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The Low Frequency Fundamental Bands of Methyl Chloride, Methyl Bromide and Methyl Iodide

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The parallel type bands ν_5 for CH_3Cl , CH_3Br and CH_3I have been found at $\lambda 13.7$, 16.4 and 18.8μ , respectively, the rotation lines of the chloride band being partially resolved. The iodide band has a particularly sharp zero branch suitable for use in calibration. Both the chloride and bromide bands are complicated by isotopic effects, the separations being 6 cm^{-1} and 1 cm^{-1} .

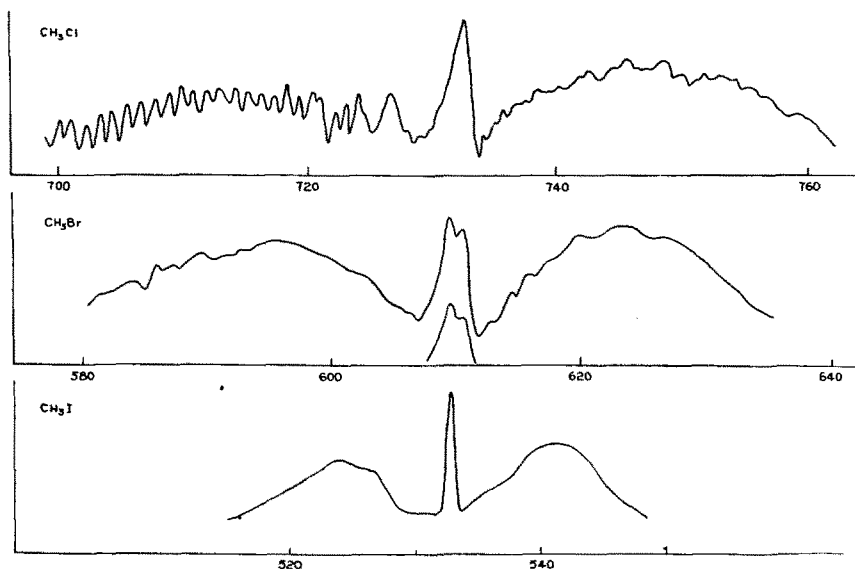
THE infrared absorption spectra of the methyl halides out to 14μ have been observed and correlated by Bennett and Meyer.¹ They were unable to reach the lowest frequency bands ν_5 for the bromide and the iodide. The corresponding chloride band was observed but not resolved, while that of the fluoride was completely analyzed. Since these observations were made the apparatus has been improved somewhat in sensitivity, and the NaCl fore prism has been replaced by one of KBr, extending the possible range of measurement out to beyond 20μ . In order to complete the series of methyl halide bands, and also to provide convenient reference wavelengths for the calibration of prism spectra in this region, we have observed the ν_5 bands of CH_3I and CH_3Br . We have also remapped the CH_3Cl band obtaining somewhat better resolution than before. The results are indicated in Fig. 1, where the ordinate is percentage absorption and the zero branches extend up to about 80 percent in each band.

The CH_3Cl band represents absorption by a column of gas 26 cm long at a pressure of 3 cm, the slit width being equivalent to 0.5 cm^{-1} .

¹ Bennett and Meyer, *Phys. Rev.* **32**, 888 (1928).

The rotation lines are partially resolved, especially on the low frequency side. The irregularities observed are not due to lack of resolving power, but to superposition of isotopic bands. The line spacing, which cannot be determined with great precision, is approximately 1.1 cm^{-1} . This indicates a moment of inertia A about an axis through the centroid and normal to the symmetry line, of about $50 \times 10^{-40}\text{ g cm}^2$. The moment of inertia C with respect to the symmetry axis is, of course, very nearly equal to that of CH_4 . The vibration ν_5 to which this band is due consists primarily of a motion of the halogen atom toward and away from the CH_3 group. It is therefore particularly sensitive to isotopic differences in the mass of the halogen atom. In first approximation the methyl group may be treated as a rigid unit, and the reduced mass computed as for a diatomic molecule. The difference in frequency thus predicted for the two bands due to Cl^{35} and Cl^{37} is 6 cm^{-1} . This agrees exactly with the observed difference between the principal zero branch at 733 cm^{-1} and the minor one at 727 cm^{-1} .

For the observations on methyl bromide a pressure of 5 cm was used in the 26 cm cell, and

FIG. 1. The parallel type absorption band ν_3 .

the slit included a spectral range of 0.3 cm^{-1} . The two isotopic bands are of nearly the same intensity in this case, and are only slightly separated, the zero branches appearing at 610 and 611 cm^{-1} . The expected displacement for Br^{81} from Br^{79} , computed as before is 1.2 cm^{-1} . The effect of partial superposition is to make the maxima appear somewhat closer together than they actually are. The interval between rotation lines should be approximately 0.5 cm^{-1} , which is very close to the limit for this spectrometer. However, it is clear that the bands superpose in such a way that no resolution is to be expected.

The third curve represents the absorption of methyl iodide at 20 cm pressure in the 26 cm cell. The zero branch is very sharp and intense,

and constitutes an excellent reference point. It appears at 532.9 cm^{-1} . Although there is no complication due to isotopes the rotation lines cannot be distinguished since their separation is below the limit of resolution of the spectrometer. There is no indication of a transition beginning at the first excited state, which must have an appreciable population. This suggests that the anharmonic constants are small. Strong absorption due to water vapor in this region may account for some of the small irregularities in the band envelope.

A comparison of the infrared observations with data obtained by Raman scattering has already been presented.²

² Adel and Barker, *J. Chem. Phys.* **2**, 627 (1934).