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REGULAR ARTICLE

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Vibrational spectrum of BiH_3: Six-dimensional variational calculations on high-level ab initio potential energy surfaces

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Abstract We report a theoretical study of the ground electronic state of BiH_3. The potential energy surface (PES) is obtained from coupled cluster CCSD(T) calculations with a large basis set (289 contracted Gaussian functions). The previously available quartic force field (P4) is extended by adding the dominant quintic and sextic stretching terms to yield improved potential functions in symmetry coordinates (P6) and Morse-type coordinates (M4). Second-order rovibrational perturbation calculations on the P4-PES and full variational calculations on the P6-PES and M4-PES yield almost identical vibrational term values which is rationalized by considering the local mode behavior of BiH_3 and the Morse-type character of the M4-PES. The remaining deviations between the computed and observed vibrational term values must thus be caused by imperfections in the CCSD(T) surface. A refinement of this ab initio surface by a restrained fit to experimental data allows an essentially perfect reproduction of the observed vibrational term values. Variational calculations on this refined surface provide predictions for several overtone and combination bands that have not yet been observed.

Keywords BiH_3 · Ab initio · Variational calculations · Vibrational spectra · Local modes

1 Introduction

Bismuthine BiH_3 is the least stable hydride of the group 15 elements. It has remained poorly characterized until 2002 when its structure and rovibrational spectrum were determined from gas phase measurements [1]. Subsequent experimental work has provided more accurate ground state parameters [2], an analysis of the high resolution infrared spectra of the fundamental bands [3], and a local mode analysis of the $2\nu_1(A_1)/\nu_1+\nu_3(E)$ band system [4]. These experimental studies have been accompanied and guided by theoretical calculations [1,3,5] at the coupled cluster CCSD(T) level which yield the equilibrium geometry and the quartic force field. The associated spectroscopic constants derived from second-order rovibrational perturbation theory generally agree well with their experimental counterparts [1,3,5].

A closer comparison between the measured and computed fundamental wavenumbers of BiH_3 shows, however, that the deviations between theory and experiment are somewhat larger than expected for CCSD(T) results with extended basis sets [5]. Part of these deviations have been traced to spin–orbit effects which lower the fundamental wavenumbers to a different extent for different modes and thereby improve the splitting between the stretching fundamentals [5]. Other possible sources of error in the theoretical treatment include the neglect of higher excitations in the coupled cluster series, basis set incompleteness, the quartic representation of the force field (without higher-order terms) and the use of the second-order rovibrational perturbation theory. In the present contribution, we explore the effects of the latter two limitations.

The paper is structured as follows. In Sect. 2 we provide an ab initio potential energy function as a quartic force field in symmetry internal coordinates. In Sect. 3 we present results of variational calculations of the vibrational term values on this surface and compare them with the results from second-order perturbation theory. In Sect. 4 we extend the ab initio potential energy function by adding selected quintic and sextic terms for the Bi–H stretching coordinates and check the effects of these additional terms on the vibrational term values. In Sect. 5 we refine the ab initio surface by fitting the potential parameters against the available experimental levels, with the restraint that the refined surface must remain close to the original ab initio surface. In Sect. 6 we offer some conclusions.

Dedicated to Hermann Stoll on the occasion of his 60th birthday

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2 Quartic force field

The quartic force field of BiH_3 has been obtained [3,5] from coupled cluster theory with all single and double excitations [6] augmented by a perturbational estimate of the effects of connected triple excitations (CCSD(T)) [7] with a formally nonrelativistic Hamiltonian. The Bi atom was described by a scalar-relativistic small-core pseudopotential [8] replacing 60 inner-core electrons ($1s$–$4f$). This pseudopotential was used in conjunction with a (12s12p10d5f3g2h)/ [8s8p7d5f3g2h] set of contracted Gaussian-type orbitals [5]. The hydrogen atoms were represented by the augmented correlation-consistent polarized valence quadruple-zeta basis aug-cc-pVQZ [9]. All 26 explicitly treated outer-core and valence electrons in BiH_3 were correlated. This approach will be denoted as CCSD(T)/EXT since the basis set has been called EXT [5].

The potential energy surface (PES) is represented by the quartic polynomial

$$V - V_e = \frac{1}{2}\sum_{i,j} F_{i,j} S_i S_j + \frac{1}{6}\sum_{i,j,k} F_{i,j,k} S_i S_j S_k + \frac{1}{24}\sum_{i,j,k,l} F_{i,j,k,l} S_i S_j S_k S_l \quad (1)$$

in symmetry adapted internal coordinates

$$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3), \quad (2)$$

$$S_2 = \frac{1}{\sqrt{3}}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3), \quad (3)$$

$$S_{3a} = \frac{1}{\sqrt{6}}(2\,\Delta r_1 - \Delta r_2 - \Delta r_3), \quad (4)$$

$$S_{3b} = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3), \quad (5)$$

$$S_{4a} = \frac{1}{\sqrt{6}}(2\,\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3), \quad (6)$$

$$S_{4b} = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_3). \quad (7)$$

Here Δr_i (i =1–3) correspond to the three Bi–H$_i$ displacements, and $\Delta\alpha_i$ (i = 1–3) denote the three H–Bi–H valence angle displacements, with α_i opposite to r_i. Throughout the paper this quartic polynomial expansion (1) is referred to as P4, where 'P' stands for the polynomial expansion and '4' for the fourth order.

The P4 symmetry force constants are given in Table 1. They have already been used [3] to compute the spectroscopic constants of BiH_3 which were found to be in reasonable agreement with experiment and served as background for the experimental assignments.

Table 1 Computed quadratic, cubic, and quartic symmetry force constants F_{ij}, F_{ijk}, and F_{ijkl} of BiH_3. Units are consistent with energies in aJ, bond lengths in Å, and bond angles in radians[a–c]

i, j, k	Value	i, j, k, l	Value	i, j, k, l	Value
11	1.9616	244	−0.3622	2234	−0.1140
12	0.0619	333	−3.3844	2244	0.0620
22	0.5279	334	−0.0815	1333	6.8510
33	1.9871	344	0.0967	1334	0.1050
34	−0.0174	444	0.2703	1344	0.0620
44	0.5625	1111	10.1210	1444	−0.1030
111	−4.7718	1112	0.4080	2333	−0.0810
112	−0.2506	1122	−0.3660	2334	0.1920
122	−0.1601	1222	0.1050	2344	−0.0280
222	0.4143	2222	1.1360	2444	−0.5720
133	−4.7730	1133	9.8590	3333	14.8350
134	0.1157	1134	−0.2580	3334	−0.0830
144	−0.2965	1144	−0.0690	3344	−0.2120
233	−0.0010	1233	0.0750	334b4b	−0.4450
234	0.1387	1234	0.0640	3444	−0.1130
244	−0.3622	1244	0.2340	4444	1.2930

[a] The quadratic and cubic force constants are from Ref. [3]
[b] Conventions for indices: 3 = 3a, 4 = 4a
[c] Quadratic force constants with spin–orbit corrections from Ref. [5] included: F_{11} = 1.9486 aJ/Å^2, F_{12} = 0.0633 aJ/Å, F_{22} = 0.5250 aJ, F_{33} = 1.9615 aJ/Å^2, F_{34} = -0.0187 aJ/Å, and F_{44} = 0.5610 aJ

3 Variational calculations

The present calculations of the vibrational levels in BiH_3 employ a variational approach which has been described in detail in Ref. [10]. This approach is designed for the calculation of the rotation–vibration spectra (including intensities, see Refs. [11,12]) of XY_3 pyramidal molecules. It is based on the Hougen–Bunker–Johns formalism [13] which provides maximum separation between different modes. The molecular motion is viewed as small-amplitude displacements (five vibrations) from a flexible *reference configuration* (of C_{3v} geometrical symmetry for BiH_3) that follows the 'umbrella' mode and rotation. The stretching motions are described by the coordinates $\Delta r_i^{(\ell)}$, i = 1, 2, 3, which are linearized versions [10] of the bond length displacements Δr_i. Likewise, the bending motions are treated by the coordinates S_{4a}^{ℓ} and S_{4b}^{ℓ} which are linearized versions of S_{4a} and S_{4b}. The 'umbrella' mode is represented by the sixth vibrational coordinate ρ which defines the molecular reference configuration [10]. This coordinate ρ is handled numerically and is therefore suitable both for single-well potentials as in BiH_3 and for double-well inversion potentials in floppy XY_3 molecules such as NH_3 [10,14]. Hence, the model is applicable to isolated electronic states of any pyramidal molecule independent of the height of the barrier; in the present case, the barrier to inversion is known to be very high in BiH_3 [15]. The rotational motion is described by means of a molecule-fixed axis system defined by Eckart–Sayvetz conditions [16,17].

In the variational calculations the basis set is truncated according to

$$P = 2(v_1 + v_3) + v_2 + v_4 \le P_{\max} = 18, \quad (8)$$

Table 2 Vibrational term values (in cm^{-1}) for the electronic ground state of BiH_3 calculated using second-order perturbation theory (PT) and variational theory (VT) for three potential energy functions P4, P6, and M4

		P4			P6		M4	
State	Obs.	PT	VT-4[a]	VT	PT	VT	PT	VT
ν_2	726.7	737.14	736.58	736.98	737.14	736.60	737.22	737.55
ν_4	751.24	759.90	759.34	760.40	759.90	759.79	759.96	760.04
ν_1	1733.25	1750.20	1749.04	1761.41	1750.20	1750.50	1750.81	1750.74
ν_3	1734.47	1759.98	1758.77	1770.98	1759.98	1759.99	1760.65	1760.57
$2\nu_1$	3406.7	3451.10	3448.47	3496.51	3451.10	3452.97	3452.28	3452.95
$\nu_1 + \nu_3$	3406.36	3452.85	3449.50	3498.12	3452.85	3453.77	3454.04	3454.02

[a] VT-4 denotes variational results with fourth-order truncation in terms of the linearized coordinates (see text for details)

where v_1, v_2, v_3, and v_4 are standard normal mode quantum numbers. In our variational scheme the nuclear kinetic energy operator and potential energy function are expressed as truncated expansions (with ρ-dependent expansion coefficients) in the coordinates $y_i^\ell = 1 - \exp(-a\Delta r_i^\ell)$ $(i = 1, 2, 3)$, S_{4a}^ℓ, and S_{4b}^ℓ, where a is a standard Morse parameter. The kinetic energy operator, given by the factor $G_{\lambda\mu}$, and the pseudopotential function U are truncated after the fourth order of the expansion [10] which has been checked to ensure convergence to better than $0.01\,cm^{-1}$ in the present case.

Table 2 lists the published experimental values [3,4] for the vibrational band centers (ν_1, ν_2, ν_3, ν_4, $2\nu_1$, and $\nu_1 + \nu_3$) and the corresponding values obtained from second-order perturbation theory (PT) and from variational theory (VT) using three different potential energy functions (P4 see above, P6 and M4 see Sect. 4). The following discussion will focus on the comparison between different sets of theoretical results, while the experimental data are included for easy reference.

We first address variational calculations (labeled VT-4) where the fourth-order polynomial expansion P4 has been transformed into a fourth-order expansion in terms of y_i^ℓ, S_{4a}^ℓ, and S_{4b}^ℓ (PES type B according to the notation from Ref. [10]) such that the transformed potential and the original expansion P4 are equivalent through fourth order. The re-expansion is performed numerically. We use $a = 1.39\,Å^{-1}$ since this value of the Morse parameter best reproduces the CCSD(T) potential curve for Bi–H in BiH_3 (see Sect. 4). Comparing the PT and VT-4 results, the fundamental wavenumbers for the bending modes (ν_2/ν_4) are quite similar, within $1\,cm^{-1}$. The differences for the stretching modes are somewhat larger, but not excessive, up to $2\,cm^{-1}$ for the fundamentals (ν_1/ν_3) and $4\,cm^{-1}$ for the overtone and combination bands ($2\nu_1/\nu_1 + \nu_3$). Relative to experiment, the VT-4 values show only a very minor improvement over the PT values, since the deviations from experiment are much larger than the differences between PT and VT-4.

We know from our previous studies on NH_3 [10] that the VT-4 treatment with a fourth-order potential re-expansion is not yet converged for a given PES: we need at least a sixth-order re-expansion to obtain reasonably stable vibrational term values, especially for the stretching modes. We have therefore re-expanded the P4-PES in terms of $\xi_i^\ell = \{y_i^\ell, S_{4a}^\ell, S_{4b}^\ell\}$ (PES type B) up to sixth order. The corresponding variational results (VT in Table 2) are higher than those from VT-4, by about $1\,cm^{-1}$ for the bending modes, $12\,cm^{-1}$ for the stretching fundamentals, and $48\,cm^{-1}$ for the stretching overtone and combination bands. Going from VT-4 to VT thus significantly increases the discrepancies from experiment for the stretching modes. It is obvious that this is due to the fact that the quartic force field P4 does not contain quintic and higher terms which are required in a complete variational treatment (unlike PT and VT-4 which only include up to quartic terms and thus yield comparable and balanced results). The need for higher-order potential energy terms in variational calculations has been recognized long ago [18,19].

We shall therefore extend the quartic expansion in Eq. (1) by adding quintic and sextic terms for bond stretching only. This is a minimalist approach for capturing the most important higher-order effects of the true potential energy surface of BiH_3. The focus on the bond stretching terms is supported by the finding that BiH_3 is a prototypical local mode molecule [4] with a heavy central Bi atom bound to three light H atoms, small intermode coupling, and a bond angle very close to 90°. It has been demonstrated [4] that the stretching modes in BiH_3 are well separated and can be approximated by three weakly coupled diatomic Morse potentials $V_i = D_e\, y_i^2$ with Morse coordinates $y_i = 1 - \exp(-a\Delta r_i)$, where D_e is the bond dissociation energy. In view of this situation, we shall not only extend the PES as indicated, but also explore PES expansions in terms of Morse coordinates.

4 Ab initio calculations and improved potential energy functions

The present quantum-chemical calculations employed the same ab initio approach as before [3,5] (see Sect. 2). They were performed with the MOLPRO2002 program [20,21]. Taking advantage of the local mode character of BiH_3, CCSD(T)/EXT energies were computed at 95 geometries that involve distortions along one particular Bi–H bond (-0.7 Bohr $\leq \Delta r_1 \leq 1.2$ Bohr) while keeping the other two Bi–H bonds and all bond angles fixed at their theoretical equilibrium values [3,5] ($r_e = 1.7784\,Å$, $\alpha_e = 90.12°$). The ab initio energies are listed in Table 3.

Table 3 Ab initio energies ($m E_h$) of the electronic ground state of BiH_3 relative to $V = -216.270508979\ E_h$

Δr_1	Energy	Δr_1	Energy	Δr_1	Energy
−0.70	54.4730	−0.10	0.6841	0.22	2.6250
−0.65	44.9781	−0.09	0.5499	0.23	2.8489
−0.60	36.7217	−0.08	0.4312	0.24	3.0802
−0.55	29.5827	−0.07	0.3276	0.25	3.3188
−0.50	23.4523	−0.06	0.2389	0.26	3.5645
−0.45	18.2319	−0.05	0.1646	0.27	3.8171
−0.40	13.8327	−0.04	0.1045	0.28	4.0764
−0.35	10.1746	−0.03	0.0583	0.29	4.3424
−0.34	9.5253	−0.02	0.0257	0.30	4.6147
−0.33	8.9023	−0.01	0.0064	0.31	4.8933
−0.32	8.3049	0.00	0.0000	0.32	5.1780
−0.31	7.7325	0.01	0.0064	0.33	5.4687
−0.30	7.1848	0.02	0.0251	0.34	5.7651
−0.29	6.6612	0.03	0.0561	0.35	6.0672
−0.28	6.1612	0.04	0.0989	0.40	7.6569
−0.27	5.6842	0.05	0.1534	0.45	9.3664
−0.26	5.2299	0.06	0.2192	0.50	11.1796
−0.25	4.7978	0.07	0.2961	0.55	13.0819
−0.24	4.3873	0.08	0.3839	0.60	15.0599
−0.23	3.9982	0.09	0.4823	0.65	17.1014
−0.22	3.6298	0.10	0.5911	0.70	19.1951
−0.21	3.2818	0.11	0.7101	0.75	21.3308
−0.20	2.9538	0.12	0.8389	0.80	23.4992
−0.19	2.6454	0.13	0.9775	0.85	25.6915
−0.18	2.3561	0.14	1.1255	0.90	27.8999
−0.17	2.0855	0.15	1.2828	0.95	30.1173
−0.16	1.8332	0.16	1.4491	1.00	32.3370
−0.15	1.5990	0.17	1.6242	1.05	34.5529
−0.14	1.3823	0.18	1.8079	1.10	36.7595
−0.13	1.1828	0.19	2.0001	1.15	38.9517
−0.12	1.0002	0.20	2.2004	1.20	41.1250
−0.11	0.8341	0.21	2.4088		

The corresponding geometries involve distortions along the Bi–H_1 bond (-0.7 Bohr $\le \Delta r_1 \le 1.2$ Bohr), while the other bond lengths and the bond angles are kept fixed at their ab initio equilibrium values [3,5] $r_e = 1.7784$ Å and $\alpha_e = 90.12^\circ$, respectively

To incorporate the new ab initio data we introduce a simple extension to P4 that will be referred to as P6:

$$V = \mathrm{P4} + \frac{f_{rrrrr}}{120}(r_1^5 + r_2^5 + r_3^5) + \frac{f_{rrrrrr}}{720}(r_1^6 + r_2^6 + r_3^6). \tag{9}$$

Taking into account the decoupling of the stretching oscillators [4] and assuming the higher-order bending terms to be negligible, we include only the dominant diagonal quintic and sextic stretching terms. The two internal coordinate force constants $f_{rrrrr} = -109.6(3)$ aJ/Å^5 and $f_{rrrrrr} = 440(10)$ aJ/Å^6 were computed numerically from the data in Table 3 using step sizes of 0.01–0.04 Bohr and 0.02–0.05 Bohr, respectively. The uncertainties in parentheses were estimated by considering the dependence of f_{rrrrr} and f_{rrrrrr} on the chosen step sizes. Corresponding symmetry force constants can be easily evaluated from f_{rrrrr} and f_{rrrrrr} using Eqs. (2), (4), (5).

Figure 1 shows how well the ab initio data (solid line) from Table 3 are reproduced by the expansions P4 (dash-dotted line) and P6 (dashed line). It is obvious that P6 is superior to P4 for larger displacements, as expected, but

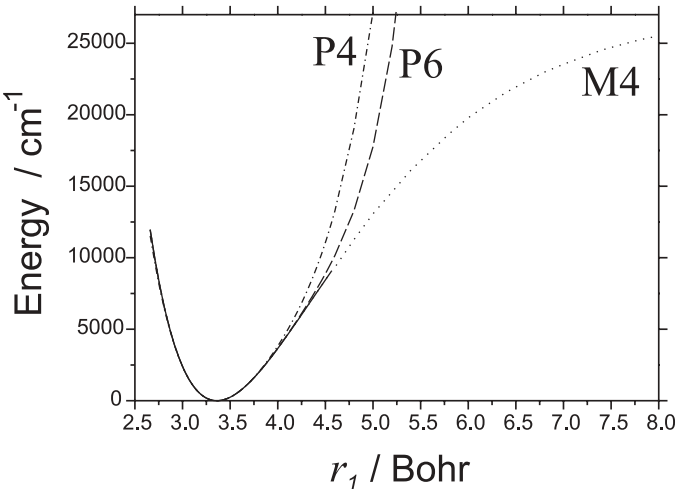

Fig. 1 Potential energy curves P4 (*dot-dash*), P6 (*dash*), and M4 (*dot*) along the Bi-H_1 bond, keeping the other bond lengths and the bond angles fixed at their ab initio equilibrium values. The ab initio data are indicated by the *solid line*

both exhibit the wrong asymptotic behavior for large Bi–H distances. Morse potentials are designed to give the correct asymptotic behavior, and we have therefore also fitted the one-dimensional (1D) Morse function

$$V_1 = f_2\, y_1^2 \tag{10}$$

to the energies from Table 3. The resulting parameters $a = 1.3668(15)$ Å^{-1} and $D_e = f_2 = 26715(57)$ cm^{-1} yield a root-mean-square (rms) error of 2.9 cm^{-1} for geometries with distortions $|\Delta r_1| < 0.4$ Bohr. They are reasonably close to the values $a = 1.353(5)$ Å^{-1} and $D_e = 26199(214)$ cm^{-1} that can be derived from the parameters ω and ωx [4] obtained by fitting to the experimental ν_1, ν_3, $2\nu_1$, and $\nu_1 + \nu_3$ band centers. When extending Eq. (10) with one extra quartic term $f_4\, y_1^4$, all ab initio energies from Table 3 can be fitted accurately ($a = 1.38817(10)$ Å^{-1}, $f_2 = 25864.8(36)$ cm^{-1}, $f_4 = 1291.4(70)$ cm^{-1}, rms deviation = 0.6 cm^{-1}).

We now introduce an alternative Morse-type representation of the P6-PES that uses a fourth-order expansion (PES type A in Ref. [10])

$$\begin{aligned} V(\xi_1, \xi_2, \xi_3, \xi_{4a}, \xi_{4b}; \sin\bar{\rho}) &= V_e + V_0(\sin\bar{\rho}) + \sum_j F_j(\sin\bar{\rho})\,\xi_j \\ &+ \sum_{j\le k} F_{jk}(\sin\bar{\rho})\,\xi_j\,\xi_k + \sum_{j\le k\le l} F_{jkl}(\sin\bar{\rho})\,\xi_j\,\xi_k\,\xi_l \\ &+ \sum_{j\le k\le l\le m} F_{jklm}(\sin\bar{\rho})\,\xi_j\,\xi_k\,\xi_l\,\xi_m \end{aligned} \tag{11}$$

in terms of the variables $\xi_1 = y_1$, $\xi_2 = y_2$, $\xi_3 = y_3$ (stretching coordinates), $\xi_{4a} = S_{4a}$, $\xi_{4b} = S_{4b}$ (two bending coordinates), and

$$\sin\bar{\rho} = \frac{2}{\sqrt{3}}\sin[(\alpha_1 + \alpha_2 + \alpha_3)/6] \tag{12}$$

for the 'umbrella' motion. The inversion potential energy function in Eq. (11) is taken to be

$$V_0(\sin\bar{\rho}) = \sum_{s=1}^{4} f_0^{(s)} (\sin\rho_e - \sin\bar{\rho})^s, \tag{13}$$

and the functions $F_{jk...}(\sin\bar{\rho})$ are defined as

$$F_{jk...}(\sin\bar{\rho}) = \sum_{s=0}^{N} f_{jk...}^{(s)} (\sin\rho_e - \sin\bar{\rho})^s, \tag{14}$$

where $\sin\rho_e$ is the equilibrium value of $\sin\bar{\rho}$ and the quantities $f_0^{(s)}$ and $f_{jk...}^{(s)}$ in Eqs. (13) and (14) are expansion coefficients. The summation limits in Eq. (14) are $N = 3$ for $F_j(\sin\bar{\rho})$, $N = 2$ for $F_{jk}(\sin\bar{\rho})$, $N = 1$ for $F_{jkl}(\sin\bar{\rho})$, $N = 0$ for $F_{jklm}(\sin\bar{\rho})$. In total there are 48 symmetrically unique potential parameters $f_{jk...}^{(s)}$. We have determined these parameters by (a) analytically transforming the Taylor expansion P4 [Eq. (1)] into the Morse-type form [Eq. (11)] and (b) adjusting the three parameters f_{11}^0, f_{111}^0, and f_{1111}^0 by least-squares fitting to the ab initio energies given in Table 3 (95 data points). The resulting values are listed in Table 4. The parameter $a = 1.39\,\text{Å}^{-1}$ is taken from the 1D Morse oscillator analysis (see above). The potential energy function defined by Eq. (11) and the ab initio parameters in Table 4 is denoted as M4, with 'M' standing for the Morse-type expansion and '4' for the fourth order.

The two potential representations P6 and M4 are equivalent in terms of the ab initio data used to generate them, and one may therefore expect that the vibrational term values computed for P6 and M4 should be quite similar. This is indeed the case (see Table 2). The corresponding differences do not exceed $1.2\,\text{cm}^{-1}$ for PT and $1.0\,\text{cm}^{-1}$ for VT. The PT values are identical for P4 and P6 by definition, while those for M4 have been calculated from normal coordinate force constants obtained numerically from the M4-PES. The VT values for P6 and M4 are all based on sixth-order potential re-expansions (see Sect. 3) which is appropriate here because the dominant quintic and sextic stretching terms are included in P6 and M4 (see above). While P6 and M4 give results of similar quality and are thus essentially equivalent in the spectroscopically relevant region, the Morse-type function M4 is our favored potential representation overall because it is superior in the asymptotic region by design.

Focusing on the results for M4 in Table 2, it is reassuring that the PT and VT vibrational term values are close to each other, within $1\,\text{cm}^{-1}$. This can be understood in terms of the pronounced local mode behavior of BiH_3 and the Morse-like character of the M4-PES. Following Mills and Robiette [22], it is possible to derive a fourth-order anharmonic analog of the $x - K$ relations: using the strict local mode limit conditions [23], $m_H \ll m_{Bi}$, $\alpha_e = 90°$, $f_{rr'} = f_{r\alpha} = f_{r\alpha'} = f_{\alpha\alpha'} = 0$, one obtains rather simple $y - K$ relations for the fourth-order anharmonic constant y_{111}:

$$y_{111} = \frac{5k_{111111}}{2} - \frac{35k_{11111}k_{111}}{2\omega} + \frac{225k_{1111}k_{111}^2}{4\omega^2} - \frac{17k_{1111}^2}{4\omega} - \frac{705k_{111}^4}{16\omega^3}, \tag{15}$$

where $\omega = \omega_1 \equiv \omega_3$ is a harmonic frequency, $k_{111...}$ denotes a normal coordinate force constant, the masses m_H and m_{Bi} refer to hydrogen and bismuth, respectively, and $f_{rr'}$, $f_{r\alpha}$, $f_{r\alpha'}$, and $f_{\alpha\alpha'}$ are non-diagonal internal coordinate force constants. Inserting in Eq. (15) the $k_{111...}$ value for a Morse oscillator yields $y_{111} = 0$. Hence, there are no extra fourth-order anharmonic corrections which implies that the second-order perturbation treatment should be essentially converged in this case. This is consistent with the excellent agreement between the PT and VT results for M4.

Comparing the previously available PT vibrational term values for P4 [3,5] with the most refined current results (VT for M4), we again find excellent agreement to within $1\,\text{cm}^{-1}$ for the fundamental modes and $2\,\text{cm}^{-1}$ for the overtone and combination bands (see Table 2) which is gratifying, but must be considered fortuitous to some extent. We are thus led to the conclusion that the use of second-order rovibrational perturbation theory in conjunction with the quartic P4-PES is not the source of the discrepancies between experiment and theory, because variational calculations with a PES that includes sextic stretching terms offer no improvement.

5 Refinement

The results in the preceding section suggest that imperfections in the CCSD(T)/EXT surface are responsible for the deviations between the observed and computed vibrational term values in Table 2. In a purely ab initio approach, one would thus need to go beyond the CCSD(T)/EXT level by including higher excitations in the coupled cluster series [24, 25], corrections for basis set incompleteness [14, 25], other minor terms such as diagonal Born–Oppenheimer corrections [25], and spin–orbit (SO) effects [5]. It has been established that the first three of these corrections cause changes of several wavenumbers in the fundamental transitions of NH_3 [25] and that spin–orbit effects lower the fundamental wavenumbers of BiH_3 by up to $12\,\text{cm}^{-1}$ [5].

Since a proper inclusion of the first two corrections requires extensive ab initio calculations, we have decided to adopt a different strategy in the refinement of the CCSD(T)/EXT surface. Following a commonly applied practice in spectroscopic work, we empirically adjust the ab initio surface by fitting to the experimental data that are available for the ground electronic state of BiH_3. In this refinement we work with the Morse-type expansion (11). Initial parameters are generated from the SO-corrected [5] CCSD(T)/EXT quadratic force constants and the CCSD(T)/EXT cubic and quartic force constants (see Table 1, especially footnote c) by transformation to the Morse-type representation (11). The corresponding potential function is labeled as M4-SO. During the fitting, the equilibrium bond length r_e and bond angle α_e are kept constant at their experimental values [3] of 1.77834 Å and 90.321°, respectively, and the Morse parameter a is kept fixed at $1.39\,\text{Å}^{-1}$ (see Sect. 4). The applied least-squares procedure has been described in detail elsewhere [26].

Table 4 Potential energy parameters (in cm^{-1} unless otherwise indicated) for BiH_3 in the Morse-type expansion of Eq. (11). We use labels 4 and 5 for the indexes 4a and 4b, respectively

	Ab initio	Fitted				Ab initio	Fitted		
	M4	I[a]	II[b]	II[b]		M4	I[a]	II[b]	II[b]
$a/Å^{-1}$	1.39	1.39	1.39	1.92		1.39	1.39	1.39	1.92
f_0^2	239660.43	235023.74[d]	239749.52	239198.30	f_{123}^0	−92.36	−92.36	121.27	−34.67
f_0^3	−560736.61	−560736.61	−564931.60	−563131.75	f_{123}^1	714.01	714.01	6118.28	268.48
f_0^4	1838287.59	1838287.59	1955148.38	1853073.22	f_{124}^0	1428.61	1428.61	1444.19	743.38
f_1^1	−5520.38	−5520.38	−5496.35	−4076.75	f_{124}^1	5451.94	5451.94	−4686.60	2841.93
f_1^2	−26909.37	−26909.37	−25221.18	−19416.95	f_{144}^0	−1676.12	−1676.12	−1629.12	−1209.07
f_1^3	3544.70	3544.70	3806.52	2555.30	f_{144}^1	−8663.00	−8663.00	−5628.56	−6260.10
f_{11}^0	25795.70[c]	25171.60[d]	25518.46	13363.46	f_{155}^0	−4545.89	−4545.89	−4289.04	−3279.20
f_{11}^1	1932.16	1932.16	2430.04	407.60	f_{155}^1	−12192.15	−12192.15	−18409.94	−8810.36
f_{11}^2	−50893.13	−50893.13	−127250.11	−29263.65	f_{455}^0	−6803.50	−6803.50	−6792.92	−6803.50
f_{12}^0	−223.15	−73.40[d]	−109.16	−58.72	f_{455}^1	−61146.82	−61146.82	−88010.23	−61254.58
f_{12}^1	9273.24	9273.24	9571.98	4833.85	f_{1111}^0	1302.30[c]	1416.36	404.56	2091.07
f_{12}^2	−14453.88	−14453.88	1039.66	−7558.09	f_{1112}^0	37.93	37.93	103.78	13.60
f_{14}^0	−516.97	−516.97	−457.17	−400.32	f_{1114}^0	121.03	121.03	−6136.29	80.84
f_{14}^1	−17481.91	−17481.91	−15978.47	−12632.87	f_{1122}^0	364.25	364.25	−1070.50	101.81
f_{14}^2	−19773.43	−19773.43	−43484.14	−14286.65	f_{1123}^0	−105.80	−105.80	2677.35	−33.48
f_{44}^0	14159.23	13856.88[d]	14168.38	14120.47	f_{1124}^0	−69.56	−69.56	863.82	77.46
f_{44}^1	38719.19	38719.19	38722.61	38787.43	f_{1125}^0	−125.66	−125.66	−3221.45	132.22
f_{44}^2	−9710.76	−9710.76	−57280.77	−9828.90	f_{1144}^0	−1532.71	−1532.71	−6138.54	−966.00
f_{111}^0	29.70[c]	−160.82	459.74	3557.97	f_{1155}^0	−4753.72	−4753.72	−12649.59	−2930.47
f_{111}^1	1228.90	1228.90	−11292.77	476.66	f_{1244}^0	817.22	817.22	2792.73	425.24
f_{112}^0	−85.20	−85.20	−644.73	−19.46	f_{1255}^0	1452.82	1452.82	1610.25	755.98
f_{112}^1	590.16	590.16	−4231.94	895.38	f_{1444}^0	−919.16	−919.16	−1708.52	−663.04
f_{114}^0	459.92	459.92	790.70	173.66	f_{1455}^0	521.80	521.80	−892.41	376.40
f_{114}^1	−19236.87	−19236.87	−46113.84	−11787.63	f_{4444}^0	2712.09	2712.09	2950.93	2712.09

[a] Morse-type force constants obtained by fitting to experimental data using approach I: Only four quadratic parameters were varied (see text for details)
[b] Morse-type force constants obtained by fitting to experimental and ab initio data using approach II: All parameters were varied (see text for details)
[c] Parameters readjusted by fitting to the 1D ab initio data from Table 3; initial values $f_{11}^0 = 25962.22\,cm^{-1}$, $f_{111}^0 = -160.82\,cm^{-1}$, $f_{1111}^0 = 1416.36\,cm^{-1}$. The remaining parameters were fixed to their ab initio values (see text for details)
[d] Parameters readjusted by fitting to experimental data; initial values $f_0^2 = 239660.43\,cm^{-1}$, $f_{11}^0 = 25962.22\,cm^{-1}$, $f_{12}^0 = -223.16\,cm^{-1}$, $f_{44}^0 = 14159.23\,cm^{-1}$. The remaining parameters were fixed to their ab initio values (see text for details)

In view of the limited amount of available experimental information, we have adopted the following two fitting approaches. In approach I we optimize only four quadratic parameters f_{11}^0, f_{12}^0, f_0^2, and f_{44}^0 with respect to the six available experimental term values (Table 2). In approach II we fit all 48 parameters entering Eq. (11), but impose the restraint that the resulting potential must remain close to the ab initio surface: following a previously described strategy [26], the reference data in approach II include the experimental term values and 3000 energies generated from the ab initio M4-SO potential function on a grid that covers the equilibrium region up to $3000\,cm^{-1}$. The optimized potential parameters from these two approaches are included in Table 4. The experimental term values are well reproduced by both refinements, with rms errors of $0.34\,cm^{-1}$ (approach I) and $0.08\,cm^{-1}$ (approach II), respectively, while the rms deviations for the 3000 M4-SO reference energies amount to $\sim 40\,cm^{-1}$ (approach I) and $\sim 10\,cm^{-1}$ (approach II). Both refined surfaces yield a dissociation limit of $D_e \approx 26400\,cm^{-1}$, which is consistent with the published local mode analysis [4], but significantly higher than the best SO-corrected theoretical value of $D_e = 19120\ cm^{-1}$ for the average Bi–H dissociation energy [5]. To explore the spectroscopic implications of such a lower dissociation limit, we have performed another fit according to approach II with a fixed Morse parameter $a = 1.92 Å^{-1}$. The resulting set of optimized parameters (Table 4) yields a dissociation energy of $D_e \approx 19700\,cm^{-1}$ and is still capable of reproducing the six experimental term values accurately, with an rms error of $0.01\,cm^{-1}$. This indicates the high flexibility of approach II with 48 optimized parameters.

Table 5 lists the vibrational term values obtained by variational calculations on the three refined surfaces. As already mentioned, the six known experimental values (Table 2) are reproduced almost exactly, while the results for the other transitions are predictions which show some obvious scatter:

Table 5 Vibrational term values (in cm^{-1}) of BiH_3 obtained from variational calculations using three refined potential energy functions[a]

	I	II	II
$a/Å^{-1}$	1.39	1.39	1.92
ν_2	726.70	726.70	726.70
$2\nu_2$	1451.03	1451.36	1450.75
$2\nu_4$	1499.07	1499.90	1499.36
ν_1	1732.96	1733.30	1733.26
$3\nu_2$	2173.36	2174.15	2173.06
$4\nu_2$	2893.73	2894.76	2892.62
$2\nu_1$	3407.08	3406.57	3406.69
$2\nu_3^0$	3466.31	3468.04	3470.77
$3\nu_1$	5019.60	5017.02	5013.53
$4\nu_1$	6571.63	6566.93	6558.39
ν_4	751.24	751.22	751.24
$\nu_2 + \nu_4$	1477.71	1474.96	1475.12
$2\nu_4^2$	1503.07	1503.70	1503.27
ν_3	1733.91	1734.56	1734.48
$3\nu_4^1$	2247.47	2250.01	2249.90
$4\nu_4^2$	2996.35	3000.67	3000.26
$\nu_1 + \nu_3$	3406.69	3406.30	3406.36
$2\nu_3^2$	3467.60	3463.78	3461.65
$3\nu_3^1$	5019.47	5017.12	5013.20
$4\nu_3^2$	6571.61	6567.04	6558.30

[a] See Table 4

the deviations between any pair of predicted term values are usually less than $2\,cm^{-1}$ below $3000\,cm^{-1}$and reach up to $9\,cm^{-1}$ above $6000\,cm^{-1}$. This is indicative of the accuracy that may be expected from the current refinements. More experimental input data are needed to further improve these surfaces.

6 Conclusions

Variational calculations of the vibrational term values of BiH_3 confirm that the quartic force field (P4) needs to be extended by higher-order terms for an adequate description. The inclusion of the dominant fifth-order and sixth-order stretching force constants in internal coordinates (f_{rrrrr}, f_{rrrrrr}) is the minimal extension (P6) that is sufficient for our purposes. Morse-type expansions can be truncated at fourth order (M4) because of their qualitatively correct asymptotic behavior with regard to bond dissociation.

Second-order rovibrational perturbation calculations on the P4-PES and full variational calculations on the P6-PES and M4-PES yield almost identical vibrational term values which is rationalized by considering the local mode behavior of BiH_3 and the Morse-type character of the M4-PES. The remaining deviations between the computed and observed vibrational term values must therefore be caused by imperfections in the underlying CCSD(T)/EXT surface. A refinement of this ab initio surface by a restrained fit to experimental data allows an essentially perfect reproduction of the observed vibrational term values. Predictions are made for several overtone and combination bands so that the accuracy of the refined surfaces can be tested by future experimental studies.

It has been demonstrated recently [4] that BiH_3 exhibits its vibrational local mode character and is close to the rovibrational local mode limit. Our theoretical model for the rotation and vibration of an XY_3 molecule [10] is designed to provide maximum separation of the rotational and vibrational motions, and it is therefore particularly suitable for variational calculations of the energies and wavefunctions of highly excited rotational states. Recently we have studied rotational excitations up to $J = 80$ in the vibrational ground state of PH_3 and found the formation of six-fold clusters of rotational energies [27]. BiH_3 is expected to show similar phenomena at significantly lower rotational excitation, and it should therefore be possible to study such effects with our variational approach also for vibrationally excited states. Corresponding investigations are in progress using the potential functions developed here.

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References

1. Jerzembeck W, Bürger H, Constantin L, Margulès L, Demaison J, Breidung J, Thiel W (2002) Angew Chem, Int Ed 41:2550
2. Jerzembeck W, Bürger H, Constantin FL, Margulès L, Demaison J (2004) J Mol Spectrosc 226:24
3. Jerzembeck W, Bürger H, Breidung J, Thiel W (2004) J Mol Spectrosc 226:32
4. Jerzembeck W, Bürger H, Hänninen V, Halonen L (2004) J Chem Phys 120:5650
5. Breidung J, Thiel W, Figgen D, Stoll H (2004) J Chem Phys 120:10404
6. Purvis GD, Bartlett RJ (1982) J Chem Phys 76:1910
7. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 157:479
8. Metz B, Stoll H, Dolg M (2000) J Chem Phys 113:2563
9. Kendall RA, Dunning TH, Harrison RJ (1992) J Chem Phys 96:6796
10. Yurchenko SN, Carvajal M, Jensen P, Lin H, Zheng JJ, Thiel W (2005) Mol Phys 103:359
11. Yurchenko SN, Carvajal M, Thiel W, Lin H, Jensen P (2005) Adv Quant Chem 48:209
12. Yurchenko SN, Carvajal M, Lin H, Zheng JJ, Thiel W, Jensen P (2005) J Chem Phys 122:104317
13. Hougen JT, Bunker PR, Johns JWC (1970) J Mol Spectrosc 34:136
14. Lin H, Thiel W, Yurchenko SN, Carvajal M, Jensen P (2002) J Chem Phys 117:11265
15. Schwerdtfeger P, Laakkonen LJ, Pykkö P (1992) J Chem Phys 96:6807
16. Eckart C (1935) Phys Rev 47:552
17. Sayvetz A (1939) J Chem Phys 7:383
18. Botschwina P (1979) Chem Phys 40:33
19. Botschwina P (1982) Chem Phys 68:41
20. Werner H-J, Knowles PJ, MOLPRO, versions 2002.3 and 2002.6, a package of ab initio programs, written with contributions from Amos RD, Bernhardsson A, Berning A Celani P, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Knowles PJ, Korona T, Lindh R, Lloyd AW, McNicholas SJ, Manby FR, Meyer W, Mura ME, Nicklass A, Palmieri P, Pitzer R, Rauhut G, Schütz M, Schumann U, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T, Werner H-J

21. Hampel C, Peterson K, Werner H-J (1992) Chem Phys Lett 190:1 and references therein. The program to compute the perturbative triples corrections has been developed by Deegan MJO, Knowles PJ (1994) ibid 227:321
22. Mills IM, Robiette AG (1985) Mol Phys 56:743
23. Halonen L, Robiette AG (1986) J Chem Phys 84:6861
24. Kállay M, Gauss J (2004) J Chem Phys 120:6841
25. Rajamäki T, Kállay M, Noga J, Valiron P, Halonen L (2004) Mol Phys 102:2297
26. Yurchenko SN, Carvajal M, Jensen P, Herregodts F, Huet TR (2003) Chem Phys 290:59
27. Yurchenko SN, Thiel W, Patchkovskii S, Jensen P (2005) Phys Chem Chem Phys 7:573