DIODE LASER SPECTROSCOPY OF BiH AND BiD

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The vibration–rotation spectra of the gas phase BiH and BiD molecules were recorded using a diode laser spectrometer. The direct reaction between the bismuth metal and hydrogen (or deuterium) provided the BiH (or BiD) molecules. The 1–0 fundamental band and several hot bands with $\Delta v = 1$ were investigated. The rotational line positions obtained were fitted separately for the BiH and BiD molecules to Dunham energy level expressions to determine the spectroscopic constants. The Bi–H and Bi–D bond lengths were calculated to be 1.80867 and 1.80671 Å, respectively.

1. Introduction

Several electronic transitions of BiH and BiD have been studied [1–9] since the early 1930s when Heimer and Hulthen discovered the $B0^+–X0^+$ transition near 4222 Å. Recently the properties of BiH have been predicted by relativistic ab initio calculations [10–12]. We report here the observation of the infrared vibration–rotation spectrum of BiH and BiD.

BiH is isovalent with NH, therefore an $X\,^3\Sigma^-$ ground state is expected from the $(6p\sigma)^2(6p\pi)^2$ configuration. However, BiH follows Hund's case (c) coupling so the $^3\Sigma_1^-$ and $^3\Sigma_0^-$ spin components are widely separated (4936 cm^{-1}) and give rise to the A1 and X0$^+$ states [2,9]. In fact the early workers called these two states A $^1\Pi$ and X $^1\Sigma^+$ because a Hund's case (a) p complex has the same energy level pattern as a Hund's case (c) $^3\Sigma^-$ state. In this paper we will use the Hund's case (c) A1 and X0$^+$ notation for the two spin components of the $^3\Sigma^-$ ground state. The A1 state was not detected in our work.

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2. Experimental methods

The gas-phase bismuth hydride or bismuth deuteride molecules were synthesized in a heat pipe oven by the reaction between the bismuth metal vapor and hydrogen or deuterium. The heat pipe is a 1 m long stainless steel tube, 50 mm in diameter, the ends of which are equipped with barium fluoride windows at Brewster's angle.

The stainless steel tube was "conditioned" to remove impurities prior to the experiment by several cycles of heating to $\approx 1000\,°$C and then cooling down to room temperature while being evacuated by a mechanical pump. Once conditioned, approximately 200 g of 99.999+% pure bismuth metal (Aesar Chemical Company) was placed in the central part of the oven and heated to $\approx 1000\,°$C to evaporate the metal. The pipe was pressurized with approximately 25 Torr with hydrogen or deuterium. Only the central part of the oven was electrically heated. The ends of the oven were water cooled to prevent the bismuth vapor from condensing on the windows and to keep the metal hydride confined to the central part of the tube. Once pressurized with H$_2$ (D$_2$), the heat pipe was sealed off by closing the valve to the vacuum pump. It was necessary to add small amounts of H$_2$ (D$_2$) into the pipe from time to time, in order to maintain the pressure inside the oven.

The heat pipe was cooled to room temperature and evacuated several times each week. Once charged

with bismuth, it was possible to re-heat the oven many times over a period of one month without re-charging. The high temperature used in this experiment promotes the oxidation of the stainless steel so the heat pipe had to be replaced several times during the course of the experiment.

The experimental schematic used in recording the vibration–rotation spectra of BiH and BiD molecules is provided in fig. 1. Three Pb–Sn–Te diode lasers (Laser Analytics) covering different spectral regions were required to record the 1–0 fundamental and several hot bands with $\Delta v = 1$ of BiH and BiD. A single longitudinal mode of the laser was first selected by passing the laser beam through a 0.33 m monochromator. As seen in fig. 1, a fraction ($\approx 25\%$) of the laser beam is then directed through an air-spaced germanium Fabry–Perot etalon, with a free spectral range of 0.029851 cm^{-1}. The fringes from the etalon provide relative frequency calibration for the spectra.

The major portion ($\approx 75\%$) of the laser beam was directed into the heat pipe and passed four times through the cell to obtain an effective path length of ≈ 2 m. The beam from the cell is passed through a 0.2 m glass cell equipped with barium fluoride windows. This cell is filled with a reference gas which has a well known infrared spectrum. The reference gas spectral line positions provide absolute calibration for the BiH and BiD line positions. NH$_3$, H$_2$O, N$_2$O [13], NO [14], H$_2$CO [15] and OCS [16] reference gases were used in this experiment to obtain
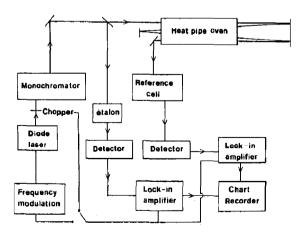
the absolute wavenumber calibration of the BiH and BiD lines.

The output from the reference cell and the Fabry–Perot etalon were focused onto two separate liquid-nitrogen-cooled Hg–Cd–Te detectors. The signals from the detectors were fed into two lock-in amplifiers. The diode laser beam was frequency modulated at ≈ 10 kHz and the absorption signal was lock-in detected at twice the modulation frequency. The spectra were recorded on a two-pen chart recorder which received its input from the two lock-in amplifiers. The absolute accuracy of the line positions is ± 0.002 cm^{-1}.

3. Results and analysis

The ground X0$^+$ state of BiH behaves like a $^1\Sigma^+$ state. A band head was observed in the R branch of the 1–0 band of BiH at $J=27$ and BiD at $J=38$. Since the B rotational constants of BiH (5.13785 cm^{-1}) and BiD (2.588813 cm^{-1}) are relatively large and a single longitudinal mode of the diode laser has continuous coverage of less than 1 cm^{-1}, only a single rotational line could be recorded in each scan. However, near the band head of the R branch of the 1–0 band of BiH, the R(25) and R(29) lines, which are separated by 0.0288 cm^{-1}, were recorded in a single scan as seen in fig. 2. The calibration lines in this spectrum were obtained by using a reference cell filled with ≈ 0.2 Torr of H$_2$CO. Water is an impurity in the H$_2$CO sample.

Fig. 3 shows two rotational lines in the R branch of the 1–0 and 2–1 bands of the BiH molecule. As seen here, the intensity of the 2–1 band lines were a factor of three lower than the intensity of the 1–0 band lines. Several water vapor lines marked on the spectrum provided absolute calibration for this spectrum. A total of 16 rotational line positions were recorded in the 1–0 fundamental and 2–1, 3–2 hot bands of BiH. These lines are reported in table 1.

For BiD, 19 rotational line positions were recorded in the 1–0 fundamental and 2–1 hot band. Fig. 4 provides one of the scans that contained two molecular rotational lines in the 1–0 and 2–1 bands. The 2–1 band lines were about 50% less intense than their 1–0 counter parts. NH$_3$ was used as the reference gas in recording these lines. The rotational line
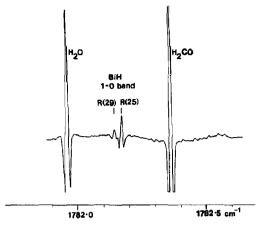

Fig. 1. Experimental diagram of the apparatus used to record the vibration–rotation spectra of the BiH and BiD molecules.

Fig. 2. A portion of the vibration–rotation spectrum of the 1–0 band of BiH. The R(25) and R(29) lines which are separated by 0.0288 cm^{-1} were recorded in a single scan. The R branch forms a band head at $J=27$. The $7_{4,3}-7_{5,2}$ rotational transition of H_2O (at 1781.96231 cm^{-1}) and the $16_{2,15}-15_{2,14}$ rotational transition of H_2CO (at 1782.3609 cm^{-1}) were used for absolute calibration.

Table 1
The rotational line positions of the 1–0, 2–1 and 3–2 bands of the BiH molecule (in cm^{-1})

Assignment	ν	$10^3\Delta\nu$
1–0 band		
R(4)	1681.8474	2
R(7)	1705.6976	−3
R(8)	1712.9962	2
R(9)	1719.9487	−2
R(11)	1732.8397	−0
R(12)	1738.7646	2
R(16)	1758.8872	0
R(17)	1763.0077	2
R(19)	1770.1154	−3
R(25)	1782.1742	0
R(29)	1782.1454	−0
P(24)	1322.1550	0
P(25)	1306.4441	0
2–1 band		
R(14)	1682.1174	0
P(21)	1311.4228	−0
3–2 band		
P(17)	1309.9661	0

positions recorded for BiD are listed in table 2. Although several attempts were made to record additional rotational lines of BiH and BiD, they were not successful due to the incomplete spectral coverage of the diode lasers.

The rotational line positions reported in tables 1 and 2 were fitted to the Dunham energy level expression [17]
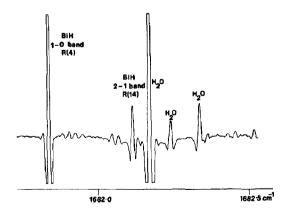
$$E_{vj} = \sum_{kj} Y_{kj}(v+\tfrac{1}{2})^k [J(J+1)]^j ,$$

where k, j are summation indices, v and J are, respectively vibrational and rotational quantum numbers and Y_{kj} are coefficients which are related to the molecular constants.

The Dunham vibration–rotation constants obtained from the fit and the corresponding constants obtained by Heimer [3,4] are reported in table 3. The BiH and BiD equilibrium bond lengths were calculated to be 1.80867 and 1.80671 Å for the BiH and BiD molecules respectively, using the $B_e \approx Y_{01}$ rotational constant.

An attempt was made to simultaneously fit the line positions of BiH and BiD molecules to obtain the isotopically invariant Watson U constants [18–20]. The fit obtained was unsatisfactory since the number of Δ's required was equal to the number of U's. The Watson Δ parameters account for the breakdown of the Born–Oppenheimer approximation. Yamada and Hirota also required a large number of Δ parameters

Fig. 3. A portion of the vibration–rotation spectrum of the 2–1 band of BiH. The R(14) line of the 2–1 band and the R(4) line of the 1–0 band appear on the same scan. As seen here, the 2–1 band lines were in general, three times lower in intensity than the 1–0 band lines.
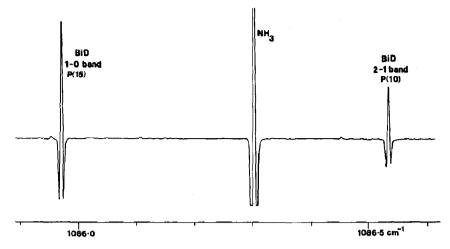
Fig. 4. A portion of the spectrum of the 1–0 and 2–1 bands of BiD. The P(15) line of the 1–0 band and the P(10) line of the 2–1 band were recorded simultaneously in this spectrum. The aR(7,7) transition of NH_3 (at 1086.30418 cm^{-1}) provided absolute calibration of the spectrum.

Table 2
The rotational line positions of the 1–0 and 2–1 bands of the BiD molecule (in cm^{-1})

Assignment	1–0 band		Assignment	2–1 band	
	ν	$10^3\Delta\nu$		ν	$10^3\Delta\nu$
P(14)	1092.4647	2	P(9)	1092.4599	3
P(15)	1085.9693	−4	P(10)	1086.5340	−2
P(16)	1079.3944	0	P(12)	1074.4102	0
P(17)	1072.7282	0	P(13)	1068.2083	−0
P(18)	1065.9805	5	P(14)	1061.9132	−2
P(20)	1052.2156	−1	R(13)	1199.9535	1
P(21)	1045.2127	−1	R(22)	1225.3165	1
R(10)	1222.4777	0	R(27)	1234.8633	−0
R(11)	1226.2593	1			
R(13)	1233.4622	−0			
R(16)	1243.3547	−2			

Table 3
The Dunham vibration–rotation constants for the BiH and BiD molecules in the X0$^+$ ground state (in cm^{-1})

Constant	BiH [a]	BiH [b]	BiD [a]	BiD [c]
Y_{10}	1697.6278(57) [d]	1699.5	1205.3843(45)	1205.6
Y_{20}	−30.6127(45)	−31.9	−16.02059(89)	−16.1
Y_{30}	−0.19756(82)	–	–	–
Y_{01}	5.13785(17)	5.141	2.588813(100)	2.592
Y_{11}	−0.148564(20)	−0.159	−0.053060(22)	−0.054
$10^3 Y_{02}$	−0.19203(35)	–	−0.04564(30)	–
$10^5 Y_{12}$	0.2281(28)	–	0.0177(37)	–
$10^8 Y_{03}$	−0.425(24)	–	−0.107(30)	–
r_e(Å)	1.80867	1.811	1.80671	1.802

[a] This work. [b] Ref. [3]. [c] Ref. [4]. [d] The numbers in parentheses are one-standard-deviation errors.

to fit the LiH and LiD vibration–rotation bands [21].

4. Discussion

The BiH and BiD molecules are formed inside the heat pipe oven, most likely, by the endothermic reaction

$$2Bi(g) + H_2(g) \rightarrow 2BiH(g), \quad \Delta H = +122 \text{ kJ mol}^{-1}.$$

According to the Le Chatelier's principle, this reaction is favored by high temperatures and high pressures. The amount of BiH formed increased with temperature but we were limited to temperatures less than $1000°C$ by the properties of the stainless steel tube. Although high pressures favor the chemistry, the total pressure inside the oven was maintained below 25 Torr, to reduce the effects of pressure broadening on the spectra of BiH and BiD molecules. The necessity to add H_2/D_2 into the oven from time to time in order to maintain this pressure indicates that the gaseous products are being slowly removed from the system. We suspect that this is due to the formation of a solid hydride, probably that of iron.

The spectra were recorded at Doppler-limited resolution of ≈ 0.01 cm^{-1}. In general the intensity of the strong 1–0 fundamental band lines of BiH indicated the absorption of $\approx 10\%$ of the infrared radiation by the molecules. The 2–1 band lines of BiH (BiD) were generally one third (one half) as intense as the fundamental band rotational lines. Additional lines were also present, probably from BiH$_2$, but the poor wavelength coverage of our diodes prevented any assignments.

The assignments for BiD and the 1–0 band of BiH are secure but only two lines of the 2–1 band and one line for the 3–2 band of BiH were observed. Two additional constants, Y_{20} ($\omega_e x_e$) and Y_{30} ($\omega_e y_e$), were required to fit these three lines of the 2–1 and 3–2 bands of BiH. Although we believe our measurements for these lines are correct, the small number of measurements contributing to the Y_{20} and Y_{30} constants increases the possibility of error. Correlation of spectroscopic parameters and unreliable standard deviations can result from this kind of data.

The relativistic configuration interaction calculations of Balusubramanian [10,11] predict the X0$^+$ internuclear distance to be 1.90 Å and the harmonic vibrational frequency to be 1619 cm^{-1}. These values are in reasonable agreement with the experimental values of $r_e = 1.80867$ Å and $\omega_e = 1697.629$ cm^{-1} reported in table 3.

In conclusion, the vibration–rotation spectra of BiH and BiD were observed for the first time. The Dunham fits of the line positions provided improved molecular constants for BiH and BiD.

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