Microwave Spectrum of the Ethylmethyl Ether Molecule

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Abstract: We have observed rotational transitions of ethylmethyl ether (CH$_3$CH$_2$OCH$_3$) in the 24-110 GHz frequency range. We newly assigned the transitions of four Q-branch series for J=1-38 with Ka=0-5 and six R-branch series of b-type transitions for J=7-37 with Ka=0-3. All these assigned transitions were observed to be split into two or four components due to the internal rotations of the methyl groups. We analyzed the averaged frequencies of the split components on the basis of the Watson $A$-reduced Hamiltonian, neglecting the effect of the internal rotations. A total of 122 transitions were fitted to eight molecular parameters to a 1σ standard deviation of 24 kHz. The parameters $A$, $B$, $C$ and $D_J$ were improved, and $D_{JK}$, $D_k$, $d_J$ and $d_K$ were determined for the first time.

Keywords: Ethylmethyl ether, spectroscopy, microwave.

Introduction

The ethylmethyl ether molecule (CH$_3$CH$_2$OCH$_3$) has internal rotations of two CH$_3$ groups of threefold symmetry. The molecular structure is shown in Figure 1. This molecule is a slightly asymmetric top molecule and has the dipole moment components along principal inertia a- and b-axis. Since the component along a-axis is so small that the transitions assigned so far are all b-type transitions. The first microwave spectra of this molecule and its isotopic species were observed in the frequency range from...
8.5 to 34 GHz by Hayashi and Kuwada, and molecular parameters $A$, $B$, $C$ and $D_J$ and components of dipole moment in the ground state were reported. They also reported the potential barrier heights 2554 and 3294 cal/mol for OCH$_3$ and CH$_3$C groups, respectively [1].

In this study, we have observed rotational transitions in the 24-110 GHz frequency range and newly assigned 111 transitions according to the prediction from the molecular parameters determined by Hayashi et al. A rotational transition split into two or four components due to the internal rotation of the two methyl groups: a transition split into two components due to the internal rotation of OCH$_3$ group, and each component further splits into two components due to the internal rotation of CH$_3$C group. However, for lower J transitions these latter splitting are too small to be observed with a conventional microwave spectrometer. We analyzed the averaged frequencies of the split components on the basis of the Watson $A$-reduced Hamiltonian [2], neglecting the effect of the internal rotations. A total of 122 transitions including 11 transitions observed by Hayashi [1] were fitted to the Hamiltonian with a 1σ standard deviation of 24 kHz.

**Figure 1.** Molecular Structure of C$_2$H$_5$OCH$_3$
Experimental

The block diagram of spectrometer is shown in Figure 2. [3] The fundamental microwave source is a microwave synthesizer (HP83642A) operating in the frequency range from 2 to 40 GHz. In the frequency range from 40 to 110 GHz, millimeter-wave source modules (Hewlett Packard, HP83556A, HP83557A and HP8358A) were used. In the measurement above 40 GHz, the source frequency was modulated by small amplitude of a 50 kHz sinusoidal-wave, and the detected microwave signal was demodulated by a lock-in amplifier operated in the 2f mode. The second derivative of an absorption line shape was recorded on a personal computer. In the measurement below 40 GHz, the square-wave Stark modulation at 100 kHz was used to prevent distortion of baselines. The accuracy of observed frequencies is estimated to be better than 70 kHz for the Stark modulation measurements and better than 50 kHz for the source modulation measurements. The observation was made at room temperature.

![Figure 2. Block diagram of Millimeter-wave-Spectrometer.](image)

Observed Spectrum and analysis

Transitions of Q-branch series for Ka=1 ← 0, 2 ← 1, and 3 ← 2 and those of R-branch series for Ka=1 ← 0, 0 ← 1, 1 ← 2, 2 ← 3, 3 ← 4 and 4 ← 5 were assigned.
(a) Q-branch transition

$J_{1,J-1} \leftarrow J_{0,0}$ series: The absorption line for the $26_{1,25} \leftarrow 26_{0,26}$ transition is shown in Figure 3 as a typical rotational line. All the lines belonging to this series show doublet structures due to the internal rotation of the -OCH$_3$ group. Separations of the components in this series are from 0.36 to 1.03 MHz, which increase with $J$. The assignment to this series was made with the help of calculated frequencies using the rotational constants reported by Hayashi et al. To find the successive $J$ transitions in the Q-branch series, we used the power series expansion of $J (J+1)$. We assigned the transitions of this series with $J=1$ to 29.

Q-branch series transitions $J_{2,J-2} \leftarrow J_{1,J-1}$ with $J = 7$ to 9, with 12 to 16, and with $J=21$ to 37, $J_{2,J-1} \leftarrow J_{1,J}$ with $J =7$ and 12 to 22, and $J_{3,J-3} \leftarrow J_{2,J-2}$ with $J = 21$ to 30 were assigned. Absorption lines for $20_{2,19} \leftarrow 20_{1,20}$ and $30_{2,27} \leftarrow 30_{2,28}$ are shown in Figures 4 and 5, respectively. Transitions belonging to $J_{2,J-2} \leftarrow J_{1,J-1}$ series show the doublet structures and those belonging to $J_{2,J-1} \leftarrow J_{1,J}$, and $J_{3,J-3} \leftarrow J_{2,J-2}$ series show the quartet structures due to the internal rotations of the two methyl groups.

![Figure 3](image_url). Absorption line for the $26_{1,25} \leftarrow 26_{0,26}$ transition.
**Figure 4.** Absorption line for the $20_{2 \ 19} \leftarrow 20_{1 \ 20}$ transition.

**Figure 5.** Absorption lines for the $30_{3 \ 27} \leftarrow 30_{2 \ 28}$ and $31_{3 \ 28} \leftarrow 30_{4 \ 27}$ transitions.
(b) R-branch transition

The absorption line for $9_1 9 \leftarrow 8_0 8$ is shown in Figure 6 and that for $31_{32} 28 \leftarrow 30_{27}$ is included in Figure 5. The R-branch series transitions $(J+1)_{J+1} \leftarrow J_0 J$ with $J = 1$ to 10, $(J+1)_{0 J+1} \leftarrow J_J J$ with $J = 5$ to 14, $(J+1)_{1 J} \leftarrow J_{2 J+1}$ with $J = 10$ to 18, $(J+1)_{2 J+1} \leftarrow J_{3 J+2}$ with $J = 18, 21, 22, 23,$ and $24$, $(J+1)_{3 J+2} \leftarrow J_{4 J+3}$ with $J = 25$ to 31, and $(J+1)_{4 J+3} \leftarrow J_{5 J+4}$ with $J = 34$ to 38 were assigned. Transitions belonging to $(J+1)_{1 J+1} \leftarrow J_{0 J}$, $(J+1)_{0 J+1} \leftarrow J_{1 J}$, and $(J+1)_{J J} \leftarrow J_{2 J+1}$ series show the doublet structures and those belonging to $(J+1)_{J J+1} \leftarrow J_{3 J+2}$, $(J+1)_{3 J+2} \leftarrow J_{4 J+3}$, and $(J+1)_{4 J+3} \leftarrow J_{5 J+4}$ series show the quartet structures.

![Figure 6. Absorption line for the $9_1 9 \leftarrow 8_0 8$ transition.](image)

(c) Rotational Constant

A total of 322 lines have been observed and listed in Table 1. 122 b-type transitions in total were assigned. In this study, we obtained the average of frequencies of split components as the transition frequencies. The 122 transition frequencies are also listed in Table 1. We fitted these frequencies to determine the rotational constants using the Watson A-reduced Hamiltonian.

\[
    H = \frac{1}{2} \left[ (B+C)P^2 + \frac{1}{2}(B-C)(P_b^2 - P_c^2) \right] P_a^2 + \frac{1}{2}(B-C)(P_b^2 - P_c^2)
\]

\[
    -D_J(P^2) - D_{JK}P_a^2 + D_KP_a^4 - 2d_JP^2(P_b^2 - P_c^2) - d_K[P_a(P_b^2 - P_c^2) + (P_b^2 - P_c^2)]P_a^2,
\]

where $P$ is total angular momentum with components $P_a$, $P_b$ and $P_c$ along the $a$, $b$ and $c$-axis, respectively.
**Table 1.** Observed frequencies of Methylethyl Ether. (MHz)

| \(J'\) | \(K_a'\) | \(K_c'\) | \(J''\) | \(K_a''\) | \(K_c''\) | obs.     | average  | calc.* | ave.-calc |
|-------|--------|--------|-------|--------|--------|---------|----------|--------|-----------|
| 1     | 1      | 0      | 1     | 0      | 1      | 24100.391| 24100.572| 24100.621| -0.049    |
| 2     | 1      | 1      | 2     | 0      | 2      | 24370.963| 24371.207| 24371.192| 0.015     |
| 3     | 1      | 2      | 3     | 0      | 3      | 24781.024| 24781.266| 24781.260| 0.006     |
| 4     | 1      | 3      | 4     | 0      | 4      | 25335.610| 25335.853| 25335.856| -0.003    |
| 5     | 1      | 4      | 5     | 0      | 5      | 26041.543| 26041.661| 26041.638| 0.023     |
| 6     | 1      | 5      | 6     | 0      | 6      | 26906.707| 26906.893| 26906.834| 0.059     |
| 7     | 1      | 6      | 7     | 0      | 7      | 27940.930| 27941.173| 27941.138| 0.035     |
| 8     | 1      | 7      | 8     | 0      | 8      | 29155.356| 29155.644| 29155.562| 0.082     |
| 9     | 1      | 8      | 9     | 0      | 9      | 30562.021| 30562.251| 30562.211| 0.040     |
| 10    | 1      | 9      | 10    | 0      | 10     | 32173.777| 32174.020| 32173.987| 0.033     |
| 11    | 1      | 10     | 11    | 0      | 11     | 34003.959| 34004.270| 34004.200| 0.070     |
| 12    | 1      | 11     | 12    | 0      | 12     | 36065.858| 36066.118| 36066.090| 0.028     |
| 13    | 1      | 12     | 13    | 0      | 13     | 38372.022| 38372.292| 38372.271| 0.021     |
| 14    | 1      | 13     | 14    | 0      | 14     | 40933.710| 40934.145| 40934.126| 0.019     |
| 15    | 1      | 14     | 15    | 0      | 15     | 43760.760| 43761.165| 43761.174| -0.009    |
| 16    | 1      | 15     | 16    | 0      | 16     | 46860.100| 46860.495| 46860.474| 0.021     |
| 17    | 1      | 16     | 17    | 0      | 17     | 50236.686| 50236.100| 50236.094| 0.006     |
| \( J' \) | \( K_a' \) | \( K_c' \) | \( J'' \) | \( K_a'' \) | \( K_c'' \) | obs.     | average | calc.* | ave.-calc |
|-------|--------|--------|------|--------|--------|---------|---------|--------|-----------|
| 18    | 1      | 17     | 18   | 0      | 18     | 53888.277 | 53888.715 | 53888.703 | 0.012     |
|       |        |        |      |        |        | 53889.152 |          |         |           |
| 19    | 1      | 18     | 19   | 0      | 19     | 57814.889 | 57815.312 | 57815.310 | 0.002     |
|       |        |        |      |        |        | 57815.734 |          |         |           |
| 20    | 1      | 19     | 20   | 0      | 20     | 62008.831 | 62009.174 | 62009.169 | 0.005     |
|       |        |        |      |        |        | 62009.517 |          |         |           |
| 21    | 1      | 20     | 21   | 0      | 21     | 66459.481 | 66459.856 | 66459.850 | 0.006     |
|       |        |        |      |        |        | 66460.231 |          |         |           |
| 22    | 1      | 21     | 22   | 0      | 22     | 71153.089 | 71153.445 | 71153.457 | -0.012    |
|       |        |        |      |        |        | 71153.820 |          |         |           |
| 23    | 1      | 22     | 23   | 0      | 23     | 76072.572 | 76072.955 | 76072.978 | -0.023    |
|       |        |        |      |        |        | 76073.337 |          |         |           |
| 24    | 1      | 23     | 24   | 0      | 24     | 81198.339 | 81198.757 | 81198.738 | 0.019     |
|       |        |        |      |        |        | 81199.174 |          |         |           |
| 25    | 1      | 24     | 25   | 0      | 25     | 86508.462 | 86508.913 | 86508.923 | -0.010    |
|       |        |        |      |        |        | 86509.364 |          |         |           |
| 26    | 1      | 25     | 26   | 0      | 26     | 91979.716 | 91980.151 | 91980.167 | -0.016    |
|       |        |        |      |        |        | 91980.586 |          |         |           |
| 27    | 1      | 26     | 27   | 0      | 27     | 97587.703 | 97588.155 | 97588.165 | -0.010    |
|       |        |        |      |        |        | 97588.606 |          |         |           |
| 28    | 1      | 27     | 28   | 0      | 28     | 103307.822 | 103308.307 | 103308.312 | -0.005    |
|       |        |        |      |        |        | 103308.791 |          |         |           |
| 29    | 1      | 28     | 29   | 0      | 29     | 109115.821 | 109116.335 | 109116.321 | 0.014     |
|       |        |        |      |        |        | 109116.848 |          |         |           |

(b) \( J_{2J'2} \leftarrow J_{1J'1} \).
Table 1. Continued

| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs.  | average | calc.* | ave.-calc |
|----|-----|-----|-----|------|------|-------|---------|---------|-----------|
| 15 | 2   | 13  | 15  | 1    | 14   | 61505.288 | 61506.020 | 61506.015 | 0.005     |
| 16 | 2   | 14  | 16  | 1    | 15   | 60925.333 | 60926.037 | 60926.050 | -0.013    |
| 21 | 2   | 19  | 21  | 1    | 20   | 60649.185 | 60649.798 | 60649.791 | 0.007     |
| 22 | 2   | 20  | 22  | 1    | 21   | 61255.456 | 61256.041 | 61256.053 | -0.012    |
| 23 | 2   | 21  | 23  | 1    | 22   | 62120.858 | 62121.436 | 62121.460 | -0.024    |
| 24 | 2   | 22  | 24  | 1    | 23   | 63259.303 | 63259.878 | 63259.873 | 0.005     |
| 25 | 2   | 23  | 25  | 1    | 24   | 64683.379 | 64683.927 | 64683.916 | 0.011     |
| 26 | 2   | 24  | 26  | 1    | 25   | 66404.416 | 66404.943 | 66404.937 | 0.006     |
| 27 | 2   | 25  | 27  | 1    | 26   | 68432.372 | 68432.858 | 68432.873 | -0.015    |
| 28 | 2   | 26  | 28  | 1    | 27   | 70775.554 | 70776.018 | 70776.025 | -0.007    |
| 29 | 2   | 27  | 29  | 1    | 28   | 73440.285 | 73440.730 | 73440.750 | -0.020    |
| 30 | 2   | 28  | 30  | 1    | 29   | 76430.674 | 76431.100 | 76431.117 | -0.017    |
| 31 | 2   | 29  | 31  | 1    | 30   | 79748.116 | 79748.521 | 79748.533 | -0.012    |
| 32 | 2   | 30  | 32  | 1    | 31   | 83391.012 | 83391.401 | 83391.415 | -0.014    |
| 33 | 2   | 31  | 33  | 1    | 32   | 87354.527 | 87354.902 | 87354.908 | -0.006    |
| 34 | 2   | 32  | 34  | 1    | 33   | 91630.373 | 91630.736 | 91630.720 | 0.016     |
| 35 | 2   | 33  | 35  | 1    | 34   | 96206.714 | 96207.068 | 96207.061 | 0.007     |
| 36 | 2   | 34  | 36  | 1    | 35   | 101068.384 | 101068.734 | 101068.726 | 0.008     |
Table 1. Continued

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | obs. average | calc.* ave.-calc |
|------|--------|-------|-------|--------|--------|--------------|-----------------|
| 37   | 2      | 35    | 37    | 1      | 36     | 106196.973   | 106197.668      |
|      |        |       |       |        |        | 106197.321   | 106197.301      | 0.020           |
|      |        |       |       |        |        |              |                 |
|      |        |       |       |        |        |              |                 |
| (c) $J_{2J'1} \leftarrow J_{1J}$ |
| 7    | 2      | 6     | 7     | 1      | 7      | 75681.685    | 75682.676       | -0.009          |
|      |        |       |       |        |        | 75681.958    | 75682.685       | -0.009          |
|      |        |       |       |        |        | 75683.395    | 75683.667       | -0.009          |
| 12   | 2      | 11    | 12    | 1      | 12     | 82536.046    | 82536.998       | -0.014          |
|      |        |       |       |        |        | 82536.284    | 82537.012       | -0.014          |
|      |        |       |       |        |        | 82537.646    | 82538.015       | -0.014          |
| 13   | 2      | 12    | 13    | 1      | 13     | 84333.665    | 84334.639       | -0.011          |
|      |        |       |       |        |        | 84333.921    | 84334.650       | -0.011          |
|      |        |       |       |        |        | 84335.399    | 84335.570       | -0.011          |
| 14   | 2      | 13    | 14    | 1      | 14     | 86275.083    | 86276.064       | -0.006          |
|      |        |       |       |        |        | 86275.332    | 86276.791       | -0.006          |
|      |        |       |       |        |        | 86277.050    | 86277.512       | -0.006          |
| 15   | 2      | 14    | 15    | 1      | 15     | 88360.471    | 88361.486       | -0.024          |
|      |        |       |       |        |        | 88360.754    | 88362.238       | -0.024          |
|      |        |       |       |        |        | 88362.480    | 88362.510       | -0.024          |
| 16   | 2      | 15    | 16    | 1      | 16     | 90589.942    | 90590.948       | 0.026           |
|      |        |       |       |        |        | 90590.244    | 90591.696       | 0.026           |
|      |        |       |       |        |        | 90591.911    | 90591.911       | 0.026           |
| 17   | 2      | 16    | 17    | 1      | 17     | 92962.950    | 92963.905       | -0.025          |
|      |        |       |       |        |        | 92963.165    | 92964.625       | -0.025          |
|      |        |       |       |        |        | 92964.881    | 92964.881       | -0.025          |
| 18   | 2      | 17    | 18    | 1      | 18     | 95478.826    | 95479.816       | 0.025           |
|      |        |       |       |        |        | 95479.086    | 95480.548       | 0.025           |
|      |        |       |       |        |        | 95480.802    | 95480.802       | 0.025           |
| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | obs.   | average | calc.* | ave.-calc |
|------|--------|--------|------|--------|--------|--------|---------|--------|-----------|
| 19   | 2      | 18     | 19   | 1      | 19     | 98136.344 | 98137.339 | 98137.372 | -0.033    |
|      |        |        |      |        |        | 98136.599 |          |          |           |
|      |        |        |      |        |        | 98138.074 |          |          |           |
|      |        |        |      |        |        | 98138.337 |          |          |           |
| 20   | 2      | 19     | 20   | 1      | 20     | 100934.115 | 100935.127 | 100935.122 | 0.005     |
|      |        |        |      |        |        | 100934.391 |          |          |           |
|      |        |        |      |        |        | 100935.870 |          |          |           |
|      |        |        |      |        |        | 100936.132 |          |          |           |
| 21   | 2      | 20     | 21   | 1      | 21     | 103870.000 | 103871.039 | 103871.058 | -0.019    |
|      |        |        |      |        |        | 103870.324 |          |          |           |
|      |        |        |      |        |        | 103871.793 |          |          |           |
|      |        |        |      |        |        | 103872.038 |          |          |           |
| 22   | 2      | 21     | 22   | 1      | 22     | 106941.696 | 106942.751 | 106942.757 | -0.006    |
|      |        |        |      |        |        | 106942.005 |          |          |           |
|      |        |        |      |        |        | 106943.485 |          |          |           |
|      |        |        |      |        |        | 106943.816 |          |          |           |
|      |        |        |      |        |        |          |          |          |           |
| (d)  |        |        |      |        |        |          |          |          |           |
|      |        |        |      |        |        |          |          |          |           |
| 21   | 3      | 18     | 21   | 2      | 19     | 109216.845 | 109218.259 | 109218.246 | 0.013     |
|      |        |        |      |        |        | 109217.248 |          |          |           |
|      |        |        |      |        |        | 109219.266 |          |          |           |
|      |        |        |      |        |        | 109219.675 |          |          |           |
| 22   | 3      | 19     | 22   | 2      | 20     | 107655.357 | 107656.756 | 107656.741 | 0.015     |
|      |        |        |      |        |        | 107655.748 |          |          |           |
|      |        |        |      |        |        | 107657.764 |          |          |           |
|      |        |        |      |        |        | 107658.154 |          |          |           |
| 23   | 3      | 20     | 23   | 2      | 21     | 106030.312 | 106031.693 | 106031.690 | 0.003     |
|      |        |        |      |        |        | 106030.685 |          |          |           |
|      |        |        |      |        |        | 106032.695 |          |          |           |
|      |        |        |      |        |        | 106033.081 |          |          |           |
| 24   | 3      | 21     | 24   | 2      | 22     | 104364.899 | 104366.268 | 104366.268 | 0.000     |
|      |        |        |      |        |        | 104365.276 |          |          |           |
|      |        |        |      |        |        | 104367.265 |          |          |           |
|      |        |        |      |        |        | 104367.633 |          |          |           |
| 25   | 3      | 22     | 25   | 2      | 23     | 102684.844 | 102686.188 | 102686.187 | 0.001     |
|      |        |        |      |        |        | 102685.202 |          |          |           |
|      |        |        |      |        |        | 102687.175 |          |          |           |
|      |        |        |      |        |        | 102687.531 |          |          |           |
Table 1. Continued

| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs. | average | calc.* | ave.-calc |
|----|-----|-----|-----|------|------|------|---------|--------|----------|
| 26 | 3   | 23  | 26  | 2    | 24   | 101017.829, 101018.179, 101020.124, 101020.474 | 101019.152 | 101019.156 | -0.004 |
| 27 | 3   | 24  | 27  | 2    | 25   | 99393.033, 99393.333, 99395.329, 99395.602 | 99394.324 | 99394.316 | 0.008 |
| 28 | 3   | 25  | 28  | 2    | 26   | 97840.436, 97840.701, 97842.601, 97842.911 | 97841.662 | 97841.647 | 0.015 |
| 29 | 3   | 26  | 29  | 2    | 27   | 96390.259, 96390.460, 96392.321, 96392.582 | 96391.406 | 96391.396 | 0.010 |
| 30 | 3   | 27  | 30  | 2    | 28   | 95072.341, 95072.555, 95074.444, 95074.683 | 95073.506 | 95073.518 | -0.012 |

(2) R-branch transitions

(a) \((J+1)_1 \ J_{+1} \leftarrow J_0 \ J\)

| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs. | average | calc.* | ave.-calc |
|----|-----|-----|-----|------|------|------|---------|--------|----------|
| 2  | 1   | 2   | 1   | 0    | 1    | 39664.870, 39665.350 | 39665.110 | 39665.143 | -0.033 |
| 3  | 1   | 3   | 2   | 0    | 2    | 47313.703, 47314.384 | 47314.044 | 47314.057 | -0.013 |
| 4  | 1   | 4   | 3   | 0    | 3    | 54832.064, 54832.753 | 54832.409 | 54832.453 | -0.044 |
| 5  | 1   | 5   | 4   | 0    | 4    | 62224.580, 62225.150 | 62224.865 | 62224.872 | -0.007 |
| 6  | 1   | 6   | 5   | 0    | 5    | 69497.300, 69497.874 | 69497.587 | 69497.582 | 0.005 |
| 7  | 1   | 7   | 6   | 0    | 6    | 76658.282, 76658.855 | 76658.569 | 76658.570 | -0.001 |
| 8  | 1   | 8   | 7   | 0    | 7    | 83717.232, 83717.788 | 83717.510 | 83717.507 | 0.003 |
| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs. | average | calc.* | ave.-calc |
|----|-----|-----|-----|------|------|------|---------|--------|-----------|
| 9  | 1   | 9   | 8   | 0    | 8    | 90685.381 | 90685.660 | 90685.668 | -0.008    |
| 10 | 1   | 10  | 9   | 0    | 9    | 97575.563 | 97575.831 | 97575.803 | 0.028     |
| 11 | 1   | 11  | 10  | 0    | 10   | 104401.662 | 104401.933 | 104401.925 | 0.008     |

(b) \((J+1)_{0,1} \leftarrow J_{1,1}\)

| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs. | average | calc.* | ave.-calc |
|----|-----|-----|-----|------|------|------|---------|--------|-----------|
| 6  | 0   | 6   | 5   | 1    | 5    | 26206.237 | 26206.479 | 26206.514 | -0.035    |
| 7  | 0   | 7   | 6   | 1    | 6    | 34953.242 | 34953.498 | 34953.503 | -0.005    |
| 8  | 0   | 8   | 7   | 1    | 7    | 43783.052 | 43783.323 | 43783.315 | 0.008     |
| 9  | 0   | 9   | 8   | 1    | 8    | 52682.093 | 52682.390 | 52682.397 | -0.007    |
| 10 | 0   | 10  | 9   | 1    | 9    | 61635.779 | 61636.037 | 61636.021 | 0.016     |
| 11 | 0   | 11  | 10  | 1    | 10   | 70628.302 | 70628.567 | 70628.569 | -0.002    |
| 12 | 0   | 12  | 11  | 1    | 11   | 79643.660 | 79643.913 | 79643.910 | 0.003     |
| 13 | 0   | 13  | 12  | 1    | 12   | 88665.588 | 88665.833 | 88665.836 | -0.003    |
| 14 | 0   | 14  | 13  | 1    | 13   | 97678.312 | 97678.552 | 97678.549 | 0.003     |
| 15 | 0   | 15  | 14  | 1    | 14   | 106666.948 | 106667.175 | 106667.171 | 0.004     |

(c) \((J+1)_{1,1} \leftarrow J_{2,1,1}\)

| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs. | average | calc.* | ave.-calc |
|----|-----|-----|-----|------|------|------|---------|--------|-----------|
| 11 | 1   | 10  | 10  | 2    | 9    | 25260.962 | 25261.775 | 25261.822 | -0.047    |
| 12 | 1   | 11  | 11  | 2    | 10   | 34826.535 | 34827.289 | 34827.328 | -0.039    |
| 13 | 1   | 12  | 12  | 2    | 11   | 44500.354 | 44501.061 | 44501.095 | -0.034    |
| 14 | 1   | 13  | 13  | 2    | 12   | 54277.305 | 54278.044 | 54278.025 | 0.019     |
| $J'$ | $K_{a}'$ | $K_{c}'$ | $J''$ | $K_{a}''$ | $K_{c}''$ | obs.     | average | calc.* | ave.-calc |
|------|---------|---------|------|----------|---------|----------|---------|--------|-----------|
| 15   | 1       | 14      | 14   | 2        | 13      | 64151.563 | 64152.285 | 64152.275 | 0.010     |
|      |         |         |      |          |         | 64153.007 |          |        |           |
| 16   | 1       | 15      | 15   | 2        | 14      | 74116.549 | 74117.276 | 74117.178 | 0.098     |
|      |         |         |      |          |         | 74118.002 |          |        |           |
| 17   | 1       | 16      | 16   | 2        | 15      | 84164.426 | 84165.146 | 84165.170 | -0.024    |
|      |         |         |      |          |         | 84165.865 |          |        |           |
| 18   | 1       | 17      | 17   | 2        | 16      | 94287.001 | 94287.716 | 94287.718 | -0.002    |
|      |         |         |      |          |         | 94288.431 |          |        |           |
| 19   | 1       | 18      | 18   | 2        | 17      | 104474.574 | 104475.263 | 104475.274 | -0.011    |
|      |         |         |      |          |         | 104475.951 |          |        |           |

(d) $(J+1)_{2} J_{1} \rightleftharpoons J_{3} J_{2}$

| $J'$ | $K_{a}'$ | $K_{c}'$ | $J''$ | $K_{a}''$ | $K_{c}''$ | obs.     | average | calc.* | ave.-calc |
|------|---------|---------|------|----------|---------|----------|---------|--------|-----------|
| 19   | 2       | 17      | 18   | 3        | 16      | 41939.196 | 41940.599 | 41940.573 | 0.026     |
|      |         |         |      |          |         | 41939.562 |          |        |           |
|      |         |         |      |          |         | 41941.617 |          |        |           |
|      |         |         |      |          |         | 41942.022 |          |        |           |
| 22   | 2       | 20      | 21   | 3        | 19      | 71703.719 | 71705.157 | 71705.170 | -0.013    |
|      |         |         |      |          |         | 71704.122 |          |        |           |
|      |         |         |      |          |         | 71706.175 |          |        |           |
|      |         |         |      |          |         | 71706.613 |          |        |           |
| 23   | 2       | 21      | 22   | 3        | 20      | 81973.114 | 81974.524 | 81974.526 | -0.002    |
|      |         |         |      |          |         | 81973.490 |          |        |           |
|      |         |         |      |          |         | 81975.550 |          |        |           |
|      |         |         |      |          |         | 81975.943 |          |        |           |
| 24   | 2       | 22      | 23   | 3        | 21      | 92407.276 | 92408.703 | 92408.705 | -0.002    |
|      |         |         |      |          |         | 92407.691 |          |        |           |
|      |         |         |      |          |         | 92409.705 |          |        |           |
|      |         |         |      |          |         | 92410.141 |          |        |           |
| 25   | 2       | 23      | 24   | 3        | 22      | 102998.435 | 102999.828 | 102999.814 | 0.014     |
|      |         |         |      |          |         | 102998.776 |          |        |           |
|      |         |         |      |          |         | 103000.849 |          |        |           |
|      |         |         |      |          |         | 103001.251 |          |        |           |

(e) $(J+1)_{3} J_{2} \rightleftharpoons J_{4} J_{3}$

| $J'$ | $K_{a}'$ | $K_{c}'$ | $J''$ | $K_{a}''$ | $K_{c}''$ | obs.     | average | calc.* | ave.-calc |
|------|---------|---------|------|----------|---------|----------|---------|--------|-----------|
| 26   | 3       | 23      | 25   | 4        | 22      | 47419.843 | 47421.609 | 47421.596 | 0.013     |
|      |         |         |      |          |         | 47420.295 |          |        |           |
|      |         |         |      |          |         | 47422.928 |          |        |           |
|      |         |         |      |          |         | 47423.369 |          |        |           |
| J' | Kα' | Kc' | J'' | Kα'' | Kc'' | obs.   | average | calc.*  | ave.-calc |
|----|-----|-----|-----|------|------|--------|---------|---------|-----------|
| 27 | 3   | 24  | 26  | 4    | 23   | 56601.309 | 56603.066 | 56603.049 | 0.017     |
|    |     |     |     |      |      | 56601.766 |         |         |           |
|    |     |     |     |      |      | 56604.362 |         |         |           |
|    |     |     |     |      |      | 56604.827 |         |         |           |
| 28 | 3   | 25  | 27  | 4    | 24   | 65945.742 | 65947.471 | 65947.480 | -0.009    |
|    |     |     |     |      |      | 65946.172 |         |         |           |
|    |     |     |     |      |      | 65948.759 |         |         |           |
|    |     |     |     |      |      | 65949.209 |         |         |           |
| 29 | 3   | 26  | 28  | 4    | 25   | 75465.481 | 75467.221 | 75467.219 | 0.002     |
|    |     |     |     |      |      | 75465.927 |         |         |           |
|    |     |     |     |      |      | 75468.512 |         |         |           |
|    |     |     |     |      |      | 75468.962 |         |         |           |
| 30 | 3   | 27  | 29  | 4    | 26   | 85171.613 | 85173.342 | 85173.352 | -0.010    |
|    |     |     |     |      |      | 85172.054 |         |         |           |
|    |     |     |     |      |      | 85174.629 |         |         |           |
|    |     |     |     |      |      | 85175.071 |         |         |           |
| 31 | 3   | 28  | 30  | 4    | 27   | 95073.555 | 95075.287 | 95075.311 | -0.024    |
|    |     |     |     |      |      | 95073.982 |         |         |           |
|    |     |     |     |      |      | 95076.581 |         |         |           |
|    |     |     |     |      |      | 95077.031 |         |         |           |
| 32 | 3   | 29  | 31  | 4    | 28   | 105178.779 | 105180.513 | 105180.519 | -0.006    |
|    |     |     |     |      |      | 105179.233 |         |         |           |
|    |     |     |     |      |      | 105181.802 |         |         |           |
|    |     |     |     |      |      | 105182.238 |         |         |           |
| (f) (J+1)_{4,3} ← J_{5,4} |
| 35 | 4   | 31  | 34  | 5    | 30   | 72014.287 | 72016.208 | 72016.219 | -0.011    |
|    |     |     |     |      |      | 72014.879 |         |         |           |
|    |     |     |     |      |      | 72017.601 |         |         |           |
|    |     |     |     |      |      | 72018.066 |         |         |           |
| 36 | 4   | 32  | 35  | 5    | 31   | 80953.050 | 80954.830 | 80954.823 | 0.007     |
|    |     |     |     |      |      | 80953.504 |         |         |           |
|    |     |     |     |      |      | 80956.143 |         |         |           |
|    |     |     |     |      |      | 80956.623 |         |         |           |
| 37 | 4   | 33  | 36  | 5    | 32   | 90009.917 | 90011.705 | 90011.707 | -0.002    |
|    |     |     |     |      |      | 90010.384 |         |         |           |
|    |     |     |     |      |      | 90013.027 |         |         |           |
|    |     |     |     |      |      | 90013.490 |         |         |           |
Table 1. Continued

| J' | K' | J'' | K'' | obs.     | average  | calc.* | ave.-calc |
|----|----|-----|-----|----------|----------|--------|----------|
| 38 | 4  | 34  | 37  | 5        | 33       |        |          |
|    |    |     |     | 99197.885 | 99199.656 | 99199.648 | 0.008   |
|    |    |     |     | 99198.340 |          |        |          |
|    |    |     |     | 99200.972 |          |        |          |
|    |    |     |     | 99201.428 |          |        |          |
| 39 | 4  | 35  | 38  | 5        | 34       |        |          |
|    |    |     |     | 108530.180 | 108531.940 | 108531.936 | 0.004   |
|    |    |     |     | 108530.636 |          |        |          |
|    |    |     |     | 108533.247 |          |        |          |
|    |    |     |     | 108533.696 |          |        |          |

* Frequencies were calculated with the molecular parameters in Table 2.

The determined rotational constants are listed in Table 2. A, B, C and DJ were refined and DJK, DK, dJ and dK were determined for the first time.

Table 2. Molecular parameters of Ethylmethyl Ether

| Parameter       | Value(MHz)        |
|-----------------|-------------------|
| A-(B+C)/2       | 23966.5365(83)    |
| (B+C)/2         | 4025.2902(12)     |
| (B-C)/2         | 134.15358(12)     |
| DJ              | 0.9734(12) ×10⁻³  |
| DJK             | -0.2476(18) ×10⁻² |
| DK              | 0.7514(70) ×10⁻¹  |
| dJ              | 0.87151(81) ×10⁻⁴ |
| dK              | -0.934(27) ×10⁻³  |

, 0.024 MHz

* The numbers in parentheses are 1σ uncertainties in units of the last quoted digits.

Conclusions

The potential barrier heights for the CH₃ torsions are relatively high, and the torsional splittings are small in the ground state. The average frequencies of these split components were determined as transition frequencies. These frequencies were fitted to the asymmetric rotor Hamiltonian with 8 molecular parameters with a 1σ standard deviation of 24 kHz.
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