

CCA-554

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Note

Far Infrared Spectra of CH_3HgBr , CH_3HgI , CD_3HgBr and CD_3HgI

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Received May 9, 1969

Far infrared spectra of the molecules CH_3HgBr , CH_3HgI , CD_3HgBr and CD_3HgI in the range $350\text{--}59\text{ cm}^{-1}$ are presented. The results include vibrational frequencies of Hg-Hal stretching (ν_4) and C-Hg-Hal bending (ν_5) modes. The band shapes are consistent with shapes of other fundamental bands of methyl mercuric halides.

Methyl mercuric halides CH_3HgX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and their perdeutero analogues have recently been studied by vibrational spectroscopy¹⁻⁴. However, most investigations lacked the data on low-lying fundamental frequencies: Hg—X stretching and C—Hg—X bending. The knowledge of these frequencies is essential for a realistic normal coordinate calculation based on a complete quadratic force field. The only formerly reported frequencies from infrared spectra below 400 cm^{-1} are due to Goggin and Woodward¹ and Green²: 313 cm^{-1} (ref. 1) and 315 cm^{-1} (ref. 2) for Hg—Cl stretching, 214 cm^{-1} for Hg—Br stretching, and two frequencies, 184 cm^{-1} and 169 cm^{-1} , for Hg—I stretching vibration². Green also reported 64 cm^{-1} for C—Hg—I skeletal bending vibration of CH_3HgI , the only molecule for which the measurements have been extended to 40 cm^{-1} . Several vibrational frequencies below 400 cm^{-1} have been obtained from Raman spectra^{1,3-5}. Since a search of the current literature failed to yield complete vibrational data for methyl mercuric halides, the infrared spectra of these molecules and of their deuterated derivatives are the subject of our investigations. In the present paper far infrared spectra of CH_3HgBr and CH_3HgI , and also of their perdeuterated derivatives in the range $350\text{--}59\text{ cm}^{-1}$ are reported.

The same samples used for recording of high-resolution infrared spectra^{4,6} were also used here. The compounds were examined as Nujol mulls placed between polyethylene plates.

Methyl mercuric halides (as well as their perdeuterated analogues) belong to the point group C_{3v} . In the spectral range $350\text{--}59\text{ cm}^{-1}$ lie two fundamental vibrations: Hg—X stretching ν_4 (species A_1) and C—Hg—X skeletal bending ν_5 (species E). The spectra recorded with Beckman IR-11 spectrophotometer (four gratings with 2,3,8, and 20 lines/mm blazed at 450, 165, 112, and 45μ respectively, and seven filters in the range $350\text{--}59\text{ cm}^{-1}$) are shown in Fig. 1 (CH_3HgBr and CH_3HgI) and Fig. 2 (CD_3HgBr and CD_3HgI). The calibration was based on water absorption lines⁷ and the frequencies are expected to be accurate to $\pm 1\text{ cm}^{-1}$. The infrared vibrational frequencies are listed in Table I. There are only two strong bands in each spectrum: the higher frequency one is

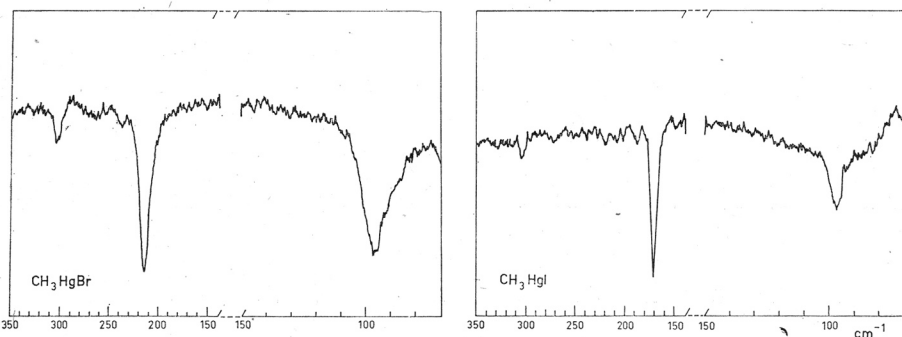


Fig. 1. Far infrared spectra of CH_3HgBr and CH_3HgI (Nujol mulls).

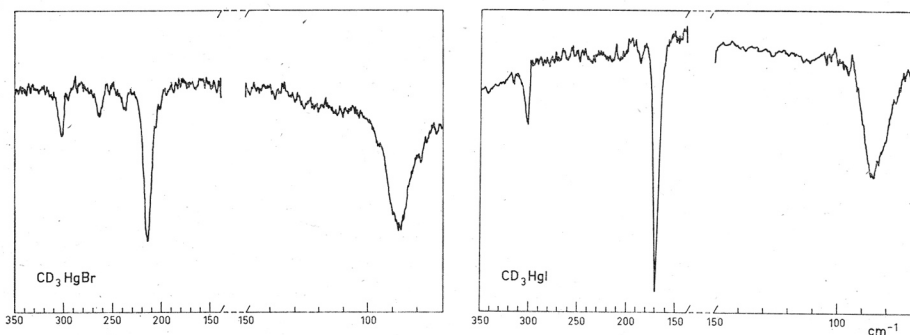


Fig. 2. Far infrared spectra of CD_3HgBr and CD_3HgI (Nujol mulls).

assigned to the fundamental ν_4 and the lower frequency one is due to the fundamental ν_8 . Peaks at 300 cm^{-1} arose from the change of filters. The origin of the minor bands at about 240 cm^{-1} and 270 cm^{-1} in the spectra of CH_3HgBr and CD_3HgBr was not subject to the investigation at this stage, which included only a search for fundamental frequencies. Band shapes are distinctively different: ν_4 is sharp and narrow (half width *ca.* 15 cm^{-1}), while ν_8 is broad (half width *ca.* 30 cm^{-1}). This is consistent with already observed differences of band contours of other fundamental frequencies of methyl mercuric halides and is an indication of molecular motion (hindered rotation about the molecular axis) in the solid.³

There is no isotopic shift for the symmetric (A_1 species) mercury-halogen stretching frequency observed, as might be expected, but for the degenerate

TABLE I
Far Infrared Fundamental Frequencies (cm^{-1})

| | CH_3HgBr | CH_3HgI | CD_3HgBr | CD_3HgI | Assignment |
|---------------|--------------------------|-------------------------|--------------------------|-------------------------|--------------|
| $\nu_4 (A_1)$ | 215 | 173 | 215 | 173 | Hg-X str. |
| $\nu_8 (E)$ | 97 | 97 | 87 | 87 | C-Hg-X bend. |

skeletal bending frequency the isotopic shift of 10 cm^{-1} is observed. Our measurements disagree with some earlier published values. Thus Green² reported for methyl mercuric iodide 64 cm^{-1} for ν_8 which we found at 97 cm^{-1} , and two bands in the region of Hg—I stretching: 184 cm^{-1} and 169 cm^{-1} , while we observed a single band at 173 cm^{-1} . However, as the actual spectra have not been published and no details were reported, it is difficult to understand these differences. The only other frequency reported here already published is the Hg—Br stretching frequency (for CH_3HgBr) which agrees with the value reported by Green.

Acknowledgment. I thank Professor M. Randić for helpful discussion and critical reading of the manuscript. My thanks are also due to Mr. I. Levstek (Nuclear Institute »Jožef Stefan«, Ljubljana) who kindly permitted the recording of the spectra in his laboratory.

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IZVOD

Spektri CH_3HgBr , CH_3HgI , CD_3HgBr i CD_3HgI u dalekom infracrvenom području

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Prikazani su spektri molekula CH_3HgBr , CH_3HgI , CD_3HgBr i CD_3HgI u dalekom infracrvenom području ($350\text{--}59\text{ cm}^{-1}$). Rezultati uključuju frekvencije osnovnih vibracija istezanja veza Hg-Hal (ν_4) i savijanja C-Hg-Hal (ν_8). Oblik apsorpcijskih vrpca u skladu je s oblicima drugih osnovnih vrpca metil živinih (II) halogenida.

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Primljeno 9. svibnja 1969.