Calculated microwave spectrum of CH_3D in the region of 3–4 cm^{-1}

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The microwave (MW) spectrum of forbidden Q-branch transitions of CH_3D has been calculated for the first time. MW CH_3D transitions of this type lie in the 3–4 cm^{-1} region, while the MW R-branch of CH_3D, according to the HITRAN-2000 database, is spread above 7 cm^{-1}. For the strongest MW CH_3D transition (11, +1) – (11, –2) the absorption coefficient $\alpha_{max} = 0.0149 \cdot 10^{-3}$ cm^{-1}. These calculations of the forbidden CH_3D spectrum show that it can be recorded by existing MW Stark modulation spectrometers or orotron spectrometers. The effective centrifugal distortion dipole moment model for molecules of trigonal symmetry is suggested on the basis of the limiting ordering scheme of an ultraspeed rotator. A possibility of construction of a Hamiltonian nonpolynomial model and the effective dipole moment based on the nonlinear transformation of a series with respect to rotational parameters is demonstrated.

Introduction

In the double harmonic and rigid rotator approximation, rotational-vibrational transitions in the fundamental bands and rotational transitions in the ground vibrational-electronic (vibronic) state of normal molecules meet the limited selection rules.[1] In polar molecules in this approximation, dipole rotational transitions with $\Delta J = 0, \pm1$, $\Delta K = 0$ are allowed,[2] where J is the quantum number of the total angular momentum and $K = |k|$ is the quantum number of the total angular momentum projection onto the molecular symmetry axis.

Rotational transitions with $\Delta K = \pm3$ in polar molecules of trigonal symmetry were predicted theoretically.[3,4] They were experimentally studied by the methods of microwave (MW), submillimeter (Submm), and far-IR (FIR) spectroscopy for NH_3, PH_3, AsH_3, and CH_3D molecules and summarized in Refs. 5–8. As a result, a complete set of rotational-vibrational constants including such constants as A_0, D_k, H_k, and others, whose values cannot be found from allowed transitions only, was determined for these molecules.

It should be noted that the values of the sextic centrifugal distortion constants found in Refs. 5–8 can be used in solving the inverse spectroscopic problem on determination of anharmonic force constants.[9]

The "forbidden" rotational spectrum was calculated in Ref. 10 for the quasipolar CH_3D molecule, namely, the R-branch and some transitions of the Q-branch, whose frequencies fall within the submillimeter region. In this paper we present the calculated MW CH_3D transitions with $\Delta K = \pm3$, which are absent in the theoretical papers[4,10] and are not studied experimentally in the MW region (and, consequently, not included in the HITRAN-2000 database) unlike the submillimeter and FIR regions.[11–13]

The calculated results for the CH_3D absorption coefficients at the line peaks corresponding to the forbidden rotational transitions with $\Delta K = \pm3$, namely, $(J, \pm1) – (J,\ \ 2)$ in the Q-branch that fall in the 3–4 cm^{-1} MW range, indicate that they are quite comparable with the absorption coefficients of other polar molecules of this type, in particular, NH_3 [Ref. 12] and PH_3 [Ref. 14], which were found for the first time with ordinary microwave Stark modulation spectrometers. Note that transitions with $\Delta K = \pm3$ in the polar molecules (NH_3, CH_3D, CD_3H, CH_3F, CD_3Cl, CH_3I, SiH_3D, CDF_3, POF_3) in the MW and submillimeter regions were also studied by the spectroscopic methods, like the double resonance method, using ordinary FIR spectrometers with signal accumulation and a submillimeter RAD spectrometer.[5–7]

Spectroscopic constants and centrifugal moments of transitions, determined from the analysis of forbidden $\Delta K = \pm3$ spectra, for some polar molecules are presented in Refs. 6 and 7.

Effective Hamiltonian, frequencies and strengths of transitions with $\Delta K = \pm3$ and $\Delta J = 0$ in molecules of trigonal symmetry

In studying purely rotational spectra formed by electrodipole transitions in the ground vibronic state, it seems rational to apply the scheme of ultraspeed rotator[15] for ordering rotational-vibrational interactions in constructing the effective Hamiltonian and the effective dipole moment operator of spectroscopic models. This scheme is characterized by the following conditions imposed on the values of vibrational and rotational operators and commutators[15,16]:

$$(q,\, p) \sim \chi^0,\ J \sim \chi^{-2+\varepsilon},\ [p,\, q] = -i,$$
$$[J_\alpha,\, J_\beta] = -i\chi^{-2+\varepsilon} \sum_\gamma e_{\alpha\beta\gamma}\, J_\gamma,\ \varepsilon \to 0, \qquad (1)$$

where χ is the Born–Oppenheimer parameter; $[a,\, b] = ab - ba$; $e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor. In this scheme, the effective Hamiltonian in the ground and excited isolated vibrational states has the form of a power series in terms of the total angular momentum for each power of the vibrational parameters[15,16]:

$$H^{\text{eff}} = \tilde{H}_V^R = \sum_n \tilde{H}_{0,2n} + \sum_n \tilde{H}_{2,n} + \ldots =$$
$$= \tilde{H}_{0,2} + \tilde{H}_{0,4} + \tilde{H}_{0,6} + \ldots. + \tilde{H}_{2,1} + \tilde{H}_{2,2} + \tilde{H}_{2,3} + \ldots, \qquad (2)$$

and the effective dipole moment operator of rotational transitions in the ground vibronic state for molecules of trigonal symmetry takes the form of a series[10,17]:

$$M^{\text{eff}}(R) = \tilde{M}(R) = \tilde{M}_{0,1} + \tilde{M}_{0,3} +$$
$$+\tilde{M}_{0,5} + \ldots. + \tilde{M}_{2,1}(R) + \tilde{M}_{2,2}(R),$$

where

$$\tilde{M}_{0,1} = \mu_z^e \lambda_{fz},$$
$$\tilde{M}_{0,3} = \Theta_z^{zz} J_z^2 + \Theta_z^{xx}\left(\mathbf{J}^2 - J_z^2\right) + \Theta_z^{xz} \sum_{\tau=\pm1} [J_z, J_\tau]_+ \lambda_{f,-\tau} =$$
$$= \sum_{\tau=\pm1}\left(\Theta_z^{xx} + \frac{\mu_z^e \tau_{xxxz}}{2(B_x - B_z)}\left[J_\tau^2,\, \lambda_{f\tau}\right]_+\right) +$$
$$+\mu_J \mathbf{J}^2 + \mu_k J_z^2 + \left(\Theta_x^{xx}\right)_{\text{eff}} \sum_{\tau=\pm1}\left[J_\tau^2,\, \lambda_{f\tau}\right]_+,$$
$$\tilde{M}_{0.5} = \mu_{JJ}\mathbf{J}^4 + \mu_{Jk}\mathbf{J}^2 J_z^2 + \mu_{kk} J_z^4 +$$
$$+\mu_{\Delta k=3}^J \mathbf{J}^2\left[J_\tau^2,\, \lambda_{f\tau}\right]_+ + \mu_{\Delta k=3}^J J_z^2\left[J_\tau^2,\, \lambda_{f\tau}\right]_+,$$

where μ_J, μ_k are the parameters in the effective dipole moment operator.

For CH$_3$D, Θ in the effective dipole moment of the forbidden transitions with $\Delta K = \pm3$ can be estimated as:

$$\left(\Theta_z^{xx}\right)_{\text{eff}} = \Theta_x^{xx} + \frac{\mu_z^e \tau_{xxxz}}{2(B_x - B_z)}.$$

Estimates of $\left(\Theta_z^{xx}\right)_{\text{eff}}$ with molecular constants from Refs. 4 and 10 give $\Theta_x^{xx} =$ 1.025 D and $\sim 10^{-3}\, \Theta_x^{xx}$ for the second term.

The relation of μ_J, μ_K to the tensor parameters $(\Theta_\gamma^{\alpha\beta})$, $(\Theta_\gamma^{\alpha\beta})_{\text{eff}}$ in Eq. (4) and their expressions through molecular constants were found in Ref. 10. The relations of the spectroscopic parameters μ_{JJ}, μ_{Jk}, μ_{kk}, $\mu_{\Delta k=3}^J$, $\mu_{\Delta k=3}^k$ in $M_{0,5}$ to the molecular parameters for molecules of trigonal symmetry can be obtained from general equations[15,16] for parameters in

$$\tilde{M}_{0.5} = \sum_{\alpha\beta\gamma\delta\varepsilon} \Theta_\varepsilon^{\alpha\beta\gamma\delta}\left[J_\alpha J_\beta J_\gamma J_\delta,\, \lambda_{f\gamma}\right]_+.$$

In this paper we present a direct numerical analysis of the MW CH$_3$D spectrum in the sextic approximation for rotational energy levels and the approximation $\tilde{M}(R) = \tilde{M}_{0,1} + \tilde{M}_{0,3}$ for the effective dipole moment of the forbidden transitions with $\Delta J = 0$, $\Delta K = \pm3$. In addition, we present a comparative analysis of forbidden spectra in the MW region and spectra of allowed $\Delta K = 0$, $\Delta J = \pm1$ transitions, calculated by us in Ref. 10 for the same J and K values of lower levels of $(J, \pm1) - (J,\ 2)$ transitions. Note that for $\Delta J = 0$ the direction cosines are determined by the following equation[8–10]:

$$(\lambda f \tau)_{\Delta J=0} = J_\tau J_f \,/\, \mathbf{J}^2, \qquad (5)$$

where J_τ, J_f are components of the total angular momentum in the molecule- and space-fixed coordinate systems, respectively. The strength of lines of the Q-type with $\Delta K = \pm3$ in the chosen approximation for $\tilde{M}(R) = \tilde{M}_{0,3}$ is described by the equation[4,14]:

$$S = \left(\Theta_x^{xx}\right)_{\text{eff}}^2 (J \mp k)(J \mp k - 1)(J \mp k - 2)(J \pm k + 1)\times$$
$$\times(J \pm k + 2)(J \pm k + 3)(2J + 1) / 4J(J + 1).$$

For MW transitions $(J, \pm1)$ $(J, \mp2)$, frequencies and line strengths are determined as

$$\nu_{J,\mp2;J,\pm1} = 3\left\{(A - B) - 5D_k - 21H_k -\right.$$
$$\left.-\left(D_{JK} - 15H_{kJ}\right)J(J + 1) + 5H_{Jk}J^2(J + 1)^2\right\}$$

and

$$S = \left(\Theta_x^{xx} + \frac{\mu_z^e \tau_{xxxz}}{2(A - B)}\right)^2 (J \mp 1)\, J\,(J \pm 1)(J \pm 2)\times$$
$$\times(J \pm 3)(J \pm 4)(2J + 1) / 4J(J + 1)$$

and for the allowed $(J,\, k) - (J + 1,\, k)$ transitions they are[4,10]:

$$\nu_{Jk,J+1,k} = 2\left(B - D_{Jk}k^2\right)(J + 1) - 4D_J(J + 1)^3 +$$
$$+H_J\left((J + 1)^6 - J^6\right) + 4H_{Jk}(J + 1)^3 k^2$$

and

$$S(J, k \to J + 1, k) = \left\{\mu_e - \Theta_z^{xz} + \left(\Theta_z^{zz} - \Theta_z^{xx} - 2\Theta_x^{xz}\right)k^2 +\right.$$
$$\left. + \Theta_z^{xx}(J + 1)^2\right\}\frac{\left[(J + 1)^2 - k^2\right]}{(J + 1)(2J + 1)}.$$

Numerical simulation of MW CH$_3$D spectrum

The absorption coefficient at the line peak of the transition $Jk - J'k'$ for symmetric-top molecules is given in Ref. 2 and adapted for CH$_3$D and normal experimental conditions in Ref. 10. For the effective dipole moments (3), presented for molecules of trigonal symmetry by Eqs. (4), it is possible to apply the method of nonlinear series transformation, in particular, the method of Pade approximants.[18] The previous analysis of higher-order centrifugal dipole moments of the methane molecule in the polynomial form (3) and in the form of Pade approximants[19] points to the principal possibility of extending the set of spectroscopic models for line intensities of MW and IR molecular spectra beyond the scope of traditional polynomial models.

The calculations of the MW spectrum of CH_3D involved the rotational and centrifugal distortion constants up to sextic ones from Ref. 20 (Table 1).

Table 1. Molecular constants for the ground vibrational state of CH_3D

B_0	3.88019606±0.00000055	$116.3253514\pm1.64886\cdot10^{-5}$
$A_0–B_0$	1.3706270±0.0000037	41.09036373±0.000110923
D_0^J	$(5.26221\pm0.00022)\cdot10^{-5}$	$0.001577571\pm6.59543\cdot10^{-8}$
D_0^K	$(-7.869\pm0.0023)\cdot10^{-5}$	$-0.002359067\pm6.89523\cdot10^{-7}$
D_0^{JK}	$(1.26337\pm0.00013)\cdot10^{-4}$	$0.003787488\pm3.8973\cdot10^{-7}$
H_0^J	$(1.4035\pm0.003)\cdot10^{-9}$	$4.20759\cdot10^{-8}\pm8.99377\cdot10^{-11}$
H_0^{JK}	$(1.1521\pm0.0027)\cdot10^{-8}$	$3.34332\cdot10^{-7}\pm8.0944\cdot10^{-10}$
H_0^{KJ}	$(-6.26\pm0.061)\cdot10^{-9}$	$-1.8767\cdot10^{-7}\pm1.82873\cdot10^{-9}$

Note. The values in the second column are in cm^{-1}, while those in the third column are in GHz.

The constants (in GHz) follow from the relation[21]: $1\ cm^{-1} = 299\,792\,458\cdot10^{-7}$ GHz. Measurement errors are presented for all constants from Ref. 20.

The calculated frequencies of microwave transitions and the absorption coefficients at line peaks are given in Table 2 and Fig. 1.

Table 2. Frequencies and absorption coefficients of MW CH_3D transitions

J	Frequency		$\alpha_{max}\cdot10^7$, cm^{-1}
	GHz	cm^{-1}	
3	123.17076	4.10853	5.81408
4	123.08107	4.10554	15.56438
5	122.96987	4.10183	32.24899
6	122.83775	4.09743	55.60832
7	122.68544	4.09235	83.14783
8	122.51378	4.08662	110.61716
9	122.32372	4.08028	133.21326
10	122.11637	4.07336	146.99872
11	121.89291	4.06591	149.96930
12	121.65467	4.05796	142.41481
13	121.40310	4.04957	126.54934
14	121.13976	4.04079	105.66629
15	120.86633	4.03167	83.18798
16	120.58463	4.02227	61.92264
17	120.29657	4.01266	43.68399
18	120.00421	4.00291	29.26474
19	119.70970	3.99309	18.64923
20	119.41535	3.98327	11.32188
21	119.12354	3.97353	6.55673
22	118.83682	3.96397	3.62638
23	118.55783	3.95466	1.91748
24	118.28933	3.94571	0.97023
25	118.03422	3.93720	0.47019
26	117.79551	3.92924	0.21842
27	117.57632	3.92192	0.09733
28	117.37990	3.91537	0.04163
29	117.20963	3.90969	0.01710
30	117.06900	3.90500	0.00675

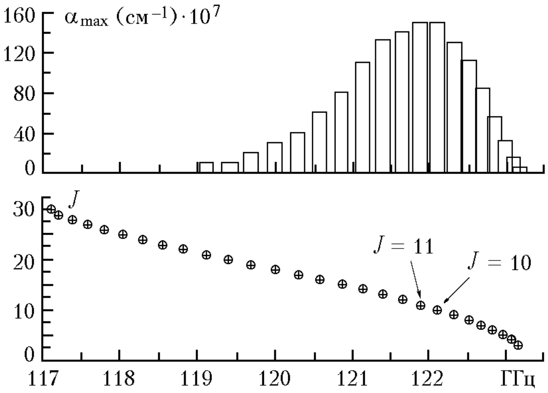

Fig. 1. Calculated frequencies and absorption coefficients of MW transitions of CH_3D.

The CH_3D sextic centrifugal distortion constant H_k, which cannot be determined from frequencies of the allowed transitions (9) and was not presented in Ref. 20, was assumed equal to zero in calculation of frequencies of forbidden transitions by Eq. (7).

Discussion

Our calculations of the low-frequency MW CH_3D spectrum formed by the forbidden $(J, \pm1) - (J, \ 2)$ transitions in the ground vibronic state show that the strongest lines of this spectrum are concentrated in the range 3–4 cm^{-1} (117–123 GHz). Strong lines of the Q-branch of forbidden $\Delta K = 3$ transitions with K = 0, 3, 6... spread out from 370 GHz with the absorption coefficients of the order of $10^{-6}\ cm^{-1}$, while strong lines of the R-branch of allowed transitions begin from 7 cm^{-1} (830 GHz). Thus, the low-frequency spectrum of forbidden MW transitions of CH_3D lies far beyond the spectra formed by other types of MW transitions.

The HITRAN-2000 data bank includes CH_3D lines starting from 7 cm^{-1}, while the lines of forbidden transitions should lie, according to our estimates, in the range 3–4 cm^{-1}. The presented calculations of the forbidden spectrum of CH_3D show that it is possible to observe this type of the low-frequency spectrum with existing MW Stark modulation spectrometers and orotron spectrometers. Experimental investigations of the MW CH_3D spectra discussed in this paper are important for problems of MW astronomy and are interesting to the applied molecular spectroscopy from the viewpoint of application of the nonpolynomial models for energy levels and dipole moments of MW transitions in symmetric molecules.

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