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Chapter 1

Introduction

Even though the word 'constant' seems to imply otherwise, it can not be taken for granted that the fundamental numbers underlying all physical theories that physicists call constants are ever unchanging. Dirac was the first to realize this, when he noticed that the ratio between the electromagnetic and gravitational forces between an electron and a proton and the ratio between the mass of the universe and the mass of the proton are approximately equal to t and t^2 , respectively, with $t \approx 10^{39}$ the age of the universe expressed in atomic units [1]. Dirac assumed that this would not be coincidental, but a fundamental truth. By then, it was already known that the observable universe is expanding, which led Dirac to two conclusions: (1) the number of protons and neutrons in the universe must increase; and (2) the ratio between the strength of the electromagnetic and gravitational forces is a function of time. As the first point would lead to a much smaller relative change in the involved quantity than the second, it was concluded that it was the gravitational 'constant' (the quotes are his) that was changing [2]. Teller showed that any variation was much smaller than would be predicted by the theory from Dirac by explaining that the temperature on earth around 250 million years ago would be such that water would be either freezing or boiling, which conflicts with life being present at that time [2].

As will be discussed later, the constraints on a variation of fundamental constants have nowadays been set much tighter, and the coincidence seen by Dirac is now seen as just that, a coincidence. Nevertheless, the search for a time or position dependency of the value of fundamental constants is ongoing. The search is aimed only at dimensionless numbers, as a variation in dimensionful numbers can not be separated from a variation in the measurement system [3]. The dimensionless numbers that are most often targeted are the fine-structure constant, α , and the proton-to-electron mass ratio, μ , with the focus of this thesis being on the latter.

An intuitive way to search for a possible variation of a fundamental constant would be to measure that constant as precisely as possible a number of times over a time interval. However, as it is not possible to measure a fundamental constant directly, this is very inefficient. To find the value of α or μ , a mea-

surement is performed and then calculations are used to extract the value of the constant itself. To experimentally find the value of a fundamental constant to a certain accuracy, one needs both measurements and calculations to this accuracy. To study whether a constant is changing over time¹, however, the exact value of the constant is not of interest. To find whether a fundamental constant is truly a constant, it is possible to directly use the results of a spectroscopic measurement, even if the dependency of the measured transition to the fundamental constant is known only to rather poor accuracy². To calculate how the energy of a transition depends on a constant to within a few percent is very much possible for molecular transitions (see, for example Chapter 6). This dependency is referred to as the sensitivity coefficient, K_X , and is defined as

$$\frac{\delta\nu}{\nu} = K_X \frac{\delta X}{X}, \quad (1.1)$$

with X a fundamental constant. This means that any relative change in a fundamental constant, $\frac{\delta X}{X}$, is accompanied by a K_X times larger relative change in the transition frequency, $\frac{\delta\nu}{\nu}$. A constraint on the size of the relative rate of change of a fundamental constant can now be determined by measuring two transitions with a different K_X over a time interval, typically of the order of one year. Two transitions with a different K_X are needed, as otherwise the relative variation will be the same in both transition, and thus remain hidden. In practice, a cesium clock is often used as the reference transition [7].

The constraint that an experiment sets on the time variation of a fundamental constant is determined by the accuracy of the measurement, the sensitivity coefficient of the measured transition and the time over which a transition is monitored. K_X is typically of order 1, however, in special cases it can have very high values up to a few hundred [8–10]. A higher than normal sensitivity is most often the result of a near degeneracy between two levels that have a different dependence on the constant under consideration. In the case of the two-photon transition in the $\alpha^3\Pi$ state of CO that will be discussed in this thesis, the energy of one of the two nearly-degenerate levels is purely rotational, while the energy of the other level is partially rotational and partially spin-orbit. The rotational energy depends only on μ , while the spin-orbit energy depends only on α . A change in α or μ will result in one level shifting with respect to the other. A near degeneracy thus raises the sensitivity coefficient, and it moves the transition frequency into the microwave regime.

¹A variation in space is equivalent to a variation in time, due to the movement of earth, and thus the laboratory, with respect to any outside reference frame. In this thesis, we will only discuss time variation.

²Spectroscopy is not the only way to study time variation of fundamental constants. For example, the evaluation of physical processes and the isotope ratios found in the Oklo natural fission reactor and the atomic abundances predicted by big bang nucleosynthesis have been used [4–6]. These methods however fall outside the scope of this thesis.

1.1 Astrophysical measurements

To make a search for a time-variation of a fundamental constant more sensitive, a very long time interval can be used. In laboratory studies this is not feasible, but it is being used in astrophysical measurements. When the light of a far-away light source travels through an interstellar gas cloud, the absorption features of the atoms and molecules that are present in the cloud are imprinted on the light. Those absorption features, that can be from the optical to the microwave regime, can be detected on earth and compared to laboratory measurements. All absorption features from the same gas cloud will be redshifted by the same relative amount. However, as not all transitions have the same sensitivity coefficient, absorption features will have shifted with respect to each other if a fundamental constant has shifted. For this purpose, absorption features of absorption in metal ions, e.g. Fe^+ and Mg^+ have been observed at high red shifts [11]. These observations were used to find a relative variation in α on the order of 10^{-5} [11]. After more data was collected and analyzed, this variation was interpreted as a spatial dipole in α , meaning that an increased α was found in one direction of the universe and a decreased α was found in the opposite direction [12].

To study a variation in μ using astrophysical observations, molecular hydrogen has been the main object of study. The transitions in hydrogen that were used in these studies, however, have a sensitivity coefficient of only order 0.01 [13]. Absorption in molecular hydrogen has been observed at redshifts corresponding to a look-back time of $\sim 10^{10}$ years, leading to a constraint on the relative change of μ on the order of 10^{-5} [14, 15]. 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, 19–21], at redshift 0.89 have resulted in more stringent limits on the variation of μ , with a most stringent limit of $\Delta\mu/\mu = (-1.0 \pm 0.8_{stat} \pm 1.0_{sys}) \times 10^{-7}$ [20] over a look-back time of 7.5 billion years.

One of the problems that faces astrophysical measurements is spatial segregation. Typically, transitions in different molecules are compared to find the most stringent constraint on a possible variation. However, if not all species are present in the same location, different conditions may apply to different molecules. To be unaffected by spatial segregation, one can use multiple transitions in one molecule that have a different sensitivity coefficient. An example of this is given in Chapter 6, where the lowest rotational transitions and lambda-doubling transitions in the lowest rotational levels of the ground state of CH are found to have very different sensitivity coefficients. Recently, these rotational transitions have been measured both in the laboratory [22] and at redshift $z = 0.89$ using ALMA [23].

1.2 α variation

The α dipole discussed before can in principle be confirmed by laboratory measurements, as earth is moving through space with respect to the α dipole. This movement through the dipole would result in $\dot{\alpha}/\alpha \approx 10^{-19} \text{ yr}^{-1}$ [24]. Here, we discuss a number of present and future laboratory experiments that search for a time variation of α .

One experiment is a comparison of two different ion-clocks, performed at NIST [25]. In this experiment, the relative frequency of a Hg^+ and a Al^+ clock are compared over a period of a year. As both clock transitions have a different dependence on α , a relative rate of change of α can be extracted from this experiment, and was found to be $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17} \text{ yr}^{-1}$.

Another experiment is the dysprosium experiment performed in the Budker group at UC Berkeley. In this experiment, a near degeneracy between two hyperfine components of two different states of dysprosium is measured. Due to large, opposite-sign relativistic corrections to the energy of both states, this transition is highly sensitive to a variation of α [26]. As the sign of the sensitivity coefficient is opposite between ^{162}Dy and ^{164}Dy , the transition is measured in both isotopes to limit common-mode effects. The transition frequencies of 235 and 754 MHz, respectively, have been measured to an accuracy of better than a hertz over a period of two years, finding $\dot{\alpha}/\alpha = (-5.8 \pm 6.9) \times 10^{-17} \text{ yr}^{-1}$, consistent with zero. The accuracy of this experiment is limited by the very short, order microseconds, lifetime of one of the states, making the transition very broad. Even though the system under study in this experiment is much less ideal than the one in the ion clock comparison, the transitions in dysprosium are $\sim 10^6$ times more sensitive to a variation of α , so the final accuracy in $\dot{\alpha}/\alpha$ is of the same order of magnitude. However, these two experiments do not have the accuracy required to confirm or exclude the α dipole.

A new development that may reach the required accuracy is the thorium nuclear clock, based on a very narrow transition between nearly-degenerate nuclear states in ^{229}Th [27]. This transition, with an energy of $7.8 \pm 0.5 \text{ eV}$ [28, 29], is very sensitive to a variation of α , as there is a cancellation between Coulomb and nuclear energies, which are both of order mega-electronvolt and depend differently on α [28, 30, 31]. It is also highly insensitive to external fields, as the nucleus couples to external electric and magnetic fields via the nuclear moments which are much smaller than the electronic equivalents. The electrons around the nucleus add an extra coupling via the hyperfine interaction, but this is still weaker than when electronic transitions are used. Furthermore, the Th^{3+} ion is alkali like, and thus amenable to laser cooling and trapping, making a single trapped ion experiment possible [27]. However, despite a search by a number of groups, this transition has not been directly observed yet [32, 33].

1.3 μ variation

In the scientific literature, many different clock comparisons can be found, for example the aforementioned comparison of Hg^+ - Al^+ clocks [25] and a comparison between Hg^+ -Cs clocks [34]. Each of these comparisons measures the relative frequency of the two clocks involved over a time interval of order 1 year, and each relative frequency has a different dependence on α and μ . Under Grand Unification models, assumptions can be made about the relation between $\dot{\alpha}/\alpha$ and $\dot{\mu}/\mu$ [7]. Using the different dependencies on the fundamental constants, and the model-dependent relations, the relative rate of change of μ was found to be $\dot{\mu}/\mu = (0.7 \pm 2.9) \times 10^{-16} \text{ yr}^{-1}$ [7].

A model-free constraint on the time variation of μ is found from a comparison of a rovibrational transition in SF_6 with a cesium fountain clock [35] over a period of two years. The transition was measured in a two-photon spatial Ramsey experiment. A CO_2 laser around $10 \mu\text{m}$ was used to detect Ramsey fringes with a periodicity of 200 Hz. A cavity was used to create a standing wave, effectively phase locking the two interrogation zones. As a vibrational transition in a molecule has a sensitivity coefficient of $K_\mu = 0.5$, the Cs clock a sensitivity coefficient of $K_\mu = -1$ and the dependence on the other constants is the same as in the Hg^+ - Al^+ clock comparison, a constraint on the variation of μ could be extracted. The end result that was found is $\dot{\mu}/\mu = (3.8 \pm 5.6) \times 10^{-14} \text{ yr}^{-1}$ [35].

1.4 Near degeneracies

The idea of using a transition between nearly degenerate levels in the search for a possible variation of fundamental constants has been mentioned already, here we will discuss this in more detail. Near degeneracies between levels with a different dependence on a fundamental constant will lead to an enhancement of the sensitivity of the transition between these levels. This has the obvious advantage that a measurement of this transition can be less accurate, while still setting a tighter constraint on a varying constant than a measurement of a transition with a low sensitivity. Another advantage is that the same transition can have a very different sensitivity coefficient in a different isotope, thereby enabling a comparison of the two using the same experimental setup. In this way, common-mode effects can be monitored by comparing the relative rate of change of both transitions. A disadvantage is that a higher absolute accuracy needs to be reached, as a constraint is set using the relative accuracy of a measurement. This is not relevant in astrophysical measurements, as the accuracy of these measurements is limited by the Doppler width of the measured transitions, which is a relative effect. The main disadvantage is that the systems that exhibit the highest sensitivity coefficients are not necessarily systems that can be measured to high accuracy, as there are only very few

highly sensitive transitions. Therefore, one will have to use a more complex system to measure, and use a more complex experimental setup.

Whereas in atoms near degeneracies are accidental and very rare, in molecules in states with $S > 0$ near degeneracies have a high probability of occurring. These states have multiple Ω manifolds, and the lowest rotational levels of each manifold are offset by the fine structure constant, A , and the rotational levels within a manifold are spaced by $BJ(J+1)$, with B the rotational constant and J the rotational quantum number. As A depends only on α , and B depends only on μ , a change in one of these two constants will move the rotational ladders with respect to each other, theoretically leading to a rotational level in one manifold crossing a rotational level in another for the right values of A and B . A near degeneracy between two levels with $\Delta J = 0$ will never lead to an increased sensitivity due to mixing of the Ω manifolds. A near degeneracy between two levels with $\Delta J = 1$ can happen in the case of a molecule with $A = 4B$, e.g. CD, but in this case the strength of this transition will unfortunately be zero, as will be shown in Chapter 6. For molecules where $A \neq 4B$, mixing of the different Ω manifolds prevents rotational levels with $\Delta J = 1$ from crossing. As there is no coupling between rotational levels in different Ω manifolds with $\Delta J = 2$, they can cross and thus become nearly degenerate. To first order, the sensitivity coefficient of a transition between these levels will be given by $K_X = E_c/\nu$, where ν is the energy difference between the two nearly degenerate levels, and E_c is the energy difference that is “canceled”, i.e. the part of the energy of the two levels that has a different dependence on the fundamental constant under consideration. Here, it is equal to the energy of the fine-structure splitting, A .

In the above case, the near degeneracy is the result of a cancellation of spin-orbit and rotational energies. Cancellations between many other types of energy also occur in molecules, for example between vibrational and electronic energy [36] or between hyperfine and rotational energy [37]. An enhanced sensitivity coefficient can also be the result of a tunneling motion, as for example in ammonia [16]. This can be understood from the fact that the tunneling probability is heavily dependent on the mass that tunnels. The effects from a tunneling motion and a cancellation of different types of energy are combined in for example methanol, leading to sensitivity coefficients ranging from -40 to +50 [8].

1.5 Metastable CO as a probe for a variation of μ

Here, we will present an experiment in CO $a^3\Pi$ to test a possible time-variation of μ . Metastable CO has a number of features that make it uniquely suitable for precision measurements; (i) Producing an intense supersonic beam of CO is straightforward, and as the ground state is a $^1\Sigma$ state there will be very few clusters. (ii) Ground state molecules can be directly laser excited to the metastable $a^3\Pi$ state [38], using a narrow-band pulsed UV laser system, pro-

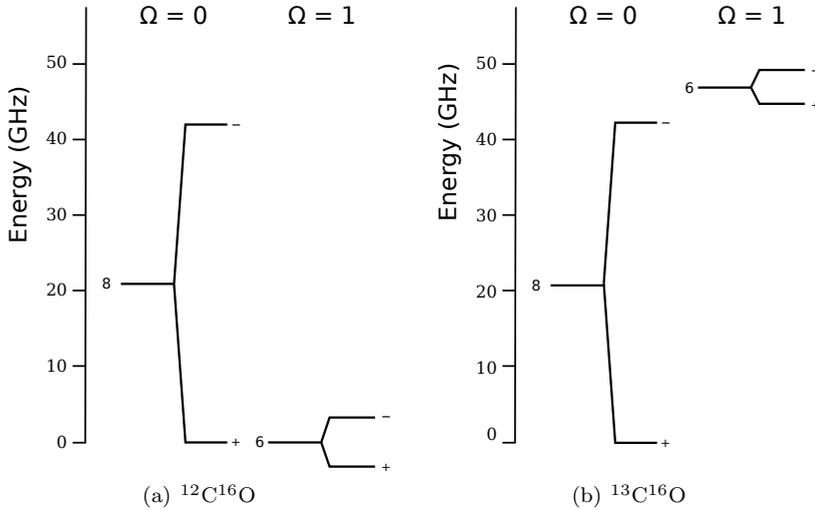


Figure 1.1: The $J = 8, \Omega = 0$ and $J = 6, \Omega = 1$ rotational levels of the CO $a^3\Pi$ state in the $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ isotopologues. The hyperfine splitting in $^{13}\text{C}^{16}\text{O}$ is neglected for clarity.

ducing a pure quantum state. (iii) Due to the long lifetime of 2.6 ms [39], transitions in this state have a low natural linewidth, on the order of a kilohertz. (iv) Excitation of the CO molecules with a pulsed nanosecond laser produces a well-defined packet of metastable molecules, both in time and in space, enabling a very precise determination of the molecular velocity. (v) Due to the high internal energy, 6 eV, of the metastable molecules, 2D detection can be performed using a multi-channel plate (MCP), a phosphor screen and a digital camera [40]. By gating the voltage on the MCP background from stray electrons and ions in the vacuum can be eliminated. (vi) Due to their high electric dipole moment, metastable CO molecules can be easily manipulated using electric fields, as for example used in the first Stark deceleration experiment [41]. (vii) $^{12}\text{C}^{16}\text{O}$ has no hyperfine structure.

Bethlem and Ubachs [9] studied the type of near degeneracy discussed in Sec. 1.4 for different molecules. It was found that the $J = 8, \Omega = 0$, the $J = 6, \Omega = 1$ and the $J = 4, \Omega = 2$ rotational levels of the $a^3\Pi$ state of CO are nearly degenerate, with the $J = 8, \Omega = 0, +$, the $J = 6, \Omega = 1, +$ levels lying only 3.3 GHz apart, a factor 10^3 smaller separation than between consecutive rotational levels within one Ω manifold around this J value. These two rotational levels are shown in the left-hand panel of Fig. 1.1. This leads to a sensitivity coefficient of $K_\mu \approx A/\nu = 1243/-3.3 = -377$, in good agreement with the more accurate calculations in Chapter 2, where it is found that $K_\mu = -334$, with the difference being due to mixing of the two Ω manifolds. As the $J = 6, \Omega = 1$ level is moving up with respect to the $J = 8, \Omega = 0$

level, the transition frequency decreases when μ increases, leading to a negative sensitivity coefficient.

As the reduced mass of $^{13}\text{C}^{16}\text{O}$ is $\sim 5\%$ larger than the reduced mass of $^{12}\text{C}^{16}\text{O}$, its rotational constant is $\sim 5\%$ smaller. This leads to a large shift of the nearly degenerate levels with respect to each other. This can be seen in the right-hand panel of Fig. 1.1 where the two nearly degenerate rotational levels in $^{13}\text{C}^{16}\text{O}$ are shown. Here, we see that the $J = 8, \Omega = 0, -$ and $J = 6, \Omega = 1, -$ levels are nearly degenerate. Here, the hyperfine splitting is neglected, the full calculation is given in Chapter 2. The ordering of the two rotational levels is inverted, leading to a positive sensitivity coefficient of $K_\mu = +128$. By studying both transitions in the same setup, common-mode effects can be studied and systematic shifts can be excluded. Instead of measuring in a different isotopologue, another vibrational level can be used. The $J = 8, \Omega = 0, + \rightarrow J = 6, \Omega = 1, +$ transition in the $v = 1$ level of $^{12}\text{C}^{16}\text{O}$ has a sensitivity coefficient of $K_\mu = 202$ [9].

1.6 Outline of this thesis

This thesis will present the progress towards setting a constraint on the possible time-variation of the proton-to-electron mass ratio using a measurement of a two-photon microwave transition in the $a^3\Pi$ state of CO. This transition between two nearly-degenerate rotational levels is highly sensitive to such a variation. In the planned experiment, a beam of metastable CO is prepared in a pure quantum state by expanding CO into vacuum and exciting the molecules using a narrow-band UV laser system. After passing two resonant microwave cavities that are separated by 50 cm, the molecules are state-selectively deflected and detected 1 meter downstream on a position sensitive detector.

In Chapter 2, to show that we have good control over the production of metastable CO, the $a^3\Pi$ state of CO is characterized by high-accuracy UV spectroscopy. We determined the frequency of the two-photon microwave transition with an accuracy of 0.5 MHz, reducing its uncertainty by well over an order of magnitude. Furthermore, mass-scaling relations were used to calculate the sensitivity coefficients of a number of transitions between nearly-degenerate levels in different isotopologues. In Chapter 3, cavity ring-down spectroscopy is performed on the $a^3\Pi$ state of two isotopologues of CO, and it is found that the mass-scaling rules for the $a^3\Pi$ state can be used to predict the transition frequencies from $v = 0, J < 8$ in $^{12}\text{C}^{16}\text{O}$ to $v = 1, J < 30$ rovibrational levels in both $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ to within the experimental accuracy of 0.2 cm^{-1} . The design of the electro-static deflection field that is used to state-selectively deflect molecules in the microwave measurements is discussed in Chapter 4. Here, the theoretical description used for the design of the deflection field is also used to study two types of storage rings for molecules in high-field seeking states. In Chapter 5 we show that high precision microwave spectroscopy can be performed on CO ($a^3\Pi$) in the planned setup. We measured the $\Omega = 1, J = 1$

lambda-doublet splitting around 394 MHz to an accuracy of 10 Hz, and discuss systematic effects that influence the result.

In Chapter 6 the sensitivity to a variation of α and μ is calculated for rotational transitions in the ground states of CH and CD molecules. It is shown that rotational levels with $\Delta J = 1$ in different Ω manifolds can become nearly degenerate, but the strength of transitions between the two levels converges to zero. This makes these near-degeneracies less interesting for the search for a variation of fundamental constants, leading to the conclusion that a two-photon transition is the best candidate.

In Chapter 7, an outlook towards measuring the highly sensitive two-photon microwave transition is given. A setup very similar to the molecular beam setup used in the one-photon microwave measurement is being planned, changes that need to be made to the setup are discussed in this chapter. As the highly sensitive transition is a two-photon transition, it requires a more intense microwave field. The transition strength is calculated, and a resonant microwave cavity is designed and tested. Also, a higher rotational level needs to be excited by the UV laser, resulting in a higher number of m_J^B sublevels, a smaller deflection and a lower population, the consequences of which are also discussed.

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