibrational energies, and the pattern of rotational and rotational–vibrational energies. The experimental results are in agreement with those from high-level ab initio calculations.

Received: March 22, 2002 [Z18958]

---

[1] A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, **1995**; N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, **1984**.

[2] E. Amberger, *Chem. Ber.* **1961**, *94*, 1447–1452.

[3] a) F. Paneth, *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 1704–1728; b) F. Paneth, E. Winternitz, *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 1728–1743.

[4] See, for example: a) M. Thompson, B. Pahlavanpur, S. J. Walton, G. F. Kirkbright, *Analyst* **1978**, *103*, 705–713; b) K. Fujita, T. Takada, *Talanta* **1986**, *33*, 203–207.

[5] F. E. Saalfeld, H. J. Svec, *Inorg. Chem.* **1963**, *2*, 46–50.

[6] a) A. M. R. P. Bopegedera, C. R. Brazier, P. F. Bernath, *Chem. Phys. Lett.* **1989**, *162*, 301–305; b) R.-D. Urban, P. Polomsky, H. Jones, *Chem. Phys. Lett.* **1991**, *181*, 485–490; c) E. H. Fink, K. D. Setzer, D. A. Ramsay, M. Vervloet, J. M. Brown, *J. Mol. Spectrosc.* **1990**, *142*, 108–116; d) H. G. Hedderich, P. F. Bernath, *J. Mol. Spectrosc.* **1993**, *158*, 170–176.

[7] L. Fusina, G. Di Lonardo, P. De Natale, *J. Chem. Phys.* **1998**, *109*, 997–1003.

[8] K. Sarka, D. Papoušek, J. Demaison, H. Mäder, H. Harder in *Vibration-Rotational Spectroscopy and Molecular Dynamics*, (Ed.: D. Papoušek), World Scientific, Singapore, **1997**, pp. 116–238.

[9] In local modes, X–H stretching excitation energy of XH_n molecules is localized the more in one single X–H bond the higher the excitation (typically in overtones), and dynamic symmetry lowering ($XH_3 \rightarrow XH'H_2$, $C_{3v} \rightarrow C_s$) occurs. See, for example: a) M. S. Child, L. Halonen, *Adv. Chem. Phys.* **1984**, *57*, 1–58; b) L. Halonen, *Adv. Chem. Phys.* **1998**, *104*, 49–179; c) P. Jensen, *Mol. Phys.* **2000**, *98*, 1253–1285; d) T. Lukka, L. Halonen, *J. Chem. Phys.* **1994**, *101*, 8380–8389.

[10] R. Marquardt, *Ber. Dtsch. Chem. Ges.* **1887**, *20,* 1518–1523.

[11] Bruker 120 HR interferometer, Globar source, KBr beam splitter, MCT 800 and MCT 600 detectors, respectively, in the ν_1/ν_3 and ν_2/ν_4 regions, low pass filters, wavenumber precision $<1 \times 10^{-3}\,cm^{-1}$, quoted resolution is 1/maximum optical path difference.

[12] Between 150 and 650 GHz the rotational spectrum was measured by using phase-locked backward-wave oscillators as sources. At 1260 GHz a far-IR laser-sideband spectrometer was used.

[13] A standard Hamiltonian complete to sextic centrifugal distortion constants, comprising off-diagonal elements taking into account $\Delta K = \pm 3$ interactions, and considering Bi nuclear quadrupole ($I = 9/2$) and spin-rotation effects was used.

[14] ν_1/ν_3: Coriolis constants $C\zeta^z = -0.0230\,cm^{-1}$ and $\sqrt{2}B\Omega_{13}\zeta^y_{13} = \pm 0.0666\,cm^{-1}$ are small. σ(fit) is $0.66 \times 10^{-3}\,cm^{-1}$ over 564 observations with $J'_{max} = 10$.

[15] The $v_2 = 1$ and $v_4 = 1$ states are strongly coupled, with x,y Coriolis resonance dominating: $\sqrt{2}B\Omega_{24}\zeta^y_{24} = 1.8193\,cm^{-1}$. Moreover, $l(2,2)$, $l(2,-1)$, and $l(2,-4)$ interactions are present. σ(fit) is $0.56 \times 10^{-3}\,cm^{-1}$ over 514 observations with $J'_{max} = 10$.

[16] a) P. Schwerdtfeger, L. J. Laakkonen, P. Pyykkö, *J. Chem. Phys.* **1992**, *96*, 6807–6819; b) P. Schwerdtfeger, G. A. Heath, M. Dolg, M. A. Bennett, *J. Am. Chem. Soc.* **1992**, *114*, 7518–7527; c) D. Dai, K. Balasubramanian, *J. Chem. Phys.* **1990**, *93*, 1837–1846.

[17] J. Breidung, W. Thiel, *J. Mol. Spectrosc.* **1995**, *169*, 166–180.

[18] The molecular geometry of BiH_3 (C_{3v} symmetry) was optimized at the CCSD(T) level of theory[19] by using counterpoise-corrected energies.[20] The innermost core electrons of the Bi atom (1s–4f) were replaced by a relativistic pseudopotential,[21] whereas the remaining 23 electrons in the Bi atom were treated explicitly by employing a (12s12p9d3f2g)/[6s6p4d3f2g] basis set.[21] The aug-cc-pVQZ basis[19] was used for the H atoms. All electrons outside the Bi core were correlated. At the CCSD(T) equilibrium geometry the harmonic force field was calculated numerically from corresponding counterpoise-corrected energies. Anharmonic normal coordinate force fields were determined at the MP2 level[19] without counterpoise corrections by employing the same basis sets as above and by using a finite difference procedure.[22] The CCSD(T) and MP2 calculations were performed with the Molpro2000[23] and Gaussian98[24] program systems, respectively.

[19] Abbreviations: CCSD(T) = coupled-cluster method with single and double excitations[25] and a perturbational treatment of triple excitations;[26] MP2 = Møller–Plesset second-order perturbation theory;[27] aug-cc-pVQZ = augmented correlation-consistent polarized valence quadruple zeta basis.[28]

[20] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566.

[21] B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563–2569.

[22] W. Schneider, W. Thiel, *Chem. Phys. Lett.* **1989**, *157*, 367–373.

[23] Molpro2000 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson.

[24] Gaussian 98 (Revision A.9), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**..

[25] G. D. Purvis III, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910–1918.

[26] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.

[27] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.

[28] R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796–6806.