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First stretching overtone of BiH_3 : An extreme local-mode case for XH_3 -type molecule?

W. Jerzembeck and H. Bürger^{a)}

Anorganische Chemie, FB 10, Bergische Universität, D-42097 Wuppertal, Germany

V. Hänninen and L. Halonen

Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

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The first stretching overtone region of short-lived, formerly inaccessible BiH₃ near 3405 cm⁻¹ has been measured by Fourier-transform infrared spectroscopy with a resolution of 0.0066 cm⁻¹. Only the $2\nu_1(A_1)/\nu_1 + \nu_3(E)$ band system has been observed. Rotational analysis, with transitions reaching $J'_{max}=14$, has revealed almost perfect local-mode behavior for the upper states denoted as $(200A_1/E)$ in the local-mode notation. Ratios of vibration–rotation interaction parameters $\bar{q}_{eff}/\alpha_{eff}^{(BB)}$ and $r_{eff}/\alpha_{eff}^{(BC)}$, and the appropriate rotational constant differences, are in good agreement with theoretical local-mode limit values. A simple stretching vibrational model reproduces the observed vibrational term values well, and the potential parameters obtained are close to true values. © 2004 American Institute of Physics. [DOI: 10.1063/1.1647055]

I. INTRODUCTION

The concept of vibrational energy localization upon single and, in particular, multiple excitation of the stretching motion has been successfully applied to hydrides XH₂, XH₃, and XH₄.¹⁻³ The X–H stretching motions are anharmonic and therefore the $\Delta v = 1$ vibrational selection rule is no longer strictly valid and $\Delta v > 1$ transitions are sufficiently intense for observation by infrared spectroscopy. On the other hand, stretch–bend combination bands are almost absent at least at high vibrational excitation indicating that the local-mode type stretching states are largely decoupled from motions involving bending states. At the same time, coupling between different X–H oscillators should also be small due to a heavy central atom X and right angle HXH bond angles in XH₂ and XH₃ systems.^{1–3} This favors the local mode behavior within the stretching vibrational manifold.

Localized vibrational states exert patterns of the rotational energy that are unique for molecules of the respective symmetry.⁴⁻⁸ There is dynamic symmetry lowering in the excited local-mode state, e.g., from C_{3v} in the ground state of an XH₃ species to C_s in a local-mode state of XH'H₂ with the excitation localized in the X-H' stretching motion. Therefore, effects of vibrational angular momentum are quenched, and both z and x, y axis Coriolis couplings are negligible. Rotational constants of the almost degenerate stretching vibrational local-mode states of XH₃, e.g., $2\nu_1(A_1)$ and $\nu_1 + \nu_3(E)$ corresponding to the $(200A_1/E)$ states, become equal. Simple relations between vibrationrotation interaction parameters are then obeyed.^{5,8} Here and throughout this paper we use the following labels for the vibrational states: In the normal mode limit we label the states $2\nu_1(A_1)$, $\nu_1 + \nu_3(E)$, and $2\nu_3(A_1 + E)$. In the local mode limit we label the states $(200A_1/E)$, and $(110A_1/E)$, where the digits 200 and 110 denote the distribution of quanta in the three bonds.

Of the series of the XH₃ species, where X is a group 15 element, stretching overtones of AsH₃ and SbH₃ have been studied in some detail while stretching overtones of PH₃ still await a thorough investigation. The NH₃ spectra do not reveal rovibrational structure as described above for localized vibrations. Although the first overtone states $(200A_1/E)$ of SbH₃ fulfill the above-mentioned local-mode requirements quite well, the corresponding states of AsH₃ are less local and particularly the $(110A_1/E)$ states of AsH₃ differ distinctly from local-mode behavior.^{9–11} Closer agreement of the $(n00A_1/E)$ stretching states with local-mode expectations becomes evident for higher excitation, $n \ge 4$ and $n \ge 3$ in AsH₃ (Refs. 12 and 13) and SbH₃,^{14,15} respectively.

The hitherto unavailable BiH₃ molecule might show local-mode behavior at lower stretching excitation than other XH₃ species. The HBiH bond angle should be very close to 90°, indicating a small kinetic energy coupling between the bond oscillators. Furthermore, the heavy Bi atom (atomic mass 209 u) most likely damps the potential energy HBi/BiH' coupling. Thus, the net coupling between bond oscillators will be small when compared with the BiH bond anharmonicity (Y_{20} = -31.92 cm⁻¹ in diatomic BiH).¹⁶ This should lead to near local-mode behavior.^{3,17,18} It would be a particularly interesting task to investigate stretching vibrational localization in this conceivably extreme case in the series of XH₃ molecules, if BiH₃ were available.

The synthesis of the BiH_3 molecule was first reported in 1961¹⁹ but could never be repeated in spite of several attempts by different researchers including ourselves. The failure to prove or disprove the first observation lies in synthetic difficulties due to the most demanding nature of the preparation and the thermal and photolytic instability of BiH_3 . In

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^{a)}Author to whom all correspondence should be addressed. Electronic mail: buerger1@uni-wuppertal.de

the gas phase, this molecule decomposes rapidly slightly above the temperature ~ -40 °C, which is also necessary for the BiH₃ formation.¹⁹ Accordingly, neither any spectroscopic data nor its structure could be determined to date.

Recently, we have been able to repeat the reported synthesis of BiH₃ so that high-resolution infrared and millimeter-wave spectra could be measured.²⁰ Ground state rotational and centrifugal distortion constants as well as the r_0 and r_e structures have been obtained thereof,²¹ and the vibrational fundamentals ν_1 , ν_2 , ν_3 , and ν_4 have been measured in the infrared region with an optical resolution of $5.5-6.6 \times 10^{-3}$ cm⁻¹.²²

Expectation that BiH₃ may be close to being vibrationally localized already in the v(BiH) = 2 overtone stretching state is supported by the finding that the HBiH angle, $\theta_e = 90.32^{\circ}$,²¹ is close to a right angle and the stretching fundamentals almost are degenerate, $(\nu_1 - \nu_3)$ $= -1.21 \text{ cm}^{-1}$, and the Coriolis parameters, $C\zeta_3^z$ = -0.0231 and B $\Omega \zeta_{1,3}^{x} = \pm 0.0656 \text{ cm}^{-1}$ are small in magnitude. We have therefore searched for this first stretching overtone band near 3400 cm⁻¹ and eventually observed it in good quality in spite of the only $\sim 1\%$ intensity relative to the ν_1/ν_3 band system and the experimental difficulties associated with the measurements at high resolution. In this contribution, we report on our observations and the analysis of the spectrum.

Section II will give some experimental details, in Sec. III the observed spectrum, the assignment, and the data fit are described. Section IV will report on rotational local-mode effects, Sec. V presents a simple vibrational calculation, and a discussion in Sec. VI concludes the study.

II. EXPERIMENTAL METHOD

Bismuthine BiH₃, which is a highly reactive, short-lived species, rapidly decomposing above $-35 \,^{\circ}\text{C}$ to give Bi (deposited on all surfaces) and H₂, was prepared as described in Refs. 19 and 20. Since no multipass cell could be employed owing to the immediate deposition of Bi on metal mirrors, the region of the first stretching overtones was studied using a double-jacketed glass cell of 1.2 m length with CaF2 windows and external cooling. The wall temperature was adjusted to -36 °C. The cell had an inner diameter of 70 mm and was placed in the external parallel beam of a Bruker 120 HR interferometer in a setup similar to that described in Ref. 23. The interferometer was equipped with a halogen source, a CaF₂ beam splitter, an InSb detector, and a 2.5–3.5 μ m optical bandpass filter. The resolution was adjusted to 0.0066 cm^{-1} (1/maximum optical path difference). Altogether 120 scans were collected. The total pressure in the cell (containing some H_2) was adjusted to 60 Pa, and the absorption cell was refilled three times with a fresh BiH₃ sample.

Calibration was carried out using H_2O lines in the 3600 cm⁻¹ region.²⁴ Wave number precision of medium to strong unblended lines is better than 5×10^{-4} cm⁻¹.



FIG. 1. Survey spectrum of the $\Delta v(BiH) = 2$ band of BiH_3 .

III. DESCRIPTION AND ASSIGNMENT OF THE SPECTRUM AND DATA FIT

The first stretching overtone band of BiH₃ is shown in Fig. 1. It is centered at $\sim 3405 \text{ cm}^{-1}$ and reveals well pronounced Q branch transitions $(\Delta J = J' - J'' = 0)$ over a spectral range of $4-5 \text{ cm}^{-1}$ degraded to smaller wave number from the sharp edge at 3406.8 cm⁻¹. The label J is the total angular momentum quantum number, and the prime and double prime refer to the upper and lower states, respectively. Toward the large wave numbers $\Delta J = +1$, R branch clusters are well pronounced and can be followed up to about J''=8. The structure of these J clusters becomes more complex as J increases. Some prominent lines stand out near the low wave number edges of these R branch clusters; at low J these can be associated with ${}^{R}R_{K}(J=K)$ lines of the (200*E*) band.

The $\Delta J = -1$, *P* branch region contains wider-spread less compact *J* clusters than the *R* branch. Moreover, the spectrum available to us is noisier in the *P* branch than in the *R* and (very dense) *Q* branch regions. At first inspection, the *Q* branch looks chaotic, and assignments could only be made when reliable predictions became available. We estimate that the intensity of the overtone band is 1%–2% of that of the ν_1/ν_3 fundamental band system.

The first assignments of the spectrum were made in the region of the compact R(0) to R(3) clusters revealing a simple structure. Use was made of ground state combination differences employing the spectroscopic parameters reported in Ref. 21. Comparison with the spectrum of the closely related $\Delta v = 2$ band of SbH₃ also helped in finding rotational assignments.11 Moreover, it was useful during the first steps of the assignment to make use of an approximate prediction of the BiH₃ spectrum obtained from scaled parameters for the $(200A_1/E)$ state of SbH₃.¹¹ An empirical scaling factor s = 0.85 was used for the appropriate most important vibration-rotation parameters (see the following). This value was obtained by a comparison of the ν_1 and ν_3 parameters of BiH₃ (Ref. 22) with those of SbH₃.²⁵ A transition moment ratio $\mu(A_1): \mu(E) = 1.0$ was chosen, in analogy to that of SbH₃, 1:1.042.¹¹ After several loops of assignments and simulations based on the least-squares optimization of spec-

TABLE I. Ground state parameters (all in cm⁻¹) of BiH₃, B reduction.^a

В	2.641 601 718
С	2.601 402 9
$D_J \times 10^6$	53.803 18
$D_{JK} \times 10^6$	-64.037 2
$D_{K} \times 10^{6}$	67.713 2
$H_J \times 10^9$	3.177 3
$H_{JK} \times 10^9$	-3.162
$H_{KJ} \times 10^9$	-3.278
$H_K \times 10^9$	5.896
$\epsilon imes 10^{6}$	12.883 3

^aFrom Ref. 21.

=

troscopic model parameters altogether 634 transitions involving also Q-branch lines were assigned. The maximum J'and K' values, which could be reached, were 14 and 13, respectively, and no medium to strong features of the spectrum remained unassigned. We did not observe any features at larger wave numbers which could be associated with the $\Delta v = 2$ band reaching the $(110A_1/E)$ state.

The fit was performed using the same nonlinear leastsquares computer program that had been employed for the $(200A_1/E)$ overtone spectrum of SbH₃.¹¹ Ground state parameters were taken from Ref. 21. For convenience, these are gathered in Table I.

For the model used in assigning the spectrum, see Refs. 4 and 11. The following ground and upper state matrix elements were employed.

The diagonal matrix elements for the ground and for the nondegenerate excited A_1 state take the customary form (s $=0 \text{ or } 200A_1)$

$$\begin{split} H_{s} &= \langle s, Jk | H/hc | s, Jk \rangle \\ &= \nu_{s} + B_{s}J(J+1) + (C_{s} - B_{s})K^{2} - D_{Js}J^{2}(J+1)^{2} \\ &- D_{JKs}J(J+1)K^{2} - D_{Ks}K^{4} + H_{Js}J^{3}(J+1)^{3} \\ &+ H_{JKs}J^{2}(J+1)^{2}K^{2} \\ &+ H_{KJs}J(J+1)K^{4} + H_{Ks}K^{6}. \end{split}$$

The corresponding expression for the doubly degenerate Estate is (t=200E)

$$H_{t} = \langle t, Jk | H/hc | t, Jk \rangle$$

$$= \nu_{t} + B_{t}J(J+1) + (C_{t} - B_{t})K^{2} - 2(C\zeta)_{t}k\ell$$

$$- D_{Jt}J^{2}(J+1)^{2} - D_{JKt}J(J+1)K^{2} - D_{Kt}K^{4}$$

$$+ H_{Jt}J^{3}(J+1)^{3} + H_{JKt}J^{2}(J+1)^{2}K^{2} + H_{KJt}J$$

$$\times (J+1)K^{4} + H_{Kt}K^{6} + \eta_{Jt}J(J+1)k\ell + \eta_{Kt}k^{3}\ell.$$
(2)

In these equations, $|i,Jk\rangle = |i\rangle |Jk\rangle$ (i=0, 200A₁, or 200E) is a product of vibrational $(|i\rangle)$ and symmetric top rigid rotor eigenfunctions $(|Jk\rangle)$. The quantum label ℓ is the vibrational angular momentum quantum number, the k quantum number corresponds to the component of the total angular momentum in the molecular fixed axis system, and K = |k|. We have also included one rotationally off-diagonal quartic distortion operator H_{04} both for the ground state and for the upper states. Its matrix elements are $(i=0, 200A_1, \text{ or } 200E)$

$$\langle i, Jk + 3 | H_{04}^{(i)} / hc | i, Jk \rangle$$

= $\epsilon_i (2k+3) F(J,k) F(J,k+1) F(J,k+2),$ (3)

where $F(J,k) = [J(J+1) - k(k+1)]^{1/2}$.

For the upper state off-diagonal elements of the Hamiltonian, we just give the formulas and refer to Ref. 11 for a more detailed discussion.

The Coriolis interaction matrix elements between the Eand A_1 bands take the form (with one higher-order term in $\zeta_{\rm eff}^{(K)})$

$$\langle 200E(\ell = +1), Jk + 1 | (H_{21} + H_{23}) / hc | 200A_1, Jk \rangle$$

= $-\langle 200A_1, Jk + 1 | (H_{21} + H_{23}) / hc | 200E(\ell = -1), Jk \rangle$
= $[2^{1/2} (B\zeta^{(A)}\Omega)_{\text{eff}} + \zeta^{(K)}_{\text{eff}} G(k)] F(J,k),$ (4)

where $G(k) = k^2 + (k+1)^2$.

All H_{22} operators are included in our model. Of these, the ℓ - and r-resonance terms couple different vibrational angular momentum states in the E vibrational band. The ℓ -resonance matrix elements (with one high-order term in $\bar{q}_{\rm eff}^{(J)}$) are

$$\langle 200E(\ell = +1), Jk + 2 | (H_{22} + H_{24}) / hc | 200E(\ell = -1), Jk \rangle$$

= $-\frac{1}{2} [\bar{q}_{eff} + \bar{q}_{eff}^{(J)} J(J+1)] F(J,k) F(J,k+1)$ (5)

and the *r*-resonance elements are

$$\langle 200E(\ell = -1), Jk + 1 | (H_{22} + H_{24}) / hc | 200E(\ell = +1), Jk \rangle$$

= 2 { [(2k+1)(r_{eff} + r^(J)_{eff} J(J+1))]
+ r^(K)_{eff} [(k+1)³ + (k+2)³] } F(J,k). (6)

There are two other H_{22} operators, the α -resonance terms, which couple the rotational states of the $200A_1$ and 200Evibrational states. The corresponding matrix elements are

$$\langle 200E(\ell = +1), Jk + 1 | (H_{22} + H_{24})/hc | 200A_1, Jk \rangle$$

$$= \langle 200A_1, Jk + 2 | (H_{22} + H_{24})/hc | 200E(\ell = -1), Jk \rangle$$

$$= \frac{1}{2} 2^{-1/2} [\alpha_{\text{eff}}^{(BC)} + \alpha_{\text{eff}}^{(BCJ)} J(J+1) + \alpha_{\text{eff}}^{(BCK)} G(k)]$$

$$\times (2k+1)F(J,k)$$

$$(7)$$

and

$$\langle 200E(\ell = -1), Jk + 2 | H_{22} / hc | 200A_1, Jk \rangle$$

= $\langle 200A_1, Jk + 2 | H_{22} / hc | 200E(\ell = +1), Jk \rangle$
= $\frac{1}{2} 2^{-1/2} \alpha_{\text{eff}}^{(BB)} F(J,k) F(J,k+1).$ (8)

Only parameters, which have been determined with statistical significance, have been optimized with the nonlinear least-squares method. The selection of fitted parameters is similar to that employed for SbH₃ although some higher order terms are different. The achieved rms deviation $\sigma(Fit)$ of ${\sim}0.8{\times}10^{-3}\,\text{cm}^{-1}$ is better than for SbH3 (2.4 and 2.2 $\times 10^{-3}$ cm⁻¹ for ¹²¹SbH₃ and ¹²³SbH₃, respectively).¹¹

TABLE II. Excited state parameters (in cm⁻¹) of BiH₃.^{a,b}

	$(200A_1)$	(200E)		
$\overline{\nu_0}$	3406.700 391(222)	3406.361 162(150)		
B	2.595 129 1(120)	2.595 587 1(187)		
С	2.558 983 5(274)	2.559 593 0(232)		
$C\zeta \times 10^3$		-6.562 3(257)		
$D_{J} \times 10^{6}$	53.965(121)	51.125(107)		
$D_{JK} \times 10^6$	-58.163(480)	-56.480(996)		
$D_K \times 10^6$	66.902(726)	66.65(130)		
$\eta_K \times 10^6$		9.063(688)		
$\epsilon \times 10^6$	13.447(119)	13.788 4(753)		
$\bar{q} \times 10^3$		-22.587 9(111)		
$\bar{q}^{(J)} \times 10^{6}$		2.458(123)		
$r \times 10^3$		7.660 67(748)		
$r^{(J)} \times 10^{6}$		0.569 7(693)		
$r^{(K)} \times 10^{6}$		-3.377(163)		
$\sqrt{2}B\Omega\zeta^{(A)}\times 10^3$	-14.15	8 8(518)		
$\zeta^{(K)} \times 10^6$	-4.419 (335)			
$\alpha^{(BC)} \times 10^3$	43.646 1(305)			
$\alpha^{(BCJ)} \times 10^{6}$	2.345(231)			
$\alpha^{(BCK)} \times 10^6$	-16.053(605)			
$\alpha^{(BB)} \times 10^3$	33.40	1 7(282)		
No. of data	634			
$\sigma(\text{Fit}) \times 10^3$	0.79	1		
$J_{\rm max}/K_{\rm max}$	14/13			

^aStandard deviations (1 σ) in parentheses refer to the least significant digits. ^bAll sextic centrifugal distortion coefficients are contrained to their ground state values given in Table I.

The results of the data fit are gathered in Table II. The rms deviation of $\sim 0.8 \times 10^{-3} \text{ cm}^{-1}$ is only 1.5 times larger than the quoted precision of unblended medium-to-strong lines. This is fully satisfactory in view of the many weak and blended lines included as data in the calculation.

We have performed spectral simulations. Experimental and calculated spectra of the R(6) cluster near 3440 cm⁻¹ are illustrated in Fig. 2. Details of the assignment of the respective transitions are available as supplementary material.²⁶ The transition moment ratio $\mu(A_1):\mu(E)$ was set to 1.0, and any significant modification of this value made the agreement between observed and simulated spectra worse. This agrees well with a bond dipole moment model³ that gives a simple interpretation for the ratio of the A_1 and Evibrational state transition moments as follows:¹¹



FIG. 2. The R(6) cluster of the $\Delta v(\text{BiH})=2$ band of BiH₃. Lower trace: experimental spectrum. Upper trace: simulated spectrum with the transition moment ratio $\mu(A_1):\mu(E)=1.0$.

$$|\mu(200A_1):\mu(200E)| = 2^{1/2} |\cos\beta/\sin\beta| = 1:1.008,$$
 (9)

where $\beta = \pi - \arcsin[(2/3^{1/2})\sin(\alpha/2)]$ and $\alpha = 90.32^{\circ}$ is the observed HBiH bond angle.²¹ The transition moments given are defined as in the paper by diLauro and Mills for Coriolis interacting A_1 and E fundamentals.²⁷ It is clear from Fig. 2 that the band contour simulations confirm the usefulness of this dipole moment model and prove that the spectrum has been correctly assigned.

IV. ROTATIONAL LOCAL-MODE EFFECTS

The vibrational dependence of the leading rovibrational parameters can be modeled with a simple approach based on the treatment of local-mode vibrations in the normalcoordinate representation. The key element in this treatment is the inclusion of quartic anharmonic resonance terms, Darling–Dennison interaction operators, to couple stretching vibrational overtone and combination states that are in strong resonance. Thus, in the harmonic normal-mode basis, one ends up in a block-diagonal Hamiltonian matrix model where only states with the same symmetry and the same total stretching vibrational quantum number are coupled. Details

TABLE III. Local-mode analysis of vibration-rotation parameters of BiH3.ª

	$(100A_1/E)$		$(200A_1/E)$		
	Obs.	Model I Calc.	Obs.	Model I Calc.	Model II Calc.
$v(A_1)$ (cm ⁻¹)	1733.25	1733.25	3406.70	3406.54	
$\nu(E) ({\rm cm}^{-1})$	1734.47	1734.46	3406.36	3406.55	
$B_0 - B_v(A_1) \text{ (cm}^{-1})$	0.022 92		0.046 47	0.046 17	0.046 17
$C_0 - C_v(A_1) \text{ (cm}^{-1})$	0.027 14		0.042 42	0.040 57	0.040 19
$B_0 - B_v(E) (\mathrm{cm}^{-1})$	0.023 17		0.046 01	0.046 17	0.046 17
$C_0 - C_v(E) (\mathrm{cm}^{-1})$	0.016 57		0.041 81	0.040 28	0.040 19
\overline{q} (cm ⁻¹)	$-0.005\ 005$		-0.02259	-0.02201	-0.02209
$r (cm^{-1})$	0.003 852		0.007 66	0.007 81	0.007 81
$\alpha^{(BC)}$ (cm ⁻¹)	0.022 24		0.043 65	0.044 18	0.044 18
$\alpha^{(BB)}$ (cm ⁻¹)	0.019 89		0.033 40	0.031 46	0.031 24
$B\zeta\Omega~(\rm cm^{-1})$	-0.04639		-0.01001	-0.00124	0.0
$C\zeta$ (cm ⁻¹)	-0.023 11		-0.00656	$-0.000\ 60$	0.0

^aThe quantities B_0 (or C_0) and B_v (or C_v) are the rotational constants of the ground and excited states,

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of the vibrational model are given in Refs. 1, 3, and 28. The eigenvectors of these matrices can be used to calculate effective spectroscopic parameters of vibrational overtone and combination states employing spectroscopic constants of the stretching fundamentals. Rotational and Coriolis constants, and the coefficients of vibrationally off-diagonal H_{22} Hamiltonian resonance coefficients, have been calculated in this way. This approach has been described before for XH₃-type molecules in Ref. 11.

The harmonic wave number $\omega = 1795.62 \text{ cm}^{-1}$, anharmonicity constant $\omega x = 30.78 \text{ cm}^{-1}$, and the bond stretch oscillator coupling parameter $\lambda = -0.404 \text{ cm}^{-1}$ of BiH₃ have been used to compute standard normal-mode theory vibrational parameters including Darling–Dennison resonance coefficients as explained in Refs. 3 and 28. Table III contains both calculated vibrational term values and effective rovibrational parameters of the $200A_1$ and 200E states (model I). Spectroscopic parameters for the stretching fundamentals²¹ used in the calculation are also given in Table III.

The BiH₃ molecule is close both to the vibrational localmode limit, where the bond oscillators are vibrationally uncoupled $(\log_{10}|\omega x/\lambda| = 1.88)$, see Ref. 29), and to the rovibrational local-mode limit, where neither vibration nor rotation couples the bond oscillators.⁸ The rovibrational local-mode limit is formally defined in a way that vibration–rotation parameters fulfill the following special relations:

$$\nu_{v}(A_{1}) = \nu_{v}(E),
B_{v}(A_{1}) = B_{v}(E),
C_{v}(A_{1}) = C_{v}(E),
\alpha_{\text{eff}}^{(BB)} = -\sqrt{2}\bar{q}_{\text{eff}},
(10)
\alpha_{\text{eff}}^{(BC)} = 4\sqrt{2}r_{\text{eff}},
(B\zeta\Omega)_{\text{eff}} = 0,
(C\zeta)_{\text{eff}} = 0,$$

where the subindex v = n00 and *n* is the local-mode vibrational quantum number. This means that the vibrational term values (v_v) and the corresponding rotational constants of the excited A_1 and *E* states (B_v or C_v) are equal, and there is no Coriolis coupling between rotational states. In addition, the special relations between the *q*, *r*, and α parameters ensure that the rotational energy level structure is that of a single vibrational state of an asymmetric rotor instead of coupled rotational states of nondegenerate A_1 and *E* vibrational states of a symmetric rotor.^{1,7} In the case, the local-mode limit vibrational wave functions are used and matrix elements are approximated by harmonic oscillator formulas, the following simple expressions for the effective overtone parameters are obtained:³⁰

$$B_{0}-B_{v}(A_{1}) = B_{0}-B_{v}(E) = (n/3)(\alpha_{1}^{(B)}+2\alpha_{3}^{(B)}),$$

$$C_{0}-C_{v}(A_{1}) = C_{0}-C_{v}(E) = (n/3)(\alpha_{1}^{(C)}+2\alpha_{3}^{(C)}),$$

$$\bar{q}_{\text{eff}} = -(1/\sqrt{2})\alpha_{\text{eff}}^{(BB)} = (n/3)(q_{3}-\sqrt{2}\alpha_{13}^{(BB)}),$$

$$r_{\text{eff}} = (1/4\sqrt{2})\alpha_{\text{eff}}^{(BC)} = (n/6)[2r_{3}+(1/\sqrt{2})\alpha_{13}^{(BC)}],$$
(11)

where B_0 and C_0 are rotational constants of the ground vibrational state and the parameters on the very right-hand side are from the upper state analysis of stretching fundamentals, see for example Ref. 4, and $B_0 - B_{\nu_1}(A_1) = \alpha_1^{(B)}$ and $B_0 - B_{\nu_3}(E) = \alpha_3^{(B)}$, etc.³¹ We have used Eq. (11) to calculate effective vibration–rotation parameters of the $(200A_1/E)$ stretching vibrational overtone states (n=2). The results are given in Table III (model II).

It is interesting to note that both models I and II give essentially identical results which on the whole agree well with experimental spectroscopic parameters. Thus, it is unnecessary to use the more sophisticated Darling–Dennison resonance model (model I) in the case of a near local-mode molecule like BiH_3 . The simple local-mode limit expressions in Eq. (11) are adequate. The only disagreement with experiment concerns the two Coriolis coupling coefficients. Experimental values are about one order of magnitude larger than results from model I. However, this is not serious, because it would be unlikely that the present simple theoretical approach would reproduce accurately these small experimental parameters. The magnitudes of Coriolis coefficients are normally about 0.1-1.0.

V. VIBRATIONAL CALCULATIONS

We have adopted a simple vibrational model to obtain information of the stretching vibrational potential energy surface of bismuthine. Following earlier work,^{1,29} our vibrational Hamiltonian is

$$H/hc = \sum_{i=1}^{3} \left(\frac{1}{2hc} g^{(rr)} p_i^2 + D_e y_i^2 \right) + \sum_{i < j} \left(\frac{1}{hc} g^{(rr')} p_i p_j + f_{rr'} a_r^{-2} y_i y_j \right), \quad (12)$$

where $g^{(rr)} = 1/m_{\rm H} + 1/m_{\rm Bi}$, $g^{(rr')} = \cos \theta_e/m_{\rm Bi}$, $p_j = -i\hbar \partial/\partial \Delta r_j$ is the momentum operator conjugate to the bond stretching displacement coordinate Δr_j for the *j*th bond, and the Morse variable $y_j = 1 - e^{-a_r \Delta r_j}$. The masses $m_{\rm H}$ and $m_{\rm Bi}$ refer to hydrogen and bismuth, respectively, θ_e = 90.3215° is the equilibrium bond angle,²¹ D_e is the Morse dissociation energy, a_r is the Morse steepness parameter, and $f_{rr'}$ is a harmonic force constant, which describes the strength of the potential energy coupling between the bond oscillators. The weight function for the volume element of integration is one.

We have also considered the effects of constraints in the Hamiltonian unlike in the earlier work on XH₃-type systems. The deep role of constraints is controversial in quantum mechanics³² but in the present types of vibrational problems the solution is known at least in classical mechanics. The vibrational tensor elements $g_c^{(ij)}$ in the presence of rigid constraints can be obtained from the unconstrained elements $g^{(ij)}$ as³³

$$g_{c}^{(rr)} = g^{(rr)} - \sum_{i=1}^{3} \sum_{j=1}^{3} g^{(r\theta_{i})} M_{ij} g^{(r\theta_{j})},$$

$$g_{c}^{(rr')} = g^{(rr')} - \sum_{i=1}^{3} \sum_{j=1}^{3} g^{(r\theta_{i})} M_{ij} g^{(r'\theta_{j})},$$
(13)

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TABLE IV. Constrained and unconstrained stretching vibrational metric tensor elements.

Molecule	$g^{(rr)}(\mathbf{u}^{-1})$	$g_c^{(rr)}(\mathbf{u}^{-1})$	$g^{(rr')}(\mathbf{u}^{-1}\mathbf{\mathring{A}}^{-1})$	$g_c^{(rr')}(\mathbf{u}^{-1}\mathrm{\AA}^{-1})$
NH ₃	1.063 63	1.058 06	-0.020516	-0.020 103
PH_3	1.024 52	1.023 49	-0.001 943	-0.002343
AsH ₃	1.005 58	1.005 40	-0.000482	-0.000560
SbH ₃	1.000 51	1.000 44	-0.000222	-0.000253
BiH ₃	0.997 02	0.997 00	$-0.000\ 040$	$-0.000\ 051$

where the indices *i* and *j* are over the three constrained bending degrees of freedom ($\Delta \theta_1$, $\Delta \theta_2$, and $\Delta \theta_3$ being the appropriate bond angle displacement coordinates) and M_{ij} is an element of the symmetrical matrix

$$M = \begin{pmatrix} g^{(\theta_1\theta_1)} & g^{(\theta_1\theta_2)} & g^{(\theta_1\theta_3)} \\ g^{(\theta_1\theta_2)} & g^{(\theta_2\theta_2)} & g^{(\theta_2\theta_3)} \\ g^{(\theta_1\theta_3)} & g^{(\theta_2\theta_3)} & g^{(\theta_3\theta_3)} \end{pmatrix}^{-1}.$$
 (14)

All unconstrained metric tensor elements can be obtained from Ref. 33.

We have calculated the constrained and the unconstrained stretching vibrational metric tensor elements for NH₃, PH₃, AsH₃, SbH₃, and BiH₃ at the respective equilibrium geometry which have been taken from Refs. 21, 34– 37. The results are gathered in Table IV. Although we have computed the constrained tensor elements only at the equilibrium geometry, it is clear that in BiH₃ there would be no real difference whether constrained or unconstrained metric tensor elements are used in Eq. (12). Therefore, all calculations have been performed with unconstrained elements.

The eigenvalues of the vibrational Hamiltonian in Eq. (12) with the unconstrained metric tensor elements have been computed variationally with a symmetrized Morse oscillator product basis as described in Ref. 29. All matrix elements have been obtained with analytical formulas.38 All basis functions with the maximum stretching quantum number 6 have been included. The nonlinear least-squares method has been employed to optimize the parameters ω , ωx , and $f_{rr'}$ instead of the true potential energy constants D_e , a_r , and $f_{rr'}$ in order to reduce correlation between the parameters. However, this is not problematic because simple relations between ω and ωx , and potential energy constants D_e and a_r allow one to readily convert one parameter set to the other.1 Experimental vibrational term values have been employed as data. We obtain the parameter values $\omega = 1795.65(66) \text{ cm}^{-1}$, $\omega x = 30.78(23) \text{ cm}^{-1}$, and $f_{rr'} = -42.0(149) \text{ cm}^{-1} \text{ Å}^{-2}$. The uncertainties in parentheses are one-standard deviation in the least significant digit. The fit to the experimental vibrational term values is given in Table V.

An inspection of the vibrational results reveals that the overall vibrational term value fit is good and the stretching potential energy parameters obtained are close to true values. However, the small splitting of the $(200A_1)$ and (200E) states is calculated to be almost absent and the order of the states is also incorrectly predicted. This indicates a slightly different coupling between different stretching states and the bending manifold. It would be of interest to perform a full

TABLE V. Vibrational energy level fit of ${\rm BiH_3}\,.$ All observations are in ${\rm cm^{-1}}.$

State	Obs.	Obscalc.
100A ₁	1733.25	-0.01
100E	1734.47	0.01
200A ₁	3406.70	0.20
200 <i>E</i>	3406.36	-0.20

six-dimensional variational vibrational calculation with an exact kinetic energy operator and an accurate state-of-the-art *ab initio* potential energy surface on this system (see Refs. 39 and 40 for this kind of approach applied to NH₃ and H_3O^+). A comparison with SbH₃ shows that, although the separation of the stretching fundamentals in stibine is larger, the (200*A*₁) and (200*E*) states of SbH₃ are more degenerate. But interestingly, also in stibine the order of the *A*₁ and *E* states is reversed when compared with stretching fundamentals. A stretching vibrational model similar to the one adopted in the present contribution does not account for this energy level order change.⁴¹

VI. CONCLUSION

We have been able to obtain a high-resolution infrared spectrum of hitherto inaccessible BiH₃ in spite of its reactivity and fast decomposition. In addition to the fundamental bands,²¹ the first stretching overtone spectrum could also be recorded. This has been assigned as the $(200A_1/E)$ local-mode band. The $2\nu_3 (A_1/E)$ stretching overtone band reaching the $(110A_1/E)$ state in the local-mode notation is apparently too weak to be observed with the experimental set-up available to us.

The nonlinear least-squares optimization of vibrational parameters of a simple model leads to a rms deviation of $\sim 0.8 \times 10^{-3} \text{ cm}^{-1}$. This is about 1/10 of the resolution $(6.6 \times 10^{-3} \text{ cm}^{-1})$ used, and the body of the data does not reveal any nonrandom residuals. Therefore, we consider the quality of the fit as fully satisfactory.

The quartic centrifugal distortion parameters of the $(200A_1)$ and (200E) states agree within 5.3% at worst. These are also similar to the ground state values with differences in the absolute value being between 1% and 15%. We noticed that constraining the *J* and *K* dependencies of the *r* and $\alpha^{(BC)}$ parameters to zero changes the D_J , D_{JK} , and D_K constants of the (200E) state to physically unsatisfactory values without altering the rms deviation of the fit. We have rejected this alternative solution when fitting the data. Supposedly, these two fit approaches respond in a slightly different manner to perturbational effects exerted by unidentified dark states.

The rotational analysis of the $(200A_1/E)$ state clearly disclosed the expected local-mode behavior. Simple local mode limit formulas explain well the vibrational dependence of the effective vibration–rotation parameters. It is of interest to know whether BiH₃ is closer to the local-mode limit than

TABLE VI. Local-mode parameters and relations of the $(200A_1/E)$ states of some XH₃ molecules.

Parameter	$^{75}\mathrm{AsH_{3}}^{a}$	$^{121}\mathrm{SbH_{3}}^{\mathrm{b}}$	²⁰⁹ BiH ₃ ^c	Theory ^d
$\overline{\nu(A_1) - \nu(E) \ (cm^{-1})}$	-1.164	0.073	0.339	0.0
$(C\zeta)/C_0 \times 10^3$	-3.94	-2.43	-2.52	0.0
$(B\Omega\zeta)/B_0 \times 10^3$	± 6.50	± 3.44	±3.79	0.0
$(B^{(A_1)} - B^{(E)}) \times 10^3$	-0.47	1.38	-0.46	0.0
(cm^{-1})				
$(C^{(A_1)} - C^{(E)}) \times 10^3$	-4.47	-1.13	-0.61	0.0
(cm^{-1})				
$\alpha_{\rm eff}^{(BB)}/\overline{q}$	-1.5163	-1.3932	-1.4787	-1.4142
$\alpha_{\rm eff}^{(BC)}/r_{\rm eff}$	5.461	5.569	5.697	5.657

^aFrom Ref. 9 with the ground state parameters from Ref. 35.

^bFrom Ref. 11.

^cThis work.

^dFrom Ref. 8.

the lighter XH_3 species AsH_3 (Refs. 9 and 10) and SbH_3 .¹¹ This comparison can be made on the basis of vibrational, rotational, and rovibrational resonance parameters as given in Table VI. It is evident that BiH_3 is closer to the theoretical values for *perfect* local-mode behavior than AsH_3 but the difference between SbH_3 and BiH_3 is small.

Vibrational analysis with a simple stretching vibrational model produces good results. The effects of the neglected bending vibrations are shown to be small and the stretching vibrational potential energy parameters obtained are close to true values. This is pleasing because, if the very highest precision is not needed, the bending vibrations can safely be decoupled from the stretches.

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