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Vibrational spectra of methyl boron difluoride and methyl-d₃ boron difluoride

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Abstract—Gas phase infrared spectra of CH_3BF_2 and CD_3BF_2 were measured from 4000 to 250 cm⁻¹, as well as Raman spectra of both species in the liquid state, including depolarization measurements. A complete vibrational assignment was made on the basis of a molecular model in which there was essentially free rotation of the methyl group about the carbon-boron bond.

THE vibration-rotation spectra of most molecules can be explained on the basis of the symmetry for the rigid equilibrium configuration of the molecule. There are, however, certain molecules whose spectra are not explained satisfactorily by conventional techniques because they possess an additional degree of rotational freedom resulting from a very low barrier for internal rotation of one part of the molecule with respect to another part. Examples of such molecules with low barriers are dimethylacetylene, nitromethane, and methyl boron diffuoride.

Dimethylacetylene, with two symmetric top rotors, has an internal rotational barrier height of only 0.46 cm⁻¹, as measured from Q-branch splitting of certain infrared bands under high resolution [1], while the barrier heights for nitromethane [2] and methyl boron diffuoride [3] have been determined to be 2.11 and 4.82 cm⁻¹, respectively, from their microwave spectra. Both molecules consist of a symmetric top rotor attached to an asymmetric framework.

Several studies of the spectrum of nitromethane have been reported. The investigation by SMITH *et al.*, [4], which is one of the more complete studies, reported the infrared and Raman spectra with depolarization measurements, for CH_3NO_2 and CD_3NO_2 . More recently, JONES and SHEPPARD [5, 6] reported observing rotational fine structure in the infrared spectrum of gaseous nitromethane which they successfully analyzed on the basis of a molecular model with free internal rotation of the methyl group.

The first vibrational spectrum of methyl boron difluoride to be reported was that of BECHER [7], who obtained the gas phase infrared spectrum with prism resolution in the region from 4000 to 660 cm⁻¹, as well as the Raman spectrum of a liquid mixture of CH_3BF_2 and $(CH_3)_2BF$. The primary purpose of this study was to determine the change in bond order for the series BF_3 , CH_3BF_2 , and $(CH_3)_2BF$, based

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^[4] D. C. SMITH, C. PAN and J. R. NIELSEN, J. Chem. Phys. 18, 706 (1950).

 ^[5] W. J. JONES and N. SHEPPARD, Spectr. Rept. Conf. Hydrocarbon Res. Group Inst. Petrol., London, pp. 181-203 (1962).

^[6] W. J. JONES and N. SHEPPARD, Proc. Roy. Soc. 304A, 135 (1968).

^[7] H. J. BECHER, Z. Anorg. Allgem. Chem. 291, 151 (1957).

on proposed vibrational assignments for CH_3BF_2 and $(CH_3)_2BF$ using a C_{2v} symmetry model for both molecules. In their earlier paper, JONES and SHEPPARD [5] also proposed virtually free rotation of the methyl group in CH_3BF_2 , which followed from observation of infrared rotational fine structure in the methyl rocking mode. In their more recent paper, published while our investigation was in progress, JONES and SHEPPARD [6] analyzed completely the infrared Q-branch sequences of the perpendicular methyl absorptions of CH_3BF_2 , and proposed a vibrational assignment by analogy with that of nitromethane, and on infrared band shape considerations.

The purpose of our investigation was to reexamine the complete vibrational spectrum of CH_3BF_2 , as well as that of the isotopic species CD_3BF_2 , and hopefully to investigate in detail the vibration-internal rotation interactions for this molecule. During the course of our work infrared spectra of the carbon-hydrogen stretching region of gaseous CH_3BF_2 were recorded on the high dispersion infrared spectrometer at the Pennsylvania State University [8]. Unfortunately no detailed rotational fine structure was observed, thus precluding a study of the vibration-internal rotation coupling. However, a complete vibrational assignment is proposed for the methyl boron diffuoride molecule that differs in certain respects from the one of JONES and SHEPPARD.

EXPERIMENTAL

Methyl boron difluoride was prepared by the following two step procedure:

$$(CH_3)_3B + B_2O_3 \rightarrow (CH_3BO)_3$$
$$(CH_3BO)_3 + 2BF_3 \rightarrow 3CH_3BF_2 + B_2O_3.$$

Trimethyl boroxol

In a typical preparation [9], 2.38 g (34.2 mmoles) B_2O_3 were placed in a 170 cm³ stainless steel bomb and 1.91 g (34.2 mmoles) (CH₃)₃B, obtained from a preparation by BROWN [10], were condensed into the cylinder by cooling to -196° C. The cylinder was then heated in a 300°C oven for 8 hours. The resulting crude product was condensed into a U-tube trap of a conventional glass vacuum system in which all ground glass surfaces were lubricated with KEL-F grease. Purification was effected by distillation at -20° C; the desired compound condensed into an adjacent U-tube trap at -45° C, while unreacted (CH₃)₃B passed through the -45° C trap and was discarded. The yield of (CH₃BO)₃ was 4.03 g (32.1 mmoles), and the final purity of the sample was determined from its infrared spectrum. The deuterated analogue of trimethyl boroxol was prepared in an identical manner from (CD₃)₃B.

Methyl boron difluoride

In a typical preparation [11], 1.62 g (12.9 mmoles) $(CH_3BO)_3$ were condensed into the 170 cm³ stainless steel cylinder cooled to $-196^{\circ}C$, followed by addition of 0.91 g (13.4 mmoles) BF₃. The cylinder was then warmed to 88°C and was maintained at this temperature for 24 hr. The resulting gaseous mixture was

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transferred to the vacuum system and was passed through a -105° C U-tube trap into a -196° C trap. Pure CH₃BF₂ condensed in the colder trap; the yield was 1.29 g (20.1 mmoles). Purity of the compound was determined from infrared and mass spectra. CD₃BF₂ was prepared in an analogous manner from (CD₃BO)₃. The purified samples were stored at liquid nitrogen temperature to prevent decomposition.

Survey infrared spectra of methyl boron diffuoride were recorded with a Perkin-Elmer model 21 spectrometer equipped with NaCl optics, and are shown in Fig. 1. Higher resolution infrared spectra covering the $4000-250 \text{ cm}^{-1}$ region were obtained with a Perkin-Elmer model 16 grating spectrometer which has been described elsewhere [12]. The monochromator was calibrated using vibration-rotation spectra of simple gases [13], or the rotational spectrum of atmospheric water vapor [14]. Unless otherwise indicated, conventional 10 cm Pyrex cells were used to obtain the gas phase results, fitted with either KBr windows for scans out to 25 μ or CsBr windows for scans at longer wavelengths. Thin polycrystalline film spectra of CH_3BF_2 and CD_3BF_2 were obtained using a low temperature cell similar to that described by WAGNER and HORNIG [15]. Raman spectra of liquid CH₃BF₂ and CD_3BF_2 were obtained with a Spex model 1401 spectrometer. The samples, approximately 0.8 ml in size, were sealed in Pyrex tubes that were 50 mm long and 3 mm in diameter, and were excited at ambient temperatures by the 5682 Å line of a Kr ion laser. Gas phase Raman spectra of CH_3BF_2 were obtained with a Spex model 1400 spectrometer, and will be discussed elsewhere.

SPECTRAL RESULTS AND DISCUSSION

Molecular model

Since the potential barrier inhibiting rotation of the CH_3 group with respect to the BF₂ framework is only 4.82 cm⁻¹ (13.77 cal/mole), CH_3BF_2 can be considered to possess essentially free internal rotation and consequently the normal modes of vibration are most accurately represented by using a symmetry point group for nonrigid molecules. An analysis of the group theory treatment for methyl boron diffuoride has been discussed in considerable detail by LONGUET-HIGGINS [16], who has shown that the correct molecular symmetry point for this molecule is one of order 12 with a character table that is isomorphous with the more familiar D_{3h} point group. There will be a total of 14 normal modes of vibration, including the free rotation of the methyl group. The vibrational representation of methyl boron diffuoride has been given by JONES and SHEPPARD [6], and for ease of comparison of spectral results, we have adopted the same numbering and designation of normal modes as was used by these workers.

Looking at the methyl boron difluoride molecule from an inertial point of view, it is not difficult to see that the mass distribution in CH_3BF_2 is such that the molecule

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Fig. 1. Gas phase infrared spectra of CH_3BF_2 and CD_3BF_2 obtained with a Perkin-Elmer model 21 spectrometer. The vapor pressures used are given in the figure. The path length was 10 cm.

is a near oblate symmetric top. That this is the case becomes more obvious if one regards the CH_3 rotor as a point mass attached to the BF_2 framework at a distance from the boron atom which corresponds to the center of mass of the methyl group. Such a configuration would possess C_{2v} point group symmetry with the smallest inertial axis co-incident with the principal rotation axis, and the largest inertial axis perpendicular to the plane of the framework, passing through the boron atom. The intermediate inertial axis must then be perpendicular to the other two axes and in the plane of the molecule. Those normal modes of vibration associated with dipole moment changes along the principal axis, would then be expected to give rise to type A infrared bands of an asymmetric top with PQR-branch structure. Those modes having dipole moment changes along the largest inertial axis should give rise to type Cinfrared bands characterized by a strong central Q-branch and weak P- and Rbranches, while the modes with dipole changes along the intermediate inertial axis were predicted to cause type B infrared bands with prominent P- and R-branch envelopes and no Q-branch.

As far as the methyl vibrations are concerned, the methyl boron diffuoride molecule can be equally viewed as consisting of a CH_3 group to which is attached a point mass representing the BF_2 group located on the principal axis of the methyl group at a point representing the center of mass of the BF_2 framework. Thus, the CH_3BF_2 molecule becomes a prolate symmetric top with the carbon-boron bond being colinear with the principal axis of symmetry. Those normal modes of vibration of the methyl group having dipole moment changes parallel to the principal axis would be



Fig. 2. The carbon-hydrogen stretching region of CH_3BF_2 obtained with a Perkin-Elmer model 16 spectrometer. The scanning speed was 4 cm⁻¹/min, and the spectral slit width was approximately 0.4 cm⁻¹. The path length was 10 cm.

expected to give rise to nondegenerate parallel infrared bands with PQR-branch structure. However, the methyl vibrations with dipole moment changes perpendicular to the principal axis, while retaining their doubly degenerate feature, have infrared band shapes that are more complex than simple theory would indicate due to the coupling of these modes with the free internal rotation of the methyl group. This matter has been described at some length by JONES and SHEPPARD [6].

CH₃ group vibrations

The assignment of the fundamental modes of vibration of $CH_{3}BF_{2}$ and $CD_{3}BF_{2}$ was based on [1] group vibrational frequencies of structurally similar molecules, [2] depolarization ratio measurements from the Raman spectra, and [3] vibrational frequency shifts which resulted from isotopic substitution. Because the methyl group vibrations are well characterized, there can be little doubt about their assignment in the spectrum of methyl boron difluoride. The symmetric and asymmetric carbonhydrogen stretching modes, r_1 and r_9 , respectively, were expected to occur in the 3000 cm^{-1} region which is shown in Fig. 2. The r_9 mode was assigned to the absorptions in the 2900–3100 cm⁻¹ region as shown in Fig. 2, while in the Raman spectrum of liquid CH_3BF_2 , r_9 appeared as a depolarized shift at 2990 cm⁻¹. The corresponding mode of CD_3BF_2 was observed at 2230 cm⁻¹ in the gas phase infrared spectrum and at 2232 cm⁻¹ in the Raman spectrum. The carbon-hydrogen symmetric stretch, v_1 , of CH₃BF₂ which was expected to occur at lower wavenumbers than the asymmetric stretch, was not so readily assigned. JONES and SHEPPARD [6] observed two strong infrared absorptions near 3020 and 2960 cm⁻¹ which are very similar to those of Fig. 2, that they interpreted as arising from the v_9 mode, and concluded that the v_1 mode of CH₃BF₂ must be quite weak. While we cannot disagree with their conclusions, it is worth pointing out that the v_1 mode of CH₃BF₂ appeared as a strong Raman shift at 2930 cm⁻¹ in both the gas and liquid phases. Consequently, we suggest that part of the infrared absorption at 2960 cm⁻¹ may, in fact, be due to the v_1 mode of CH₃BF₂. In the infrared spectrum of CD₃BF₂ the assignment of the v_1 mode was much easier. It appeared as a weak parallel type band without any overlapping structure centered at 2138 cm⁻¹, while in the Raman spectrum of liquid CD₃BF₂ there was an intense polarized shift at 2138 cm⁻¹ which was assigned to this mode.

The symmetric and asymmetric carbon-hydrogen deformations, v_2 and v_{10} , normally occur in the 1450–1200 cm⁻¹ region, but in the gas phase spectrum of the light molecule these modes were badly obscured by absorptions of the BF₂ stretching modes. However, the infrared spectrum of a thin polycrystalline film of CH₃BF₂ at 77°K revealed several sharp absorptions in this region from which it was concluded that the CH₃ asymmetric deformation gave rise to an absorption at 1440 cm⁻¹ and the symmetric deformation to an absorption at 1410 cm⁻¹. The corresponding modes of the deuterated species should, of course, be shifted to lower wavenumbers and a broad infrared absorption extending from 1150 to 900 cm⁻¹ was observed in the gas phase spectrum of CD₃BF₂. A thin film spectrum of this region again proved to be more revealing and showed the v_2 absorption to be centered at 1026 cm⁻¹ and the v_{10} absorption at 1040 cm⁻¹. Corroborating evidence for the assignment of these two modes was obtained from the Raman spectrum of CD₃BF₂, where a polarized shift occurred at 1020 cm⁻¹ and a depolarized shift at 1050 cm⁻¹.

The methyl rocking mode of CH_3BF_2 , v_{11} , appeared in the gas phase infrared spectrum as a weak structural absorption in the 860 cm⁻¹ region, and is shown in Fig. 3. The rotational fine structure associated with this absorption has been completely explained by JONES and SHEPPARD [6]. In the spectrum of the deuterated molecule, the v_{11} mode was expected to shift to the region near 750 cm⁻¹, however, the band center was uncertain since it was overlapped by another absorption which proved to be due to the boron-carbon stretching vibration. In the thin film spectrum several absorptions were observed in this region and the v_{11} fundamental was assigned to the absorption at 710 cm⁻¹.

While the boron-carbon stretching mode, ν_4 , proved to be too weak to be observed in the gas phase infrared spectrum of CH_3BF_2 , it did appear as a doublet absorption near 775 cm⁻¹ in the thin film spectrum of the light molecule. There are two naturally occurring isotopes of boron, ¹⁰B and ¹¹B, the latter being the predominant one (80.4%). Accordingly, the weaker absorption at 780 cm⁻¹ was assigned to the ¹⁰B—C stretch and the stronger absorption at 774 cm⁻¹ to the ¹¹B—C stretch. Further evidence for the correctness of this assignment was the observation of a very strong polarized Raman shift at 772 cm⁻¹ in the spectrum of the light molecule and an equally strong polarized shift at 725 cm⁻¹ in the spectrum of the deuterated species. As mentioned above, in the gas phase infrared spectrum of CD_3BF_2 the v_4 mode was overlapped by the CD_3 rocking mode, but in the solid state spectrum of this species the boron-carbon stretch was assigned to a doublet absorption at 728 and 718 cm⁻¹.



Fig. 3. The CH₃ rocking mode and BF₂ wagging mode of CH₃BF₂ obtained with a Perkin-Elmer model 16 spectrometer. The path length was 1.2 m, scanning speed 4 cm⁻¹/min, and the spectral slit width was approximately 0.4 cm^{-1} .

BF₂ group vibrations

The five normal modes of vibration remaining to be assigned are all associated with the BF₂ framework, and the assignment was made either by analogy with the vibrational assignment of BClF₂ [17], or by polarization measurements from the Raman spectrum of methyl boron diffuoride. In the gas phase infrared spectrum of BClF₂, the asymmetric and symmetric BF₂ stretches occurred at 1421 and 1247 cm⁻¹, respectively. By analogy, in the infrared spectrum of CH₃BF₂ the asymmetric stretch, ν_7 , was assigned to a very intense structureless absorption at 1366 cm⁻¹, while the BF₂ symmetric stretch, which was expected to occur at a lower wavenumber as a type A band, was assigned to an absorption at 1249 cm⁻¹. In the spectrum of the deuterated species, these two modes had frequencies of 1348 and 1211 cm⁻¹, respectively.

The BF₂ wagging mode of CH_3BF_2 was assigned to a doublet absorption in the 930–900 cm⁻¹ region which is shown in Fig. 3. Isotopic splitting was clearly evident in this band system, with the more intense line at 908 cm⁻¹ being assigned to the wagging mode of the ¹¹BF₂ species, while the weaker transition at 924 cm⁻¹ was due to the ¹⁰BF₂ group. Upon deuteration of the methyl group it was found that this vibration was significantly shifted to lower wavenumbers, appearing as an isotopically split doublet at 834 and 812 cm⁻¹, respectively. It was anticipated that in the Raman spectrum of CH_3BF_2 the ν_6 mode would appear as a depolarized shift near 900 cm⁻¹, however there was no experimental evidence for this mode, nor was there any trace of it in the Raman spectrum of CD_3BF_2 .

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CH ₃ BF ₃			CD ₃ BF ₃			A	Annuarimete normal mode	
Infrared (cm ⁻¹)	Raman† (cm ⁻¹)	ρ	Infrared (cm ⁻¹)	$\frac{\text{Raman}^{\dagger}}{(\text{cm}^{-1})}$	ρ	Assignment	Approximate normal mode	
~2990	2990	depol.	2230 2148 <i>R</i>	2232	0.85	vg	CH ₃ asymmetric stretch	
~2960	2930	0.04	$2138 Q \\ 2125 P$	2138	0.03	v ₁	CH_3 symmetric stretch	
1440*	~1458		1150 to	1050	0.75	v_{10}	CH_3 asymmetric deformation	
1410*			900	1020	0.25	Va	CH, symmetric deformation	
	_		1374	_	_	v .	¹⁰ BF, asymmetric stretch	
1366	1338	depol.	1348			,	¹¹ BF, asymmetric stretch	
_			1212 Q			V a	¹⁰ BF, symmetric stretch	
1263 R			-			u u		
1249Q	1240	0,38	1193Q				¹¹ BF ₂ symmetric stretch	
1239 P			1184 P					
924 Q	_		834 Q	—		ve	¹⁰ BF ₃ wag (out-of-plane)	
908 Q			$\begin{array}{c} 812 \ Q \\ 795 \ P \end{array}$				¹¹ BF ₂ wag (out-of-plane)	
860			710*			<i>v</i> ₁₁	CH ₃ rock	
780*			728 Q	_	_	v4	¹⁰ BC stretch	
774*	772	0.04	718 Q 710 P 481 R	725	0.03		¹¹ BC stretch	
493 ()			472 0			v.	¹⁰ BF, scissors	
485 Q	482	0.51	470 Q 459 P	470	0.28	- 3	¹¹ BF ₂ scissors	
346	335	depol.	305	305	0.48	Vg	BF ₂ rock (in-plane)	

Table 1. Fundamental vibrational wavenumbers of methyl boron diffuoride

* These values were obtained from thin film spectra cooled to 77°K. † Raman shifts are for the liquid state.

Table 2.	Overtone a	nd combination	wavenumbers	of methyl	boron	difluoride

CH ₃ BF ₃ (cm ⁻¹)	CD_8BF_8 (cm ⁻¹)	Assignment	
3750	2875	V1 + VA	
	3395	$v_s + v_s$	
<u> </u>	3180		
2700		220	
	2635	?	
2575		$v_2 + v_2$	
2490	_	27	
	2320	?	
2130	2085	$v_{4} + v_{7}$	
	2113	2	
	2102	2	
	2091	2	
2020	1897	v. + v.	
1825		2v	
1010	1803		
1722		vo + v-	
	1722	v, + v,	
1840		* <u>+</u> * .	
1040	1698	$p_4 + p_{11}$	
1529	1020	V7 T V8	
1999	1491	9ai	
	1421	² <i>V</i> ₄	
	402	1	

The BF₂ scissoring mode, ν_5 , was assigned to an absorption at 485 cm⁻¹ in the gas phase infrared spectrum of CH₃BF₂, and to a pair of absorptions at 472 and 470 cm⁻¹ in the infrared spectrum of the deuterated species. Further evidence for the correctness of this assignment was the appearance of a strong polarized Raman shift at 482 cm⁻¹ in the spectrum of the light molecule which shifted to 470 cm⁻¹ in the Raman spectrum of CD₃BF₂. JONES and SHEPPARD [6] proposed that this mode be assigned to an isotopically split absorption near 595 cm⁻¹, however, we were unable to observe any absorption in this region either in the infrared or Raman spectrum of CH₃BF₂.

Finally, the BF₂ in-plane rocking mode, v_8 , occurred as a depolarized shift at 335 cm⁻¹ in the Raman spectrum of liquid CH₃BF₂, and as a weak band at 346 cm⁻¹ in the infrared spectrum. In the spectrum of the deuterated species this mode was observed at 305 cm⁻¹ in both the infrared and Raman spectra.

Table 1 summarizes the assignment of the fundamental modes of vibration for CH_3BF_2 and CD_3BF_2 , which we believe to be more complete than any proposed to date. In Table 2 are listed weaker infrared absorptions that were observed which must arise from overtone and combination modes. While the complexity of the vibrational spectrum precludes an unambiguous assignment of these bands, a tentative assignment is proposed.

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