Calculated “forbidden” rotational spectrum of CH_3D

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The rotational dependence of the dipole moment of CH_3D molecule determined from Stark measurements and intensities of *R*-branch rotational lines is theoretically obtained:

$$\mu_I(J,\ k) = \pm\ \{5.655 + 0.0588\ k^2 - 0.00932\ (J + 1)^2\} \cdot 10^{-3}\ \text{D};$$

$$\mu_{\text{St}}(J,\ k) = \pm\ \{5.655 + 0.0588\ k^2 - 0.0390\ J\ (J + 1)\} \cdot 10^{-3}\ \text{D}.$$

Peak-absorption coefficients of rotational lines of CH_3D are calculated. It is shown that in the region of 400 GHz the intensities of the strongest lines of forbidden transitions are two orders of magnitude lower than intensities of allowed transitions, but in the high frequency region (~4000 GHz) the intensity ratio of forbidden and allowed transitions is 1/10. In the region of 6000 GHz, some calculated forbidden transitions of CH_3D are comparable with that of allowed transitions.

Introduction

The molecules like methane and their deuterated isotopic species occupy a particular place among simple polyatomic molecules. Almost all reviews on microwave and infrared spectroscopy include the results of studies of the molecules from this class.[1–5] This is connected, on the one hand, with the basic peculiarities of the force field and structure of rotational-vibrational levels and, on the other hand, with a wide use of methane and methane-type molecules in various experiments of laser physics.

In the double harmonic approximation, tetrahedral molecules like methane have no rotational spectrum in the ground vibronic state, whereas polar molecules like CH_3D have rotational absorption spectrum formed by electric-dipole transitions with limited selection rules in terms of the quantum number of projection of total angular momentum onto the symmetry axis of the molecule, $\Delta k = 0$ (Refs. 1–6).

In the papers by Fox, Watson, Aliev, and Mikhailov,[3–5] it was shown that allowance for centrifugal distortion when constructing rotational wave functions leads to appearance of dipole-type rotational transitions in the ground vibronic state of a certain class of non-polar molecules, among which there is methane, and to relief of prohibition from $\Delta k \neq 0$ transitions in polar molecules, which include CH_3D (Refs. 3–6).

The first experimental confirmation of the centrifugal mechanism of activation of forbidden rotational transitions was given by Ozier for the methane molecule.[2,3] Then, rotational spectra of non-polar molecules and forbidden transitions in microwave spectra of polar molecules were studied by various spectroscopic methods: molecular beam spectroscopy, FIR spectroscopy, double resonance method, and MW absorption spectroscopy.[3–5] Methane was found in the atmosphere of Jupiter and other planets just because of the lines of forbidden rotational transitions. There is reason to think that deuterated isotopic species of methane, including CH_3D, are present in planetary atmospheres of the solar system. Thus, our calculations of the forbidden rotational spectrum of CH_3D can be applied to MW spectroscopy and astrophysical observations.

In this paper, we present detailed calculations of the forbidden rotational spectrum of CH_3D. The calculations were made based on the refined results on dipole moments of the forbidden and allowed transitions obtained in Refs. 6 and 7 and recalculated in this work. The molecule of CH_3D can be considered as quasi-polar. This class of molecules is characterized by low constant dipole moments induced by centrifugal distortion. Therefore, the forbidden and allowed rotational transitions may have comparable intensities in a certain frequency region. This effect is studied in this paper as applied to the CH_3D molecules.

The methane CH_4 molecule has no constant dipole moment in the ground rovibronic state, however CH_3D has a low dipole moment because of a broken tetrahedral symmetry. The following chains of molecules and their symmetry groups illustrate the effect of symmetry lowering in tetrahedral AX_4 molecules, due to the isotopic substitution:

$$AX_4(T_d) \Rightarrow \begin{matrix} AX_3Y(C_{sv}) \\ AX_2Y_2(D_{2d}) \end{matrix}.$$

From the viewpoint of site symmetry, the symmetry group of a molecule is a product of subgroups: group of site symmetry G_S of some function of atoms and group of permutations of equivalent atoms G_I:

$$G = G_I\ G_S.$$

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For methane and deuterated methane, the group relation from the position of site symmetry is in the well known equation of the theory of group representations: $Td = C_{3v} \otimes D_2$.

Let us give some examples of site symmetry and the group of permutations of equivalent atoms for some molecular systems ($G = G_I \otimes G_S$) (Table 1).

Table 1

Point group	Molecule	Ligand	G_S	G_F
T_d	AX_4	X	C_{3v}	D_2
C_{3v}	AX_3	X	C_S	C_3
D_{2d}	$A\,X_2Y_2$	X(Y)	C_S	D_2

The constant dipole moment of CH_3D was determined from measured intensities of the FIR rotational spectrum[9] to be $(5.68 \pm 0.3) \cdot 10^{-3}$ D. The dipole moment of CH_3D in different rotational states was measured by the method of double IR-IR resonance between Stark components,[8] and the obtained values differ from the above value. In the theoretical part of Ref. 8 it was proved that the rotational dependence of the CH_3D dipole moment determined from first-order Stark shifts is absolutely predictable from the centrifugal dipole moment Θ_z^{xy} of methane.

Ozier et al.[9] have found experimentally from the intensities of $J \to J + 1$ rotational spectral lines that the dipole moment depends slightly on the quantum number J. Since every line consists of many lines with $k \le J$, the effective dipole moment of such a transition can be described as[8]:

$$\mu_{J,\text{eff}} = \left\{ \frac{\sum\limits_{k=0}^{J} [\mu_I(J,\,k)]^2\, w(J,\,k)}{\sum\limits_{k=0}^{J} w(J,\,k)} \right\}^{1/2},$$

where the weighting factor $w(J, k)$ is determined by the equation $w(J, k) = [(J + 1)^2 - k^2]\, f_k \exp [- (A - B)\, k^2/kT]$ with $f_k = 1$ for $k = 0$ and $k \ne 3n$ and $f_k = 2$ for $k = 3n$ $(n \ne 0)$.

The calculations we have made based on the rotational dependence of the CH_3D dipole moment determined or calculated for intensities of lines of the R-branch[6,7]:

$$\mu_I(J,k) = \pm \{5.655 + 0.0588\, k^2 - 0.00932\, (J + 1)^2\} \cdot 10^{-3}\ \text{D}$$

demonstrate a weak dependence of $\mu_{J,\text{eff}}$, the dipole moment of the transition $J \to J + 1$, on the quantum number J. The results of numerical analysis of the rotational dependence of $\mu_{J,\text{eff}}$ will be given in Tables 2 and 3 and in Fig. 1. In this paper, we also present the results of numerical analysis of the absorption spectrum of allowed ($\Delta k = 0$) and forbidden ($\Delta k \ne 0$) rotational transitions of CH_3D.

1. Operator of effective centrifugal dipole moment of CH_3D

Using the perturbation method, the operator of the effective dipole moment can be represented as a power series over vibrational (q, $p = - i\partial/\gamma q$) and rotational operators $[J(J_\alpha, J_\beta, J_\gamma)]$ (Refs. 10 and 11):

$$\tilde{M}^f = \sum_{m,n} \tilde{M}^f_{m,n}, \tag{1}$$

$$\tilde{M}^f_{m,n} = \frac{1}{2} \sum_{\alpha=x,y,z} [\tilde{\mu}_\alpha^{m,n-1},\, \lambda_{f\alpha}]_+ \tag{2}$$

where f and α denote the space- and molecule-fixed Cartesian coordinate systems; λ_{f_α} are directional cosines; $[a, b]_+ = ab + ba$;

$$\mu_\alpha^{m,n} = \sum_{\{i,j\}} c^{\,i_1 \ldots i_m}_{\,j_1 \ldots j_n} (q,\, p)^m\, (\mathbf{J})^n. \tag{3}$$

The operator of effective dipole moment for rotational transitions in the ground and excited vibrational states meets the following conditions[10–13]

$$\langle \tilde{M} \rangle = \tilde{M}(R),$$
$$[\tilde{M}(R),\, H_{20}] = 0, \tag{4}$$

where H_{20} is the Hamiltonian of the set of harmonic oscillators of a molecule.

For the considered problem of studying purely rotational spectra, it seems more rational to use the "ultraspeed rotator" ordering scheme[10,14] in calculating parameters in the M^{eff} and constructing spectroscopic models. This scheme is characterized by the following conditions imposed on the orders of vibrational and rotational operators and commutators[10–14]:

$$q \sim \chi^0,\ \ J \sim \chi^{-2+\varepsilon},\ \ [p,\, q] = - i,$$
$$[J_\alpha,\, J_\beta] = -i\, \chi^{-2+\varepsilon} \sum e_{\alpha\beta\gamma} J_\gamma,\ \ \varepsilon \to 0, \tag{5}$$

where χ is the Born–Oppenheimer parameter; $e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor. In this scheme, the operator of effective dipole moment for rotational transitions in the ground vibronic state has the form of a series:

$$\tilde{M}(R) = M_{01} + \tilde{M}_{03} + \tilde{M}_{05} + \ldots +$$
$$+ \tilde{M}_{21}(R) + \tilde{M}_{22}(R) + \ldots\ . \tag{6}$$

It can be shown that for polar symmetric-top molecules $\tilde{M}(R)$ represented as a series (6) for the first-order Stark effect in the ground vibronic state it takes the form of a power series over total angular momentum $\mathbf{J}^2$ and J_z^2 is the projection of $\mathbf{J}$ on the symmetry axis z of the molecule:

$$\tilde{M}(R)_{\text{St}} = \{\mu_e + \mu_J\, \mathbf{J}^2 + \mu_k\, J_z^2 + \mu_{JJ}\, \mathbf{J}^4 +$$
$$+ \mu_{Jk}\, \mathbf{J}^2 J_z^2 + \mu_{kk}\, J_z^4 + \ldots\}\, \lambda_{Z_z}. \tag{7}$$

The parameters μ_{JJ}, μ_{Jk}, and μ_{kk} are functions of the coefficients $\Theta_{\varepsilon}^{\alpha\beta\gamma\delta}$ in the operator $\widetilde{M}_{05}$. For $\Delta J = 0$, λ_{Z_z} is determined by the equation $\lambda_{Z_z} = J_z J_z / \mathbf{J}^2$ (Ref. 15).

Let us present the known procedure for calculation of the parameters in $\widetilde{M}_{mn}$ (Refs. 6, 7, 10–12), which is adapted to calculation of $\widetilde{M}_{03}$, from which follow the equations for spectroscopic parameters μ_J and μ_k in Eq. (7) and dipole moments of forbidden transitions through molecular constants.

For molecules of the trigonal symmetry, the scheme of lower rotational-vibrational levels and dominant interactions leading to appearance of $\widetilde{M}_{03}$ has been given in Ref. 16. Let us briefly present the procedure of construction and reduction of the centrifugal Hamiltonian [12,14] for molecules of $\mathrm{C_{3v}}$ symmetry. The initial Hamiltonian has the form:

$$H_{\mathrm{VR}} = H_{20} + H_{02} + H_{12}, \tag{8}$$

where the centrifugal distortion H_{12} for molecules of $\mathrm{C_{3v}}$ symmetry is determined by the equation

$$H_{12} = B_t^{xx} \sum_{\tau = \pm 1} q_{t_\tau} J_\tau^2$$
$$(q_{t_\tau} = q_{t_x} - i\tau q_{t_y},\ J_\tau = J_x + i\tau J_y). \tag{9}$$

In Eq. (9) B_t^{xx} is the parameter defined for the first time in Ref. 6 as a rotational derivative.

After vibrational contact transformations, we obtain for the centrifugal Hamiltonian that:

$$H^{\mathrm{eff}} = \mathrm{e}^{iS_{12}} H_{\mathrm{VR}}\, \mathrm{e}^{-iS_{12}} = H_{02} + H_{20} + \widetilde{H}_{04},$$
$$\widetilde{H}_{04} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta. \tag{10}$$

For molecules of $\mathrm{C_{3v}}$ symmetry, the operator $\widetilde{H}_{04}$ breaks into a sum of parts that are diagonal and off-diagonal in the basis $H_{02} = B_x \mathbf{J}^2 + (B_z - B_x) J_z^2$,

$$\langle \widetilde{H}_{04} \rangle = D_J \mathbf{J}^4 + D_{Jk} \mathbf{J}^2 J_z^2 + D_k J_z^4, \tag{11}$$

$$H_{\mathrm{split}} = \varepsilon \sum_\tau [J_\tau^3, J_z]_+,\ \varepsilon = 1/4\, \tau_{xxxz}. \tag{12}$$

After reduction transformations

$$\widetilde{H}(\mathrm{Red}) = \mathrm{e}^{iS_{03}} H^{\mathrm{eff}}\, \mathrm{e}^{-iS_{03}}\ , \tag{13}$$

in which the generators for the symmetry $\mathrm{C_{3v}}$ have the form

$$S_{03} = i \sum_\tau S^{\tau\tau\tau} (\tau J_\tau^3),\ \ (S^{+++} = S^{---}), \tag{14}$$

the reduced Hamiltonian takes the form

$$\widetilde{H}(\mathrm{Red}) = H_{02} + H_{20} + \langle \widetilde{H}_{04} \rangle + \tilde{\varepsilon}\, [J_\tau^3, J_z]_+,$$
$$\tilde{\varepsilon} = \{\varepsilon + S^{\tau\tau\tau} (B_z - B_x)\}. \tag{15}$$

Assuming $\tilde{\varepsilon} = 0$, we obtain one of the forms of the effective Hamiltonian and the condition for determination of the parameter S^{+++}:

$$S^{+++} = -\frac{\varepsilon}{B_z - B_x}\ . \tag{16}$$

The operator of the effective dipole moment is constructed by the method of contact transformations (CT) by the scheme similar to that used to construct the effective rotational Hamiltonian.[10,12,14] In this approach, the operator $\widetilde{M}_{03}$ in the commutator form is determined by the following equation:

$$\widetilde{M}_{03} = \sum_{\alpha\beta\gamma} \Theta_\varepsilon^{\alpha\beta} [J_\alpha J_\beta, J_{f\gamma}]_+ + i\, [S_{03}, \mu_{01}] =$$
$$= \sum_{\alpha\beta\gamma} \widetilde{\Theta}_\varepsilon^{\alpha\beta} J_\alpha J_\beta \lambda_\gamma =$$
$$= \sum_{\alpha\beta\gamma} \left\{ \sum_s \frac{B_s^{\alpha\beta}}{\omega_s} \mu_s^\gamma + 3 \sum_{\delta\varepsilon} S_{\alpha\beta\delta}\, e_{\delta\varepsilon\gamma}\, \mu_\varepsilon^{(\mathrm{e})} \right\} J_\alpha J_\beta \lambda_\gamma\ . \tag{17}$$

For molecules of $\mathrm{C_{3v}}$ symmetry, the operator structure of $\widetilde{M}_{03}$ is as follows:

$$\widetilde{M}_{03}(C_{3v}) = \{\Theta_z^{zz} J_z^2 + \Theta_z^{xx} (\mathbf{J}^2 - J_z^2)\} \lambda_{fz} + \Theta_z^{xz} ([J_x, J_z]\, \lambda_{fx} +$$
$$+ [J_y, J_z]\, \lambda_{fy}) + \sum_{\tau = \pm 1} \left(\Theta_x^{xx} + \frac{\mu_e\, \tau_{xxxz}}{2(B_x - B_z)} \right) [J_\tau^2, \lambda_{f\tau}]_+. \tag{18}$$

In deriving Eq. (18), we took into account the equations for nonzero $\Theta_\gamma^{\alpha\beta}$ parameters,[6,7] Θ_z^{zz}, $\Theta_z^{xx} = \Theta_z^{yy}$, $\Theta_x^{xz} = \Theta_y^{yz}$ for all groups $\mathrm{C_n}$, $\mathrm{C_{nv}}$, and $\Theta_z^{xx} = -\Theta_y^{yy} = -\Theta_y^{xy}$ for the groups $\mathrm{C_{3v}}$, $\mathrm{C_3}$, $\mathrm{D_{3h}}$, $\mathrm{D_3}$, $\mathrm{C_{3h}}$. It should be noted that in the groups $\mathrm{C_{nv}}$ the axis x lies in the plane σ_v, and in the dihedral groups $\mathrm{D_{3h}}$ and $\mathrm{D_3}$ the axis x is directed along the axis $\mathrm{C_2}$.

The strengths of the rotational transitions (*R*-branch) allowed when considering $\widetilde{M}_{03}$ in the operator of the effective dipole moment are given in Refs. 6 and 7, as well as in Ref. 8 for the Stark effect.

Determine the rotational dependence of the constant dipole moment of polar molecules, including a molecule of the symmetry $\mathrm{C_{3v}}$. This dependence follows from the results obtained earlier[6,7,8] and from Eq. (18):

$$\tilde{\mu}_I(J, k) = \{\mu_{\mathrm{e}} - \Theta_x^{xz} + (\Theta_z^{zz} - \Theta_z^{xx} - 2\Theta_x^{xz})\, k^2 +$$
$$+ \Theta_z^{xx} (J + 1)^2\} = \mu_{\mathrm{e}} - \Theta_x^{xz} + \mu_k k^2 + \mu_J^I (J + 1)^2,$$
$$\tilde{\mu}_{\mathrm{St}}(J, k) = \{\mu_{\mathrm{e}} - \Theta_x^{xz} + (\Theta_z^{zz} - \Theta_z^{xx} - 2\Theta_x^{xz})\, k^2 + \tag{19}$$
$$+ (\Theta_z^{xx} + 2\Theta_x^{xz})\, J\, (J + 1)^2\} =$$
$$= \mu_{\mathrm{e}} - \Theta_x^{xz} + \mu_k k^2 + \mu_J^{\mathrm{St}} J\, (J + 1)^2.$$

The dependence $\tilde{\mu}_{\mathrm{St}}(J, k)$ is determined from measured Stark shifts, whereas the dependence $\tilde{\mu}_I(J, k)$ is determined from the measured intensities of lines in the *R*-branch.

To summarize this section, let us give the general equations for calculation of the parameters $\Theta_\gamma^{\alpha\beta}$ (Refs. 6, 7, 10, 14, 16, and 17):

$$\Theta_\gamma^{\alpha\beta} = \left\{ \begin{array}{c} -\sum_k \frac{B_k^{\alpha\beta}}{\omega_k} \left(\frac{\partial\mu_\gamma}{\partial q_k}\right) \\ \frac{\hbar^2}{2I_\alpha I_\beta} \sum_k \frac{a_k^{\alpha\beta}}{\lambda_k} \left(\frac{\partial\mu_\gamma}{\partial Q_k}\right) \\ \frac{\hbar^2}{2I_\alpha I_\beta} \sum_{mn} (\mathrm{F}^{-1})_{mn} J_n^{\alpha\beta} \left(\frac{\partial\mu_\gamma}{\partial S_m}\right) \\ \frac{\hbar^2}{2I_\alpha I_\beta} \sum_{uv} (\mathrm{FG})_{uv}^{-1} Y_u^{\alpha\beta} \left(\frac{\partial\mu_\gamma}{\partial S_v}\right) \end{array} \right. . \qquad (20)$$

These equations were derived from the following equations and definitions. In Eq. (20) q_k and Q_k are dimensionless and dimensional normal coordinates; S_u are the inner symmetry coordinates; $a_k^{\alpha\beta}$ and $B_k^{\alpha\beta}$ are inertial and rotational derivatives:

$$B_k^{\alpha\beta} = \frac{a_k^{\alpha\beta}\,\omega_k}{2I_\alpha I_\beta\,\gamma_k^{3/2}}, \qquad (21)$$

$$a_k^{\alpha\beta} = \sum_u J_u^{\alpha\beta} L_{uk}, \qquad (22)$$

where $J_u^{\alpha\beta} = (\partial I_{\alpha\beta}/\partial S_u)$; $L_{uk} = (\partial S_u/\partial Q_k)$ is the matrix determined by Kivelson and Wilson[18] for different types of the inner coordinates. They are rather complicated because the Eckart conditions must be imposed.[19] Significant simplification was achieved by Aliev and Aleksonyan[20] and later by other authors[21]; it consists in representation of the inertial derivatives in the form

$$a_k^{\alpha\beta} = \sum_u Y^{\alpha\beta}(L^{-1})_{ku}; \qquad (23)$$

$$Y_u^{\alpha\beta} = \sum_v J_v^{\alpha\beta} G_{vu}, \qquad (24)$$

where G_{vu} is the matrix of the kinematic coefficients,

$$Y_u^{\alpha\beta} = Y_u^{\beta\alpha} = 2\left\{\delta_{\alpha\beta} \sum_{\gamma i} B_{u,\gamma i}\, r_{\gamma i}^{(e)} - \sum_{\alpha i} B_{u,\alpha i}\, r_{\alpha i}^{(e)}\right\}, \qquad (25)$$

$B_{u,\gamma i}$ are elements of the matrix of Wilson S-vectors,[19] $r_{\gamma i}^{(e)}$ is the equilibrium γ-coordinate of the atom i. In this formulation, the Eckart conditions are fulfilled automatically. Using Eqs. (21)–(24) and the equations that follow

$$\left(\frac{\partial\mu_k}{\partial q_k}\right) = \left(\frac{\partial\mu_\gamma}{\partial Q_k}\right)\left(\frac{\hbar^2}{2\pi c\omega_k}\right)^{1/2},$$

$$\left(\frac{\partial\mu_\gamma}{\partial Q_k}\right) = \sum_u L_{uk}\left(\frac{\partial\mu_k}{\partial S_u}\right), \qquad (26)$$

$$\Lambda^{-1} = L^{-1}\,(GF)^{-1}\,L^{1},\quad G = L\tilde{L},\quad \Lambda_{kk} = 1/\lambda_k,$$

where F is a matrix of force constants and $\tilde{L}$ is a transposed matrix, we obtain $\Theta_\gamma^{\alpha\beta}$ represented by Eq. (20) in equivalent forms. In calculating $\Theta_\gamma^{\alpha\beta}$ for CH$_3$D in Refs. 6 and 7, the second form of Eq. (20) was used along with the data by Sverdlov et al.[22] for molecular constants.

2. Rotational absorption spectrum of CH$_3$D molecule

The CH$_3$D molecule is of the class of quasi-polar molecules, it has a low ($\mu_z^{(e)} \sim 5 \cdot 10^{-3}$ D) constant dipole moment and a weak rotational spectrum.

To calculate the centrifugal dipole moment $\Theta_x^{xx} + \mu_z^{(e)}\,\tau_{xxxz}/2(B_z - B_x)$, we used, in Refs. 6 and 7, frequencies, forms of vibrations, and dipole moment derivatives found by Sverdlov.[22] Depending on the relative signs of $(\partial\mu/\partial Q_k)$ and Θ_x^{xx}, we have obtained four sets of values, which were reported in Refs. 6 and 7. Note that the rotational term $\mu_z^{(e)}\,\tau_{xxxz}/2(B_z - B_x)$ is small for CH$_3$D (only ~ $10^{-3}\,\Theta_x^{xx}$) and it is neglected in calculations. The parameters $\Theta_\gamma^{\alpha\beta}$ depend strongly on the signs of $(\partial\mu/\partial Q_k)$, and the value of Θ_x^{xx} was the largest ($\pm\,1.025 \cdot 10^{-5}$ D) at the signs recommended in Ref. 22. It was just this value that we used in calculating the absorption coefficient of forbidden transitions.

Let us present here the calculated values of all $\Theta_\gamma^{\alpha\beta}$ (in units of 10^{-5} D) at the selected set of signs of electrooptical parameters: ∓, ±, ±. This set of the signs of μ_k corresponds to μ_k^z (k = 1, 2, 3) for Θ_z^{zz} and Θ_x^{xx}, and μ_k^x (k = 4, 5, 6) for Θ_z^{xx} and Θ_x^{xz}.

$$\Theta_x^{xx} = \mp\,1.025,\ \Theta_x^{xz} = \mp\,1.483,$$
$$\Theta_z^{xx} = \mp\,0.932,\ \Theta_z^{zz} = \pm\,2.080. \qquad (27)$$

In Ref. 8, it was shown that the parameters $\Theta_\gamma^{\alpha\beta}$ of CH$_3$D can be completely predicted from the parameter Θ_z^{xy} of CH$_4$. Table 2 gives the new re-calculated (for comparison with Ref. 6) set of parameters $\Theta_\gamma^{\alpha\beta}$ of CH$_3$D and the experimental values from Ref. 8.

Table 2

$\Theta_\gamma^{\alpha\beta}$, 10^{-5} D	Experiment, Ref. 8	Theory, Refs. 6, 7, and this work
Θ_z^{zz}	∓ 2.783	∓ 2.080
Θ_z^{xx}	± 1.328	± 0.932
Θ_x^{xz}	± 1.421	± 1.483
Θ_x^{xx}	∓ 1.080	∓ 1.025

The agreement with the values of $\Theta_\gamma^{\alpha\beta}$ of CH$_3$D calculated from molecular parameters taken from Ref. 22 can be considered good. The discrepancy between the calculated and experimental parameters can be attributed to the uncertainty in determination of molecular parameters in Ref. 22.

Let us give the values of $\tilde{\mu}_z^{\mathrm{e}}$, μ_J^{St}, and μ_k in Eq. (19) for CH$_3$D that were obtained taken into account the experimental data from Ref. 24:

$$\tilde{\mu}_z^{(e)} = \mu_z^e - \Theta_x^{xz} = \pm\,(5.655 \pm 0.003)\cdot 10^{-3},$$
$$\mu_J^{St} = \Theta_x^{xx} + 2\Theta_x^{xz} = \mp\, 3.897 \cdot 10^{-5}, \qquad (28)$$
$$\mu_k = \Theta_z^{zz} - \Theta_z^{xx} - 2\Theta_x^{xz} = \pm\, 5.878 \cdot 10^{-5}.$$

The superscript in Θ-parameters agrees with the selected signs of electrooptical parameters in Ref. 22 and *ab initio* calculations.[8]

The results of numerical analysis of the rotational dependence of μ_J are given in Table 3 and in Fig. 1.

Table 3. Measured and calculated effective dipole moments $\mu_{J,\mathrm{eff}}$ (10^{-3} D)

J	Exp., Ref. 6	This work	Coefficient from Ref. 8	This work
	From intensities of $J \to J + 1$			Stark
0	–	5.6457	5.6437	5.6550
1	–	5.6417	5.6331	5.6075
2	–	5.6330	5.6143	5.5165
3	–	5.6263	5.5951	5.3891
4	–	5.5986	5.5485	5.2077
5	5.45(38)	5.5517	5.4768	4.9760
6	5.66(29)	5.4886	5.3837	4.6990
7	5.48(34)	5.4109	5.2709	4.3812
8	5.50(29)	5.3198	5.1401	4.0288
9	5.25(45)	5.2163	4.9927	3.6509
10	5.42(35)	5.1011	4.8297	3.2621
11	5.44(29)	4.9748	4.6524	2.8870
12	5.58(33)	4.8380	4.4617	2.5672
13	–	4.6913	4.2590	2.3672
14	–	4.5353	4.0458	2.3634
15	–	4.3705	3.8241	2.6006
16	–	4.1978	3.5965	3.0623
17	–	4.0181	3.3664	3.6994
18	–	3.8327	3.1388	4.4678
19	–	3.6429	2.9200	5.3378
20	–	3.4507	2.7190	6.2914

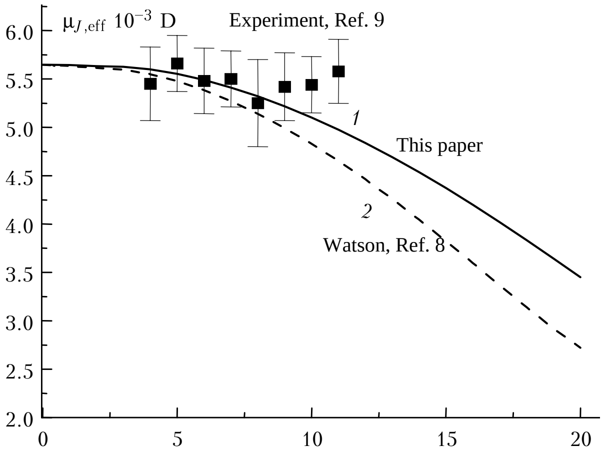

Fig. 1. Rotational dependence of the effective dipole moment $\mu_{J,\mathrm{eff}}$ (10^{-3} D) as judged from the intensities of $J \to J + 1$ transitions: this work (*1*) and Ref. 8 (*2*).

The peak absorption coefficient of the line corresponding to the transition $JK \to J'K'$ ($E_{JK} < E_{J'K'}$) for symmetric-top molecules is calculated by the equation[1]:

$$\alpha_{\max}(\mathrm{cm}^{-1}) = \frac{12.22\cdot 10^{-4}\, F_V\, i_c\, \sigma\, g_I\, g_K\, g_J\, B\sqrt{A}\, \nu^2\, \{M_{JK}\}^2}{T^{5/2}(\Delta\nu)_1}, \qquad (29)$$

$$F(J \to J',\, k \to k'')\left[1 - \frac{0.024\,\nu}{T}\right] e^{-0.048E_{JK}/T}.$$

Here $K = |k|$

$$g_K = \begin{cases} 1 \text{ for } k = 0 \\ 2 \text{ for } k > 0\text{'} \end{cases}$$

$$g_J = 2J + 1,\ \nu = E_{J'K'} - E_{JK};$$

$$E_{JK} = BJ\,(J+1) + (A - B)\,k^2 - D_J\,J^2\,(J+1)^2 - D_{JK}\,J\,(J+1)\,k^2 - D_K\,k^4; \qquad (30)$$

F_v is a fraction of molecules in the given vibrational state; i_c is the concentration of the observed isotopic species, σ is the symmetry number; g_I is the reduced nuclear statistical weighting factor; $(\Delta\nu)_1$ is the line width for $P = 1$ mm Hg; T is the absolute temperature, in K. The parameters in Eqs. (29) and (30) have the following dimensions: A, B, D_J, D_{Jk}, D_k in GHz; T in K; $(\Delta\nu)_1$ in MHz; M_{JK} in D.

For CH_3D we have the following values of rotational and centrifugal constants for the ground vibrational state (in cm^{-1}) from Ref. 24:

$$\begin{aligned} B_0 &= (3.880\,088 \pm 0.000\,016),\\ A_0 - B_0 &= (1.370\,615 \pm 0.000\,053),\\ A_0 &= (5.250\,703 \pm 0.000\,056),\\ D_0^J &= (5.1739 \pm 0.0051)\cdot 10^{-5},\\ D_0^{Jk} &= (1.2375 \pm 0.0023)\cdot 10^{-4},\\ D_0^k &= -\,(7.680 \pm 0.037)\cdot 10^{-5}. \end{aligned} \qquad (31)$$

In units of GHz the constants have the following values:

$$\begin{aligned} B_0 &= (116.332\,113\,429\,665 \pm 0.004\,796\,679\,392),\\ A_0 - B_0 &= (41.090\,004\,530\,413 \pm 0.001\,588\,900\,048),\\ A_0 &= (157.412\,117\,960\,079 \pm 0.001\,678\,837\,787),\\ D_0^J &= (15.510\,962\,191\,418 \pm 0.015\,289\,415\,562)\cdot 10^{-4},\\ D_0^{Jk} &= (37.099\,377\,172\,500 \pm 0.068\,952\,266\,260)\cdot 10^{-4},\\ D_0^k &= -(23.024\,061\,081\,600 \pm 0.110\,923\,210\,940)\cdot 10^{-4}. \end{aligned} \qquad (32)$$

In calculation of the absorption coefficient $\alpha_{\max}$ (in cm^{-1}) and frequencies of the transitions for CH_3D, we used $T = 300$°K, $(\Delta\nu)_1 = 1$ MHz, $\sigma g_I = 3$ for $k = 3n$ and $\sigma g_I = 3/2$ for other k, the strengths of forbidden $|\Delta k = 3|$ (from Refs. 6 and 7) and allowed $\Delta k = 0$ transitions with the allowance for the rotational dependence $\mu_I(J,k)$ (19), and values of rotational and centrifugal constants (32).

Calculation of the parameters μ_J^I and μ_k^I in $\mu_I(J,k)$ (19) with the values of $\Theta_\gamma^{\alpha\beta}$ from Table 2 gives the following rotational dependence of the constant dipole moment that is determined from (or calculated for) intensities of lines of the R-branch

$$\mu_I(J,k) = \pm \{5.655 - 0.00932\ (J + 1)^2 + 0.0588\ k^2\} \cdot 10^{-3}\ \text{D}. \qquad (33)$$

Table 4 for $K = 0, 3, 6, 9$ and Fig. 2 give the calculated results on $\alpha_{\max}$ and on frequencies of the forbidden rotational transitions $J, k \to J + 1, k + 3$.

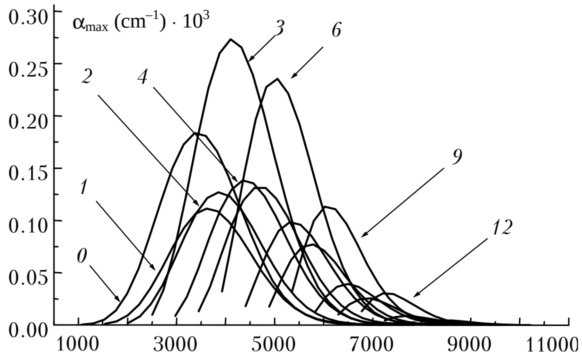

Fig. 2. Absorption coefficient of CH_3D molecule for forbidden transitions $J \to J + 1$, $K \to K + 3$.

Table 5 for $K = 3, 6, 9$ and Fig. 3 give the calculated results on $\alpha_{\max}$ and frequencies of the forbidden rotational transitions $J \to J + 1$, $k \to k - 3$. Table 6 for $K = 0, 3, 6, 9$ presents the calculated results on $\alpha_{\max}$ and frequencies of forbidden rotational transitions $J \to J$, $k \to k + 3$. Table 7 for $J = 3, 6, 9, 12, 15$ and Fig. 4 give the calculated values of $\alpha_{\max}$, frequencies, and effective dipole moments of the allowed rotational transitions $J, k \to J + 1, k$. Note that for this type of (allowed) transitions the value of $\alpha_{\max}$ for $k \neq 0$ was calculated by Eq. (29) and Eq. (6.54) from Ref. 1:

$$\alpha_{\max}\ (k \neq 0) = 4g_I\ \alpha_{\max}\ (k = 0) \left[1 - \frac{k^2}{(J + 1)^2}\right] \times \exp\left[-\frac{0.48\ (A - B)\ k^2}{T}\right], \qquad (34)$$

where $g_I = 1/2$ for $k = 3n$ $(n \neq 0)$, $g_I = 1/4$ for $k \neq 3n$ and $k = 0$.

The microwave region formed by rotational transitions of molecules extends up to the submillimeter region ($\lambda = 0.43$ mm). For optimal detection of molecules, it is important to know in what region various molecules have strongest absorption lines. This is important for molecules with small dipole moments, as well as in observing lines of rare isotopes and rotational lines of molecules due to transitions from thinly populated vibrational states. To determine J for the strongest $J \to J + 1$ transition, one has to differentiate $\alpha_{\max}$ with respect to J in Eq. (29) or (34), equalize the derivative to zero, and solve the equation for J. The following results was obtained in Ref. 1:

$$J_{\text{opt}}\ (\text{for strongest lines}) \approx 5.5 \left(\frac{T(\text{K})}{B(\text{GHz})}\right)^{1/2}. \qquad (35)$$

Table 4. Absorption coefficient α_ν^* and frequencies of forbidden transitions $J \to J + 1$, $K \to K + 3$

J	$K = 0$		$K = 3$		$K = 6$		$K = 9$	
	Frequency, ν	$\alpha_\nu \cdot 10^3$	Frequency, ν	$\alpha_\nu \cdot 10^3$	Frequency, ν	$\alpha_\nu \cdot 10^3$	Frequency, ν	$\alpha_\nu \cdot 10^3$
2	1067.36115	0.00010						
3	1299.50875	0.00069						
4	1531.44065	0.00258						
5	1763.11965	0.00695	2502.14526	0.00964				
6	1994.50850	0.01491	2732.53243	0.03336				
7	2225.56999	0.02695	2962.45868	0.07232				
8	2456.26689	0.04237	3191.88678	0.12298	3933.01840	0.03200		
9	2686.56197	0.05926	3420.77951	0.17754	4160.37520	0.08560		
10	2916.41801	0.07485	3649.09963	0.22616	4387.02590	0.14540		
11	3145.79777	0.08634	3876.80992	0.25988	4612.93310	0.19640	5358.64346	0.03158
12	3374.66404	0.09175	4103.87315	0.27320	4838.05980	0.22760	5581.69996	0.07020
13	3602.97957	0.09039	4330.25211	0.26530	5062.36860	0.23540	5803.80506	0.09974
14	3830.70716	0.08300	4555.90955	0.23966	5285.82230	0.22140	6024.92154	0.11316
15	4057.80957	0.07134	4780.80825	0.20244	5508.38380	0.19200	6245.01217	0.11078
16	4284.24958	0.05759	5004.91100	0.16058	5730.01570	0.15500	6464.03972	0.09704
17	4509.98995	0.04380	5228.18055	0.12000	5950.68090	0.11700	6681.96696	0.07764
18	4734.99347	0.03146	5450.57969	0.08470	6170.34210	0.08300	6898.75668	0.05744
19	4959.22290	0.02138	5672.07119	0.05660	6388.96210	0.05560	7114.37163	0.03964
20	5182.64101	0.01378	5892.61781	0.03586	6606.50370	0.03520	7328.77460	0.02566
21	5405.21059	0.00843	6112.18234	0.02160	6822.92960	0.02100	7541.92836	0.01566
22	5626.89441	0.00490	6330.72755	0.01236	7038.20260	0.01200	7753.79568	0.00902
23	5847.65523	0.00271	6548.21621	0.00674	7252.28560	0.00640	7964.33933	0.00494
24	6067.45584	0.00143	6764.61109	0.00350	7465.14120	0.00320	8173.52210	0.00256
25	6286.25900	0.00072	6979.87498	0.00174	7676.73220	0.00160	8381.30674	0.00126
26	6504.02749	0.00035	7193.97063	0.00082	7887.02150	0.00060	8587.65604	0.00060
27	6720.72408	0.00016	7406.86082	0.00038	8095.97170	0.00020	8792.53277	0.00026
28	6936.31155	0.00007	7618.50834	0.00016	8303.54570	0.00000	8995.89971	0.00012

Note. * α_ν is equal to $\alpha_{\max}$, in cm^{-1}.

Table 5. Absorption coefficient α_ν and frequencies of the forbidden transitions $J \rightarrow J + 1$, $K \rightarrow K - 3$

J	$K = 3$			$K = 6$		$K = 9$	
	Frequency, ν		$\alpha_\nu \cdot 10^3$	Frequency, ν	$\alpha_\nu \cdot 10^3$	Frequency, ν	$\alpha_\nu \cdot 10^3$
3	560.58415	0.00002					
4	793.11706	0.00017					
5	1025.53063	0.00079					
6	1257.78761	0.00239	0.00478	517.89387	0.00004		
7	1489.85078	0.00555	0.01110	750.82517	0.00032		
8	1721.68292	0.01053	0.02106	983.65899	0.00122		
9	1953.24680	0.01709	0.03418	1216.35811	0.00316	471.42003	0.00002
10	2184.50519	0.02436	0.04872	1448.88530	0.00628	705.08246	0.00012
11	2415.42087	0.03106	0.06212	1681.20333	0.01030		
12	2645.95661	0.03591	0.07182	1913.27499	0.01448		
13	2876.07517	0.03803	0.07606	2145.06303	0.01796		
14	3105.73935	0.03719	0.07438	2376.53023	0.01996		
15	3334.91191	0.03378	0.06756	2607.63938	0.02020		
16	3563.55561	0.02864	0.05728	2838.35323	0.01876		
17	3791.63325	0.02275	0.04550	3068.63457	0.01612		
18	4019.10758	0.01700	0.03400	3298.44616	0.01290		
19	4245.94139	0.01197	0.02394	3527.75078	0.00966		
20	4472.09744	0.00797	0.01594	3756.51121	0.00678		
21	4697.53851	0.00503	0.01006	3984.69022	0.00448		
22	4922.22738	0.00301	0.00602	4212.25058	0.00280		
23	5146.12681	0.00171	0.00342	4439.15506	0.00166		
24	5369.19958	0.00092	0.00184	4665.36644	0.00092		
25	5591.40847	0.00048	0.00096	4890.84749	0.00050		
26	5812.71624	0.00023	0.00046	5115.56098	0.00026		
27	6033.08567	0.00011	0.00022	5339.46969	0.00012		

Table 6. Absorption coefficient α_ν and frequencies of the forbidden transitions $J \rightarrow J$, $K \rightarrow K + 3$

J	$K = 0$		$K = 3$		$K = 6$		$K = 9$	
	Frequency,ν	$\alpha_\nu \cdot 10^3$	Frequency,ν	$\alpha_\nu \cdot 10^3$	Frequency,ν	$\alpha_\nu \cdot 10^3$	Frequency, ν	$\alpha_\nu \cdot 10^3$
2	369.79619	0.00000						
3	369.59586	0.00001						
4	369.32874	0.00005						
5	368.99484	0.00013	1109.22247	0.00000				
6	368.59417	0.00025	1108.02045	0.00027				
7	368.12672	0.00042	1106.61809	0.00092				
8	367.59248	0.00061	1105.01539	0.00192	1849.15211	0.00000		
9	366.99147	0.00078	1103.21235	0.00306	1846.14705	0.00060		
10	366.32368	0.00090	1101.20898	0.00410	1842.80809	0.00177		
11	365.58911	0.00095	1099.00527	0.00481	1839.13524	0.00315	2590.45491	0.00000
12	364.78776	0.00093	1096.60122	0.00508	1835.12849	0.00432	2584.84546	0.00045
13	363.91963	0.00085	1093.99683	0.00491	1830.78785	0.00499	2578.76856	0.00117
14	362.98472	0.00072	1091.19211	0.00438	1826.11331	0.00506	2572.22421	0.00182
15	361.98304	0.00058	1088.18705	0.00364	1821.10488	0.00464	2565.21240	0.00219
16	360.91457	0.00044	1084.98165	0.00283	1815.76255	0.00390	2557.73314	0.00222
17	359.77933	0.00031	1081.57592	0.00208	1810.08633	0.00303	2549.78643	0.00199
18	358.57730	0.00021	1077.96985	0.00143	1804.07621	0.00220	2541.37226	0.00161
19	357.30850	0.00014	1074.16344	0.00094	1797.73219	0.00150	2532.49064	0.00119

Table 7. Absorption coefficient α_ν and frequencies of the allowed transitions $J \to J + 1$, $K \to K$

K	$J = 15$	$\alpha_\nu \cdot 10^3$	$J = 12$	$\alpha_\nu \cdot 10^3$	$J = 9$	$\alpha_\nu \cdot 10^3$	$J = 6$	$\alpha_\nu \cdot 10^3$	$J = 3$	$\alpha_\nu \cdot 10^3$
0	3696.89519	0.17294	3010.74450	0.74100	2320.23833	1.65557	1626.38180	1.79742	930.18001	0.70063
1	3695.70799	0.08899	3009.77990	0.37859	2319.49633	0.84253	1625.86240	0.91261	929.88321	0.35528
2	3692.14639	0.09664	3006.88610	0.40297	2317.27033	0.88678	1624.30420	0.95422	928.99281	0.37010
3	3686.21039	0.21932	3002.06310	0.88775	2313.56033	1.92077	1621.70720	2.04611	927.50881	0.78909
4	3677.89999	0.12832	2995.31090	0.50139	2308.36633	1.06266	1618.07140	1.11798		
5	3667.21519	0.15273	2986.62950	0.57504	2301.68833	1.19180	1613.39680	1.23672		
6	3654.15599	0.36542	2976.01890	1.32678	2293.52633	2.68856	1607.68340	2.75082		
7	3638.72239	0.21758	2963.47910	0.76372	2283.88034	1.51449				
8	3620.91439	0.25613	2949.01010	0.87190	2272.75034	1.69459				
9	3600.73199	0.59319	2932.61190	1.96490	2260.13634	3.74953				
10	3578.17519	0.33674	2914.28450	1.08893						
11	3553.24400	0.37411	2894.02791	1.18445						
12	3525.93840	0.81240	2871.84211	2.52468						
13	3496.25840	0.43077								
14	3464.20400	0.44606								
15	3429.77520	0.90198								

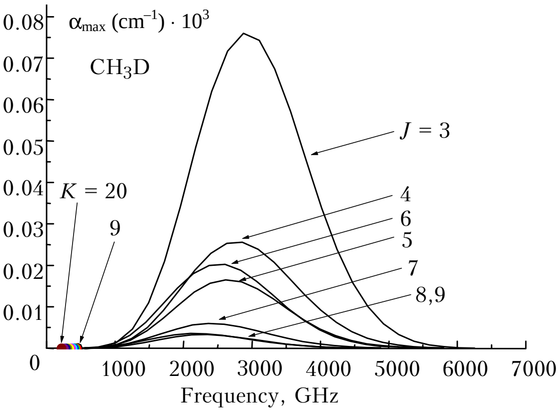

Fig. 3. Absorption coefficient of forbidden transitions $J - J + 1$, $K - K - 3$ for CH$_3$D molecule.

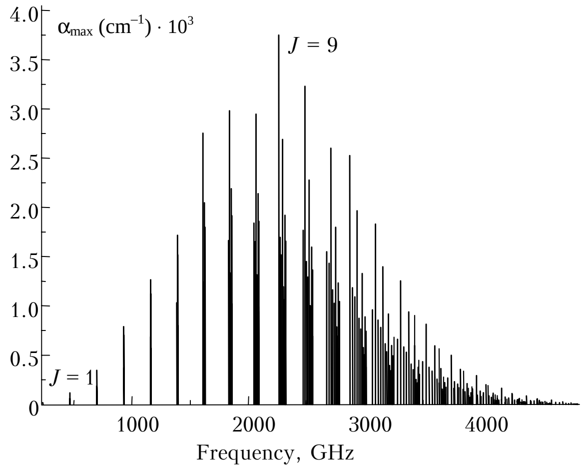

Fig. 4. Absorption coefficient of allowed transitions $J - J + 1$, $K - K$ for CH$_3$D molecule.

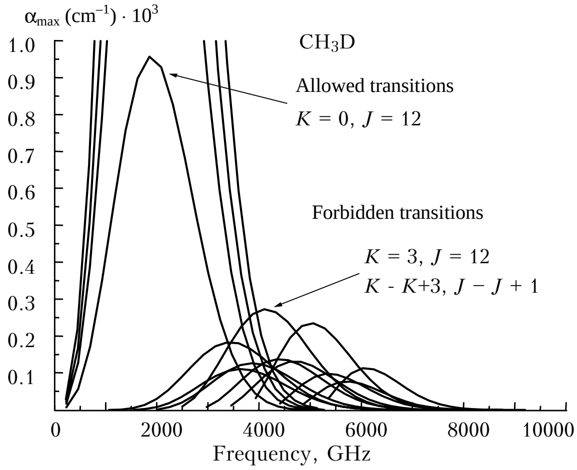

Fig. 5. Absorption coefficient of allowed and forbidden transitions in the region of 4000–6000 GHz.

Having obtained J_{opt}, we can readily find the optimal frequency region for detecting the absorption spectrum of a molecule from the equation

$$\nu_{opt} \text{ (for strongest lines)} \approx$$
$$\approx 2\,(J_{opt} + 1) = 2B + 11(BT)^{1/2}. \qquad (36)$$

Estimation of α_{max} by Eq. (35) and calculation of α_{max} by Eq. (29) give the same value for J_{opt}; it is roughly equal to 9 for CH$_3$D at T = 300 K according to estimates by Eq. (35).

As seen from Tables 3–6 and Figs. 2–5, in the region of low frequencies ~ 400 GHz the intensity of forbidden transitions is two orders of magnitude lower than the intensity of the allowed ones; from Tables 4 and 7 and Figs. 2 and 4 it follows that in the region of 3000–4000 GHz the intensities of forbidden transitions are roughly an order of magnitude lower than those of allowed ones, and in the region of 5000–6000 GHz the intensities of forbidden and allowed transitions may be comparable. This result is illustrated in Fig. 5. The same conclusion can be drawn for deuterated isotopic species of methane and, generally, most deuterated isotopic species of nonpolar molecules. However, in the high-frequency (> 4000 GHz) region, one can expect rotational-vibrational transitions of hot absorption bands, but these two types of transitions have different selection rules and different dependence of intensities on the temperature and quantum numbers J and k.

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