

VU Research Portal

Molecular radicals in the search for drifting constants

de Nijs, A.J.

2014

document version

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

citation for published version (APA)

de Nijs, A. J. (2014). *Molecular radicals in the search for drifting constants*.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:

vuresearchportal.ub@vu.nl

Chapter 6

Sensitivity of rotational transitions in CH and CD to a possible variation of fundamental constants

Abstract

The sensitivity of rotational transitions in CH and CD to a possible variation of fundamental constants has been investigated. Largely enhanced sensitivity coefficients are found for specific transitions which are due to accidental degeneracies between the different fine-structure manifolds. These degeneracies occur when the spin-orbit coupling constant is close to four times the rotational constant. CH and particularly CD match this condition closely. Unfortunately, an analysis of the transition strengths shows that the same condition that leads to an enhanced sensitivity suppresses the transition strength, making these transitions too weak to be of relevance for testing the variation of fundamental constants over cosmological time scales. We propose a test in CH based on the comparison between the rotational transitions between the e and f components of the $\Omega' = 1/2, J = 1/2$ and $\Omega' = 3/2, J = 3/2$ levels at 532 and 536 GHz and other rotational or lambda-doublet transitions in CH involving the same absorbing ground levels. Such a test, to be performed by radioastronomy of highly redshifted objects, is robust against systematic effects.

*This chapter was published as Phys. Rev. A **86**, 032501 (2012).*

6.1 Introduction

A possible variation of the fundamental constants can be detected by comparing transitions between levels in atoms and molecules that have a different functional dependence on these constants. The limit that can be derived from such

a test is proportional to the relative accuracy of the experiment and inversely proportional to both the time interval covered by the experiment and the sensitivity of the transition to a possible variation. The duration of tests that are conducted in the laboratory is typically limited to a few years, but these tests have the advantage that one can choose transitions in atoms or molecules that are very sensitive to a variation, transitions that can be measured to an extremely high precision, or both. Tests over cosmological time scales, on the other hand, typically span 10^9 years, but have the disadvantage that only a limited number of molecular transitions are observed at high redshift, and the accuracy of the observed lines is relatively low.

Up to very recently, tests of the time-variation of the proton-to-electron mass ratio, $\mu = m_p/m_e$, over cosmological time scales were based exclusively on molecular hydrogen, the most abundant molecule in the universe and observed in a number of high redshift objects. The transitions in molecular hydrogen correspond to the transitions between different electronic states and exhibit sensitivity coefficients, K_μ , ranging from -0.05 to $+0.01$ [13, 14]. Recently, the observations of the inversion transition in ammonia ($K_\mu = -4.2$) [16–18] and torsion-rotation transitions in methanol (K_μ ranging from -33 to -1) [8, 21, 132], at high redshift, have resulted in more stringent limits on the variation of μ .

In this chapter, we discuss the sensitivity of rotational transitions in CH and its deuterated isotopologue, CD to a variation of the proton-to-electron mass ratio, μ , and the fine structure constant, α . CH is a small diatomic radical that is frequently targeted in astrophysical studies, as it is a well established and well understood proxy of H_2 [133]. These studies have been targeting primarily the interstellar medium in the local galaxy. However, a survey for CH at high redshift is currently being conducted at the Atacama Large Millimeter Array (ALMA) [23]. CH and CD have a spin-orbit coupling constant, A , that is close to two and four times their respective rotational constant, B . This leads to near degeneracies between rotational levels of different spin-orbit manifolds. As a result, the rotational transitions between the near-degenerate levels have an increased sensitivity to a variation of μ . The work presented in this chapter is complementary to that of Kozlov [134], who calculated the sensitivity coefficients of lambda-doublet transitions in CH and other diatomic radicals.

6.2 Energy level structure of a $^2\Pi$ state

In this chapter, we investigate CH and CD in their $^2\Pi$ ground state. Molecules in $^2\Pi$ states have three angular momenta that need to be considered; the electronic orbital angular momentum, \mathbf{L} , the spin angular momentum, \mathbf{S} , and the rotational angular momentum, \mathbf{R} . Depending on the energy scales associated with these momenta, the coupling between the vectors is described by the different Hund’s cases. In Hund’s case (a), \mathbf{L} is strongly coupled to the inter-

nuclear axis and \mathbf{S} couples to \mathbf{L} via spin-orbit interaction. States are labeled by J , the quantum number associated with the total angular momentum, and Ω , the sum of Λ and Σ , the projections of \mathbf{L} and \mathbf{S} on the internuclear axis, respectively. When the rotational energy becomes comparable to the energy of the spin-orbit interaction, \mathbf{S} decouples from the internuclear axis, and Hund's case (b) is more appropriate. In this case the molecular levels are labeled by $N = R + \Lambda$, and J .

In heavy molecules at low J , the spin-orbit interaction is much larger than the rotational energy splitting. As a result, the energy level structure consists of two spin-orbit manifolds separated by an energy A , each having a pattern of rotational levels with energies given by Bz , with $z = (J + 1/2)^2 - 1$. In light molecules, $A \sim Bz$ already at low J . In this case the two manifolds are considerably mixed and the energies are not described by a simple formula. To describe a situation that is intermediate between Hund's case (a) and (b), the wavefunction of a state is written as a superposition of pure Hund's case (a) wavefunctions:

$$|\Omega', J\rangle = c_{\Omega', J, \Omega=1/2} |\Omega = 1/2, J\rangle + c_{\Omega', J, \Omega=3/2} |\Omega = 3/2, J\rangle \quad (6.1)$$

where $c_{\Omega', J, \Omega=1/2}$ and $c_{\Omega', J, \Omega=3/2}$ are coefficients signifying the $\Omega = 1/2$ and $\Omega = 3/2$ character, respectively, of the wavefunction of the state $|\Omega', J\rangle$. Note that Ω' is used to label the rotational levels of the different spin-orbit manifolds, while Ω is used to denote the pure Hund's case (a) wave functions. The coefficients are the eigenvectors of the Hamiltonian matrix that is given, for instance, by Amiot *et al.* [135]. When the lambda-doublet splitting, centrifugal distortion and hyperfine splitting are neglected, the Hamiltonian matrix reduces to [136]:

$$\begin{pmatrix} \frac{1}{2}A + Bz & -B\sqrt{z} \\ -B\sqrt{z} & -\frac{1}{2}A + B(z + 2) \end{pmatrix}. \quad (6.2)$$

The first row represents the ${}^2\Pi_{\Omega=3/2}$ component, the second the ${}^2\Pi_{\Omega=1/2}$ component. Although most of our calculations use the extensive matrix, all relevant features can be understood from the simplified matrix.

The level scheme of CH is depicted in Fig. 6.1. In CH ($A = 1.98B$), the $\Omega' = 1/2, J = 3/2$ level lies about 200 GHz below the $\Omega' = 3/2, J = 5/2$ level, whereas in CD ($A = 3.65B$) the energy difference is only 30 GHz. In Fig. 6.1, the lambda-doublet splittings are exaggerated by a factor of 10. It was shown by Kozlov [134] that, as a result of an inversion of the lambda-doublet splitting in the $\Omega' = 3/2$ -manifold, the different components of the lambda doublet become near-degenerate at $\Omega' = 3/2, J = 3/2$ for CH, leading to enhanced sensitivity coefficients of the lambda-doublet transitions.

Let us now consider the sensitivity of rotational transitions to a possible variation of μ . The sensitivity coefficient of a transition is defined as

$$K_\mu = \frac{\mu}{\nu} \frac{\partial \nu}{\partial \mu} = \frac{\mu_{red}}{\nu} \frac{\partial \nu}{\partial \mu_{red}} \quad (6.3)$$

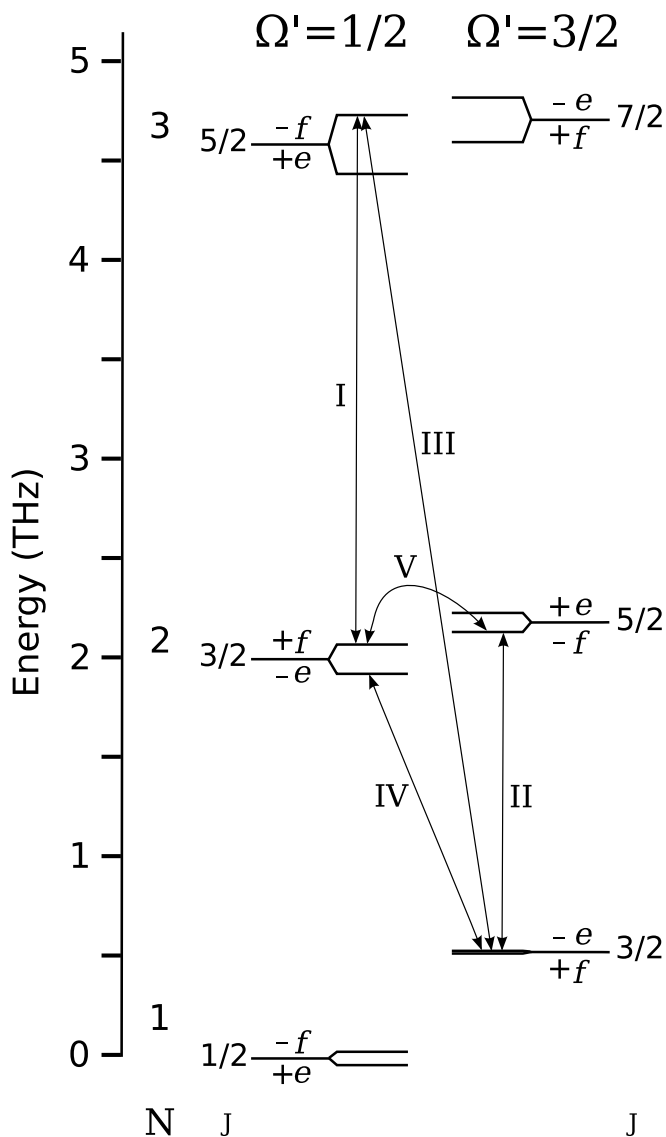


Figure 6.1: Level scheme of the ground state of CH, calculated using the Hamiltonian matrix from Amiot *et al.* [135] and the molecular constants given by McCarthy *et al.* [137]. Indicated are five different types of rotational transitions, labeled I through V. The lambda-doublet splitting is exaggerated by a factor of 10. Also indicated are the symmetries of the electronic part of the wave function, denoted by e and f and the total parity, denoted by $+$ and $-$. Note: The e and f labels of the $\Omega = 1/2$ manifold were inverted in the published version, the correct version is shown above.

with

$$\nu = (E_{\Omega'_f, J_f} - E_{\Omega'_i, J_i})/h \quad (6.4)$$

the transition frequency, and μ_{red} the reduced mass of the molecule. Note that it is assumed here that the neutron and proton masses vary in the same way. The K_μ and K_α coefficients can now be calculated using the Hamiltonian matrix by including the dependence of the molecular constants on the reduced mass of the molecule and α , given, for instance, in Bely *et al.* [138], and the values of the molecular parameters for CH from McCarthy *et al.* [137] and for CD from Halfen *et al.* [139]. As the effective Hamiltonian used for these molecules is an accurate physical representation, the sensitivity coefficients that are found in this way are very accurate. For instance, in previous work on CO, the transition frequencies in different isotopologues could be predicted to a relative accuracy well within 10^{-4} [10][Chapter 2]. However, for actual tests of the variation of fundamental constants, an accuracy of 1% is sufficient and the sensitivity coefficients will be given to this level only.

We have calculated K_μ and K_α for rotational transitions in CH and CD using both the extensive and the reduced matrix. For clarity, we separate the transitions into five different types, I through V, as shown in Fig. 6.1. The transitions from J to $J + 1$ within the $\Omega' = 1/2$ and $\Omega' = 3/2$ manifolds are labeled by I and II, respectively. The transitions from $\Omega' = 1/2$ to $\Omega' = 3/2$ with $\Delta J = -1, 0, +1$ are labeled by III through V, respectively. From the calculations, we found that for both CH and CD, transitions of types I and II have K_μ close to -1 and K_α close to 0. Transitions of types III through IV also have K_μ close to -1 and K_α close to 0, except for transitions involving the lowest rotational levels, which have K_μ between -0.5 and -1 and a K_α between 1 and 0. Interestingly, transitions of type V were found to be extremely sensitive to a variation of α and μ . The K_μ for these transitions are listed in the third column of Table 6.1 and range from -67 to 18 for CD and -6.2 to 2.7 for CH. The fourth column of Table 6.1 lists the values of K_α . Note, that $K_\alpha \sim 2 + 2K_\mu$, a relation that is exact when lambda-type doubling is neglected.

The calculations are most easily understood by plotting the sensitivity coefficients for the different transitions as a function of A/B , as shown in Fig. 6.2. The upper panel shows the K_μ for transitions of types I through IV, while the lower panel shows K_μ for transitions of type V, calculated using the reduced matrix from Eq. (6.2). The black curves show the sensitivity coefficients for transitions starting from $J = 3/2$. To indicate the progression towards higher values of J , transitions starting from $J = 7/2$ and $J = 15/2$ are plotted in gray. We see that for large $|A/B|$, K_μ approaches -1 for transitions of types I and II and 0 for transitions of types III through V. This can be understood by realizing that for large $|A/B|$, a Hund's case (a) coupling scheme applies. Consequently, transitions of types I and II are pure rotational transitions which are proportional to B , while transitions of types III through IV are pure electronic transitions and proportional to A . When $A \sim Bz$, the manifolds become mixed

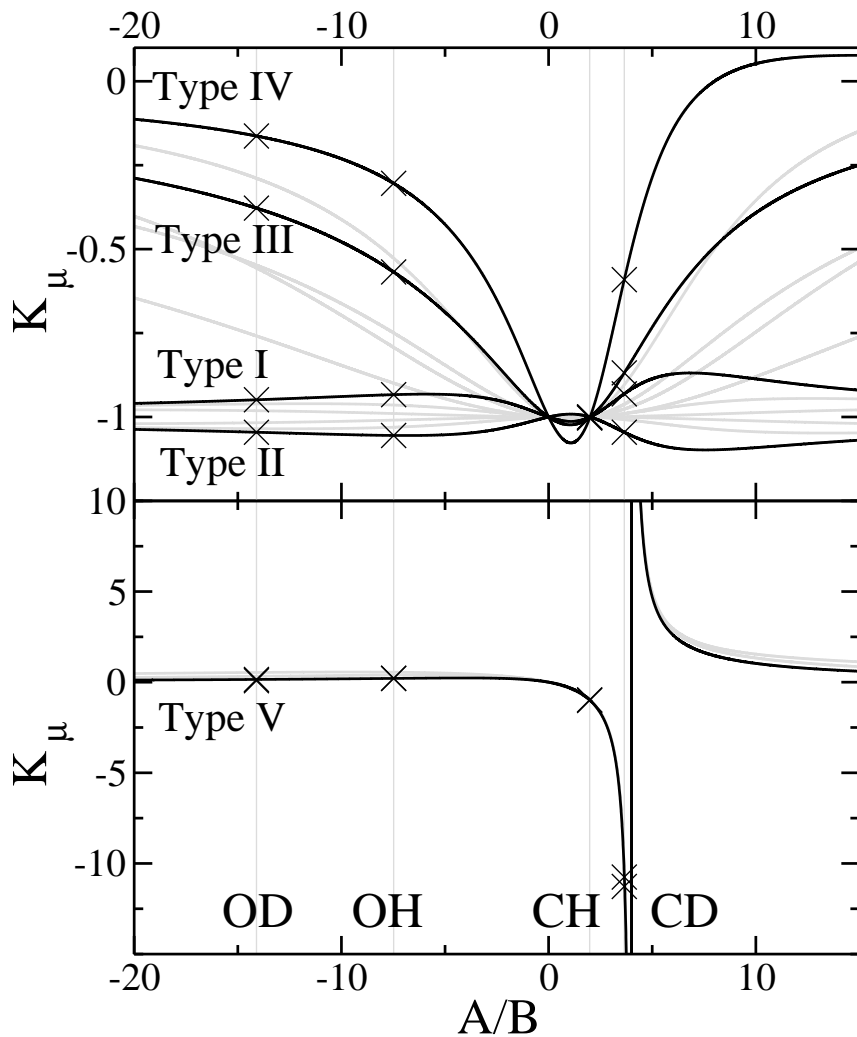


Figure 6.2: Sensitivity coefficient K_μ of transition types I through IV (upper panel) and V (lower panel) starting from $J = 3/2$, in black, and $J = 7/2$ and $J = 15/2$, in gray, calculated using the reduced matrix given in Eq. (6.2). The crosses indicate the sensitivity coefficients calculated for the transitions from $J = 3/2$ for the listed molecules using the complete matrix.

and the sensitivity of the different types of transitions is between 0 and -1 . When $A = 0$, corresponding to a pure Hund's case (b), all types of transitions have a sensitivity coefficient K_μ of -1 , as expected. When $A = 2B$ the two spin-orbit manifolds are fully mixed, also causing K_μ to become -1 . Another special case is when $A = 4B$. Here, $\Omega' = 3/2, J$ levels are degenerate with $\Omega' = 1/2, J + 1$ levels. This gives rise to an enhancement of the sensitivity coefficient for transitions that connect these levels (i.e., transitions of type V). The enhancement is expected to be on the order of A/ν [9, 140], which is in reasonable agreement with our calculations. Note, that the sensitivity coefficients found from the simplified model are almost independent of J .

The crosses, also shown in Fig. 6.2, are the values of K_μ calculated using a full set of molecular parameters for CH ($A = 1.98B$), CD ($A = 3.65B$), OH ($A = -7.48B$), [141] and OD ($A = -14.1B$) [142]. The correspondence between the simplified model and the full description is very good for transitions at low J , but less good for higher J when effects of the lambda-type doubling become increasingly important. The lambda-type doubling shifts the energy levels, leading to a decrease or increase of the energy difference between the $\Omega' = 1/2, J$ and $\Omega' = 3/2, J + 1$ levels, and henceforth to a corresponding increase or decrease of the sensitivity coefficients.

6.3 Transition strengths

To be relevant for astrophysical tests of the time-variation of the proton-to-electron mass ratio, the highly sensitive transitions in CH and CD discussed in the previous section need to be sufficiently strong. In Hund's case (a), the transitions between different Ω manifolds (i.e., transitions of types III through V) are forbidden. However, as discussed in the previous section, the Ω manifolds of CH and CD are mixed and transitions are allowed.

The transition strength of a transition between rotational states i and f , is given by $|\langle i|T|f\rangle|^2$, with $|i\rangle$ and $|f\rangle$ given by Eq. (6.1). The transition strength of a transition $i \rightarrow f$ is then given by:

$$\begin{aligned} |\langle i|T|f\rangle|^2 = & |c_{i,1/2} c_{f,1/2} \langle 1/2, J_i|T|1/2, J_f\rangle \\ & + c_{i,3/2} c_{f,1/2} \langle 3/2, J_i|T|1/2, J_f\rangle \\ & + c_{i,1/2} c_{f,3/2} \langle 1/2, J_i|T|3/2, J_f\rangle \\ & + c_{i,3/2} c_{f,3/2} \langle 3/2, J_i|T|3/2, J_f\rangle|^2. \end{aligned} \quad (6.5)$$

The expressions $\langle \Omega, J_i|T|\Omega, J_f\rangle$ are the Hund's case (a) dipole transition matrix elements given in, for example, Brown and Carrington [143]. As a result of the Hund's case (a) selection rules, the second and third terms on the right-hand side of Eq. (6.5) are zero. Using the simplified Hamiltonian matrix given in Eq. (6.2), we have calculated the amplitude of the remaining terms as a function of A/B . In Fig. 6.3, the transition strength is plotted for type V

transitions starting from different J levels. It is seen that when $|A/B|$ becomes smaller, the levels become increasingly mixed and the transition strength becomes larger. Near $A = 4B$ the transition strength becomes smaller, due to the destructive interference between the two different paths that combine to form this transition. At $A = 4B$ the two paths are equally strong, but due to the orthogonality of the eigenvectors they have a different sign and the transition strength becomes zero. The last column of Table 6.1 lists the transition strength, calculated using the full Hamiltonian, but neglecting hyperfine splitting. For comparison, note that purely rotational transitions have a transition strength of order unity. The crosses shown in Fig. 6.3 again correspond to a calculation for CH, CD, OH, and OD using a complete set of parameters and are in good agreement with the calculations using the reduced matrix. We have validated that these calculations are also in agreement with calculations using the PGOPHER software package [63]. Note, that the dipole moment is set to unity in the calculations.

6.4 Relevance for tests on drifting constants over cosmological time scales

In the previous section, we have shown that transitions of type V that have an enhanced sensitivity to a variation of μ are too weak to be observed in astrophysical objects at high redshift. The only transitions in CH that have a non-vanishing transition strength and a K_μ that deviates significantly from -1 are the $\Omega' = 1/2, J = 1/2$ to $\Omega' = 3/2, J = 3/2$ transitions at 532 and 536 GHz that have $K_\mu = -0.2$. By comparing these transitions with a rotational transition, typically exhibiting $K_\mu = -1$, in any other molecule observed in the same object, a test of the time variation of μ over cosmological time scales can be performed. If μ varies, the transition frequency of a pure rotational transition will vary while the frequency of the discussed transition in CH will change five times less (i.e., the CH transition will act as an anchor line). Ideally, the CH anchor transitions are compared with other transitions in CH, and preferably with transitions from the same absorbing levels. This eliminates one of the main systematic effects that limits astrophysical tests, namely the effect of spatial segregation. Astrophysical tests rely on the assumption that the transitions that are being compared originate from the same space-time location and hence the same apparent redshift. Spatial segregation of the absorbers may mimic or hide frequency shifts due to a variation of μ [18].

We propose a test of the time variation of μ by comparing the CH anchor transitions to other rotational or lambda-doublet transitions in CH involving the same absorbing ground levels (i.e. to the $\Omega' = 1/2, J = 1/2$ to $\Omega' = 1/2, J = 3/2$ transition near 2 THz and/or the $\Omega' = 3/2, J = 3/2$ to $\Omega' = 3/2, J = 5/2$ transition near 1.5 THz that has $K_\mu = -1$ or to the lambda-doublet transition in the $\Omega' = 1/2, J = 1/2$ at 3.3 GHz that has $K_\mu = -1.7$ and the lambda-doublet transition in the $\Omega' = 3/2, J = 3/2$ near 700 MHz

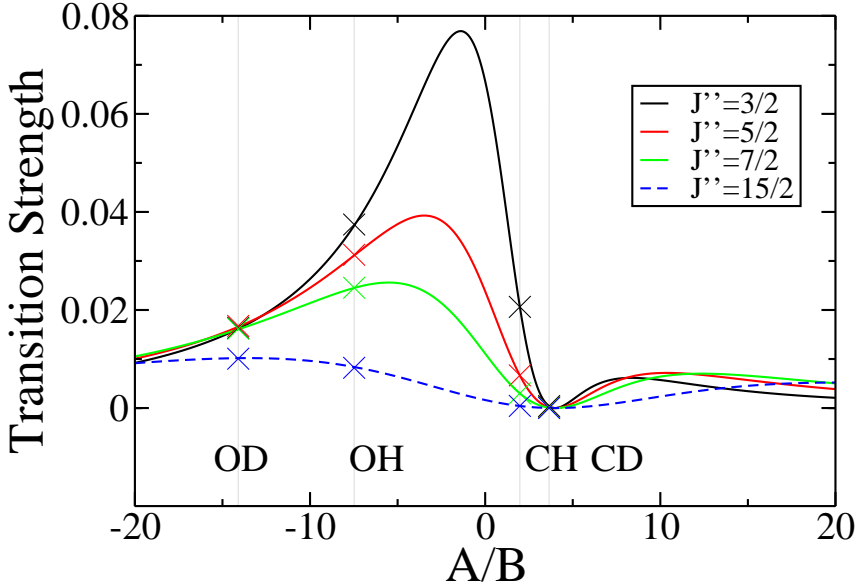


Figure 6.3: Transitions strengths of type V transitions, following from Eq. (6.5), starting from different J levels. The transition strength is zero at $A = 4B$ for all J , making the transitions with the highest sensitivity exceedingly weak. The crosses correspond to a calculation for CH, CD, OH, and OD using a complete set of parameters. The molecules are also indicated by the vertical gray lines.

that has $K_\mu = -6.2$ [134]). This test is based on transitions within the lowest four levels of a single species making it very robust against possible shifts due to spatial segregation of the absorbing molecules. The transitions that are relevant to this test are listed in Tables 6.3 and 6.4, including the hyperfine splitting, with their respective sensitivity coefficients and transitions strengths, calculated using PGOPHER [63]. Our values for the sensitivity coefficients of the lambda-doubling transitions correspond well to those found by Kozlov [134], but our sensitivity coefficients are more exact as we use a more complete set of molecular parameters.

6.5 Conclusion

In this chapter, we have analyzed the sensitivity to a possible variation of μ and α for rotational transitions in $^2\Pi$ states, in particular for rotational tran-

J	freq. (MHz)	K_μ	K_α	Tr. Str.
<i>e</i> parity				
1/2	536772.4	-0.22	1.57	$6.6 \cdot 10^{-1}$
3/2	191101.3	-1.02	-0.0068	$2.1 \cdot 10^{-2}$
5/2	137163.5	-1.09	-0.041	$6.7 \cdot 10^{-3}$
7/2	115440.4	-1.20	-0.074	$3.0 \cdot 10^{-3}$
9/2	107620.7	-1.32	-0.10	$1.6 \cdot 10^{-3}$
11/2	107870.7	-1.44	-0.12	$9.7 \cdot 10^{-4}$
13/2	113649.5	-1.55	-0.14	$6.3 \cdot 10^{-4}$
15/2	123632.5	-1.65	-0.14	$4.3 \cdot 10^{-4}$
<i>f</i> parity				
1/2	532741.0	-0.20	1.59	$6.6 \cdot 10^{-1}$
3/2	178904.5	-0.94	0.039	$2.1 \cdot 10^{-2}$
5/2	111119.2	-0.85	0.020	$6.7 \cdot 10^{-3}$
7/2	71064.4	-0.64	-0.012	$3.0 \cdot 10^{-3}$
9/2	40500.9	-0.11	-0.086	$1.6 \cdot 10^{-3}$
11/2	13698.2	2.56	-0.42	$9.7 \cdot 10^{-4}$
13/2	11758.8	-6.40	0.68	$6.3 \cdot 10^{-4}$
15/2	37049.6	-3.16	0.27	$4.3 \cdot 10^{-4}$

Table 6.1: Transition frequencies, sensitivity coefficients to variation of μ and α and transition strengths of transitions from $\Omega' = 1/2, J$ to $\Omega' = 3/2, J + 1$, type V transitions in CH, calculated using the Hamiltonian matrix from Amiot *et al.* [135] and the molecular constants given by McCarthy *et al.* [137] for CH and Halfen *et al.* [139] for CD. Note that the values of K_μ for transitions starting from $\Omega' = 1/2, J = 1/2$ are always between 0 and -1 , as the $\Omega' = 1/2, J = 1/2$ is unmixed. The transition strengths are following from Eq. (6.5). freq.: Frequency, Tr. Str.: Transition Strength.

sitions in the ground states of CH and CD. For certain rotational transitions, we found a significantly enhanced sensitivity due to accidental degeneracies between rotational levels of different fine-structure manifolds. These degeneracies occur when the spin-orbit coupling constant is close to four times the rotational constant. CH ($A = 1.98B$) and particularly CD ($A = 3.65B$), match this condition closely (as discussed in the introduction of this thesis). The fact that enhancement occurs is unexpected, as it was shown by Bethlem and Ubachs [9] that in molecules such as CO, the transition from Hund's (a) to Hund's case (b) coupling scheme prohibits levels that are connected by one-photon transitions to become near degenerate. Here we show that for $A \sim 4B$ this does not apply. Unfortunately, the same condition that leads to an enhanced sensitivity suppresses the transition strength. Thus, one-photon transitions between different spin-orbit manifolds of molecular radicals are either insensitive or too weak to be of relevance for tests of the variation of fundamental constants over

J	freq. (MHz)	K_μ	K_α	Tr. Str.
<i>e</i> parity				
1/2	439799.0	-0.46	1.09	9.5×10^{-1}
3/2	31493.8	-10.6	-19.1	4.1×10^{-4}
5/2	23326.3	-10.0	-17.9	1.7×10^{-4}
7/2	20438.4	-9.09	-15.8	8.6×10^{-5}
9/2	20133.3	-7.91	-13.2	4.9×10^{-5}
11/2	21473.9	-6.74	-10.6	3.1×10^{-5}
13/2	24037.3	-5.71	-8.27	2.1×10^{-5}
15/2	27598.2	-4.89	-6.44	1.5×10^{-5}
<i>f</i> parity				
1/2	439262.1	-0.45	1.10	9.5×10^{-1}
3/2	29320.6	-11.1	-20.3	4.2×10^{-4}
5/2	17073.0	-12.7	-24.0	1.7×10^{-4}
7/2	8787.4	-18.0	-35.9	8.6×10^{-5}
9/2	1771.6	-67.1	-146	4.9×10^{-5}
11/2	4894.4	18.0	44.7	3.1×10^{-5}
13/2	11611.1	5.38	16.4	2.1×10^{-5}
15/2	18576.6	2.12	9.14	1.5×10^{-5}

Table 6.2: Transition frequencies, sensitivity coefficients to variation of μ and α and transition strengths of transitions from $\Omega' = 1/2, J$ to $\Omega' = 3/2, J + 1$, type V transitions, in CD. For a full discription of the table, see caption of Table 6.1

cosmological time scales. However, the high sensitivity coefficients could possibly be used in laboratory tests (note that experiments are being planned to decelerate CH molecules using electric fields [148] which open the prospect of measuring its rotational and microwave spectrum at high resolution).

We propose a test in CH based on the comparison between the rotational transitions between the *e* and *f* components of the $\Omega' = 1/2, J = 1/2$ and $\Omega' = 3/2, J = 3/2$ levels at 532 and 536 GHz, which have $K_\mu = -0.2$, with other rotational or lambda-doublet transitions in CH. Such a test, to be performed by far infrared spectroscopy of highly redshifted objects, is robust against systematic effects.

Ω', J	F'	freq (MHz)	o-c (kHz)	K_μ	K_α	Trans. Str.
$\frac{1}{2}, \frac{1}{2} f \rightarrow \frac{1}{2}, \frac{1}{2} e$	0→1	3263.795 ^a	16	-1.71	0.58	0.33
	1→1	3335.481 ^a	-10	-1.70	0.61	0.67
	1→0	3349.194 ^a	6	-1.69	0.62	0.33
$\frac{1}{2}, \frac{3}{2} f \rightarrow \frac{1}{2}, \frac{3}{2} e$	1→2	7275.004 ^a	15	-2.13	-0.26	0.14
	1→1	7325.203 ^a	27	-2.12	-0.24	0.68
	2→2	7348.419 ^a	-15	-2.12	-0.24	1.23
	2→1	7398.618 ^a	-4	-2.11	-0.22	0.14
$\frac{1}{2}, \frac{5}{2} f \rightarrow \frac{1}{2}, \frac{5}{2} e$	2→3	14713.78 ^b	190	-2.02	-0.04	0.04
	2→2	14756.670 ^a	36	-2.01	-0.03	0.54
	3→3	14778.962 ^a	-28	-2.01	-0.03	0.77
	3→2	14821.88 ^b	-160	-2.01	-0.02	0.04
$\frac{3}{2}, \frac{3}{2} f \rightarrow \frac{3}{2}, \frac{3}{2} e$	2→2	701.667 ^c	-8	-6.14	-8.28	1.17
	1→2	704.008	–	-6.11	-8.23	0.13
	2→1	722.452	–	-5.98	-7.96	0.13
	1→1	724.788 ^c	3	-5.96	-7.92	0.65

Table 6.3: Transition frequencies, sensitivity to variation of μ and α and transitions strengths of specific lambda-doubling transitions in CH calculated using PGOPHER [63] with the molecular constants from McCarthy *et al.* [137], including hyperfine splitting. Measured frequencies are given where possible, the difference with calculations is given for these transitions. The letters correspond to references: a: McCarthy *et al.* [137]; b: Brazier and Brown [144]; c: Ziurys and Turner [145]; d: Amano [146]; e: Davidson *et al.* [147]. freq., Frequency; o-c, Observed - Calculated; Trans. Str., Transition Strength. Tab. 6.4 lists rotational transitions.

Ω', J	F	freq (MHz)	o-c (kHz)	K_μ	K_α	Trans. Str.
$\frac{1}{2}, \frac{1}{2} f \rightarrow \frac{3}{2}, \frac{3}{2} f$	1→1	532721.333 ^d	-314	-0.20	1.59	0.17
	1→2	532723.926 ^d	-54	-0.20	1.59	0.85
	0→1	532793.309 ^d	-50	-0.20	1.59	0.34
$\frac{1}{2}, \frac{1}{2} e \rightarrow \frac{3}{2}, \frac{3}{2} e$	1→2	536761.145 ^d	-1	-0.22	1.57	0.86
	1→1	536781.954 ^d	31	-0.22	1.57	0.17
	0→1	536795.678 ^d	58	-0.22	1.57	0.34
$\frac{3}{2}, \frac{3}{2} f \rightarrow \frac{1}{2}, \frac{3}{2} e$	2→1	1470689.444	–	-1.00	0.00	0.03
	1→1	1470691.777	–	-1.00	0.00	0.17
	2→2	1470739.632	–	-1.00	0.00	0.30
	1→2	1470741.965	–	-1.00	0.00	0.03
$\frac{3}{2}, \frac{3}{2} e \rightarrow \frac{1}{2}, \frac{3}{2} f$	1→1	1477292.168	–	-1.00	0.00	0.16
	2→1	1477312.946	–	-1.00	0.00	0.03
	1→2	1477365.614	–	-1.00	0.00	0.03
	2→1	1477386.391	–	-1.00	0.00	0.30
$\frac{3}{2}, \frac{3}{2} f \rightarrow \frac{3}{2}, \frac{5}{2} f$	2→3	1656961.185	–	-1.00	0.00	2.32
	2→2	1656970.448	–	-1.00	0.00	0.17
	1→2	1656972.781	–	-1.00	0.00	1.49
$\frac{3}{2}, \frac{3}{2} e \rightarrow \frac{3}{2}, \frac{5}{2} e$	2→3	1661107.278	–	-1.00	0.00	2.32
	1→2	1661118.045	–	-1.00	0.00	1.49
	2→2	1661138.822	–	-1.00	0.00	0.17
$\frac{1}{2}, \frac{1}{2} e \rightarrow \frac{1}{2}, \frac{3}{2} e$	1→1	2006748.915	–	-0.79	0.42	0.16
	0→1	2006762.612	–	-0.79	0.42	0.32
	1→2	2006799.103	–	-0.79	0.42	0.81
$\frac{1}{2}, \frac{1}{2} f \rightarrow \frac{1}{2}, \frac{3}{2} f$	1→1	2010738.601	–	-0.79	0.42	0.16
	0→1	2010810.46 ^e	150	-0.79	0.42	0.33
	1→2	2010811.92 ^e	-130	-0.79	0.42	0.81

Table 6.4: Transition frequencies, sensitivity to variation of μ and α and transitions strengths of specific rotational transitions in CH. For a full description, see caption of Tab. 6.3

Bibliography

- [1] P. A. M. Dirac, *The cosmological constants*, Nature **139**, 323 (1937).
- [2] E. Teller, *On the change of physical constants*, Phys. Rev. **73**, 801 (1948).
- [3] J. P. Uzan, *The fundamental constants and their variation: observational and theoretical status*, Rev. Mod. Phys. **75**, 403 (2003).
- [4] A. Shlyakhter, *Direct test of the constancy of fundamental nuclear constants*, Nature **264**, 340 (1976).
- [5] C. R. Gould, E. I. Shapapov, and S. K. Lamoreaux, *Time variability of alpha from realistic models of Oklo reactors*, Phys. Rev. C **74**, 024607 (2006).
- [6] K. A. Olive, G. Steigman, and T. P. Walker, *Primordial nucleosynthesis: theory and observations*, Phys. Rep. **333-334**, 389 (2000).
- [7] M. C. Ferreira, M. D. Julião, C. J. A. P. Martins, and A. M. R. V. L. Monteiro, *Probing unification scenarios with atomic clocks*, Phys. Rev. D **86**, 125025 (2012).
- [8] P. Jansen, L. H. Xu, I. Kleiner, W. Ubachs, and H. L. Bethlem, *Methanol as a sensitive probe for spatial and temporal variations of the proton-to-electron mass ratio*, Phys. Rev. Lett. **106**, 100801 (2011).
- [9] H. L. Bethlem and W. Ubachs, *Testing the time-invariance of fundamental constants using microwave spectroscopy on cold diatomic radicals*, Faraday Discuss. **142**, 25 (2009).
- [10] A. J. de Nijs, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, and H. L. Bethlem, *UV-frequency metrology on CO $a^3\Pi$: Isotope effects and sensitivity to a variation of the proton-to-electron mass ratio*, Phys. Rev. A **84**, 052509 (2011).
- [11] J. K. Webb et al., *Further evidence for cosmological evolution of the fine structure constant*, Phys. Rev. Lett. **87**, 091301 (2001).
- [12] J. K. Webb, J. A. King, M. T. Murphy, V. Flambaum, R. F. Carswell, and M. B. Bainbridge, *Indications of a spatial variation of the fine structure constant*, Phys. Rev. Lett. **107**, 191101 (2011).
- [13] W. Ubachs, R. Buning, K. S. E. Eikema, and E. Reinhold, *On a possible variation of the proton-to-electron mass ratio: H₂ spectra in the line of sight of high-redshift quasars and in the laboratory*, J. Mol. Spectrosc. **241**, 155 (2007).

- [14] F. van Weerdenburg, M. T. Murphy, A. L. Malec, L. Kaper, and W. Ubachs, *First constraint on cosmological variation of the proton-to-electron mass ratio from two independent telescopes.*, Phys. Rev. Lett. **106**, 180802 (2011).
- [15] A. L. Malec et al., *Keck telescope constraint on cosmological variation of the proton-to-electron mass ratio*, Mon. Not. R. Astron. Soc. **403**, 1541 (2010).
- [16] J. van Veldhoven, J. Küpper, H. L. Bethlem, B. Sartakov, A. J. A. van Rooij, and G. Meijer, *Decelerated molecular beams for high-resolution spectroscopy*, Eur. Phys. J. D **31**, 337 (2004).
- [17] V. V. Flambaum and M. G. Kozlov, *Limit on the cosmological variation of m_p/m_e from the inversion spectrum of ammonia*, Phys. Rev. Lett. **98**, 240801 (2007).
- [18] M. T. Murphy, V. V. Flambaum, S. Muller, and C. Henkel, *Strong limit on a variable proton-to-electron mass ratio from molecules in the distant universe*, Science **320**, 1611 (2008).
- [19] J. Bagdonaite, P. Jansen, C. Henkel, H. L. Bethlem, K. M. Menten, and W. Ubachs, *A stringent limit on a drifting proton-to-electron mass ratio from alcohol in the early universe*, Science **339**, 46 (2013).
- [20] J. Bagdonaite et al., *Robust constraint on a drifting proton-to-electron mass ratio at $z=0.89$ from methanol observation at three radio telescopes*, Phys. Rev. Lett. **111**, 231101 (2013).
- [21] S. Muller et al., *Molecules at $z=0.89$ A 4-mm-rest-frame absorption-line survey toward PKS 1830-211*, Astron. Astrophys. **535**, A103 (2011).
- [22] S. Truppe, R. J. Hendricks, E. A. Hinds, and M. R. Tarbutt, *Measurement of the lowest millimeter-wave transition frequency of the CH radical*, ApJ **780**, 71 (2014).
- [23] S. Muller et al., *An ALMA Early Science survey of molecular absorption lines toward PKS 1830-211*, Astron. Astrophys. **566**, A112 (2014).
- [24] J. C. Berengut and V. V. Flambaum, *Manifestations of a spatial variation of fundamental constants in atomic and nuclear clocks, Oklo, meteorites, and cosmological phenomena*, Eur. Phys. Lett. **97**, 20006 (2012).
- [25] T. Rosenband et al., *Frequency ratio of Al^+ and Hg^+ single-ion optical clocks; metrology at the 17th decimal place*, Science **319**, 1808 (2008).
- [26] N. Leefer, C. T. M. Weber, A. Cingöz, J. R. Torgerson, and D. Budker, *New limits on variation of the fine-structure constant using atomic dysprosium*, Phys. Rev. Lett. **111**, 060801 (2013).

- [27] E. Peik and C. Tamm, *Nuclear laser spectroscopy of the 3.5 eV transition in Th-229*, Europhys. Lett. **61**, 181 (2003).
- [28] B. R. Beck et al., *Energy Splitting of the Ground-State Doublet in the Nucleus ^{229}Th* , Phys. Rev. Lett. **98**, 142501 (2007).
- [29] B. R. Beck et al., *Improved Value for the Energy Splitting of the Ground-State Doublet in the Nucleus ^{229}Th* , Proc. of the 12th Int. Conf. on Nuc. Reac. Mech. **LLNL-PROC-415170**, 255 (2009).
- [30] V. Flambaum, *Enhanced effect of temporal variation of the fine structure constant and the strong interaction in Th-229*, Phys. Rev. Lett. **97**, 092502 (2006).
- [31] J. C. Berengut, V. A. Dzuba, V. Flambaum, and S. G. Porsev, *Proposed experimental method to determine α sensitivity of splitting between ground and 7.6 eV isomeric states in ^{229}Th* , Phys. Rev. Lett. **102**, 210801 (2009).
- [32] M. P. Hehlen, R. R. Greco, W. G. Rellergert, S. T. Sullivan, D. D. R. A. Jackson, E. R. Hudson, and J. R. Torgerson, *Optical spectroscopy of an atomic nucleus: Progress toward direct observation of the ^{229}Th isomer transition*, J. Lumin. **133**, 91 (2013).
- [33] C. J. Campbell, A. G. Radnaev, and A. Kuzmich, *Wigner Crystals of ^{229}Th for Optical Excitation of the Nuclear Isomer*, Phys. Rev. Lett. **106**, 223001 (2011).
- [34] T. M. Fortier et al., *Precision atomic spectroscopy for improved limits on variation of the fine structure constant and local position invariance*, Phys. Rev. Lett. **98**, 070801 (2007).
- [35] A. Shelkvnikov, R. J. Butcher, C. Chardonnet, and A. Amy-Klein, *Stability of the proton-to-electron mass ratio*, Phys. Rev. Lett. **100**, 150801 (2008).
- [36] D. DeMille, S. Sainis, J. Sage, T. Bergeman, S. Kotochigova, and E. Tiesinga, *Enhanced sensitivity to variation of m_e/m_p in molecular spectra*, Phys. Rev. Lett. **100**, 043202 (2008).
- [37] V. V. Flambaum, *Enhanced effect of temporal variation of the fine-structure constant in diatomic molecules*, Phys. Rev. A **73**, 034101 (2006).
- [38] M. Drabbels, S. Stolte, and G. Meijer, *Production of an intense pulsed beam of oriented metastable CO $a^3\Pi$* , Chem. Phys. Lett. **200**, 108 (1992).
- [39] J. J. Gilijamse, S. Hoekstra, S. A. Meek, M. Metsälä, S. Y. T. van de Meeakker, G. Meijer, and G. C. Groenenboom, *The radiative lifetime of metastable CO ($a^3\Pi$, $v=0$)*, J. Chem. Phys. **127**, 221102 (2007).

- [40] R. T. Jongma, G. von Helden, G. Berden, and G. Meijer, *Confining CO molecules in stable orbits*, Chem. Phys. Lett. **270**, 304 (1997).
- [41] H. L. Bethlem, G. Berden, and G. Meijer, *Decelerating neutral dipolar molecules*, Phys. Rev. Lett. **83**, 1558 (1999).
- [42] W. H. B. Cameron, *The production of some spectra of carbon, oxygen, and nitrogen in the presence of neon*, Philos. Mag. **1**, 405 (1926).
- [43] R. S. Freund and W. Klemperer, *Radio-Frequency Spectrum of the $a^3\Pi$ State of Carbon Monoxide*, J. Chem. Phys. **43**, 2422 (1965).
- [44] B. G. Wicke, R. W. Field, and W. Klemperer, *Fine-structure, dipole-moment, and perturbation analysis of $a^3\Pi$ CO*, J. Chem. Phys. **56**, 5758 (1972).
- [45] R. J. Saykally, T. A. Dixon, T. G. Anderson, P. G. Szanto, and R. C. Woods, *The microwave-spectrum of CO in the $a^3\Pi$ state. 1. The $J=0-1$ transitions in CO, ^{13}CO and C^{18}O* , J. Chem. Phys. **87**, 6423 (1987).
- [46] N. Carballo, H. E. Warner, C. S. Gudeman, and R. C. Woods, *The microwave-spectrum of CO in the $a^3\Pi$ state. 2. The submillimeter wave transitions in the normal isotope*, J. Chem. Phys. **88**, 7273 (1988).
- [47] A. Wada and H. Kanamori, *Submillimeter-wave spectroscopy of CO in the $a^3\Pi$ state*, J. Mol. Spectrosc. **200**, 196 (2000).
- [48] M. Havenith, W. Bohle, J. Werner, and W. Urban, *Vibration-rotation spectroscopy of excited electronic states faraday-LMR spectroscopy of CO $a^3\Pi$* , Molec. Phys. **64**, 1073 (1988).
- [49] P. B. Davies and P. A. Martin, *Infrared-laser spectroscopy of the fundamental band of $a^3\Pi$ CO*, Chem. Phys. Lett. **136**, 527 (1987).
- [50] C. Effantin, F. Michaud, F. Roux, J. d'Incan, and J. Verges, *High-resolution fourier spectrometry of the CO infrared-emission spectrum - perturbation analysis of the $a'^3\Sigma-a^3\Pi$ system*, J. Mol. Spectrosc. **92**, 349 (1982).
- [51] R. W. Field, S. G. Tilford, R. A. Howard, and J. D. Simmons, *Fine-structure and perturbation analysis of the $a^3\Pi$ state of CO*, J. Mol. Spectrosc. **44**, 347 (1972).
- [52] R. H. Gammon, R. C. Stern, M. E. Lesk, B. G. Wicke, and W. Klemperer, *Metastable $a^3\Pi$ ^{13}CO - Molecular-beam electric-resonance measurements of fine structure, hyperfine structure, and dipole moment*, J. Chem. Phys. **54**, 2136 (1971).
- [53] G. Klapper, F. Lewen, R. Gendriesch, S. P. Belov, and G. Winnewisser, *Sub-Doppler measurements of the rotational spectrum of ^{13}CO* , J. Mol. Spectrosc. **201**, 124 (2000).

- [54] R. T. Jongma, T. Rasing, and G. Meijer, *2-Dimensional imaging of metastable CO molecules*, J. Chem. Phys. **102**, 1925 (1995).
- [55] S. Hannemann, E. J. Salumbides, S. Witte, R. T. Zinkstok, E. J. van Duijn, K. S. E. Eikema, and W. Ubachs, *Frequency metrology on the $EF^1\Sigma_g^+ \leftarrow X^1\Sigma_g^+$ (0,0) transition in H_2 , HD, and D_2* , Phys. Rev. A **74**, 062514 (2006).
- [56] S. Hannemann, E. J. Salumbides, S. Witte, R. T. Zinkstok, E. J. van Duijn, K. S. E. Eikema, and W. Ubachs, *Frequency metrology on the $Mg\ 3s^2\ ^1S \rightarrow 3s4p\ ^1P$ line for comparison with quasar data*, Phys. Rev. A **74**, 012505 (2006).
- [57] S. Hannemann, E. J. Salumbides, and W. Ubachs, *Reducing the first-order Doppler shift in a Sagnac interferometer*, Opt. Lett. **32**, 1381 (2007).
- [58] G. C. Groenenboom, private communication.
- [59] B. Minaev, O. Plachkevych, and H. Ågren, *Multiconfiguration response calculations on the cameron bands of the CO molecule*, J. Chem. Soc. Faraday Trans. **91**, 1729 (1995).
- [60] S. Witte, R. T. Zinkstok, W. Ubachs, W. Hogervorst, and K. S. E. Eikema, *Deep-ultraviolet quantum interference metrology with ultrashort laser pulses*, Science **307**, 400 (2005).
- [61] E. J. Salumbides, D. Bailly, A. Khramov, A. L. Wolf, K. S. E. Eikema, M. Vervloet, and W. Ubachs, *Improved laboratory values of the H_2 Lyman and Werner lines for constraining time variation of the proton-to-electron mass ratio*, Phys. Rev. Lett. **101**, 223001 (2008).
- [62] J. M. Brown and A. J. Merer, *Lambda-type doubling parameters for molecules in Π -electronic states of triplet and higher multiplicity*, J. Mol. Spectrosc. **74**, 488 (1979).
- [63] C. M. Western, *PGOPHER, a program for simulating rotational structure, Version 6.0.111*, University of Bristol (2009), <http://pgopher.chm.bris.ac.uk>.
- [64] G. Winnewisser, S. P. Belov, T. Klaus, and R. Schieder, *Sub-Doppler measurements on the rotational transitions of carbon monoxide*, J. Mol. Spectrosc. **184**, 468 (1997).
- [65] J. M. Brown, I. Kopp, C. Malmberg, and B. Rydh, *Analysis of hyperfine interactions in electronic-spectrum of AlF*, Phys. Scripta **17**, 55 (1977).
- [66] C. Puzzarini, L. Dore, and G. Cazzoli, *Rotational spectrum of $^{13}C^{17}O$ and $^{13}C^{18}O$: completely resolved nuclear hyperfine structures due to ^{13}C and ^{17}O* , J. Mol. Spectrosc. **217**, 19 (2003).

- [67] J. A. Coxon and P. G. Hajigeorgiou, *Direct potential fit analysis of the $X^1\Sigma^+$ ground state of CO*, J. Chem. Phys. **121**, 2992 (2004).
- [68] W. Ubachs, I. Velchev, and P. Cacciani, *Predissociation in the $E^1\Pi$, $v=1$ state of the six natural isotopomers of CO*, J. Chem. Phys. **113**, 547 (2000).
- [69] P. Cacciani, F. Brandi, I. Velchev, C. Lyngå, C. G. Wahlström, and W. Ubachs, *Isotope dependent predissociation in the $C^1\Sigma^+$, $v=0$ and $v=1$ states of CO*, Eur. Phys. J.D. **15**, 47 (2001).
- [70] R. J. Le Roy, *LEVEL 8.0: A computer program for solving the radial Schrödinger equation for bound and quasibound levels*, University of Waterloo Chemical Physics Research Report CP-663 (2007), see <http://leroy.uwaterloo.ca/programs/>.
- [71] R. J. Le Roy, private communication.
- [72] I. Angeli, *Recommended values of rms charge radii*, Acta Phys. Hung. New Ser.-Heavy Ion Phys. **8**, 23 (1998).
- [73] V. V. Flambaum, D. B. Leinweber, A. W. Thomas, and R. D. Young, *Limits on variations of the quark masses, QCD scale, and fine structure constant*, Phys. Rev. D **69**, 115006 (2004).
- [74] T. Dent, *Composition-dependent long range forces from varying m_p/m_e* , J. Cosmol. Astropart. Phys. **1**, 13 (2007).
- [75] M. Sneep, S. Hannemann, E. J. van Duijn, and W. Ubachs, *Deep-UV cavity ring-down spectroscopy*, Opt. Lett. **29**, 1378 (2004).
- [76] D. Ityaksov, H. Linnartz, and W. Ubachs, *Deep-UV absorption and Rayleigh scattering of carbon dioxide*, Chem. Phys. Lett. **462**, 31 (2008).
- [77] R. T. Jongma, M. G. H. Boogaarts, I. Holleman, and G. Meijer, *Trace gas-detection with cavity ring down spectroscopy*, Rev. Sci. Instrum. **66**, 2821 (1995).
- [78] G. Cazzoli, C. Puzzarini, and A. V. Lapinov, *Precise laboratory frequencies for the $J = 1-0$ and $J = 2-1$ rotational transitions of $C^{18}O$* , Astrophys. J. **592**, L95 (2003).
- [79] S. Y. T. van de Meerakker, H. L. Bethlem, and G. Meijer, *Taming molecular beams*, Nature Phys. **4**, 595 (2008).
- [80] D. Auerbach, E. E. A. Bromberg, and L. Wharton, *Alternate-gradient focusing of molecular beams*, J. Chem. Phys. **45**, 2160 (1966).
- [81] G. Lambertson, *Beam dynamics in a storage ring for neutral (polar) molecules*, Proc. 2003 Part. Acc. Conf. **1-5**, 410 (2003).

- [82] W. Gerlach and O. Stern, *The experimental evidence of direction quantisation in the magnetic field*, Zeitschrift für Physik **9**, 349 (1922).
- [83] B. Friedrich and D. Herschbach, *Stern and Gerlach: How a bad cigar helped reorient atomic physics*, Phys. Today **56**, 53 (2003).
- [84] H. Kallmann and F. Reiche, *Über den Durchgang bewegter Moleküle durch inhomogene Kraftfelder*, Zeitschrift für Physik **6**, 352 (1921).
- [85] E. Wrede, *Über die Ablenkung von Molekularstrahlen elektrischer Dipolmoleküle im inhomogenen elektrischen Feld*, Zeitschrift für Physik **44**, 261 (1927).
- [86] G. E. Chamberlain and J. C. Zorn, *Alkali polarizabilities by the atomic beam electrostatic deflection method*, Phys. Rev. **129**, 677 (1963).
- [87] R. Antoine, P. Dugourd, D. Rayane, E. Benichou, M. Broyer, F. Chandezon, and C. Guet, *Direct measurement of the electric polarizability of isolated C₆₀ molecules*, J. Chem. Phys. **110**, 9771 (1999).
- [88] M. Berninger, A. Stefanov, S. Deachapunya, and M. Arndt, *Polarizability measurements of a molecule via a near-field matter-wave interferometer*, Phys. Rev. A **76**, 013607 (2007).
- [89] R. Moro, R. Rabinovitch, C. Xia, and V. V. Kresin, *Electric dipole moments of water clusters from a beam deflection measurement*, Phys. Rev. Lett. **97**, 123401 (2006).
- [90] R. Moro, X. Xu, S. Yin, and W. A. de Heer, *Ferroelectricity in free niobium clusters*, Science **300**, 1265 (2003).
- [91] N. F. Ramsey, *Molecular beams* (Oxford University Press, 1956).
- [92] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper, and G. Meijer, *Laser-induced alignment and orientation of quantum-state-selected large molecules*, Phys. Rev. Lett. **102**, 023001 (2009).
- [93] F. Filsinger et al., *Pure samples of individual conformers: The separation of stereoisomers of complex molecules using electric fields*, Angew. Chem. Int. Ed. **48**, 6900 (2009).
- [94] A. Stefanov, M. Berninger, and M. Arndt, *A novel design for electric field deflectometry on extended molecular beams*, Meas. Sci. Technol. **19**, 055801 (2008).
- [95] J. Kalnins, G. Lambertson, and H. Gould, *Improved alternating gradient transport and focusing of neutral molecules*, Rev. Sci. Instrum. **73**, 2557 (2002).
- [96] H. L. Bethlem, M. R. Tarbutt, J. Küpper, D. C. Carty, K. Wohlfart, E. A.

- Hinds, and G. Meijer, *Alternating gradient focusing and deceleration of polar molecules*, J. Phys. B **39**, R263 (2006).
- [97] J. Reuss, *State selection by nonoptical methods*, in G. Scoles (Ed.), *Atomic and molecular beam methods, Vol I*, p. 276 (Oxford University Press, New York, 1988).
- [98] E. O. Lawrence and M. S. Livingston, *The production of high speed protons without the use of high voltages*, Phys. Rev. **38**, 834 (1931).
- [99] H. A. Bethe and M. E. Rose, *The maximum energy obtainable from the cyclotron*, Phys. Rev. **52**, 1254 (1937).
- [100] D. W. Kerst and R. Serber, *Electronic orbits in the induction accelerator*, Phys. Rev. **60**, 53 (1941).
- [101] W. Ketterle and D. E. Pritchard, *Trapping and focusing ground-state atoms with static fields*, Appl.Phys.B **54**, 403 (1992).
- [102] H. Nishimura, G. Lambertson, J. G. Kalnins, and H. Gould, *Feasibility of a storage ring for polar molecules in strong-field-seeking states*, Eur. Phys. J. D **31**, 359 (2004).
- [103] F. M. H. Crompvoets, H. L. Bethlem, R. T. Jongma, and G. Meijer, *A prototype storage ring for neutral molecules*, Nature (London) **411**, 174 (2001).
- [104] S. K. Sekatskii, *Electrostatic traps for polar molecules*, JETP Lett. **62**, 916 (1995).
- [105] S. K. Sekatskii and J. Schmiedmayer, *Trapping polar molecules with a charged wire*, Eur. Phys. Lett. **36**, 407 (1996).
- [106] H.-J. Loesch and B. Scheel, *Molecules on Kepler orbits: An experimental study*, Phys. Rev. Lett. **85**, 2709 (2000).
- [107] E. D. Courant and H. S. Snyder, *Theory of the alternating-gradient synchrotron*, Annals of Physics **3**, 1 (1958).
- [108] D. Kakati and D. C. Lainé, *Alternate-gradient focusing of a molecular beam of ammonia*, Phys. Lett. **24A**, 676 (1967).
- [109] D. Thompson, R. V. E. Lovelace, and D. M. Lee, *Storage-rings for spin-polarized hydrogen*, J.Opt.Soc.Am.B **6**, 2227 (1989).
- [110] M. R. Tarbutt et al., *Slowing heavy, ground-state molecules using an alternating gradient decelerator*, Phys. Rev. Lett. **92**, 173002 (2004).
- [111] F. Filsinger, U. Erlekam, G. von Helden, J. Küpper, and G. Meijer, *Selector for structural isomers of neutral molecules*, Phys. Rev. Lett. **100**, 133003 (2008).
- [112] T. E. Wall, S. Armitage, J. J. Hudson, B. E. Sauer, J. M. Dyne, E. A.

- Hinds, and M. R. Tarbutt, *Transport of polar molecules by an alternating-gradient guide*, Phys. Rev. A **80**, 043407 (2009).
- [113] P. C. Zieger, S. Y. T. van de Meerakker, C. E. Heiner, H. L. Bethlem, A. J. A. van Roij, and G. Meijer, *Multiple packets of neutral molecules revolving for over a mile*, Phys. Rev. Lett. **105**, 173001 (2010).
- [114] C. E. Heiner, *A molecular synchrotron*, Ph.D. thesis, Radboud University Nijmegen (2009).
- [115] M. R. Tarbutt, J. J. Hudson, B. E. Sauer, and E. A. Hinds, *Prospects for measuring the electric dipole moment of the electron using electrically trapped polar molecules*, Faraday Discuss. **142**, 37 (2009).
- [116] S. E. Maxwell et al., *High-flux beam source for cold, slow atoms or molecules*, Phys. Rev. Lett. **95**, 173201 (2005).
- [117] D. Patterson and J. M. Doyle, *Bright, guided molecular beam with hydrodynamic enhancement*, J. Chem. Phys. **126**, 154307 (2007).
- [118] N. Huntemann, M. Okhapkin, B. Lipphardt, S. Weyers, C. Tamm, and E. Peik, *High-accuracy optical clock based on the octupole transition in $^{171}\text{Yb}^+$* , Phys. Rev. Lett. **108**, 090801 (2012).
- [119] T. L. Nicholson et al., *Comparison of two independent Sr optical clocks with 1×10^{-17} stability at 10^3 s*, Phys. Rev. Lett. **109**, 230801 (2012).
- [120] J. J. Hudson, D. M. Kara, I. J. Smallman, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, *Improved measurement of the shape of the electron*, Nature **473**, 493 (2011).
- [121] The ACME Collaboration, *Order of Magnitude Smaller Limit on the Electric Dipole Moment of the Electron*, Science **343**, 269 (2014).
- [122] C. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, C. J. Bordé, and C. Chardonnet, *Limit on the parity nonconserving energy difference between the enantiomers of a chiral molecule by laser spectroscopy*, Phys. Rev. Lett. **83**, 1554 (1999).
- [123] M. Quack, *Frontiers in spectroscopy*, Faraday Discuss. **150**, 533 (2011).
- [124] G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki, and W. Ubachs, *Fundamental vibration of molecular hydrogen*, Phys. Rev. Lett. **110**, 193601 (2013).
- [125] E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema, and W. Ubachs, *Bounds on fifth forces from precision measurements on molecules*, Phys. Rev. D **87**, 112008 (2013).
- [126] P. Jansen, H. L. Bethlem, and W. Ubachs, *Tipping the scales: Search for drifting constants from molecular spectra*, J. Chem. Phys. **140**, 010901 (2014).

- [127] S. Truppe et al., *A search for varying fundamental constants using hertz-level frequency measurements of cold CH molecules*, Nat. Comm. **4**, 2600 (2013).
- [128] S. A. Meek, G. Santambrogio, B. G. Sartakov, H. Conrad, and G. Meijer, *Suppression of nonadiabatic losses of molecules from chip-based microtraps*, Phys. Rev. A **83**, 033413 (2011).
- [129] S. Hannemann, E. J. van Duijn, and W. Ubachs, *A narrow-band injection-seeded pulsed titanium:sapphire oscillator-amplifier system with on-line chirp analysis for high-resolution spectroscopy*, Rev. Sci. Instrum. **78**, 103102 (2007).
- [130] A. J. de Nijs and H. L. Bethlem, *On deflection fields, weak-focusing and strong-focusing storage rings for polar molecules*, Phys. Chem. Chem. Phys. **13**, 19052 (2011).
- [131] N. F. Ramsey, *Experiments with separated oscillatory fields and hydrogen masers*, Rev. Mod. Phys. **62**, 541 (1990).
- [132] S. P. Ellingsen, M. A. Voronkov, S. L. Breen, and J. E. J. Lovell, *First cosmological constraints on the proton-to-electron mass ratio from observations of rotational transitions of methanol*, Astrophys. J. Lett. **747**, L7 (2012).
- [133] Y. Sheffer, M. Rogers, S. R. Federman, N. P. Abel, R. Gredel, D. L. Lambert, and G. Shaw, *Ultraviolet survey of CO and H₂ in diffuse molecular clouds: the reflection of two photochemistry regimes in abundance relationships*, Astrophys. J. **687**, 1075 (2008).
- [134] M. G. Kozlov, *Lambda-doublet spectra of diatomic radicals and their dependence on fundamental constants*, Phys. Rev. A **80**, 022118 (2009).
- [135] C. Amiot, J. P. Maillard, and J. Chauville, *Fourier spectroscopy of the OD infrared-spectrum - merge of electronic, vibration-rotation, and microwave spectroscopic data*, J. Mol. Spectrosc. **87**, 196 (1981).
- [136] J. M. Brown and K. M. Evenson, *The far-infrared laser magnetic-resonance spectrum of the CD radical and determination of ground-state parameters*, J. Mol. Spectrosc. **136**, 68 (1989).
- [137] M. C. McCarthy, S. Mohamed, J. M. Brown, and P. Thaddeus, *Detection of low-frequency Lambda-doublet transitions of the free ¹²CH and ¹³CH radicals*, Proc. Natl. Acad. Sci. U. S. A. **103**, 12263 (2006).
- [138] K. Beloy, M. G. Kozlov, A. Borschevsky, A. W. Hauser, V. V. Flambaum, and P. Schwerdtfeger, *Rotational spectrum of the molecular ion NH⁺ as a probe for α and m_e/m_p variation*, Phys. Rev. A **83**, 062514 (2011).
- [139] D. T. Halfen, L. M. Ziurys, J. C. Pearson, and B. J. Drouin, *Direct*

- measurements of the fundamental rotational transitions of CD and ^{13}CH ($X^2\Pi_r$), Astrophys. J. **687**, 731 (2008).*
- [140] P. Jansen, I. Kleiner, L. H. Xu, W. Ubachs, and H. L. Bethlem, *Sensitivity of transitions in internal rotor molecules to a possible variation of the proton-to-electron mass ratio*, Phys. Rev. A **84**, 062505 (2011).
- [141] J. M. Brown, C. M. L. Kerr, F. D. Wayne, K. M. Evenson, and H. E. Radford, *The far-infrared laser magnetic-resonance spectrum of the OH radical*, J. Mol. Spectrosc. **86**, 544 (1981).
- [142] J. M. Brown and J. E. Schubert, *The EPR spectrum of the OD radical - a determination of molecular-parameters for the ground-state*, J. Mol. Spectrosc. **95**, 194 (1982).
- [143] J. M. Brown and A. Carrington, *Rotational spectroscopy of diatomic molecules* (Cambridge University Press, 2003).
- [144] C. R. Brazier and J. M. Brown, *The microwave-spectrum of the CH free-radical*, J. Chem. Phys. **78**, 1608 (1983).
- [145] L. M. Ziurys and B. E. Turner, *Detection of interstellar rotationally excited CH*, Astrophys. J. **292**, L25 (1985).
- [146] T. Amano, *The lowest submillimeter-wave transitions of CH: The laboratory measurement of the rest frequencies*, Astrophys. J. **531**, L161 (2000).
- [147] S. A. Davidson, K. M. Evenson, and J. M. Brown, *A measurement of the rotational spectrum of the CH radical in the far-infrared*, Astrophys. J. **546**, 330 (2001).
- [148] M. R. Tarbutt, private communication.
- [149] T. van Oudheusden, *Electron source for sub-relativistic single-shot femtosecond diffraction*, Ph.D. thesis, Technische Universiteit Eindhoven (2010).
- [150] J. Vanier and C. Audoin, *The Quantum Physics of Atomic Frequency Standard* (IOP Publishing, 1989).
- [151] T. W. Hänsch and B. Couillaud, *Laser frequency stabilization by polarization spectroscopy of a reflecting reference cavity.*, Opt. Commun. **35**, 441 (1980).