Ab Initio Study of the Vibrational Frequencies of H_nBNH_n ($n = 1, 2, 3$) and Related Compounds

Paul Brint* and Benchang Sangchakr

Department of Chemistry, University College, Cork, S. Ireland

Patrick W. Fowler

Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD

The equilibrium geometries and vibrational frequencies of the H_nBNH_n ($n = 1, 2, 3$) molecules have been calculated at the SCF level using a 4-31G** basis set. Comparative calculations were carried out for the isoelectronic hydrocarbons. The borane-ammonia adduct was treated at the correlated second-order Møller-Plesset level, with analytic calculation of second derivatives. The B—N stretching vibration in H_3BNH_3 is poorly described at the SCF level and shifts from 604 to 679 cm^{-1} on inclusion of electron correlation. Over the whole set of molecules, calculated SCF harmonic frequencies are uniformly higher than the experimental fundamentals by 10%, with a few exceptions that lead to proposed reassignments of some spectroscopic bands. A correlation between BH stretching frequency and nominal hybridisation is determined and its application to some related compounds discussed.

It is well established that the infrared absorption frequencies of CH bonds are diagnostic of the hybridisation of the carbon atom, the frequency increasing with the carbon 2s component.[1] It is reasonable, therefore, to expect a similar variation for BH bonds. This effect appears never to have been quantified, however, and although some spectroscopic work of high quality exists for simple BH-containing compounds, it is not comprehensive. We have therefore carried out a purely theoretical investigation of this effect using *ab initio* calculations and comparing results with experiment wherever possible. The object is not to show that the effect occurs (it obviously must), but to gauge its magnitude and determine whether observed vibrational frequencies are a sensitive test of boron hybridisation. The interest arises from a long-term study of the bonding of boranes and related clusters in which we have used theoretical and spectroscopic methods.[2] We are currently investigating the information content of the infrared spectra of borane molecules and their correspondence with theories of borane bonding. An application of the following to the spectra of *closo*-boranes will be reported in a later paper.

The methodology of this study was first to establish an appropriate basis set and level of treatment of electron correlation, by calculating the equilibrium geometry of HCCH, a molecule which is sufficiently small to be computationally tractable and also contains a multiple bond, which is demanding in accuracy. The chosen level of calculation was then applied to H_3CCH_3 and H_2CCH_2 for equilibrium geometry and to all three hydrocarbons for the evaluation of fundamental vibrational frequencies, which were found to compare well with experiment. The same level of calculation was then applied to the boron-containing analogues H_3BNH_3, H_2BNH_2 and HBNH to provide data to illustrate the frequency/hybridisation relationship.

Method of Calculation

The GAUSSIAN 82 *ab initio* program[3] was used for most of the calculations, taking the internal basis sets and default convergence criteria ($10^{-9}E_h$ in energy). Vibrational

Table 1. Equilibrium geometries of HCCH calculated with various basis sets at SCF and post-SCF levels

	CH	CC
STO-3G	1.065	1.168
4-31G	1.051	1.189
6-31G	1.053	1.194
4-31G**	1.056	1.183
6-31G**	1.057	1.186
MP2/4-31G**	1.061	1.215
CID/4-31G**	1.059	1.199
expt	1.061	1.203

All geometries were linear. The values are given in Å and the experimental results are taken from an r_e structure in ref. (5).

frequencies were calculated using numerical fits to the potential-energy minima. In the cases of H_3CCH_3 and H_3BNH_3, the geometry was further optimised using the CADPAC program[4] with a tolerance on gradients of 10^{-5} a.u.; the vibrational frequencies of these molecules were then calculated using analytic second derivatives with the CRAY1S (ULCC) version of that program.

The optimised structures all coincide in symmetry with those deduced from experiment. The symmetries were checked as follows: for each molecule the geometry was optimised within an assumed point group and the Hessian matrix (matrix of second derivatives of the energy) determined. Diagonalisation of the Hessian gave the correct number of zero frequencies ($3N-6$ or $3N-5$), thus characterising the stationary point as a true minimum. If the assumed symmetry had been too high, at least one imaginary frequency would have been found. If the assumed symmetry were too low, the optimised structure would exhibit a higher symmetry than the initial guess.

Results

The equilibrium geometry of HCCH calculated with various basis sets and at SCF and post-SCF levels is shown in table 1. As a compromise between accuracy and computational time the 4-31G** basis set was chosen and used at the SCF level in the rest of this work. It is a genuine compromise as it is clear from table 1 that electron correlation definitely improves the accuracy of the calculated CC bond length.[5]

The geometries and vibrational frequencies of H_3CCH_3, H_2CCH_2 and HCCH are given in tables 2–5 together with the experimental values. The agreement between calculated and experimental geometries is generally better in the saturated molecules, showing that multiple bonds are computationally more demanding. The calculated vibrational frequencies are higher than experimental frequencies, but consistently so, average percentage errors being $9.8 \pm 2.1\%$ for H_3CCH_3 and $10.0 \pm 2.1\%$ for H_2CCH_2. Such errors have been shown by Pople[6] to be typically *ca.* 13% as a percentage of the experimental value, equivalent to our 10% of the calculated value. Allowing for this systematic error, the only values in significant disagreement with experiment are the degenerate modes of HCCH, both of which involve the triple bond and whose low value make any absolute error more significant, and for similar reasons the low-energy a_{1u} mode of H_3CCH_3. The π_g bending frequency of acetylene is notoriously dependent upon basis set; it is claimed[7] that f functions are required for its correct description at SCF and correlated levels.

Table 2. Equilibrium geometries calculated at the SCF level with the 4-31G** basis set

species	symmetry	energy	dipole moment	geometric parameters	
H_3BNH_3	C_{3v}	−82.546510	5.5625	B—H 1.208 (1.210)[a]	∠HBN 104.4 (104.5)
				B—N 1.685 (1.672)	∠HNB 110.7 (109.9)
				N—H 1.002 (1.014)	
H_2BNH_2	C_{2v}	−81.419944	1.8322	B—H 1.192	∠HBN 119.4
				B—N 1.385	∠HNB 123.1
				N—H 0.993	
HBNH	$C_{\infty v}$	−80.217379	0.6917	B—H 1.165	
				B—N 1.221	
				N—H 0.978	
H_3CCH_3	D_{3d}	−79.162010		C—H 1.076 (1.091)[b]	∠HCH 111.2 (108.0)
				C—C 1.525 (1.536)	
H_2CCH_2	D_{2h}	−77.961291		C—H 1.076 (1.086)[b]	∠HCC 121.8 (121.2)
				C—C 1.312 (1.339)	
HCCH	$D_{\infty h}$	−76.744379		C—H 1.056 (1.060)[b]	
				C—C 1.183 (1.203)	

[a] Ref. (18). [b] Ref. (4). Distances are quoted in Å and angles in degrees. Experimental values are given in brackets (where known). The total energy is quoted in hartree, dipole moments in D.

Table 3. Ground-state vibrational frequencies of H_3BNH_3 and H_3CCH_3 calculated in the 4-31G** basis set

H_3BNH_3				H_3CCH_3			
assignment	calc.	expt	error (%)	assignment	calc.	expt	error (%)
7,e	3820.3	3386	11.4	$10,e_u$	3256.5	2995.5	8.0
$1,a_1$	3692.1	3337	9.6	$7,e_g$	3230.8	2950.0	8.7
8,e	2589.3	2415	6.7	$1,a_{1g}$	3183.2	2953.8	7.2
$2,a_1$	2544.0	2340	8.0	$5,a_{2u}$	3178.2	2895.7	8.9
9,e	1802.6	1608	10.7	$11,e_u$	1635.8	1472.2	10.0
$3,a_1$	1446.0	1343	7.1	$8,e_g$	1630.2	1468.7	9.9
10,e	1302.7	1301	0.1	$2,a_{1g}$	1567.7	1388.4	11.4
$4,a_1$	1289.9	(1052)[a]	18.0	$6,a_{2u}$	1535.3	1379.1	10.1
11,e	1133.7	(1186)[a]	−4.7	$9,e_g$	1332.8	1190.0	10.6
12,e	681.2	603	11.4	$3,a_{1g}$	1059.2	944.8	10.7
$5,a_1$	604.2	(968)[b]	−60.0	$12,e_u$	889.7	821.5	7.4
$6,b_2$	257.1	(232)[a]	9.7	$4,a_{1u}$	328.5	278.0	15.2

[a] Assignment disputed. See discussion in the text. [b] Estimated [see ref. (10)]. Assignments are $(\nu_n,$ symmetry species) and frequencies are reported in cm^{-1}.

When making a comparison between theoretical and experimental frequencies, it is useful to bear in mind that the calculation gives purely *harmonic* frequencies for an *isolated* molecule. The fundamental bands measured in the i.r. spectrum are contaminated by anharmonic contributions from the cubic and quartic terms in the force field, leading to values consistently lower than the true harmonic frequencies. Extrapolation from results for diatomics[8] would suggest that anharmonic effects account for *ca.* one third of the previously noted 10% discrepancy. Torsional vibrations may be poorly modelled by the single-well harmonic oscillator, and weak dative bonds (*e.g.* $H_3B \leftarrow NH_3$) are likely to show large anharmonicities. Spectra of transient species such as HBNH are recorded for molecules trapped in inert-gas matrices; matrix shifts of up to $60\ cm^{-1}$ have been observed for hydrogen halides in Xe.[9]

Table 4. Ground-state vibrational frequencies of H_2BNH_2 and H_2CCH_2 calculated in the 4-31G** basis set

H$_2$BNH$_2$				H$_2$CCH$_2$			
assignment	calc.	expt[a]	error (%)	assignment	calc.	expt	error (%)
9,b$_2$	3941.5	3534	11.5	8,b$_{2u}$	3396.1	3105.3	8.5
1,a$_1$	3837.4	3451	11.2	10,b$_g$	3369.1	3102.5	7.9
10,b$_2$	2746.9	2564	7.1	1,a$_g$	3317.5	3026.4	5.7
2,a$_1$	2681.2	2495	7.4	5,b$_{1u}$	3293.4	2988.6	9.2
3,a$_1$	1789.2	1625	10.1	2,a$_g$	1860.6	1622.6	12.7
4,a$_1$	1450.9	1337	8.5	6,b$_{1u}$	1600.7	1433.5	9.8
5,a$_1$	1232.0	1225	0.6	3,a$_g$	1493.2	1342.2	10.1
11,b$_2$	1226.9	1131	8.4	11,b$_{3g}$	1350.0	1236	8.3
7,b$_1$	1110.9	1005	10.4	4,a$_u$	1159.6	1027	11.5
6,a$_2$	879.9	763	15.3	7,b$_{2g}$	1106.1	950	14.1
12,b$_2$	769.8	593	34.4	12,b$_{3u}$	1096.6	949.2	13.4
8,b$_1$	641.9	670	−4.1	9,b$_{2u}$	896.1	810.3	9.6

[a] Ref. (20). Assignments are (ν_n, symmetry species).

Table 5. Ground-state vibrational frequencies of HBNH and HCCH calculated in the 4-31G** basis set

HBNH				HCCH			
assignment	calc.	expt	error (%)	assignment	calc.	expt	error (%)
1,σ	4132.0	3700	10.4	1,σ_g	3697.5	3372.5	8.2
2,σ	3002.9			3,σ_u	3584.5	3294.9	8.0
3,σ	1983.1	1785	8.1	2,σ_g	2256.8	1973.5	12.5
4,π	837.5			5,π_u	879.1	729.2	17.0
5,π	578.5	460	20.4	4,π_g	801.6	611.7	23.7

[a] Ref. (24). Assignments are (ν_n, symmetry species).

Tables 2–5 give equivalent data for the isoelectronic–isostructural boron–nitrogen compounds. Again the geometries agree very well with experimental structures, where these are known, and the vibrational frequencies, with a few notable exceptions, are close to or within the +10% error expected from the hydrocarbons. The overall agreement between calculation and experiment is extremely good and shows that SCF calculations in the 4-31G** basis provide a good representation of the vibrational ground state of these molecules. This conclusion is undoubtedly limited to the lower vibrational levels of the ground electronic state of these molecules as work on the dissociation of H_3BNH_3 has shown that a much larger basis and inclusion of electron correlation is required for accurate calculation away from the minimum.[10] The vibrational frequencies of H_3BNH_3 have been calculated previously[11] at the 6-31G** level and the results are essentially identical to ours. The only large difference between the two sets of theoretical results is in the lowest-energy ν_6 mode, the i.r.-inactive hindered rotation about the BN bond. The value in table 3 shows the expected error of *ca.* +10%, whilst that of ref. (11) is 11% *below* the estimated experimental value. We are reporting the harmonic frequency, whereas the authors of ref. (10) have used a hindered-rotor model to calculate a torsional fundamental of 198 cm^{-1}. The 'experimental' frequency of 232 cm^{-1} is itself not directly observed, and the value depends upon use of the same model of the torsional barrier.[11] The *harmonic* frequencies in 4-31G** and 6-31G* bases are very similar.

Of the notable deviations between calculated and experimental frequencies the following seem worth further consideration.

(a) ν_5, a_1 Mode of H_3BNH_3

The -60% error reported in table 3 clearly suggests a major problem with the BN stretching mode. Independently of any disagreement with calculation, difficulties with the assignment of this mode have been noted before.[12] Although H_3BNH_3 is highly polar ($\mu = 5.216$ D†),[13] the BN stretch is predicted to be only weakly i.r.-active. In the matrix-isolation spectrum[14] a weak band at 968 cm^{-1} was assigned to ^{11}BN stretching, and various weak features in the range 931-987 cm^{-1} were assigned to the BN stretch in different isotopomers. All previous work[15-17] on the free molecule, or on H_3BNH_3 in various solvents, gave $\nu(BN)$ from 776 to 790 cm^{-1}. A matrix shift of *ca.* 200 cm^{-1} is larger than would be expected, even for this dissociative stretching mode. The authors of ref. (14) point out that their assignment gives a force constant 1.6 times greater than previous estimates and one that is larger than the estimated value for $H_3BN(CH_3)_3$.[17] On chemical grounds one would expect the BN bond in the latter compound to have a much higher force constant since trimethylamine is a stronger base than ammonia.

Our 4-31G** calculations give a force constant for the BN stretch of 177 N m^{-1}, which is in moderate agreement with early experimental estimates of 290 and 295 N m^{-1}, but not with the value of 456 N m^{-1} derived in ref. (14). An independent estimate of the BN stretching force constant can be made from the microwave spectrum of H_3BNH_3. In a pseudo-diatomic model, taking the borane and ammonia subunits as rigid, the BN force constant is

$$k_{BN} = \frac{16\pi^2 \mu B^3}{D_J}$$

where B is the rotational constant, D_J is the centrifugal distortion constant and μ is the reduced mass of the oscillator. If B and D_J are in MHz and μ in kg, then k_{BN} is given in N m^{-2}. Results from seven isotopic forms [table III, ref. (18)] give $k_{BN} = 220 \pm 60$ N m^{-2}, with five of the values lying within the range 220 ± 10 N m^{-2}. Although not expected to be very accurate estimates, these values are clearly more compatible with our lower BN stretching force constant, casting further doubt on the assignment made in ref. (14). However, even if it is accepted that the ν_5 mode has an experimental frequency of 780 ± 10 cm^{-1}, there is still a discrepancy of some 180 cm^{-1} (-29%) between the 4-31G** SCF value and experiment. Why should an SCF calculation underestimate this frequency in particular? It is conventional to describe the BN bond as a dative bond formed by donation of the ammonia lone pair to the empty p_z orbital of BH_3. A single-determinant SCF treatment does not give a correct account of the dissociation energy of this molecule. Several studies[10,11] have shown that SCF wavefunctions recover only *ca.* two thirds of the estimated experimental D_e; a correlated wavefunction is needed for the remaining third. Electron correlation would be expected to have an effect of similar magnitude on the BN force constant, causing both it and ν_5 to increase.

To check this hypothesis, the geometry of the H_3BNH_3 molecule was optimised at the second-order Møller–Plesset level using version 4.0 of the CADPAC program[19] to calculate the MP2 force constants analytically. The results show minor changes in most of the geometric parameters when compared with the SCF calculations: $r(B-H) = 1.200$ Å (-0.008 Å), $r(B-N) = 1.654$ Å (-0.031 Å), $r(N-H) = 1.013$ Å (-0.001 Å), $\angle HBN\ 104.5°$ ($+0.1°$), $\angle HNB\ 107.8°$ (-2.9). The main effect is a shortening in the BN bondlength (by rather too much when compared with experiment). The MP2 frequencies are compared with the SCF and experimental values in table 6. Most of the modes fall in frequency. ν_2 and ν_8 increase by small amounts (1.9 and 0.6%, respectively) but the

† 1 D $= 3.335\,64 \times 10^{-30}$ C m.

Table 6. Effects of electron correlation on the vibrational frequencies of H_3BNH_3, calculated at the MP2 level in the 4-31G** basis

assignment	MP2	Δ	expt	error (MP2) (%)
7e	3683.6	−136.7	3386	8.1
1a₁	3541.2	−150.9	3337	5.8
8e	2639.6	50.3	2415	8.5
2a₁	2559.7	15.7	2340	8.6
9e	1715.1	−87.5	1608	6.2
3a₁	1373.1	−72.9	1343	2.2
10e	1270.7	−32.0	1301	−2.3
4a₁	1254.6	−35.3	(1052)^a	(16.1)
11e	1108.5	−25.2	(1186)^a	(−7.0)
12e	660.3	−20.9	603	8.7
5a₁	679.0	74.8	(968)^a	(−42.6)
6a₂	275.9	18.8	(232)^b	(15.9)

^{a} Assignment disputed. See discussion in the text. ^{b} Estimated [see ref. (10)]. The column headed Δ shows the change in frequency from the SCF calculations reported in table 3.

significant changes are in the BN stretch ν_5 (+12.4%) and the torsional frequency ν_6 (+7.3%). Overall agreement with experiment is improved. The stretching force constant for the BN bond is 216 N m^{-1} at the MP2 level, in better agreement with the estimate from centrifugal distortion constants.

There is not yet sufficient experience with MP2 frequencies to give a precise estimate of their expected accuracy, but available calculations suggest that for DZP (double-zeta plus polarisation) basis sets MP2 frequencies are *ca.* twice as accurate as SCF results in the same basis, although with errors that may be of either sign, unlike the generally positive SCF error.[20,21] It is not claimed here that the present 4-31G** basis gives a quantitative account of the MP2 correlation effects, but it does seem likely that the broad conclusions (a BN stretching constant that is unusually sensitive to electron correlation and larger than the SCF value) will be stable against improvement in the basis.

The BN stretching vibration in this complex is something of a special case, in that the SCF force constant is too small. The present authors agree with the conclusion of Binkley and Thorne[10] that such large errors are likely to be confined to those modes directly involving stretching of the dative bond. For other frequencies H_3BNH_3 shows only the 'normal' 10% SCF overestimation. Conclusions about the NH and BH stretches may usefully be drawn, even from an SCF calculation.

(b) ν_4, a₁ and ν_{11}, e Modes of H_3BNH_3

These are the symmetric and antisymmetric angular deformation modes of the BH_3 group. The assignment in ref. (14) was $\nu_4 = 1052$, $\nu_{11} = 1186$ cm^{-1}, made on the ground that antisymmetric vibrations are usually higher in energy. The opposite assignment for the corresponding frequencies (1026 and 1175 cm^{-1}) was made by Taylor.[15] The present calculation finds that the e mode has a higher frequency, both at SCF and MP2 levels. Reversing the experimental assignment would give SCF errors of 8.1% and 7.2%, respectively, which would be more consistent with the expected behaviour.

(c) ν_8, b₁ and ν_{12}, b₂ Modes of H_2BNH_2

Table 4 shows poor agreement for both these modes and in this case the experimental assignments[22] should be much more certain, being based both on characteristic

Table 7. Variation of the average X—H stretching frequency
with nominal hybridisation

	X		
hybridisation	B	C	N
sp^3	2368	2964	3169
sp^2	2497	3077	3578
sp	2763	3350	3801
approx. range	400	390	730

The average calculated value is increased by 8% to allow
for the systematic overestimation of experimental frequen-
cies. Frequencies are quoted in cm^{-1}.

frequencies and also on symmetry assignment from rotational structure. It happens,
however, that for these two modes there is no direct evidence. Their frequencies were
inferred from combination bands $\nu_6 - \nu_8$, $\nu_2 + \nu_{12}$ and even these are observed only
through their interference with the rotational structure of the ν_4 fundamental. Whilst
the analysis appears sound there is some scope for uncertainty in this rather complex
assignment procedure, and it may be worth reconsideration as simply reversing the
assignment of the two modes produces errors of the expected magnitude (1.6 and 7.6%,
respectively).

Conclusions

The variation of experimentally observed vibrational frequency of BH stretches with
nominal hybridisation is summarised in Table 7, and is clearly large enough to be used
as a diagnostic of hybridisation.† The NH stretches show a considerably wider range
and therefore a potentially more useful correlation. The values for CH stretches are in
near perfect agreement with those quoted in standard texts. The values given in table
7 are, of course, only typical ones corresponding approximately to precise hybridisation
and should really have a range on them, which from experimental data seems to be of
the order of ± 50 cm^{-1}. Alternatively the vibrational frequency can be considered as a
continuous function of hybridisation and used to predict the s-p mixing in particular
molecules. We note that the experimental BH stretching frequencies in borazole (2530,
2535 cm^{-1})[23] and $H_3BN_2H_4$ (2210-2360 cm^{-1})[16] are within the predicted ranges for sp^2
and sp^3 hybridisation, respectively. Price *et al.*[23] find an NH stretching mode at 3490 cm^{-1}
and note that this is higher than typical amine frequencies. It is in reasonable agreement
with the sp^2 value in table 7.

The only question left in deciding the usefulness of the correlation for other molecules
containing boron-hydrogen bonds is whether the B—N bonding is a sufficient perturba-
tion to the nominal hybridisation to distort the result. As a check we consider the
experimentally determined frequencies of B_2H_6. These are (for the BH stretches):
a_g 2524, 2104 cm^{-1}, b_{1u} 2612 cm^{-1}, b_{2g} 2591 cm^{-1}, b_{2u} 1915 cm^{-1} and b_{3u} 2525 cm^{-1}.[5]
The correspondence with hybridisation suggests that the four terminal BH bonds are
intermediate between sp^2 and sp hybridised, whilst the modes involving the bridging
hydrogens are outside the range of table 7, having more p character than sp^3, clearly

---

† The nominal hybridisation is, of course, judged on the molecular geometry and atom connectivities (the
nearness of the geometries to classic tetrahedron, trigonal and linear shapes). Other factors can effect the
geometry-hydrisation relationship, but given the simplicity of these molecules and the small range of
electronegativities involved the classic relationship is certainly applicable.

Vibrational Frequencies of H_nBNH_n

Table 8. Stretching force constants of H_nBNH_n molecules calculated at the SCF level with the 4-31G** basis set

force constant/10^2 N m^{-1}	H_3BNH_3	H_2BNH_2	HBNH
B—H	3.62	4.02	4.70
B—N	1.77	7.58	16.3
N—H	7.78	8.39	9.33

MP2 correlation corrections raises the B—N force constant of H_3BNH_3 to 216 N m^{-1} (see text).

very different from the simplest description of two sp^2 hybridised BH_3 groups weakly associated. This is supported by the geometric structure of the molecule which shows an H_b—B—H_b bond angle of 96.5°,[25] consistent with large p character. BH_3 should have hybridisation very close to sp^2 (exact in the absence of polarisation functions) and a calculation on this molecule finds one of the BH stretches in very good agreement with table 7 and the degenerate pair at slightly higher frequency than expected. This small inconsistency could arise because BH_3 contains only one heavy atom whereas all other molecules considered contain two.

Finally, table 8 summarises the stretching force constants calculated in the course of this work.

References

1 C. A. Coulson, *Valence* (Oxford University Press, Oxford, 2nd edn, 1961), p. 210.
2 B. Sangchakr and P. Brint, *J. Chem. Soc., Dalton Trans.*, 1988, 105.
   P. Brint, K. O'Cuill, and T. R. Spalding, *Polyhedron*, 1985, **5**, 1791.
3 J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, G. Fluder and J. A. Pople, GAUSIAN 82, Carnegie-Mellon University, Pittsburgh, PA 15213.
4 R. D. Amos, CADPAC—*The Cambridge Analytic Derivatives Package*, S.E.R.C., Daresbury CCP1/84/4, 1984.
5 All geometric data and vibrational frequencies for the hydrocarbons were taken from: G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
6 J. A. Pople, H. B. Schegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch and R. A. Whiteside, *Int. J. Quantum Chem. Symp.*, 1981, **15**, 269.
7 E. D. Simandiras, J. E. Rice, T. J. Lee, R. D. Amos and N. C. Handy, *J. Chem. Phys.*, 1988, **88**, 3187.
8 W. J. Hehre, L. Radom, P.v.R. Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986), p. 233.
9 A. J. Barnes, in *Vibrational Spectroscopy of Trapped Species*, ed. H. E. Hallam (Wiley, Chichester, 1973).
10 C. Zirc and R. Ahlrichs, *J. Chem. Phys.*, 1981, **75**, 4980.
11 J. S. Binkley and L. R. Thorne, *J. Chem. Phys.*, 1983, **79**, 2932.
12 W. Sawodny, in *Gmelin Handbuch der Anorganischen Chemie, Band 52, Tiel 18 Borverbindungen* (1978), p. 39.
13 R. D. Suendram and L. R. Thorne, *Chem. Phys. Lett.*, 1981, **78**, 157.
14 J. Smith, K. S. Seshadri and D. White, *J. Mol. Spectrosc.*, 1973, **45**, 327.
15 R. C. Taylor, *Adv. Chem. Ser.*, 1964, **42**, 59.
16 J. Goubeau and E. Ricker, *Z. Anorg. Allg. Chem.*, 1961, **310**, 123.
17 W. Sawodny and J. Goubeau, *Z. Phys. Chem. (Frankfurt)*, 1965, **44**, 227.
18 L. R. Thorne, R. D. Suendram and F. J. Lovas, *J. Chem. Phys.*, 1983, **78**, 167.
19 R. D. Amos and J. E. Rice, *CADPAC: The Cambridge Analytic Derivative Package*, issue 4.0, Cambridge, 1987.
20 E. D. Simandiras, R. D. Amos and N. C. Handy, *Chem. Phys. Lett.*, 1987, **133**, 324.
21 N. C. Handy, J. F. Gaw and E. D. Simandiras, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 1577.
22 M. C. L. Gerry, W. Lewis-Bevan, A. J. Merer and N. P. C. Westwood, *J. Mol. Spectrosc.*, 1985, **110**, 153.

23 W. C. Price, R. D. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.
24 E. R. Lory and R. F. Porter, *J. Am. Chem. Soc.*, 1973, **95**, 1766.
25 K. Kuchitsu, *J. Chem. Phys.*, 1968, **49**, 4456; W. J. Lafferty, A. G. Maki and T. D. Coyle, *J. Mol. Spectrosc.*, 1970, **33**, 345.