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Three-dimensional *ab initio* dipole moment surfaces and stretching vibrational band intensities of the XH_3 molecules*

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Stretching vibrational band intensities of XH_3 (X=N, Sb) molecules are investigated employing three-dimensional dipole moment surfaces combined with the local mode Hamiltonian model. The dipole moment surfaces of NH_3 and SbH_3 are calculated with the density functional theory and at the correlated MP2 level, respectively. The calculated band intensities are in good agreement with the available experimental data. The contribution to the band intensities from the different terms in the polynomial expansion of the dipole moments of four group V hydrides (NH_3, PH_3, AsH_3 and SbH_3) are discussed. It is concluded that the breakdown of the bond dipole approximation must be considered. The intensity "borrowing" effect due to the wave function mixing among the stretching vibrational states is found to be less significant for the molecules that reach the local mode limit.

Keywords: overtone, dipole moment, infrared band intensity, local mode
PACC: 3120A, 3310G, 3320E

1. Introduction

The quantum chemistry calculations have shed light on the area of molecular spectroscopy. The positions and intensities of ro-vibrational transitions can be predicted by correctly calculated potential energy surfaces (PES) and dipole moment surfaces (DMS). Up to now, the line positions can be calculated with a satisfactory accuracy by the variational calculations based on a sufficiently accurate PES. The recent progress on the calculated water vapour spectrum stands for a good example.[1,2] Based on an *ab initio* PES and followed by a careful adjustment according to the available observations of ro-vibrational transitions, the resulting PES can produce the energy levels below 25000 cm^{-1} of variant isotopes of water with a sub 1 cm^{-1} accuracy. However, it has also been found that the DMS model from quantum chemistry calculations often gives poor predictions for the intensities of high overtones.[3−10] About 3–10 times over- or under-estimation of the observed band intensities is common. This is mainly due to the inaccurate high-order terms in the DMS, which would make significant contribution to the transitions in a highly excited energy region.[9−12] Meanwhile, the calculated intensities are found to be less sensitive to the potential energy surface.[7,12−15] In a previous paper, we studied the stretching overtones and combination bands of the XH_4 (X=C, Si, Ge, Sn) type group IV hydrides. By applying four-dimensional *ab initio* dipole moment surfaces and local mode potential energy surfaces, most of the observed band intensities were reproduced within a factor of 1.5.[16]

Here we concentrate on the group V hydrides (NH_3, PH_3, AsH_3 and SbH_3). The study has been carried out on PH_3.[5] and AsH_3.[17] It is a fact that PH_3, AsH_3 and SbH_3 are good local mode molecules whose stretching vibrational energy levels can be well described by the local mode theory, for instance, the anharmonically coupled anharmonic oscillator (ACAO) model. But it is not the case for NH_3 because of complicated interactions like the strong

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Fermi resonance between the bending and stretching vibrations.[18] The potential energy surface parameters of NH_3 and SbH_3 have been calculated by local modes with Fermi resonance model,[18,19] by the effective normal mode model,[20] and also by the high level *ab initio* method.[21] Recently, six-dimensional PES and DMS were calculated at the CCSD(T) (coupled cluster theory with all single and double substitutions from the Hartree-Fock reference determinant[22] augmented by a perturbative treatment of connected triple excitations)[23,24] level, which could reproduce the experimental energy values of ammonia below $15000\,cm^{-1}$ with a deviation around $5\,cm^{-1}$.[25] A global analytical representation of the electric dipole hyper-surface for ammonia is also introduced by Marquardt *et al.*[26] However, the local mode picture is also acceptable for the high overtones of NH_3.[18] It is also a good approximation assuming the bending bands just "borrow" intensities from corresponding stretching bands through wave function mixing due to the Fermi Resonance. So it will be instructive to apply the crude local mode picture to NH_3 so as to compare it with other XH_3 species. In the present paper, the local mode Hamiltonian and stretching dipole moment models are given in Section 2, and the band intensities of SbH_3 and NH_3 are presented in Section 3. Section 4 includes discussion and concluding remarks.

2. Dipole moment and Hamiltonian models

The dipole moment vector $\boldsymbol{M}$ is projected as

$$\begin{aligned}\boldsymbol{M}(r_1,r_2,r_3) =& u_1(r_1,r_2,r_3)\boldsymbol{e}_1 + u_2(r_1,r_2,r_3)\boldsymbol{e}_2 \\ &+ u_3(r_1,r_2,r_3)\boldsymbol{e}_3, \end{aligned} \tag{1}$$

where $\boldsymbol{e}_i$ $(i=1,2,3)$ is the unit vector along the X-H_i bond. Since XH_3 molecules belong to C_{3V} point group, there are following relations for u_i $(i=1,2,3)$

$$u_2(r_1,r_2,r_3) = u_1(r_2,r_1,r_3), \tag{2}$$

$$u_3(r_1,r_2,r_3) = u_1(r_3,r_2,r_1). \tag{3}$$

In this work, only the X-H bond stretching bands are considered, and $u_1(r_1,r_2,r_3)$ is expanded with the polynomial functions in terms of the bond displacements $(r_i, i=1,2,3)$,

$$\begin{aligned}&u_1(r_1,r_2,r_3) \\ &= \sum_{i,j\geq k} C^{\mathrm{B}}_{ijk} r_1^i (r_2^j r_3^k + r_2^k r_3^j)/(1+\delta_{jk}), \end{aligned} \tag{4}$$

where i, j, and k are non-negative integers, C^B_{ijk} is the expansion coefficient, and δ_{jk} equals 1 if $j=k$, and otherwise equals 0. Note that the expansion of the dipole moment function u_1 can be divided into two parts:

$$u_1 = u_1^{\mathrm{d}} + u_1^{\mathrm{c}}, \tag{5}$$

$$u_1^{\mathrm{d}} = C^{\mathrm{B}}_{i00} r_1^{\mathrm{i}}, \tag{6}$$

where u_1^{d} is the dipole moment (along the direction of the X-H_1 bond) introduced by a corresponding bond displacement, which is a polynomial function of r_1, we call it "diagonal" part. Another part u_1^{c} is refereed to as "crossing" part. It comes into play when the displacements also happen to other bonds. In our recent paper on the XH_4 type molecules, we have pointed out that this part might be important and inappropriate to be neglected.[16]

The procedure of calculating the 3D X-H stretching DMS of XH_3 (X=N, Sb) is similar to that used in the previous study on either PH_3[5] or AsH_3.[17] It includes two steps: equilibrium geometry optimization, and single point calculation. The 3D DMS calculations are carried out with the B3PW91 method (Becke's three parameter hybrid method with Perdew and Wang's gradient-corrected correlation functional)[27,28] for NH_3, and at the correlated MP2 level (second-order Møller–Plesset perturbation theory)[29] for SbH_3, by using the GAUSSIAN 98 package.[30] The cc-pVQZ (correlation-consistent polarized valence quadruple zeta) basis set[31,32] is employed for the hydrogen and nitrogen atoms. The Hay and Wadt (HW)[33] effective core potentials are used with the corresponding double-zeta valence basis sets in a (3s3p)/[2s2p], augmented with one set of six Cartesian d polarization functions (the exponent[34] is 0.25) to the antimony atom. The optimized equilibrium geometry data compared with experimental values[35,36] are presented in Table 1. It is shown that our results are close to the experimental values. The dipole moments of NH_3 are calculated analytically in the B3PW91 implementation, while for SbH_3, they are obtained by finite difference at the MP2 level with the equation which can be described by

$$M_i = \frac{E(p_i) - E(-p_i)}{2p_i}, \tag{7}$$

where $i = x, y, z$, $E(p_i)$ and $E(-p_i)$ are, respectively, the correlated MP2 energies of SbH_3 molecule in the electric field with positive and negative strengths of p_i along the molecular fixed i axis,[8] and p_i is chosen to be 0.005 atomic units.

Table 1. Optimized and experimental equilibrium geometric structure of NH_3 and SbH_3.

	NH_3		SbH_3	
	Cal.	Exp.[a]	Cal.	Exp.[b]
R_{XH}/0.1nm	1.0122	1.0166	1.6937	1.7000127
ϕ_{HXH}/(°)	106.66	106.68	91.5652	91.55662

[a] From Ref.[35]. [b] From Ref[36].

The method to fit the 3D DMS is referred to Ref.[5]. It is shown that it is unnecessary to include many high order terms in the fit of the three-dimensional DMS.[9] All terms with higher than fourth order are neglected here, and the C^{B}_{021} of NH_3 and SbH_3 are also constrained to zero for the same reason. The expanded coefficients of NH_3 and SbH_3 are given in Table 2. Figure 1 provides parts of the *ab initio* calculated dipole moments along the X–H_1(X=N, Sb) bond to show the difference between NH_3 and SbH_3. The dipole moments along the X–H_1 bond at different fixed values of r_2 and r_3 show nonlinear dependence on the r_1 value for NH_3, while quite linear for PH_3,[5] AsH_3,[37] and SbH_3. Particularly, it is clearly shown that when r_1 is fixed the dipole moment along the X–H_1 bond of NH_3 varies markedly at different values of r_2 and r_3. Note that the upper and lower panels in this figure have different vertical scales, we shall point out that actually, it is almost the same situation as SbH_3. It is interesting to note that a similar phenomenon is also found in XH_4 type hydrides.[16]

Table 2. Three-dimensional stretching vibrational DMS coefficients of NH_3 and SbH_3.*

	NH_3	SbH_3
C_{000}	1.373413(65)	–0.259647(30)
C_{100}	–0.03718(39)	–2.13842(17)
C_{010}	–0.17436(22)	0.09295(16)
C_{200}	–0.51644(95)	–0.16489(43)
C_{020}	0.25334(75)	0.07070(42)
C_{110}	–0.27934(79)	–0.04449(36)
C_{011}	–0.14499(65)	–0.01970(30)
C_{300}	–0.2832(39)	0.5039(17)
C_{030}	0[a]	–0.0839(17)
C_{210}	–0.3358(33)	0.0816(15)
C_{021}	0[a]	0[a]
C_{120}	0.2985(33)	0.2472(15)
C_{111}	–0.3029(28)	–0.0359(13)
rms[b]/10^{-3}	1.91	0.84

* Units are defined as follows: the dipole moment is in Debye (= 3.33564×10^{-30} C m), the bond length displacement is in 0.1nm. The value in each parenthesis is one standard error in the last significant digit. [a] Constrained values. [b] Root mean squares of the fitting residual.

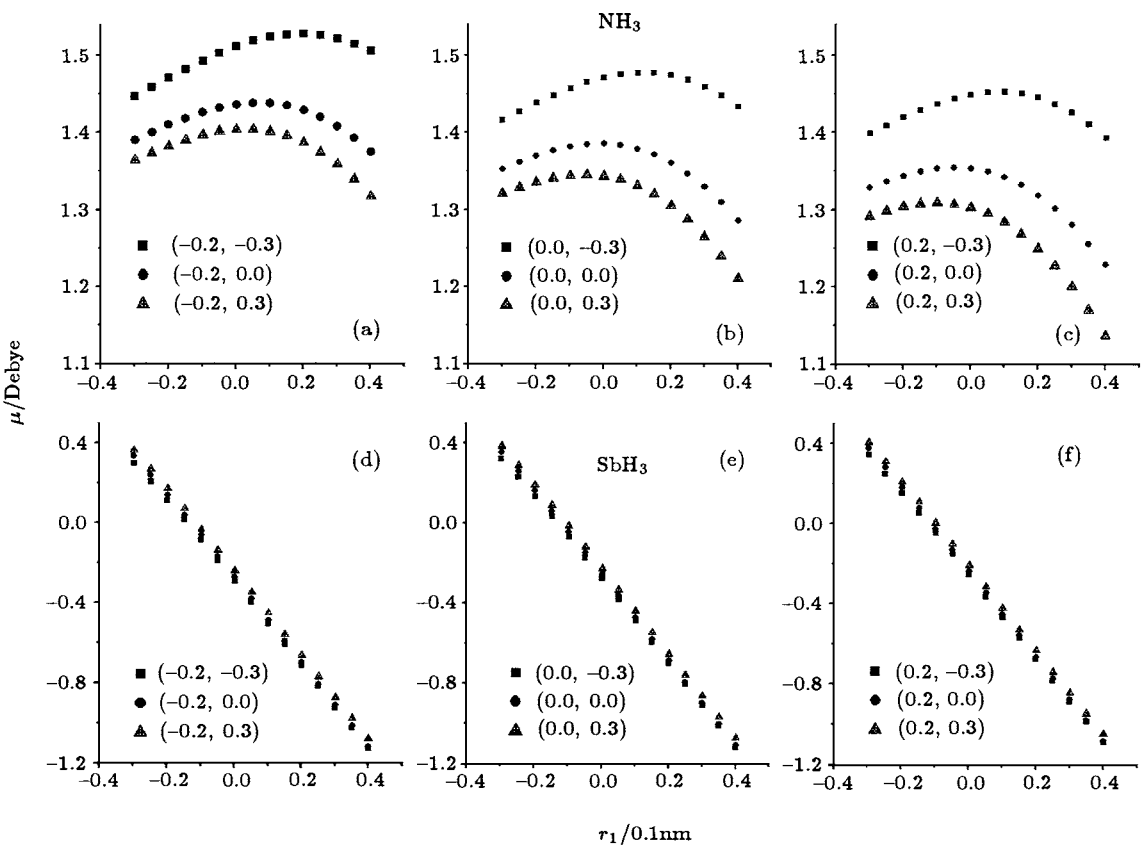

Fig.1. The dipole moments along the X–H_1 bond in NH_3 and SbH_3 according to the bond length displacement r_1 at different values of r_2 and r_3 respectively. Values in parentheses are for r_2 and r_3. The upper and lower panels are for NH_3 and SbH_3, respectively.

The ACAO I model is used to calculate the vibrational wavefunctions:

$$H = \sum_{i=1}^{3} \left(\frac{1}{2} G_{rr} p_i^2 + D_e y_i^2 \right) + \sum_{i<j} (G_{rr'} p_i p_j + F_{rr'} r_i r_j). \quad (8)$$

Here m_{H} and m_X are the mass of the H and X atoms, respectively, ϕ is the experimental equilibrium value for the H-X-H angle, p_i is the momentum conjugate to r_i, D_e and α are the Morse potential parameters, and $F_{rr'}$ is the inter-bond potential coupling parameter. For NH_3, the parameters D_e and α are optimized by the least-squares fitting to thirteen observed vibrational band centers, while $F_{rr'}$ is constrained to the calculated value by Esa Kauppi *et al.*[18] The results are $D_e = 41535(326)\,\mathrm{cm}^{-1}$, $\alpha = 2.0560(106)$ $(0.1\mathrm{nm})^{-1}$, and $F_{rr'} = 455.08\,\mathrm{cm}^{-1}$ $(0.1\mathrm{nm})^{-2}$, where the value in each parenthesis is one standard error in units of the last quoted digit. The root mean square of the fitting residual is $16.8\,\mathrm{cm}^{-1}$. For SbH_3, the effective parameters are $D_e = 28566(52)\,\mathrm{cm}^{-1}$, $\alpha = 1.4135(17)$ $(0.1\mathrm{nm})^{-1}$, $F_{rr'} = -191(56)\,\mathrm{cm}^{-1}$ $(0.1\mathrm{nm})^{-2}$, and the root-mean-square of the fitting residual is $1.94\,\mathrm{cm}^{-1}$. The deviations from the observed values of the band centers of NH_3 and SbH_3 are presented in Table 3.

Table 3. Observed and calculated stretching vibrational band centers (in cm^{-1}) and calculated band intensities (in 10^{-22}cm/molec) of NH_3 and SbH_3.

band	NH_3				SbH_3			
	ν_{obs} [a]	ν_{calc}	$\delta_{\mathrm{o-c}}$	I_{cal}	ν_{obs} [b]	ν_{calc}	$\delta_{\mathrm{o-c}}$	I_{cal}
$(100; A_1)$	3336.2	3337.5	–1.3	0.514×10^4	1890.502	1890.789	–0.29	0.246×10^6
$(100; E)$	3443.4	3426.9	16.5	0.166×10^4	1894.497	1896.425	–1.93	0.701×10^6
$(200; A_1)$	6606.0	6593.5	12.5	0.370×10^1	3719.933	3721.197	–1.26	0.443×10^4
$(200; E)$	6609.2	6635.2	–26.0	0.310×10^4	3719.860	3721.605	–1.74	0.993×10^4
$(110; A_1)$	6796.0	6810.5	–14.5	0.244×10^3		3785.505		0.584×10^2
$(110, E)$	6850.4	6833.1	17.3	0.385×10^2		3790.799		0.147×10^2
$(300; A_1)$		9713.8		0.520×10^1	5480.285	5481.248	–0.96	0.926×10^2
$(300; E)$	9689.8	9722.5	–32.7	0.184×10^3	5480.235	5481.263	–1.03	0.991×10^2
$(210; A_1)$		9939.6		0.690×10^1	5607	5609.560	–2.56	0.100×10^2
$(210; lE)$		10002.3		0.500×10^1		5612.481		0.268×10^1
$(210; hE)$		10093.1		0.330×10^2		5619.014		0.335×10^1
$(400; A_1)$		12665.2		0.900×10^0	7173.799	7173.600	0.20	0.250×10^1
$(400; E)$	12675.5	12666.2	9.3	0.145×10^2	7173.783	7173.601	0.18	0.153×10^0
$(310; A_1)$		13043.2		0.300×10^0		7372.465		0.643×10^0
$(310; lE)$		13085.0		0.110×10^1		7373.048		0.160×10^{-2}
$(310; hE)$		13139.1		0.200×10^1		7376.484		0.453×10^0
$(500; A_1)$	15449.1	15459.0	–9.9	0.138×10^0		8798.525		0.719×10^{-1}
$(500; E)$	15449.9	15459.1	–9.2	0.145×10^1		8798.525		0.125×10^0
$(410; A_1)$		16018.1		0.240×10^{-1}		9064.979		0.428×10^{-1}
$(410; lE)$		16030.8		0.200×10^0		9065.010		0.153×10^{-2}
$(410; hE)$		16085.6		0.770×10^{-1}		9068.758		0.323×10^{-1}
$(600; A_1)$	18109.3	18100.3	9.0	0.230×10^{-1}	10358	10356.034	2	0.148×10^{-2}
$(600; E)$	18108.5	18100.3	8.2	0.179×10^0	10358	10356.035	2	0.533×10^{-1}
$(510; A_1)$		18822.7		0.200×10^{-2}		10689.623		0.360×10^{-2}
$(510; lE)$		18824.7		0.210×10^{-1}		10689.624		0.200×10^{-3}
$(510; hE)$		18885.0		0.600×10^{-2}		10693.389		0.290×10^{-2}

[a] From Ref.[18]. [b] From Ref.[19].

3. Calculated stretching band intensities

The absolute vibrational band intensity can be calculated by

$$I = \frac{8\pi^3\nu_0}{3hcQ_{\rm v}(T)}\left[1-\exp\left(-\frac{hc\nu_0}{kT}\right)\right]\nu_0|\langle N \mid \boldsymbol{M} \mid 0\rangle|^2 \doteq K\nu_0|\langle N \mid \boldsymbol{M} \mid 0\rangle|^2, \quad (9)$$

where $|0\rangle$ and $|N\rangle$ denote the vibrational ground and exited states respectively, ν_0 is the band center in cm^{-1}, $Q_{\rm v}(T)$ is the vibrational partition function at temperature T, c is the speed of light, h and k are Planck and Boltzmann constants, respectively. The approximation in the second line of Eq.(9) is fulfilled since $Q_{\rm v}(T) \doteq 1$ and $\exp\left(-\frac{hc\nu_0}{kT}\right) \ll 1$ under the present conditions. The constant K equals $4.1623755 \times 10^{-19}\,\mathrm{cm^2 Debye^{-2}}$ ($1\,\mathrm{Debye} = 3.33564 \times 10^{-30}\,\mathrm{C\,m}$).

3.1. SbH_3

The calculated absolute band intensities of SbH_3 are listed in the column 7 in Table 3. Due to the lack of observed data, we only compare the relative band intensities which are calculated by

$$I_{\rm rel}(i) = \frac{I_{\rm abs}(i)}{I_{\rm abs}(100)}, \quad (10)$$

where $I_{\rm rel}(i)$ and $I_{\rm abs}(i)$ are the relative and absolute intensities of the band i, respectively. $I_{\rm abs}(100)$ is the overall intensity of bands $(100, A_1)$ and $(100, E)$. The calculated and observed relative band intensities are given in columns 2 and 3 of Table 4. For the first and second overtone bands, our calculated values are in good agreement with the experimental values given by Ref.[38], and the accuracy is similar to the one calculated from an empirical bond dipole model in the same reference (values also given in the column 4 of Table 4). For the third overtone, our result is only one fifth of the experimental value and the empirical bond dipole model gives one half. But for the combination band (210, A_1), we reproduce the experimental band intensity very well, while the value obtained by the empirical bond dipole model is more than one hundred times smaller. Actually, the relative intensities of combination bands calculated by the empirical bond dipole model[38,39] have large differences from the observed values for both AsH_3 and SbH_3. This may result from the inappropriate neglect of the contribution from inter-bond coupling terms in their dipole moment model.

Table 4. Observed and calculated relative band intensities of SbH_3.

band	$I^{\rm a)}_{\rm obs}$	$I^{\rm a)}_{\rm cal}$	$I^{\rm b)}_{\rm cal}$
$(100, A_1/E)$	1.0	1.0	1.0
$(200, A_1/E)$	0.022	0.015	0.021
$(300, A_1/E)$	0.32×10^{-3}	0.47×10^{-3}	0.20×10^{-3}
$(210, A_1)$	0.11×10^{-4}	0.82×10^{-7}	0.11×10^{-4}
$(400, A_1/E)$	0.14×10^{-4}	0.78×10^{-5}	0.28×10^{-5}

a) From Ref.[38]. b) This work.

3.2. NH_3

The observed and calculated vibrational energy levels, along with the band intensities calculated from the DFT DMS are listed in columns 2, 3 and 4 in Table 3. It is not surprising that there are large discrepancies between the observed and calculated energy levels since the strong Fermi resonance and inverse splitting are not included in our simple ACAO model. For the band intensities of NH_3, to the best of our knowledge, the available experimental data on band intensities is surprisingly limited. The intensities of the (100, A_1) and (100, E) bands were determined by Kleiner *et al*,[40] they are 9498 and 4747 (in units of $10^{-22}\,\mathrm{cm/Molecule}$), respectively. Coy and Lehmann [41] gave the line intensities for 39 and 15 prominent lines in the five and six quanta bands, respectively. The summed values of the intensities of these prominent lines can be considered as an estimation of the lower limit of the band intensities. They are 0.455 for the (500, A_1/E) band and 0.041 (in unit of $10^{-22}\,\mathrm{cm/molecule}$) for the (600, A_1/E) band. The calculated intensities of (100, A_1) and (100, E) are 2–3 times smaller than these available experimental values, which may result from the deviation of the wave functions since the ACAO model should not describe the low exited vibrational states of NH_3. Our calculated intensities of (500, A_1/E) and (600, A_1/E) bands are about triple larger than the experimental values. The discrepancy seems large here, but on the one hand, the discrepancy should be much smaller since the "experimental" intensities we used here are most likely lower limits of the true values, on the other hand, as a rough estimation on the difficult issue of the band intensities, such discrepancy is already acceptable. We expect more experimental data, especially for the high excited overtones and combination bands to be available to test the result listed in Table 3.

4. Discussion and conclusions

In the earlier work,[16] we discussed the contributions to the overtone transition moments from diagonal and crossing terms in the polynomial expansion of the dipole moments according to the bond displacements. Actually, if we take a "bond dipole" approximation, which means that the assumption is made that the "crossing" terms are all negligible and only the "diagonal" terms remain in the dipole moment expansion, then the vibration induced dipole moment must be aligned with the vibrating bond. This approximation is simple but as we have examined in the study on the group IV hydrides XH_4 (X=C, Si, Ge, Sn), large deviation will be found if the crossing terms are neglected, particularly when the combination bands are considered. For those contributions from such crossing terms, as the breakdown of the "bond dipole" approximation, we call it "crossing" effect. Another effect is the so-called "borrowing" effect, which comes from the wave function mixing. Due to the miscellaneous vibrational interaction resonance or the complexity of the potential energy surface, each vibrational state will not be a "pure" local-mode vibration state but a combination of all interacting states. As a consequence, the transition moments will be re-distributed among all the interacting vibrational bands. For example, a "dark" combination band could "borrow" some strengths from other "bright" bands, for example, the corresponding overtone within the same vibrational polyad. We believe that, for those molecules which could be well described by the local-mode model, like SiH_4, GeH_4, and SnH_4 in the group IV hydrides and PH_3, AsH_3, and SbH_3 in the group V hydrides discussed in present paper, the "borrowing" effect will be less important when the energy grows up or the local-mode limit is reached. Since NH_3 and CH_4 are not such local-mode molecules, for those molecules the local mode model is poor to describe the vibrational states, there by the "borrowing" effect will remain significant.

In order to understand the origin of the stretching vibrational band intensities of the polyatomic hydrides, we focus on the investigation of the "crossing" and "borrowing" effects, and calculate the contributions to the band intensities from different terms for the XH_3 (X=N, P, As, Sb) molecules. Three cases which correspond to three different limits are considered: 1) I_1 is the intensity calculated when the "borrowing" effect is neglected, and the wave function of the upper energy state is assumed to be a "pure" local-mode state; 2) I_2 is the intensity calculated when the "crossing" effect is neglected, the dipole function is simplified into a bond dipole function, and all crossing terms in the DMS expansion are neglected, while the "borrowing" effect is included; 3) I_3 is the intensity calculated on the assumption that only the crossing terms in the DMS expansion are important and all other diagonal terms are neglected. For each case, the intensities of the overtones—from the ground state to the (n 0 0) states, and of the usually strongest combination bands in each polyad—from the ground state to the (n-1 1 0) states, are calculated. The resulting values are then normalized to the true values when both the "borrowing" and "crossing" effects are included. The results of (n 0 0) overtones and (n-1 1 0) combinations are shown in the upper and lower panels of Fig.2, respectively. The following points can be concluded from the figure: (1) The "borrowing" effect can be neglected for the (n 0 0) overtones of all these molecules and also for the combination bands of local mode molecules (PH_3, AsH_3 and SbH_3) when close to the local-mode limit ($n > 2$). The "borrowing" effect seems to be only accountable in the combination bands of NH_3. This point can be easily concluded from plots a and b. (2) For the overtones, both the diagonal and "crossing" terms in the DMS expansion are important for most molecules (plots c and e). The "crossing" effect is the leading contribution to the high excited combination bands which is clearly shown in plots e and f.

So we may conclude that the "crossing" effect is the leading contribution to the combination bands and also an important part to the overtones for most XH_n type hydrides. When we limit our discussion to the band intensity distribution among different stretching bands within a polyad, the "borrowing" effect seems negligible for the molecules in the local-mode limit, for example, high vibrational excited states of PH_3, AsH_3, and SbH_3 in the present discussion. We think it can be also considered as an alternative character for the molecule reaching the local-mode limit other than the pattern of energy levels.

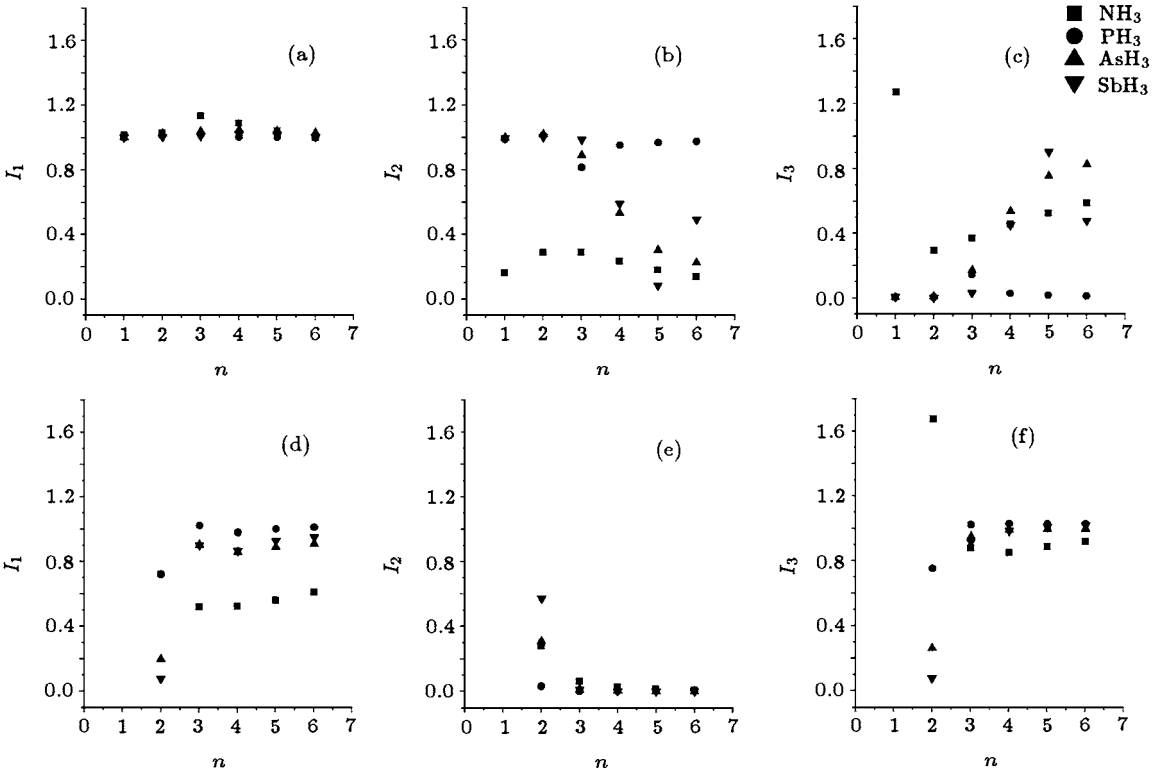

Fig.2. The relative contributions to the band intensities, calculated in three cases (see in text). The upper panels are for the (n 0 0) overtones, and the lower panels are for the (n-1 1 0) combination bands.

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