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Preliminary communication

Rotation-vibration spectra of dimethylmercury and perdeutero-dimethylmercury

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The structure of dimethylmercury has been the subject of several investigations using electron diffraction methods[1,2], Raman[3-8] and infrared[5-10] spectroscopy. Gutowsky has shown that the vibrational data are consistent with a linear CHgC structure, and favour the methyl groups in the eclipsed position (symmetry D_{3h}), or having free rotation (D'_{3h}), rather than having the staggered position (D_{3d})[5]. The most convincing argument for the free rotational model is based on the rotational structure of the infrared perpendicular band, ν_8, as reported by Boyd, Thompson and Williams[11].

In the present study of the spectra of gaseous dimethylmercury and its perdeutero derivative we have measured six out of the seven infrared active fundamental bands in the respective spectra. The instrument used was a Perkin—Elmer 225 grating spectrophotometer equipped with a 1 m gas cell (the deuterium content of $Hg(CD_3)_2$ being better than 99% as determined by mass spectrometry). The perpendicular bands present in the spectra exhibit a definite fine structure, with the Q branches split into two or more components; the exact rotational assignment, however, was very difficult at the resolution level of the present instrument.

The mean spacing of the centres of the group of branches for the CH stretching mode, ν_8, was found to be 4.16 cm^{-1}. Using the values of rotational constants A and B as determined by Rao, Stoicheff and Turner from the pure rotational Raman spectra[12] of this compound, and assuming free rotation, yields a Coriolis Coupling factor ξ of 0.18. With a fixed configuration this factor would have a value of -0.64. Since, as a rule, the ξ value for the fundamental bands corresponding to CH stretching vibrations is small and positive, it seems likely that the smaller positive value quoted above is the correct one. Thus, it is reasonable to assume that the internal rotation is essentially free both in dimethylmercury[11] and perdeutero-dimethylmercury. This conclusion is consistent with results arising from an investigation of the vibrational spectra of these compounds[7,8].

Studies of the other perpendicular vibrational-rotational bands in the spectra showed that the methyl asymmetrical deformation, ν_9, was not sufficiently band resolved and that the fine structure of the methyl rocking band, ν_{10}, was rather difficult to obtain.

The centre of these bands could not be located with certainty but their probable values and mean spacing, together with the probable Coriolis constants, are presented in Table 1.

Although the fine structure of the parallel bands could not be resolved, the line spacing in the *P*- and *R*-branches should be about 0.23 and 0.18 cm^{-1} respectively for dimethylmercury and perdeuterated dimethylmercury. These molecules have larger values of the ratio I_B/I_A, so that the central *Q*-branches have a low intensity. In Table 2 the frequency data for the centre, the intensity maxima of *P*- and *R*-branches, and the band separation of the parallel bands are shown. Some of the combination modes were found in our spectra. Using the formulae of Gerhard and Dennison[13], the values for the separation of

TABLE 1

THE MEAN SPACING OF SUBBRANCHES AND THE CORIOLIS CONSTANTS FOR THE PERPENDICULAR BANDS IN THE IR SPECTRA OF DIMETHYLMERCURY AND PERDEUTERO-DIMETHYLMERCURY

	$Hg(CH_3)_2$	$Hg(CD_3)_2$
ν_8	2978.5[a] cm^{-1}	2231.3 cm^{-1}
ν_9	1384.3 cm^{-1}	1041.8 cm^{-1}
ν_{10}	791.9 cm^{-1}	604.9 cm^{-1}
$\Delta\nu_8$	9.29 cm^{-1}	4.16 cm^{-1}
$\Delta\nu_9$	–	6.40 cm^{-1}
$\Delta\nu_{10}$	3.25 cm^{-1}	1.01 cm^{-1}
ξ_8	0.10[a]	0.18
ξ_9	–	–0.24
ξ_{10}	0.66	0.77

[a] Values from ref. 11.

TABLE 2

THE OBSERVED PARALLEL BANDS IN THE INFRARED SPECTRA OF DIMETHYLMERCURY AND PERDEUTERO-DIMETHYLMERCURY

Band	Frequency (cm^{-1})			
	Centre	*P*-branch	*R*-branch	*P–R*
$Hg(CH_3)_2$				
ν_5	2921.6	2913.7	2929.7	16.0
ν_6	1200.1	1191.8	1207.0	15.2
ν_7	546.3	536.0	552.7	16.7
$\nu_9 + \nu_{13}$	2831.1	2825.0	2840.0	15.0
$\nu_2 + \nu_6$	2375.0	2368.2	2383.2	15.0
$\nu_2 + \nu_7, \nu_3 + \nu_6$	1718.9	1710.1	1727.0	16.9
$\nu_{10} + \nu_{14}$	1465.1	1458.6	1472.4	13.8
$Hg(CD_3)_2$				
ν_5	2125.3	2118.4	2132.2	13.8
ν_6	938.9	932.2	945.1	12.9
ν_7	497.7	488.3	504.6	16.3
$\nu_9 + \nu_{13}$	2060.0	2054.8	2065.3	10.5
$\nu_2 + \nu_7, \nu_3 + \nu_6$	1402.0	1396.3	1408.6	12.3
$\nu_3 + \nu_7$	973.3	966.5	981.0	14.5

P- and *R*-branch at 35° were calculated as 15.1 cm^{-1} and 13.4 cm^{-1} for dimethylmercury and perdeutero-dimethylmercury, respectively. The values found are in satisfactory agreement with one another.

The assignments of the measured frequencies are listed in Table 3.

TABLE 3

THE ORIGIN OF THE OBSERVED INFRARED BANDS OF GASEOUS $Hg(CH_3)_2$ AND $Hg(CD_3)_2$

Frequency $\nu(cm^{-1})$		Symmetry species for D'_{3h}	Assignment	
$Hg(CH_3)_2$	$Hg(CD_3)_2$			
2978.5 vs	2231.3 vs	E'	ν_8	CH stretching
2921.6 vs	2125.3 vs	A''_2	ν_5	CH stretching
2831.1 m	2060.0 m	$A''_1 + A''_2 + E''$	$\nu_9 + \nu_{13}$	
2375.0 m	1837.1 vw	A''_2	$\nu_2 + \nu_6$	
	1450.3 w	E'	$\nu_6 + \nu_{14}$	
1718.9 w,m	1402.5 m	A''_2	$\nu_3 + \nu_6, \nu_2 + \nu_7$	
1465.1 m	(1122.5 m)	$A''_1 + A''_2 + E''$	$\nu_{10} + \nu_{14}$	
1384.3 w	1041.8 m	E'	ν_9	CH_3 deformation
1352.0 vw		E'	$\nu_2 + \nu_{11}$	
1258.0 vw		E'	$\nu_7 + \nu_{14}$	
1200.1 w	938.9 m	A''_2	ν_6	CH_3 deformation
1160.0 sh ?				
1132.8 m ?				
1068.2 w	973.3 m	A''_2	$\nu_3 + \nu_7$	
791.9 vs	604.9 vs	E'	ν_{10}	CH_3 rocking
546.3 vs	497.7 vs	A''_2	ν_7	CHgC stretching
153 m [a]	141 [b]	E'	ν_{11}	CHgC deformation

[a] Value from ref. 14. [b] From the Raman spectrum of the liquid sample[8]. Band intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

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