

Rotational dependence of the dipole moment of CH₃D

James K. G. Watson

Department of Chemistry, The University, Southampton SO9 5NH, England

Michio Takami^{a)} and Takeshi Oka

Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada
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Radio frequency modulated side bands of the C¹⁸O₂ P(18) laser line were used to perform infrared-infrared double resonance between the first order Stark components of the ν_6 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 $(1.03 \pm 0.1) \times 10^{-3}$ 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, Muentert, and Klemperer, we have obtained the rotational dependence of the dipole moment derived from Stark measurements in the form $\mu_{\text{Stark}}(J, K) = \mp \{ (5.657 \pm 0.004) - (0.0427 \pm 0.0009)J(J+1) + (0.0696 \pm 0.0026)K^2 \} \times 10^{-3}$ 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 K^2 for CH₃D. It has been demonstrated that they can be completely predicted from the θ_2^{ν} 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 $(5.68 \pm 0.3) \times 10^{-3}$ D from the intensity of the far infrared rotational spectrum,¹ 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.²

We have used the rf modulated side bands of infrared laser radiation³⁻⁵ to perform infrared-infrared double resonance between Stark components exploiting the accidental coincidence between the ν_6 P(10, 1) transition of CH₃D and the C¹⁸O₂ P(18) 9.3 μ m 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 $(9.14 \pm 0.1) \times 10^{-3}$ and $(1.03 \pm 0.1) \times 10^{-3}$ 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 CH₄.⁶⁻⁹ Normally, in polar molecules, such a dipole moment is a small fraction of the permanent dipole moment,¹⁰⁻¹² but in CH₃D, it is comparable to the latter for $J \sim 10$.

^{a)}NRCC Visiting Scientist, Summer 1978. Permanent address: The Institute of Physical and Chemical Research, Wako, Saitama, Japan 351.

Therefore, an attempt was made to use the rotational dependence of the dipole moment of CH₃D theoretically calculated by Aliev and Mikhaylov¹³ 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_2^{ν} 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.*¹ 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 $\tilde{\mu}_z$ of the effective dipole moment operator is given as⁶

$$\tilde{\mu}_z = \sum_{\alpha} (\lambda_{z\alpha} \tilde{\mu}_{\alpha} + \tilde{\mu}_{\alpha} \lambda_{z\alpha}) / 2, \quad (1)$$

where $\lambda_{z\alpha}$ are direction cosines and $\tilde{\mu}_{\alpha}$ are the molecule-fixed dipole operators which can be expressed in terms of the distortion dipole coefficients $\theta_{\alpha}^{\beta\gamma}$ as

$$\tilde{\mu}_{\alpha} = \tilde{\mu}_{\alpha}^{(0)} + \sum_{\beta, \gamma} \theta_{\alpha}^{\beta\gamma} J_{\beta} J_{\gamma}. \quad (2)$$

From symmetry considerations, we find for a molecule with C_{3v} symmetry that there are only four independent nonvanishing $\theta_{\alpha}^{\beta\gamma}$'s, $\theta_1^{\alpha\alpha} = \theta_2^{\alpha\alpha}$, $\theta_1^{\alpha\beta} = \theta_2^{\alpha\beta}$, $\theta_1^{\beta\alpha} = \theta_2^{\beta\alpha} = \theta_1^{\alpha\beta} = \theta_2^{\alpha\beta}$, and

$\theta_{\xi}^{\xi\xi} = -\theta_{\xi}^{\eta\eta} = -\theta_{\eta}^{\xi\xi} = -\theta_{\eta}^{\eta\xi}$, where the ξ axis is taken along the C_3 axis, the ξ axis on a σ_v plane, and the η axis perpendicular to them.

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

$$\mu_s(J, K) = \mu_s^{(0)} - \theta_{\xi}^{\xi\xi} + (\theta_{\xi}^{\xi\xi} + 2\theta_{\xi}^{\eta\xi})J(J+1) + (\theta_{\xi}^{\xi\xi} - \theta_{\xi}^{\eta\xi} - 2\theta_{\xi}^{\eta\xi})K^2. \quad (3)$$

On the other hand, the rotational dependence of the dipole moment μ_r determined from the intensities of R branch rotational lines is obtained by calculating $\langle J+1, K, m | \bar{\mu}_z | J, K, m \rangle$ to be¹³

$$\mu_r(J, K) = \mu_s^{(0)} - \theta_{\xi}^{\xi\xi} + \theta_{\xi}^{\xi\xi}(J+1)^2 + (\theta_{\xi}^{\xi\xi} - \theta_{\xi}^{\eta\xi} - 2\theta_{\xi}^{\eta\xi})K^2. \quad (4)$$

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

B. θ constants of CH₃D

The theoretical formula for the distortion dipole coefficients $\theta_{\alpha}^{\beta\gamma}$ is⁶

$$\theta_{\alpha}^{\beta\gamma} = \frac{\hbar^2}{2I_{\beta}I_{\gamma}} \sum_k \frac{1}{\lambda_k} \left(\frac{\partial \mu_{\alpha}}{\partial Q_k} \right)_e \left(\frac{\partial I_{\beta\gamma}}{\partial Q_k} \right)_e \quad (5)$$

$$= \frac{\hbar^2}{2I_{\beta}I_{\gamma}} \sum_{m,n} (F^{-1})_{mn} \left(\frac{\partial \mu_{\alpha}}{\partial S_m} \right)_e \left(\frac{\partial I_{\beta\gamma}}{\partial S_n} \right)_e, \quad (6)$$

where Q_k are normal coordinates and S_m are internal coordinates. We wish to employ Eq. (6) to relate the θ constants of CH₃D to $\theta_{\alpha}^{\beta\gamma}$ of CH₄. The compliance constants $(F^{-1})_{mn}$ are isotopically invariant if the same internal coordinates are used for both molecules. The isotopic variation of the dipole derivatives $(\partial \mu_{\alpha} / \partial S_m)_e$ 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 CH₄ should be chosen with the C_{3v} orientation appropriate to CH₃D. The inertial derivatives $(\partial I_{\beta\gamma} / \partial S_n)_e$ can be calculated by the method of Aliev and Aleksanyan^{15,16} as

$$(\partial I_{\beta\gamma} / \partial S_n)_e = \sum_p (G^{-1})_{np} Y_p^{\beta\gamma}, \quad (7)$$

where

$$Y_p^{\beta\beta} = 2 \sum_i \left[r_{i\beta}^e \left(\frac{\partial S_p}{\partial r_{i\beta}} \right) + r_{i\beta}^e \left(\frac{\partial S_p}{\partial r_{i\beta}} \right) \right], \quad \beta \neq \gamma \neq \delta \neq \beta, \quad (8)$$

$$Y_p^{\beta\gamma} = -2 \sum_i r_{i\beta}^e \left(\frac{\partial S_p}{\partial r_{i\beta}} \right) = -2 \sum_i r_{i\gamma}^e \left(\frac{\partial S_p}{\partial r_{i\beta}} \right), \quad \beta \neq \gamma.$$

For the same orientation of axes for different isotopes, the $Y_p^{\beta\gamma}$ are isotopically invariant.

For CH₄, the xyz axes are customarily taken along the three S_4 symmetry axes, essentially a D_{2d} 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

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1/\sqrt{6} & 1/\sqrt{2} & 1/\sqrt{3} \\ -1/\sqrt{6} & -1/\sqrt{2} & 1/\sqrt{3} \\ 2/\sqrt{6} & 0 & 1/\sqrt{3} \end{pmatrix} \begin{pmatrix} \xi \\ \eta \\ \zeta \end{pmatrix}. \quad (9)$$

The bond CH₍₁₎ (which becomes CD of CH₃D) is assumed to lie along the ζ axis and the bond CH₍₄₎ in the $\xi\zeta$ plane. Six of the nine C_{3v} coordinates are taken as

$$A_1 \begin{cases} S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4), \\ S_{3\xi} = \frac{1}{2\sqrt{3}}(3r_1 - r_2 - r_3 - r_4), \\ S_{4\xi} = \frac{R_e}{\sqrt{6}}(\alpha_{23} + \alpha_{24} + \alpha_{34} - \alpha_{12} - \alpha_{13} - \alpha_{14}), \end{cases} \quad (10)$$

$$E_a \begin{cases} S_{2\xi} = \frac{R_e}{2\sqrt{3}}(2\alpha_{23} - \alpha_{24} - \alpha_{34} + 2\alpha_{14} - \alpha_{12} - \alpha_{13}), \\ S_{3\xi} = \frac{1}{\sqrt{6}}(2r_4 - r_2 - r_3), \\ S_{4\xi} = \frac{R_e}{2\sqrt{3}}(2\alpha_{23} - \alpha_{24} - \alpha_{34} - 2\alpha_{14} + \alpha_{12} + \alpha_{13}), \end{cases} \quad (11)$$

and the remaining three coordinates $S_{2\eta}$, $S_{3\eta}$, and $S_{4\eta}$ are the E_b partners of the three E_a coordinates [Eq. (11)]. In these equations, r_i is the extension of the CH_(i) bond and α_{ij} is the increase of the H_(i)CH_(j) angle. The above choice of coordinates preserves the partitioning of the force constant matrix into blocks according to the symmetry species of the tetrahedral group T_d .

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

$$\mu_3' = (\partial \mu_x / \partial S_{3\xi}) = (\partial \mu_y / \partial S_{3\eta}) = (\partial \mu_z / \partial S_{3\xi}), \quad (12)$$

$$\mu_4' = (\partial \mu_x / \partial S_{4\xi}) = (\partial \mu_y / \partial S_{4\eta}) = (\partial \mu_z / \partial S_{4\xi}), \quad (13)$$

which are equal to the derivatives in the D_{2d} orientation

$$\mu_3' = (\partial \mu_x / \partial S_{3x}) = (\partial \mu_y / \partial S_{3y}) = (\partial \mu_z / \partial S_{3z}), \quad (14)$$

$$\mu_4' = (\partial \mu_x / \partial S_{4x}) = (\partial \mu_y / \partial S_{4y}) = (\partial \mu_z / \partial S_{4z}). \quad (15)$$

The elements of the tensor $Y_p^{\beta\gamma}$ are readily calculated by means of Eq. (8) from the derivatives $(\partial S_p / \partial r_{i\beta})_e$, which are the same as Wilson's s vector components.¹⁸ They are

p	$Y_p^{\xi\xi}/R_e$	$Y_p^{\eta\xi}/R_e$	$Y_p^{\zeta\xi}/R_e$
1	8/3	8/3	0
3 ξ	-8/3 $\sqrt{3}$	4/3 $\sqrt{3}$	0
4 ξ	8/3 $\sqrt{3}$	-4/3 $\sqrt{3}$	0
2 ξ	0	4/ $\sqrt{6}$	4/ $\sqrt{3}$
3 ξ	0	-8/3 $\sqrt{6}$	4/3 $\sqrt{3}$
4 ξ	0	8/3 $\sqrt{6}$	-4/3 $\sqrt{3}$

The inversion of the A_1 and E_a blocks of the G matrix for use in Eq. (7) is tedious but straightforward. The expressions finally obtained for the independent θ constants of CH₃D are

$$\theta_{\xi}^{\xi\xi} = \frac{2\hbar^2 m_H R_e}{3\sqrt{3} I_{\xi}^2} (-2M_3' + M_4'), \quad (17)$$

$$\theta_{\xi}^{\eta\xi} = \frac{\hbar^2 R_e}{6\sqrt{3} M I_{\xi}^2} [(9m_C m_D - 5m_C m_H + 28m_D m_H - 12m_H^2)M_3' - 2m_H(m_C + 7m_D - 3m_H)M_4'], \quad (18)$$

$$\theta_{\xi}^{\xi\xi} = \frac{\hbar^2 R_e}{12\sqrt{3} M I_{\xi}^2} [(5m_C m_H + 3m_C m_D + 32m_D m_H) M_3' - 2(3m_C m_D - m_C m_H + 8m_D m_H) M_4'] , \quad (19)$$

$$\theta_{\xi}^{\xi\xi} = \frac{2\hbar^2 m_H R_e}{3\sqrt{6} I_{\xi}^2} (-2M_3' + M_4') , \quad (20)$$

where

$$M = m_C + m_D + 3m_H , \quad (21)$$

$$I_{\xi} = \frac{2}{3} m_H R_e^2 , \quad (22)$$

$$I_{\xi} = \frac{R_e^2}{3M} [m_C(5m_H + 3m_D) + 4m_H(3m_H + 5m_D)] , \quad (23)$$

$$M_n' = \sum_m \mu_m'(F^{-1})_{mn} . \quad (24)$$

The quantities M_3' and M_4' are isotopically invariant.

The constant $\theta_{\xi}^{\xi\xi}$, being independent of m_D , has the same value for CH₃D and CH₄. For the latter molecule, it is related to the constant $\theta_{\xi}^{\xi\xi}$ according to

$$\theta_{\xi}^{\xi\xi} = \frac{2}{\sqrt{3}} \theta_{\xi}^{\xi\xi} . \quad (25)$$

From Eqs. (17)–(20), we obtain

$$\theta_{\xi}^{\xi\xi} + 2\theta_{\xi}^{\xi\xi} = - \frac{3(m_C m_D + 5m_D m_H - m_H^2) I_{\xi}^2}{2m_H M I_{\xi}^2} \theta_{\xi}^{\xi\xi} , \quad (26)$$

$$\theta_{\xi}^{\xi\xi} = \frac{1}{\sqrt{2}} \frac{I_{\xi}^2}{I_{\xi}^2} \theta_{\xi}^{\xi\xi} . \quad (27)$$

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 CH₄ parameter. On the other hand, the μ_I given in Eq. (4) requires the independent parameter $\theta_{\xi}^{\xi\xi}$.

The dipole derivatives μ_3' and μ_4' can be derived from the intensities of the infrared fundamentals of CH₄. The usual sign ambiguities in the transition moments allow four different solutions. The principal information obtained from the experimental value of $|\theta_{\xi}^{\xi\xi}|$ ⁸ is the relative sign of μ_3' and μ_4' , which proves to be the same as that previously calculated *ab initio*.¹⁹ The remaining ambiguity is in the overall sign, which could be determined by measuring the sign of $\theta_{\xi}^{\xi\xi}$. We thus have

$$\theta_{\xi}^{\xi\xi} = \mp 2.783 \times 10^{-5} \text{ D} ,$$

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_{ξ} increases. From Eq. (26), the value of $\theta_{\xi}^{\xi\xi} + 2\theta_{\xi}^{\xi\xi}$ for CH₃D is

$$\theta_{\xi}^{\xi\xi} + 2\theta_{\xi}^{\xi\xi} = -1.5908 \theta_{\xi}^{\xi\xi} = \pm 4.427 \times 10^{-5} \text{ D} .$$

The independent constant $\theta_{\xi}^{\xi\xi}$ cannot be obtained by mass scaling of $\theta_{\xi}^{\xi\xi}$, and must be calculated from Eq. (18). With the data employed previously,⁶ the calculated value is

$$\theta_{\xi}^{\xi\xi} = \pm 1.328 \times 10^{-5} \text{ D} .$$

III. EXPERIMENT AND RESULTS

The infrared-infrared double resonance was carried out by using a CO₂ laser line (ν_r) and its amplitude mod-

ulation side bands ($\nu_r \pm \nu_r$). The side bands were generated by passing the CO₂ laser radiation through a Cd-Te electro-optic crystal to which a high radiofrequency (ν_r) 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.³ The quarter wave plate³ was not used in this experiment so that ϕ 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 ($\Delta M = 2$)

$$\frac{2K}{J(J+1)} \cdot \frac{\mu E}{h} = 2\nu_r . \quad (28)$$

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 $E_{\parallel} = E \sin^2 \theta$ and $E_{\perp} = E \sin \theta \cos \theta$, and for a small angle, $E_{\perp} \gg E_{\parallel}$. 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 ν_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-C¹⁸O₂ laser lines and CH₃D absorption were searched for based on the recent high resolution infrared results of Pinkley *et al.*²⁰ About 20 near coincidences have been tested by the method of zero-field level crossing.^{21, 3-5} It was found that only the coincidence between the C¹⁸O₂ P(18) line and the ν_6 ^rP(10, 1) transition of CH₃D is sufficiently close ($|\nu_1 - \nu_0| \lesssim 100$ 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 ν_6 state. The signals marked 0, ν , and 2ν correspond, respectively, to the resonance condition $2\mu E/J(J+1)h = 0$, ν_r , and $2\nu_r$. The 0 signal was caused by level crossings.²¹ The derivative shape of the resonance is due to square wave Stark modulation (\sim 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 ν_6 state. The frequencies and the corresponding resonant electric fields for the ν signal are listed in Table I. The dipole moment in the $\nu_6(9, 2)$ level has been determined to be

$$|\mu_{\nu_6(9, 2)}| = (3.75 \pm 0.05) \times 10^{-3} \text{ D} .$$

Figure 1(b) shows the ν 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.

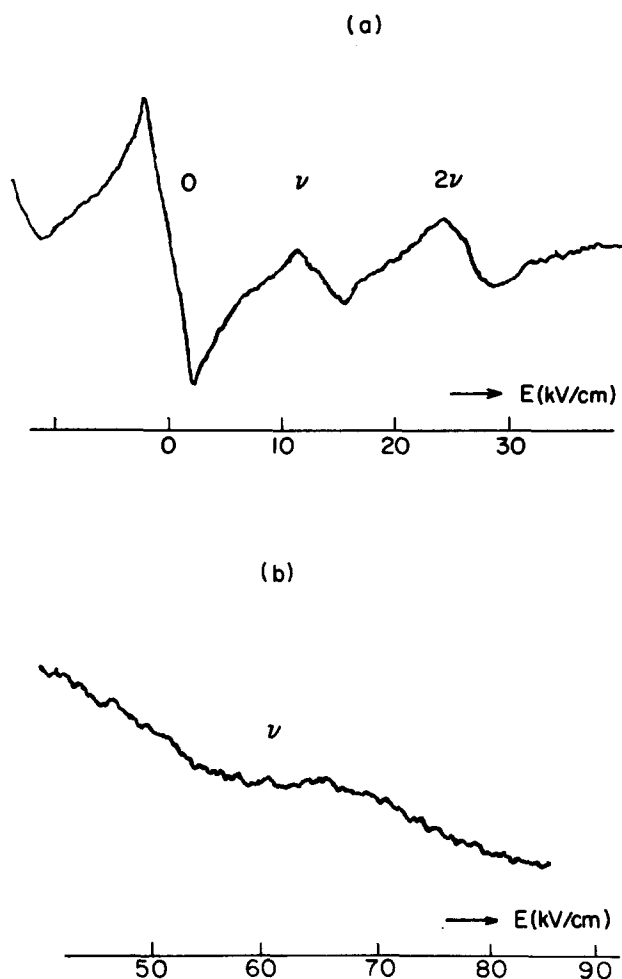


FIG. 1. Double resonance signals between Stark components of CH₃D. (a) Signals caused by the first order Stark shift of the $J=9$, $K=2$ level in the ν_6 state; $\nu_{rf}=1.139$ MHz, $P=4$ mTorr, $\theta=20^\circ$. (b) Signals caused by the first order Stark shift of the $J=10$, $K=1$ level in the ground state; $\nu_{rf}=0.5722$ MHz, $P=4$ mTorr, $\theta=20^\circ$. See the text for more detail.

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

$$|\mu_0(10, 1)| = (1.03 \pm 0.1) \times 10^{-3} \text{ D}.$$

TABLE I. Resonant electric fields and radiofrequencies.

	Radiofrequency (MHz)	E (kV/cm)	μ (D)
Ground state $J=10$, $K=1$	0.5722	60.60	1.03×10^{-3}
ν_6 State $J=9$, $K=2$	1.139	13.57	3.75×10^{-3}
	2.727	32.41	3.76×10^{-3}
	4.990	59.46	3.75×10^{-3}

TABLE II. Summary of the dipole moments of CH₃D (in 10^{-3} D).

	Observed	Theoretical
$ \mu_0(1, 1) ^a$	5.6409(30)	5.6412
$ \mu_0(2, 2) ^a$	5.6794(30)	5.6792
$ \mu_0(10, 1) $	1.03(10)	0.86
$ \mu_6(9, 2) $	3.75(5)	...
$\mu_\xi^{(0)} - \theta_\xi^{\xi\xi}$	$\mp 5.657(4)$...
$\theta_\xi^{\xi\xi} + 2\theta_\xi^{\xi\xi}$	$\pm 0.0427(9)$	± 0.0443
$\theta_\xi^{\xi\xi}$	$\mp 0.0269(26)$	∓ 0.0278

^aReference 2.

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

$$\mu_\xi^{(0)} - \theta_\xi^{\xi\xi} = \mp (5.657 \pm 0.004) \times 10^{-3} \text{ D},$$

$$\theta_\xi^{\xi\xi} + 2\theta_\xi^{\xi\xi} = \pm (4.27 \pm 0.09) \times 10^{-5} \text{ D},$$

$$\theta_\xi^{\xi\xi} = \mp (2.69 \pm 0.26) \times 10^{-5} \text{ D}.$$

The latter two values agree well with the theoretical values given in the previous section of $\pm 4.427 \times 10^{-5}$ and $\mp 2.783 \times 10^{-5}$ D, respectively. The signs of the experimentally determined values indicate that the permanent dipole moment μ_0 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 CH₃D can be predicted from that of CH₄. Since $\theta_\xi^{\xi\xi}$ of CD₄ is also predictable from that of CH₄, this means in general that once $\theta_\xi^{\xi\xi}$ of XH₄ is known, the rotational dependence of the dipole moment of XH₃D, XHD₃, and XD₄, 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 CH₃D 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

$$\mu_{J, \text{eff}} = \left\{ \sum_{K=0}^J [\mu_r(J, K)]^2 w(J, K) / \sum_{K=0}^J w(J, K) \right\}^{1/2}, \quad (29)$$

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

$$w(J, K) = [(J+1)^2 - K^2] f_r \exp[-(A-B)hK^2/kT], \quad (30)$$

with $f_r = 1$ for $K \neq 3n$ and 0 and $f_r = 2$ for $K = 3n$ ($n \neq 0$).

TABLE III. Observed and calculated effective dipole moments $|\mu_{J,\text{eff}}|$ (in 10^{-3} D) of CH₃D determined from the intensities of $J+1 \rightarrow J$ transitions.

J	Observed ^a	Calculated
5	5.45 ± 0.38	5.637
6	5.66 ± 0.29	5.687
7	5.48 ± 0.34	5.682
8	5.50 ± 0.29	5.651
9	5.25 ± 0.45	5.691
10	5.42 ± 0.35	5.682
11	5.44 ± 0.29	5.642
12	5.58 ± 0.33	5.660

^aReference 1.

Using the values $\mu_{\xi}^{(0)} - \theta_{\xi}^{\xi\xi} = \mp 5.657 \times 10^{-3}$ and $\theta_{\xi}^{\xi\xi} - \theta_{\xi}^{\xi\xi} - 2\theta_{\xi}^{\xi\xi} = \mp 6.96 \times 10^{-5}$ D which are experimentally determined and $\theta_{\xi}^{\xi\xi} = \pm 1.328 \times 10^{-5}$ D which is theoretically calculated, together with the rotational constants $A = 5.240 \text{ cm}^{-1}$ ²² and $B = 3.882 \text{ cm}^{-1}$,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.*

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