Low Frequency Vibrations of Molecular Crystals. XIII. CH₃AsCl₂, CH₃AsBr₂, CH₃Asl₂, and CD₃Asl₂*

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The ir spectra from 4000 to 33 cm⁻¹ have been recorded of CH₃AsCl₂, CH₃AsBr₂, CH₃AsI₂, and CD₃AsI₂. The Raman spectra of each of these compounds have been recorded and depolarization values measured for CH₃AsCl₂ and CH₃AsBr₂. The observed spectra have been successfully interpreted on the basis of a pyramidal skeletal structure of C_s symmetry. The observed values for the Teller–Redlich product rule for the assignments of the normal modes of the CH₃AsI₂ and CD₃AsI₂ molecules are in reasonable agreement with the theoretical values for both symmetry species. The As–CH₃ torsional mode was tentatively assigned in the ir spectrum of solid CH₃AsBr₂ at 134 cm⁻¹ and the torsional barrier calculated to be 461 ± 30 cm⁻¹ (1.32 ± 0.08 kcal/mole). The low frequency bending modes of solid CH₃AsI₂ and CD₃AsI₂ have been found to show correlation field splitting and have been successfully explained in terms of the four molecules per unit cell with a space group of C_{24}^6 .

INDEX HEADINGS: Infrared spectra; Far infrared spectra; Molecular structure; Raman spectra.

INTRODUCTION

The study of the vibrational motions of organometallic compounds in the low frequency region of the spectrum $(<200 \text{ cm}^{-1})$ has been the subject of several recent investigations.¹⁻⁴ These investigations were for the purposes of characterizing the molecular motions giving rise to the low frequency modes and of studying the effects on the barriers hindering internal rotation of the CH₃ group by the addition of various substituents. As a continuation of these studies, we have investigated the far ir spectra of CH₃AsCl₂, CH₃AsBr₂, CH₃AsI₂, and CD₃AsI₂. No previous far infrared data have been published for these molecules, but rather complete Raman data have been reported for the first two molecules.⁵ Partial Raman data were previously given for the CH_3AsI_2 molecule but these data were not consistent with the observed far infrared bands. Therefore, we have recorded the Raman spectra of all the methyl haloarsines with laser excitation.

A microwave study⁶ has been carried out on CH_3AsF_2 and the barrier hindering the methyl rotation was found to be 463 cm⁻¹. Similarly the barrier for methyl arsine was determined from far infrared data⁷ to be about 500 cm⁻¹. Therefore, it was hoped that the study of the methyldihaloarsines might reveal some substituent effects on the torsional barriers for these arsines if such effects exist.

I. EXPERIMENTAL METHOD

The chloride and bromide samples were prepared as suggested by Van der Kelen and Herman⁵ and the

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iodide by the method of Millar *et al.*⁸ The chloride and bromide were purified by fractional distillation and the iodides were purified by sublimation. The CD_3AsI_2 compound was prepared and purified using the same procedures followed for CH_3AsI_2 , but with the substitution of CD_3I for CH_3I .

The spectral region from 4000 to 250 cm^{-1} was investigated with a Perkin–Elmer model 621 ir spectrophotometer. The instrument was calibrated with standard gases⁹ and was continuously flushed with dry air during operation. Spectral data were obtained from liquid films of each compound supported between heated CsI plates. Infrared spectra between 4000 and 250 cm⁻¹ are presented in Fig. 1.

The spectral region from 650 to 33 cm⁻¹ was investigated with a Beckman model IR-11 far ir spectrophotometer. The instrument was calibrated with atmospheric water vapor and the assignments of Randall *et al.*¹⁰ Spectral data were obtained from samples which were sublimed onto a silicon plate cooled to -190° C. It was necessary to anneal each sample several times before bands reached their final breadth and intensity. All data taken at low temperature were obtained by using the cell described by Baglin *et al.*¹¹ The spectra observed from 250 to 33 cm⁻¹ are presented in Fig. 2.

Raman data were obtained from a Cary model 81 Raman spectrophotometer which has a helium-neon laser operated at 6328 Å for excitation. The instrument was calibrated from 0-4000 cm⁻¹ by neon emission lines. Spectral data were obtained from solid or liquid samples of each compound. Raman spectra are presented in Fig. 3. Frequencies of the observed infrared and Raman bands are reported in Tables I–IV. All frequencies are expected to be accurate to $\pm_t 2$ cm⁻¹ for sharp bands.

II. RESULTS AND DISCUSSION

Microwave results⁶ on CH₃AsF₂ established that this molecule is in a pyramidal arrangement with the

APPLIED SPECTROSCOPY

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methyl group presumed to be in the staggered conformation. An x-ray¹² study of a single crystal of CH₃AsI₂ revealed a similar structure for this molecule. Therefore, it is not unreasonable to assume that both CH₃AsCl₂ and CH₃AsBr₂ would also have pyramidal skeletal structures. These molecules can have at most a single plane of symmetry and thus would fall under the point group C_s . Under C_s symmetry there should be 15 fundamental vibrational frequencies, nine class a' and six class a'' modes, and they should all be active in the ir and Raman spectra. The nine class a' modes should be polarized in the Raman spectrum and the six class a'' depolarized.

No crystal data are available for either CH_3AsCl_2 or CH_3AsBr_2 but the space group was determined to be $C_{2/c}-C_{2\hbar}^6$ with four molecules per primitive cell for the

 CH_3AsI_2 crystal.¹² Thus, in the spectra of the solid both the ir and Raman bands may be split into two modes which would represent the A_u-B_u and A_g-B_g components, respectively. Also because of the center of symmetry in the unit cell, there may be mutual exclusion between the ir and Raman frequencies (see Table V). This factor group splitting will depend upon the strength of the correlation field and is expected to be the most pronounced for the As-I motions. The effects of the correlation field will be discussed in detail after the vibrational assignment is given.

Spectral data and vibrational assignments are available for the molecules $AsCl_{,,1^{3},1^{4}} AsBr_{,,1^{5}} AsI_{,3},^{16,17}$ and $As(CH_{3})_{,3},^{5,18}$ Harvey and Wilson have also reported their spectral results and normal coordinate analysis of $CH_{3}AsH_{2}^{7}$ as well as three of its deuterated derivatives.



FIG. 2. A Far infrared spectrum from 250 to 33 cm⁻¹ of CH₃AsCl₂; B far infrared spectrum from 250 to 33 cm⁻¹ of CH₃AsBr₂; C far infrared spectrum from 250 to 33 cm⁻¹ of CH₃AsI₂: D far infrared spectrum from 250 to 33 cm⁻¹ of CD₃AsI₂.

The choice of fundamental vibrational assignments for CH_3AsCl_2 , CH_3AsBr_2 , CH_3AsI_2 , and CD_3AsI_2 will be based on depolarization values, band intensities in the ir and Raman spectra, deuterium shift factors, and comparisons with similar molecules. The fundamental vibrations will be discussed in the following order: carbon-hydrogen, arsenic-carbon, and arsenic-halogen vibrations. The methyl torsional oscillation for the isolated molecules and the crystal effects will be dis-

cussed separately. As a matter of simplicity the CH_3AsCl_2 , CH_3AsBr_2 , and CH_3AsI_2 molecules will be referred to as the chloride, bromide, and iodide, respectively, in the following discussion.

A. Carbon-Hydrogen Vibrations

Three carbon-hydrogen stretches are expected, two of class a' and one of class a'' symmetry. The anti-

Table I. Infrared and Raman spectra of methyldichloroarsine."

Infrared (liquid) (cm ⁻¹)	In- ten- sity	Raman (liquid) (cm ⁻¹)	In- ten- sity	Depo- lariza- tion	Assignments
3012	m	3012	1		ν_{10} CH ₃ antisymmetric
2994	m	2995	1		ν_1 CH ₃ antisymmetric
2916	m	2915	5		v2 CH3 symmetric stretch
2780	w.				$2\nu_3 = 2794$
2482	w				$2\nu_4 = 2496$
2224	w	• • •			$\nu_3 + \nu_5 = 2229$
2083	m				$\nu_4 + \nu_5 = 2080$
1827	m	• • •			$\nu_4 + \nu_6 = 1829$
1598	w	• • •			$\nu_{10} - \nu_{11} = 1597$
1415	$^{\rm sh}$	• • •			\$\nu_{11} CH_3\$ antisymmetric
1397	•	1397	· 2		deformation ν_3 CH ₃ antisymmetric deformation ***
1248	8	1248	2		ν_4 CH ₃ symmetric
1925	sh				-1242?
1200	sn				$p_3 - p_9 - 1242$; $p_{31} - 1162$
020	n	834	9		$2\nu_6 = 1102$
751	a w	001	4		$v_5, v_{12} = 752$
581	5	581	57		ve As-C stretch
388	4	379	100	n	v ₇ As-Cl symmetric
000		0.0	200	Р	stretch
364	ŝ	363	59	•••	ν_{13} As-Cl antisym-
224^{b}	w	219	12	р	ν_8 AsCl ₂ symmetric
201b	sh	205	12	dn	$^{\text{wag}}_{\text{wu}}$ As-CH ₂ bend
160 ^b	w	155	$\frac{12}{29}$	n D	v ₉ AsCl ₂ deformation
1446	vw	200		12	ν_{15} As-CH ₃ torsion?
108 ^b	vw				Lattice
102 ^b	vw				Lattice

 $^{\rm a}$ m (Medium), s (strong), w (weak), sh (shoulder), v (very), p (polarized), dp (depolarized).

^b Frequencies obtained from sample at -190° C.

symmetric C-H stretching mode of class a'' is assigned to the highest frequency bands observed at 3012, 3010, and 3004 cm⁻¹ in the chloride, bromide, and iodide compounds, respectively. The corresponding band in CD₃AsI₂ is observed at 2251 cm⁻¹. The two class a'modes, one symmetric and one antisymmetric, are found in the chloride at 2916 and 2994 cm⁻¹, respectively, and are found to shift only slightly to lower frequency in the bromide and iodide compounds. The 2916 cm⁻¹ band is of greater intensity in the Raman spectrum and corresponds to the symmetric stretching mode for a methyl group with C_{3v} symmetry. The corresponding bands in the heavy compound were found at 2113 and 2240 cm⁻¹, respectively.

Five carbon-hydrogen bending modes are expected, three of class a' and two of class a'' symmetry. They can be approximately described as one a'' CH₃ deformation, two a' CH₃ deformations, one a'' and one a'CH₃ rocking modes. The antisymmetric a'' CH₃ deformation was observed in the ir spectra at 1415, 1411, and 1409 cm⁻¹ for the chloride, bromide, and iodide compounds, respectively. The class a' antisymmetric vibration was observed at 1397, 1393, and 1384 cm⁻¹ in the three spectra and the class a' symmetric vibration at 1248, 1243, and 1239 cm⁻¹, respectively. These vibrations are well characterized in both intensity and frequency and their assignment is therefore straightforward. These three deformational vibrations in the CD_3AsI_2 compound were observed at 1026, 1019, and 947 cm⁻¹ in the Raman spectrum.



FIG. 3. A Raman spectrum of CH_3AsCl_2 ; B Raman spectrum o CH_3AsBr_2 ; C Raman spectrum of CH_3AsI_2 ; D Raman spectrum of CD_3AsI_2 .

Table II. Infrared and Raman spectra of methyldibromoarsine."

Infrared (liquid) (cm ⁻¹)	In- ten- sity	Raman (liquid) (cm ⁻¹)	In- ten- sity	Depo- lariza- tion	Assignments
3010	m	3008	1		ν_{10} CH ₃ antisymmetric
2991	m	2988	1		$\nu_1 CH_3$ antisymmetric
2912	m	2910	2		ν_2 CH ₃ symmetric stretch
2853	w				2991 - 134 = 2857?
2775	w				$2\nu_3 = 2786$
2474	w				$2\nu_4 = 2486$
2221	w				$\nu_3 + \nu_5 = 2224$
2078	m				$\nu_4 + \nu_5 = 2074$
1818	m				$\nu_4 + \nu_5 = 1818$
1597	vw				$v_{11} + v_8 = 1600$
1560	vw				?
1411	(sh)	1407	1		ν_{11} CH ₃ antisymmetric deformation
1393	s	1392	1		ν_3 CH ₃ antisymmetric
1243	s	1244	1		$\nu_4 \text{ CH}_3 \text{ symmetric}$
1142	vw				$2\nu_{\rm f} = 1150$
831	s	829	1		vs. vie CHe rock
575	ŝ	573	$2\overline{1}$		ve As-C stretch
374	m	0.0			$2\nu_{\rm e} = 378$
269	s	268	100	р	ν_{7} , ν_{13} As-Br symmet- ric and antisymmet- ric stretch
233^{b}	w(sh)				$2 \times 135 = 230$
$\overline{198^{b}}$	w	189	8	р	ν_{8} , ν_{14} AsBr ₂ wag and As-CH ₃ bend
134^{b}	vw				ν_{15} As-CH ₃ torsion
115^{b}	m	100	36	p	ν_{9} AsBr ₂ deformation
$94^{\rm b}$	w		- 5	1-	Lattice

^a See Table I for explanation of symbols used.

^b Frequencies obtained from sample at -190 °C.

The two CH_3 rocking modes appeared to be degenerate and a single, strong ir band at 832 cm⁻¹ was observed in all the spectra. The Raman spectrum of the heavy compound showed these two modes to be split by about 5 cm⁻¹ at 632 and 627 cm⁻¹, respectively. Thus, the use of deuterium substitution in the iodide made this assignment unequivocal.

B. Arsenic–Carbon and Arsenic–Halogen Vibrations

The arsenic-carbon stretching mode was observed at 583 cm⁻¹ in $As(CH_3)_{3^5}$; therefore, the strong ir bands at 581, 575, 563, and 520 $\rm cm^{-1}$ in the spectra of the chloride, bromide, iodide, and iodide- d_3 compounds, respectively, are confidently assigned to the arsenic-carbon stretching motion. The shift with deuteration is exactly the calculated value. The symmetric AsX_3 stretching modes were observed at 411, 287, and 216 cm⁻¹ for AsCl.,¹⁴ AsBr₃,¹⁵ and AsI₃,^{16,17} respectively. The symmetric AsX_2 stretching vibrations should be the strongest Raman lines below 1000 cm^{-1} and should have frequencies similar to those found for the symmetric stretching modes of the AsX_3 compounds. Thus, these symmetric stretching motions are assigned to the intense, polarized Raman bands at 379, 268, 200, and 195 cm^{-1} for the chloride, bromide, iodide, and iodide- d_3 compounds, respectively. The antisymmetric stretching vibration exhibited interesting behavior for this series of molecules. This mode was observed at 363 cm⁻¹ for the chloride, 16 cm⁻¹ lower than the symmetric stretching mode, at 268 cm⁻¹ for the bromide, which is degenerate with the symmetric motion, and at 222 cm⁻¹ for the iodide, 22 cm⁻¹ higher than the symmetric mode. There can be no doubt that these assignments for the stretching modes are correct because of the relative intensities in both the ir and Raman spectra as well as the depolarization values of the Raman lines. Similar relative behavior of the corresponding stretching modes is found for the AsX₃ molecules.

In the earlier work of Van der Kelen and Herman,⁵ two bands were reported at 278 and 263 cm⁻¹ in the Raman spectrum of the bromide. Our spectra, both infrared and Raman, clearly indicate the presence of only one band at 268 cm⁻¹ for this compound. The spectrum of CH₃AsI₂ reported by Van der Kelen and Herman⁵ contained two bands of equal intensity at 220 and 283 cm⁻¹. Our spectral data revealed three Raman and ir bands in this region at 200, 222, and 288 cm⁻¹. The intensity of the 288 cm⁻¹ band indicates that it is

Table III. Infrared and Raman spectra of methyldiiodoarsine.^a

Infrared (liquid) (cm ⁻¹)	In- ten- sity	Raman (solid) (cm ⁻¹)	In- ten- sity	Assignments
3004	m	3005	1	ν_{10} CH ₃ antisymmetric stretch
2982	m	2988	1	ν_1 CH ₃ antisymmetric stretch
2905	m	2909	1	ν_2 CH ₃ symmetric stretch
2853	VW			$\nu_3 + \nu_{11} + \nu_9 = 2857$
2812	VW			$2\nu_{11} = 2818$
2769	w			$2\nu_3 = 2768$
2461	W			$2\nu_4 = 2478$
2215	w			$\nu_3 + \nu_5 = 2216$
2072	m			$\nu_4 + \nu_5 = 2071$
1799	m			$\nu_4 + \nu_6 = 1802$
1656	vw			$2\nu_5 = 1664$
1409	\mathbf{sh}	1405	1	ν_{11} CH ₃ antisymmetric
				deformation
1384	s	1371	1	ν_3 CH ₃ antisymmetric
				deformation
1239	s	1229	1	ν_4 CH ₃ symmetric deformation
1116	w			$2\nu_6 = 1126$
1055	vw			$\nu_5 + \nu_{13} = 1048$ (?)
832	s	826	1	ν_5 , ν_{12} CH ₃ symmetric and anti-
				symmetric rock
773	w			$\nu_6 + \nu_{13} = 778$
728	w			
563	s	560	2	$\nu_{\rm f}$ As–C stretch
478	w			
445	w			$2 \times \nu_{13} = 450$
		422	1	$\nu_7 + \nu_{13} = 422$
346	vw			$2\nu_{14} = 354$
331	w			$\nu_7 + \nu_{15} = 344?$
283^{b}	w	288	1	$\nu_8 + \nu_7 = 287$
225^{b}	s	222	12	ν_{13} As–I antisymmetric stretch
$204^{\mathrm{b},\mathrm{c}}$	s	200	100	ν_7 As–I symmetric stretch
180 ^{b,c}	m	176	19	ν_{14} As-CH ₃ bend; ν_8 CH ₃ AsI ₂
				wag
		140	$^{\mathrm{sh}}$	ν_{15} torsion or $\nu_9 + 44 = 139$?
95 ^{b,c}	s	87	49	ν_9 AsI ₂ deformation
86 ^{b,c}	w(sh)			
$64^{\mathrm{b,c}}$	s	72	7	Lattice mode
44 ^b	w			Lattice mode

^a See Table I for explanation of symbols used.

^b Spectrum of the sample at -190 °C.

• See discussion of crystal field effects.

probably a combination band $(200+87=287 \text{ cm}^{-1})$. The band at 200 cm⁻¹ is the strongest line observed in the Raman spectrum below 1000 cm⁻¹. This line clearly must be due to the symmetric AsI₂ stretching motion as discussed above and not the AsI₂ symmetric deformation as described by the Dutch workers. The medium intensity band at 222 cm⁻¹ then must be due to the antisymmetric AsI₂ stretching motion. The Dutch workers have assigned the antisymmetric AsI₂ stretching motion to a band at 108 cm⁻¹. We observe no band at this frequency and believe the 108 cm⁻¹ line can not arise from a molecular motion of the CH₃AsI₂ molecule.

The study of $CH_3AsH_2^7$ showed that the low frequency skeletal modes could be described as a symmetric AsH_2 deformation (a'), a symmetric (a') AsH_2 wagging, and a symmetric (a'') AsH_2 twisting mode.

In the latter mode the methyl group moves extensively. When the mass of hydrogen is changed to that of the halogen the primary motion of the antisymmetric bending mode becomes one of mainly methyl motion because of the much lighter mass of the methyl group in relation to the mass of the halogens. The study of As X_3 (where X = Cl, Br, and I) established the frequency range for the two bending motions which are found at 195 and 159 cm^{-1} in the chloride, at 130 and 100 cm^{-1} in the bromide, and at 94 and 70 $\rm cm^{-1}$ in the iodide for the symmetric and antisymmetric deformational modes, respectively. The assignment of these three fundamentals in CH₃AsCl₂ is straightforward for only three strong bands are observed in the expected spectral region and two of these bands are found to be polarized in the Raman spectrum. The two polarized lines at 219 and 155 cm^{-1} are assigned to the AsCl₂ wagging and AsCl₂ scissors, respectively, by analogy with the assignments of AsCl₃. The depolarized line (205 cm^{-1}) is assigned to the Cl_2As-CH_3 antisymmetric bending motion. In the bromide only two bands were observed in the expected region at 198 and 115 cm^{-1} in the ir and the Raman spectra of the solid and at 189 and 100 cm^{-1} in the Raman spectrum of the liquid. An inspection of the two spectra [Figs. 2(B) and 3(B)] clearly shows that the two higher frequency bands in the chloride merge into the single band at 198 cm^{-1} in the bromide. This single broad band is then assigned to both the CH₃AsBr₂ wagging mode and the antisymmetric bending motion in CH₃AsBr₂. It should be pointed out that the CH₃AsBr₂ wagging mode will involve a considerable amount of CH₃-As bending motion since the halogen mass has increased to more than four times the mass of the methyl group. The 115 cm^{-1} band is assigned to the AsBr₂ deformational mode. The Raman spectrum of liquid CH_3AsI_2 also contains only two bands in the expected region at 170 and 74 $\rm cm^{-1}$. The assignment of these two bands follows that given for the bromide: the symmetric and antisymmetric CH_3 -As-I bending modes to the 170 cm⁻¹ band and the AsI_2 deformation to the 72 cm⁻¹ band. The spectral data obtained from the CD_3AsI_2 molecule are of great value in confirming the above assignments. In the ir

Table IV. Infrared and Raman spectra of methyldiiodoarsine-d₃.^a

Infrared (liquid) (cm ⁻¹)	In- ten- sity	Raman (solid) cm ⁻¹	In- ten- sity	Assignments
3265	w			$\nu_{10} + \nu_3 = 3270$
3250	w			$\nu_1 + \nu_3 = 3252$
3204	w			$\nu_{10} + \nu_4 = 3208$
3185	vw			$\nu_1 + \nu_4 = 3190$
2877	w			$\nu_1 + \nu_5 = 2873$
2745	$\mathbf{v}\mathbf{w}$			$\nu_2 + \nu_5 = 2748$
2631	vw			$\nu_2 + \nu_6 = 2631$
2379	w			?
2254	m	2251	2	ν_{10} CD ₃ antisymmetric stretch
2236	m	2240	3	ν_1 CD ₃ antisymmetric stretch
2111	m	2113	11	ν_2 CD ₃ symmetric stretch
2029	w			$2\nu_3 = 2032$
1975	vw			$\nu_3 + \nu_4 = 1970$
1652	w			$\nu_3 + \nu_5 = 1653$
1587	m			$\nu_4 + \nu_5 = 1591$
1467	m			$\nu_4 + \nu_6 = 1474$
1245	w			
1150	w			$\nu_5 + \nu_6 = 1157$
1016	s	1026	1	ν_3 , ν_{11} CD ₃ antisymmetric
		1019	3	deformation
996	\mathbf{sh}			?
954	s .	947	8	ν_4 CD ₃ symmetric deformation
737	w			$\nu_6 + \nu_{13} = 744$
722	w			
637	s	632	7	$\nu_5 \text{ CD}_3 \text{ rock}$
•••		627	6	ν_{12} CD ₃ rock
520	s	516	50	ν_6 As–C stretch
443	w			$2\nu_{13} = 448$
		412	4	$\nu_{13} + \nu_4 = 413$
		396	2	$2\nu_7 = 390$
368	W			$\nu_7 + \nu_{14} = 365$
		283	3	$\nu_7 + \nu_8 = 281$
224^{b}	s	218	15	ν_{13} AsI ₂ antisymmetric stretch
199^{b}	s	195	100	ν_7 AsI ₂ symmetric stretch
172 ^{b,o}	w	162	4	V14 As-CD3 bend; V8 CD3AsI2
$161^{b,c}$				wag
		134	1	? Ü
93ь	s	86	34	ν_9 AsI ₂ deformation
$84^{b,c}$	w			
$64^{b,c}$	m	71	5	Lattice mode

^a See Table I for explanation of symbols used.

^b Spectrum of the sample at -190 °C.

• See discussion of crystal field effects.

spectrum of solid CD_3AsI_2 the high frequency band was found to be split into a doublet at 172 and 161 cm^{-1} . The shifts observed in the AsX₂ deformation and symmetric and antisymmetric bending modes in going from the chloride to the iodide reveal that there is considerable methyl motion involved in both the symmetric and antisymmetric bending modes but very little methyl contribution in the AsX_2 deformational mode. There can be no clear distinction between the symmetric and antisymmetric bending modes in the d_3 compound since depolarization data cannot be obtained in the solid. However, without having the Raman and ir spectra of all four of the compounds, both liquid and solid, the assignment of the low frequency modes would have been very difficult. There are one or two very strong lattice modes for all the solid $CH_3(D_3)AsX_2$ compounds at or below 100 cm⁻¹. For instance, the iodide compounds have a very strong lattice mode at 64 cm^{-1} which could have easily been assigned to one of the low frequency bending modes which were observed at 94 and 70 cm⁻¹ in AsI₃. However, the ir spectrum of CH_3AsI_2 in solution did not

Table V. Correlation diagram for solid methyldiiodorarsine.

Molecule	Site	Crystal		
<i>C</i> .	C_1	C _{2ħ} ⁶ ∫Ag(Raman)		
A' (4	$A_u(\mathrm{ir})$		
A''	А	$B_{g}(\text{Raman})$		
J		$(B_u(\mathrm{ir}))$		

indicate the presence of this band. The Raman spectrum of liquid CH_3AsI_2 showed a very strong line at 74 cm⁻¹ which accounts for one of the modes and the ir spectrum of solid CD_3AsI_2 indicates that the 180 cm⁻¹ d_0 band is made up of two components which appear at 172 and 161 cm⁻¹ in the d_3 compound; however, factor group splitting can not be definitely ruled out. It must also be pointed out that there are extensive frequency shifts in going from liquid to the solid in both the ir and Raman spectra. If one has access only to data taken from the ir or Raman spectra of solid samples, erroneous assignments of the low frequency bending modes could easily be made.

C. Crystal Field Effects

The frequency for the AsI_2 deformational motion is not the same in the ir and Raman spectra. These differences are real and can be explained on the basis of factor group splitting in the crystal (see Table V). For example, the Raman line at 87 cm^{-1} represents both the A_g and B_g AsI₂ deformation whereas the two outof-phase motions of A_u and B_u symmetry are found at 86 and 95 cm⁻¹. This correlation field splitting is quite large in comparison to the frequency of the normal modes (it represents a 10% shift of the in-phase and out-of-phase motions). These splittings should be taken into consideration when force constant calculations are made but this point seems to have been neglected in a recent paper on the vibrational spectrum of AsI_{3} .¹⁷ Stammreich *et al.*¹⁶ reported a frequency of 94 cm⁻¹ for the AsI₃ symmetric mode in the Raman effect whereas a frequency of 102 cm⁻¹ was reported for this normal mode in the far infrared spectrum recorded by Manley and Williams.¹⁷ Although Manley and Williams¹⁷ state that they prefer the 102 cm⁻¹ assignment on the basis of their force constant calculations, it is believed that the difference in frequency between the two spectra represents factor group splitting.

D. Methyl Torsional Oscillation

The remaining vibration to be discussed is the CH_3 - torsional oscillation. The observation of the bands owing to this mode is the most difficult of all to obtain for they are generally quite weak, broad bands. Microwave data⁶ established that the barrier to internal rotation in CH_3AsF_2 was 463 ± 6 cm⁻¹. An ir study of $CH_3AsH_2^7$ failed to establish an exact value for the barrier to $-CH_3$ rotation, but arrived at an estimate of about 500 cm⁻¹ for this barrier. This as

well as other evidence¹⁹ suggests that the replacement of hydrogen by fluorine does not greatly change the barrier height. These values allow one to estimate a range of frequencies for the As-CH₃ torsion of 135 to 185 cm⁻¹. From the spectra of the chloride and the iodide one cannot make a definitive assignment for the torsional mode. There is a very weak shoulder at 144 cm⁻¹ in the ir spectrum of solid CH₃AsCl₂ which may be due to the torsion. No other bands were observed in the region between 200 and 100 cm^{-1} which could be assigned to this mode. The ir spectrum of the iodide gives no clear indication of a band which could be attributed to the torsional motion. However, there is a weak band at ~ 140 cm⁻¹ in the Raman spectrum of this compound. This may be due to the torsion or to an overtone $(95+44=139 \text{ cm}^{-1})$; therefore this cannot be regarded as a definitive assignment of the torsion. The ir spectrum of the bromide has a band at 134 cm^{-1} which is clearly separated from the other low frequency bands. This band cannot be assigned to any reasonable combination nor to a lattice mode. Therefore; it is felt that the 134 cm^{-1} band is due to the methyl torsion.

From the observed frequency of the torsional oscillation and assumptions about the structure of the molecule, one can calculate the height of the potential barrier to rotation. For groups of threefold local symmetry oscillating about an asymmetric framework the potential energy may be represented by

$$V(\alpha) = (V_3/2)(1 + \cos 3\alpha) + (V_6/2)(1 + \cos 6\alpha) + \cdots,$$

where α is the angle of rotation, V_3 is the height of the threefold potential barrier, V_6 the height of the sixfold one, and so forth. The terms higher than the first may be dropped, therefore, the torsional energy is

$$E_{\nu\sigma} = 2.25 \, \mathrm{Fb}_{\nu\sigma},$$

where $b_{\nu\sigma}$ is an eigenvalue of the Mathieu equation and $F = h^2/8\pi^2 r I \alpha$. By using the structural parameter given in Table VI the F values for CH₃AsCl₂, CH₃AsBr₂, CH₃AsI₂, and CD₃AsI₂ may be calculated (Table VI). From the F value and the absorption frequency, a $\Delta b_{\nu\sigma}$ may be calculated and from $\Delta b_{\nu\sigma}$ a dimensionless s value may be obtained from tables of solutions for the

Table VI. Structural data on CH₃AsX₂ and CD₃Asl₂.

Bond distances and angles	CH3AsF2ª	CH3AsCl2 b	CH3AsBr2 ^b	CH3AsI2c	CD₃AsI₂ ^b
r(As-C)(A ⁰)	1.92	1.97	2.02	2.07	2.07
$r(As-X)(A^0)$	1.74	2.01	2.27	2.54	2.54
<c-as-x< td=""><td>95°50′</td><td>94°</td><td>102°</td><td>104°</td><td>104°</td></c-as-x<>	95°50′	94°	102°	104°	104°
< X - As - X	96°	98°	102°	104°	104°
Moments of in	ertia				
$I_A \operatorname{amu} \operatorname{\AA}^2$	93.66	131.75	184.73	230.39	252.01
Is amu Å ²	93.943	203.82	546.59	1072.19	1083.27
Ic amu Ų	130.565	254.61	634.89	1194.97	1208.67
$F(\mathrm{em}^{-1})$	5.333	5.303	5.257	5.243	2.649
8	37.9		39.0		

^a L. J. Nugent and C. D. Cornwell, J. Chem. Phys. 18, 1109 (1950).

^b Bond distances and angles estimated.

• N. Camerman and J. Trotter, Acta Cryst. 16, 922 (1963).

Mathieu equation. Then the barrier height is

$V_3 = 2.25$ Fs.

The F value for CH_3AsBr_2 is 5.26 cm⁻¹ which gives a barrier height V_3 of 461 ± 30 cm⁻¹ or 1.32 ± 0.08 kcal/mole. This agreement between the value found in CH_3AsF_2 and CH_3AsBr_2 is undoubtedly fortuitous. The agreement, however, does indicate the substituents have very little if any effect on the torsional barrier in these compounds. This effect, or lack of it, has been observed also in the case of another fourth row element (germanium).⁴ The barrier height V_3 has been found to be essentially independent of substitution on the metal atom.

E. Overtones, Combinations, and Lattice Modes

Tables I-IV present possible assignments for overtones and combination bands. Several bands are observed in the low frequency region which are thought to be due to external modes in the solid phase. They are listed as lattice modes in Tables I-IV.

Table VII. Summary of the fundamental frequencies (cm⁻¹) of methyldihaloarsines.

Funda- mental	Approximate description	CH ₃ AsCl ₂	CH3AsBr2	CH ₂ AsI ₂	CD₄AsI2
	S	pecies A'			
1	C-H antisymmetric stretch	2994	2991	2982	2240
2	C-H symmetric stretch	2916	2912	2905	2113
3	C-H antisymmetric defor- mation	1397	1392	1384	1016
4	C-H symmetric defor- mation	1248	1244	1239	954
5	C-H rock	832	831	832	637
6	As-C stretch	581	575	563	520
7	As- X symmetric stretch	388	269	204	199
8	As-X ₂ wag	224	189ª	176ª	172
9	As- X_2 scissor	160	100ª	87ª	86ª
	S	pecies A''			
10	C-H antisymmetric stretch	3012	3010	3004	2251
11	C-H antisymmetric defor- mation	1415	1411	1409	1016
12	C-H rock	832	831	832	627ª
13	As- X antisymmetric stretch	364	269	225	224
14	As-CH3 bend	201	۱89 ۰	176ª	162ª
15	As-CH ₃ torsion	(144) ^b	134		•••

* Frequencies taken from Raman spectrum.

^b Estimated frequencies.

III. SUMMARY AND CONCLUSIONS

The 15 fundamental vibrations of CH₃AsCl₂, CH₃AsBr₂, CH₃AsI₂, and CD₃AsI₂ have been assigned on the basis of a pyramidal skeletal structure. These assignments are summarized in Table VII. The frequency of the methyl torsional oscillation is observed for methyl dibromoarsine. Using assumed geometric parameters the *F* and *s* values for this molecule are evaluated and the barrier to internal rotation was calculated to be 461 ± 30 cm⁻¹ (1.32 ± 0.08 kcal/mole).

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