# Vibrational Spectra of Vinylarsine and Vinylstibine. An Experimental and Theoretical Study

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The infrared spectra (3200 to 600 cm$^{-1}$) of gaseous vinylarsine and vinylstibine and their As-dideuterated and Sb-dideuterated derivative were recorded at 1 cm$^{-1}$ resolution. Both the infrared absorption bands of the syn and gauche conformers of the vinylarsine and vinylstibine were observed and assigned. The integrated intensities of isolated and overlapping vibrational bands were determined experimentally. Density functional theory calculations at the B3LYP/6-311G(d) level were performed to obtain the values of the harmonic vibrational frequencies. The results obtained are in good agreement with the experimental spectra and help in the assignment of the vibrational bands within the complex absorption region between 1100 and 600 cm$^{-1}$.

## Introduction

The enamine functional group has received a great deal of attention, because among other reasons, it exhibits versatile chemistry due to its ambident reactant nature,[1−3] since it can react at both the heteroatom and the $\beta$-carbon atom. For similar reasons the vinylphosphines, arsines, and stibines could be used as bidentate ligands in organometallic chemistry. Actually, these phosphorus and arsenic derivatives are the precursors of the corresponding phosphaalkenes[4] and arsaalkenes,[5] respectively. However, unsubstituted primary vinylamine, -phosphine, -arsine, and -stibine have a low stability at room temperature in the condensed phase.[6−9] Vinylarsine and vinylstibine exhibit a similar stability but are highly less stable than the vinylphosphine. Vinylamine is unambiguously the least stable of the four but due to the availability of several precursors, this molecule has been extensively studied, while information on the other three compounds is rather scarce and fragmentary. As a matter of fact, while the infrared spectrum of vinylamine was reported for the first time almost 20 years ago,[10−12] that of vinylphosphine was described only very recently,[13] and those of the vinylarsine and vinylstibine have not previously been reported. In fact, vinylic primary arsines and stibines were synthesized for the first time[7,8] only six years ago and, as a consequence, their NMR, mass, photoelectron,[8,14] and microwave spectra[15,16] were not recorded until very recently. Similarly, the gas-phase acidity of vinylarsine was determined by FT-ICR and theoretical calculations[17] only four years ago. Hence, the aim of this paper is to contribute to a better understanding of the properties of vinylarsine and vinylstibine through the analysis of their infrared spectra.

As in the case of the vinylphosphine, the vinylarsine and the vinylstibine have a structure of three conformers: syn, gauche, and anti. All ab initio calculations[13,15,16] indicate that the syn form is more stable than the gauche form, the anti form being the least stable. The infrared spectra of the vinylphosphine and its P-dideuterated derivative in our preceding work[13] confirmed this result where only the syn and the gauche forms were observed and their corresponding bands were assigned. In the present paper we report infrared gas-phase measurements of the $CH_2{=}CHAsH_2$ and $CH_2{=}CHSbH_2$ molecules. Vibrational bands in the range 3200−600 cm$^{-1}$ of the two thermodynamically stable isomers were observed. The deuteration of the arsine and the stibine groups was necessary to assess the assignment of the absorption bands in the complex absorption region between 1100 and 600 cm$^{-1}$. Observed vibrational frequencies and measured absolute intensities of isolated bands were compared to density functional theory calculations performed using the Gaussian 98 series of programs[18] and the B3LYP approach.[19,20] The results obtained were in good agreement with the experimental measurements.

## Experimental Procedure

The flask containing the reducing agent $Bu_3SnH$ (20 g, 68 mmol) with about 50 mg of duroquinone was fitted on a vacuum line, cooled to −30 °C, and degassed. The pure vinyldichloroarsine or vinyldichlorostibine (20 mmol) was then slowly added with a flex-needle through the septum in about 15 min. During and after the addition, the vinylarsine or vinylstibine formed was distilled off in vacuo from the reaction mixture. A cold trap (−80 °C) selectively removed the less volatile products and the product was condensed in a second cold trap (−110 °C) to remove the most volatile products (mainly $AsH_3$ or $SbH_3$ respectively). After disconnecting from the vacuum line by stopcocks, the product was kept in liquid nitrogen and transferred into the IR gas cell just before collecting the spectrum. To get an order of magnitude of the band intensities, the spectra

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**TABLE 1: Rotational Constants (MHz/cm$^{-1}$) of Vinylarsine and Vinylstibine**

| | vinylarsine | | | | vinylstibine | |
|---|---|---|---|---|---|---|
| | *syn* conformer | | *gauche* conformer | | *syn* conformer | |
| | calc | exp[a] | calc | exp[a] | calc | exp[b] |
| A | 36618.3/1.2214 | 36323.3/1.2116 | 37742.0/1.2589 | 37441.6/1.2489 | 33302.6/1.1108 | 32773.2/1.0932 |
| B | 3866.3/0.1289 | 3941.3/0.1315 | 3777.5/0.1260 | 3848.8/0.1284 | 3069.1/0.1024 | 3116.0/0.1039 |
| C | 3617.9/0.1207 | 3678.6/0.1227 | 3541.4/0.1181 | 3597.8/0.1200 | 2907.2/0.0969 | 2944.7/0.0982 |

[a] Values taken from ref 15. [b] Values taken from ref 16.

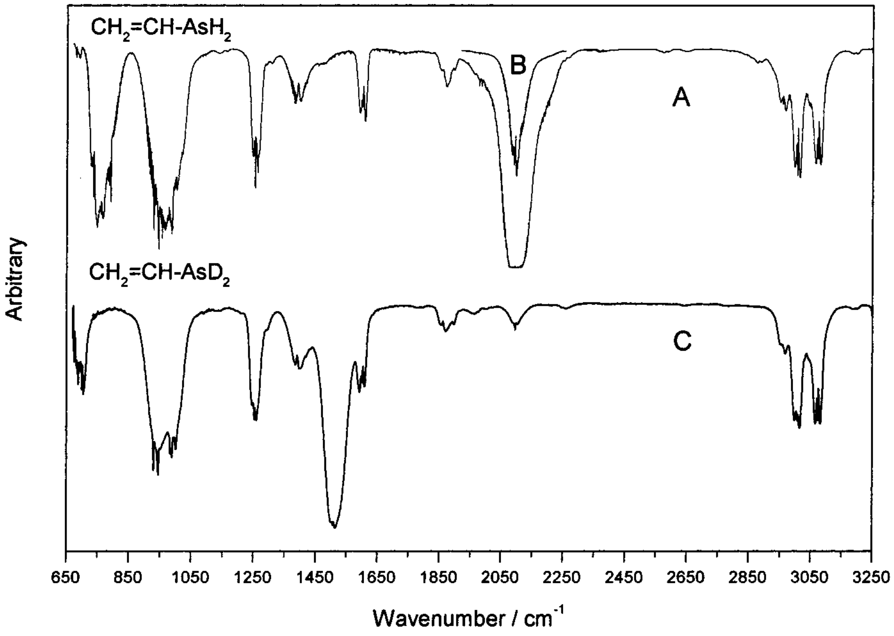


**Figure 1.** Infrared gas-phase spectra of vinylarsine and its As-dideuterated derivative recorded at 1 cm$^{-1}$ resolution. (A) Spectrum of $CH_2{=}CHAsH_2$ at a partial pressure of 40 Torr. (B) Stretching bands of $AsH_2$ group at a partial pressure of 5 Torr. (C) Spectrum of $CH_2{=}CHAsD_2$.

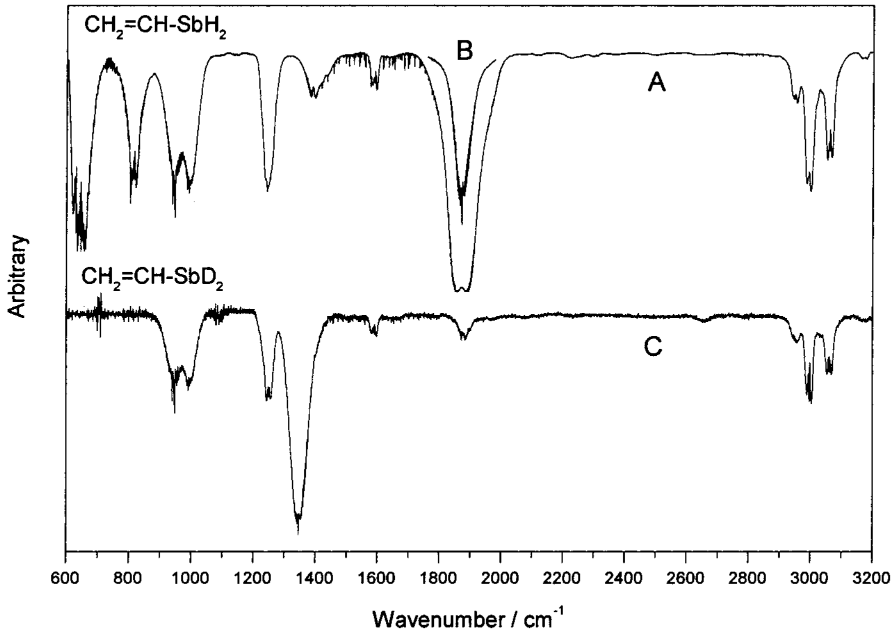


**Figure 2.** Infrared gas-phase spectra of vinylstibine and its Sb-dideuterated derivative recorded at 1 cm$^{-1}$ resolution. (A) Spectrum of $CH_2{=}CHSbH_2$ at a partial pressure of 40 Torr. (B) Stretching bands of $SbH_2$ group at a partial pressure of 5 Torr. (C) Spectrum of $CH_2{=}CHSbD_2$.

were recorded for different values (2−40 Torr) of partial pressure of vinylarsine and vinylstibine, respectively. An inert gas (760 Torr pure $N_2$) was systematically added to produce a broadening effect of the bands of interest. Similar experiments with $Bu_3SnD$ as reducing agent were used to prepare the dideuterated derivatives. Yields of 55% and 53% were respectively obtained for vinylarsine and vinylstibine.

The spectra were recorded with a Fourier transform IR spectrometer 120 HR Bruker equipped with a KBr beam splitter and a liquid nitrogen cooled MCT detector. A 20-cm-long gas

**TABLE 2: Observed and Calculated Vibrational Frequencies (freq, cm$^{-1}$), Relative Intensities (int), and Assignments for the Syn and Gauche Forms of $CH_2{=}CHAsH_2$[a]**

| observed | | | | calculated | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| gauche | | syn | | gauche | | syn | | | |
| freq | | freq | | freq | int | freq | int | assignments | |
| 3081.6 | R | 3081.6 | R | | | | | | |
| 3075.6 | Q | 3075.6 | | 3194 | 19.04 | 3193 | 17.31 | $CH_2$ | antisymmetric stretching |
| 3065.6 | P | 3065.6 | P | | | | | | |
| 3014 | R | 3014 | R | | | | | | |
| 3006 | Q | 3006 | Q | 3131 | 14.01 | 3146 | 9.28 | $CH_2$ | symmetric stretching |
| 2998 | P | 2998 | P | | | | | | |
| 2968 | R | 2968 | R | | | | | | |
| 2959 | Q | 2959 | Q | 3112 | 15.22 | 3113 | 17.03 | CH | symmetric stretching |
| 2950 | P | 2950 | P | | | | | | |
| 2103 | R | 2104 | R | | | | | | |
| 2095 | Q | 2095 | Q | 2170 | 110.61 | 2150 | 129.49 | $AsH_2$ | antisymmetric stretching |
| 2092 | Q | 2092 | Q | 2147 | 119.69 | 2144 | 118.91 | $AsH_2$ | symmetric stretching |
| 2086 | P | 2086 | P | | | | | | |
| 1892 | | 1892 | | | | | | 2n CH | wagging |
| 1860.5 | | 1860.5 | | | | | | 2n $CH_2$ | wagging |
| 1608 | R | 1608 | R | | | | | | |
| 1601 | Q | 1601 | Q | 1662 | 2.93 | 1664 | 4.89 | C=C | stretching |
| 1591.6 | P | 1591.6 | P | | | | | | |
| 1400 | R | | | | | | | | |
| 1391 | ctr | 1391 | | 1439 | 8.06 | 1437 | 9.24 | $CH_2$ | scissors |
| 1380.7 | P | | | | | | | | |
| | | 1264 | R | | | | | | |
| 1262. | Q | 1253 | Q | 1297 | 8.77 | 1287 | 18.47 | CH | bending in-plane |
| | | 1247 | P | | | | | | |
| | | 1001.8 | | 1044 | 6.76 | 1034 | 7.61 | $CH_2$ | rocking |
| 982 | | 989 | | 1021 | 9.49 | 1023 | 23.37 | CH | bending out-of-plane |
| 956 | | 976 | | 991 | 30.1 | 1010 | 17.06 | $AsH_2$ | scissors |
| 929.3 | | 945 | | 948 | 35.23 | 969 | 35.27 | $CH_2$ | wagging |
| | | 790 | Q1 | | | | | | |
| 773 | | 786 | Q2 | 795 | 39.12 | 817 | 24.41 | $AsH_2$ | twisting |
| | | 784 | Q3 | | | | | | |
| 765 | R | 745 | R | | | | | | |
| 758 | Q | 737 | Q1 | 781 | 14.2 | 763 | 31.85 | $AsH_2$ | wagging |
| 747 | P | 735 | Q2 | | | | | | |
| | | 728 | P | | | | | | |
| | | | | 540 | 5.05 | 572 | 6.34 | C−As | stretching |
| | | | | 482 | 8.53 | 491 | 8.74 | $CHCH_2$ | twisting |
| | | | | 302 | 2 | 288 | 1.29 | As−C−C | bending |
| | | | | 169 | 1.28 | 134 | 0.3 | $AsH_2$ | rocking |

[a] Calculated values were obtained at the B3LYP/6-311G(d) Level. R, Q, and P refer to band contours; ctr refers to the center of the band.

cell, equipped with 8-mm-thick KBr windows, was used. The spectra of $CH_2{=}CHAsH_2$, $CH_2{=}CHAsD_2$, $CH_2{=}CHSbH_2$, and $CH_2{=}CHSbD_2$ (average of 30 scans) were collected at ambient temperature, at a resolution of 1 cm$^{-1}$.

## Computational Details

As mentioned in the Introduction, the geometries of vinylarsine and vinylstibine were optimized using the B3LYP density functional theory approach. This method combines Becke's three-parameter nonlocal hybrid exchange potential[19] with the nonlocal correlation functional of Lee, Yang, and Parr.[20] In general, geometries obtained using the aforementioned DFT method are in fairly good agreement with experimental values.[21−25] More importantly, the harmonic vibrational frequencies are closer to experiment than those obtained by using other correlated methods such as MP2.[26,27] Furthermore, also as far as the infrared intensities are concerned, the B3LYP approach is more accurate than MP2, yielding values in close agreement with those obtained at high (QCISD) ab initio levels.[28] For the vinylarsine geometry optimization, and the evaluation of the harmonic vibrational frequencies, a 6-311G(d,p) basis set expansion, since it is particularly well suited to account for electron correlation effects, was used. For antimony, no 6-311G(d,p) expansion has been previously reported and we used the polarized basis set proposed by González et al.[29] This basis set is used in conjunction with the SKBJ relativistic potential of Stevens et al.,[30] which employs a (5s,5p)/[2s,2p] basis set to describe the valence electrons of Sb. However, we have used a completely uncontracted scheme, which formally corresponds to a quintuple $\zeta$ basis set, instead of this [4,1] contraction scheme. The corresponding polarization functions for Sb are those optimized in ref 29. This polarized, uncontracted [11111,11111,1] scheme, used together with a 6-311G(d,p) basis set for first and second row atoms, will be named 6-311G(d), for the sake of consistency.

## Results and Discussion

The rotational constants of vinylarsine and vinylstibine, derived from their microwave Fourier transform spectra, have been reported recently in the literature.[15,16] These values can be readily used to assess the reliability of our optimized geometries. In Table 1 we compare our B3LYP/6-311G(d,p) calculated rotational constants with the experimental ones for both the syn and the gauche conformers of vinylarsine. It can be seen that the agreement between both sets of values is good, the deviation varying between 0.8% for the A constants and 1.9% for the B constants. In the same table the rotational constants of vinylstibine are also given. In this case the comparison is restricted to the most stable syn conformer, since only one set of experimental values have been reported.[16] The

**TABLE 3: Observed and Calculated Vibrational Frequencies (freq, $cm^{-1}$), Relative Intensities (int), and Assignments for the Syn and Gauche Forms of $CH_2{=}CHAsD_2$[a]**

| observed | | | | calculated | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| gauche | | syn | | gauche | | syn | | | |
| freq | | freq | | freq | int | freq | int | assignments | |
| 3082 | R | 3082 | R | | | | | | |
| 3073.5 | Q | 3073.5 | Q | 3195 | 18.85 | 3193 | 17.29 | $CH_2$ | antisymmetric stretching |
| 3066 | P | 3066 | P | | | | | | |
| 3014.8 | R | 3014.8 | R | | | | | | |
| 3006.4 | Q | 3006.4 | Q | 3133 | 13.66 | 3146 | 9.32 | $CH_2$ | symmetric stretching |
| 2997.6 | P | 2997.6 | P | | | | | | |
| 2967.9 | R | 2967.9 | R | | | | | | |
| 2961.7 | Q | 2961.7 | Q | 3113 | 15.47 | 3113 | 16.96 | CH | symmetric stretching |
| 2958.4 | Q | 2958.4 | Q | | | | | | |
| 2952 | P | 2952 | P | | | | | | |
| 1892.5 | | 1892 | | | | | | 2n CH | wagging |
| 1889 | | | | | | | | | |
| 1861 | | 1860.5 | | | | | | 2n $CH_2$ | wagging |
| 1608 | R | 1608 | R | | | | | | |
| 1600.6 | Q | 1600.6 | Q | 1662 | 3.32 | 1664 | 4.93 | C=C | stretching |
| 1590.8 | P | 1590.8 | P | | | | | | |
| 1520 | R | 1520 | R | | | | | | |
| 1514.6 | Q | 1514.6 | Q | 1540 | 54.06 | 1531 | 66.46 | $AsD_2$ | antisymmetric stretching |
| 1507.4 | Q | 1507.4 | Q | 1515 | 62.77 | 1526 | 58.39 | $AsD_2$ | symmetric stretching |
| 1499.5 | P | 1499.5 | P | | | | | | |
| 1398.4 | R | 1398.5 | R | | | | | | |
| 1390.7 | ctr | 1390.7 | ctr | 1439 | 9.67 | 1437 | 10.43 | $CH_2$ | scissors |
| 1383.5 | P | 1383.5 | P | | | | | | |
| | | 1259.8 | R | | | | | | |
| 1261 | Q | 1252.8 | Q | 1297 | 9.2 | 1287 | 18.33 | CH | bending in-plane |
| | | 1245.8 | P | | | | | | |
| | | 1000.3 | | 1036 | 6.08 | 1028 | 5.43 | $CH_2$ | rocking |
| 983 | | 989.7 | | 1016 | 18.27 | 1024 | 23.59 | CH | bending out-of-plane |
| 929.2 | | 945.8 | | 948 | 36.68 | 969 | 34.41 | $CH_2$ | wagging |
| 681 | | 691 | | 706 | 9.13 | 720 | 8.08 | $AsD_2$ | scissors |
| | | | | 641 | 37.42 | 656 | 25.19 | $AsD_2$ | twisting |
| | | | | 618 | 5.3 | 609 | 26.3 | $AsD_2$ | wagging |
| | | | | 504 | 5.72 | 531 | 0.98 | C−As | stretching |
| | | | | 428 | 3.2 | 441 | 2.84 | $CHCH_2$ | twisting |
| | | | | 292 | 1.61 | 282 | 1.47 | As−C−C | bending |
| | | | | 118 | 0.74 | 105 | 0.07 | $AsD_2$ | rocking |

[a] Calculated values were obtained at the B3LYP/6-311G(d) level. R, Q, and P refer to band contours; ctr refers to the center of the band.

agreement between calculated and experimental values is again very good: the average deviation being about 1.5%. It is also worth noting that our optimized value for the C−Sb bond length (2.146 Å) is in very good agreement with the experimental estimate (2.13(3) Å).[16]

The spectra of the vinylarsine and its As-dideuterated derivative are given in Figure 1 and the spectra of the vinylstibine and its Sb-dideuterated derivative are given in Figure 2. As indicated previously, these species have two stable conformers: the syn form and the gauche form. They present an infrared spectral signature varying up to 20 $cm^{-1}$ between the two isomers. This complicates considerably the assignment of the vibrational bands especially in the region above 1000 $cm^{-1}$. Also, we take advantage of the comparison between the spectra of the vinylarsine and the vinylstibine and their corresponding As-dideuterated and Sb-dideuterated derivatives as well as the estimated frequencies obtained in our DFT calculations. Tables 2−5 summarize the frequencies observed and calculated for the $CH_2{=}CH{-}AsH_2$ and $CH_2{=}CH{-}SbH_2$ molecules and their $-XD_2$ ($X = As$ or Sb) derivatives.

The CH stretching vibrations of the vinyl group appear in the region around 3000 $cm^{-1}$. One observes three bands characteristic of the antisymmetric and the symmetric stretching of the $CH_2$ group and the stretching of the CH group. For the $CH_2{=}CH{-}AsH_2$ molecule, these bands appear at 3075, 3006, and 2959 $cm^{-1}$, respectively. For the $CH_2{=}CH{-}SbH_2$ molecule, they are shifted about 10 $cm^{-1}$ toward the red. It is also observed that the spacing of frequencies between the syn and the gauche forms for these bands is more appreciable in the case of the vinylstibine than in the case of the vinylarsine. We do not observe any tangible effect on these bands when one substitutes hydrogen by deuterium in the $AsH_2$ and $SbH_2$ groups.

The C=C double bond stretching and the CH in-plane deformations of the vinyl group are easily identified and assigned in the two molecules. These bands are not sensitive to the presence of deuterium atoms at the $AsH_2$ and $SbH_2$ groups. In the case of the vinylarsine, the C=C stretching vibration absorbs at 1601 $cm^{-1}$ whereas in the case of the vinylstibine, this band appears at 1590 $cm^{-1}$ and we detect the same red shift as before. As in the case of the vinylphosphine,[13] the experimental contour of this band in vinylarsine shows two distinct P and R branches with a central structure appearing as series of the Q branches. We assigned the most intense Q branch to the center of the band. This structure is not resolved in the case of the vinylstibine.

The $CH_2$ scissoring of the vinyl group occurs at 1400 $cm^{-1}$ in the vinylarsine and in the vinylstibine. It seems to be insensitive to the nature of the substituent groups, namely $-AsH_2$ or $-SbH_2$. Indeed, most of the vinyl compounds absorb at the same frequency so that this band is usually a good indication of the presence of the $-CH{=}CH_2$ fragment. The peaks of the P and R branches have a regular spacing of $2(A - B) = 2.1$ $cm^{-1}$ for the vinylarsine and of $2(A - B) = 2.0$ $cm^{-1}$ for the vinylstibine. The absence of the Q branch in these bands renders the assignment to syn and gauche isomers difficult. Hence, we assigned the same frequency to the two

**TABLE 4: Observed and Calculated Vibrational Frequencies (freq, cm$^{-1}$), Relative Intensities (int), and Assignments for Syn and Gauche Forms of $CH_2$=$CHSbH_2$[a]**

| observed | | | | calculated | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| gauche | | syn | | gauche | | syn | | | |
| freq | | freq | | freq | int | freq | int | assignments | |
| 3069.2 | R | 3069.2 | R | | | | | | |
| 3065.6 | Q | 3061.0 | Q | 3188 | 19.03 | 3183 | 19.9 | $CH_2$ | antisymmetric stretching |
| 3054.5 | P | 3054.5 | P | | | | | | |
| 3001 | R | 3001 | R | | | | | | |
| 2988.5 | Q | 2993.7 | Q | 3125 | 25.36 | 3136 | 11.95 | $CH_2$ | symmetric stretching |
| 2988 | P | 2988 | P | | | | | | |
| 2955.4 | R | 2955.4 | R | | | | | | |
| 2945 | Q | 2949.3 | Q | 3104 | 18.81 | 3105 | 24.95 | CH | symmetric stretching |
| 2942.8 | P | 2942.8 | P | | | | | | |
| 1893.7 | | 1877 | | 1941 | 200.9 | 1927 | 237.5 | $SbH_2$ | antisymmetric stretching |
| 1867.3 | | 1872.9 | | 1917 | 227.8 | 1924 | 223.2 | $SbH_2$ | symmetric stretching |
| 1595.4 | R | 1595.4 | R | | | | | | |
| 1589.7 | Q | 1589.7 | Q | 1654 | 0.35 | 1656 | 2.81 | C=C | stretching |
| 1581.7 | P | 1581.7 | P | | | | | | |
| 1398.7 | R | 1398.7 | R | | | | | | |
| 1390.3 | ctr | 1390.3 | ctr | 1441 | 9.17 | 1441 | 10.56 | $CH_2$ | scissors |
| 1382.6 | P | 1382.6 | P | | | | | | |
| 1259.0 | R | 1248.3 | R | | | | | | |
| 1254 | Q | 1243.6 | Q | 1287 | 17.39 | 1274 | 33.96 | CH | bending in-plane |
| 1248.3 | P | 1237.7 | P | | | | | | |
| 996 | | 992 | | 1034 | 13.76 | 1031 | 23.57 | CH | bending out-of-plane |
| 987.4 | | 987.4 | | 1022 | 12.74 | 1020 | 11.4 | $CH_2$ | rocking |
| 939.3 | | 948 | | 963 | 37.29 | 974 | 34.03 | $CH_2$ | wagging |
| | | 822.4 | R | | | | | | |
| 804 | | 817 | Q | 839 | 51.85 | 855 | 50.14 | $SbH_2$ | scissors |
| | | 808.7 | P | | | | | | |
| 663 | | 663 | | 686 | 82.81 | 687 | 35.7 | $SbH_2$ | twisting |
| 645 | | 629 | | 667 | 15.53 | 654 | 76.87 | $SbH_2$ | wagging |
| | | | | 482 | 11.55 | 504 | 6.16 | C−Sb | stretching |
| | | | | 435 | 5.93 | 435 | 5.26 | $CHCH_2$ | twisting |
| | | | | 270 | 2.16 | 252 | 2.85 | Sb−C−C | bending |
| | | | | 119 | 0.3 | 109 | 0.08 | $SbH_2$ | rocking |

[a] Calculated values were obtained at the B3LYP/6-311G(d) level. R, Q, and P refer to band contours; ctr refers to the center of the band.

conformers in agreement with the prediction of our DFT calculations, which envisage a negligible difference of less than 2 cm$^{-1}$ between the two isomers.

For the CH in-plane bending mode, the isomeric effect is more clearly discerned. The two conformers have a frequency difference of 8 cm$^{-1}$ in the case of vinylarsine and 10 cm$^{-1}$ in the case of the vinylstibine. DFT calculations estimate these differences to be about 10 and 13 cm$^{-1}$, respectively. Furthermore, in agreement with calculated values, we observed a ratio of intensity of about 2 in favor of the syn form.

The $CH_2$ rocking mode occurs around 990 cm$^{-1}$ with a medium intensity. Guided by our theoretical calculations, we assigned the same frequencies to the syn and the gauche isomers in the case of the vinylstibine, while in the case of the vinylarsine, only the syn form is observed and assigned.

The most useful infrared bands to elucidate the structure of the $-CH$=$CH_2$ group are the strongest absorption bands of the CH out-of-plane bending and the $CH_2$ wagging vibrations. These bands appear around 990 and 915 cm$^{-1}$, respectively, and present two characteristic harmonic bands at 1980 and 1830 cm$^{-1}$, respectively. However, in this region of the spectrum, other vibrational modes, namely the $-XH_2$ ($X$ = As or Sb) scissoring, twisting, and wagging, appear. All these bands are sensitive to the isomeric effect and exhibit a contour typical of the overlapping of several vibrational bands. Hence, to assign the individual vibrational modes in this particularly complicated spectral region, we have used three different criteria: the calculated harmonic frequencies, the comparison between the two spectra of the vinylarsine and the vinylstibine, and the expected isotopic effects on their As- and Sb-dideuterated species (see Figure 3). Following this strategy, we assign the

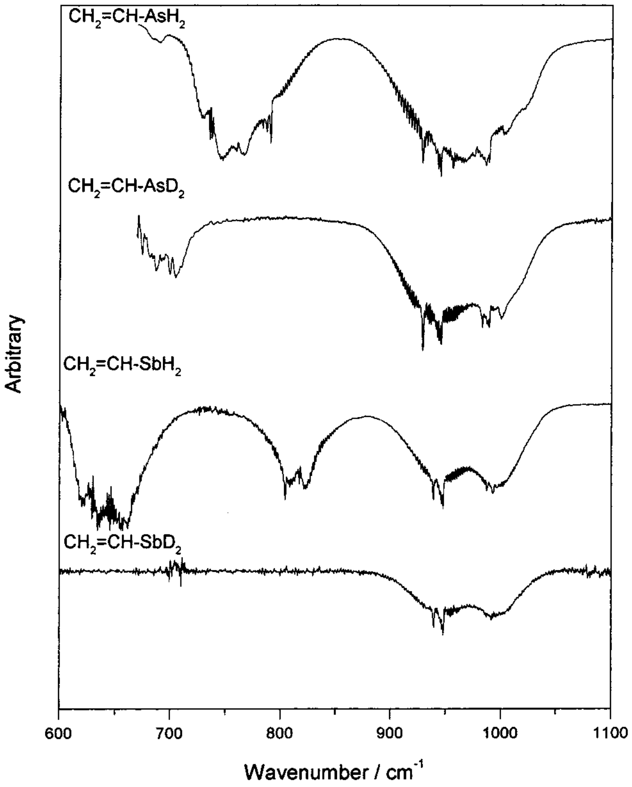


**Figure 3.** Spectral region showing the expected isotope effects by substitution of the group $AsD_2$ in the vinylarsine molecule and a substitution of the group $SbD_2$ in the vinylstibine molecule. $XH_2$ with ($X$ = As, Sb) scissors, twisting and wagging vibrational modes are significantly affected by this isotopic distribution.

**TABLE 5: Observed and Calculated Vibrational Frequencies (freq, cm$^{-1}$), Relative Intensities (int), and Assignments for Syn and Gauche Forms of $CH_2{=}CHSbD_2$**[a]

| observed | | | | calculated | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| gauche | | syn | | gauche | | syn | | | |
| freq | | freq | | freq | int. | freq | int. | assignments | |
| 3069.6 | R | 3069.6 | R | | | | | | |
| 3065.3 | Q | 3065.3 | Q | 3188 | 19 | 3183 | 19.84 | $CH_2$ | antisymmetric stretching |
| 3054.6 | P | 3054.6 | P | | | | | | |
| 3004.2 | R | 3004.2 | R | | | | | | |
| 2997.4 | Q | 2997.4 | Q | 3125 | 25.04 | 3136 | 12 | $CH_2$ | symmetric stretching |
| 2989.6 | P | 2989.6 | P | | | | | | |
| 2956.9 | R | 2956.9 | R | | | | | | |
| 2948.7 | Q | 2948.7 | Q | 3104 | 19.65 | 3105 | 24.87 | CH | symmetric stretching |
| 2942.7 | P | 2942.7 | P | | | | | | |
| 1596.3 | R | 1596.3 | R | | | | | | |
| 1590.6 | Q | 1590.6 | Q | 1654 | 0.36 | 1655 | 2.45 | C=C | stretching |
| 1582 | P | 1582 | P | | | | | | |
| | | | | 1441 | 3.78 | 1440 | 7.07 | $CH_2$ | scissors |
| 1353.6 | R | 1353.6 | R | | | | | | |
| 1347 | Q | 1347 | Q | 1378 | 107.2 | 1369 | 121.34 | $SbD_2$ | antisymmetric stretching |
| 1342.6 | Q | 1342.6 | Q | 1362 | 115.6 | 1366 | 115.2 | $SbD_2$ | symmetric stretching |
| 1338.7 | P | 1338.7 | P | | | | | | |
| 1257.4 | R | 1257.5 | R | | | | | | |
| 1258 | Q | 1250.2 | Q | 1286 | 18.89 | 1273 | 34.18 | CH | bending in-plane |
| 1244 | P | 1244 | P | | | | | | |
| 996.1 | | 991.6 | | 1033 | 15.79 | 1032 | 23.47 | CH | bending out-of-plane |
| 987.2 | | 987.2 | | 1019 | 9.9 | 1017 | 7.88 | $CH_2$ | rocking |
| 939.4 | | 948 | | 963 | 35.73 | 974 | 33.16 | $CH_2$ | wagging |
| | | | | 598 | 33.9 | 608 | 25.45 | $SbD_2$ | scissors |
| | | | | 571 | 47.4 | 574 | 32.6 | $SbD_2$ | twisting |
| | | | | 546 | 4.96 | 542 | 46.57 | $SbD_2$ | wagging |
| | | | | 436 | 15.62 | 451 | 7.36 | C−Sb | stretching |
| | | | | 377 | 4.98 | 375 | 0.51 | $CHCH_2$ | twisting |
| | | | | 261 | 1.49 | 243 | 3.38 | Sb−C−C | bending |
| | | | | 100 | 0.19 | 91 | 0.07 | $SbD_2$ | rocking |

[a] Calculated values were obtained at the B3LYP/6-311G(d) Level. R, Q. and P refer to band contours; ctr refers to the center of the band.

**TABLE 6: Absolute Intensity of the Strongest Isolated Vibrational Bands and the Estimated Sum Intensities for Overlapping Vibrational Bands**

| isolated and overlapping vibration bands | absolute intensity (cm$^{-2}$ atm$^{-1}$) |
|---|---|
| $C_2H_3AsH_2$ | |
| $AsH_2$ twisting + $AsH_2$ wagging | 170 ± 5 |
| $AsH_2$ scissors + CH wagging + $CH_2$ rocking + $CH_2$ wagging | 292 ± 10 |
| CH deformation | 43 ± 1 |
| $CH_2$ deformation | 27.4 ± 0.6 |
| C=C stretching | 20.0 ± 0.5 |
| 2n CH deformation + 2n $CH_2$ deformation | 9.9 ± 0.4 |
| $AsH_2$ antisymmetric stretching + $AsH_2$ symmetric stretching | 813 ± 28 |
| $CH_2$ antisymmetric stretching + $CH_2$ symmetric stretching + CH symmetric stretching | 147 ± 5 |
| $C_2H_3SbH_2$ | |
| $SbH_2$ scissors | 103 ± 4 |
| CH wagging + $CH_2$ rocking + $CH_2$ wagging | 193 ± 19 |
| CH deformation | 92 ± 11 |
| $CH_2$ deformation | 34.7 ± 3.4 |
| C=C stretching | 9.7 ± 0.9 |
| $SbH_2$ antisymmetric stretching + $SbH_2$ symmetric stretching | 1350 ± 27 |
| $CH_2$ antisymmetric stretching + $CH_2$ symmetric stretching + CH symmetric stretching | 146.9 ± 5.8 |

CH out-of-plane bending to absorptions at 989 and 982 cm$^{-1}$ for the syn and the gauche forms of vinylarsine and to bands at 996 and 992 cm$^{-1}$ for vinylstibine. The $CH_2$ wagging vibrations for the syn and the gauche forms of $CH_2{=}CHAsH_2$ appear at 929 and 945 cm$^{-1}$ and at 939 and 948 cm$^{-1}$ in the case of the $CH_2{=}CHSbH_2$ molecule. The last vibrational modes in the vinyl group, namely, the skeletal $-C{=}C$ deformation and $-CH{=}CH_2$ twisting lie below 600 cm$^{-1}$ and therefore out of the range of our spectrometer. Accordingly, only their calculated frequency values are given.

Concerning the $AsH_2$ and the $SbH_2$ groups, the assignment of their observed vibrational bands has been carried out by taking advantage of the expected isotope effects on the $AsD_2$ and $SbD_2$ compounds. We found the $AsH_2$ stretching modes around 2095 cm$^{-1}$ and the $SbH_2$ stretching modes near 1880 cm$^{-1}$. The two symmetric and antisymmetric stretching vibrations are observed and assigned. Shifts of frequencies of these vibrational bands when we substitute hydrogen by deuterium are about 560 cm$^{-1}$ and the ratios of $\nu(-AsH_2)/\nu(-AsD_2)$ and $\nu(-SbH_2)/\nu(-SbD_2)$ are found to be 1.39 and are consistent with the factor of $\sqrt{2}$ provided by the H−D mass change. In the case of the vinylstibine, spacing between the frequency values of the syn and the gauche forms are in good agreement with the calculated value. A good agreement between observed and computed values for the shift between the symmetric and the asymmetric stretch is also found. On the contrary, in the

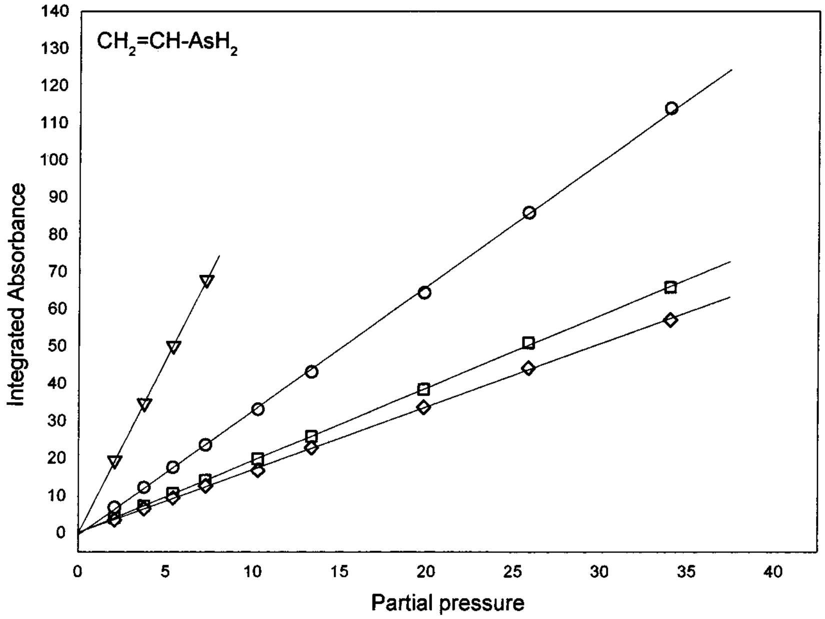


**Figure 4.** Variation of the integrated absorbance as a function of the pressure of vinylarsine: (down triangle) absorbance of symmetric and asymmetric $AsH_2$ stretching vibrations, (circle) absorbance of the overlapping vibration modes ($AsH_2$ scissors, CH wag, $CH_2$ wag, and $CH_2$ rock); (square) absorbance of the $AsH_2$ twist + $AsH_2$ wag; (diamond) absorbance of symmetric and asymmetric stretching of $CH_2$ and CH stretching groups.

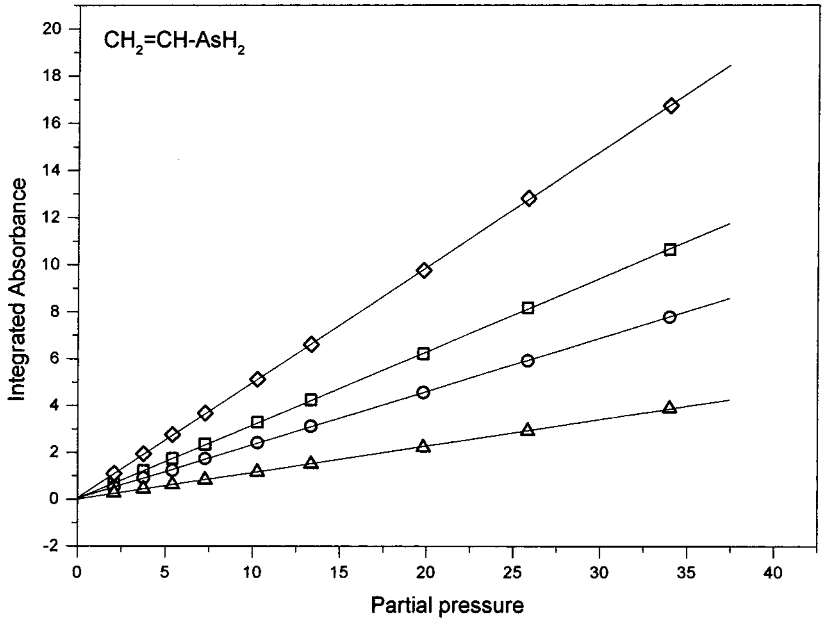


**Figure 5.** Variation of the integrated absorbance as a function of the pressure of vinylarsine: (diamond) absorbance of the CH deformation; (square) absorbance of the $CH_2$ deformation; (circle) absorbance of the C=C stretching vibration; (up triangle) absorbance of the overtone of CH and $CH_2$ wagging groups.

case of the vinylarsine, we do not observe any appreciable spacing between the two isomers and the observed spacing between the symmetric and the asymmetric stretch is only about 3 $cm^{-1}$, while our calculation predicts a difference up to 23 $cm^{-1}$.

Other vibrational modes of the $-XH_2$ (X = As or Sb) groups, namely the scissoring, twisting, and wagging, are very sensitive to the isomeric effect. With the only exception of the $SbH_2$ twisting mode, which presents the same frequency for the syn and the gauche conformers, the other vibrational modes are spaced about 15 $cm^{-1}$ in the case of the vinylarsine and about 20 $cm^{-1}$ in the case of the vinylstibine. All these modes are observed and assigned. Finally, vibrational values of the rocking mode of the $-AsH_2$ and the $-SbH_2$ appears below 600 $cm^{-1}$; only their calculated value are given.

Finally, it is worth noting that the C=C and C−H vibrational modes of vinylarsine and vinylstibine are sensitive to the nature of the substituent. Indeed, our results, both experimental and theoretical, show that the C=C stretching mode is slightly red-shifted (13 $cm^{-1}$) on going from $H_2C{=}CHAsH_2$ to $H_2C{=}CHSbH_2$. This is consistent with a slightly greater contribution of the **b** type resonance structure (see Scheme 1)[6] in the case of the vinylstibine, reflecting the lower electronegativity of Sb with respect to As. Similarly, the $CH_2$ and the C−H stretches, as well as the $CH_2$ rocking and the C−H in-plane bending, are red-shifted by 16, 19, 13, and 8 $cm^{-1}$,

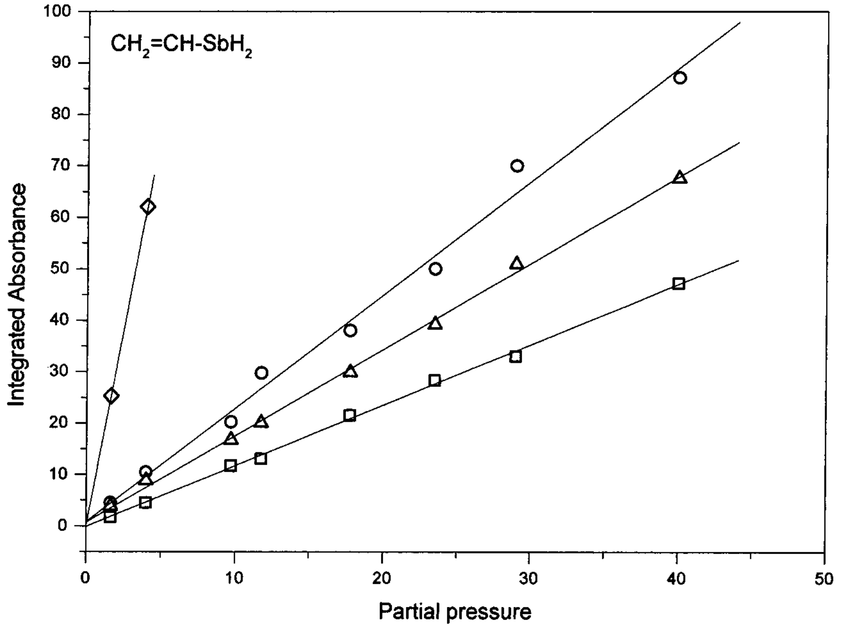


**Figure 6.** Variation of the integrated absorbance as a function of the pressure of vinylstibine: (diamond) absorbance of symmetric and asymmetric $SbH_2$ stretching vibrations; (circle) absorbance of the overlapping vibration modes (CH wag, $CH_2$ wag, and $CH_2$ rock); (square) absorbance of the $SbH_2$ scissors; (up triangle) absorbance of symmetric and asymmetric stretching of $CH_2$ and CH stretching groups.

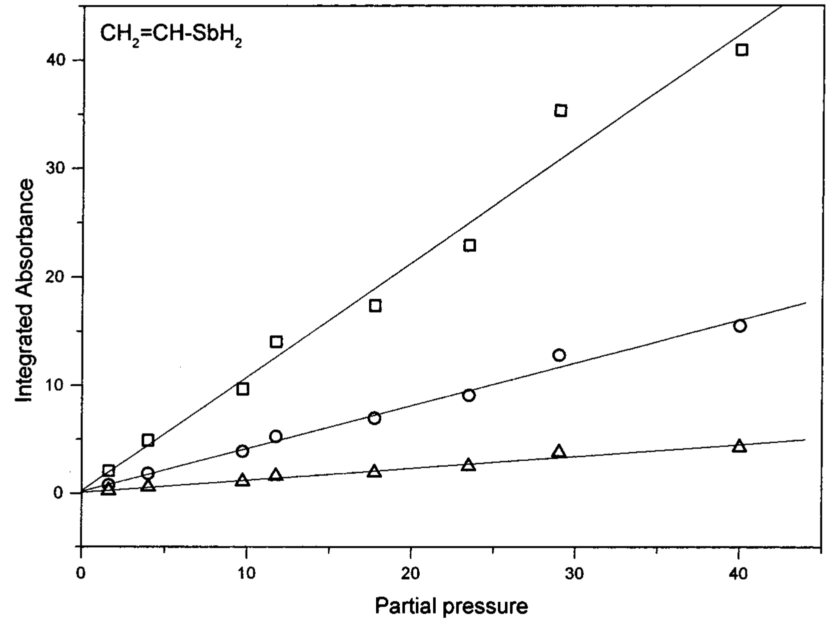
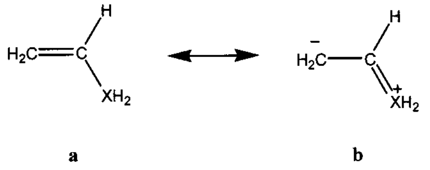


**Figure 7.** Variation of the integrated absorbance as a function of the pressure of vinylstibine: (square) absorbance of the CH deformation; (circle) absorbance of the $CH_2$ deformation; (up triangle) absorbance of the C=C stretching vibration.

**SCHEME 1**



respectively. Also consistently, both the C−H out-of-plane bending and the $CH_2$ wagging are blue-shifted by 10 $cm^{-1}$.

## Intensity Measurements

For vinylarsine and vinylstibine, we have determined absolute intensities for identified vibrational bands by plotting their integrated absorbance, $A_\nu$, as a function of the partial pressure. For all the bands studied, we observed a linear variation, and the straight line obtained passes through the (0,0) point. This indicates that Beer's law is indeed followed, as shown in Figures 4−7.

One can easily derive the value of the absolute band intensity, $S_\nu$, from the slope of the corresponding straight lines

$$A_\nu = S_\nu l P$$

where $l$ is the length of the gas cell and $P$ the partial pressure. In addition, the standard deviation from linearity gives a quantitative estimate of the uncertainty on the $S_\nu$ value. We have followed this approach for all of the observed bands of $CH_2{=}CHAsH_2$ and $CH_2{=}CHSbH_2$. In the case of overlapping of several vibrational bands, only the sum of their integrated absorbances has been estimated, because they cannot be calculated separately for each component. Table 6 summarizes the measured intensities and their associated uncertainties. $S_\nu$ values are given in atm$^{-1}$ cm$^{-2}$ determined at 300 K, base e.

Double bond stretching in vinyl hydrocarbons is a medium intensity band. We observe that the absolute intensity of this band is twice as significant in the case of the vinylarsine than in the case of the vinylstibine. On the contrary, the CH deformation band presents an absolute intensity 2 times weaker in the case of the vinylarsine than in the case of vinylstibine. The $CH_2$ deformation, CH stretching, and $CH_2$ symmetric and antisymmetric stretching bands have about the same absolute intensity for the two molecules. For all the isolated bands, the intensity ratio for the two molecules is practically the same than that obtained by DFT calculations.

## Conclusions

In agreement with the predictions of DFT calculations carried out at the B3LYP/6-311G(d,p) level, both the syn and gauche conformers of the vinylarsine and vinylstibine were experimentally detected through the analysis of their gas-phase infrared spectra in the region from 3200 to 600 cm$^{-1}$. The spectra of the corresponding As-dideuterated and Sb-dideuterated derivatives were also recorded at 1 cm$^{-1}$ resolution, and were crucial, together with the DFT harmonic vibrational frequencies, to achieve an unambiguous assignment of the absorption bands in the region between 1100 and 600 cm$^{-1}$. The integrated intensities of isolated and overlapping vibrational bands were determined experimentally. The experimental results obtained were in good agreement with the predictions of theory.

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