Rotation-vibration Spectra of Gaseous Methyl Mercuric Halides and [$^2H_3$]Methyl Mercuric Halides

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AMONG the several i.r. spectroscopic studies of methyl mercuric halides are included reports on methyl mercuric bromide and [$^2H_3$]methyl mercuric bromide.[1] We now report, for the first time, the fundamental vibrational frequencies of solid CD_3HgCl and CD_3HgI (Table 1) and also spectra of gaseous methyl mercuric halides. Although some of the vibrational-rotational bands are not well-resolved a number of Coriolis ζ constants were obtained (Table 2). These compounds are normally crystalline but at *ca.* 200° their vapour pressures permit i.r. spectra of gaseous samples to be recorded. The molecules belong to C_{3v} point group with all heavy atoms on the molecular axis. The rotational constants A are therefore large, (*ca.* 5 and 2·5 cm.$^{-1}$ for MeHgX and CD_3HgX respectively) leading to widely-spaced Q-sub-branches of perpendicular bands, several of which have been resolved. The figure shows a well-resolved rotational structure of the methyl rocking band of MeHgCl. The instrument used was a grating Perkin-Elmer M521 with a high temperature cell RIIC GK-5. The sequence of the intensity of Q-branches, strong–weak–weak, characteristic for molecules with a three-fold rotational axis, is pronounced. The assignment of K to Q_K was possible only for the methyl rocking bands of those which were sufficiently

TABLE 1

*Fundamental frequencies of solid methyl mercuric halides (cm.$^{-1}$)**

	MeHgCl	MeHgBr	MeHgI	CD_3HgCl	CD_3HgBr	CD_3HgI
A_1						
ν_1	2922	2921	2913	2124	2124	2119
ν_2	1191	1186	1173	921	916	905
ν_3	539	539	526	499	495	483
ν_4	304	202†	170†	304	201†	170†
E						
ν_5	3008	3005	3000	2255	2255	2252
ν_6	1403	1404	1403	1030	1027	1026
ν_7	788	785	775	598	597	587
ν_8		123†	118†(2)			113†

Approximate description: ν_1 and ν_5, C–H (C–D) stretching; ν_2 and ν_6, CH_3 deformation; ν_3, C–Hg stretching; ν_7, CH_3 rocking; ν_4, Hg–X stretching; and ν_8, C–Hg–X bending.

* The frequencies reported may be a few wavenumbers in error since no check on the calibration of the instrument was made. The difference between the results in Table 1 and those reported in ref. may not be therefore significant.

† Raman spectra of powdered samples.

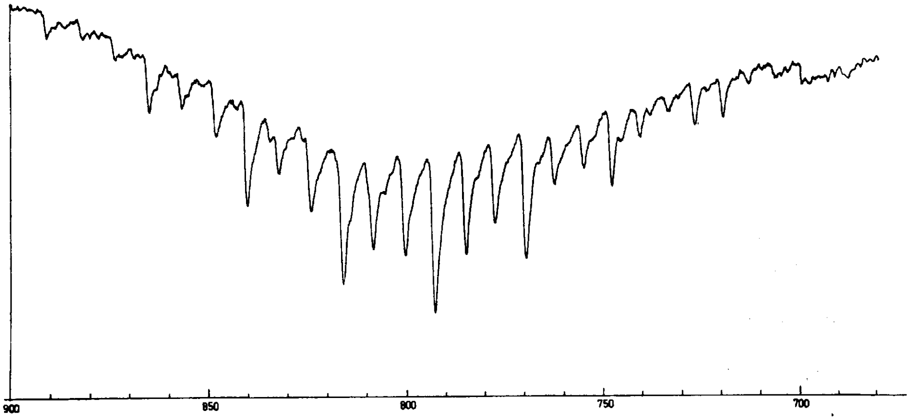

FIGURE. *Rotational structure of methyl rocking band of* MeHgCl.

TABLE 2

Rotational constants, the mean spacing of Q-sub branches (cm.$^{-1}$) and the Coriolis ζ constants for methyl mercuric halides

	MeHgCl	MeHgBr	MeHgI	CD_3HgCl	CD_3HgBr	CD_3HgI
A		5·0668			2·5334	
B	0·0687	0·0376	0·0252	0·0634	0·0355	0·0240
$\Delta\nu_5$	9·15	9·29	9·32	4·04	4·06	
$\Delta\nu_6$				6·75	6·11	
$\Delta\nu_7$	7·71*	7·69*	7·60*			4·20
ζ_5	0·08	0·06	0·075	0·18	0·18	
ζ_6				−0·36	−0·33	
ζ_7	0·22	0·23	0·23			0·16

*Linear term in the expression for Q_K. ζ_8 is not known.

well-resolved. For these bands the Q-sub-branches are represented by the following quadratic expressions:

Me–Hg–Cl $Q_{\pm K} = 792{\cdot}7 + 2{\cdot}713K \pm 0{\cdot}0421K^2$
Me–Hg–Br $Q_{\pm K} = 792{\cdot}2 + 2{\cdot}694K \pm 0{\cdot}0417K^2$
Me–Hg–I $Q_{\pm K} = 777{\cdot}9 + 2{\cdot}562K \pm 0{\cdot}0717K^2$

Several other bands were partly resolved, showing 10—20 well-spaced Q-branches, but it was not possible to locate the band centres. In these cases an average spacing was used in evaluating the corresponding Coriolis ζ values (Table 2). The rotational constants A and B used for calculation of the ζ constants are based on the microwave structural parameters of Gordy and Sheridan[2] for MeHgCl and MeHgBr, who assumed values for the C–H distance (1·10 Å) and the angle H–C–H (110° 42′). These same values are used for MeHgI and CD_3HgI which with the available data on C–Hg and Hg–I bond lengths[3] permit the calculation of the respective B-constants.

The Coriolis ζ values agree with the values found in structurally related molecules, being close to the expected values:[4] zero, $-\frac{1}{3}$, and $+\frac{1}{3}$ for CH-stretching, CH_3-deformation, and CH_3-rocking modes respectively. More detailed analysis of the rotational structure, re-investigation of some bands, especially the CH_3-deformation bands which have been obscured by atmospheric absorption (not well compensated when the high temperature cell was introduced in the sample beam), as well as an extensive force constants calculation are in progress.

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[2] W. Gordy and J. Sheridan, *J. Chem. Phys.*, 1954, **22**, 92. CH_3HgBr and CH_3HgCl are reinvestigated to give more precise parameters (personal communication from Professor J. Sheridan).

[3] 'Tables of Interatomic Distances,' *Chem. Soc. Special Publ.*, No. 18, 1965.

[4] M. Randić and N. Sheppard (to be published).