

Sensitivity to variation of fundamental constants of rotational spectra of light diatomic radicals

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(Dated: May 3 2012 – June 29, 2012)

This is a brief note on the sensitivities Q_α and Q_μ for rotational transitions in CH, CD, OH, and other molecules, where the fine structure parameter A is comparable to the rotational constant B . In this case rotational transitions appear to be sensitive to both fundamental constants with sensitivity coefficients of the order of unity. Further enhancement of the sensitivity can take place for low frequency transitions $\omega \ll B$.

PACS numbers: 06.20.Jr, 06.30.Ft, 33.20.Bx

I. MOTIVATION

Six lowest rotational lines of CH were recently detected with Herschel telescope towards Orion KL [1]. That pushed me to calculate sensitivities for these transitions. I used the same model which had been used for the paper [2]. It turned out that CH is close to a very special case: when $A = 2B$ the sensitivities Q_α almost turn to zero for most rotational transitions. For the isotopologue CD, where rotational constant is two times smaller and $A \approx 4B$, all sensitivities for the low rotational transitions are nonzero. In addition, for CD molecule there is a low frequency transition between close rotational levels $N = 2, J = 5/2$ and $N = 2, J = 3/2$ with enhanced sensitivities to fundamental constants. The laboratory spectrum of CD was measured in [3], but I do not know about any astronomical observations.

Another molecule of astrophysical importance is OH. For this molecule $A \approx -7B$. This molecule is observed more often from the interstellar medium (ISM). Sergei Levshakov provided following bibliography on OH. In Ref. [4] many rotational lines were detected in the close galaxies NGC 4418 [$V = 2105$ km/s, distance is probably about 100 Mly] and APR 220 [$V = 5434$ km/s, distance 250 Mly]. Several emission lines were detected from the Orion Molecular Cloud 1 in [5]. In Ref. [6] the hyperfine structure was resolved for the 1837 GHz line from a star forming region. Two rotational lines were detected in from a protoplanetary disk around the star HD100546 in [7]. Finally, rotational OH lines were seen from the young stellar object [8] and from comets [9].

II. ROTATIONAL SPECTRUM

Rotational spectra of CH, CD, and OH radicals are shown on Fig. 1, Fig. 2, and Fig. 3. To a first approximation rotational energy of the diatomic molecule is described by the Hamiltonian:

$$H_{\text{rot}} = B(\mathbf{J} - \mathbf{J}_e)^2 \quad (1a)$$

$$= B\mathbf{J}^2 - B(J_+J_{e,-} + J_-J_{e,+}) - B\Omega^2 \quad (1b)$$

where B is rotational constant, \mathbf{J} is the total angular momentum of the molecule, and \mathbf{J}_e is electronic angular mo-

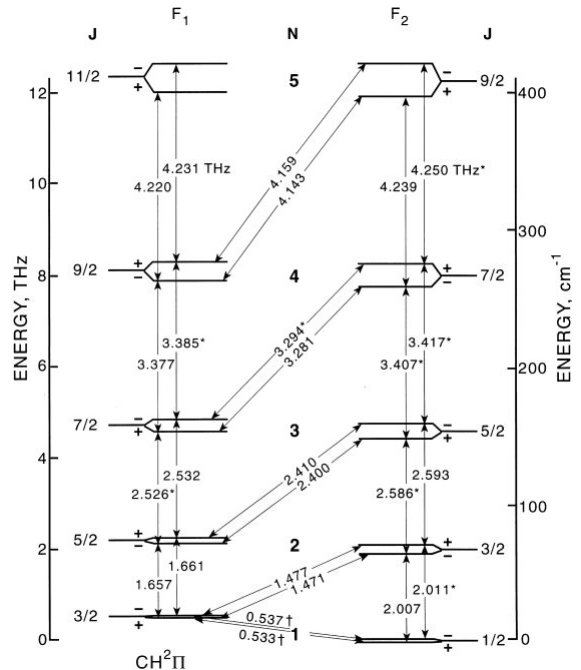


FIG. 1: Rotational spectrum of CH from Ref. [10]. A doubling is not to scale.

mentum. The first term in expression (1b) describes conventional rotational spectrum. The last term is constant for a given electronic state (we used that $J_\zeta = J_{e,\zeta} = \Omega$). The second term is known as Coriolis interaction H_{Cor} . It is responsible for the mixing of $\Pi_{1/2}$ and $\Pi_{3/2}$ states, as well as Π and Σ states.

If we neglect Coriolis interaction, the eigenvectors of Hamiltonian (1) have definite projections M and Ω of the molecular angular momentum \mathbf{J} on the laboratory axis z and on the molecular axis ζ respectively. In this approximation the states $|J, M, \Lambda, \Sigma, \Omega\rangle$ and $|J, M, -\Lambda, -\Sigma, -\Omega\rangle$ are degenerate. Adding the spin-orbit interactions term to the rotational energy we get:

$$E_{J,\pm\Omega} = A\Lambda\Sigma + BJ(J+1) - B\Omega^2. \quad (2)$$

If we neglect $\Pi - \Sigma$ mixing, the only nondiagonal term is the Coriolis matrix element between $\Pi_{1/2}$ and $\Pi_{3/2}$

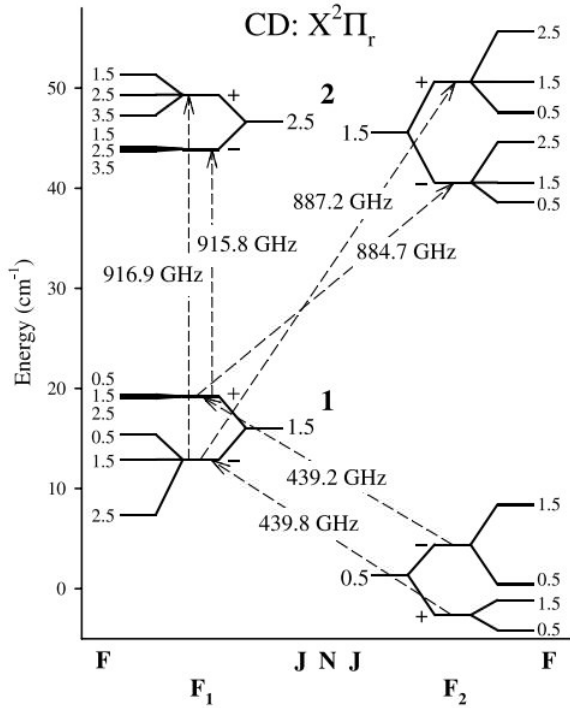


FIG. 2: Rotational spectrum of CD from Ref. [3]. Λ doubling and hyperfine structure are not to scale.

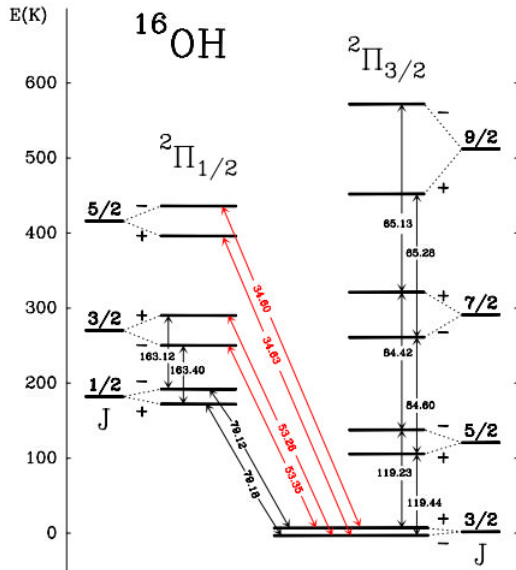


FIG. 3: Rotational spectrum of OH from Ref. [5]. Transition frequencies are in μm . Λ doubling is not to scale.

states [11]:

$$\langle \Pi_{1/2} | H_{\text{Cor}} | \Pi_{3/2} \rangle = B \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})}. \quad (3)$$

We see from (2) that in the diagonal approximation the splitting between $\Pi_{1/2}$ and $\Pi_{3/2}$ states is equal to

$A - 2B$, rather than simply A . This is because for a given quantum number J the rotational angular momentum \mathbf{R} depends on the electronic angular momentum \mathbf{J}_e : $\mathbf{R} = \mathbf{J} - \mathbf{J}_e$.

If we take into account mixing (3), the energies are given by the expressions:

$$E_{J>1/2,\pm} = B \left(J + \frac{1}{2} \right)^2 - \frac{5}{4}B \quad (4)$$

$$\pm \sqrt{\left(\frac{A}{2} - B \right)^2 + B^2 \left(J - \frac{1}{2} \right) \left(J + \frac{3}{2} \right)}.$$

$$E_{J=1/2} = -\frac{1}{2}A + \frac{3}{4}B. \quad (5)$$

For $A \gg B$ these expressions are reduced to Eq. (2) with the upper and lower signs in (4) corresponding to $|\Omega| = \frac{3}{2}$ and $\frac{1}{2}$ respectively. When A and B are of the same order of magnitude the states $\Pi_{3/2}$ and $\Pi_{1/2}$ are strongly mixed. For $A = 2B$ we get exactly 50-50 mixing and for smaller values of A the upper sign corresponds to the state, which is closer to $\Pi_{1/2}$. Clearly, for $A \approx 2B$ the energies (4) very weakly depend on A . At the same time, the lower level (5) always depend on A linearly.

We conclude that for CH molecule, where $|A - 2B| \ll B$ all rotational transitions frequencies between levels with $J > \frac{1}{2}$ are almost independent on A . Consequently, for these transitions $Q_\alpha \approx 0$. On the other hand, the dependence on B is almost linear, thus $Q_\mu \approx 1$. Transitions from the level $J = \frac{1}{2}$, on the contrary, depend on both A and B with $Q_\alpha \sim Q_\mu \sim 1$.

For the isotopologue CD the rotational constant is approximately two times smaller, while spin-orbit constant remains unchanged. Consequently, now $A \approx 4B$ and both terms under the square root in Eq. (4) are comparable for small values of J . As a result, rotational energies depend on both constants and both sensitivities are of the same order of magnitude. According to the general rule the large absolute values of sensitivities may appear for the low frequency transitions $\omega \ll B$.

The simple discussion in this section seems to explain all important features of the numerical results for rotational transitions given below.

A. Λ doubling

Up to now we neglected Λ doubling and the states $|\Lambda\rangle$ and $|\Lambda\rangle$ were degenerate. In the higher orders in Coriolis and spin-orbit interactions this degeneracy is removed and new eigenstates are the states of definite parity $p = \pm 1$ [12]. To account for Λ doubling one can add phenomenological corrections to the Hamiltonian (1) as I did in [2]. It is important though that for each phenomenological parameter we need to define its dependence on fundamental constants α and μ . This can be done only for sufficiently simple Hamiltonians, where all parameters can be unambiguously associated with particular terms of the perturbation theory. An adequate

model for our purposes can be based on the Hamiltonian suggested by Meerts and Dymanus [11]. It includes only two additional parameters S_1 and S_2 . The former appears in the second order as a cross term in Coriolis and spin-orbit interaction and the latter is quadratic in Coriolis interaction. These parameters are related to the more widely used parameters p and q . *It would be good to give explicit relation, as it would allow using parameters from the NIST database [13].*

Λ doubling is much smaller than rotational intervals. Because of that both components of the doublet have almost identical sensitivity coefficients, which are independent of the details of Λ doubling Hamiltonian. Microwave transitions between two Λ doublet parity states, on the contrary, are determined by the parameters S_1 and S_2 . For CH molecule I fitted these parameters to the experimental spectrum [2]. For CD molecule I simply scaled them assuming that $S_1 \propto M^{-1}$ and $S_2 \propto M^{-2}$. For the more reliable predictions of the Λ doubling frequencies and sensitivity coefficient these parameters should be also fitted.

III. RESULTS

TABLE I: Parameters of the spin-rotational Hamiltonian for CH, CD, and OH molecules which were used for the estimates of the transition frequencies and sensitivity coefficients.

Molecule	A (GHz)	A (GHz)	S_1 (MHz)	S_2 (MHz)
CH	843.81757	425.47685	251.47	827.75
CD	842.309	230.895	126.0	144.0
OH	-4161.75018	557.93957	-1753.294	575.521

TABLE II: Frequencies (GHz) and sensitivities of the rotational transitions in CH.

N, J, p	N', J', p'	ν_{theor}	ν_{expt} [14]	Q_α	Q_μ
$1, \frac{3}{2}, +$	$1, \frac{1}{2}, -$	533.9	532.7	1.59	0.20
$1, \frac{3}{2}, -$	$1, \frac{1}{2}, +$	537.9	536.8	1.57	0.22
$2, \frac{3}{2}, +$	$1, \frac{3}{2}, -$	1477.2	1477.4	0.00	1.00
$2, \frac{3}{2}, -$	$1, \frac{3}{2}, +$	1470.6	1470.7	-0.01	1.00
$2, \frac{5}{2}, +$	$1, \frac{3}{2}, -$	1663.0	1661.1	0.00	1.00
$2, \frac{5}{2}, -$	$1, \frac{3}{2}, +$	1658.8	1657.0	0.00	1.00
$2, \frac{3}{2}, +$	$1, \frac{1}{2}, -$	2011.8	2010.8	0.42	0.79
$2, \frac{3}{2}, -$	$1, \frac{1}{2}, +$	2007.8	2006.8	0.42	0.79
$2, \frac{5}{2}, +$	$2, \frac{3}{2}, -$	193.1	191.1	0.01	1.03
$2, \frac{5}{2}, -$	$2, \frac{3}{2}, +$	180.9	178.9	0.06	0.94

We estimate sensitivity coefficients for rotational transitions in CH, CD, and OH molecules using simple four parameter spin-rotational Hamiltonian described in [2]. The values of the parameters used here are listed in Table I. For CH and OH molecules we use the same parameters as in [2]. Parameters A and B for CD are taken

TABLE III: Frequencies (GHz) and sensitivities of the rotational transitions in CD.

N, J, p	N', J', p'	ν_{theor}	ν_{expt} [14]	Q_α	Q_μ
$1, \frac{3}{2}, +$	$1, \frac{1}{2}, -$	439.9	439.2	1.10	0.45
$1, \frac{3}{2}, -$	$1, \frac{1}{2}, +$	440.3	439.8	1.09	0.46
$2, \frac{3}{2}, +$	$1, \frac{3}{2}, -$	886.8	887.2	0.82	0.59
$2, \frac{3}{2}, -$	$1, \frac{3}{2}, +$	884.7	884.7	0.82	0.59
$2, \frac{5}{2}, +$	$1, \frac{3}{2}, -$	917.6	916.9	0.14	0.93
$2, \frac{5}{2}, -$	$1, \frac{3}{2}, +$	916.7	915.8	0.14	0.93
$2, \frac{5}{2}, +$	$2, \frac{3}{2}, -$	32.3	31.5	-19.1	10.6
$2, \frac{5}{2}, -$	$2, \frac{3}{2}, +$	30.5	29.3	-20.3	11.2
$2, \frac{3}{2}, +$	$1, \frac{1}{2}, -$	1326.0	1325.8	0.91	0.55
$2, \frac{3}{2}, -$	$1, \frac{1}{2}, +$	1325.6	1325.3	0.91	0.54

TABLE IV: Frequencies (GHz) and sensitivities of the rotational transitions in OH.

Ω, J, p	Ω', J', p'	ν_{theor}	ν_{expt} [14]	Q_α	Q_μ
$\frac{3}{2}, \frac{5}{2}, +$	$\frac{3}{2}, \frac{3}{2}, -$	2527.4	2514.3	0.13	0.93
$\frac{3}{2}, \frac{5}{2}, -$	$\frac{3}{2}, \frac{3}{2}, +$	2523.0	2509.9	0.13	0.93
$\frac{1}{2}, \frac{1}{2}, +$	$\frac{3}{2}, \frac{3}{2}, -$	3776.7	3789.2	2.14	-0.07
$\frac{1}{2}, \frac{3}{2}, -$	$\frac{3}{2}, \frac{3}{2}, +$	3773.7	3786.2	2.14	-0.07
$\frac{1}{2}, \frac{3}{2}, +$	$\frac{1}{2}, \frac{1}{2}, -$	1843.7	1834.7	-0.14	1.07
$\frac{1}{2}, \frac{3}{2}, -$	$\frac{1}{2}, \frac{1}{2}, +$	1846.7	1837.8	-0.13	1.07
$\frac{1}{2}, \frac{3}{2}, +$	$\frac{3}{2}, \frac{5}{2}, -$	3094.3	3110.9	2.41	-0.20
$\frac{1}{2}, \frac{3}{2}, -$	$\frac{3}{2}, \frac{5}{2}, +$	3096.1	3112.7	2.42	-0.21
$\frac{1}{2}, \frac{3}{2}, +$	$\frac{3}{2}, \frac{3}{2}, -$	5615.7	5619.2	1.39	0.31
$\frac{1}{2}, \frac{3}{2}, -$	$\frac{3}{2}, \frac{3}{2}, +$	5625.1	5628.7	1.39	0.30
$\frac{3}{2}, \frac{7}{2}, +$	$\frac{3}{2}, \frac{5}{2}, -$	3565.9	3543.8	0.10	0.95
$\frac{3}{2}, \frac{7}{2}, -$	$\frac{3}{2}, \frac{5}{2}, +$	3573.3	3551.2	0.10	0.95

from [3]. For the parameters S_1 and S_2 we use CH values scaled according to their assumed dependence on the reduced mass M , i.e. $S_1 \sim M^{-1}$ and $S_2 \sim M^{-2}$.

Tables II – IV list results of the calculations and experimental frequencies from [14] averaged over the hyperfine structure. For CH and CD molecules we use quantum numbers N, J, p , $\mathbf{N} = \mathbf{J} - \mathbf{S}$. Quantum number N is well defined when electron spin decouples from the molecular axis. For OH molecule the spin-orbit interaction is stronger and decoupling of the spin takes place only for $J > \frac{9}{2}$ [2]. Because of that here we use quantum numbers Ω, J, p .

Table II demonstrates the anomaly discussed Sec. II that only transitions to the states with $J = \frac{1}{2}$ depend on α while all other transitions have $Q_\alpha \approx 0$ and $Q_\mu \approx 1$. For CD molecule all transition frequencies depend on both fundamental constants. Finally, for OH molecule transitions with $\Delta\Omega = 0$ are almost pure rotational ($Q_\alpha \approx 0$, $Q_\mu \approx 1$). Transitions with $\Delta\Omega = \Delta J = 1$, on the contrary, depend only on α .

A lot of the stuff from this note has just ap-

peared in the Ref. [15].

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