Rotational dependence of the dipole moment of CH₃D

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Radio frequency modulated side bands of the C¹⁴O₂ P(18) laser line were used to perform infrared--infrared double resonance between the first order Stark components of the ν₂ P(10,1) transition of CH₃D. The dipole moment in the J = 10, K = 1 level in the ground state has been measured to be (1.03 ± 0.01) × 10⁻³ D, which is very different from the previously reported values of around 5.65 × 10⁻³ D. This difference has been explained as due to rotational dependence of the dipole moment. Combining the present result with the previous molecular beam measurements by Wofsy, Muentner, and Klempner, we have obtained the rotational dependence of the dipole moment derived from Stark measurements in the form μ_22(J, K) = ±[(5.657 ± 0.004) - (0.0427 ± 0.0009)J(J + 1)] + (0.0696 ± 0.0026)K² × 10⁻³ D. The upper sign would be consistent with ab initio calculations of the signs of the dipole derivatives. A theory was developed to calculate the above coefficients of J(J + 1) and K² for CH₃D. It has been demonstrated that they can be completely predicted from the θ'' parameter of CH₄. The prediction agreed with the observed values within the quoted uncertainties. This theoretical information was indispensable in determining which of the two observed double resonance signals corresponded to the ground state. The apparent contradiction of the present result with that of Ozier, Ho, and Birnbaum, who reported that the dipole moments of CH₃D determined from the intensities of R branch spectral lines are independent of J, is explained as due to the fact that the rotational dependence of the dipole moment is different depending on the method of determination. Their measurements are shown to be consistent with the above parameters.

I. INTRODUCTION

Although the CH₄ molecule does not possess a permanent dipole moment in the ground rovibrational state, its deuterated species CH₃D has a small dipole moment due to the breakdown of tetrahedral symmetry. This dipole moment has been measured to be (5.68 ± 0.3) × 10⁻³ D from the intensity of the far infrared rotational spectrum, and to be 5.6409 × 10⁻³ and 5.6794 × 10⁻³ D for the (J, K) = (1, 1) and (2, 2) rotational levels, respectively, from the Stark shifts of molecular beam electric resonances.

We have used the rf modulated side bands of infrared laser radiation to perform infrared--infrared double resonance between Stark components exploiting the accidental coincidence between the ν₂ P(10,1) transition of CH₃D and the C¹⁴O₂ P(18) 9.3 µm band laser line. This method gives two sets of resonances corresponding to the first order Stark shifts in the excited and the ground state, but it is difficult to tell experimentally which of the sets corresponds to the ground state. We have obtained two possible values (9.14 ± 0.1) × 10⁻³ and (9.03 ± 0.1) × 10⁻³ D for the CH₃D dipole moment in the (10,1) level of the ground state. In either case, the dipole moment is very different from previous values mentioned earlier. With hindsight, it occurred to us that the dipole moment induced by the centrifugal distortion may explain this difference; such a dipole moment causes observable rotational transitions in CH₄. Normally, in polar molecules, such a dipole moment is a small fraction of the permanent dipole moment, but in CH₃D, it is comparable to the latter for J > 10.

Therefore, an attempt was made to use the rotational dependence of the dipole moment of CH₃D theoretically calculated by Aliev and Mikhailov to decide which of the two values of the dipole moment is the correct one. In this process, we have discovered that the rotational dependence of the dipole moment of CH₃D determined from the first order Stark shift is completely predictable from the distortion dipole coefficient θ'' of CH₄. In this paper, we present the theoretical basis of this fact and our experimental results which agree with the theory.

Ozier et al. studied the intensities of rotational spectral lines of CH₃D and concluded that the dipole moment of CH₃D is independent of J, a result which apparently contradicts our observation. This problem is also discussed.

II. THEORY

A. Rotational dependence of dipole moment

The theoretical expression for the rotational dependence of the dipole moment depends on how it is measured. The space-fixed component μₓ of the effective dipole moment operator is given as

$$\muₓ = \sum_a (\lambda_2 a \bar{\mu}_a + \bar{\mu}_a \lambda_2) / 2,$$

(1)

where λ₂a are direction cosines and μ_a are the molecule-fixed dipole operators which can be expressed in terms of the distortion dipole coefficients θ'' as

$$\bar{\mu}_a = \bar{\mu}_a^{(3)} + \sum_{a,t} \theta''_a \bar{J}_a \bar{J}_t .$$

(2)

From symmetry considerations, we find for a molecule with C₃v symmetry that there are only four independent nonvanishing θ''s, θ''₁ = θ''₄, θ''₂ = θ''₅, θ''₃ = θ''₆ = θ''₇ = θ''₈, and

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\[ \theta^1_{\xi} = -\theta^1_{\eta} = -\theta^1_{\xi} = -\theta^1_{\eta}, \]
where the \( \xi \) axis is taken along the \( C_3 \) axis, the \( \eta \) axis on a \( \sigma_\parallel \) plane, and the \( \eta \) axis perpendicular to them.

The rotational dependence of the dipole moment \( \mu \) determined from the first order Stark shift is obtained by calculating \( \langle J, K, m | \mu \sigma_{\parallel} | J, K, m \rangle \). Substituting Eq. (2) into (1) and using matrix elements of direction cosines, we find

\[
\mu_{\xi}(J, K) = \mu_{\xi}^{(1)} - \theta_{\xi}^1 + (\theta_{\xi}^{1} + 2\theta_{\xi}^{1}J(J+1))\frac{K^2}{2}.
\]

On the other hand, the rotational dependence of the dipole moment \( \mu \) determined from the intensities of \( R \) branch rotational lines is obtained by calculating \( \langle J+1, K, m | \mu \sigma_{\parallel} | J, K, m \rangle \) to be\(^{13} \)

\[
\mu_{\xi}(J, K) = \mu_{\xi}^{(1)} - \theta_{\xi}^1 + (\theta_{\xi}^{1} + 2\theta_{\xi}^{1}J(J+1))\frac{K^2}{2}.
\]

The difference between Eqs. (3) and (4) explains the apparent contradiction between our measurement and that by Ozier et al.\(^{1} \)

**B. \( \theta \) constants of CH\(_3\)D**

The theoretical formula for the distortion dipole coefficients \( \theta^p \) is\(^3 \)

\[
\theta^p_{\alpha} = \frac{\hbar^2}{2 \pi I_r} \sum_{\nu} \frac{1}{\lambda_{\alpha}} \left( \frac{\theta_{\mu \alpha}}{Q_{\nu \alpha}} \right) \left( \theta_{\nu \alpha}^{(1)} \right)_a \left( \theta_{\nu \alpha}^{(1)} \right)_b,
\]

\[
\theta^p_{\alpha} = \frac{\hbar^2}{2 \pi I_r} \sum_{\nu \alpha} \left( \theta_{\nu \alpha}^{(1)} \right)_a \left( \theta_{\nu \alpha}^{(1)} \right)_b,
\]

where \( Q_{\alpha} \) are normal coordinates and \( S_{\alpha} \) are internal coordinates. We wish to employ Eq. (6) to relate the \( \theta \) constants of CH\(_3\)D to \( \theta^p \) of CH\(_4\). The compliance constants \( \left( F^{-1} \right)_{\alpha \alpha} \) are isotopically invariant if the same internal coordinates are used for both molecules. The isotopic variation of the dipole derivatives \( \partial \theta_{\nu \alpha}^{(1)}/\partial S_{\alpha} \) depends on the equilibrium dipole moment,\(^14 \) but this vanishes for a nonpolar molecule like methane and the derivatives are invariant, assuming that the equilibrium axes have the same orientation for different isotopes. Therefore, the axes for CH\(_4\) should be chosen with the \( C_3 \) orientation appropriate to CH\(_3\)D. The inertial derivatives \( \partial \theta_{\nu \alpha}^{(1)}/\partial S_{\alpha} \) can be calculated by the method of Aliev and Aleksanyan\(^{15,16} \)

\[
(\theta_{\nu \alpha}^{(1)}/\partial S_{\alpha}) = \sum_{p} (G^{(1)})_{\alpha \beta} Y_{\nu \alpha}^p,
\]

where

\[
Y_{\nu \alpha}^p = 2 \sum_{i} \left[ r_{\alpha i} \left( \frac{\partial S_{\beta}}{\partial y_{\nu i}} \right)_e + r_{\alpha i} \left( \frac{\partial S_{\beta}}{\partial y_{\nu i}} \right)_e \right], \ \ \beta \neq \gamma \neq \delta \neq \beta,
\]

\[
Y_{\nu \alpha}^p = -2 \sum_{i} \left[ r_{\alpha i} \left( \frac{\partial S_{\beta}}{\partial y_{\nu i}} \right)_e - r_{\alpha i} \left( \frac{\partial S_{\beta}}{\partial y_{\nu i}} \right)_e \right], \ \ \beta \neq \gamma.
\]

For the same orientation of axes for different isotopes, the \( Y_{\nu \alpha}^p \) are isotopically invariant.

For CH\(_4\), the \( xyz \) axes are customarily taken along the three \( S_{\alpha} \) symmetry axes, essentially a \( D_{3h} \) type of orientation. For the \( C_{3v} \) molecules, the axes employed are the \( \xi \eta \zeta \) axes of Dorney and Watson,\(^17 \) the direction cosines between the two systems being

\[
\begin{bmatrix}
  x \\
  y \\
  z \\
\end{bmatrix} = \begin{bmatrix}
  -1/\sqrt{6} & 1/\sqrt{2} & 1/\sqrt{3} \\
  -1/\sqrt{6} & -1/\sqrt{2} & 1/\sqrt{3} \\
  2/\sqrt{6} & 0 & 1/\sqrt{3} \\
\end{bmatrix} \begin{bmatrix}
  \xi \\
  \eta \\
  \zeta \\
\end{bmatrix}.
\]

The bond CH\(_{3}\) (which becomes CD of CH\(_3\)D) is assumed to lie along the \( \xi \) axis and the bond CH\(_{4}\) in the \( \zeta \) plane.

Six of the nine \( C_{3v} \) coordinates are taken as

\[
\begin{align*}
S_1 &= \frac{1}{2}(r_1 + r_2 + r_3 + r_4), \\
S_2 &= \frac{1}{\sqrt{6}}(3r_1 - r_2 - r_3 - r_4), \\
S_4 &= \frac{R}{\sqrt{6}}(\alpha_{13} + \alpha_{24} + \alpha_{14} - \alpha_{13} - \alpha_{14}), \\
S_5 &= \frac{R}{\sqrt{6}}(2\alpha_{13} - \alpha_{14} - \alpha_{13} - 2\alpha_{14} - \alpha_{12} - \alpha_{13}), \\
S_6 &= \frac{2}{\sqrt{3}}(2r_1 - r_2 - r_3), \\
S_8 &= \frac{R}{\sqrt{6}}(2\alpha_{13} - \alpha_{14} - \alpha_{13} - 2\alpha_{14} + \alpha_{12} + \alpha_{13}),
\end{align*}
\]

and the remaining three coordinates \( S_3, S_6, S_8 \) and \( S_w \) are the \( E \) partners of the three \( E \) coordinates \([Eq. (11)](\text{ref:11})\). In these equations, \( r_1 \) is the extension of the CH\(_{3}\) bond and \( \alpha_{14} \) is the increase of the H(\( \xi \))CH(\( \xi \)) angle.

From the symmetry of the charge distribution, the nonzero dipole derivatives are

\[
\begin{align*}
\mu_1^{(1)} &= (\mu_{\xi}/\partial S_{3}) = (\mu_{\xi}/\partial S_{3}) = (\mu_{\xi}/\partial S_{3}), \\
\mu_5^{(1)} &= (\mu_{\xi}/\partial S_{3}) = (\mu_{\xi}/\partial S_{4}) = (\mu_{\xi}/\partial S_{4}), \\
\mu_6^{(1)} &= (\mu_{\xi}/\partial S_{3}) = (\mu_{\xi}/\partial S_{4}) = (\mu_{\xi}/\partial S_{4}).
\end{align*}
\]

The elements of the tensor \( Y_{\nu \alpha}^p \) are readily calculated by means of Eq. (8) from the derivatives (\( \partial \theta_{\nu \alpha}^{(1)}/\partial y_{\nu \alpha} \)), which are the same as Wilson's \( s \) vector components.\(^18 \) They are

\[
\begin{align*}
\rho & Y_{\nu \alpha}^{(1)}/R_e, \\
1 & 8/3, 8/3, 0, \\
8/3 & -8/3, 8/3, 0, \\
4/3 & 4/3, 4/3, 0, \\
2/3 & 0, 4/3, 4/3, \\
3/3 & 0, -8/3, 8/3, 0, \\
4/3 & 0, 8/3, 0, 4/3, \\
4/3 & 0, 8/3, 0, -4/3, 0
\end{align*}
\]

The inversion of the \( A_1 \) and \( E \) blocks of the \( G \) matrix for use in Eq. (7) is tedious but straightforward. The expressions finally obtained for the independent \( \theta \) constants of CH\(_3\)D are

\[
\begin{align*}
\theta_{\xi}^2 &= \frac{2F^2m_R}{3/3} (2M_3 + M_3), \\
\theta_{\eta}^2 &= \frac{F^2}{6/3} M_2 \left[ (9m_m m_D - 5m_c m_B + 28m_D m_h - 12m_m^2)M_3 \\
- 2m_m (m_c + 7m_D - 3m_B)M_3 \right],
\end{align*}
\]

\[ J. Chem. Phys., Vol. 70, No. 12, 15 June 1979 \]
\( \delta_{T}^2 = \frac{\hbar^2 R_x}{12 \sqrt{3} M_1^2} [(5m_c m_D + 3 m_c m_D + 32 m_D m_D) M_1^2 \]
\[ - 2(3m_c m_D - m_c m_D + 8 m_D m_D) M_1^2 \]
\[ + 2 \frac{h^2}{\sqrt{3} M_1^2} R_4 \{ - 2 M_1^2 + M_1^3 \}, \]
\[ \delta_T = \frac{2h^2 m_R R_4}{3 \sqrt{6} M_1^2} \]

where
\[ M = m_c + m_D + 3 m_H, \]
\[ I = \frac{8}{3} m_R R_4, \]
\[ I = \frac{R^2}{3M} [m_c (5m_H + 3m_D) + 4m_H (3m_H + 5m_D)], \]
\[ M_1^2 = \sum \mu_n^2 (F_n^3)_{\text{max}}, \]

The quantities \( M_1^2 \) and \( M_1^3 \) are isotopically invariant.

The constant \( \delta_T^2 \), being independent of \( m_D \), has the same value for CH3D and CH3H. For the latter molecule, it is related to the constant \( \delta_T^2 \) according to
\[ \delta_T^2 = \frac{2 \sqrt{3}}{3} \delta_T^2. \]

From Eqs. (17)–(20), we obtain
\[ \delta_T^2 + 2 \delta_T = \frac{3(m_c m_D + 5 m_D m_D - m_D m_H)}{2 m_H M_1^2} \]
\[ \delta_T^2 = \frac{1}{\sqrt{3}} \delta_T^2. \]

Equations (25) and (26) allow the rotational dependence of the linear Stark effect of CH3D [Eq. (3)] to be predicted by appropriate mass scaling of the CH parameter. On the other hand, the \( \mu_n \) given in Eq. (4) requires the independent parameter \( \delta_T^2 \).

The dipole derivatives \( \mu_1^2 \) and \( \mu_1^4 \) can be derived from the intensities of the infrared fundamentals of CH3H. The usual sign ambiguities in the transition moments allow four different solutions. The principal information obtained from the experimental value of \( \delta_T^2 \) is the relative sign of \( \mu_1^2 \) and \( \mu_1^4 \), which proves to be the same as that previously calculated ab initio. The remaining ambiguity is in the overall sign, which could be determined by measuring the sign of \( \delta_T^2 \). We thus have
\[ \delta_T^2 = 2.783 \times 10^{-5} \text{ D}, \]

where the upper sign is favored by the ab initio calculation. This upper sign implies that the D end of the molecule becomes increasingly negative as \( J \) increases. From Eq. (26), the value of \( \delta_T^2 + 2 \delta_T \) for CH3D is
\[ \delta_T^2 + 2 \delta_T = -1.5908 \delta_T^2 = 4.427 \times 10^{-5} \text{ D}. \]

The independent constant \( \delta_T^2 \) cannot be obtained by mass scaling of \( \delta_T^2 \), and must be calculated from Eq. (18). With the data employed previously, \( \delta_T^2 \) calculated value is
\[ \delta_T^2 = 1.328 \times 10^{-5} \text{ D}. \]

### III. EXPERIMENT AND RESULTS

The infrared–infrared double resonance was carried out by using a CO2 laser line (\( \nu_1 \)) and its amplitude modulation side bands (\( \nu_i \pm \nu_j \)). The side bands were generated by passing the CO2 laser radiation through a Cd–Te electro-optic crystal to which a high radiofrequency (\( \nu_f \)) field (~2 kV) was applied. The side bands as well as the carrier were passed through a Stark cell filled with ~4 mTorr of CH3D which contained Stark electrodes separated by 1 mm quartz spacers. A linear polarizer placed after the electro-optic modulator and in front of the Stark cell was used to adjust the condition of double resonance. The quarter wave plate was not used in this experiment so that \( \phi \) was always equal to zero. The polarization of the laser initially was parallel to the Stark field. Therefore, if the polarizer was set perpendicular to the Stark field (\( \theta = 0 \)), the double resonance was caused solely from the two side bands with polarization perpendicular to the Stark field. The resonance condition for this is \( \Delta M = 2 \)
\[ \frac{2K}{J(J+1)} = \frac{\mu E}{\hbar} = 2\nu_r. \]

When the polarizer was slightly tilted (\( \theta \neq 0 \)), the carrier also contributed to double resonance. After the polarizer, the carrier electric field had components \( E_x = E \sin \beta \) and \( E_y = E \cos \beta \), and for a small angle, \( E_x \gg E_y \). Therefore, the double resonance caused by the carrier and a side band is still dominantly \( \Delta M = \pm 2 \), for which the resonance condition is obtained by replacing \( 2\nu_r \) in Eq. (28) with \( \nu_r \). A smaller signal with the \( \Delta M = \pm 1 \) selection rule caused by the carrier and a side band overlaps with the signal given in Eq. (28).

The possible coincidences between the CO2-13CO2-\( ^{14} \text{O}_2 \) laser lines and CH3D absorption were searched for based on the recent high resolution infrared results of Pinkley et al. About 20 near coincidences have been tested by the method of zero-field level crossing. It was found that only the coincidence between the \( ^{14} \text{O}_2 P(18) \) line and the \( \nu_r P(10, 1) \) transition of CH3D is sufficiently close (\( \nu_1 - \nu_0 \approx 100 \text{ MHz} \)) to carry out the double resonance experiment.

Examples of the observed double resonance signals are shown in Fig. 1. Figure 1(a) shows a set of double resonance signals which was assigned to the \( J = 9, K = 2 \) level in the \( \nu_6 \) state. The signals marked 0, \( \nu_0 \), and \( 2\nu_r \) correspond, respectively, to the resonance condition \( \mu E/J(J+1)k = 0, \nu_r, \) and \( 2\nu_r \). The 0 signal was caused by level crossings. The derivative shape of the resonance is due to square wave Stark modulation (~kV/cm, 10 kHz) and phase sensitive detection. The applied radiofrequency was 1.138 MHz and the polarizer setting was \( \theta = 20^\circ \). Three radio frequencies were used for the \( \nu_6 \) state. The frequencies and the corresponding resonant electric fields for the \( \nu_r \) signal are listed in Table I. The dipole moment in the \( \nu_r \) state is listed in Table I. The dipole moment in the \( \nu_r \) state is listed in Table I. The dipole moment in the \( \nu_r \) state is listed in Table I.

Figure 1(b) shows the \( \nu_r \) signal which was assigned to the ground state with \( J = 10, K = 1 \) based on the theoretical calculation given in the previous section. This corresponds to a very small dipole moment and the double resonance was observable only with a low rf frequency of 0.5722 MHz and a high electric field of 60.6 kV/cm.
The slope overlapping with the double resonance signal is due to the normal laser Stark spectrum which is not resolved into individual \( m \) components and appear rather strongly due to the required high voltage of Stark modulation. Because of this background and because of the slow Stark shift, the measurement of this double resonance signal is less accurate than that for the signal given in Fig. 1(a). The dipole moment of the ground state with \( J = 10, \ K = 1 \) has been determined to be

\[
|\mu_\delta(10, 1)| = (1.03 \pm 0.1) \times 10^{-3} \text{ D}.
\]

**TABLE I. Resonant electric fields and radiofrequencies.**

<table>
<thead>
<tr>
<th>Radiofrequency (MHz)</th>
<th>( E ) (kV/cm)</th>
<th>( \mu ) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state, ( J = 10, K = 1 )</td>
<td>0.5722</td>
<td>60.60</td>
</tr>
<tr>
<td>( \nu_\alpha ) State, ( J = 9, K = 2 )</td>
<td>1.139</td>
<td>13.57</td>
</tr>
<tr>
<td>( \nu_\beta ) State, ( J = 10, K = 1 )</td>
<td>2.727</td>
<td>32.41</td>
</tr>
<tr>
<td>( \nu_\gamma ) State, ( J = 9, K = 2 )</td>
<td>4.990</td>
<td>59.46</td>
</tr>
</tbody>
</table>

**TABLE II. Summary of the dipole moments of CH\(_3\)D (in \( 10^{-6} \) D).**

<table>
<thead>
<tr>
<th>Observed</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_\delta(1, 1) ) ( ^a )</td>
<td>5.6409(30)</td>
</tr>
<tr>
<td>( \mu_\delta(2, 2) ) ( ^a )</td>
<td>5.6798(30)</td>
</tr>
<tr>
<td>( \mu_\delta(10, 1) )</td>
<td>1.03(10)</td>
</tr>
<tr>
<td>( \mu_\delta(9, 2) )</td>
<td>3.75(5)</td>
</tr>
<tr>
<td>( \mu_\delta^{(1)} - \theta_\delta )</td>
<td>( \pm 5.657(4) )</td>
</tr>
<tr>
<td>( \theta_\delta + 2\theta_\delta )</td>
<td>( \pm 0.0427(9) )</td>
</tr>
<tr>
<td>( \theta_\delta )</td>
<td>( \pm 0.0268(26) )</td>
</tr>
</tbody>
</table>

\( ^a \) Reference 2.

Using this dipole moment and the values by Wofay et al.\(^2\) for the \( (1, 1) \) and \( (2, 2) \) levels, we obtain the following values from Eq. (3):

\[
\begin{align*}
\mu_\delta^{(1)} - \theta_\delta &= (5.657 \pm 0.004) \times 10^{-3} \text{ D}, \\
\theta_\delta + 2\theta_\delta &= (4.27 \pm 0.09) \times 10^{-3} \text{ D}, \\
\theta_\delta &= (2.69 \pm 0.26) \times 10^{-3} \text{ D}.
\end{align*}
\]

The latter two values agree well with the theoretical values given in the previous section of \( \pm 4.427 \times 10^{-4} \) and \( \pm 2.783 \times 10^{-4} \) D, respectively. The signs of the experimentally determined values indicate that the permanent dipole moment \( \mu_\delta \) is such that the \( D \) end of the molecule is negative, according to the discussion given in the previous section. The slight discrepancy between the observed and calculated values may be due to the effects of zero-point vibrations in producing departures from the isotopic relations, but is in any case close to the uncertainties of quantities used in the calculation.

**IV. DISCUSSION**

The theoretical and experimental results described in this paper and summarized in Table II indicate that the rotational dependence of the dipole moment of CH\(_3\)D can be predicted from that of CH\(_4\). Since \( \theta_\delta \) of CH\(_3\)D is also predictable from that of CH\(_4\), this means in general that once \( \theta_\delta \) of CH\(_4\) is known, the rotational dependence of the dipole moment of CH\(_3\)D, CHD\(_3\), and XD\(_4\), can be predicted with accuracy, where X can be any of C, Si, Ge, etc.

One remaining problem to be discussed is the observation by Ozier et al.\(^1\) that the dipole moment of CH\(_3\)D determined from the intensities of the \( J + 1 - J \) rotational spectral lines has a very small \( J \) dependence. Since each of the lines is composed of many lines with \( K \leq J \), the effective dipole moment for such a transition can be expressed as

\[
\mu_{J, \text{eff}} = \left\{ \sum_{K=0}^{J} \left| \mu_\delta(J, K) \right|^2 w(J, K) \right\}^{1/2},
\]

where the dipole moment \( \mu_\delta(J, K) \) is given in Eq. (4) and the weight factor \( w(J, K) \) is

\[
w(J, K) = (J + 1)^{2} - K^{2} \right|_{A}^{B} \exp[-(A - B)hK^{2}/kT] ,
\]

with \( f_{X} = 1 \) for \( K \neq 3n \) and 0 and \( f_{X} = 2 \) for \( K = 3n \) (\( n \neq 0 \)).
TABLE III. Observed and calculated effective dipole moments $|\mu_{e,eff}|$ (in $10^{-3}$ D) of CH$_3$D determined from the intensities of $J+1-J$ transitions.

<table>
<thead>
<tr>
<th>$J$</th>
<th>Observed$^a$</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.45 ± 0.38</td>
<td>5.637</td>
</tr>
<tr>
<td>6</td>
<td>5.66 ± 0.29</td>
<td>5.687</td>
</tr>
<tr>
<td>7</td>
<td>5.48 ± 0.34</td>
<td>5.682</td>
</tr>
<tr>
<td>8</td>
<td>5.50 ± 0.29</td>
<td>5.651</td>
</tr>
<tr>
<td>9</td>
<td>5.25 ± 0.45</td>
<td>5.691</td>
</tr>
<tr>
<td>10</td>
<td>5.42 ± 0.35</td>
<td>5.682</td>
</tr>
<tr>
<td>11</td>
<td>5.44 ± 0.29</td>
<td>5.642</td>
</tr>
<tr>
<td>12</td>
<td>5.58 ± 0.33</td>
<td>5.660</td>
</tr>
</tbody>
</table>

$^a$Reference 1.

Using the values $\mu_{x}^{\langle 0 \rangle} - \theta_{x}^{\langle 0 \rangle} = \pm 5.657 \times 10^{-3}$ D and $\theta_{u}^{ \langle 0 \rangle} - 2\theta_{x}^{\langle 0 \rangle} = \pm 6.96 \times 10^{-5}$ D which are experimentally determined and $\theta_{u}^{\langle 0 \rangle} = \pm 1.328 \times 10^{-3}$ D which is theoretically calculated, together with the rotational constants $A = 5.240$ cm$^{-1}$ and $B = 3.882$ cm$^{-1}$, we calculate the effective values of the dipole moment as listed in Table III. It is seen that the calculated values agree well with the observed values reported by Ozier et al.

We would like to thank I. Ozier for his critical reading of the manuscript and helpful discussions.


