Vibration-Rotation Spectra, the Coriolis Coupling Constants and the Intramolecular Fore Field of Symmetric Top Molecules. II. Analysis of the Overtones and Combination Tones of Methyl Bromide

By Yonezo MORINO, Junko NAKAMURA* and Seiya YAMAMOTO

(Received August 10, 1964)

The infrared spectra of the overtones and combination tones of methyl bromide, CH_3Br, have been studied by many investigators;[1-4] six A_1-type bands and ten E-type bands have been observed. For the bands, $2\nu_4$, $\nu_1+\nu_4$, $\nu_1+\nu_5$, $\nu_2+\nu_4$, $\nu_4+\nu_5$ and $\nu_4+2\nu_5$, in particular, the rotational fine structures have been analyzed.

It seems, however, that no study has yet been undertaken with the particular intention of determining the second-order molecular parameters, that is, the vibrational anharmonic terms (x_{ij}), the rotational correction terms (α_i and β_i), and the effective Coriolis coupling constants (ζ_{eff}). The primary object of this paper will be, therefore, to measure the

---

* Present address: The Institute of Physical and Chemical Research, Komagome, Bunkyo-ku, Tokyo

[1] C. P. Courtoy, *Ann. Soc. Sci. Bruxelles*, **LX**, 122 (1946).

[2] D. H. Rank, H. D. Rix and T. A. Wiggins, *J. Opt. Soc. Am.*, **43**, 157 (1953).

[3] H. B. Weissman, R. B. Bernstein, S. E. Rosser, A. G. Meister and F. F. Cleveland, *J. Chem. Phys.*, **23**, 544 (1955).

[4] R. G. Brown and T. H. Edwards, ibid., **37**, 1029 (1962); ibid., **40**, 2740 (1964).

infrared spectra of methyl bromide for this purpose. The parameters obtained in the present work will be used later to investigate the harmonic and anharmonic potential constants of this molecule.

Experimental

A commercial sample of methyl bromide was dried by passing it through phosphorous pentoxide. Infrared spectra were recorded on a Perkin-Elmer 112G grating spectrometer, which has a resolution of about 0.6 cm^{-1}, an accuracy of the absolute frequency of about 0.5 cm^{-1}, and an accuracy of the relative frequency of about 0.05 cm^{-1}. A long-path cell (about 6 m. long) was used with a sample pressure varying from 100 to about 760 mmHg.

Theory

The methyl bromide molecule has the C_{3v} symmetry and six normal modes; three of them belong to the A_1-type, and the other three to the E-type. The energy level of the molecule is, to a second order of approximation, given by:[6]

$$T = G(v_1,\ v_2, \cdots) + F_v(J,\ K) \tag{1}$$

where G is the vibrational energy and F is the rotational energy, including the vibration-rotation interactions:

$$\begin{aligned} G = &\sum_i \omega_i (v_i + d_i/2) \\ &+ \sum_i \sum_{j\geq i} x_{ij} (v_i + d_i/2)(v_j + d_j/2) \\ &+ \sum_t \sum_{t'\geq t} g_{tt'}\ |l_t| \cdot |l_{t'}| \end{aligned} \tag{2}$$

and

$$\begin{aligned} F = &B_v J(J+1) + (A_v - B_v) K^2 - D_J J^2 (J+1)^2 \\ &- D_{JK} J(J+1) K^2 - D_K K^4 - 2A_v \sum_t \zeta_t l_t K \\ &+ A_v (\sum_t \zeta_t l_t)^2 \end{aligned} \tag{3}$$

The term G can be referred to the ground state $G(0,\ 0,\ \cdots)$,

$$\begin{aligned} G_0 = &\sum_i \omega_i^0 v_i + \sum_i \sum_{j\geq i} x_{ij} v_i v_j \\ &+ \sum_t \sum_{t'\geq t} g_{tt'} |l_t| \cdot |l_{t'}| \end{aligned} \tag{4}$$

Where

$$\omega_i^0 = \omega_i + x_{ii} d_i + 1/2 \sum_{j\neq i} x_{ij} d_j \tag{5}$$

Here ω_i is the normal frequency of the ith mode: v_i, its vibrational quantum number, and $d_i = 1$ or 2, depending on whether i refers to a totally symmetric or to a doubly-degenerate vibration. The suffix t denotes a doubly-degenerate mode, and the vibrational angular momentum, $|l_t|$, takes the values v_t, $(v_t - 2), \cdots$, 1 or 0. The coefficients x_{ij} and $g_{tt'}$ are the vibrational anharmonic terms, and A_v and B_v are the rotational constants which depend on the vibrational state, v. The coefficients D_J, D_{JK} and D_K are the centrifugal distortion constants and do not depend on the vibrational state in this approximation.[7] The ζ_t is a first-order Coriolis coupling constant, which does not appear when no doubly-degenerate vibrations are excited.

As may be seen from Eq. 4, the band center of a fundamental (ν_i) is given by:

$$(\nu_i) = \omega_i^0 + x_{ii}, \text{ for the } A_1\text{-type mode} \tag{6}$$

and

$$(\nu_t) = \omega_t^0 + x_{tt} + g_{tt}, \text{ for the E-type mode} \tag{7}$$

If the centrifugal distortion terms are ignored because of their small size, the rotational structure for a parallel band is given by the selection rules $\Delta K = 0$ and $\Delta J = 0, \pm 1$:

$$\begin{aligned} {}^{Q}R_{|K|}(J) = &\nu_i + [(A' - A'') - (B' - B'')] K^2 \\ &+ 2B' + (3B' - B'')J + (B' - B'')J^2 \\ {}^{Q}Q_{|K|}(J) = &\nu_i + [(A' - A'') - (B' - B'')] K^2 \\ &+ (B' - B'')J(J+1) \\ {}^{Q}P_{|K|}(J) = &\nu_i + [(A' - A'') - (B' - B'')] K^2 \\ &- (B' + B'')J + (B' - B'')J^2 \end{aligned} \tag{8}$$

where J denotes the quantum number of the lower level, and the symbols $''$ and $'$ indicate the lower and upper states respectively.

For a perpendicular band whose selection rules are $\Delta K = \pm 1$ and $\Delta J = 0, \pm 1$, the rotational structure is given by:

$$\begin{aligned} {}^{P}_{R}R_{|K|}(J) = &{}^{P}_{R}\nu_o^{\text{sub}} + 2B' + (3B' - B'')J \\ &+ (B' - B'')J^2 \\ {}^{P}_{R}Q_{|K|}(J) = &{}^{P}_{R}\nu_o^{\text{sub}} + (B' - B'')J(J+1) \\ {}^{P}_{R}P_{|K|}(J) = &{}^{P}_{R}\nu_o^{\text{sub}} - (B' + B'')J + (B' - B'')J^2 \end{aligned} \tag{9}$$

where

$$\begin{aligned} {}^{P}_{R}\nu_o^{\text{sub}} = &\nu_t + [A'(1 - \zeta_t)^2 - B'] \mp 2[A'(1 - \zeta_t) \\ &- B']|K| + [(A' - A'') - (B' - B'')] K^2 \end{aligned} \tag{10}$$

and J and K are the values of the lower state. In Eq. 10, the upper sign corresponds to the P branch, and the lower sign, to the R branch.

Overtones and Combination Tones. — The features of the overtones of the fundamentals belonging to the A_1-type symmetry are similar to those of the fundamentals since $(a_1)^2 = A_1$. The band center of the overtone, $(2\nu_i)$, is given by:

---

[5] Y. Morino and J. Nakamura, This Bulletin, 38, 443 (1965).

[6] G. Herzberg, "Infrared and Raman Spectra II," D. Van Nostrand Company, Inc., Princeton, New Jersey (1945).

[7] H. H. Nielsen, *Revs. Mod. Phys.*, 23, 90 (1951).

$$(2\nu_i) = 2(\nu_i) + 2x_{ii} \tag{11}$$

The overtones of the E-type fundamentals have two components, A_1 and E, since $(e)^2 = A_1 + E$. The band center of the A_1-type component is:

$$(2\nu_t) = 2(\nu_t) + 2x_{tt} - 2g_{tt} \tag{12}$$

and that of the E-type component is:

$$(2\nu_t) = 2(\nu_t) + 2x_{tt} + 2g_{tt} \tag{13}$$

It is important to note that in this case the ζ_t in Eq. 10 must be replaced by:[8)]

$$\zeta_{\mathrm{eff}} = -2\zeta_t \tag{14}$$

Since $a_1 \cdot a_1 = A_1$, the fine structure of a combination tone between two different A_1-type modes is similar to that of the fundamentals, and

$$(\nu_i + \nu_j) = (\nu_i) + (\nu_j) + x_{ij} \tag{15}$$

The fine structure of the combination tone between an A_1- and an E-type mode is similar to that of the E-type fundamental, since $a_1 \cdot e = E$,

$$(\nu_i + \nu_t) = (\nu_i) + (\nu_t) + x_{it} \tag{16}$$

and

$$\zeta_{\mathrm{eff}} = \zeta_t \tag{17}$$

The combination tones between two E-type modes have two components, since $e \cdot e = A_1 + A_2 + E$, the A_2-type not being infrared-active. The band center is given, for both of the A_1 and E components, by:

$$(\nu_t + \nu_{t'}) = (\nu_t) + (\nu_{t'}) + x_{tt'} + g_{tt'} \tag{18}$$

and, for the E component, by:

$$\zeta_{\mathrm{eff}} = -(\zeta_t + \zeta_{t'}) \tag{19}$$

The Method of the Analysis of the Observed Bands.—If we assume that $B' = B''$, the Eqs. 8 for parallel bands become:

$$\begin{aligned} {}^{Q}R_{|K|}(J) &= \nu_i + (A' - A'')K^2 + 2B''(J+1) \qquad (20) \\ {}^{Q}Q_{|K|}(J) &= \nu_i + (A' - A'')K^2 \\ {}^{Q}P_{|K|}(J) &= \nu_i + (A' - A'')K^2 - 2B''J \end{aligned}$$

The line spacing due to the J value is $2B''$ in the P and R branches, and all lines of different J values coincide with the band center, ν_i, in the Q branch. The spacing due to the K value, on the other hand, is $(A' - A'')(2K+1)$ in the P, Q, and R branches. In the case of methyl bromide, the value of $(A' - A'')$ is about $0.05\,\mathrm{cm}^{-1}$, though those of different bands are not equal. The value of $2B''$ is $0.63\,\mathrm{cm}^{-1}$. Since the resolving power of the spectrometer used is about $0.6\,\mathrm{cm}^{-1}$, there may be a splitting of the lines which have different J values, and, in fact, the splittings have been observed in several bands. The K splitting may not be observed in the region of small K numbers. In fact, most of the bands did not show their fine structures, and only the envelopes of the P, Q, and R branches were observed. The Q branches showed two types of envelopes, depending on whether $(A' - A'')$ is positive or negative. When $(A' - A'')$ was negative, the intensity of the absorption increased slowly from the lower frequency side, reached a maximum, and decreased rapidly toward the higher frequency side. The band origin of this band was determined by measuring the frequency at which the absorption disappeared at the higher frequency side. The case must be reversed if $(A' - A'')$ is positive, and the band origin determined at the lower frequency side. Since the envelopes of the P and R branches intersect near the band origin, the frequencies determined by the above method were proved consistent.

For perpendicular bands, if $B' = B''$, then Eq. 9 becomes:

$$\begin{aligned} {}^{P}_{R}R_{|K|}(J) &= {}^{P}_{R}\nu_o^{\mathrm{sub}} + 2B''(J+1) \\ {}^{P}_{R}Q_{|K|}(J) &= {}^{P}_{R}\nu_o^{\mathrm{sub}} \\ {}^{P}_{R}P_{|K|}(J) &= {}^{P}_{R}\nu_o^{\mathrm{sub}} - 2B''J \qquad (21) \end{aligned}$$

With a few exceptions, no bands show the J splitting in the P and R branches, and lines which originate from different J values form a background for the absorption curve. In the Q branch, all lines of different J values appear at nearly the same point, ${}^{P}_{R}\nu_o^{\mathrm{sub}}$; therefore, they show a sub-bands series, which have much stronger intensities than the lines of the P and R branches, as peaks above the background with an interval of about $2[A'(1-\zeta) - B'']$. Naturally, they have an unresolved J structure and show envelopes like the Q branches of the parallel bands, due to $(B' - B'')$ and also to a slit function characteristic of the spectrometer used.

If ${}^{P}_{R}\nu_o^{\mathrm{sub}}$ is rewritten as $\nu(m)$, where $m = -|K|$ in ${}^{P}Q_{|K|}$ and $m = |K|$ in ${}^{R}Q_{|K|}$, then:

$$\begin{aligned} \Delta\nu(m) &= \nu(m+1) - \nu(m) \\ &= 2[(A' - A'') - (B' - B'')]m \\ &\quad + 2[A'(1 - \zeta_{\mathrm{eff}}) - B'] \\ &\quad + [(A' - A'') - (B' - B'')] \qquad (22) \end{aligned}$$

If $\Delta\nu(m)$ is plotted against m, it lies on a straight line, and $[(A' - A'') - (B' - B'')]$ and $[A'(1 - \zeta_{\mathrm{eff}}) - B']$ can be determined from the slope and $\Delta\nu(-1/2)$ respectively. If the values of A'' and B'' are known and if B' is assumed to be equal to B'', the parameters A', ζ, and ν_t can then be determined.

The frequencies of the subbands at the

---

8) D. R. J. Boyd and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A 231**, 55 (1952).

maximum intensities were measured, and the method described above was taken as a first step of the analysis. The assignment of m was made by the use of the fact that the sub-bands whose m numbers are a multiple of 3 have stronger intensities than the others. The values of $\zeta_{\rm eff}$ obtained in this way were compared with the values to be expected from those of the fundamentals. This procedure confirms whether or not the vibrational assignment is correct. The coefficients of m in Eq. 22 and the values of A', ζ, and ν_t were then determined by the method of least squares.

The values of A'' and B'' are taken to be 5.127 cm^{-1} from the results of the analysis of the fundamentals,⁵⁾ and 0.3186 cm^{-1} from the results of the microwave spectroscopy⁹⁾.

Experimental Results

a) Parallel Bands.—The overtone and combination tone bands of the A_1-type fundamentals were all observed. Moreover, the A_1 components of the overtones $2\nu_4$ and $2\nu_5$, and the combination tone $\nu_4+\nu_6$, were also observed. Most of them, however, showed only envelopes, and no fine structures were resolved. The bands $\nu_1+\nu_2$ and $\nu_4+\nu_6$ showed fine structures, as Fig. 1 and Fig. 2 show, but the analysis has not been made in detail. For the band of $\nu_1+\nu_3$ it seems that the Q branch was split into fine structures (Fig. 3), but it was difficult to distinguish each line because of the noise, so the band center was determined from the point of intersection of the envelopes of the P and R branches. Two Q branches observed in the band $2\nu_3$ (Fig. 4) are probably due to ^{79}Br and ^{81}Br. The results are summarized in Table I.

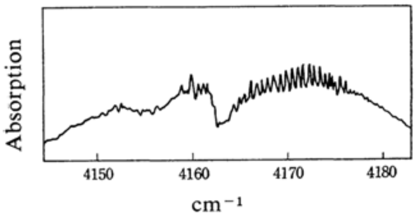

Fig. 1. The parallel band $\nu_1+\nu_2$ of CH_3Br.

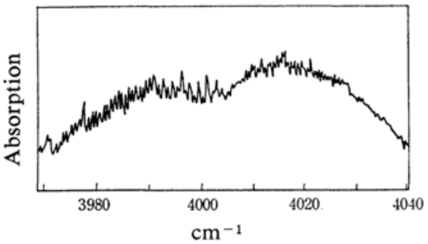

Fig. 2. The parallel band $\nu_4+\nu_6$ of CH_3Br.

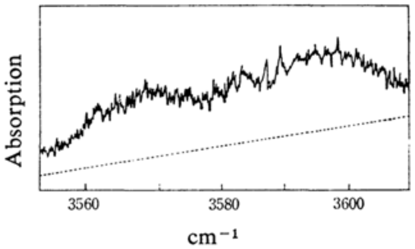

Fig. 3. The parallel band $\nu_1+\nu_3$ of CH_3Br. The dotted curve represents the blank curve.

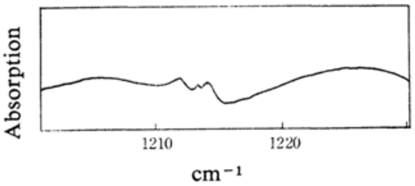

Fig. 4. The parallel band $2\nu_3$ of CH_3Br.

b) Perpendicular Bands. — All the E-type bands of the overtones and the combination tones except $\nu_3+\nu_4$, $\nu_3+\nu_5$, $\nu_3+\nu_6$, $\nu_4+\nu_6$ and $2\nu_5$ were observed.

1) Region 1500 — 2000 cm^{-1}.—A perpendicular band was observed and assigned to $2\nu_6$ (1869 cm^{-1}). The quality of the spectra of this region was poor for the following reasons. First, this band has a weak intensity. This band was observed at the pressure of about 760 mmHg. Second, this region was interfered with by a strong absorption band of water. Finally, on the higher frequency side there was an absorption of the A_1-type band $\nu_2+\nu_3$. The observed frequencies and molecular constants are given in Table XII.

2) Region 2000 — 2500 cm^{-1}. — Two bands were observed in this region. They were assigned to $\nu_2+\nu_6$ (2256 cm^{-1}) and $\nu_5+\nu_6$ (2389 cm^{-1}). These bands were disturbed by the absorption of carbon dioxide. The higher

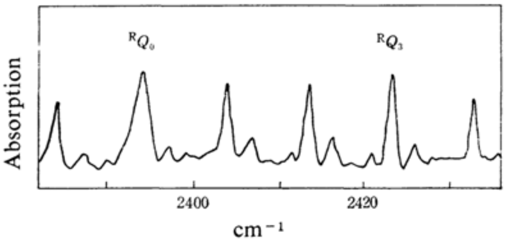

Fig. 5. The perpendicular band $\nu_5+\nu_6$ of CH_3Br.

---

9) W. J. O. Thomas, J. F. Cox and W. Gordy, *J. Chem. Phys.*, **22**, 1718 (1954).

10) I. A. Kraitchman and B. P. Dailey, ibid., **22**, 1477 (1954).

11) C. Hirose, Private communication.

frequency side of $\nu_2+\nu_6$ and the lower frequency side of $\nu_5+\nu_6$ were overlapped by a band of carbon dioxide. Between the lines of the band $\nu_5+\nu_6$, there were other lines (Fig. 5) which were considered to be a hot band or lines due to isotopic species; they are left unassigned. The observed frequencies are given in Tables VIII and XI.

3) Region 2500—3000 cm^{-1}.—There was one band, which was assigned to $\nu_2+\nu_5$. The observed frequencies are given in Table VII.

4) Region 3500—4000 cm^{-1}.—One E-type band was observed and assigned to $\nu_1+\nu_6$. This band was disturbed by the absorption of water. The observed frequencies of the subbands could not be described by an ordinary quadratic function of K (Fig. 6). It is not clear whether or not this situation originated from an overlapping with the absorption of water alone. The constants were, tentatively, calculated from the observed frequencies of $^PQ_1$, $^RQ_0$ and $^RQ_1$. The observed frequencies are given in Table V.

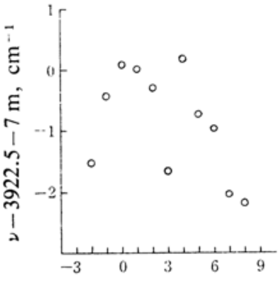

Fig. 6. The observed frequencies vs. m for the perpendicular band $\nu_1+\nu_6$ of CH_3Br.

5) Region 4000—4500 cm^{-1}.—Three E-type bands were observed and assigned to $\nu_2+\nu_4$ (4352 cm^{-1}), $\nu_1+\nu_5$ (4411 cm^{-1}) and $\nu_4+\nu_5$ (4483 cm^{-1}). Brown et al.[4] measured this region with a high resolution spectrometer. Although their first assignments were different from those of this work, their revised values are in good agreement with the present results. An ambiguity lies, however, in the assignment of the $^RQ_0$ subband. For the band $\nu_1+\nu_5$, two subbands at 4418.25 cm^{-1} and 4452.66 cm^{-1} have about the same intensity. If one takes the latter as the $^RQ_0$, ζ_5 becomes -0.18, whereas the assignment of the former to the $^RQ_0$ leads to the ζ_5 value of -0.22. Therefore, the latter assignment ($^RQ_0=4418.25$ cm^{-1}) was preferred in view of the knowledge of the fundamental ζ_5 value of -0.244. The $^PQ_{|K|}$ lines in $\nu_1+\nu_5$ show an anomaly, as Fig. 7 shows. The origin of this anomaly is unknown. The observed frequencies are given in Tables IV, VI and X.

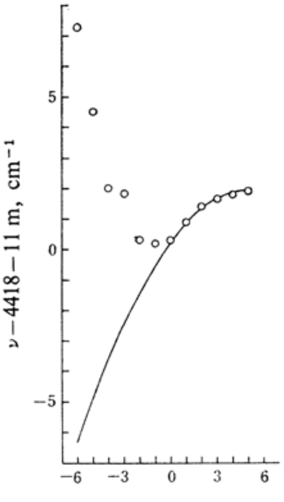

Fig. 7. The observed frequencies vs. m for the perpendicular band $\nu_1+\nu_5$ of CH_3Br. The solid curve represents the calculated one.

6) Region 5500—6500 cm^{-1}.—In this region, four perpendicular bands were observed. They were assigned to $\nu_2+\nu_4+\nu_5$ (5781 cm^{-1}), $\nu_4+2\nu_5$ (5879 cm^{-1}), $\nu_1+\nu_4$ (5941 cm^{-1}) and $2\nu_4$ (6095 cm^{-1}). The bands $\nu_4+2\nu_5$, $\nu_1+\nu_4$ and $2\nu_4$ have also been observed by Rank et al.[2] Their results are in good agreement with those obtained in the present work.

The spectrum of the band $\nu_2+\nu_4+\nu_5$, given in Fig. 8, shows that the band is disturbed on the higher-frequency side by other absorption lines.

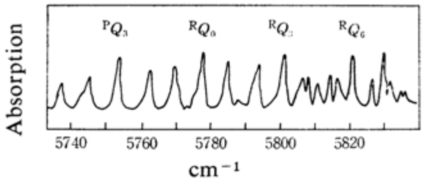

Fig. 8. The perpendicular band $\nu_2+\nu_4+\nu_5$ of CH_3Br.

For $\nu_4+2\nu_5$, since $e\cdot(e)^2=A_1+A_2+E+E$, there are two E-type components, that is, the state where $l_4=1$, $l_5=0$ and the state where $l_4=-1$, $l_5=2$. For the former, the predicted value of ζ_{eff} is 0.059, and for the latter it is -0.547. The observed value is -0.021; therefore, the observed transition is probably related to the former state, even though the difference between the observed and the predicted values of ζ is appreciable. There is presumably a resonance among these states. It seems that, because of this resonance, the ternary combination bands, $\nu_4+2\nu_5$ and $\nu_2+\nu_4+\nu_5$, appeared with sufficient intensities.

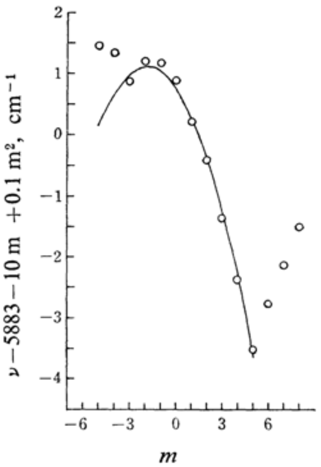

Fig. 9. The observed frequencies vs. m for the perpendicular band $\nu_4+2\nu_5$ of CH_3Br. The solid curve represents the calculated one.

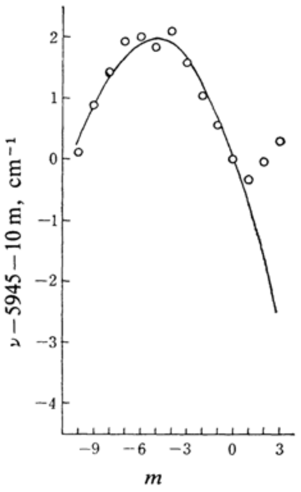

Fig. 10. The observed frequencies vs. m for the perpendicular band $\nu_1+\nu_4$ of CH_3Br. The solid curve represents the calculated one.

The observed frequencies are given in Tables III, IX, XIII and XIV. Those of $\nu_4+2\nu_5$ and $\nu_1+\nu_4$ are shown graphically in Figs. 9 and 10 respectively. The anomalies shown in the figures may also be the result of the resonance.

7) Summary.—The results described above are summarized in Table XV. The errors associated with the molecular constants given in Tables III through XIV are taken to be 2.5 σ, where σ is the standard deviation; 2.5 σ is the 99% confidence interval, and it is thought to be a reasonable limit of error. However, these results do not include systematic errors; for example, the frequencies of the band centers are uncertain by an order of 0.1 cm^{-1}, since they are derived from the assumption that $B'=B''$. The values in the brackets in the tables show the subbands which were omitted from the least-squares calculations because they are either obscured by the presence of foreign bands, such as those of carbon dioxide and water, or are at apparently irregular positions.

Discussion

It can be seen from Table XV that the differences between the observed and the predicted values of ζ are about 0.03. These differences indicate that the ζ values of the overtones and combination tones can not be expressed by the sums of those of the corresponding fundamentals. However, before concluding whether this is true or not, one must take into account the resonances among various vibrational states; this has not been done, and it would require complicated computations. The results of this work simply show that the values of the overtones and the combination tones can be expressed by the sums of the corresponding fundamentals, with proper signs, to within 0.03 in the case of CH_3Br.

The vibrational anharmonic terms obtained in this work are given in Table XVI. These values are still tentative, because the observed frequencies of the E-type bands are the frequencies of the maximum intensity; they must be corrected for the band origins, as has been discussed in the previous section.

The effective rotational constants for a given vibrational state can be expressed by the following relations:[6,7]

$$A_v=A_e-\textstyle\sum_i\alpha_i(v_i+d_i/2)$$
$$B_v=B_e-\textstyle\sum_i\beta_i(v_i+d_i/2)$$

where A_e and B_e are the rotational constants for the equilibrium position and α_i and β_i are the rotational correction terms. The value of $(A'-A'')-(B'-B'')$ is obtained as the coefficient of K^2 from the analysis of the perpendicular band, and it is rewritten in terms of α_i and β_i as follows:

$-\alpha_i+\beta_i$ for the ith fundamental,

$-2\alpha_i+2\beta_i$ for the overtone of the ith vibration,

$-(\alpha_i+\alpha_j)+(\beta_i+\beta_j)$ for the combination tone between the ith and jth vibrations.

The observed values are summarized in the third column of Table XVII. The values due to $(B'-B'')$ are shown in the fifth column. The values β_i used are given in Table XVIII. It can be seen that the largest value of $(B'-B'')$ is 0.003 cm^{-1} for $\nu_2+\nu_6$; nevertheless, this is within the range of error of the measurement of $(A'-A'')-(B'-B'')$. Therefore, the assumption that $B'=B''$, which was used in the analysis of the perpendicular band, seems reasonable.

The appropriate combinations of observed values and the already-known values of α_i or β_i determine some unknown rotational correction terms, α_i.

The most probable values for α_i are given in Table XVIII. The values $(A'-A'')-(B'-B'')$ calculated by using α_i and β_i in Table XVIII are given in the fourth column of Table XVII. They are in rather good agreement with the observed values.

Summary

The infrared spectra of most of the overtones and combination tones of methyl bromide have been obtained. In the perpendicular band, the rotational fine structures have been observed. The values of the Coriolis coupling constants obtained from the analysis of the rotational fine structures are consistent with those obtained from the analysis of the fundamentals. It has been seen that, if one takes 0.03 as the error of the observed values of the Coriolis coupling constants, one can use the observed values to calculate the force constants.

Most of the vibrational anharmonic terms, x_{ij}, have been obtained, but they are tentative yet.

The rotational correction terms, α_1 and α_2 have been estimated from the combination-bands analyses.

This work was supported by a grant-in-aid for fundamental scientific research from the Ministry of Education, to which the authors' thanks are due.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

TABLE I. THE OBSERVED FREQUENCIES OF THE PARALLEL BANDS OF CH_3Br

	ν_0^{obs} cm^{-1}	ν_0^{pred} cm^{-1}	$\varDelta$ cm^{-1}
$2\nu_1$	5882	5944	−62
$\nu_1+\nu_2$	4163	4277	−114
$\nu_1+\nu_3$	3582	3583	−1
$2\nu_2$	2596	2610	−14
$\nu_2+\nu_3$	1911	1916	−5
$2\nu_3$ (^{79}Br)	1215	1222	−8
(^{81}Br)	1213		
$2\nu_4$	6046	6113.2	−67
$\nu_4+\nu_6$	4003	4010.9	−8
$2\nu_5$	2863	2885.6	−23

TABLE II. VIBRATIONAL FREQUENCIES AND CORIOLIS COUPLING CONSTANTS OF THE FUNDAMENTALS FOR CH_3Br[3,5)]

	ν_0, cm^{-1}	ζ
ν_1	2972	—
ν_2	1305	—
ν_3	611	—
ν_4	3056.6	0.059
ν_5	1442.8	−0.244
ν_6	954.3	0.216

TABLE III. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_1+\nu_4$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	$\varDelta$ cm^{-1}
−10	5845.09	5845.26	−0.17
−9	55.87	55.88	−0.01
−8	66.42	66.35	0.07
−7	76.92	76.69	0.23
−6	87.00	86.88	0.12
−5	96.84	96.94	−0.10
−4	5907.09	5906.85	0.24
−3	16.54	16.62	−0.08
−2	26.01	26.26	−0.25
−1	35.53	35.75	−0.22
0	44.98	45.10	−0.12
1	54.65	54.31	0.34
2	(64.94)	63.38	(1.56)
3	(75.26)	72.31	(2.95)

$\nu_0+[A'(1-\zeta)^2-B']=5945.1\pm0.3$ cm^{-1}
$2[A'(1-\zeta)-B']=9.3\pm0.1$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.07\pm0.01$ cm^{-1}
$\nu_0=5940.6\pm0.3$ cm^{-1}
$\zeta=0.01_9\pm0.01_2$

TABLE IV. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_1+\nu_5$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	$\varDelta$ cm^{-1}
−6	(4359.23)	4345.53	(13.70)
−5	(67.49)	58.02	(9.47)
−4	(76.00)	70.36	(5.64)
−3	(86.81)	82.55	(4.26)
−2	(96.28)	94.60	(1.68)
−1	(4407.12)	4406.50	(0.62)
0	18.25	18.26	−0.01
1	29.88	29.87	0.01
2	41.35	41.33	0.02
3	52.66	52.65	0.01
4	63.76	63.82	−0.06
5	74.88	74.85	0.03

$\nu_0+[A'(1-\zeta)^2-B']=4418.3\pm0.1$ cm^{-1}
$2[A'(1-\zeta)-B']=11.68\pm0.09$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.07\pm0.02$ cm^{-1}
$\nu_0=4411.1\pm0.2$ cm^{-1}
$\zeta=-0.22\pm0.01$

TABLE V. THE OBSERVED FREQUENCIES OF THE BAND $\nu_1+\nu_6$

m	ν^{obs}, cm^{-1}
−2	3906.99
−1	15.09
0	22.60
1	29.52
2	36.24
3	41.84
4	50.67
5	56.78
6	63.54
7	69.46
8	76.33

TABLE VI. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_2+\nu_4$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−8	4283.91	4283.74	0.17
−7	92.69	92.86	−0.17
−6	4301.86	4301.97	−0.11
−5	11.07	11.07	0.00
−4	20.18	20.15	0.03
−3	29.20	29.22	−0.02
−2	38.33	38.28	0.05
−1	47.50	47.33	0.17
0	56.50	56.36	0.14
1	65.40	65.38	0.02
2	74.34	74.39	−0.05
3	83.17	83.38	−0.21
4	92.27	92.36	−0.09
5	4401.25	4401.33	−0.08
6	10.50	10.29	0.21
7		19.23	
8	(28.84)	28.16	(0.68)

$\nu_0+[A'(1-\zeta)^2-B']=4356.4\pm0.2$ cm^{-1}
$2[A'(1-\zeta)-B']=9.03\pm0.02$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.006\pm0.005$ cm^{-1}
$\nu_0=4352.1\pm0.1$ cm^{-1}
$\zeta=0.057\pm0.005$

TABLE VII. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_2+\nu_5$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−10	2629.03	2628.98	0.05
−9	41.59	41.51	0.08
−8	54.01	53.98	0.03
−7	(66.11)	66.39	(−0.28)
−6	78.61	78.74	−0.13
−5	90.91	91.03	−0.12
−4	2703.11	2703.26	--0.15
−3	15.38	15.44	−0.06
−2	27.59	27.55	0.04
−1	39.58	39.60	−0.02
0	51.59	51.59	0.00
1	(63.72)	63.52	(0.20)
2	75.47	75.39	0.08
3	(87.41)	87.21	(0.20)
4	98.97	98.96	0.01
5	2810.53	2810.65	−0.12
6	22.25	22.28	−0.03

$\nu_0+[A'(1-\zeta)^2-B']=2751.59\pm0.07$ cm^{-1}
$2[A'(1-\zeta)-B']=11.96\pm0.02$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.030\pm0.003$ cm^{-1}
$\nu_0=2744.13\pm0.11$ cm^{-1}
$\zeta=-0.236\pm0.005$

TABLE VIII. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_2+\nu_6$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−9	2194.75	2194.73	0.02
−8	2201.44	2201.48	−0.04
−7	(08.03)	08.33	(−0.30)
−6	15.35	15.27	0.08
−5	22.33	22.32	0.01
−4	29.39	29.47	−0.08
−3	36.63	36.71	−0.08
−2	(44.31)	44.06	(0.25)
−1	51.59	51.50	0.09
0	58.99	59.04	−0.05
1	66.73	66.68	0.05
2	74.49	74.42	0.07
3	82.26	82.26	0.00
4	90.08	90.20	−0.12
5	98.28	98.24	0.04

$\nu_0+[A'(1-\zeta)^2-B']=2259.04\pm0.07$ cm^{-1}
$2[A'(1-\zeta)-B']=7.59\pm0.02$ cm^{-1}
$(A'-A'')-(B'-B'')=0.050\pm0.004$ cm^{-1}
$\nu_0=2256.09\pm0.08$ cm^{-1}
$\zeta=0.205\pm0.003$

TABLE IX. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $2\nu_4$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−8	(6013.55)	6012.13	(1.42)
−7	23.77	23.69	0.08
−6	35.10	35.14	−0.04
−5	46.39	46.48	−0.09
−4	57.62	57.70	−0.08
−3	68.80	68.81	−0.01
−2	79.93	79.81	0.12
−1	90.80	90.70	0.10
0	6101.51	6101.48	0.03
1	12.17	12.15	0.02
2	22.66	22.70	−0.04
3	33.10	33.14	−0.04
4	43.47	43.47	0.00
5	53.57	53.69	−0.12
6	63.81	63.80	0.01
7	73.88	73.79	0.09
8	83.58	83.68	−0.10
9	93.52	93.45	0.07
10	(6203.29)	6203.11	(0.18)
11	(12.25)	12.66	(−0.41)
12	(19.98)	22.09	(−2.11)

$\nu_0+[A'(1-\zeta)^2-B']=6101.48\pm0.07$ cm^{-1}
$2[A'(1-\zeta)-B']=10.72\pm0.01$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.056\pm0.002$ cm^{-1}
$\nu_0=6095.44\pm0.09$ cm^{-1}
$\zeta=-0.120\pm0.005$

TABLE X. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_4+\nu_5$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−9	4410.50	4410.44	0.06
−8	19.35	19.46	−0.11
−7	28.32	28.31	0.01
−6	37.02	37.01	0.01
−5	45.62	45.55	0.07
−4	53.94	53.93	0.01
−3	62.23	62.16	0.07
−2	70.10	70.23	−0.13
−1	78.14	78.14	0.00
0	85.92	85.89	0.03
1	93.49	93.48	0.01
2	4500.86	4500.92	−0.06
3	08.19	08.20	−0.01
4	(15.15)	15.32	(−0.17)
5	22.29	22.29	0.00
6	29.14	29.09	0.05
7	(36.17)	35.74	(0.43)

$\nu_0+[A'(1-\zeta)^2-B']=4485.89\pm0.07$ cm^{-1}
$2[A'(1-\zeta)-B']=7.67\pm0.01$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.079\pm0.002$ cm^{-1}
$\nu_0=4482.79\pm0.07$ cm^{-1}
$\zeta=0.177\pm0.003$

TABLE XI. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_5+\nu_6$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−6	(2335.15)	2336.27	(−1.12)
−5	(45.37)	45.91	(−0.54)
−4	(55.09)	55.55	(−0.46)
−3	(64.83)	65.20	(−0.37)
−2	(74.48)	74.86	(−0.38)
−1	84.51	84.53	−0.02
0	94.23	94.21	0.02
1	2403.95	2403.90	0.05
2	13.57	13.59	−0.02
3	23.27	23.29	−0.02
4	32.99	33.00	−0.01
5	42.67	42.72	−0.05
6	52.47	52.44	0.03
7	62.25	62.18	0.07
8	71.88	71.92	−0.04

$\nu_0+[A'(1-\zeta)^2-B']=2394.21\pm0.07$ cm^{-1}
$2[A'(1-\zeta)-B']=9.68\pm0.04$ cm^{-1}
$(A'-A'')-(B'-B'')=0.004\pm0.005$ cm^{-1}
$\nu_0=2389.40\pm0.09$ cm^{-1}
$\zeta=-0.005\pm0.005$

TABLE XII. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $2\nu_6$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−6	(1791.62)	1795.70	(−4.08)
−5	1809.01	1809.38	−0.37
−4	23.63	23.14	0.49
−3	37.02	36.97	0.05
−2	50.77	50.88	−0.11
−1	64.91	64.86	0.05
0	78.75	78.91	−0.16
1	93.19	93.04	0.15
2		1907.24	
3	1921.52	21.51	0.01
4	35.56	35.86	−0.30
5	50.31	50.28	0.03
6	64.93	64.77	0.16

$\nu_0+[A'(1-\zeta)^2-B']=1878.9\pm0.3$ cm^{-1}
$2[A'(1-\zeta)-B']=14.09\pm0.06$ cm^{-1}
$(A'-A'')-(B'-B'')=0.04\pm0.02$ cm^{-1}
$\nu_0=1868.8\pm0.3$ cm^{-1}
$\zeta=-0.426\pm0.009$

TABLE XIII. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_2+\nu_4+\nu_5$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−6	5728.62	5728.57	0.05
−5	37.27	37.22	0.05
−4	45.69	45.71	−0.02
−3	53.95	54.05	−0.10
−2	62.16	62.23	−0.07
−1	70.21	70.26	−0.05
0	78.02	78.13	−0.11
1	(85.23)	85.85	(−0.62)
2	93.53	93.41	0.12
3	5801.05	5800.81	0.24
4	08.15	08.06	0.09
5	14.90	15.15	−0.25
6	(22.21)	22.09	(0.12)

$\nu_0+[A'(1-\zeta)^2-B']=5778.1\pm0.2$ cm^{-1}
$2[A'(1-\zeta)-B']=7.80\pm0.03$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.08\pm0.01$ cm^{-1}
$\nu_0=5781.1\pm0.2$ cm^{-1}
$\zeta=0.165\pm0.005$

TABLE XIV. THE OBSERVED AND CALCULATED FREQUENCIES OF THE BAND $\nu_4+2\nu_5$

m	ν^{obs} cm^{-1}	ν^{calcd} cm^{-1}	Δ cm^{-1}
−6	(5820.85)	5819.53	(1.32)
−5	(31.81)	31.17	(0.64)
−4	42.26	42.39	−0.13
−3	53.31	53.22	0.09
−2	63.76	63.65	0.11
−1	73.78	73.67	0.11
0	83.20	83.29	−0.09
1	92.47	92.51	−0.04
2	5901.21	5901.33	−0.12
3	09.70	09.74	−0.04
4	17.85	17.75	0.10
5	(27.71)	25.36	(2.35)
6	(37.23)	32.57	(4.66)
7	(46.59)	39.38	(7.21)

$\nu_0+[A'(1-\zeta)^2-B']=5883.3\pm0.2$ cm^{-1}
$2[A'(1-\zeta)-B']=9.42\pm0.04$ cm^{-1}
$(A'-A'')-(B'-B'')=-0.201\pm0.005$ cm^{-1}
$\nu_0=5878.6\pm0.2$ cm^{-1}
$\zeta=-0.021\pm0.005$

TABLE XV. VIBRATIONAL FREQUENCIES AND CORIOLIS COUPLING CONSTANTS OF THE PERPENDICULAR BANDS OF CH_3Br

	Observed values		Predicted values		$\nu_0^{obs}-\nu_0^{pred.}$ cm^{-1}
	ν_0, cm^{-1}	ζ	ν_0, cm^{-1}	ζ	
$\nu_1+\nu_4$	5940.6	0.02	6029.0	0.059	−88.4
$\nu_1+\nu_5$	4411.1	−0.22	4415.2	−0.244	−4.1
$\nu_1+\nu_6$	3920	0.23	3926.7	0.216	−7
$\nu_2+\nu_4$	4352.1	0.057	4361.6	0.059	−9.5
$\nu_2+\nu_5$	2744.13	−0.236	2747.8	−0.244	−3.7
$\nu_2+\nu_6$	2256.1	0.205	2259.3	0.216	−3.2
$2\nu_4$	6095.44	−0.120	6113.2	−0.118	−17.8
$\nu_4+\nu_5$	4482.79	0.177	4499.4	0.185	−16.6
$\nu_5+\nu_6$	2389.40	−0.005	2397.1	0.028	−7.7
$2\nu_6$	1868.8	−0.426	1908.6	−0.432	−39.8
$\nu_2+\nu_4+\nu_5$	5781.1	0.165	5804.4	0.185	−23.3
$\nu_4+2\nu_5$	5878.6	−0.021	5942.2	$\begin{cases}-0.547\\ 0.059\end{cases}$	−63.6

TABLE XVI. VIBRATIONAL ANHARMONIC TERMS OF CH_3Br, cm^{-1}

x_{11}	−31	x_{13}	−1
x_{12}	−114	x_{23}	−5
x_{22}	−7	x_{33}	−4
$x_{44}+g_{44}$	−8.9	$x_{56}+g_{56}$	−7.7
$x_{45}+g_{45}$	−16.6	$x_{66}+g_{66}$	−19.9
$x_{46}+g_{46}$	−8		
$x_{44}-g_{44}$	−34		
$x_{55}-g_{55}$	−12		
x_{44}	−21		
g_{44}	+12		
x_{14}	−88	x_{24}	−10
x_{15}	−4	x_{25}	−4
x_{16}	−7	x_{26}	−3

TABLE XVII. THE OBSERVED AND CALCULATED VALUES FOR $(A'-A'')-(B'-B'')$ OF CH_3Br, cm^{-1}

		$(A'-A'')-(B'-B'')$		$-(B'-B'')$
		obs.	calcd.	
1	$\nu_1+\nu_4$	−0.07	−0.06	−0.00009*
2	$\nu_1+\nu_5$	−0.07	−0.08	−0.00066*
3	$\nu_2+\nu_4$	−0.006	−0.008	0.00191
4	$\nu_2+\nu_5$	−0.030	−0.027	0.00134
5	$\nu_2+\nu_6$	0.050	0.050	0.0031
6	$2\nu_4$	−0.056	−0.060	−0.00018
7	$\nu_4+\nu_5$	−0.079	−0.079	−0.00075
8	$\nu_5+\nu_6$	0.004	−0.020	0.00044
9	$2\nu_6$	0.04	0.056	0.0022
10	$\nu_2+\nu_4+\nu_5$	−0.08	−0.057	0.00125
11	$\nu_4+2\nu_5$	−0.201	−0.127	−0.00141

* It is assumed that $\beta_1=0$.

TABLE XVIII. THE ROTATIONAL CORRECTION TERMS OF CH_3Br, cm^{-1}

α_1	0.03	the present work
α_2	−0.020	the present work
α_3		
α_4	0.030	Morino et al.5), Rank et al.2), the present work
α_5	0.048	Brown et al.4) with $\alpha_4=0.030$, Morino et al.5), the present work
α_6	−0.027	Morino et al.,5) the present work
β_1		
β_2	0.00200	Brown et al.4) with $\beta_4=-0.00009$
β_3	0.0024	Kraitchman et al.10)
β_4	−0.00009	Rank et al.2)
β_5	−0.00066	Brown et al.4) with $\beta_4=-0.00009$
β_6	0.0011	Hirose11)