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Absolute local mode vibrational band intensities of AsH_3

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Abstract

The local mode vibrational absolute band intensities of AsH_3 molecule were studied experimentally and theoretically. The stretching vibrational band intensities of AsH_3 were derived from the infrared spectra recorded by a Bruker IFS 120 HR Fourier transform spectrometer. A three-dimensional As–H stretching dipole moment surface (DMS) was calculated by the density functional theory method. The DMS was used to calculate the absolute band intensities, which agreed well with the observed values. The inter-bond coupling terms in the DMS expansion are found to be essential in reproducing overtone and combination band intensities in the high-energy regions. © 2002 Published by Elsevier Science B.V.

1. Introduction

AsH_3 is important in planetary study since it was detected in the atmospheres of Jupiter and Saturn [1–3]. It is very suitable to study the local mode effects because it is close to the local mode limit. An anharmonically coupled anhormonic oscillators (ACAO) model was successfully applied to explain and to predict the stretching vibrational overtone spectra in the region of 1800–8000 cm^{-1} in [4]. Later, a vibrational Hamiltonian model was applied to the observed vibrational term value by Lukka et al. [5], in which Fermi resonance interactions between the stretching and bending modes were taken into account. Many works on high-resolution ro-vibrational spectrum from fundamental to the fifth stretching vibrational overtone bands [6–11] and some local mode combination bands [12–14] have also been reported.

The present work mainly contributes to the absolute band intensities of the As–H stretching vibrations. In a previous work, Halonen et al. [4] gave the relative infrared absorption intensities for the stretching vibrational bands from the experiment and calculations based on a bond dipole model. But this model gave far too low intensities for local mode combination bands. In 1993, Dana et al. [15] estimated the absolute band intensities of the fundamental ν_1 and ν_3 from line intensities in high-resolution spectra. Later, they reported five absolute band intensities with the same method such as $2\nu_2, \nu_2 + \nu_4, 2\nu_4, \nu_1$, and ν_3 [16]. In this work, we re-recorded the medium resolution Fourier transform infrared (FTIR) spectra from the fundamental to the fourth overtone of the As–H stretching motion and investigate the absolute

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band intensities from the experiment and the calculation. A three-dimensional (3D) As–H stretching dipole moment surface was calculated by density functional theory (DFT). This method has been successfully used to predict the absolute stretching vibrational band intensities of PH_3 [17].

2. Experiment

The AsH_3 samples were purchased from Nanjing Special Gas with the stated purity of 99.9% and 5.01%, the latter was mixed with argon gas. A Bruker IFS 120 HR Fourier transform spectrometer was used to record the infrared absorption spectra of AsH_3 from $V = 1$ to $V = 5$ (here, $V = n_1 + n_2 + n_3$, $(n_1 n_2 n_3; \Gamma)$ is the local mode notation [18]), and it was equipped with a path length adjustable multi-pass gas cell. All spectra were recorded at an unapodized resolution of 0.2 cm^{-1}. The details of experimental conditions are listed in Table 1. If the sample pressure is too low or too high, a manometer used to measure the pressure will give a relatively larger measurement uncertainty. So it is an advantage that we used the mixed sample gas in stead of the 'pure' one from the fundamental to the second overtone region. But in the region of $V = 4$ and $V = 5$ the absorption is very weak, and we must use pure sample. Water absorption lines are too weak to be observed in our spectra, so they can be ignored. The absolute intensity can be given by

$$I_{\mathrm{obs.}} = I_0 PL/(kT), \tag{1}$$

where $I_{\mathrm{obs.}}$ and I_0 are the observed and absolute intensity, P, L, k and T are the sample pressure, absorption path length, *Boltzmann* constant and temperature in the measurement, respectively. All the spectra were recorded at room temperature which varied from 26 to 28 °C in the measurement.

The observed intensities are obtained by directly integrating the absorbance spectra

$$I(v_0)_{\mathrm{obs.}} = \int_{v_0 - v_L}^{v_0 + v_H} -\ln[S(v)/S_0(v)]\,\mathrm{d}v, \tag{2}$$

where v_0 is the band center, v_L and v_H are the appropriate values for the integral limits, $S(v)$ and $S_0(v)$ are the transmittance and baseline spectra, respectively. The $(1\,1\,0; A_1/E)$ bands are not only overlapped with the R branch of $(2\,0\,0; A_1/E)$ in Fig. 1, but also much more weaker than the $(2\,0\,0; A_1/E)$ bands. In this case, the v_L and v_H in Eq. (2) are chosen such that the integral range includes all the spectra of $(2\,0\,0; A_1/E)$ and $(1\,1\,0; A_1/E)$, so total band intensities are obtained. But in the region of $V = 3$ the band centers are well isolated and the intensity of $(2\,1\,0; A_1/E)$ is comparable with that of $(3\,0\,0; A_1/E)$ so the v_L and v_H are chosen in the middle of the two neighboring band centers. The results are listed in Table 2. The difference of total intensity of fundamental v_1 and v_3 between ours and that given by Dana et al. [15] is within 10%, also the intensities obtained agree with the relative intensities given by Halonen et al. [4] in 1992. So we can consider our experimental results are reliable. The uncertainty of the experimental values is estimated from 20% to 40%.

Table 1
The details of the experimental conditions[a]

Vibration band	Sample (%)	Source	Detector	Path-length (m)	Pressure[b] (Pa)
(1 0 0)	5.01[c]	Globar	InSb[d]	15	9
(2 0 0)/(1 1 0)	5.01	Tungsten	InSb[d]	87	62
(3 0 0)/(2 1 0)	5.01	Tungsten	Insb[d]	87	3768
(4 0 0)/(3 1 0)	99.9	Tungsten	Ge diode	105	3150
(5 0 0)/(4 1 0)	99.9	Tungsten	Si diode	105	26 660

[a] The room temperature was varied within ±1 K for each spectrum.

[b] It is the total pressure of the sample.

[c] AsH_3 is mixed with argon.

[d] Liquid nitrogen cooled.

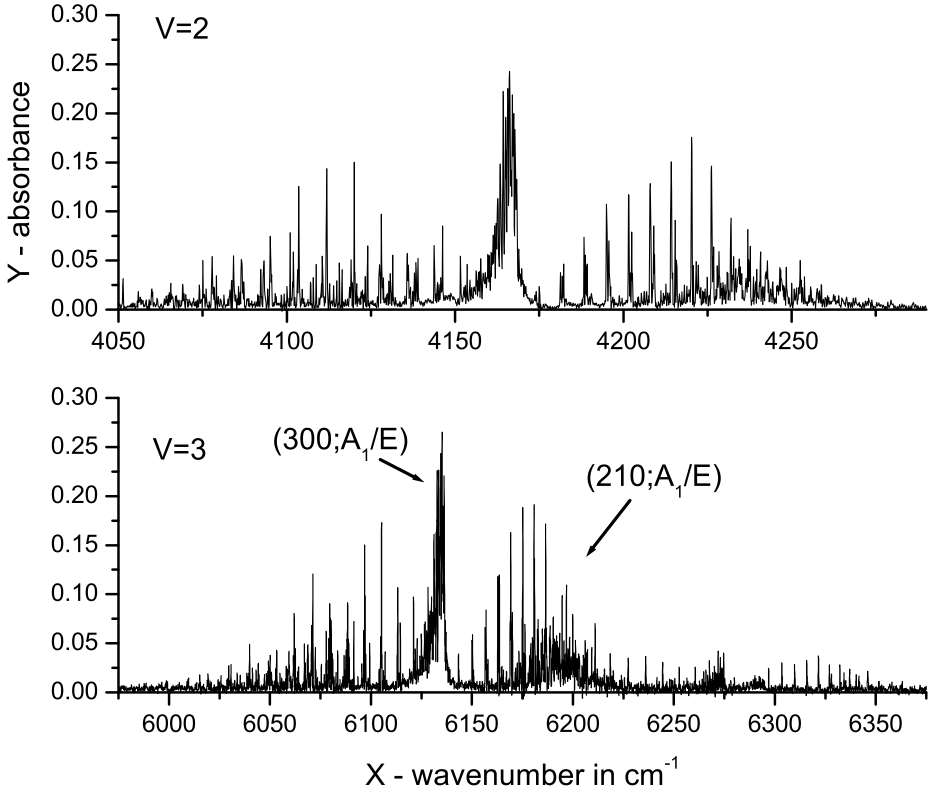

Fig. 1. FTIR spectra of AsH_3 molecule in $V = 2$ and $V = 3$ region. The experimental conditions are listed in Table 1.

3. Dipole moment model and dipole moment surface

The procedure of calculating the 3D As–H stretching DMS of AsH_3 by the DFT method is similar to the one used for PH_3 in our earlier work [17]. The calculations were done by using GAUSSIAN 98 package [19]. In our calculations, the B3PW91 (Becke's three parameter hybrid method with Perdew and Wang's gradient-corrected correlation functional) [20,21] method with the 6-311++G(3df, 2pd) basis set [22] were adopted. The optimized As–H bond length and H–As–H bond angle in equilibrium configuration are 1.5218 Å and 92.0474°, which agree well with the experimental values [23] 1.511060(14) Å and 92.0690(14)°, respectively. The method of scanning the 3D DMS can be referred to [17].

The calculated DFT dipole moment vectors are projected to molecule-fixed reference system. The dipole moment vector **M** is projected as [17]

$$\mathbf{M}(r_1,r_2,r_3) = u_1(r_1,r_2,r_3)\mathbf{e}_1 + u_2(r_1,r_2,r_3)\mathbf{e}_2 + u_3(r_1,r_2,r_3)\mathbf{e}_3, \tag{3}$$

where $\mathbf{e}_i$ $(i = 1,2,3)$ is the unit vector along the As–H_i bond, and H_i is the ith H atom in AsH_3.

In this work, only the As–H bond stretching motion is included, so DMS is expanded as the polynomial functions in terms of the bond length displacements. Because the AsH_3 molecule has the symmetry of point group C_{3v}, we have the following relations for u_1, u_2 and u_3,

$$u_2(r_1,r_2,r_3) = u_1(r_2,r_1,r_3), \tag{4}$$

$$u_3(r_1,r_2,r_3) = u_1(r_3,r_2,r_1). \tag{5}$$

The $u_1(r_1,r_2,r_3)$ can be expanded as

$$u_1(r_1,r_2,r_3) = \sum_{i,j\geqslant k} C_{ijk} r_1^i (r_2^j r_3^k + r_2^k r_3^j)/(1+\delta_{jk}), \tag{6}$$

Table 2
Observed and calculated band intensities (in 10^{-22} cm) of AsH_3[a]

$(n_1n_2n_3;\Gamma)$	ν_0[b]	$I_{Cal.}$	$I_{obs.}$
$(1\,0\,0;A_1)$	2115.16	0.114E + 6/0.441E + 6[c]	0.107E + 6/0.404E + 6[d]
$(1\,0\,0;E)$	2126.42	0.327E + 6	0.297E + 6[d]
$(2\,0\,0;A_1)$	4166.77	0.157E + 4/0.427E + 4	/0.618E + 4[e]
$(2\,0\,0;E)$	4167.94	0.270E + 4	
$(1\,1\,0;A_1)$	4237.70	0.117E + 3/0.123E + 3	
$(1\,1\,0;E)$	4247.53	0.671E + 1	
$(3\,0\,0;A_1)$	6136.34	0.456E + 2/0.656E + 2	/0.989E + 2
$(3\,0\,0;E)$	6136.33	0.200E + 2	
$(2\,1\,0;A_1)$	6275.83	0.112E + 2/0.182E + 2	/0.275E + 2
$(2\,1\,0;lE)$	6282.36	0.104E + 1	
$(2\,1\,0;hE)$	6294.72	0.596E + 1	
$(1\,1\,1;A_1)$	6365.97	0.650E + 0	
$(4\,0\,0;A_1)$	8028.97	0.277E + 1/0.287E + 1	/0.428E + 1
$(4\,0\,0;E)$	8028.97	0.959E − 1	
$(3\,1\,0;A_1)$	8249.52	0.716E + 0/0.176E + 1	/0.165E + 1
$(3\,1\,0;lE)$	8257.27	0.122E + 0	
$(3\,1\,0;hE)$	8258.38	0.924E + 0	
$(5\,0\,0;A_1)$	9841.09	0.258E + 0/0.259E + 0	/0.487E + 0
$(5\,0\,0;E)$	9841.18	0.102E − 2	
$(6\,0\,0;A_1)$	11 576.33	0.316E − 1/0.325E − 1	
$(6\,0\,0;E)$	11 576.34	0.891E − 3	

[a] The ACAOI Hamiltonian model is used to calculate the wavefunctions.

[b] Refs. [6–14].

[c] The value under / is the total intensity of the bands with the same quantum numbers $n_1n_2n_3$.

[d] From [15]. Our result is 0.374×10^6 for total band intensity of $(1\,0\,0;A_1)$ and $(1\,0\,0;E)$.

[e] It is the total intensity of all $V = 2$ bands. See for details in the text.

where i, j, and k are non-negative integers, C_{ijk} is the expansion coefficient, and $\delta_{jk} = 1$ if $j = k$, or else $\delta_{jk} = 0$. This DMS model can be called the improved bond dipole model [17], which includes the inter-bond coupling terms.

The expansion coefficients are fitted with the DFT calculated data points. In our fitting, all terms higher than fourth-order are constrained to zero, since they cannot be determined well. The results are listed in Table 3.

4. Intensities calculation

The absolute vibrational band intensity I can be calculated as

$$I(\nu_0) = K\nu_0|\langle N|\mathbf{M}|0\rangle|^2, \tag{7}$$

where K is a constant concerning the absolute value in intensity and the value is 4.1623755×10^{-19} cm^2 Debye^{-2} in this work, ν_0 is the transition wavenumber in cm^{-1}, $|0\rangle$ and $|N\rangle$ denote the vibrational ground and excited states, respectively.

To calculate I in Eq. (7), $\mathbf{M}$ described in the previous section is used, the vibrational wavefunctions $|0\rangle$ and $|N\rangle$ are computed variationally based on the ACAO local mode model [24–26]. The stretching vibrational Hamiltonian takes the form

$$H = \frac{1}{2}g_{rr}\sum_{i=1}^{3}p_i^2 + g_{rr'}\sum_{i<j}^{3}p_ip_j + V(r), \tag{8}$$

where p_i is the moment operator conjugate to the bond displacement coordinate r_i of the ith bond. $g_{rr} = 1/m_H + 1/m_{As}$, here m_H is the mass of the H atom and m_{As} the As atom, $g_{rr'} = \cos(\phi)/m_{As}$ and $\phi = 92.069°$ is used in this work. The potential energy function $V(r)$ can take two different forms. In model I

$$V(r) = D_e\sum_{i=1}^{3}y_i^2 + f_{rr'}\sum_{i<j}^{3}r_ir_j, \tag{9}$$

Table 3
Expansion coefficients[a] of the dipole moment surfaces of AsH_3 molecule

C_{000}	0.183365(13)
C_{100}	−1.440819(85)
C_{010}	0.038976(75)
C_{200}	−0.30568(43)
C_{020}	0.09236(17)
C_{110}	−0.07000(37)
C_{011}	−0.06531(38)
C_{300}	0.1604(11)
C_{030}	−0.0698(74)
C_{210}	0.01778(78)
C_{021}	0.00531(77)
C_{120}	0.30237(77)
C_{111}	−0.06683(57)
C_{400}	0.1403(38)
C_{040}	0[b]
C_{310}	0.0764(32)
C_{031}	0.0290(32)
C_{130}	−0.1061(32)
C_{211}	0.0862(27)
rms[c] ($\times 10^{-4}$)	3.4

[a] Units are defined that the dipole moment is in Debye ($= 3.33564 \times 10^{-30}$ C m), the bond length displacement in Å. The value in the parentheses is one standard error in the last significant digit.

[b] Constrained value.

[c] Root-mean squares of the fitting residual.

and in model II

$$V(r) = D_e \sum_{i=1}^{3} y_i^2 + (f_{rr'}/a^2) \sum_{i<j}^{3} y_i y_j. \tag{10}$$

The Mores variables y_i are defined as $y_i = 1 - \exp(-ar_i)$, where a is a Mores potential energy parameter, D_e is the Mores dissociation energy and $f_{rr'}$ is the inter-bond potential coupling parameter. The Hamiltonian with the potential energy model in Eqs. (9) and (10) are called ACAOI and ACAOII, respectively. Halonen et al. [4] and Lin et al. [14] gave the vibrational analysis of the Arsine molecule. The values obtained in the Lin's work [14] are adopted here to calculate the wavefunctions: $D_e = 31\,643.7$ cm^{-1}, $a = 1.501156$ $\mathring{\mathrm{A}}^{-1}$ and $f_{rr'} = -412.1$ cm^{-1} $\mathring{\mathrm{A}}^{-2}$ for ACAOI, $D_e = 31\,669.1$ cm^{-1}, $a = 1.500129$ $\mathring{\mathrm{A}}^{-1}$ and $f_{rr'} = -455.1$ cm^{-1} $\mathring{\mathrm{A}}^{-2}$ for ACAOII. The details of the variational calculation can be referred to the [4]. So the band intensities were then calculated according to Eq. (7). The results by ACAOII model are omitted because they are almost the same.

5. Results and discussion

From Table 2, the calculation agrees with the observation within a factor of 1.5 for most bands. In 1993, Dana et al. [15] studied the absolute line intensities in the fundamental v_1 and v_3 of AsH_3 molecule and also estimated the band intensities, which are 1.07×10^5 and 2.97×10^5 (in 10^{-22} cm), respectively, and agree with the calculation in this work. In some cases, the empirical bond dipole model may not be very suitable for intensity calculation. The main reason may be this model ignores the contribution of the inter-bond coupling terms. From Table 3, it is obvious that all the coefficients C_{i00} are relatively large and others are smaller except C_{120} and C_{130}. To understand the effect of the inter-bond coupling term in the overtone and combination band intensities calculation, we calculated the absolute transition moments from the coupling terms and non-coupling terms in the DMS expansion separately. The results are shown in Table 4, which indicate the contributions to the intensities from different terms in the DMS expansion. In the fundamental the transition moment from inter-bond coupling terms is so little that can be neglected. But in the overtone region it becomes more and more important, especially in the high overtone region it is even larger than that from non-coupling terms. From $V = 3$ and $V = 4$ vibrational bands, we can see that the transition moments of combination bands in the column II are larger than those of the column III by about one order of magnitude. It indicates that the combination band intensity arises mainly from the coupling terms. So we can conclude that the inter-bond coupling terms are very essential for reproducing both combination and overtone band intensities in the high-energy regions.

Considering the separation of vibrational and rotational motion, the reference system which obeys Eckart conditions should be used [27,28]. So we also use this reference system to fit the DMS and calculate the intensities. But it gives similar

Table 4
Absolute transition moments (*D*) from different terms in the DMS expansion

Band	$\vert\langle N\vert\mathbf{M}_{\text{non-coupling}}\vert 0\rangle\vert$[a]	$\vert\langle N\vert\mathbf{M}_{\text{coupling}}\vert 0\rangle\vert$[b]
$(1\,0\,0;\mathrm{A}_1)$	0.12421E+0	0.71668E−2
(1 0 0; E)	0.26201E+0	0.68931E−2
$(2\,0\,0;\mathrm{A}_1)$	0.87460E−2	0.10097E−2
(2 0 0; E)	0.18748E−1	0.12938E−2
$(1\,1\,0;\mathrm{A}_1)$	0.11977E−2	0.14450E−2
(1 1 0; E)	0.11186E−2	0.25740E−3
$(3\,0\,0;\mathrm{A}_1)$	0.85564E−3	0.51641E−3
(3 0 0; E)	0.18203E−2	0.58412E−3
$(2\,1\,0;\mathrm{A}_1)$	0.47065E−4	0.62367E−3
(2 1 0; lE)	0.65405E−4	0.21395E−3
(2 1 0; hE)	0.59790E−4	0.72681E−3
$(1\,1\,1;\mathrm{A}_1)$	0.37023E−5	0.15713E−3
$(4\,0\,0;\mathrm{A}_1)$	0.12340E−3	0.17199E−3
(4 0 0; E)	0.26259E−3	0.18769E−3
$(3\,1\,0;\mathrm{A}_1)$	0.44787E−5	0.14377E−3
(3 1 0; lE)	0.94119E−5	0.96449E−4
(3 1 0; hE)	0.16067E−5	0.23093E−3
$(5\,0\,0;\mathrm{A}_1)$	0.25345E−4	0.56140E−4
(5 0 0; E)	0.53952E−4	0.60946E−4
$(6\,0\,0;\mathrm{A}_1)$	0.70122E−5	0.19280E−4
(6 0 0; E)	0.14922E−4	0.20934E−4

[a] From the non-coupling terms in the DMS expansion.
[b] From the coupling terms in the DMS expansion.

results, which are not listed here. As mentioned in [17], the Eckart conditions are not crucial in studying this kind of problems – the stretching vibrational band intensities of XH_3 molecules ($X = P$, As, Sb).

In summary, in this work we study the absolute local mode vibrational band intensities of AsH_3 molecule experimentally and theoretically. The DFT calculation 3D DMS was given in molecule-fixed reference system. The 3D DMS and wavefunction given by ACAO model reproduce the absolute local mode vibrational band intensities quite well. In this work, we only give the total intensity of all $V = 2$ bands, but we can get each band intensity by integrating all the assigned lines in high-resolution spectrum. So studying the absolute line intensities will be our future work.

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