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INFRARED SPECTRUM AND VIBRATION-ROTATION ANALYSIS OF THE ν_1 BAND OF METHYL-d_3 IODIDE

Hiroatsu MATSUURA* and Hiromu MURATA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730

Infrared spectrum of the ν_1 band of methyl-d_3 iodide was measured by a Fourier transform spectrometer with a resolution of 0.08 cm^{-1}. The analysis of the spectrum gave the following constants: $(\nu_0)_1$ 2155.437±0.006 cm^{-1}, α_1^A 0.02221±0.00006 cm^{-1}, and α_1^B 0.000113±0.000002 cm^{-1}. The centrifugal distortion constants were also determined.

The vibration-rotation spectra of methyl halides and their deuterated species have been extensively studied and various spectroscopic constants have been determined. However, some of the constants, particularly those for the parallel bands, were obtained from the spectra with relatively low resolution and in consequence their values are less accurate than others.

The infrared spectrum of the ν_1 band of methyl-d_3 iodide (CD_3I) has been studied previously by Jones et al.[1] with medium resolution. In the present work, the higher-resolution spectrum of this band was measured and the spectroscopic constants were determined through the spectral analysis.

The infrared spectrum of the ν_1 band of gaseous CD_3I was measured on a JEOL JIR-40X Fourier transform spectrometer equipped with a TGS detector and the interferogram was accumulated by scanning 400 times. A sample pressure of about 8.5 Torr in a 1-m cell was utilized. The effective resolution achieved was 0.08 cm^{-1}. The observed wavenumbers were calibrated by using the IUPAC wavenumber data.[2]

The observed spectrum in the whole ν_1 band region is shown in Fig. 1. In the spectral region between 2120 and 2190 cm^{-1}, about 350 vibration-rotation lines were observed, but most of them were revealed to be composite of two or more transition lines.

The spectral analysis was started with assigning the Q branch lines in the 2151 – 2156 cm^{-1} region. On the basis of the intensity alteration expected for

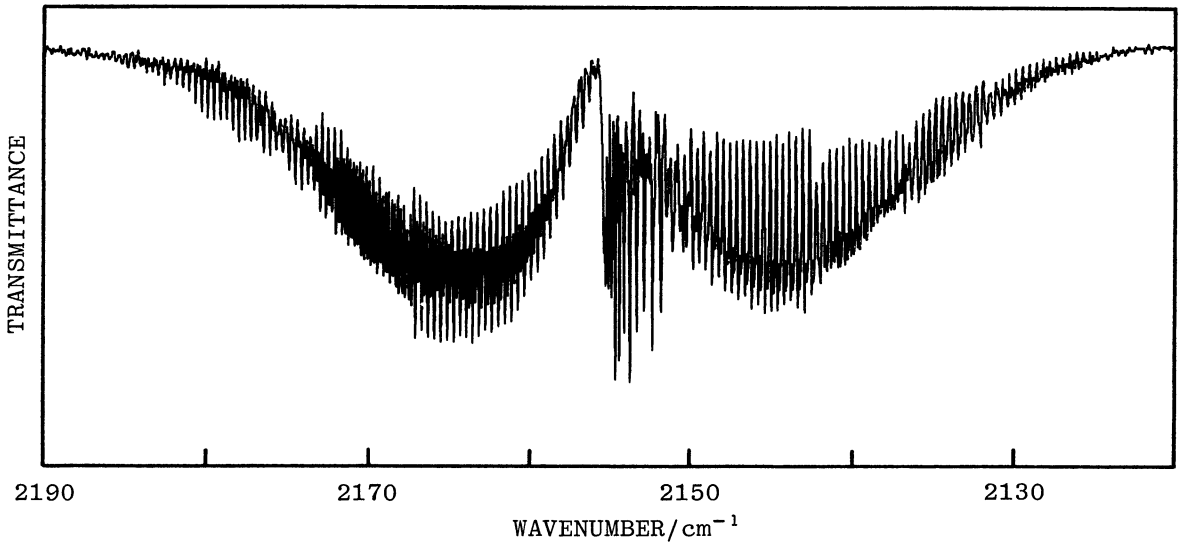

Fig. 1. Infrared spectrum of the ν_1 band of gaseous CD_3I.

CD_3X-type molecules, the K-assignment of the Q branch was readily made and $Q(J,K=2)-Q(J,K=13)$ were identified. The observed wavenumbers for these twelve lines gave approximate values for $(\nu_0)_1$ and $[(A_1-B_1)-(A_0-B_0)]$. Since the ground-state rotational constant B_0 has been determined by microwave spectroscopy,[3] its value was used throughout the present analysis. The previous value[1] for B_1 and the microwave value for B_0 were incorporated with the results of the Q-branch analysis to make a preliminary simulation of the spectrum. By comparing the observed and the simulated spectra, J- and K-assignments of the P- and R-branch lines were performed and J_{max} values, which are the J values corresponding to the Q-branch maxima, were estimated.

The observed wavenumbers for the P- and R-branch lines thus assigned and those for the Q-branch maxima were jointly used in the least-squares calculation to determine the spectroscopic constants for the ν_1 band. The spectrum was again simulated by using the constants determined, and the J- and K-assignments and the J_{max} assignment were examined. By repeating the least-squares calculation of the constants and the spectral simulation, the line assignment was extended to higher J transitions. In the final stage, the P- and R-branch lines of J values up to about 70 were identified. The simulation of the spectrum was important in the analysis of this band, since many transition lines were blended into a few series of the P and R branches and the individual transition lines were not identified in most cases. Thus such overlapped lines were actually assigned to two or more

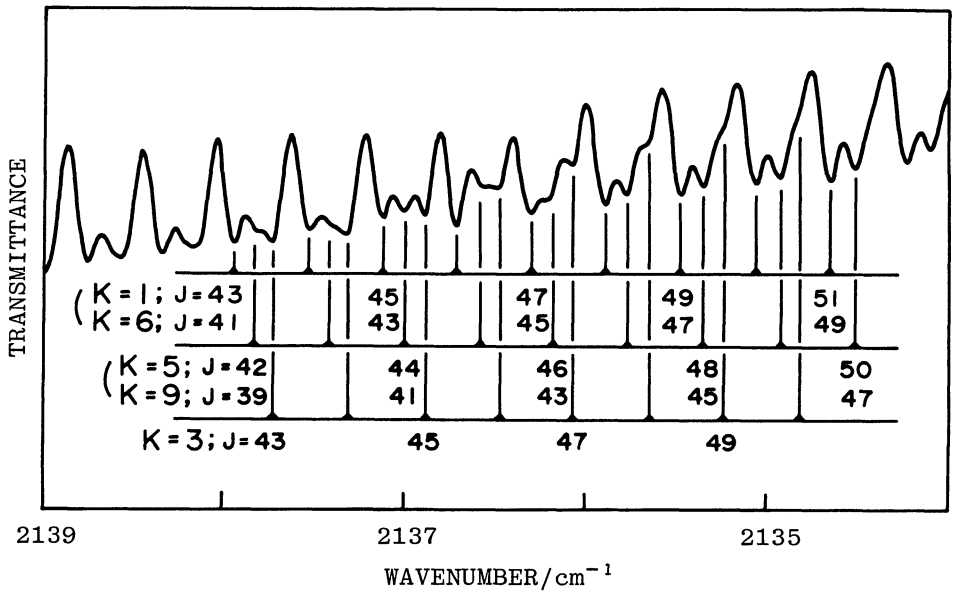

Fig. 2. J- and K-assignments in the P-branch region.

transitions. The J- and K-assignments of the P branch in the 2134 – 2139 cm^{-1} region are shown in Fig. 2.

The spectroscopic constants for the ν_1 band of CD_3I were finally determined from the observed wavenumbers for 421 transitions. Throughout the present analysis, the constants for the ground state, B_0, $(D_J)_0$, and $(D_{JK})_0$, were constrained to the microwave values.[3] The weights for the Q-branch lines were chosen, in the least-

Table 1. Spectroscopic constants for the ν_1 band of CD_3I

Constant	Value/cm^{-1}	
	Present work	Previous work[a]
$(\nu_0)_1$	2 155.437±0.006	2 155.42
$[(A_1-B_1)-(A_0-B_0)]$	-0.022 10±0.000 06	
B_1	0.201 370±0.000 002	
$(D_J)_1$	$(1.209\pm0.005)\times10^{-7}$	
$(D_{JK})_1$	$(1.69\pm0.03)\times10^{-6}$	
$[(D_K)_1-(D_K)_0]$	$(-3.2\pm0.4)\times10^{-6}$	
B_0	0.201 483 03[b]	0.202 0
$(D_J)_0$	1.197×10^{-7}[b]	
$(D_{JK})_0$	1.61×10^{-6}[b]	
α_1^A $(=A_0-A_1)$	0.022 21±0.000 06	0.021 7
α_1^B $(=B_0-B_1)$	0.000 113±0.000 002	0.000 135

a) Ref. 1. b) Constrained in the least-squares calculation.

squares treatment, to be 25 times greater than those for the P- and R-branch lines. This was necessary to get a good wavenumber fit evenly for all the transitions. The results obtained are given in Table 1, in comparison with the previous ones.[1)]

The spectral analysis in the present work gave the constants for the ν_1 band with higher accuracy than in the previous work.[1)] The differences in the values obtained in the two analyses are due, at least in part, to the facts that Jones et al.[1)] ignored the term in K^2 in analyzing the P and R branches and that the observed lines were therefore all assigned to the transitions of K=0. They observed in their spectrum two series of P- and R-branch lines which were severely overlapped with each other, and assigned the main series to the fundamental ν_1 band and the sub-series to the hot band $\nu_1+\nu_3-\nu_3$. The present analysis clarified that these series are in fact the P- and R-branch lines of the ν_1 band with different K values. The lines assignable definitely to the hot band were not identified in the present spectrum. Such assignments of the transition lines, namely a main series to the fundamental band and sub-series to hot band(s), have been sometimes made in the past in analyses of parallel bands with lower resolution. Therefore care must be taken in evaluating the derived values of the constants.

Anderson and Overend[4)] have studied a number of overtone and combination bands of CD_3I and obtained an effective value for $\alpha_1^A + \alpha_5^A$ from the analysis of the $\nu_1 + \nu_5$ band. This value was combined with the α_5^A obtained from the ν_5 band to give α_1^A. The value derived was 0.0226 ± 0.0004 cm^{-1} in good agreement with the present value of 0.02221 cm^{-1} determined directly from the ν_1 band. The constants α_r^A and α_r^B for CD_3I have been compiled in a previous paper.[5)] The present values for α_1^A and α_1^B are updated data to the previous ones.

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