
16 Variation of the Fundamental Constants as Revealed by Molecules: Astrophysical Observations and Laboratory Experiments

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16.1 INTRODUCTION

In this chapter, we describe the application of precision molecular spectroscopy to the study of a possible temporal and spatial variation of the fundamental constants. As we will show below, molecular spectra are mostly sensitive to two such dimensionless constants, namely the fine-structure constant $\alpha = e^2/\hbar c$ and the electron-to-proton mass ratio $\mu = m_e/m_p$ (note that some authors define μ as an inverse value, i.e., the proton-to-electron mass ratio). At present, NIST lists the following values of these constants [1]: $\alpha^{-1} = 137.035999679(94)$ and $\mu^{-1} = 1836.15267247(80)$.

The fine-structure constant α determines the strength of the electromagnetic (and, more generally, electroweak) interactions. In principle, there is a similar coupling constant α_s for quantum chromodynamics (QCD). However, because of the highly nonlinear character of the strong interaction, this constant is not well defined. Therefore, the strength of the strong interaction is usually characterized by the parameter Λ_{QCD} , which has the dimension of mass and is defined as the position of the Landau pole in the logarithm for the strong coupling constant, $\alpha_s(r) = \text{const.}/\ln(r\Lambda_{\text{QCD}}/\hbar c)$, where r is the distance between the interacting particles.

In the Standard Model (SM), there is another fundamental parameter with the dimension of mass—the Higgs vacuum expectation value (VEV), which determines the electroweak unification scale. The electron mass m_e and quark masses m_q are proportional to the Higgs VEV. Consequently, the dimensionless parameters $X_e = m_e/\Lambda_{\text{QCD}}$ and $X_q = m_q/\Lambda_{\text{QCD}}$ link the electroweak unification scale with the strong scale. For the light u and d quarks, $X_q \ll 1$. As a result, the proton mass m_p is proportional to Λ_{QCD} and hence X_e is proportional to μ . In what follows, we use μ instead of X_e as it is more directly linked to the experimentally accessible atomic and molecular observables.

Below we show that a huge enhancement of the relative variation takes place in transitions between close-lying atomic, molecular, and nuclear energy levels. Recently, several new systems have been found where the levels are both very close to one another and narrow. Also, a large enhancement of the variation effects can be expected to occur in cold collisions of atoms and molecules near Feshbach resonances.

We begin by reviewing the state of the art of the search for the variation of α and μ . Next, we discuss, in some detail, the results that follow from the astrophysical observations of the optical and microwave spectra of molecules. Finally, we describe possible laboratory experiments with molecules on time variation. Such experiments are a novelty, and the accuracy of the laboratory results cannot yet compete with that of the astrophysical observations (see, nevertheless, Section 16.7). However, there are proposals for significant improvements, and several groups have already started implementing them.

The analysis of the data from the Big Bang nucleosynthesis [2], quasar absorption spectra, and the Oklo natural nuclear reactor yields the space–time variation of the constants on the timescale of the lifetime of the Universe, that is, from a few billion to more than ten billion years. In comparison, the frequencies of various atomic and molecular transitions in the laboratory experiments yield a time variation on the timescale from a few months to a few years. There is no model-independent connection between the variations on such different timescales. However, in order to

compare the astrophysical and laboratory results, we will often assume a linear time dependence of the constants. In this way, we can interpret all the results in terms of the time derivatives of the fundamental constants. Within this assumption, we can use the quasar absorption spectra to obtain the best current limit on the variation of the mass ratio μ and of X_e [3],

$$\dot{\mu}/\mu = \dot{X}_e/X_e = (1 \pm 3) \times 10^{-16} \text{ yr}^{-1}. \quad (16.1)$$

Combining this result with the atomic clock results [4] yields the best upper bound on the variation of α [5–7]:

$$\dot{\alpha}/\alpha = (-0.8 \pm 0.8) \times 10^{-16} \text{ yr}^{-1}. \quad (16.2)$$

The measurements at the Oklo natural reactor provide the best bound on the variation of $X_s = m_s/\Lambda_{\text{QCD}}$, where m_s is the strange quark mass [8–10],

$$|\dot{X}_s/X_s| < 10^{-18} \text{ yr}^{-1}. \quad (16.3)$$

Note that the Oklo data cannot yield any bound on the variation of α since the effect of α there is much smaller than the effect of X_s and should be neglected within the accuracy of the present theory [10].

In addition to the time variation, one may also consider the spatial variation of the constants. Massive bodies (stars or galaxies) may also affect the physical constants. In other words, the fundamental constants may depend on the gravitational potential, for example,

$$\delta\alpha/\alpha = k_\alpha \delta(GM/rc^2), \quad (16.4)$$

where G is the gravitational constant and r is the distance from the mass M . The most stringent limit on such a variation,

$$k_\alpha + 0.17k_\mu = (-3.5 \pm 6) \times 10^{-7}, \quad (16.5)$$

is obtained in Ref. [6] from the measurements of the dependence of the atomic frequencies on the distance from the Sun due to the ellipticity of the Earth's orbit [4,11] (the parameter k_μ is defined by analogy with Equation 15.4). Below we also discuss some other results, including those that indicate nonzero variation of the fundamental constants.

16.2 THEORETICAL MOTIVATION

How may the variation of the physical constants and the violation of the local position invariance come about? Light scalar fields very naturally appear in modern cosmological models, affecting parameters of the SM including α and μ (for the whole list of SM parameters see Ref. [12]). Cosmological variations of these scalar fields are, in turn, expected to arise because of the drastic changes in the composition of the Universe during its evolution.

Theories unifying gravity and other interactions suggest the possibility of spatial and temporal variation of physical “constants” in the Universe [13]. Moreover, there exists a mechanism for making all coupling constants and masses of elementary particles both space- and time-dependent, and influenced by the local environment (see review in Ref. [14]). Variation of the coupling constants could be nonmonotonic, such as, for example, damped oscillations.

These variations are usually associated with the effect of massless (or very light) scalar fields. One such field is the dilaton: a scalar that appears in string theories together with the graviton, in a massless multiplet of closed-string excitations. Other scalars naturally appear in those cosmological models in which our Universe is a “brane” floating in a space of a larger dimension. The scalars are simply brane coordinates in extra dimensions. However, the only relevant scalar field recently discovered, the cosmological dark energy, has not shown visible variations so far. Observational limits on the variation of the physical constants given in Section 16.1 are quite stringent, allowing only for scalar couplings, which are tiny in comparison with gravity.

A possible explanation was suggested by Damour and colleagues [15,16], who pointed out that cosmological evolution of scalars naturally leads to their self-decoupling. Damour and Polyakov [16] have further suggested that the variations should take place when the scalars become excited by some physical change in the Universe, such as phase transitions, or by other drastic changes in the equation of state of the Universe. They considered several phase transitions, but since the publication of their paper a new transition has been discovered, one from a matter dominated (decelerating) era to a dark-energy-dominated (accelerating) era. This transition is a relatively recent event, corresponding to a cosmological redshift $z \approx 0.5$, or a look-back time of approximately 5 billion years.

The time dependence of the perturbation related to the transition from the decelerating to the accelerating era could be calculated [17,18]. The calculation shows that the self-decoupling process is effective enough to explain why *after* this transition the variation of the constants is as small as observed in the present-time laboratory experiments. However, the calculated time dependence is also consistent with the observations of the variation of the electromagnetic fine-structure constant at $z \gtrsim 1$ [19–21].

16.3 DEPENDENCE OF ATOMIC AND MOLECULAR SPECTRA ON α AND μ

Atomic and molecular spectra are most naturally described in atomic units ($\hbar = m_e = e = 1$), with the energy measured in Hartrees (1 Hartree = $\frac{e^4 m_e}{\hbar^2} = 2 \text{ Ry} = 219474.6313705(15) \text{ cm}^{-1}$).

One could argue that the atomic energy unit itself depends on α as it can be expressed as $\alpha^2 m_e c^2$, with $m_e c^2$ the rest energy of a free electron. However, an experimental search for a possible variation of the fundamental constants relies on the observation of the time variation of the ratios of different transition frequencies to one another. In such ratios, the dependence of the units on the fundamental constants cancels out. Below we will use atomic units unless stated otherwise.

In the atomic units, the nonrelativistic Schrödinger equation for an atom with an infinitely heavy, pointlike nucleus does not include any dimensional parameters. The dependence of the spectrum on α enters only through relativistic corrections, which describe the *fine-structure*, the Lamb shift, and so on. The dependence of atomic energies on μ is known as the *isotope effect* and is caused by a finite nuclear mass and volume. There are even smaller corrections to atomic energies, which depend on both α and μ and are known as the *hyperfine structure*.

The relativistic corrections to the binding energies of the atomic valence electrons are on the order of $\alpha^2 Z^2$, where Z is the atomic number, and become quite large for heavy elements. For our purposes, it is convenient to consider the dependence of the atomic transition frequencies on α^2 in the form

$$\omega = \omega_0 + qx, \quad (16.6)$$

where $x = (\frac{\alpha}{\alpha_0})^2 - 1 \approx \frac{2\delta\alpha}{\alpha}$ and ω_0 is a transition frequency for $\alpha = \alpha_0$. Rough estimates of the q -factors can be obtained from simple one-particle models, but in order to obtain accurate values, one has to account for electronic correlations via large-scale numerical calculations. Recently, such calculations have been carried out for many atoms and ions [22–29].

Isotope effects in atoms are on the order of $\mu \sim 10^{-3}$ and the magnetic hyperfine structure scales roughly as $\alpha^2 \mu Z g_{\text{nuc}} \approx 10^{-7} Z g_{\text{nuc}}$, where g_{nuc} is the nuclear g -factor. One has to keep in mind that g_{nuc} also depends on μ and the quark parameters X_q . This dependence has to be considered when comparing, for example, the frequency of the hyperfine transition in ^{133}Cs (Cs frequency standard) [5] or the hydrogen 21 cm hyperfine line [30,31] with various optical transitions [5].

At present, there are many accurate experiments comparing different optical and microwave atomic clocks [4,32–39]. These experiments put stringent limits on the time variation of the different combinations of α , μ , and g_{nuc} . As we mentioned above, the limit on the α -variation (2) follows from the experiment of Ref. [4] and the limit (1) from the assumption of a linear time-dependence of all constants. A detailed discussion of the atomic experiments can be found in recent reviews [40,41].

A comparison of the hyperfine transition in atomic hydrogen with optical transitions in ions on a cosmological timescale was described in Refs [30] and [31]. This allows one to study the time variation of the parameter $F = \alpha^2 g_p \mu$, where g_p is the proton g -factor. The analysis of the absorption spectra of nine quasars with redshifts $0.23 \leq z \leq 2.35$ yielded

$$\delta F/F = (6.3 \pm 9.9) \times 10^{-6}, \quad (16.7)$$

$$\dot{F}/F = (-6 \pm 12) \times 10^{-16} \text{ yr}^{-1}, \quad (16.8)$$

which is consistent with a zero variation of μ and α .

Molecular spectroscopy opens additional possibilities for studying the variation of the fundamental constants. It is known that μ defines the scales of electronic, vibrational, and rotational intervals in molecular spectra, $E_{\text{el}} : E_{\text{vib}} : E_{\text{rot}} \sim 1 : \mu^{1/2} : \mu$. In addition, molecules have fine and hyperfine structure, Λ -doubling, hindered rotation,

and so on. All these effects have different dependencies on the fundamental constants. Obviously, a comparison of these effects allows one to study different combinations of the fundamental constants.

The sensitivity to temporal variation of the fundamental constants may be strongly enhanced in transitions between narrow close-lying levels of different types. Huge enhancement of the relative variation $\delta\omega/\omega$ can be expected in transitions between nearly degenerate levels of atoms [22,24,25,42,43], molecules [3,44–46,49], and nuclei [50,51].

An interesting case of the enhancement of the effect of the variation of fundamental constants arises in collisions of ultracold atoms and molecules near Feshbach resonances [52]. The scattering length A near a resonance is extremely sensitive to the μ -variation:

$$\frac{\delta A}{A} = K \frac{\delta\mu}{\mu}, \quad (16.9)$$

because the enhancement factor K can be quite large; for example, for Cs–Cs collisions, $K \sim 400$ [52]. The enhancement can be further increased by tuning the resonance using external fields. Near a narrow magnetic or optical Feshbach resonance, the enhancement factor K may be increased by many orders of magnitude.

The calculation of the factor K in Ref. [52] is based on the analytic formula for the scattering length derived in Ref. [53]. This formula is valid for an arbitrary interatomic potential with an inverse-power long-range tail ($1/r^6$ for neutral atoms); that is, it includes all anharmonic corrections.

To the best of our knowledge, it is the only suggested experiment on time variation where the observable is not a frequency. However, another parameter L with the dimension of length is needed to compare with A , and thus render it dimensionless. In Ref. [52], the scattering length was defined in atomic units (a_B). However, it is important, because of the large enhancement in Equation 16.9, that the possible dependence of L on μ becomes irrelevant. For example, if we measure A in conventional units, meters, which are linked to the Cs standard, then $\delta L/L = -\delta\mu/\mu$, and

$$\frac{\delta(A/L)}{(A/L)} = (K + 1) \frac{\delta\mu}{\mu}. \quad (16.10)$$

As long as $K \gg 1$, the dependence of the units used on the fundamental constants can be neglected. Below, we discuss several other experiments with huge enhancement factors, where this argument can be also applied.

16.4 ASTROPHYSICAL OBSERVATIONS OF H₂

H₂ is the most abundant molecule in the universe and its UV spectrum has been used in the studies of the possible μ -variation for a long time. For a given electronic transition, the frequency of each rovibrational line has different dependence on μ [54,55]. Therefore, comparing rovibrational frequencies from astrophysical observations with laboratory data can provide information on μ .

In the adiabatic approximation, the rovibrational levels of the electronic state Λ with vibrational and rotational quantum numbers v and J are given by the Dunham expansion [56]:

$$E(v, J) = \sum_{k, l \geq 0} Y_{k, l} \left(v + \frac{1}{2} \right)^k \left[J(J+1) - \Lambda^2 \right]^l, \quad (16.11)$$

where each term depends on μ in the following way:

$$Y_{k, l} \propto \mu^{l+k/2}. \quad (16.12)$$

Because of the smallness of the parameter μ , the $Y_{k, l}$ coefficients rapidly decrease with both k and l , and for small v and J , one ends up with the usual vibrational ($k = 1$) and rotational ($l = 1$) terms. The zeroth term of the Dunham expansion ($k = l = 0$) corresponds to the electronic energy.

One can define the sensitivity coefficient K_i for each rovibrational transition i of a given electronic band $e - g$ as [55]:

$$\begin{aligned} K_i &\equiv \left(\frac{dv_i}{v_i} \right) / \left(\frac{d\mu}{\mu} \right) \\ &= \frac{\mu}{E_e - E_g} \left(\frac{dE_e}{d\mu} - \frac{dE_g}{d\mu} \right), \end{aligned} \quad (16.13)$$

where both energies, E_g and E_e , are given by expansion 16.11. The sign of K_i depends on the rovibrational energies of the excited (e) and ground (g) states (in the absorption spectra of the quasars, only transitions from the ground electronic state are seen). The electronic energy, represented by the term $Y_{0,0}$, dominates the expansion and the coefficients K_i are rather small. Typically they are on the order 10^{-2} , but can reach 0.05 for large values of the quantum numbers v and J .

The Dunham coefficients of Equation 16.11 are determined by fitting the measured spectra. The sensitivity coefficients K_i can be found by making use of Equations 16.12 and 16.13. Some rovibrational levels of different electronic excited states lie very close to each other. For such levels, additional nonadiabatic corrections can be included within the two-level approximation [57].

A purported μ -variation, $\delta\mu$, leads to a difference in the observed redshifts z_i for different lines

$$\zeta_i \equiv \frac{z_i - z_{q, \text{abs}}}{1 + z_{q, \text{abs}}} = -\frac{\delta\mu}{\mu} K_i, \quad (16.14)$$

where $z_{q, \text{abs}}$ represents the redshifts of a quasar absorption system. One can estimate $\delta\mu/\mu$ by plotting the reduced redshifts ζ_i against the sensitivity coefficients K_i . The most recent study [20] of the possible μ -variation using astrophysical data on H_2 was based on the observation of the two redshifts $z_{q, \text{abs}} = 3.02$ and 2.59 . An analysis of 76 lines from two UV bands of H_2 gave the following result:

$$\frac{\delta\mu}{\mu} = (-20 \pm 6) \times 10^{-6}. \quad (16.15)$$

This result indicates, at a 3.5σ confidence level, that μ has increased during the past 12 billion years. Assuming a linear time dependence, we can rewrite Equation 16.15 as

$$\frac{\dot{\mu}}{\mu} = (17 \pm 5) \times 10^{-16} \text{ yr}^{-1}. \quad (16.16)$$

Q1 This has to be compared with the ammonia result of Equation 16.1, which corresponds to a timescale of about 6.5 billion years and is discussed in more detail in Section 16.6.

16.5 ASTROPHYSICAL OBSERVATIONS OF MICROWAVE MOLECULAR SPECTRA

In the previous section, we discussed astrophysical observations of UV spectra of H_2 . The corresponding absorption bands are very strong and can be observed even for objects with very high redshifts. On the other hand, as we have seen, the sensitivity coefficients K_i in Equation 16.13 are rather small. This is because of the smallness of the rovibrational energy compared with the total transition energy. Therefore, it is expedient to study the microwave spectra of molecules, where the relative frequency changes due to a possible variation of the constants are larger.

16.5.1 ROTATIONAL SPECTRA

In 1996, Varshalovich and Potekhin [58] compared redshifts for the microwave rotational transitions ($J = 3 \rightarrow J = 2$) and ($J = 2 \rightarrow J = 1$) in the CO molecule with redshifts of optical lines of light atomic ions from the same astrophysical objects at redshifts $z = 2.286$ and $z = 1.944$. Because the atomic frequencies are independent of μ while the rotational transition frequencies are proportional to μ , this comparison made it possible to set the following limits on the variation of μ :

$$\frac{\delta\mu}{\mu} = (-0.6 \pm 3.7) \times 10^{-4}, \quad \text{at } z = 2.286, \quad (16.17a)$$

$$\frac{\delta\mu}{\mu} = (-0.7 \pm 1.0) \times 10^{-4}, \quad \text{at } z = 1.944. \quad (16.17b)$$

In the same paper [58], the authors compared the ($J = 0 \rightarrow J = 1$) CO absorption line with the 21 cm hydrogen line for an object with $z = 0.2467$. They did not find any significant difference in the respective redshifts, and interpreted this result as yet another limit on the variation of μ . However, as noted above, the frequency of the hydrogen hyperfine line is proportional to $\alpha^2 \mu g_p$, and so this result actually puts a limit on the variation of the parameter $F = \alpha^2 g_p$ [59]. Recently, a similar analysis was undertaken by Murphy and colleagues [60] using more accurate data for the same object at $z = 0.247$ and for a more distant object at $z = 0.6847$, which led to

the following limits:

$$\frac{\delta F}{F} = (-2.0 \pm 4.4) \times 10^{-6}, \quad \text{at } z = 0.2467, \quad (16.18a)$$

$$\frac{\delta F}{F} = (-1.6 \pm 5.4) \times 10^{-6}, \quad \text{at } z = 0.6847. \quad (16.18b)$$

The object at $z = 0.6847$ is associated with the gravitational lens toward quasar B0218+357 and corresponds to the look-back time of ~ 6.5 Gyr. This object was also used by other authors, as will be discussed in Sections 16.5.2 and 16.6.

16.5.2 THE 18 cm TRANSITIONS IN OH

Here we consider transitions between the hyperfine substates of the ${}^2\Pi_{3/2}$ ground-state Λ -doublet of the OH molecule [61–63]. The Λ -doubling for ${}^2\Pi_{3/2}$ states appears in the third order of the Coriolis interaction and the corresponding energy interval is inversely proportional to the spin–orbit splitting between the ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ states, that is, it scales as $\mu^3\alpha^{-2}$, while the hyperfine structure intervals scale as $\alpha^2\mu g_{\text{nuc}}$. Therefore, the ratio of the hyperfine interval to the Λ -doubling interval depends on the combination $\tilde{F} = \alpha^4\mu^{-2}g_{\text{nuc}}$. Higher-order corrections modify this parameter to $\tilde{F} = \alpha^{3.14}\mu^{-1.57}g_{\text{nuc}}$ [64].

The hyperfine structure splitting for the OH molecule is approximately 50 MHz and is much smaller than the Λ -doubling interval, which is about 1700 MHz. Because of that, it is actually easier to compare the Λ -doubling transitions in OH to the 21 cm hydrogen line, or to rotational lines of the HCO^+ molecule [61–64].

The most stringent limit on the variation of \tilde{F} was obtained from observations of the $z = 0.765$ absorber and the $z = 0.685$ gravitational lens [64],

$$\delta\tilde{F}/\tilde{F} = (0.44 \pm 0.36^{\text{stat}} \pm 1.0^{\text{syst}}) \times 10^{-5}, \quad (16.19)$$

where the systematic error mostly accounts for the possible Doppler noise, due to the difference in the velocities of the molecules in a molecular cloud.

The frequencies of the OH Λ -doublet were recently remeasured in the laboratory with a higher precision using cold molecules produced by a Stark decelerator [65]. That may be of relevance to more accurate future astrophysical observations.

16.6 LIMIT ON THE TIME VARIATION OF μ FROM THE INVERSION SPECTRUM OF AMMONIA

In 2004, van Veldhoven and colleagues suggested using a decelerated molecular beam of ND_3 to search for the variation of μ in a laboratory experiment [46]. The ammonia molecule has a pyramidal structure with an inversion frequency depending on the exponentially small probability of tunneling of the three hydrogen (or deuterium) atoms through the potential barrier [66]. Therefore, it is very sensitive to any changes of the parameters of the system, particularly to the reduced mass entering the vibrational inversion mode. Van Veldhoven and colleagues found that for the ND_3

molecule, $\delta\omega/\omega = 5.6 \delta\mu/\mu$. Therefore, the inversion frequency of ND_3 is nearly an order of magnitude more sensitive to μ -variation than typical molecular vibrational frequencies (note that Ref. [46] contains a misprint in the sign of the effect).

However, even such enhanced sensitivity is insufficient to make a laboratory experiment on the time variation of μ using conventional or Stark-decelerated molecular beams competitive. A molecular fountain seems to be necessary to increase the sensitivity by the several orders of magnitude needed for a competitive experiment. Work on the molecular fountain is in progress [67].

On the other hand, an only slightly smaller enhancement exists for the inversion spectrum of NH_3 , often observed in astrophysics even for high z objects. This spectrum was used in Ref. [3] to obtain limit 16.1, which we will now discuss in more detail.

Q1

There are two bound vibrational states pertaining to the inversion vibration of ammonia. These two levels are split by tunneling through the barrier into inversion doublets. The splitting of the lower doublet corresponds to a wavelength $\lambda \approx 1.25$ cm and is used in ammonia masers. Molecular rotation leads to a centrifugal distortion of the potential energy curve, and so the inversion splitting depends on the rotational angular momentum J and its projection K on the molecular symmetry axis:

$$\omega_{\text{inv}}(J, K) = \omega_{\text{inv}}^0 - c_1[J(J+1) - K^2] + c_2K^2 + \dots, \quad (16.20)$$

where we omitted terms with higher powers of J and K . The measured values of the parameters are $\omega_{\text{inv}}^0 \approx 23.787$ GHz, $c_1 \approx 151.3$ MHz, and $c_2 \approx 59.7$ MHz [68].

In addition to the rotational structure 16.20, the inversion spectrum has a hyperfine structure. For the main nitrogen isotope ^{14}N , the hyperfine structure is dominated by the electric quadrupole interaction (~ 1 MHz) [69]. Because of the dipole selection rule, $\Delta K = 0$ and the levels with $J = K$ are metastable. In beam experiments, the width of the corresponding inversion lines is usually determined by collisional broadening. In astrophysical observations, the lines with $J = K$ are also narrower and stronger than others, but the hyperfine structure of the spectra with high redshifts is unresolved.

For our purposes, it is important to know how the parameters in Equation 16.20 depend on the fundamental constants. The molecular electrostatic potential in atomic units does not depend on the fundamental constants (here we neglect small relativistic corrections, which give a weak α dependence). Therefore, the inversion frequency ω_{inv}^0 and the constants $c_{1,2}$ are functions of μ only. Note that the coefficients c_i depend on μ through the reduced mass of the inversion mode and because they are inversely proportional to the molecular moments of inertia. This implies a different scaling of ω_{inv}^0 and c_i with μ .

The inversion spectrum of Equation 16.20 can be approximately described by the Hamiltonian

$$H_{\text{inv}} = -\frac{1}{2M_1}\partial_x^2 + U(x) + \frac{1}{I_1(x)}[J(J+1) - K^2] + \frac{1}{I_2(x)}K^2, \quad (16.21)$$

where x is the distance from the N nucleus to the H-plane, I_1 and I_2 are the moments of inertia perpendicular and parallel to the molecular axis, respectively, and M_1 is the

reduced mass for the inversion mode. If we assume that the length d of the N–H bond does not change during the inversion, then $M_1 = 2.54 m_p$ and

$$I_1(x) \approx \frac{3}{2} m_p d^2 [1 + 0.2(x/d)^2], \quad (16.22)$$

$$I_2(x) \approx 3 m_p d^2 [1 - (x/d)^2]. \quad (16.23)$$

The dependence of $I_{1,2}$ on x generates a correction to the potential energy of the form $C(J, K) x^2 \mu$. This changes the vibrational frequency and the effective height of the potential barrier, thereby changing the inversion frequency ω_{inv} given by Equation 16.20.

Following Ref. [70], we can write the potential $U(x)$ in Equation 16.21 as

$$U(x) = \frac{1}{2} k x^2 + b \exp(-c x^2). \quad (16.24)$$

Fitting the vibrational frequencies for NH_3 and ND_3 gives $k \approx 0.7598$ au, $b \approx 0.05684$ au, and $c \approx 1.3696$ au. A numerical integration of the Schrödinger equation with the potential 16.24 for different values of μ gives the following result:

$$\frac{\delta \omega_{\text{inv}}^0}{\omega_{\text{inv}}^0} \approx 4.46 \frac{\delta \mu}{\mu}. \quad (16.25)$$

It is instructive to reproduce this result analytically. Within the WKB approximation, **Q2** the inversion frequency is estimated as [71]:

$$\omega_{\text{inv}}^0 = \frac{\omega_{\text{vib}}}{\pi} \exp(-S) \quad (16.26a)$$

$$= \frac{\omega_{\text{vib}}}{\pi} \exp\left(-\frac{1}{\hbar} \int_{-a}^a \sqrt{2M_1(U(x) - E)} dx\right), \quad (16.26b)$$

where ω_{vib} is the vibrational frequency of the inversion mode, S is the action in units of \hbar , $x = \pm a$ are the classical turning points at energy E ; for the lowest vibrational state, $E = U_{\text{min}} + \frac{1}{2} \omega_{\text{vib}}$. Using the experimental values $\omega_{\text{vib}} = 950 \text{ cm}^{-1}$ and $\omega_{\text{inv}} = 0.8 \text{ cm}^{-1}$, we obtain $S \approx 5.9$.

Expression 16.26b allows one to calculate the dependence of ω_{inv}^0 on the mass ratio μ . Let us write the action as $S = A \mu^{-1/2} \int_{-a}^a \sqrt{U(x) - E} dx$, where A is a numerical constant and the square root depends on μ via E . Then

$$\frac{d\omega_{\text{inv}}^0}{d\mu} = \omega_{\text{inv}}^0 \left(\frac{1}{2\mu} - \frac{dS}{d\mu} \right) \quad (16.27a)$$

$$= \omega_{\text{inv}}^0 \left(\frac{1}{2\mu} - \frac{\partial S}{\partial \mu} - \frac{\partial S}{\partial E} \frac{\partial E}{\partial \mu} \right). \quad (16.27b)$$

It is easy to see that $\partial S/\partial\mu = -S/2\mu$. The value of the third term in Equation 16.27b depends on the form of the potential barrier

$$\frac{\partial S}{\partial E} = -\frac{q}{4} \frac{S}{U_{\max} - E}, \quad (16.28)$$

where for a square barrier $q = 1$, and for a triangular barrier $q = 3$. For a more realistic barrier shape, $q \approx 2$. Using the parametrization 16.24 to determine U_{\max} we obtain

$$\frac{\delta\omega_{\text{inv}}^0}{\omega_{\text{inv}}^0} \approx \frac{\delta\mu}{2\mu} \left(1 + S + \frac{S}{2} \frac{\omega_{\text{vib}}}{U_{\max} - E} \right) = 4.4 \frac{\delta\mu}{\mu}, \quad (16.29)$$

which is close to the numerical result of Equation 16.25.

We see that the inversion frequency of NH_3 is an order of magnitude more sensitive to the change of μ than typical vibrational frequencies. The reason for this is clear from Equation 16.29: it is the large value of the action S for the tunneling process.

Using Equations 16.21 to 16.23, one can also find the dependence of the constants $c_{1,2}$ in Equation 16.20 on μ (Ref. [3])

$$\frac{\delta c_{1,2}}{c_{1,2}} = 5.1 \frac{\delta\mu}{\mu}. \quad (16.30)$$

It is clear that the above consideration is directly applicable to ND_3 , where the inversion frequency is 15 times smaller and Equation 16.26b gives $S \approx 8.4$. According to Equation 16.29, this leads to a somewhat higher sensitivity of the inversion frequency to μ , in agreement with Ref. [46],

$$\text{ND}_3 : \begin{cases} \frac{\delta\omega_{\text{inv}}}{\omega_{\text{inv}}} \approx 5.7 \frac{\delta\mu}{\mu} \\ \frac{\delta c_2}{c_2} \approx 6.2 \frac{\delta\mu}{\mu}. \end{cases} \quad (16.31)$$

We see from Equations 16.25 and 16.30 that the inversion frequency ω_{inv}^0 and the rotational intervals $\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)$ have different dependencies on μ . In principle, this allows one to study time variation of μ by comparing different intervals in the inversion spectrum of ammonia. For example, if we compare the rotational interval to the inversion frequency, then Equations 16.25 and 16.30 give

$$\frac{\delta\{[\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)]/\omega_{\text{inv}}^0\}}{[\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)]/\omega_{\text{inv}}^0} = 0.6 \frac{\delta\mu}{\mu}. \quad (16.32)$$

The relative effects are substantially larger if we compare the inversion transitions with the transitions between the quadrupole and magnetic hyperfine components. However, in practice, this method does not work because the hyperfine splitting is much smaller than typical linewidths in astrophysical spectra.

Again, as in the case of Λ -doubling in the OH molecule, it is more promising to compare the inversion spectrum of NH_3 with the rotational spectra of other molecules, where

$$\frac{\delta\omega_{\text{rot}}}{\omega_{\text{rot}}} = \frac{\delta\mu}{\mu}. \quad (16.33)$$

In astrophysical observations, any frequency shift is related to a corresponding apparent redshift

$$\frac{\delta\omega}{\omega} = -\frac{\delta z}{1+z}. \quad (16.34)$$

According to Equations 16.25 and 16.33, for a given astrophysical object with $z = z_0$, variation of μ leads to a change of the apparent redshifts of all rotational lines $\delta z_{\text{rot}} = -(1+z_0)\delta\mu/\mu$. The corresponding shifts of all inversion lines of ammonia therefore are $\delta z_{\text{inv}} = -4.46(1+z_0)\delta\mu/\mu$. By comparing the apparent redshift z_{inv} for NH_3 with the apparent redshifts z_{rot} for the rotational lines, we find

$$\frac{\delta\mu}{\mu} = 0.289 \frac{z_{\text{rot}} - z_{\text{inv}}}{1+z_0}. \quad (16.35)$$

High-precision data on the redshifts of NH_3 inversion lines exist for the already mentioned object B0218+357 at $z \approx 0.6847$ [72]. Comparing them with the redshifts of the rotational lines of CO, HCO^+ , and HCN molecules from Ref. [73], one can obtain the following conservative limit from Equation 16.35

$$\frac{\delta\mu}{\mu} = (-0.6 \pm 1.9) \times 10^{-6}. \quad (16.36)$$

Taking into account that the redshift $z \approx 0.68$ for the object B0218+357 corresponds to the look-back time of about 6.5 Gyr, this limit translates into the most stringent present limit 16.1 on the variation rate $\dot{\mu}/\mu$.

Q1

16.7 EXPERIMENT WITH SF_6

Here we discuss ongoing experiments on the time variation using the SF_6 molecule. We start with a recent experiment on the two-photon vibrational transition ($v = 0, J = 4$) \rightarrow ($v = 2, J = 3$) in SF_6 [47]. This is a Ramsey-type experiment with a supersonic beam of SF_6 molecules. The beam velocity $u = 400$ m/sec and the length of the interaction region $D = 1$ m correspond to a linewidth of $u/2D = 200$ Hz.

A CO_2 laser was used to drive the two-photon transition and its frequency was controlled by a Cs standard [48]. This means that the vibrational frequency ω_{vib} in SF_6 was compared with the hyperfine transition frequency ω_{hfs} in Cs. Therefore, the experiment was sensitive to the combination of the fundamental constants $F = g_{\text{nuc}}\mu^{-1/2}\alpha^{2.83}$. The measurements were in progress for 18 months, and the following result was obtained:

$$\dot{F}/F = (1.4 \pm 3.2) \times 10^{-14} \text{yr}^{-1}. \quad (16.37)$$

This limit is weaker than the most stringent limit obtained with atomic clocks. On the other hand, it constrains a different combination of the fundamental parameters. Most importantly, in atomic experiments, the parameters g_n and μ always scale as a product $g_n\mu$, while here we have the combination $g_n\mu^{-1/2}$. That makes it possible to combine the atomic clock results [4,35,37] with the limit 16.37 to obtain the best laboratory limit on μ -variation:

$$\dot{\mu}/\mu = (3.4 \pm 6.5) \times 10^{-14} \text{ yr}^{-1}. \quad (16.38)$$

This limit is significantly weaker than the astrophysical limit 16.1, but it will likely soon be markedly improved.

16.8 NARROW CLOSE-LYING LEVELS OF DIATOMIC MOLECULES

In this section we focus on narrow, close-lying levels of varying nature in diatomic molecules. Such levels may come about due to a quasi-degeneracy of either hyperfine and rotational levels [45], or between the fine and vibrational levels within the molecular electronic ground state [49] (see Figure 16.1). The transitions between the quasi-degenerate levels correspond to microwave frequencies, which are experimentally accessible, and have narrow linewidths, typically $\sim 10^{-2}$ Hz. The sensitivity K of the relative variation can exceed 10^5 in such cases.

16.8.1 MOLECULES WITH QUASIDEGENERATE HYPERFINE AND ROTATIONAL LEVELS

Consider a diatomic molecule with a $^2\Sigma$ ground state (one unpaired electron). Examples of such molecules include LaS, LaO, LuS, LuO, and YbF [74]. The hyperfine interval Δ_{hfs} is proportional to $\alpha^2 Z F_{\text{rel}}(\alpha Z)\mu g_{\text{nuc}}$, where F_{rel} is an additional relativistic (Casimir) factor [76]. The rotational interval $\Delta_{\text{rot}} \propto \mu$ is approximately

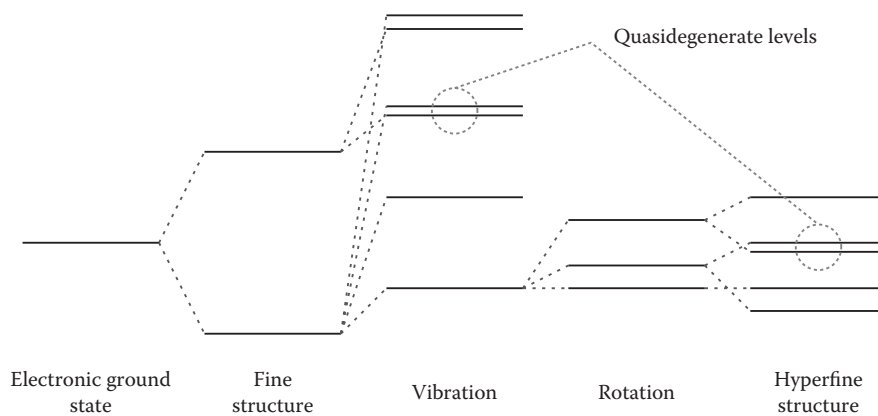


FIGURE 16.1 Energy levels within the ground electronic state of a diatomic molecule (not to scale).

independent of α . For a molecule with $\Delta_{\text{hfs}} \approx \Delta_{\text{rot}}$, the splitting ω between the hyperfine and the rotational levels depends on the following combination

$$\omega \propto \mu \left[\alpha^2 F_{\text{rel}}(\alpha Z) g_{\text{nuc}} - \text{const.} \right]. \quad (16.39)$$

The relative variation is then given by

$$\frac{\delta\omega}{\omega} \approx \frac{\Delta_{\text{hfs}}}{\omega} \left[(2 + K) \frac{\delta\alpha}{\alpha} + \frac{\delta g_{\text{nuc}}}{g_{\text{nuc}}} \right] + \frac{\delta\mu}{\mu}, \quad (16.40)$$

where the factor K comes from the variation of $F_{\text{rel}}(\alpha Z)$; for $Z \sim 50$, $K \approx 1$. As long as $\Delta_{\text{hfs}}/\omega \gg 1$, we can neglect the last term in Equation 16.40.

The data on the hyperfine structure of diatomics are hard to come by and usually not very accurate. Using the data from Ref. [74], one can find that $\omega = (0.002 \pm 0.01) \text{ cm}^{-1}$ for $^{139}\text{La}^{32}\text{S}$ [45]. Note that for $\omega = 0.002 \text{ cm}^{-1}$, the relative frequency shift is

$$\frac{\delta\omega}{\omega} \approx 600 \frac{\delta\alpha}{\alpha}. \quad (16.41)$$

As new data on molecular hyperfine constants become available, it is likely that other molecular candidates with the requisite quasidegeneracy will be found.

16.8.2 MOLECULES WITH QUASIDEGENERATE FINE-STRUCTURE AND VIBRATIONAL LEVELS

The fine-structure interval ω_f increases rapidly with the nuclear charge Z :

$$\omega_f \sim Z^2 \alpha^2, \quad (16.42)$$

In contrast, the vibrational energy quantum decreases with the atomic mass

$$\omega_{\text{vib}} \sim M_r^{-1/2} \mu^{1/2}, \quad (16.43)$$

where the reduced mass for the molecular vibration is $M_r m_p$. Therefore, we obtain an equation $Z = Z(M_r, v)$ for the spectral lines at fixed Z, M_r where we can expect an approximate cancellation between the fine-structure and vibrational intervals:

$$\omega = \omega_f - v \omega_{\text{vib}} \approx 0, \quad v = 1, 2, \dots \quad (16.44)$$

Using Equations 16.42 to 16.44, it is easy to find the dependence of the transition frequency on the fundamental constants

$$\frac{\delta\omega}{\omega} = \frac{1}{\omega} \left(2\omega_f \frac{\delta\alpha}{\alpha} + \frac{v}{2} \omega_{\text{vib}} \frac{\delta\mu}{\mu} \right) \approx K \left(2 \frac{\delta\alpha}{\alpha} + \frac{1}{2} \frac{\delta\mu}{\mu} \right), \quad (16.45)$$

where the enhancement factor $K = \frac{\omega_f}{\omega}$ is due to the relative frequency shift for a given change of the fundamental constants. Large values of the factor K are experimentally

favorable, as the correspondingly large relative shifts can be more easily detected. However, large values of K do not always guarantee a more sensitive measurement. For some quasidegenerate levels, this factor may become irrelevant [42]. Thus, it is also important to consider the absolute values of the shifts and compare them with the linewidths of the transitions considered.

Because the number of different molecules is finite, we cannot expect to find a molecule with $\omega = 0$. However, for many molecules we do have $\omega/\omega_f \ll 1$ and thus $|K| \gg 1$. Moreover, an additional “fine tuning” may be achieved by isotopic substitution and the use of suitable rotational, Ω -doublet, and hyperfine components. Therefore, there are two large manifolds available, one arising from the fine structure and the other from the vibrational structure of the same or of different electronic states. If these manifolds overlap, one may select two or more transitions with different signs of ω . In this case, the expected sign of the $|\omega|$ -variation must be different (because the variation $\delta\omega$ has the same sign) and so one can eliminate some systematic errors. Such an elimination of the systematic errors was carried out by Budker and colleagues [42, 43, 75] for the transitions between the close-lying levels in two dysprosium isotopes. The signs of the energy differences between two levels belonging to different configurations were opposite for the ^{163}Dy and ^{162}Dy transitions used in that work.

In Table 16.1, we present a list of molecules reported in Ref. [74] whose ground state is split into two fine-structure levels such that Equation 16.44 is approximately fulfilled. The molecules Cl_2^+ and SiBr are of particular interest. For both molecules, the frequency ω , as defined by Equation 16.44, is on the order of 1 cm^{-1} and thus comparable to the rotational constant B . This means that ω can be further reduced by a proper choice of isotopes, the rotational quantum number J , and the hyperfine components. New measurements are needed to determine the exact values of the transition frequencies and to identify the best transitions. The required accuracy of the frequency-shift measurements is easily found: according to Equation 16.45, the expected frequency shift is

$$\delta\omega = 2\omega_f \left(\frac{\delta\alpha}{\alpha} + \frac{1}{4} \frac{\delta\mu}{\mu} \right). \quad (16.46)$$

TABLE 16.1
Diatomic Molecules with Quasidegeneracy between the
Ground-State Vibrational and Fine-Structure Excitations

Molecule	Electronic States	ω_f	ω_{vib}	K
Cl_2^+	$^2\Pi_{3/2,1/2}$	645	645.6	1600
CuS	$^2\Pi$	433.4	415	24
IrC	$^2\Delta_{5/2,3/2}$	3200	1060	160
SiBr	$^2\Pi_{1/2,3/2}$	423.1	424.3	350

Note: All frequencies are in cm^{-1} . Enhancement factor K is estimated using Equation 16.45.

Source: Data are taken from Huber, K.P. and Herzberg, G., *Constants of Diatomic Molecules*, Van Nostrand, New York, 1979.

Assuming $\delta\alpha/\alpha \sim 10^{-15}$ and $\omega_f \sim 500 \text{ cm}^{-1}$, we obtain $\delta\omega \sim 10^{-12} \text{ cm}^{-1} \sim 3 \times 10^{-2} \text{ Hz}$. In order to obtain a similar sensitivity from a comparison of the hyperfine transition frequencies of Cs or Rb, one would have to measure the shifts with an accuracy of $\sim 10^{-5} \text{ Hz}$.

16.8.3 THE MOLECULAR ION HfF^+

The list of molecules in Table 16.1 is incomplete due to a lack of data in Ref. [74]. Let us briefly discuss one interesting case, which has been recently brought to our attention. The HfF^+ ion and similar ions are being considered by Cornell and colleagues as candidates for a search for the EDM of the electron [77,78]. The ions are to be trapped in a quadrupole radio-frequency trap, to achieve long coherence times. A similar experimental setup can be used to study a possible time variation of the fundamental constants. A recent calculation by Petrov and colleagues [79] suggests that the ground state of HfF^+ is a $^1\Sigma^+$ state and that the first excited state, $^3\Delta_1$, lies only 1633 cm^{-1} higher in energy. The calculated vibrational frequencies for these two states are 790 and 746 cm^{-1} , respectively. For these parameters the vibrational level $v = 3$ of the ground state is separated by only 10 cm^{-1} from the $v = 1$ level of the $^3\Delta_1$ state. Thus, instead of Equation 16.44, we now have

$$\omega = \omega_{\text{el}} + \frac{3}{2}\omega_{\text{vib}}^{(1)} - \frac{7}{2}\omega_{\text{vib}}^{(0)} \approx 0, \quad (16.47)$$

where the superscripts 0 and 1 correspond to the ground and excited electronic states, respectively. The electronic transition with the frequency ω_{el} is not a fine-structure transition, and so Equation 16.42 is not applicable. Instead, by analogy with Equation 16.6, we can write

$$\omega_{\text{el}} = \omega_{\text{el},0} + qx, \quad x = \alpha^2/\alpha_0^2 - 1. \quad (16.48)$$

In order to calculate the q -factor for the HfF^+ ion, one needs to perform a relativistic molecular calculation for several values of α , which has not yet been done. However, we can make an order-of-magnitude estimate using an atomic calculation for the Yb^+ ion [24]. According to Ref. [79], the $^1\Sigma_1^+ - ^3\Delta_1$ transition is the same, in the first approximation, as the $6s-5d$ transition of the hafnium ion. It is well known that valence s - and d -orbitals of heavy atoms have a different dependence on α : while the binding energy of the s -electrons increases with α , the binding energy of the d -electrons decreases [22–25]. For the same transition of the Yb^+ ion, Ref. [24] gives $q_{sd} = 10,000 \text{ cm}^{-1}$. Using this value as an estimate, we can write by analogy with Equation 16.45:

$$\frac{\delta\omega}{\omega} \approx \left(\frac{2q}{\omega} \frac{\delta\alpha}{\alpha} + \frac{\omega_{\text{el}}}{2\omega} \frac{\delta\mu}{\mu} \right) \approx \left(2000 \frac{\delta\alpha}{\alpha} + 80 \frac{\delta\mu}{\mu} \right) \quad (16.49)$$

$$\delta\omega \approx 20,000 \text{ cm}^{-1} (\delta\alpha/\alpha + 0.04\delta\mu/\mu). \quad (16.50)$$

Assuming $\delta\alpha/\alpha \sim 10^{-15}$ we obtain $\delta\omega \sim 0.6 \text{ Hz}$.

16.8.4 ESTIMATE OF THE NATURAL WIDTHS OF THE QUASIDEGENERATE STATES

As pointed out above, it is important to compare the frequency shifts caused by a possible time variation of the fundamental constants with the linewidths of the corresponding transitions. Let us first estimate the natural width Γ_v of the vibrational level v :

$$\Gamma_v = \frac{4\omega_{\text{vib}}^3}{3\hbar c^3} |\langle v | \hat{D} | v-1 \rangle|^2. \quad (16.51)$$

In order to estimate the magnitude of the dipole matrix element, we can write

$$\hat{D} = \left. \frac{\partial D(R)}{\partial R} \right|_{R=R_0} (R - R_0) \sim \frac{D_0}{R_0} (R - R_0), \quad (16.52)$$

where D_0 is the dipole moment of the molecule at the equilibrium internuclear distance R_0 . Using the result for the harmonic oscillator, $\langle v | x | v-1 \rangle = (\hbar v / 2m\omega)^{1/2}$, we obtain

$$\Gamma_v = \frac{2\omega_{\text{vib}}^2 D_0^2 v}{3c^3 M_r m_p R_0^2}. \quad (16.53)$$

For the homonuclear molecule Cl_2^+ , $D_0 = 0$ and Γ_v vanishes. For the SiBr molecule, Equation 16.53 gives $\Gamma_1 \sim 10^{-2}$ Hz, where we assume $D_0^2/R_0^2 \sim 0.1 e^2$.

Let us now estimate the width Γ_f of the upper state ${}^2\Pi_{3/2}$ of the fine-structure doublet, ${}^2\Pi_{1/2,3/2}$. By analogy with Equation 16.51 we can write

$$\Gamma_f = \frac{4\omega_f^3}{3\hbar c^3} \left| \langle {}^2\Pi_{3/2} | D_1 | {}^2\Pi_{1/2} \rangle \right|^2. \quad (16.54)$$

This dipole matrix element is written in the molecular frame and includes the summation over all final rotational states. It corresponds to a spin flip and must be zero in the nonrelativistic approximation. The spin-orbit interaction mixes the ${}^2\Pi_{1/2}$ and ${}^2\Sigma_{1/2}$ states

$$\left| {}^2\Pi_{1/2} \right\rangle \rightarrow \left| {}^2\Pi_{1/2} \right\rangle + \xi \left| {}^2\Sigma_{1/2} \right\rangle, \quad (16.55)$$

and the matrix element in Equation 16.54 becomes [80]

$$\left\langle {}^2\Pi_{3/2} | D_1 | {}^2\Pi_{1/2} \right\rangle \approx \xi \langle \Pi | D_1 | \Sigma \rangle \sim \frac{\alpha^2 Z^2}{10(E_\Pi - E_\Sigma)}, \quad (16.56)$$

where E_Σ is the energy of the lowest Σ -state. Substituting Equation 16.56 into Equation 16.54 and using energies from Ref. [74], we obtain the following estimate for the SiBr molecule

$$\Gamma_f \sim 10^{-2} \text{ Hz}. \quad (16.57)$$

Here we assumed that the unpaired electron in the SiBr molecule is predominantly located on Si ($Z = 14$) rather than on Br ($Z = 35$). As a result, the fine-structure splitting in SiBr comes out smaller than that of Cl_2^+ , where $Z = 17$ (see Table 16.1). For the homonuclear molecule Cl_2^+ the matrix element in Equation 16.54 vanishes due to the $g \leftrightarrow u$ selection rule. We conclude that the natural widths of the molecular levels considered here are on the order of 10^{-2} Hz or less. For comparison, the natural width of the level $^2D_{5/2}$ of Hg^+ ion (used in an atomic clock experiment [4]) is 12 Hz. The lifetime of levels as narrow as 10^{-2} Hz may depend on the interaction with the black-body radiation [81]. According to Ref. [81], the lifetimes of the rovibrational levels of polar molecules at room temperature vary from 1 to 100 sec. Again, we can expect that lifetimes for homonuclear molecules are significantly longer. This makes them very promising candidates for superhigh precision experiments [82].

16.9 PROPOSED EXPERIMENTS WITH Cs_2 AND Sr_2

In this section we discuss two recently proposed experiments with cold diatomic molecules, one with Cs_2 at Yale [44,83] and one with Sr_2 at JILA [84].

The Yale experiment is based on the idea, described in Ref. [44] of matching the electronic energy with a large number of vibrational quanta. The difference compared with the case described by Equations 16.42 to 16.44 is that here the electronic transition is between a $^1\Sigma_g^+$ ground state and a $^3\Sigma_u^+$ excited state and thus, in the first approximation, its frequency is independent of α . The energy of this transition is about 3300 cm^{-1} and the number of the vibrational quanta needed to match it is on the order of 100 (see Figure 16.2). For the vibrational quantum number $v \sim 100$, the

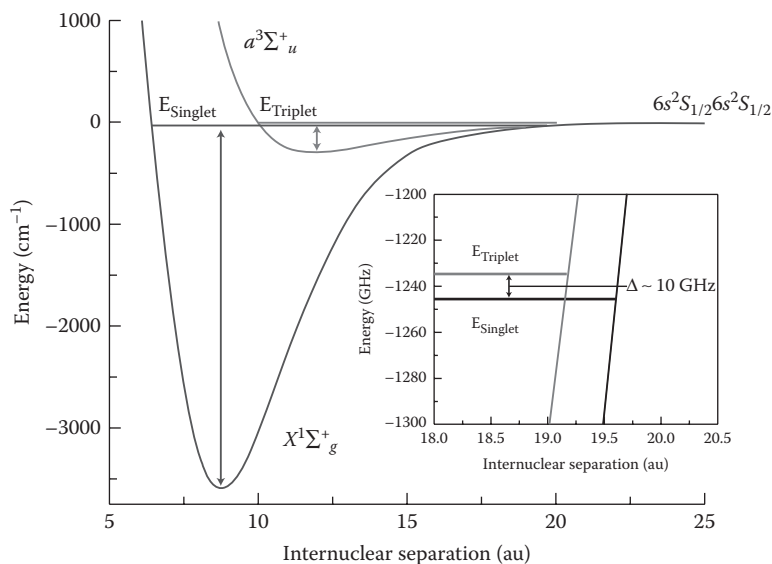


FIGURE 16.2 Levels $^3\Sigma_u^+$ and $^1\Sigma_g^+$ in Cs_2 molecule. (From Sainis, S, Ph.D. Thesis, Yale University, 2005.)

density of the levels is high due to the anharmonicity of the potential and hence it is possible to find two nearby levels belonging to two different potential energy curves. This leads to an enhanced sensitivity to variation of μ (cf. Equation 16.44). Cold Cs_2 molecules in a particular quantum state can be produced by the photoassociation of Cs atoms in a trap.

Let us estimate the sensitivity of this proposed experiment to the variation of α and μ . The electronic transition energy can be determined from Equation 16.48. If we neglect the anharmonicity, we can write the transition frequency between the closely spaced vibrational levels of the two electronic terms as

$$\omega = \omega_{\text{el},0} + qx + \left(v_2 + \frac{1}{2}\right) \omega_{\text{vib},2} - \left(v_1 + \frac{1}{2}\right) \omega_{\text{vib},1}, \quad (16.58)$$

where $v_2 \ll v_1$. The dependence of this frequency on α and μ is given by

$$\delta\omega \approx 2q \frac{\delta\alpha}{\alpha} - \frac{\omega_{\text{el},0}}{2} \frac{\delta\mu}{\mu}, \quad (16.59)$$

where we made use of the inequality $\omega \ll \omega_{\text{el},0}$. For the ground state of atomic Cs, the q -factor is about 1100 cm^{-1} , which is close to $\frac{1}{4}\alpha^2 Z^2 \varepsilon_{6s}$, where ε_{6s} is the ground-state binding energy. If we assume that the same relation holds for the electronic transition in the molecule, we obtain $|q| \sim \frac{1}{4}\alpha^2 Z^2 \omega_{\text{el},0} \sim 120 \text{ cm}^{-1}$. Using this rough estimate and Equation 16.59 we have

$$\delta\omega \approx -240 \frac{\delta\alpha}{\alpha} - 1600 \frac{\delta\mu}{\mu}, \quad (16.60)$$

where we assumed that the relativistic corrections reduce the dissociation energy of the molecule, as a result of which q is negative. This estimate shows that the experiment with Cs_2 is mostly sensitive to the variation of μ .

As noted above, for high vibrational states, the potential is highly anharmonic. This significantly decreases the sensitivity as estimated from Equation 16.60. This can be seen either from the WKB approximation [44,83], or from an analytic solution for the Morse potential [84]. The quantization condition for the vibrational spectrum in the WKB approximation

$$\int_{R_1}^{R_2} \sqrt{2M(U(r) - E_n)} dr = \left(v + \frac{1}{2}\right) \pi \quad (16.61)$$

yields, by differentiation with respect to μ , the following result

$$\delta E_v = \frac{v + \frac{1}{2}}{2\rho(E_v)} \frac{\delta\mu}{\mu}, \quad (16.62)$$

where $\rho(E_v) \equiv (\partial E_v / \partial v)^{-1} \approx (E_v - E_{v-1})^{-1}$ is the level density. For the harmonic part of the potential, ρ is constant, and the shift δE_v increases linearly with v , but for vibrational states near the dissociation limit, the level density $\rho(E) \rightarrow \infty$ and

$\delta E_v \rightarrow 0$. Consequently, the maximum sensitivity of about 1000 cm^{-1} is reached at $v \approx 60$, and rapidly drops for higher v . The Yale group has found a conveniently close vibrational level of the upper ${}^3\Sigma_u$ state with $v = 138$. The sensitivity for this level is, however, only about 200 cm^{-1} [83]. There are still good prospects for finding other close-lying levels with smaller v , for which the sensitivity may be several times higher.

The sensitivity as given by Equation 16.60 for the variation of α is in addition reduced by the anharmonicity of the potential. For the highest vibrational levels of the electronic ground state as well as for all levels of the upper (weakly bound) electronic state, the separation between the nuclei is large, $R \gtrsim 12 \text{ au}$ (see Figure 16.2). Thus, both electronic wavefunctions are close to either symmetric (for ${}^1\Sigma_g^+$) or antisymmetric combination (for ${}^3\Sigma_u^+$) of the atomic $6s$ functions,

$$\Psi_{g,u}(r_1, r_2) \approx \frac{1}{\sqrt{2}} \left(6s^a(r_1)6s^b(r_2) \pm 6s^b(r_1)6s^a(r_2) \right). \quad (16.63)$$

As a result, all the relativistic corrections are (almost) the same for both electronic states.

The deleterious effect of the anharmonicity on the sensitivity to the variation of μ and α can be also obtained from the analysis of the Morse potential. Its eigenvalues are given by

$$E_v = \omega_0 \left(v + \frac{1}{2} \right) - \frac{\omega_0^2 \left(v + \frac{1}{2} \right)^2}{4d} - d, \quad (16.64)$$

with $\omega_0 = 2\pi a\sqrt{2d/M}$ and d the dissociation energy. The last eigenvalue E_N is found from the conditions $E_{N+1} \leq E_N$ and $E_{N-1} \leq E_N$. Clearly, E_N is very close to zero and is independent of μ and α and thus of their variation.

We conclude that the highest absolute sensitivity can be expected for vibrational levels in the middle of the potential energy curve. However, in this part of the spectrum, there are no close-lying vibrational levels pertaining to different electronic states that would allow to maximize the relative sensitivity $\delta\omega/\omega$. An option would be to make use of a frequency comb to perform a high-accuracy measurement. This idea has been proposed by Zelevinsky and colleagues [84], who suggested using an optical lattice to trap Sr_2 molecules formed in one of the uppermost vibrational levels of the ground electronic state by photoassociation (see Figure 16.3). As we saw above, this level is not sensitive to the variation of μ . In the next step, a Raman transition is proposed to create molecules in one of the most sensitive levels in the middle of the potential well. In this way, it might be feasible to achieve the highest possible absolute sensitivity for a given molecule. Unfortunately, the dissociation energy of Sr_2 is only about 1000 cm^{-1} , which is three times smaller than that of Cs_2 . Consequently, the highest sensitivity for the Sr_2 molecule occurs at about 270 cm^{-1} , that is, only slightly higher than for the $v = 138$ level in Cs_2 . Therefore, it may be useful to try to apply this scheme to another molecule with a larger dissociation energy. Finally, we note that the sensitivity to α -variation in the Sr_2 experiment is additionally reduced by a factor $(38/55)^2 \approx 1/2$ because of the smaller Z .

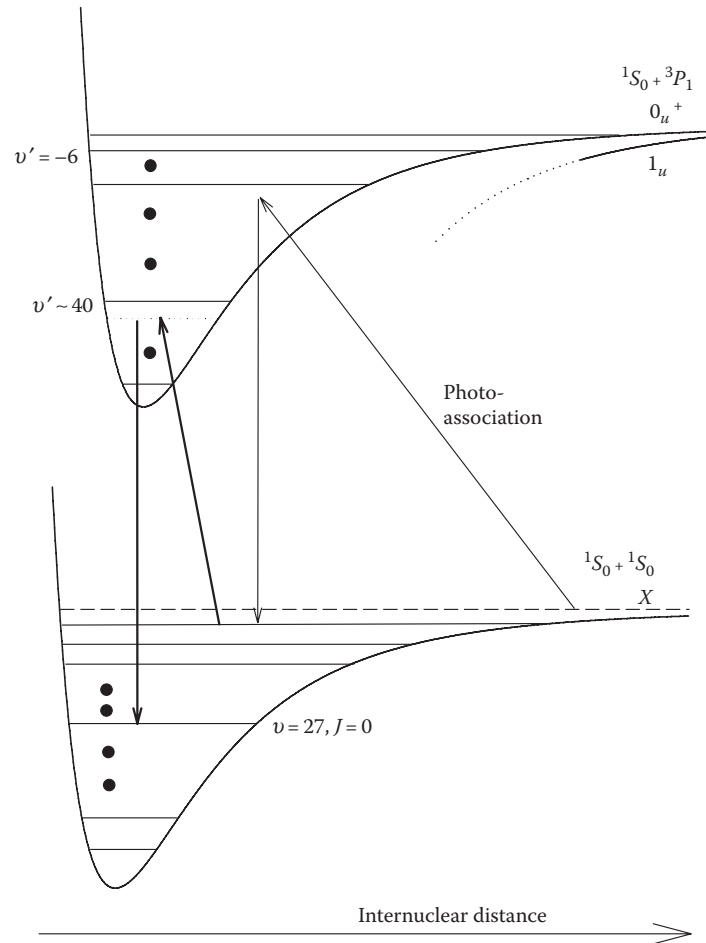


FIGURE 16.3 The scheme for Raman spectroscopy of Sr_2 ground-state vibrational spacings. A two-color photoassociation pulse prepares molecules in the $v = v_{\text{max}} - 2$ vibrational state (labeled in the figure as $v = -3$). Subsequently, a Raman pulse couples the $v = -3$ and $v = 27$ states via the $v' \approx 40$ level of the excited 0_u^+ state. (From Zelevinsky, T. et al., *Phys. Rev. Lett.*, 100, 043201, 2008. With permission.)

16.10 EXPERIMENTS WITH HYDROGEN MOLECULAR IONS H_2^+ AND HD^+

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The hydrogen molecular ion is very attractive for fundamental studies because of its simplicity and the feasibility of its cooling and trapping (compare with Chapter X by Schiller). The use of H_2^+ and HD^+ ions for the study of the time variation of the electron-to-proton and the proton-to-deuteron mass ratios $\mu = m_e/m_p$ and m_p/m_d has been suggested in Refs [86] and [87]. Because of the anharmonicity of the ion's potential, the ratio of the two vibrational transitions with very different vibrational quantum numbers is μ -dependent [86]. As a result, there is no enhancement of the

relative sensitivity here, but the lines are very narrow and high-precision measurements are possible using frequency combs.

Recently, HD^+ ions have been cooled to 50 mK and trapped in a linear radio-frequency trap [88]. This made it possible to measure the rovibrational transition $v, N = 0, 2 \rightarrow v', N' = 4, 3$ with an absolute accuracy of 0.5 MHz. By making use of the sensitivity coefficient from Ref. [87], one can see that this accuracy translates into a 5×10^{-9} (5 ppb) accuracy for μ . Note that modern molecular theory of HD^+ has achieved a comparable accuracy [89]. Thus, a direct comparison between theory and experiment allows the determination of the absolute value of μ to 5 ppb.

16.11 CONCLUSIONS

Astrophysical observations of the spectra of diatomic and polyatomic molecules can reveal a possible variation of the electron-to-proton mass ratio μ on a timescale from 6 to 12 billion years. However, the astrophysical results obtained so far are inconclusive; see Equations 16.15, 16.19, and 16.36. Much of the same can be said about the astrophysical search for an α -variation. In principle, the astrophysical observations can be explained by a complex evolution of μ and α in space and time. Likely, there are also systematic errors in the measurements that have not been fully understood. Therefore, it is imperative to complement the astrophysical studies with laboratory measurements of the present-day variation of these constants. This work is under way in a number of laboratories. Most use atomic frequency standards and atomic clocks. In this chapter we discussed several recent ideas and proposals on how to increase the sensitivity of the laboratory tests by using molecules instead of atoms.

The only molecular experiment [47,48] capable of putting a limit on the time variation of the fundamental constants, Equation 16.37, has made use of a supersonic beam of SF_6 . Although this experiment is less sensitive than the best atomic experiments, it probes a different combination of the fundamental constants. In combination with the results of the atomic-clock experiments, [4,35,37], it provides the most stringent laboratory limit, Equation 16.38, on the time variation of μ . The linewidth in this experiment, $\Gamma \approx 200$ Hz, was determined by the time of flight through a 1 m Ramsey interferometer. A similarly broad linewidth has been a liability in an ND_3 experiment [46]. The use of cold molecules holds the promise of reducing the linewidth by several orders of magnitude and hence to dramatically enhance the sensitivity of the molecular experiments.

We have seen that, for diatomic radicals, such as Cl_2^+ and SiBr , there are narrow levels belonging to different electronic states that are separated by $\lesssim 1 \text{ cm}^{-1}$, while the natural widths of these levels are on the order of 10^{-2} Hz. This comes close to what is needed in order to reach the sensitivity of $\delta\alpha/\alpha \sim 10^{-15}$, similar to that achieved in the best atomic laboratory tests. In the high-precision frequency measurements, the accuracy is typically better than the linewidth by a few orders of magnitude. In order to be able to benefit from such narrow lines, the molecules need to be cooled. In this respect, the Cl_2^+ ion seems particularly promising.

An even higher sensitivity to the temporal variation of α is found in HfF^+ and similar molecular ions, which are being considered as candidates for the search for the electron EDM at JILA [77–79]. The transition amplitude between the $^3\Delta_1$ and

$^1\Sigma_0$ states of HfF^+ is suppressed. The transition width is larger than those of Cl_2^+ and SiBr because of the larger value of Z and the higher frequency ω_f . In Ref. [79], the width of the $^3\Delta_1$ state was estimated to be about 2 Hz. This width is of the same order of magnitude as the expected frequency shift for $\delta\alpha/\alpha \sim 10^{-15}$. At present, not much is known about these molecular ions. More spectroscopic and theoretical data are required in order to estimate the sensitivity to α -variation reliably. We hope that this monograph will further stimulate such studies. An added benefit is the possibility to measure the electron EDM and the α -variation on the same molecule and with a similar experimental setup.

A preliminary spectroscopic experiment with the Cs_2 molecule has been recently performed at Yale [83]. The electronic transition between the $^3\Sigma_u^+$ and $^1\Sigma_g^-$ states of Cs_2 is independent, in the first approximation, of α . On the other hand, the sensitivity to the μ -variation may be enhanced because of the large number of vibrational quanta needed to match the electronic transition. However, the anharmonicity of the potential suppresses this enhancement for very high vibrational levels near the dissociation limit. As a result, the sensitivity to the variation of μ for the $v = 138$ level is about the same as in Equation 16.46. It is possible that there are other close-lying levels with smaller vibrational quantum number that, consequently, allow for a higher sensitivity. Even if such levels are not found, the experiment with the $v = 138$ level may improve the current limit on the time variation of μ by several orders of magnitude.

An experiment with the Sr_2 molecule has recently been proposed at JILA [84]. This experiment has a similar sensitivity to the time variation of μ as the experiment with Cs_2 ; these experiments are complementary to the experiments with the molecular radicals, which are mostly sensitive to the time variation of α [49].

Finally, we have shown that the inversion spectra of polyatomic molecules, such as NH_3 and ND_3 , are potentially even more sensitive to the time variation of μ . This has already been used in astrophysical measurements to put the most stringent limit, Equation 16.36, on the time variation of μ on a cosmological timescale. The corresponding laboratory experiments would require slow molecules, and molecular fountains and traps hold the promise of providing them [46].

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