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published in
Physical Review A. Atomic, Molecular and Optical Physics
2011

DOI (link to publisher)
10.1103/PhysRevA.84.062505

document version
Publisher's PDF, also known as Version of record

Link to publication in VU Research Portal

citation for published version (APA)

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Download date: 08. Aug. 2024
Sensitivity of transitions in internal rotor molecules to a possible variation of the proton-to-electron mass ratio

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(Received 23 September 2011; published 7 December 2011)

Recently, methanol was identified as a sensitive target system to probe variations of the proton-to-electron mass ratio \( \mu \) [Jansen et al., Phys. Rev. Lett. 106, 100801 (2011)]. The high sensitivity of methanol originates from the interplay between overall rotation and hindered internal rotation of the molecule; that is, transitions that convert internal rotation energy into overall rotation energy, or vice versa, have an enhanced sensitivity coefficient, \( K_\mu \). As internal rotation is a common phenomenon in polyatomic molecules, it is likely that other molecules display similar or even larger effects. In this paper we generalize the concepts that form the foundation of the high sensitivity in methanol and use this to construct an approximate model which makes it possible to estimate the sensitivities of transitions in internal rotor molecules with \( C_{3v} \) symmetry, without performing a full calculation of energy levels. We find that a reliable estimate of transition sensitivities can be obtained from the three rotational constants \((A, B, \text{ and } C)\) and three torsional constants \((F, V_1, \text{ and } \rho)\). This model is verified by comparing obtained sensitivities for methanol, acetaldehyde, acetamide, methyl formate, and acetic acid with a full analysis of the molecular Hamiltonian. Of the molecules considered, methanol is by far the most suitable candidate for laboratory and cosmological tests searching for a possible variation of \( \mu \).

DOI: 10.1103/PhysRevA.84.062505
PACS number(s): 33.15.-e, 06.20.Jr, 98.80.—k

I. INTRODUCTION

Physical theories extending the standard model have presented scenarios that allow for, or even predict, spatiotemporal variations of the constants of nature [1]. Currently, a number of laboratory experiments and astronomical observations are conducted to search for signatures of such variations [2]. One of the dimensionless constants that are hypothesized to vary is the proton-to-electron mass ratio, \( \mu = m_p/m_e \). A variation of \( \mu \) can be detected by comparing frequencies of spectral lines in molecules as a function of time and/or position. A fractional change in \( \mu \) will manifest itself as a fractional frequency shift. As a measure for the inherent sensitivity of a transition, the sensitivity coefficient, \( K_\mu \), is defined by

\[
\frac{\Delta \nu}{\nu} = K_\mu \frac{\Delta \mu}{\mu}.
\]

(1)

For pure rotational transitions \( K_\mu = -1 \), for pure vibrational transitions \( K_\mu = -\frac{1}{2} \), while for pure electronic transitions \( K_\mu = 0 \) [3]. Transitions between the inversion levels of ammonia [4,5] and hydronium (\( \text{H}_3\text{O}^+ \)) [6] have a sensitivity of \( K_\mu = -4.2 \) and \( K_\mu = -2.5 \), respectively. It was shown that the sensitivity of a transition between two near-degenerate levels that have a different functional dependence on \( \mu \) is enhanced significantly [6–10]. Recently, we reported such an enhancement for torsional-rotational transitions in methanol [11].

Methanol (\( \text{CH}_3\text{OH} \)), schematically depicted in Fig. 1, consists of an OH group attached to a methyl group. The OH and methyl group may rotate with respect to each other about the C–O bond. On the left-hand side of the figure, the potential energy curve is shown as a function of the torsional angle, \( \gamma \). The interaction between the OH and methyl group results in a threefold barrier. Tunneling between the three wells results in a splitting of each rotational level into three levels of different torsional symmetries [12]. Transitions between the different torsional levels have a sensitivity coefficient, \( K_\mu = -2.5 \). As the torsional levels A and E belong to different symmetries, transitions between them are not allowed. It was shown in Jansen et al. [11] that transitions converting internal rotation energy into overall rotation energy, or vice versa, have sensitivity coefficients, \( K_\mu \), that range from \(-88 \) to \(+330 \) in the different isotopologues of methanol.

Hindered internal rotation is a common phenomenon found in many polyatomic molecules. Hence, other molecules may have similar or larger sensitivities to a variation of \( \mu \). In this paper we calculate the sensitivities for methanol, acetaldehyde, acetamide, methyl formate, and acetic acid, five relatively small molecules that have a group of \( C_{3v} \) symmetry that rotates with respect to the remainder of the molecule. These five molecules have been detected in the interstellar medium of the local galaxy [13] and some at high redshift [14]. Methylamine, another relatively small internal rotor molecule is computationally more complex and will be treated in a separate paper [15].

This paper is organized as follows. In Sec. II, we give a brief review of the theory of internal rotor molecules and outline how the torsional-rotational levels are numerically calculated using the BELGI code [16]. In addition, we present approximate expressions for obtaining the torsional energy splitting as function of the barrier height and the reduced moment of inertia, and compare this to the output of numerical calculations of a full Hamiltonian. In Sec. III, we discuss how the molecular constants that appear in the torsional-rotational Hamiltonian scale with \( \mu \). These scaling relations are then used to determine...
the sensitivities of selected transitions in five different internal rotor molecules using BELGI. In Sec. IV the analytical expressions for the torsional energy splitting presented in Sec. II are used to construct a simple model for obtaining the sensitivity coefficients.

II. HINDERED INTERNAL ROTATION

A review of hindered internal rotation can be found in the seminal paper by Lin and Swalen [12], while a recent review to estimate the sensitivity of other internal rotor molecules.

A. Hamiltonian

The potential energy of an internal rotor molecule is a periodic function of the torsional angle \( \gamma \) between the \( C_3 \) group and the remainder of the molecule, as shown in Fig. 1. Hence, it can be expanded in a Fourier series as

\[
V(\gamma) = \frac{V_3}{2}(1 - \cos 3\gamma) + \frac{V_6}{2}(1 - \cos 6\gamma) + \cdots, \tag{2}
\]

where typically \( V_6 \) is about 100 times smaller than \( V_3 \), but provides information on the shape of the torsional potential. If only the first term of the expansion is taken into account, the torsional wave functions and energies follow from the solutions of the Mathieu equation [12].

To express the kinetic part of the Hamiltonian an axis system. The inertia tensor then takes the form

\[
I = \begin{bmatrix}
I_c & 0 & 0 \\
0 & I_b & -I_{ab} \\
0 & -I_{ab} & I_a
\end{bmatrix}, \tag{3}
\]

with \( I_a = \sum_i m_i (b_i^2 + c_i^2) \) being the moment of inertia of the molecule about the \( a \) axis. The subscript \( i \) runs over all atoms with mass \( m_i \) in the molecule. Expressions for \( I_b \) and \( I_c \) can be found by cyclic permutation of the \( a, b, \) and \( c \) labels. \( I_{ab} = \sum_i m_i a_i b_i \) is the product of inertia about the \( a \) and \( b \) axis. The kinetic energy can be expressed as [12]

\[
T = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2 - I_{ab} \omega_a \omega_b + \frac{1}{2} I_{a2} \gamma^2 + I_{a2} \omega_a \gamma, \tag{4}
\]

where \( \omega_a, \omega_b, \) and \( \omega_c \) are the angular velocity components around the \( a, b, \) and \( c \) axis, respectively, and \( I_{a2} \) is the moment of inertia of the top along its own symmetry axis. For a given vibrational state, the zeroth-order torsion-rotation Hamiltonian can be separated into a symmetric top part, an asymmetric top part, and a torsional part [18,19]

\[
H^0 = H_{RS}^0 + H_{RA}^0 + H_{tors}^0, \tag{5a}
\]

where

\[
H_{RS}^0 = \frac{1}{2}(B + C)(P_a^2 + P_b^2) + AP_a^2, \tag{5b}
\]

\[
H_{RA}^0 = \frac{1}{2}(B - C)(P_a^2 - P_b^2) + D_{ab}(P_a P_b + P_b P_a), \tag{5c}
\]

\[
H_{tors}^0 = F(p_\gamma + \rho P_a)^2 + V(\gamma). \tag{5d}
\]

\( P_a, P_b, \) and \( P_c \) are the usual angular momentum operators along the \( a, b, \) and \( c \) axis, respectively, and \( p_\gamma = -i\partial/\partial \gamma \) is the angular momentum operator associated with the internal rotation of the top with respect to the frame. The coupling between the internal rotation and overall rotation in Eq. (5d) can be eliminated partly by transforming to a different axis system, the so-called “rho-axis system.” In the resultant “rho-axis method” (RAM), which is implemented in the BELGI code used hereafter, the torsional Hamiltonian operator contains only the +2FP_aP_bP_\gamma term. It is important to note here that two sign conventions are used in the literature for the torsion-rotation operator in Eq. (5d), that is, \( F(p_\gamma + \rho P_a)^2 \) and \( F(p_\gamma - \rho P_a)^2 \). If the latter convention is adopted the \( \pm K \) labeling of the \( E \) levels (vide infra) is reversed [20]. In this paper we adopt the convention with the “+” sign, that is, \( F(p_\gamma + \rho P_a)^2 \). The effective rotational and torsional constants are defined by

\[
A = \frac{1}{2}\hbar^2 \left( \frac{I_a + I_b}{I_a I_b - I_{ab}^2} - \frac{I_b}{I_b^2 + I_{ab}^2} \right), \tag{6}
\]

\[
B = \frac{1}{2}\hbar^2 \frac{I_b}{I_b^2 + I_{ab}^2}, \tag{7}
\]

\[
C = \frac{1}{2}\hbar^2 \frac{1}{I_c}, \tag{8}
\]

\[
D_{ab} = \frac{1}{2}\hbar^2 \frac{I_{ab}}{I_b^2 + I_{ab}^2}, \tag{9}
\]

\[
F = \frac{1}{2}\hbar^2 \frac{I_a I_b - I_{ab}^2}{I_{a2}(I_a I_b - I_{ab}^2)}. \tag{10}
\]
TABLE I. Some low-order Hamiltonian terms for an asymmetric top containing a C₃ᵥ internal rotor and a partial parameter list as used in the BELGI code (taken from Kleiner [17]). The ρ dependence of the molecular constants is given in parentheses. The product of the parameter and operator from a given row yields the term actually used in the torsion-rotation Hamiltonian of the fitting program, except for F, ρ, and A, which occur in the Hamiltonian in the form F(Pᵢρ + ρPᵢ)² + A Pᵢ² (see text).

<table>
<thead>
<tr>
<th>Rotational</th>
<th>( \frac{1}{(\mu^0)} )</th>
<th>( 1 - \cos 3\gamma )</th>
<th>( P^2 )</th>
<th>( 1 - \cos 6\gamma )</th>
<th>( A P^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( (\mu^0) )</td>
<td>( V₁/2 )</td>
<td>( F )</td>
<td>( V₂/2 )</td>
<td>( k₁ )</td>
</tr>
<tr>
<td>( P^2 )</td>
<td>( (\mu^0) )</td>
<td>( (B + C)/2 )</td>
<td>( F_1 )</td>
<td>( G_1 )</td>
<td>( L_1 )</td>
</tr>
<tr>
<td>( P^2 )</td>
<td>( (\mu^0) )</td>
<td>( A - (B + C)/2 )</td>
<td>( k₂ )</td>
<td>( k₃ )</td>
<td>( k₄ )</td>
</tr>
<tr>
<td>( P^2_1 - P_2^2 )</td>
<td>( (\mu^0) )</td>
<td>( (B - C)/2 )</td>
<td>( c₂ )</td>
<td>( c₃ )</td>
<td>( c₄ )</td>
</tr>
<tr>
<td>( P_a P_b + P_b P_a )</td>
<td>( (\mu^0) )</td>
<td>( D_{ab} )</td>
<td>( \delta_{ab} )</td>
<td>( \Delta_{ab} )</td>
<td>( \delta_{ab} )</td>
</tr>
</tbody>
</table>

where \( Iₐ₁ \) is the moment of inertia attributed to the frame, defined by \( Iₐ₁ = I_a - I_a₂ \). A dimensionless parameter \( \rho \) is introduced by the axis transformation described earlier. For a symmetric top, \( \rho \) is simply defined as the ratio between the moment of inertia of the top divided by the moment of inertia of the molecule along the \( a \) axis; that is, \( \rho = Iₐ₂/I_a \).

For asymmetric molecules, \( \rho \) is a more complicated function of the moments of inertia:

\[
\rho = \frac{Iₐ₁ \sqrt{Iₐ₂ + Iₐ₃} - Iₐ₂ \sqrt{Iₐ₁ + Iₐ₃}}{Iₐ₁ \sqrt{Iₐ₂ + Iₐ₃} + Iₐ₂ \sqrt{Iₐ₁ + Iₐ₃}}.
\]  

(11)

The Hamiltonian of Eq. (5) can be expanded by adding additional distortion and interaction terms. Many of these higher-order constants multiply torsional operators by rotational operators and can be considered as effective constants after the van Vleck transformations of the torsion-rotation Hamiltonian [17,19,21]. Some low-order symmetry-allowed torsion-rotation terms for an asymmetric top containing a C₃ᵥ internal rotor are listed in Table I.

The overall Hamiltonian can now be written as

\[
H = H^0 + H_{int} + H_{cd},
\]

(12)

where \( H_{cd} \) corresponds to the centrifugal distortion Hamiltonian and \( H_{int} \) contains higher-order torsional-rotation interaction terms.

### B. Eigenfunctions and eigenvalues

#### 1. Torsion

Herbst et al. [19] suggested to evaluate the Hamiltonian of Eq. (12) in two steps. In the first step, the torsional Hamiltonian \( H^0_{tors} \) is diagonalized in a product basis set composed of free rotor torsional eigenfunctions of \( p \), and eigenfunctions \( |K\rangle \) = \((2\pi)^{-1/2}\exp(-iK\chi)\) of \( P_a \), where \( \chi \) is the Euler angle:

\[
|K_{\sigma}\rangle = \frac{1}{\sqrt{2\pi}} |K\rangle \exp(i[3k + \sigma]n),
\]

(13)

where \( \sigma \) can take the values \(-1, 0, \) or \(+1\) and \( k \) can be any integer. The eigenvalues of \( P_a \) are \( 3k + \sigma \) as required by the periodicity of the potential. Due to the symmetry of the torsional Hamiltonian, basis functions of different \( \sigma \) do not mix. Moreover, basis functions of different \( K \) do not mix either, as \( P_a \) and \( H^0_{tors} \) commute. The resulting Hamiltonian matrix for each value of \( \sigma \) and \( K \) is infinite in size, but it was found that truncating it to a \( 21 \times 21 \) matrix \((-10 \leq k \leq 10) \) is sufficient to obtain experimental accuracy for the molecules under study here [19]. The torsional eigenfunctions can be written as

\[
|K_{\nu_1\sigma}\rangle = \frac{1}{\sqrt{2\pi}} |K\rangle \sum_{k=-10}^{10} A_{3k+\sigma}^K \exp(i[3k + \sigma]n),
\]

(14)

where \( \nu_1 \) is the torsional vibration quantum number and \( A_{3k+\sigma}^K \) are expansion coefficients. States with \( \sigma = 0 \) are labeled as \( A \), and states with \( \sigma = +1 \) and \( \sigma = -1 \) are labeled as \( E1 \) and \( E2 \), respectively. For \( A \) torsional states, \( \pm K \) levels are degenerate, whereas for \( E \) states a degeneracy exists between \( E1 \), \( K \) and \( E2 \), \(-K \) levels. Although the torsional \( E1 \) and \( E2 \) state have different labels, transitions between these two states are allowed. It was therefore suggested by Lees [22] to refer to \( E1 \) and \( E2 \) levels as \( E \) levels where the sign of \( K \) distinguishes the two symmetries.

The eigenvalues of the torsional Hamiltonian for methanol [23], acetaldehyde [24], and acetic acid [25] are depicted in Fig. 2 as a function of \( K \) for the ground torsional state \( \nu_1 = 0 \) of those molecules. The solid circles, open circles, and open triangles represent values numerically calculated using the BELGI code [16] for the \( A \), \( E1 \), and \( E2 \) torsional states, respectively. It is seen that the torsional energies are periodic functions of \( K \) with a period that is proportional to \( \rho^{-1} (\rho = 0.81, 0.33, \) and 0.07 for methanol, acetaldehyde, and acetic acid, respectively).

In order to obtain an analytical model for estimating the sensitivities of transitions in internal rotor molecules, discussed in Sec. IV, we now derive approximate solutions to the torsional Hamiltonian. It is clear from Eq. (14) that substituting \( \sigma \) with \( \sigma + 3 \) results in identical eigenvalues; consequently, the eigenvalues may be regarded as periodic functions which can be expanded in a Fourier series as [12]

\[
E_{\text{tors}} = F \left[ a_0 + a_1 \cos \left( \frac{2\pi}{3} (\rho K + 3) \right) + \cdots \right],
\]

(15)

where \( a_0,a_1 \) and higher-order terms are (dimensionless) expansion coefficients. It can be shown [12] that these coefficients

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are functions of the reduced barrier height \( s \), with

\[
s = \frac{4V_3}{9F},
\]

and that in the moderate-to-high-barrier limit, the series converges quickly. The solid curves shown in Fig. 2 are obtained by fitting the first two terms of Eq. (15) for \( \sigma = 0 \), \( E1 (\sigma = +1) \), and \( E2 (\sigma = -1) \) states. The resulting coefficients for methanol, acetaldehyde, and acetic acid, as well as those for acetamide and methyl formate, are plotted as the open diamonds in Fig. 3. By diagonalizing \( H_{\text{top}}^0 \) for several values of \( s \) and \( \rho > 0 \), while all other constants are set to zero, and fitting the torsional energies according to Eq. (15), \( a_1 \) coefficients were obtained for each value of \( s \). These generic coefficients are plotted as the solid diamonds in Fig. 3. According to Lin and Swalen [12], the \( a_1 \) coefficients are given by the following equation:

\[
a_1 = A_{15} s^8 e^{-C_1 s^7}. \tag{17}
\]

The solid line shown in Fig. 3 is obtained by fitting Eq. (17) to the generic \( a_1 \) values, using \( A_{15} = -5.296, B_1 = 1.111 \), and \( C_1 = 2.120 \). Note that these fit parameters deviate from those given in Table IV of Ref. [12], but the curves agree with the curves shown in Fig. 7 of the same paper. Small differences between the curves and the \( a_1 \) coefficients obtained for the different molecules can be attributed to higher-order torsional terms which were not taken into account to obtain the fits.

### 2. Rotation

At this point the torsional Hamiltonian is diagonalized and the first step of the approach by Herbst et al. is complete. The second step of the approach consists of evaluating the remainder of the full Hamiltonian, that is, overall rotation and coupling terms, in the basis set

\[
|JK\nu_t\sigma\rangle = |JK\rangle |K\nu_t\sigma\rangle, \tag{18}
\]

with \( |JK\rangle \) the symmetric top rotational eigenfunctions [19]. The eigenvalues of the Hamiltonian of Eq. (5b) are

\[
\langle JK\nu_t\sigma|H_{\text{sym}}^0|JK\nu_t\sigma\rangle = \frac{1}{2}(B + C)J(J + 1) + \left(A - \frac{B + C}{2}\right)K^2. \tag{19}
\]

Note that, in the case of an asymmetric top, torsional \( A \) levels are split in \( \pm \) components for \( K > 0 \) due to the asymmetry of the molecule.

### C. Level schemes and selection rules

In Fig. 4 the lowest energy levels of \( ^{12}\text{CH}_3^{16}\text{OH} \) are shown for the \( A \) and \( E \) species. \( A \) and \( E \) symmetry species can be considered as two different molecular species in the same sense as \( \text{para-} \) and \( \text{ortho-hydrogen} \): Radiative transitions between \( A \) and \( E \) species do not occur. The arrangement of energy levels within a symmetry state is quite similar to the structure of the \( K \) ladders in a (prolate) symmetric top; however, in the case of internal rotation each \( K \) ladder attains an additional offset,
FIG. 4. Energy of the lowest rotational levels in the torsion-vibrational ground state \((v_t = 0)\) of methanol \((^{12}\text{CH}_3\text{OH})\) [23]. The levels are denoted by \(J\) (indicated on the left side of each level), \(K\). For the \(A\) levels the so-called parity quantum number \((\mp)\) is also used. The panel on the left displays the \(A\) state levels, whereas the panel on the right displays the \(E\) state levels. High sensitivities are expected for transitions that connect near degenerate levels with different \(K\).

\[ E_{\text{tors}}(K), \text{ induced by the tunneling splitting. The } \pm \text{ or } - \text{ component of the } A \text{ state refers to the } |J,K,v_t,0\rangle \pm |J,-K,v_t,0\rangle \text{ and } |J,K,v_t,0\rangle \mp |J,-K,v_t,0\rangle \text{ linear combinations of basis functions for } K \text{ even and } K \text{ odd, respectively. The overall parity of the levels is given by } \pm (-1)^{J+v_t} [19]. \]

The selection rules for allowed transitions within a torsion-vibrational state are [19]

\[
\begin{align*}
A \text{ levels: } & \pm \pm \pm \triangle J = 0 \ |\Delta K| = 0 (K \neq 0), 1,
\pm \pm \pm |\Delta J| = 1 \ |\Delta K| = 0, 1,
E \text{ levels: } & \triangle J = 0 \ |\Delta K| = 1,
\triangle J = 1 \ |\Delta K| = 0, 1,
\end{align*}
\]

where \(K\) is only a good quantum number in the limit of a symmetric top. As a consequence, transitions with \(|\Delta K| > 1\) are allowed in asymmetric top molecules.

### III. SCALING AND SENSITIVITY COEFFICIENTS

The sensitivity to a variation of \(\mu\) of a transition between states \(|\nu_0', J'', K'', T_s''\rangle\) and \(|\nu_0', J', K', T_s'\rangle\) is given by

\[
K_\mu(\nu_0', J'', K'', T_s'' \rightarrow \nu_0', J', K', T_s') = \frac{\mu(\partial E/\partial \mu)_{\nu_0', J'', K'', T_s''} - \mu(\partial E/\partial \mu)_{\nu_0', J', K', T_s'}}{E(\nu_0', J'', K'', T_s'') - E(\nu_0', J', K', T_s')}. \tag{20}
\]

Thus, in order to calculate the \(K_\mu\) coefficients, the energy of each level and its dependence on \(\mu\) has to be obtained. This translates into knowing the values of the molecular constants that go into BELGI and how these constants scale with \(\mu\).

We first examine the scaling relations for the lowest-order constants. We implicitly assume that the neutron-electron mass ratio follows the same behavior as the proton-electron mass ratio and that no effects depending on quark structure persist [26]. As a consequence, the atomic masses and hence the moments of inertia are directly proportional to \(\mu\). The rotational, centrifugal, and torsional constants \(A, B, C, D_{ab},\) and \(F\) and the factor \(\rho\) are explicit functions of \(I_a, I_b, I_c,\) and \(I_{ab}\), their \(\mu\) dependence is obtained from Eqs. (6)–(11). Within the Born-Oppenheimer approximation, the torsional potential \(V_3\) is independent of the mass of the nuclei and hence of \(\mu\).

The scaling relations for higher-order constants are derived from combinations of lower-order torsional and rotational operators. Some symmetry-allowed torsion-rotation terms are listed in Table I. Let us, for example, inspect the constant \(M_3\), which can be considered as a product of the torsional operator \(P_3\) with the rotational operator \(P^2\). As the term with \(P_3^2\) scales as \(\mu^{-2}\) and the term with \(P^2\) scales as \(\mu^{-1}\), we expect \(M_3\) to scale as \(\mu^{-3}\). The scaling relations of constants associated with other operators follow in a similar manner. The supplementary material of Ref. [11] lists the scaling relations for all constants used for methanol.

In this work, as well as in our previous work [11], we interpreted higher-order terms multiplying operators with powers of \(P_3, P_0\) [such as \(\rho_j(L_j), \rho_k(k_1), \rho_m(k_3)\)] as the \(J, K,\) and \(m\) dependence of \(\rho\) (hence, we assumed these terms
should be scaled as $\mu^{-1}$. It was, however, kindly brought to our attention [27] that those terms might have been interpreted as powers of $2F\rho$ (in which case they should be scaled as $\mu^{-2}$). Interestingly, when we use these alternative scaling relations, the obtained sensitivities for the various transitions calculated using 119 constants are much closer to the values found when using only 7 constants ($A$, $B$, $C$, $D_{ab}$, $F$, $V_3$, and $\rho$). This might be taken as an indication (but not a proof) that the latter scaling relations are, in fact, the correct ones. To fully understand the implications of this finding, a careful study is needed where (i) proper expressions for the higher-order terms should be derived explicitly as functions of the mass (or the moment of inertia) and (ii) a consistent set of axis system must be assured for all parameters to be scaled. Although understanding the physical meaning of the higher-order constants is relevant in its own right, the exact scaling relations do not alter the obtained sensitivities significantly.

In order to determine the sensitivity coefficients, we have written a computer code that generates the molecular constants as a function of $\mu$ using the discussed scaling relations, calls BELGI with these constants as input, and subsequently stores the computed level energies.

As an example, the top panel of Fig. 5 shows the energies of the $2_2E$, $2_1E$, $3_{-1}E$, and $2_0E$ levels in methanol as a function of $\Delta\mu/\mu$. The sensitivity coefficient of the $2_0 \rightarrow 3_{-1}E$ and $2_1 \rightarrow 2_2E$ transitions can be obtained by dividing the difference in slope by the difference in energy [cf. Eq. (20)].

![Fig. 5. (Color online) Energies of selected rotational levels in methanol ($^{12}$CH$_4$OH) as a function of the fractional change in the proton-to-electron mass ratio. The insets in the top panel show magnifications of the regions where the levels cross. It can be seen that levels with same $J$ give rise to avoided crossings, whereas levels with different $J$ do not. The bottom panel depicts the sensitivity coefficients of the $2_1 \rightarrow 2_2E$ and $2_0 \rightarrow 3_{-1}E$ transitions as a function of $\Delta\mu/\mu$. For transitions between levels with same $J$, $K_\mu$ goes to zero at the (avoided) crossing, whereas transitions between levels with different $J$, $K_\mu$ diverges to infinity at the crossing.](image)

The sensitivity coefficients of these transitions as a function of the relative variation of the proton-electron mass ratio, $\Delta\mu/\mu$, are shown in the bottom panel of Fig. 5. As expected from Eq. (20), the sensitivity is strongly enhanced when the energy difference between the levels becomes small.

The behavior of the sensitivity coefficient close to the resonance depends on the quantum numbers of the levels involved. For instance, in methanol, $K_\mu$ is not a good quantum number due to the asymmetry of the molecule, and levels with equal $J$ mix. As a consequence, the $2_2E$ and $2_1E$ levels shown in Fig. 5 display an avoided crossing, and the sensitivity coefficient for the $2_1 \rightarrow 2_2E$ transition is zero at the resonance. In contrast, $J$ is a good quantum number and levels of different $J$ will not mix. As a consequence, the sensitivity coefficient for the $2_0 \rightarrow 3_{-1}E$ transition becomes infinite at the resonance. In practice, we are only interested in the value of $K_\mu$ at $\Delta\mu/\mu < 10^{-5}$ and the effects of avoided crossings are relevant only if the levels cross extremely close to $\Delta\mu/\mu = 0$.

In our study we have only come across one transition that has a significantly reduced sensitivity coefficient as a result of mixing of the energy levels involved, namely, the $8_0 \rightarrow 8_{-1}E$ transition in $^{12}$CD$_5^{16}$OD at 4.2 GHz with $K_\mu = 0.7$. Note that the sign of the sensitivity coefficients at $\Delta\mu/\mu = 0$ is positive if the levels cross at $\Delta\mu/\mu < 0$, and negative if the levels cross at $\Delta\mu/\mu > 0$.

Using the recipe described above, the sensitivity coefficient of any desired transition in a molecule containing a $C_3v$ symmetry group can be calculated. We have calculated the sensitivity coefficients of many (> 1000) transitions in methanol, acetaldehyde, acetamide, methyl formate, and acetic acid, using the constants listed in Refs. [23–25, 29, 30], respectively.

In Table II sensitivity coefficients of selected transitions in the vibrational ground state ($v_i = 0$) of these molecules are listed. For methanol, the most sensitive transitions involving levels with $J \leq 10$ are listed. For the other molecules no large sensitivities were found for the vibrational ground state and the eight lowest transition frequencies that have been observed in the interstellar medium have been listed [28]. From the table, we see in particular that transitions in methanol are much more sensitive to a variation of $\mu$ than the transitions listed for the other molecules. Except for the $1_{-1} \rightarrow 1_{1}E$ transition in acetaldehyde with $K_\mu = -3.7$, all transitions in acetaldehyde, acetamide, methyl formate, and acetic acid have $-1.57 \leq K_\mu \leq -0.74$.

The error in the last digit of the $K_\mu$ coefficients is quoted in brackets, and is conservatively taken to be 5% if $|K_\mu| > 1$ or 0.05 if $|K_\mu| < 1$. The error in the sensitivity coefficients has three sources. (i) The first consists of errors due to the uncertainty in the determination of the molecular constants. As the simulations reproduce almost all transitions < 100 kHz, this error is negligible small. (ii) The second source consists of errors due to inexactness of the scaling relations of higher-order constants. Many of the higher-order constants are products of torsional and rotational operators and may also be fairly correlated. Therefore, the exact relationships between the higher-order parameters and the moments of inertia (and masses) are not obvious. For methanol we have investigated the influence of the higher-order parameters by comparing $K_\mu$ coefficients calculated by scaling only the first 7 and the first 31 constants to $K_\mu$ coefficients obtained by
TABLE II. Selected transitions [28] and $K_\mu$ coefficients for different molecules, calculated with BELGI (fourth column) using the constants from Refs. [23–25,29,30] and the approximate model (fifth column) discussed in the text. For methanol the most sensitive lines are shown, whereas for the other molecules the eight lowest transitions that have been observed in the interstellar medium as listed in the review by Lovas [28] are given. The error in the last digit(s) is given within brackets. Molecules marked with an asterisk (*) are labeled according to the sign convention opposite to the one as used in the text to be consistent with literature, that is, $F(p_\gamma - \rho P_\alpha)^2$ instead of $F(p_\gamma + \rho P_\alpha)^2$. As a consequence, the sign of the $\pm K$ labeling of the $E$ transitions is reversed for these molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition, $J_K$</th>
<th>Transition (MHz)</th>
<th>$K_\mu^{\text{BELGI}}$</th>
<th>$K_\mu^{\text{toy}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>$5_1 \rightarrow 6_0 A^+$</td>
<td>6 668.5192(8)</td>
<td>−42.2 (2)</td>
<td>−46</td>
</tr>
<tr>
<td></td>
<td>$9_{-1} \rightarrow 8_{-1} E$</td>
<td>9 936.202(4)</td>
<td>11.6 (5)</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>$5_2 \rightarrow 4_1 A^+$</td>
<td>9 978.686(4)</td>
<td>53.3 (3)</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>$5_2 \rightarrow 4_1 A^-$</td>
<td>10 058.257(12)</td>
<td>52.3 (3)</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>$2_0 \rightarrow 3_{-1} E$</td>
<td>12 178.593(4)</td>
<td>−33.2 (2)</td>
<td>−32</td>
</tr>
<tr>
<td></td>
<td>$2_1 \rightarrow 3_0 E$</td>
<td>19 967.396(2)</td>
<td>−5.9 (3)</td>
<td>−5.0</td>
</tr>
<tr>
<td></td>
<td>$9_{-2} \rightarrow 10_{1} A^+$</td>
<td>23 121.024(2)</td>
<td>−11.7 (6)</td>
<td>−10.8</td>
</tr>
<tr>
<td></td>
<td>$3_2 \rightarrow 3_1 E$</td>
<td>24 928.715(14)</td>
<td>17.9 (9)</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>$2_2 \rightarrow 2_1 E$</td>
<td>24 934.382(5)</td>
<td>17.9 (9)</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>$8_2 \rightarrow 9_1 A^-$</td>
<td>28 969.954(20)</td>
<td>−9.5 (6)</td>
<td>−8.8</td>
</tr>
<tr>
<td></td>
<td>$4_{-1} \rightarrow 3_0 E$</td>
<td>36 169.290(14)</td>
<td>9.7 (5)</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>$6_2 \rightarrow 5_1 A^-$</td>
<td>38 293.292(14)</td>
<td>−15.1 (8)</td>
<td>−10.4</td>
</tr>
<tr>
<td></td>
<td>$6_2 \rightarrow 5_1 A^+$</td>
<td>38 452.653(14)</td>
<td>−15.0 (8)</td>
<td>−10.4</td>
</tr>
<tr>
<td></td>
<td>$7_0 \rightarrow 6_1 A^+$</td>
<td>44 069.476(15)</td>
<td>5.2 (3)</td>
<td>5.9</td>
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<tr>
<td></td>
<td>$1_0 \rightarrow 2_{-1} E$</td>
<td>60 531.489(10)</td>
<td>−7.4 (4)</td>
<td>−7.3</td>
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<td></td>
<td>$1_1 \rightarrow 2_0 E$</td>
<td>68 305.680(7)</td>
<td>−2.4 (1)</td>
<td>−2.2</td>
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<tr>
<td>Acetaldehyde</td>
<td>$1_{-1} \rightarrow 1_1 E$</td>
<td>1 849.634(7)</td>
<td>−3.7 (2)</td>
<td>−4.2</td>
</tr>
<tr>
<td></td>
<td>$1_1 \rightarrow 2_0 A^+$</td>
<td>8 243.462(3)</td>
<td>−1.11 (6)</td>
<td>−1.15</td>
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<tr>
<td></td>
<td>$1_0 \rightarrow 0_1 E$</td>
<td>19 262.140(4)</td>
<td>−1.00 (5)</td>
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<td></td>
<td>$1_0 \rightarrow 0_0 A^+$</td>
<td>19 265.137(1)</td>
<td>−1.00 (5)</td>
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<tr>
<td></td>
<td>$2_0 \rightarrow 1_0 E$</td>
<td>38 506.035(3)</td>
<td>−1.00 (5)</td>
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<td></td>
<td>$2_0 \rightarrow 1_1 A^+$</td>
<td>38 512.081(3)</td>
<td>−1.00 (5)</td>
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<tr>
<td></td>
<td>$1_{-1} \rightarrow 1_0 E$</td>
<td>47 746.980(5)</td>
<td>−1.03 (5)</td>
<td>−0.93</td>
</tr>
<tr>
<td></td>
<td>$1_1 \rightarrow 1_0 A^+$</td>
<td>47 820.620(4)</td>
<td>−1.02 (5)</td>
<td>−1.03</td>
</tr>
<tr>
<td>Acetamide$^*$</td>
<td>$2_2 \rightarrow 2_1 A^+$</td>
<td>9 254.418(4)</td>
<td>−1.04 (5)</td>
<td>−1.12</td>
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<tr>
<td></td>
<td>$1_0 \rightarrow 1_1 E$</td>
<td>13 388.703(4)</td>
<td>−1.57 (8)</td>
<td>−1.34</td>
</tr>
<tr>
<td></td>
<td>$4_1 \rightarrow 3_2 A^+$</td>
<td>14 210.349(4)</td>
<td>−1.03 (5)</td>
<td>−1.12</td>
</tr>
<tr>
<td></td>
<td>$3_3 \rightarrow 3_2 A^+$</td>
<td>14 441.705(4)</td>
<td>−1.05 (5)</td>
<td>−1.12</td>
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<tr>
<td></td>
<td>$2_0 \rightarrow 1_1 E$</td>
<td>15 115.748(4)</td>
<td>−1.43 (7)</td>
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<td></td>
<td>$2_2 \rightarrow 1_1 E$</td>
<td>22 095.527(4)</td>
<td>−0.74 (5)</td>
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<tr>
<td></td>
<td>$3_3 \rightarrow 3_2 A^+$</td>
<td>22 769.635(4)</td>
<td>−1.03 (5)</td>
<td>−1.08</td>
</tr>
<tr>
<td></td>
<td>$4_2 \rightarrow 3_1 E$</td>
<td>47 373.320(4)</td>
<td>−1.04 (5)</td>
<td>−1.11</td>
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<td>Methyl formate$^*$</td>
<td>$1_1 \rightarrow 1_{-1} E$</td>
<td>1 610.900(2)</td>
<td>−1.00 (5)</td>
<td>−0.70</td>
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<tr>
<td></td>
<td>$2_{-1} \rightarrow 1_{-1} E$</td>
<td>22 827.741(8)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
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<tr>
<td></td>
<td>$2_1 \rightarrow 1_1 A^+$</td>
<td>22 828.134(8)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
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<td>$2_0 \rightarrow 1_0 E$</td>
<td>24 296.491(8)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
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<tr>
<td></td>
<td>$2_0 \rightarrow 1_1 A^+$</td>
<td>24 298.481(8)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>$2_1 \rightarrow 1_1 E$</td>
<td>26 044.796(8)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
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<tr>
<td></td>
<td>$2_1 \rightarrow 1_1 A^-$</td>
<td>26 048.534(8)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>$4_0 \rightarrow 3_0 E$</td>
<td>47 534.069(16)</td>
<td>−1.00 (5)</td>
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<tr>
<td>Acetic acid$^*$</td>
<td>$8_{-1} \rightarrow 7_{-1} E$</td>
<td>90 203.444(20)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>$8_{-1} \rightarrow 7_0 E$</td>
<td>90 203.444(20)</td>
<td>−1.00 (5)</td>
<td>−0.97</td>
</tr>
<tr>
<td></td>
<td>$8_0 \rightarrow 7_{-1} E$</td>
<td>90 203.444(20)</td>
<td>−1.00 (5)</td>
<td>−1.03</td>
</tr>
<tr>
<td></td>
<td>$8_0 \rightarrow 7_1 E$</td>
<td>90 203.444(20)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>$8_0 \rightarrow 7_0 A^+$</td>
<td>90 246.250(50)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>$8_0 \rightarrow 7_1 A^+$</td>
<td>90 246.250(50)</td>
<td>−1.00 (5)</td>
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<td></td>
<td>$8_1 \rightarrow 7_0 A^+$</td>
<td>90 246.250(50)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
<tr>
<td></td>
<td>$8_1 \rightarrow 7_1 A^+$</td>
<td>90 246.250(50)</td>
<td>−1.00 (5)</td>
<td>−1.00</td>
</tr>
</tbody>
</table>

scaling all 119 constants. Sensitivity coefficients were found to typically agree within 5% or 0.5% if 7 or 31 constants were scaled, respectively. The results of Levshakov et al. [31] are exactly identical to ours if only 7 constants are scaled. Differences in calculated $K_\mu$ coefficients due to alternative scaling relations for some higher-order terms.
TABLE III. Rotational and torsional energy differences and associated sensitivity coefficients. Expressions for differences in rotational energy are only valid in the limit of a symmetric top molecule.

<table>
<thead>
<tr>
<th></th>
<th>ΔE</th>
<th>K_μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation</td>
<td>ΔJ = 0</td>
<td>ΔK = ±1</td>
</tr>
<tr>
<td></td>
<td>ΔJ = ±1</td>
<td>ΔK = 0</td>
</tr>
<tr>
<td></td>
<td>ΔJ = ±1</td>
<td>ΔK = ±1</td>
</tr>
<tr>
<td></td>
<td>ΔJ = ±1</td>
<td>ΔK = ±1</td>
</tr>
<tr>
<td>Torsion</td>
<td>ΔK = 0^a</td>
<td>±√3FA1 sin (2π [ρK ± 1/2])</td>
</tr>
<tr>
<td></td>
<td>ΔK = ±1</td>
<td>±2FA1 sin (2π [ρK ± 1/2])</td>
</tr>
</tbody>
</table>

^aNote that the transitions involving different overall symmetry species of the torsional levels (A ↔ E) are forbidden; thus, transitions with ΔK = 0, ΔJ = 0 do not occur.

(vide supra) are therefore expected to be small. (iii) The third source consists of errors due to neglecting the μ dependence of the torsional potential. Within the Born-Oppenheimer approximation the torsional potential, V_3, is independent of the mass of the nuclei and hence of μ. It is known, however, that V_3 does vary between isotopologues. For instance, for $^{12}$CH$_{16}$OH the torsional potential $V_3 \approx 373$ cm$^{-1}$, and for $^{12}$CD$_{16}$OD $V_3 \approx 362$ cm$^{-1}$. A reliable model for this variation is not available. As a check, we have assumed $V_3$ to be a linear function of $I_{rot} = I_1I_2/I_s$; $V_3 = V_0(12^{12}$CH$_{16}$OH) - 19.4[$I_{rot} - I_{red}(12^{12}$CH$_{16}$OH)]. As $I_{red}$ is directly proportional to μ, this introduces a μ dependence in the potential. We found that the $K_μ$ coefficients for $^{12}$CH$_{16}$OH calculated by including the linear scaling for V_3 are typically 3% smaller than those obtained when the potential is assumed to be independent of μ.

IV. “TOY” MODEL

Although the numerical calculations described in the previous section yield the sensitivity coefficient for any desired transition, they provide limited insight. In this section, we devise a simple model which provides an intuitive picture of the physics involved and aids in the identification of other internal rotor molecules that possibly exhibit large sensitivity coefficients. In this model, we neglect coupling between vibrational, rotational, and torsional motion. In this case, the μ dependence of the energy of a certain state $|v, J, K, T_S>$ can be written as

$$\mu \left( \frac{dE}{d\mu} \right)_{v, J, K, T_S} = K_v^{vib} E_v^{vib} + K_μ^{rot} E_μ^{rot} + K_μ^{tors} E_μ^{tors},$$ (21)

where $K_v^{vib}$, $K_μ^{rot}$, and $K_μ^{tors}$ are the sensitivities to a possible variation of the proton-to-electron mass ratio of a vibrational, rotational, and torsional transition, respectively. We neglect vibrational excitation and use Eq. (21) to rewrite Eq. (20) as

$$K_μ = \frac{K_μ^{rot} ΔE_μ^{rot} + K_μ^{tors} ΔE_μ^{tors}}{ΔE_μ^{rot} + ΔE_μ^{tors}},$$ (22)

with ΔE_μ^{rot} and ΔE_μ^{tors} being the difference in rotational and torsional energy between the two energy levels involved, respectively. From this equation it immediately follows that $K_μ$ diverges for ΔE_μ^{rot} = −ΔE_μ^{tors} and $K_μ^{rot} ≠ K_μ^{tors}$. This implies that the highest sensitivities are expected for transitions that convert overall rotation into internal rotation or vice versa.

Furthermore, Eq. (22) indicates that the $K_μ$ coefficients are proportional to the amount of energy that is canceled. We now derive analytical expressions for ΔE_μ^{rot}, ΔE_μ^{tors}, $K_μ^{rot}$, and $K_μ^{tors}$ using the results of Sec. II.

The rotational energy is given by Eq. (19), from which it is straightforward to calculate the energy differences for different transitions. The results are listed in Table III. Note that these expressions are valid only for a nearly symmetric molecule.

$K_μ^{rot}$ follows from the μ dependence of the rotational constants. From Eqs. (6)–(8) A, B, and C are inversely proportional to the moments of inertia that are proportional to μ. Consequently, in first-order approximation $K_μ^{rot} = -1$.

The torsional energy is given by Eq. (15), from which the splitting between the A (σ = 0) and E (σ = ±1) states can be calculated:

$$ΔE_μ^{A↔E} = FA1 \left[ \cos \left( \frac{2π}{3} (ρK ± 1) \right) - \cos \left( \frac{2π}{3} ρK \right) \right]$$

$$= ± √3FA1 \sin \left( \frac{2π}{3} ρK ± 1 \frac{1}{2} \right).$$ (23)

Analogously, the splitting between E1 (σ = +1) and E2 (σ = -1) levels is given by

$$ΔE_μ^{E1↔E2} = √3FA1 \sin \left( \frac{2π}{3} ρK \right).$$ (24)

Equations (23) and (24) are plotted in Fig. 6 as function of $s$ for K = 0 and |K| = 1, respectively, using the A_1, B_1, and C_1 parameters obtained in Sec. II. Also shown are data points for the various isotopologues of methanol derived from experiments. Within the Born-Oppenheimer approximation $s$ is proportional to $I_{red} = \frac{1}{2}h^2F^{-1}$.

As transitions between different symmetry states (A ↔ E) are not allowed, we are interested in transitions within the same torsional states that differ in ΔK. The difference in torsional energy for such transition with ΔK = ±1 can be derived from Eq. (15) to be

$$ΔE_μ^{ tors} = ± 2FA1 \sin \left( \frac{π}{3} ρ \right) \sin \left( \frac{2π}{3} \left[ \rho \left( K ± \frac{1}{2} \right) + σ \right] \right).$$ (25)

Due to the a_1 coefficient appearing in Eqs. (23)–(25) all torsional splittings have the same dependence on $s$, and hence
on $\mu$. The sensitivity of a torsional transition, $K_{\mu}^{\text{tors}}$, can be obtained from Eq. (1) by writing

$$K_{\mu}^{\text{tors}} = \left( \frac{\partial \Delta E_{\text{tors}}}{\partial s} \right) \left( \frac{\partial \mu}{\partial s} \right) \frac{\Delta E_{\text{tors}}}{s F} = \frac{\partial (\Delta E_{\text{tors}}/F)}{\partial s} s F - 1,$$

(26)

where we have used the fact that $F$ scales with $\mu^{-1}$. The $-1$ appearing in the second line is introduced by the substitution of $\Delta E_{\text{tors}}$ with $\Delta E_{\text{tors}}/F$. By inserting Eq. (25) in Eq. (26) we obtain

$$K_{\mu}^{\text{tors}} = (B_1 - 1) - \frac{1}{2} C_1 \sqrt{s} \simeq 0.111 - 1.060 \sqrt{s},$$

(27)

where we have used the dimensionless fit values for $B_1$ and $C_1$ obtained in Sec. II. Hence, within our approximations, $K_{\mu}^{\text{tors}}$ is only a function of $s$. For $^{12}\text{CH}_3^{16}\text{OH}$, with $s = 6.01$, this results in $K_{\mu}^{\text{tors}} \approx -2.5$, in agreement with the value found in Jansen et al. \[11\].

With the help of Eq. (22) and the expressions for $\Delta E_{\text{rot}}$, $\Delta E_{\text{tors}}$, $K_{\mu}^{\text{rot}}$, and $K_{\mu}^{\text{tors}}$ as listed in Table III, we can now determine which transitions are likely to have an enhanced sensitivity and estimate the $K_\mu$ coefficients of these transitions. From Eq. (22), we saw that the highest sensitivities are expected when $\Delta E_{\text{rot}} \simeq -\Delta E_{\text{tors}}$. In Fig. 7 the difference in rotational energy, $\Delta E_{\text{rot}}$, (solid curves) and negated torsional energy, $-\Delta E_{\text{tors}}$ (dashed curves) are shown for $|J, K \rangle \rightarrow |J + 1, K - 1 \rangle A^+$ transitions in methanol. The highest sensitivities are expected when the lines representing the difference in rotational energy $\Delta E_{\text{rot}}$ and the negated difference in torsional energy $-\Delta E_{\text{tors}}$ cross. For this to happen at low $J$ and $K$ it requires that the rotational constants $A$, $B$, and $C$ are of the same order as the difference in torsional energy. If the rotational constants are much smaller or larger than $\Delta E_{\text{tors}}$, the crossings will only occur for high $J$ and/or $K$ quantum numbers. With the help of Fig. 7, it is straightforward to select transitions that are likely to have a large $K_\mu$ coefficient. For instance, the solid line representing the difference in rotational energy for $K = 1$ (solid circles) crosses the dashed line representing the negated difference in torsional energy near $J = 5$. As the lines cross near the maximum of torsional energy that may be attained, represented by the border of the gray shaded area, we may expect a large $K_\mu$ for the $5_1 \rightarrow 6_0 A^+$ transition. Indeed, this transition has $K_\mu = -42$.

The sensitivity coefficients $K_\mu$ of the transitions can be estimated using Eq. (22). Unfortunately, we found that the agreement between the $K_\mu$ coefficients obtained from this simple model and the values found from the full calculation was unsatisfactory, mainly as a result of neglecting the asymmetry of the molecules. Hence, we chose to use the experimental energy difference between the levels, $h\nu$, rather than $(\Delta E_{\text{rot}} + \Delta E_{\text{tors}})$. In this case, Eq. (22) can be written as

$$K_\mu = \left[ K_\mu^{\text{rot}} (h\nu - \Delta E_{\text{tors}}) + K_\mu^{\text{tors}} \Delta E_{\text{tors}} \right]/h\nu$$

$$= \frac{K_\mu^{\text{rot}} + \Delta E_{\text{tors}} (K_\mu^{\text{tors}} - K_\mu^{\text{rot}})}{h\nu}$$

$$= -1 \mp 2FA_1 s^3 e^{-C_1 \sqrt{s}} \left( B_1 - \frac{1}{2} C_1 \sqrt{s} \right) \times \sin \left( \frac{\pi}{3} \rho \right) \sin \left( \frac{2\pi}{3} \left[ \rho \left( K \pm \frac{1}{2} \right) + \sigma \right] \right)/h\nu$$

$$\equiv -1 \mp F(s) \sin \left( \frac{\pi}{3} \rho \right) g(\rho, K, \sigma)/h\nu,$$

(28)

The calculated $K_\mu$ coefficients from this model for selected transitions are listed in Table II and are seen to agree rather well with the numerical calculations.

We are now ready for a qualitative discussion of the sensitivity coefficients obtained for the different molecules.
In the last line of Eq. (28), we have separated the expression for the sensitivity coefficient in four different parts: the molecular constant \( F \); a function \( f(s) \) that depends only on \( s \); a function that depends only on \( \rho \); and a function \( g(\rho, K, \sigma) \) that depends on the rotational quantum number \( K \), on the torsional symmetry \( \sigma \), and on \( \rho \). This last function takes on a value between \(-1\) and \(1\) for the different \( \sigma, K \) levels. Although this function determines the sensitivity of a specific level, it is not important for comparing different molecules. The product \( f(s) \sin(\frac{\pi}{3} \rho) \) can be used as a means to compare the sensitivity for different molecules. In Fig. 8 this product is plotted as a function of \( s \) with \( \rho \) as indicated in the figure. The curves can be regarded as the maximum sensitivity one may hope to find for different molecules. In Fig. 8 this product is plotted as a function of \( s \) with \( \rho \) as indicated in the figure. Also shown are data points for each molecule investigated in this paper; values of \( s \) and \( \rho \) can be found in Table IV.

In Table IV the structure and lowest-order molecular constants of the molecules investigated in this paper are listed as well as the results from our analytical model. The last columns of the table are hypothetical sensitivities that may be expected for transitions of \(1\) GHz and with \( g(\rho, K, \sigma) = 1 \). Molecular constants are taken from Refs. [23–25,29,30].

### TABLE IV. Structure and some lower-order constants of the molecules investigated in this paper. The \( A \leftrightarrow E = 0 \) torsional splitting from Eq. (23) is listed for the vibrational ground state \( v_1 = 0 \) of these molecules. Note that the magnitude of the torsional splitting only depends on the reduced barrier height \( \rho = 4V_{ij}/9F \). The magnitude of \( K_{\mu}^{\text{gas}} \) for each molecule follows from Eq. (26). The \( K_{\mu}^{\text{gas}} \) values given in the last column of the table are hypothetical sensitivities that may be expected for transitions of \(1\) GHz and with \( g(\rho, K, \sigma) = 1 \). Molecular constants are taken from Refs. [23–25,29,30].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Isotopologue</th>
<th>( V_3 ) (cm(^{-1}))</th>
<th>( F ) (cm(^{-1}))</th>
<th>( s )</th>
<th>( \rho )</th>
<th>( \Delta E_{\text{gen}} ) (cm(^{-1}))</th>
<th>( K_{\mu}^{\text{gas}} )</th>
<th>( K_{\mu}^{\text{gas}} + 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>(^{12}\text{CH}_3\text{OH} )</td>
<td>373.555</td>
<td>27.647</td>
<td>6.01</td>
<td>0.810</td>
<td>9.07</td>
<td>-2.5</td>
<td>\pm 398</td>
</tr>
<tr>
<td></td>
<td>(^{13}\text{CH}_3\text{OH} )</td>
<td>373.777</td>
<td>27.642</td>
<td>6.01</td>
<td>0.810</td>
<td>9.06</td>
<td>-2.5</td>
<td>\pm 397</td>
</tr>
<tr>
<td></td>
<td>(^{12}\text{CH}_3\text{OH} )</td>
<td>374.067</td>
<td>27.428</td>
<td>6.06</td>
<td>0.809</td>
<td>8.88</td>
<td>-2.5</td>
<td>\pm 392</td>
</tr>
<tr>
<td></td>
<td>(^{12}\text{CD}_3\text{OH} )</td>
<td>370.055</td>
<td>24.994</td>
<td>6.58</td>
<td>0.895</td>
<td>7.12</td>
<td>-2.6</td>
<td>\pm 363</td>
</tr>
<tr>
<td></td>
<td>(^{12}\text{CH}_3\text{OD} )</td>
<td>366.340</td>
<td>17.428</td>
<td>9.34</td>
<td>0.699</td>
<td>2.58</td>
<td>-3.1</td>
<td>\pm 145</td>
</tr>
<tr>
<td></td>
<td>(^{12}\text{CD}_3\text{OD} )</td>
<td>362.122</td>
<td>14.758</td>
<td>10.91</td>
<td>0.822</td>
<td>1.54</td>
<td>-3.4</td>
<td>\pm 110</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>(^{12}\text{CH}_3\text{C}^{18}\text{OH} )</td>
<td>407.716</td>
<td>7.600</td>
<td>23.84</td>
<td>0.332</td>
<td>0.065</td>
<td>-5.1</td>
<td>\pm 3.6</td>
</tr>
<tr>
<td>Acetamide</td>
<td>(^{12}\text{CH}_3\text{C}^{16}\text{O}^{14}\text{NH}_2 )</td>
<td>25.044</td>
<td>5.617</td>
<td>1.98</td>
<td>0.068</td>
<td>4.85</td>
<td>-1.4</td>
<td>\pm 5.2</td>
</tr>
<tr>
<td>Methyl formate</td>
<td>(^{12}\text{CH}_3\text{O}^{12}\text{C}^{16}\text{OH} )</td>
<td>370.924</td>
<td>5.490</td>
<td>30.03</td>
<td>0.084</td>
<td>0.017</td>
<td>-5.7</td>
<td>\pm 0.3</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>(^{12}\text{CH}_3\text{C}^{16}\text{O}^{16}\text{OH} )</td>
<td>170.174</td>
<td>5.622</td>
<td>13.45</td>
<td>0.072</td>
<td>0.34</td>
<td>-3.8</td>
<td>\pm 2.8</td>
</tr>
</tbody>
</table>
column lists the generic maximum sensitivity $K^\text{gen}$ that may be expected for a hypothetical transition with a frequency of 1 GHz. For methanol, this number is 10–100 times larger than for the other investigated molecules, following from the fact that methanol has a large $F$, an effective barrier close to the optimal value of 4, and a relatively large $\rho$.

Application of the toy model to excited torsional states

So far, we have limited the discussion to transitions in the ground torsional state ($\nu_t = 0$). In this paragraph we discuss the application of the model to excited torsional states. Transitions within excited torsional states are both unlikely to be observed in the interstellar medium and of less interest for laboratory tests due to the added complexity of the experiment; hence, the following discussion is merely intended for providing a more complete picture. In excited torsional states the splitting between the different torsional symmetry levels becomes larger as tunneling through the torsional potential becomes more likely. This implies that the energy that can be canceled also becomes larger, but, at the same time, the sensitivity coefficient of a pure torsional transition, $K^\text{tors}$, becomes smaller. As we will see, the first effect is more important.

In Fig. 3 the solid squares represent $a_1^\nu=1$ coefficients for the $\nu_t = 1$ state obtained by fitting the second eigenvalues of the torsional Hamiltonian as function of $K$ to the Fourier expansion of Eq. (15). The dashed line in Fig. 3 represents a fit using an expression similar to Eq. (17) with an additional term, that is,

$$a_1^\nu=1 = A_1 s^\nu_1 e^{-C_1 s^\nu_1 D_1 s^\nu_1},$$

with $A_1 = 10.388$, $B_1 = 0.829$, $C_1 = 1.108$, and $D_1 = -0.058$. The open squares, also shown in Fig. 3, are $a_1$ coefficients for the first excited torsional state of the five molecules investigated in this paper. The additional term modifies Eq. (28) only slightly. With the known coefficients, $A_1$, $B_1$, $C_1$, and $D_1$, we can again plot the parts that depend only on $s$ and $\rho$, as was done for $\nu_t = 0$ shown in Fig. 8. As compared to the $\nu_t = 0$, the curves for the $\nu_t = 1$ are broadened and the center of the peak is shifted from $s = 4$ to $s = 7$. Moreover, the generic sensitivity is 5 times larger at the peak. As a consequence, the generic sensitivity, that is, the sensitivity for a transition with $\nu = 1$ GHz and $g(\rho,K,s) = 1$, of molecules with unfavorable $s$ and $\rho$ in the ground torsional state, can be large in the $\nu_t = 1$ state. For instance, acetaldehyde in the $\nu_t = 1$ state has a generic sensitivity $K^\text{gen} + 1 = \pm 82$ as compared to $K^\text{gen} + 1 = \pm 3.6$ in the torsional ground state. For methanol, the generic sensitivity will also increase; however, as the torsional splitting in the $\nu_t = 1$ state is much larger than the rotational splittings, resonances are expected to occur only at high $J$ and $K$ values. Note that the sensitivities for transitions from the $\nu_t = 0$ to the $\nu_t = 1$ state will not be significantly enhanced as compared to ordinary vibrational transitions; that is, $K^\nu \approx -0.5$.

V. CONCLUSION AND OUTLOOK

In the present study we have demonstrated that transitions in internal rotor molecules that convert internal rotation energy into overall rotation energy of the molecule exhibit an enhanced sensitivity to a possible variation of the proton-to-electron mass ratio. We have calculated the $K^\nu$ coefficients for five, relatively small, internal rotor molecules that are of astrophysical relevance: methanol, acetaldehyde, acetamide, methyl formate, and acetic acid. In addition to full calculations using advanced codes, such as the BELGI program, that achieve spectroscopic accuracy on the level energies, we have developed an approximate model, dubbed as the “toy” model, in which the molecular structure is described by the six most relevant of the molecular parameters. Based on this model we produce insight in the question as to why certain molecules of $C_{3v}$ symmetry with hindered internal rotation are sensitive to $\mu$ variation. In particular, molecules in the torsional ground state are expected to have large $K^\nu$ coefficients if they have (i) an effective barrier height, $s$, around 4, (ii) a ratio between the moment of inertia of the top and the whole molecule, $\rho$, close to unity, and (iii) a large value for the molecular constant that relates to the internal rotation, $F$. If the torsional splittings are of the same order as the rotational constants, sensitive transitions will occur between levels with low $J$ and $K$ quantum numbers.

From the approximate toy model we learn that of the five molecules studied, methanol has by far the largest sensitivity, due to its favorable value of the effective barrier $s$ and the fact that in methanol $\rho$ is near unity. Moreover, methanol has a fairly large value of $F$. The other investigated molecules either have too large a barrier (acetaldehyde), have too heavy a frame attached to the methyl group and consequently a very small $\rho$ (acetamide and acetic acid), or have both a high barrier and a small $\rho$ (methyl formate). Based on these criteria, other interesting molecules containing a $C_{3v}$ symmetry group include mercaptan, CH$_3$SH, ($F = 15$ cm$^{-1}$, $V_3 = 439$ cm$^{-1}$, and $\rho = 0.65$ [32], resulting in $K^\nu + 1 = \pm 67$) and methylvamine (which will be topic of a separate publication [15]). Other interesting candidate molecules, although of $C_2$ symmetry, are H$_2$O$_2$ (recently treated by Kozlov [33]) and H$_2$S$_2$. These molecules require a modification in the definition of $s$ and will have different $A_1$, $B_1$, and $C_1$ coefficients.

The high sensitivities of internal rotor molecules, particularly methanol, make them excellent target species to search for a variation of the proton-to-electron mass ratio over cosmological time scales. It is important to note that the sensitivity coefficients of the transitions in these molecules have both large positive and large negative values, that is, if $\mu$ varies, some transitions will shift to higher frequencies while others shift to lower frequencies. This makes it possible to perform a test of the variation of $\mu$ using transitions pertaining to a single species, thus avoiding the many systematic effects that plague tests based on comparing transitions in different molecules.

Currently, the most stringent bounds on a cosmological variation of $\mu$ is set by observations of hydrogen molecules in high ($z = 2–3$) redshift objects [34,35] and a comparison between the ammonia tunneling frequencies and rotational transitions in anchor molecules at intermediate redshift ($z = 0.5–1$) objects [36–38]. Methanol provides a system that should result in more stringent bounds for $\mu$ variation. Recently, methanol, as well as methylamine and acetaldehyde have been observed in the gravitationally lensed system, PKS 1830-211 at $z = 0.89$ [14,39]. The $1_0 \rightarrow 2_{–1}$ $E$ transition in methanol reported by Muller et al. was calculated to have
\( K_\mu = -7.4 \). We have also calculated the \( K_\mu \) coefficients for the nine observed transitions in acetaldehyde and found that all lines have sensitivities of \( K_\mu \approx -1 \). Sensitivity coefficients for methanol, for which three lines were observed in the same survey, will be calculated in a separate paper \cite{Ilyushin}. For methylamine, for which three lines were observed in the present calculations, we found that all lines have sensitivities of \( K_\mu \approx 0 \) at high (terrestrial) and low (interstellar) densities of baryonic matter and observed a statistically significant variation of \( \Delta K_\mu \) as a result of chameleonlike scalar fields. These fields predict a dependence of \( \Delta K_\mu \) on the local matter density. Note that the physical origin of these chameleonlike theories is very different from theories describing temporal \( \mu \) variation. Levshakov et al. \cite{Levshakov} compared ammonia spectra taken at high (terrestrial) and low (interstellar) densities of baryonic matter and found that methanol was performed by Levshakov et al. \cite{Levshakov}. This test obtained similar results as for ammonia but can be further improved if more accurate laboratory data become available.

Methanol is also a promising candidate for laboratory tests on a possible variation of \( \mu \). Laboratory experiments can make use of rare isotopologues (in contrast to cosmological searches). Hence, the most sensitive transitions deriving from the present calculations can be targeted; a combined measurement of the \( 2_1 \rightarrow 1_1 E \) and \( 3_0 \rightarrow 2_1 E \) lines in \( \text{CD}_2\text{OH} \) exhibit a sensitivity spread \( \Delta K_\mu \) that is more than 400 times larger than a pure rotational transition \cite{Bethlem}. Measurements of these transitions in slow (Stark decelerated \cite{DeMille, Kozlov}) molecular beams may result in more stringent bounds on the variation of the proton-to-electron mass ratio in the current epoch.

**ACKNOWLEDGMENTS**

This research has been supported by NWO via a VIDI grant and by the ERC via a Starting Grant. I.K. acknowledges the financial support provided by Grant No. ANR-08-BLAN-0054. L.H.X. gratefully acknowledges financial support from the Natural Science and Engineering Research Council of Canada. W.U. acknowledges support from the Netherlands Foundation for the Research of Matter (FOM). We thank Mikhail Kozlov, Jon Hougen, and Vadim Ilyushin for helpful discussions.

\begin{thebibliography}{99}
\bibitem{Uzan} J.-P. Uzan, Rev. Mod. Phys. \textbf{75}, 403 (2003), and references therein.
\bibitem{Lin} C. C. Lin and J. D. Swalen, Rev. Mod. Phys. \textbf{31}, 841 (1959).
\bibitem{Ilyushin} V. V. Ilyushin et al. (to be submitted).
\bibitem{Ilyushin} V. V. Ilyushin et al., J. Mol. Spectrosc. \textbf{205}, 286 (2001).
\bibitem{Ilyushin} V. V. Ilyushin (private communication).
\bibitem{Murphy} M. T. Murphy, V. V. Flambaum, S. Muller, and C. Henkel, Science \textbf{320}, 1611 (2008).
\bibitem{Henkel} C. Henkel (private communication).
\end{thebibliography}