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Analysis of Vibration-rotational Spectra of BiH

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Analysis of measurements of vibration-rotational transitions of $^{209}Bi^1H$ and $^{209}Bi^2H$ in electronic ground state X 0^+ yielded values of coefficients of radial functions that represent the internuclear potential energy and adiabatic and nonadiabatic rotational effects of the hydrogen atomic centre. Both these effects have exceptionally large magnitudes, tentatively attributed in part to interaction with nearby electronically excited state A 1. The maximum range of validity of radial functions of BiH is $1.49 \le R/10^{-10}$ m ≤ 2.4; the equilibrium internuclear distance R_e is $(1.8041955 \pm 0.00000186) \times 10^{-10}$ m.

INTRODUCTION

Precise measurements of infrared spectra of diatomic molecules by means of both tunable lasers and interferometric spectrometers challenge development of quantitative theoretical treatments. Besides the internuclear potential energy that is the dominant effect on vibration-rotational energies and hence on transitions between such states, one must take into account that a diatomic molecule consists of not merely two atoms lacking internal structure but rather two nuclei with their associated electrons. Both the finite mass of an individual nucleus, not infinitely large relative to the mass of an electron, and the finite volume of each individual nucleus, not zero, impress their effects on measurable frequencies or wavenumbers of transitions under conditions of sufficiently great spectral resolution.

For LiH, in analysis of available spectra we supplemented these data with calculated values of the electric dipolar moment and rotational g factor.[1] Although in principle the latter information of both kinds might be readily derived from spectra measured with the Stark and Zeeman effects, available measurements are insufficient for the purpose; the few electrons per molecule made practicable accurate computation of the required data. In this way we discovered that for LiH adiabatic effects — that internuclear potential energy depends on not only internuclear separation but also relative nuclear momenta — were generally larger than both nonadiabatic rotational and vibrational effects, whereby electrons fail to follow perfectly nuclei in their rotation and vibration, respectively, with respect to the centre of mass. For CO,[2] AlCl,[3] SiS[3] and InF[4] the adiabatic effects become increasingly small relative to nonadiabatic rotational effects. For TlF, although corresponding analysis of available spectra appeared to indicate extraordinarily large adiabatic effects for Tl, a more reasonable explanation is that large nuclear sizes, or finite volumes and their isotopic variation, of ^{203}Tl and ^{205}Tl in contrast to ^{113}In and ^{115}In for instance, exert a detectable influence on the spectra of their diatomic fluorides,[4] confirming earlier evidence based on only pure rotational spectra.[5]

Which effects might be important for BiH is thus enigmatic to predict: adiabatic effects are associated with small nuclear masses of H and D that become detectable by means of isotopic substitution, but either adiabatic effects or effects of finite nuclear volume of Bi are indeterminate because spectral data for only one stable nuclide ^{209}Bi are available. Although vibration-rotational spectra of both BiH and BiD are reported, neither pure rotational spectra nor even calculated values of the rotational g factor and electric dipolar moment are known. Because of lack of isotopes of Bi, we are prevented from estimating both the rotational g factor and the electric dipolar moment of BiH from spectra measured in the absence of applied external electric or magnetic fields, as we endeavoured to do for GaH with some success.[6] A further complication is that coupling of electronic angular momenta yields an electronic ground state denoted X 0^+ and a related state A 1 of BiH; the energy of the latter is near that of vibrational state v=3 of BiH to which transitions are reported. In previous analyses of vibration-rotational spectra of BiH and BiD the authors derived only spectral parameters,[7-9] and no single analysis included all pertinent data. Hence an analysis of all data in terms of radial functions can yield further insight into intramolecular dynamics not only of this molecular species but also, by comparison with other diatomic species, of the general range and applicability of the various effects. For these rea-

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Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

sons we undertook this analysis of spectral data of BiH and BiD in the light of our quantitative treatment of relevant phenomena.[10]

SUMMARY OF THEORY AND TREATMENT OF EXPERIMENTAL DATA

Our procedure is based on a theoretical formalism[11] and its implementation in an algorithm[10] already applied to and tested with several compounds.[1-4,6,10] We review here briefly the salient features of the procedure that enable us to extract the molecular properties of interest.

In an effective hamiltonian for nuclear motion of form[11]

$$H_{eff} = \hat{P}[1 + \beta(R)]\hat{P}/2\mu + V(R) + V'(R) + hcB_e[1 + \alpha(R)]J(J+1)R_e^2/R^2 \qquad (1)$$

R_e is the equilibrium internuclear separation and $\hat{P}$ the operator for linear momentum of the nuclei; other quantities are defined below. To apply these functions we transform to the reduced displacement variable

$$z = 2(R - R_e)/(R + R_e) \qquad (2)$$

that possesses the property of remaining finite throughout the range of molecular existence: for $0 \le R < \infty$, $-2 \le z < 2$.[12,13] With SI units of wavenumber, we represent the potential energy $V(R)$ independent of nuclear mass in the form[12]

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j) \qquad (3)$$

For a diatomic molecule AB having nuclei of unlike protonic numbers and reduced mass μ, the remaining functions dependent on individual nuclear masses M_a and M_b we represent by means of separate expansions for the nucleus of each type A and B; we have for nonadiabatic vibrational effects,[10]

$$\beta(R) \rightarrow m_e \sum_{j=0} s_j^a z^j/M_a + \sum_{j=0} s_j^b z^j/M_b] \qquad (4)$$

for nonadiabatic rotational effects,[10]

$$\alpha(R) \rightarrow m_e[\sum_{j=0} t_j^a z^j/M_a + \sum_{j=0} t_j^b z^j/M_b] \qquad (5)$$

and for adiabatic effects[10] (combined with any residual nonadiabatic vibrational effects[11]),

$$V'(R) \rightarrow m_e[\sum_{j=1} u_j^a z^j/M_a + \sum_{j=1} u_j^b z^j/M_b] \qquad (6)$$

The molecular energies within a particular electronic state, or vibration-rotational terms, we express in the form[10]

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{r,a} + Z_{kl}^{r,b} + Z_{kl}^{v,a} + Z_{kl}^{v,b})(v + 1/2)^k (J^2 + J)^l \qquad (7)$$

in which the dependence of various term coefficients Y_{kl} and Z_{kl} on the radial coefficients is explained elsewhere.[10]

Available infrared spectral data of BiH of usable quality result from absorption by $^{209}Bi^1H$ and $^{209}Bi^2H$ separately of light from laser diodes,[8] and of emission of separate samples of these species measured with an interferometric spectrometer.[9] Because characteristics of the lasers precluded continuous tuning over broad ranges, many lines in each band were immeasurable; for this reason only 90 lines of $^{209}Bi^1H$, up to $v' = 4$ and $J = 33$, and 60 lines of $^{209}Bi^2H$ up to $v' = 3$ and $J = 28$, in progressions with $\Delta v = 1$ were measured, with nominal accuracy 0.1 m^{-1}.[8] In emission spectra 126 lines of $^{209}Bi^1H$ up to $v' = 3$ and $J = 26$ and 125 lines of $^{209}Bi^2H$ up to $v' = 3$ and $J = 38$, also in progressions with $\Delta v = 1$, were measured, with assigned accuracy variable from 0.03 m^{-1} to much larger values.[9] Because of extensive, but incomplete, overlap between these data sets, we combined them such that each line was assigned an uncertainty reflecting both the source of the data and its goodness of fit. Thus we selected for analysis in total 290 transitions with only slight duplication (in cases in which there was some discrepancy between the measurements and in which the interferometric measurements were not usable at the minimum uncertainty). Before combining these lines we verified by means of duplicated lines that no discernible general systematic shift of wavenumbers exists between measurements made with the diode laser[8] and the interferometer,[9] although significant divergences between the data sets appeared to occur near the limits of P and R branches of some bands; undoubtedly small intensities of the ultimately detectable lines caused precision of measurement to become degraded to some extent.

Of various models (sets of parameters) tested during the fitting process according to the criterion of the maximum F statistic,[14] the results of the best fit in Table 1 constitute parameters, each with its estimated (single) standard er-

Table 1. Coefficients of Radial Functions and Other Molecular Properties of ^{209}BiH X 0^{+} [a]

j	c_j	t_j^H	$u_j^H/10^6\ m^{-1}$
0	$(14000970.07 \pm 3.70)\ m^{-1}$	[0]	
1	-1.5858055 ± 0.0000223	17.0606 ± 0.0215	-124.291 ± 0.034
2	1.106944 ± 0.000131	-31.835 ± 0.157	392.081 ± 0.116
3	-0.64968 ± 0.00077		-619.60 ± 1.18
4	0.1902 ± 0.0056		842.11 ± 6.6
5	-0.7423 ± 0.0240		-894.04 ± 18.4
6	3.5056 ± 0.141		617.4 ± 108.0
7	-7.434 ± 0.54		

$U_{1,0}/m^{-1}\ u^{1/2} = 170303.567 \pm 0.079$
$U_{0,1}/m^{-1}\ u = 517.88028 \pm 0.00062$
$k_e/N\ m^{-1} = 170.882671 \pm 0.000187$
$R_e/10^{-10}\ m = 1.8041955 \pm 0.00000186$
range of validity $1.49 \leq R/10^{-10}\ m \leq 2.4$

[a] Each stated uncertainty represents one estimated standard error; the normalised standard deviation of the fit of 290 data was 0.99 and the F value was 2.9×10^{14}; the value of t_0^H was constrained in the final fit.

ror, in a set evaluated from specified spectral data of both isotopic variants of BiH by means of computer programme Radiatom.[10] For comparison with results from other sources this programme generates secondarily values of U_{kl} and $\Delta_{kl}^{a,b}$ in a commonly applied empirical relation[15]

$$E_{vJ} = \sum_{k=0} \sum_{l=0} U_{kl}\, \mu^{-(1/2k+1)} (v+1/2)^k [J(J+1)]^l \\ [1+m_e(\Delta_{kl}^{a}/M_a + \Delta_{kl}^{b}/M_b)] \tag{8}$$

for which our work[11] provides the first systematic theoretical justification. Our values of Δ_{kl}^H are derived directly from the sum of term coefficients $Z_{kl}^{v,H} + Z_{kl}^{r,H}$, but no values of Δ_{kl}^{Bi}, nor correspondingly $Z_{kl}^{v,Bi}$ and $Z_{kl}^{r,Bi}$, were evaluated because of lack of isotopes of Bi; all purely *mechanical* effects are taken into account in the principal term coefficients Y_{kl} in equation 7 or U_{kl} in equation 8 that include all pertinent contributions of whatever order. Values of Δ_{kl}^H generally reported[8,9] include implicitly contributions to Y_{kl} of order greater than that of $U_{kl} \equiv Y_{kl}^{(0)}\ \mu^{(1/2k+1)}$; hence values of $\Delta_{kl}^{a,b}$ from other sources reflect not only adiabatic and nonadiabatic effects but also mechanical effects in $Y_{kl}^{(2)}$, and we incorporated the latter contributions into values of Δ_{kl}^H presented in Table 2. Because of their secondary generation in the programme Radiatom based on various nonlinear combinations of primary parameters that are coefficients in radial functions (presented in Table 1), most values of U_{kl} and Δ_{kl}^H in Table 2 lack associated standard errors.

DISCUSSION

By means of 17 independently adjustable parameters in Table 1, we reproduced wavenumbers of 290 lines of BiH in two isotopic variants within the best estimates of uncertainties of their measurements.[8,9] That these parameters are fewer than those used previously, numbering 18 to 26[8] or 19 to 26[9] depending on whether U_{kl} and Δ_{kl}^H or Y_{kl} were applied,

Table 2. Auxiliary Parameters U_{kl} and Δ_{kl}^H of BiH[a]

k l	$U_{kl}/m^{-1}\ u^{1/2k+1}$	Δ_{kl}^H
1 0	170303.567 ± 0.079	-1.06156
2 0	-3202.3140	-0.2889
3 0	3.68131	34.9525
4 0	-0.76433	...
0 1	517.880278 ± 0.00062	-8.91845
1 1	-14.984290	-4.64275
2 1	0.0167287	236.1212
3 1	-6.22087×10^{-3}	...
4 1	-1.170×10^{-4}	...
0 2	$-1.9155814 \times 10^{-2}$	-41.5882
1 2	1.09414×10^{-4}	43.684
2 2	-1.3992×10^{-5}	29.813
3 2	-9.457×10^{-7}	...
0 3	2.9348×10^{-7}	-224.7037
1 3	-1.865×10^{-8}	-6.003
0 4	-1.4060×10^{-10}	-108.6
1 4	-1.386×10^{-12}	4.0024
0 5	-7.028×10^{-14}	842.99
0 6	-3.931×10^{-20}	-82.55

[a] The notation ... signifies that this parameter was not evaluated.

to reproduce fewer spectral lines implies that the radial coefficients in Table 1 constitute a more compact set of parameters than U_{kl} and Δ^H_{kl} or Y_{kl}. Because in neither previous analysis were all these data used, these parameters yield the best representation of all currently available data. Furthermore because previous analyses[8,9] were conducted in terms of only term coefficients Y_{kl} or U_{kl} and Δ^H_{kl}, our results provide greater chemical and physical insight into extra-mechanical effects that affect wavenumbers of transitions apart from the potential energy. Because there are no spectral data for nuclides of Bi other than ^{209}Bi, the potential energy provided by V(z) is not truly independent of mass, as it thus includes not only adiabatic and nonadiabatic effects associated with Bi but also the (probably significant) effect of nuclear volume.[5] Because of insufficient information from available spectra or otherwise, the parameters t_j, $1 \leq j \leq 2$, and u_j, $2 \leq j \leq 6$, incorporate the unknown and unresolvable nonadiabatic vibrational effects. The coefficient u_1 is formally a measure of purely adiabatic effects.

To ensure that the effects of the term coefficients $Z^{r,H}_{kl}$ were properly separated from those of $Z^{v,H}_{kl}$, in a preliminary fit we used only data for ^{209}Bi^{1}H; by this means we proved that only two values of t_j (beyond t_0) were required, and the resulting values t^H_1 ~17.5 and t^H_2 ~-34.2 are satisfactorily similar to the corresponding final values (Table 1) reflecting wavenumber data of both ^{209}Bi^{1}H and ^{209}Bi^{2}H. We tested whether any value of t^H_0 could be evaluated significantly, but discovered that free fits yielded only small magnitudes surpassed by their standard errors.

Comparison in Table 2 of values of coefficients U_{kl} and Δ^H_{kl} between present indirect fits to these parameters and previous direct fits[8,9] indicates that agreement is close for $\Delta^H_{0,1}$, $\Delta^H_{1,0}$ and $\Delta^H_{0,2}$, but less so for $\Delta^H_{1,1}$ and $\Delta^H_{2,0}$. The divergence in the latter values presumably reflects the greater extent both of the spectral data in our analysis and of parameters Δ^H_{kl} that are generated from our large set of coefficients $Z^{v,H}_{kl}$ and $Z^{r,H}_{kl}$ from which these parameters are derived. Therefore the exceptionally large magnitudes of these parameters Δ^H_{kl} in Table 2 are essentially confirmed by previous work. The correspondingly large magnitudes of the coefficients t^H_j and u^H_j are in turn confirmed. As additional evidence of these exceptional magnitudes for BiH, we recall that for LiH[1] magnitudes of t^H_j are less than 2.5, so of the order of a tenth those of BiH, and of u^H_j less than 6×10^6 m^{-1}, of the order of one hundredth those of BiH. For GaH, t^H_1 = 7.4, t^H_2 = -15.1 and t^H_3 = 16.3,[6] less than half the magnitudes for BiH, whereas for GaH u^H_1 = -10.8×10^6 m^{-1} and u^H_4 attained -257 $\times$ 10^6 m^{-1},[6] from one tenth to a quarter of magnitudes for BiH. To explain these results, there are clearly exceptional conditions to be elucidated. These magnitudes of t^H_j and u^H_j reflect the existence of nonadiabatic and adiabatic effects. For LiH the nonadiabatic vibrational, nonadiabatic rotational and adiabatic effects were separately evaluated because computed values of rotational g factor and electric dipolar moment supplemented spectral data; in this case adiabatic effects are prominent.[1] For GaH for which t^H_0 was evaluated from spectral data to have the value -3.17,[6] nonadiabatic rotational effects are thereby relatively large, but according to our spectral analysis of BiH only a small magnitude of t^H_0 is indicated, in fact zero within the modest standard error when this parameter was freely fitted.

To explain tentatively these results we recall the electronically excited state A 1 of BiH, which lies about 4.9×10^5 m^{-1} above the ground state X 0^+,[9] thus about the same energy as the vibrational state v = 3 of BiH or v = 4 of BiD above the corresponding states v = 0. Relatively large deviations between observed wavenumbers of some transitions affecting the states v = 3 and 4 of BiH are evident in not only our calculations but also the original reports of these spectra.[8,9] Whether these deviations are due to mere uncertainty or error of measurement, or whether they indicate specific heterogeneous perturbations between the two states, remains to be ascertained. Our method of analysis is based on the implicit assumption that interactions between the state of interest (within which measured vibration-rotational transitions are treated in our analysis) and other electronic states are weak and homogeneous, so that these interactions can be treated as a perturbation. These interactions are assessed according to magnitudes of coefficients t^H_j and u^H_j (in the absence of effects attributed to nonadiabatic vibrational effects through s^H_j). The notable points in this regard are that u^H_1 = $(-124.291 \pm 0.034) \times 10^6$ m^{-1} — both having a large magnitude and being well defined, which reflects purely adiabatic effects, and that t^H_0 ~0 ± 0.2 — possessing such a small magnitude that it defies evaluation, which might thereby indicate absence or cancellation of purely nonadiabatic rotational effects.

Expressing the rotational g factor, g_J, in terms of contributions due to the nonadiabatic rotational part g^{na}_J and to the electric dipolar moment μ_e, for masses M_a of atom A and M_b of atom B in a molecule of relative polarity $^+$AB$^-$, we invoke the relation[16]

$$g_J = g^{na}_J + m_p(M_a^{-1} - M_b^{-1})\mu_e/(eR_e) \tag{9}$$

in which m_p is the mass of the proton and e its charge. Hence according to an assumed relative polarity $^+$BiH$^-$ the coefficients t^{Bi}_0 and t^H_0 become accordingly

$$t_0^{Bi} = \mu g_J^{na}/m_p + \mu_e/(eR_e) \qquad (10)$$

and

$$t_0^{H} = \mu g_J^{na}/m_p - \mu_e/(eR_e) \qquad (11)$$

in which μ is the reduced mass $\mu = M_aM_b/(M_a+M_b)$. Then a fortuitous near cancellation $\mu g_J^{na}/m_p \approx \mu_e/(eR_e)$ would result in t_0^H having a small magnitude, consistent with the experimental result, despite genuinely nonadiabatic rotational effects being large as a result of rotationally induced interaction between electronic states X and A. As values of neither g_J (or thereby g_J^{na}) nor μ_e are known for BiH, and as we cannot estimate t_0^{Bi} without spectra of a bismuth isotope, we cannot at present confirm this deduction. Because electronic angular momenta of states X and A differ by one unit, we expect nonadiabatic rotational effects to be more important than nonadiabatic vibrational effects, according to van Vleck's original analysis.[17] An explanation of the exceptionally large adiabatic effects is lacking because these effects are associated with expectation values of various operators in the electronic state of interest;[17] there is no particular reason for the large nonadiabatic rotational effects, expected because of the proximity of the two electronic states X and A, to be accompanied by relatively large adiabatic effects, even though electronic expectation values (of state X) that define adiabatic effects involve the same operators as those that appear in matrix elements connecting separate electronic states (i.e. states X and A) to define nonadiabatic rotational effects.[17]

In summary our analysis of available vibration-rotational spectra of BiH and BiD in electronic ground state X 0^+ yielded the discovery of exceptionally large nonadiabatic rotational and adiabatic effects; the former we attribute in part to the presence to rotationally induced electronic interactions with nearby electronic state A 1.

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Key Words

Vibration-rotational spectra; Isotopic effects; Metal hydrides; Spectral reduction; Intramolecular dynamics.

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