Tests of time independence of the electron and nuclear masses with ultracold molecules

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We propose to use laser spectroscopy of ultracold molecules to establish improved limits on the time independence of electron-to-nuclear and nuclear-nuclear mass ratios by comparing, via an optical frequency comb, the frequencies of suitable sets of transitions in the ground electronic state. Hydrogen molecular ions trapped in a radiofrequency trap, sympathetically cooled by atomic ions, are identified as an accessible system. We show that the dipole-allowed rovibrational transition frequencies of HD^+ are suitable probes for a time dependence of m_e/m_p or m_p/m_d. Separate bounds on the time independence of these constants can be obtained from a comparison of HD^+ and H_2^+ transitions frequencies. Spectroscopy of single molecular ions via a quantum jump method is proposed as an approach toward ultrahigh precision.

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I. INTRODUCTION

The difficulty in developing a theory unifying the standard model with general relativity is motivating significant experimental efforts to test the Einstein equivalence principle (EEP), the foundation of metric theories of gravity [1]. One approach for testing the EEP consists in testing the principle local position invariance, which states that the fundamental constants of nature, such as the fine structure constant α, the mass ratios of the elementary particles, etc. are independent of time and position. Tests of the time independence of the fundamental constants can be performed with high precision both by laboratory experiments and astronomical observations [2,3]. The search for a time dependence of the constants has also acquired significance after the discovery of dark energy. Cosmological fields proposed to explain its existence could couple to matter and thereby induce changes of the coupling constants and particle masses over cosmological times [4]. Tests of time independence of the fundamental constants are considered to be complementary to tests of deviations from the weak equivalence principle (universality of free fall), although in some models the time independence violation correlates with violation of free fall universality [3,5]. For an overview of theoretical ideas, see [3].

Recent astronomical observations claim to have detected a variation of α on the order of a few parts in 10^5 over cosmological time scales [6]. These results are in contradiction with others [7]; improved observations are currently being pursued to resolve this issue.

In the laboratory, experiments with significantly improved precision have become possible by using atomic clocks based on ultracold atoms and atomic ions together with new methods of precise comparison of optical and radio frequencies. This has led to an improvement of more than an order of magnitude of the most stringent laboratory limits over those obtained with more traditional atomic beam microwave or Doppler-free laser spectroscopy. In particular, a recent high-precision test using hyperfine transitions of ultracold atoms yielded a test of the time independence of $g_{Cs}/g_{Rb}\alpha^{0.44}$, where g denotes a nuclear gyromagnetic ratio, at the level of 7×10^{-16}/yr [8]. A comparison of an optical transition in Hg^+ and the hyperfine frequency of Cs gave a limit of 7×10^{-15}/yr for the combination $g_{Cs}\alpha^6 m_e/m_p$ [9]. It should be noted that until recently precise laboratory limits such as this concerned *combinations* of fundamental constants. Methods that permit tests which are sensitive to a single constant are possible. For example, tests of α can be implemented by a comparison of optical transition frequencies of different atoms or of different transitions of the same atomic species where relativistic or spin-orbit effects are relevant [10]. This method has also been applied to quasar spectra, e.g., in Ref. [6]. A very recent laboratory measurement has now established a direct upper limit for α variability at the level of 2×10^{-15}/yr [11]. With the availability of such accurate laboratory results for $d\alpha/dt$, the hyperfine clock comparison results will therefore yield limits for the time independence of ratios of g factors.

Among the fundamental constants, investigations of the ratios of masses of fundamental particles appear worthy of increased experimental efforts because of several reasons: (i) theoretical analyses that find that the fractional time rate of change of m_e/m_p could be significantly larger than that of α [12,13]; (ii) the ratios of nuclear masses have not been tested at levels better than 10^{-12}/yr [14]. Tests of the ratios of nuclear masses are also tests of time independence of QCD interaction through the mass scale Λ_{QCD}, and are complementary to tests of the time independence of the g factors of nuclei: (iii) model-independent laboratory tests of m_e/m_p are desirable: the three comparisions mentioned in the previous paragraph can only be used to set limits to the individual constant m_e/m_p if a theoretical model of the nuclear g factors is assumed [15].

Sensitive tests of the constancy of mass ratios can be performed using molecules. In laboratory experiments early measurements performed with Doppler-free spectroscopy on room-temperature molecular gases included a comparison of a midinfrared vibrational transition frequency of methane (CH_4) and the hyperfine frequency of Cs that led to an upper

limit on the order 10^{-12}/yr for the time dependence of the combination $g_{Cs}\alpha^2\sqrt{m_e/m_p}$ [16]. A measurement of the far-infrared vibrational transition of the molecule OsO_4 led to the limit 2×10^{-13}/yr for the same combination [17]. In stating these limits, it was assumed that the ratios of nuclear masses are constant.

In astronomical tests, the time-dependence of the single constant m_e/m_p was probed by comparing various vibrational energies of neutral H_2 molecules in interstellar clouds with present-day laboratory values [18]. An upper limit for the time drift of the order 40 ppm was set for redshifts $z\simeq3$ (12 Gyr ago) [19], recently improved to 25 ppm [20]. A recent study showed that the measurement of (microwave) transition frequencies between Λ-doubled levels of the *same* molecular species is sensitive to both α and m_e/m_p. A maximum time drift of 10 ppm and 7 ppm was deduced for m_e/m_p and α, respectively, at a redshift $z\simeq0.7$ (6.4 Gyr ago) [21]. The time dependence of nuclear mass ratios and of g_p was assumed to vanish in this analysis. In the future, the detection of additional suitable transitions may allow one to set limits for both m_e/m_p and α without the assumption of constant g_p.

In this paper, we propose methods for laboratory tests of the time independence of mass ratios, that have the potential to set very stringent limits, at the 10^{-15} level. The methods are based on vibrational laser spectroscopy of ultracold molecules and are applicable to a large variety of molecules. A particularly advantageous application is to molecular ions. We consider explicitly molecular hydrogen ions, which have been recently trapped and cooled [22].

II. GENERAL ASPECTS

In the following, we consider diatomic molecules for simplicity.

As is well known, for molecules where a nonrelativistic treatment of electron motion is appropriate, the Born-Oppenheimer approximation shows that the vibrational quanta have an energy on the order of $\sqrt{m_e/\mu}E_R$, where E_R is the Rydberg energy and μ is the reduced nuclear mass, while rotational quanta have an energy on the order of $(m_e/\mu)E_R$. The ratio of a rotational and a vibrational transition frequency is thus proportional to $\sqrt{m_e/\mu}$ and allows a time independence test [see approaches (i,A) and (ii) below].

However, the vibrational quanta follow the $\sqrt{m_e/\mu}$ scaling only for the lowest-lying vibrational states, for which the nuclear potential is close to parabolic. As vibrational states approach the dissociation limit, the energy difference between two adjacent levels shows a significantly different dependence on m_e/μ. Therefore a time independence test of this quantity can be peformed by comparing different vibrational transition frequencies [see case (i,B) below] of a single molecular species.

Based on these observations, we can therefore consider the following approaches.

(i) Comparison of frequencies of two transitions of a single homonuclear molecular species X_2. This allows us to set limits on the time dependence of the ratio of electron-to-nuclear mass m_e/m_X. Examples are neutral diatomics (e.g., Rb_2, Cs_2) and molecular ions, e.g., H_2^+, D_2^+, T_2^+. The two transitions can be one vibrational and one rotational (case A) or two vibrational (case B).

(ii) Comparison of frequencies of two transitions of a single heteronuclear molecular species XY. Excluding the unlikely case of a cancellation, this allows us to test for the time dependence of both m_e/m_X and the ratio of nuclear masses m_X/m_Y, but not to set individual limits.

(iii) Comparison of transition frequencies of different molecular species, e.g., between X_2 and Y_2 or between X_2 and XY, allows obtaining limits on the time dependence of the ratio of nuclear masses m_X/m_Y. Several nuclear mass ratios can be tested by including at least as many molecular species in the comparison. An example is the set HD^+, DT^+, and HT^+, which allows us to test m_e/m_p, m_p/m_d, and m_p/m_t.

(iv) Because of (small) nonadiabtic contributions of the molecular energies, a single heteronuclear diatomic molecule species XY allows us to set simultaneous limits for both the electron-to-nuclear mass ratio and the nuclear-to-nuclear mass ratio m_X/m_Y, by a choice of at least three suitable transitions.

As a general statement we emphasize that in the field of time independence tests, consistency checks are crucial; therefore one should, if possible, perform comparisons of as many transitions in as many species as possible.

In general, we need to consider the normalized sensitivities s_k^j,

$$\frac{\eta^j}{\Delta E_k}\frac{\partial \Delta E_k}{\partial \eta^j} \equiv s_k^j, \tag{1}$$

where η^j are all independent mass ratios occurring in a particular molecular species (e.g., m_e/m_X, m_X/m_Y, etc.) and ΔE_k is the energy of transition k.

If we consider the transition pairs within a single molecular species, e.g., between levels A and B (transition energy $\Delta E_{AB}=E_A-E_B$), and between levels C and D ($\Delta E_{CD}=E_D-E_C$), the relevant normalized time dependence is

$$\frac{d\ln\left(\frac{\Delta E_{AB}}{\Delta E_{CD}}\right)}{dt} = \sum_j (s_{AB}^j - s_{CD}^j)\left(\frac{d\ln\eta^j}{dt}\right). \tag{2}$$

To set limits to all individual time drifts $d\eta^j/dt$, an equal number of transition pair frequencies must be measured over the course of time. The corresponding inversion of the set of equations (2) is possible if they are linearly independent. This can generally be ensured, since there are many more vibrational levels than differing nuclei in a molecule.

III. HYDROGEN MOLECULAR IONS

The hydrogen molecular ions are useful candidates for tests of the time independence of m_e/m_p because they are also being studied with the goal of measuring the value of m_e/m_p [23,24]. They are special among all molecules in that they are three-body systems. Their relative simplicity make them amenable to an *ab inito* treatment so that quantities of interest can be calculated with high precision.

The Schrödinger equation for such systems can be solved with essentially arbitrary precision ($\sim10^{-14}$–10^{-18} a.u.)

[23,25–27]. The required relativistic and QED corrections have so far been worked out to an accuracy of the order 10^{-8} a.u. [28]. Currently these corrections are being computed to higher accuracy ($\sim 10^{-10}$–10^{-11} a.u.) [29].

In what follows we will use the molecular notation to describe a particular state A, namely $A=(\nu,N)$, where ν is the vibrational quantum number and N is the total orbital angular momentum.

The dependence of the $N=0$, 1-state energies of H_2^+ on m_p/m_e and of the $N=0$, 1-state energies of D_2^+ on m_d/m_e has been calculated by Hilico *et al.* [23].

As an example, we apply Eq. (2) to the homonuclear H_2^+, where the only relevant mass ratio is $\eta^{ep}\equiv m_e/m_p$. For the lowest rotational transition $\{A\rightarrow B:(0,0)\rightarrow(0,1)\}$ we have $s_{AB}^{ep}\simeq 1$ and for the overtone transition $\{C\rightarrow D:(0,0)\rightarrow(2,0)\}$ (reachable by a two-photon excitation) we have $s_{CD}^{ep}=0.45495$ [23]. Thus

$$\frac{d\ln\left(\frac{\Delta E_{AB}}{\Delta E_{CD}}\right)}{dt}=0.545\frac{d\ln(m_e/m_p)}{dt}. \tag{3}$$

Comparing instead the $C\rightarrow D$ transition with the overtone transition $\{E\rightarrow F:(2,0)\rightarrow(4,0),s_{EF}^{ep}=0.403\}$ or $\{G\rightarrow H:(13,0)\rightarrow(15,0),s_{GH}^{ep}=-1.00\}$, we have

$$\frac{d\ln\left(\frac{\Delta E_{CD}}{\Delta E_{EF}}\right)}{dt}=0.052\frac{d\ln(m_e/m_p)}{dt}, \tag{4}$$

$$\frac{d\ln\left(\frac{\Delta E_{CD}}{\Delta E_{GH}}\right)}{dt}=1.45\frac{d\ln(m_e/m_p)}{dt}. \tag{5}$$

The sensitivity of the second transition pair considered is substantially larger because the anharmonicity of the potential is relevant for the high-lying vibrational levels G and H.

We now turn to the heteronuclear ion HD^+. This ion is of interest because it is the simplest one that allows us to test both $d(m_e/m_p)/dt$ and $d(m_p/m_d)/dt$. On the experimental side, compared to the alternative of the homonuclear H_2^+ and D_2^+, spectroscopy on HD^+ is likely to be easier since its vibrational transitions are dipole allowed.

For the purpose of calculating the sensitivities required in Eq. (2) it is sufficient to solve the (nonadiabatic) Schrödinger equation omitting relativistic, hyperfine, and QED effects.

To be general, we consider a three-body system with nuclear masses m_d, m_p, corresponding charges z_d, z_p, and a single electron (mass m_e, charge z_e). In atomic units (1 a.u. $=2E_R, m_e=1$) the nonrelativistic Hamiltonian of this three-body system is (in the center of mass frame)

$$H_0=-\frac{1}{2}(1+\eta^{pd})\eta^{ep}\nabla_{\mathbf{r}_1}^2-\frac{1}{2}(1+\eta^{pd}\eta^{ep})\nabla_{\mathbf{r}_2}^2-\eta^{pd}\eta^{ep}\nabla_{\mathbf{r}_1}\nabla_{\mathbf{r}_2}+V_C, \tag{6}$$

where $\eta^{pd}=m_p/m_d$ is the proton-deuteron mass ration, $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of proton and electron with respect to the deuteron, and V_C is the Coulomb interaction potential. The sensitivity of the energy of any state of the system to changes of an arbitrary parameter ξ may be calculated as follows. The Schrödinger equation reads

$$H_0(\xi)|\psi(\xi)\rangle=E(\xi)|\psi(\xi)\rangle, \tag{7}$$

where E is the internal energy in a.u. Therefore,

$$\frac{\partial\langle\psi(\xi)|H_0(\xi)-E(\xi)|\psi(\xi)\rangle}{\partial\xi}\equiv 0. \tag{8}$$

The left-hand side may be evaluated explicitly as

$$\left\langle\psi(\xi)\left|\frac{\partial H_0(\xi)}{\partial\xi}\right|\psi(\xi)\right\rangle-\frac{\partial E(\xi)}{\partial\xi}+2\left\langle\frac{\partial\psi(\xi)}{\partial\xi}\left|H_0(\xi)-E(\xi)\right|\psi(\xi)\right\rangle. \tag{9}$$

Since the last term is zero, we have

TABLE I. Nonrelativistic energies for the HD^+ hydrogen molecular ion, in atomic units.

	$\nu=0$	$\nu=1$	$\nu=2$	
$N=0$	−0.597897968645036	−0.5891818296538696	−0.580903700369888	
$N=1$	−0.597698128231121	−0.5889911120916558	−0.580721828274966	
$N=2$	−0.597299643396469	−0.588610829494785	−0.580359195358916	
$N=3$	−0.596704882815161	−0.588043264275825	−0.579818002194323	
$N=4$	−0.595917342277359	−0.5872917844977067	−0.579101495741694	
	$\nu=3$	$\nu=4$	$\nu=10$	$\nu=18$
$N=0$	−0.573050546751956	−0.56561104231965	−0.5292336359	
$N=1$	−0.57287727729663	−0.56544616652256		−0.5025423865
$N=2$	−0.57253181053302	−0.56511745001299		
$N=3$	−0.57201626944644	−0.56462694231765		
$N=4$	−0.571333786268944	−0.563977667131535		

TABLE II. Derivatives $\eta^{ep}\partial E/\partial\eta^{ep}\times 10^2$ of nonrelativistic energies of the HD^+ hydrogen molecular ion with respect to the electron/proton mass ratio (in atomic units). v is the vibrational quantum number; N is the rotational quantum number.

	$\nu=0$	$\nu=1$	$\nu=2$	$\nu=3$	$\nu=4$	$\nu=10$	$\nu=18$
$N=0$	0.244262	0.657496	1.02799	1.35753	1.64756	2.59793	
$N=1$	0.263983	0.675865	1.04506	1.37334	1.66215		1.52417
$N=2$	0.303187	0.712375	1.07898	1.40476	1.69114		
$N=3$	0.361407	0.766581	1.12933	1.45138	1.73414		
$N=4$	0.437958	0.837828	1.19548	1.51260	1.79057		

$$\frac{\partial E(\xi)}{\partial\xi}=\left\langle\psi(\xi)\left|\frac{\partial H_0(\xi)}{\partial\xi}\right|\psi(\xi)\right\rangle. \tag{10}$$

The sensitivities of the energy to the mass ratios are easily obtained from Eq. (6) as

$$\eta^{pd}\frac{\partial E}{\partial\eta^{pd}}=\eta^{pd}\eta^{ep}\left[-\frac{1}{2}\langle\nabla^2_{\mathbf{r}_1}\rangle-\frac{1}{2}\langle\nabla^2_{\mathbf{r}_2}\rangle-\langle\nabla_{\mathbf{r}_1}\nabla_{\mathbf{r}_2}\rangle\right], \tag{11}$$

$$\eta^{ep}\frac{\partial E}{\partial\eta^{ep}}=\eta^{pd}\frac{\partial E}{\partial\eta^{pd}}-\frac{1}{2}\eta^{ep}\langle\nabla^2_{\mathbf{r}_1}\rangle. \tag{12}$$

The expectation values are computed with respect to a particular state.

The numerical calculations for HD^+ have been performed using the variational approach described in [25]. Table I gives the computed energies. The masses adopted for calculations are $m_p=1836.152701m_e$ and $m_d=3670.483014m_e$. The numbers in the Table are accurate to the last significant digit, as verified by studying convergence for each state. Increasing basis sets with $N=2000-4000$ functions have been used to ensure and check convergence. The results are in agreement with those given by Moss in [28], but extend the precision by about 5–7 orders of magnitude.

Table II lists the energy derivatives of the nonrelativistic energies with respect to the electron-to-proton mass ratio η^{ep}, while Table III gives the energy derivatives with respect to the proton-to-deuteron mass ratio η^{pd}.

Let us consider the vibrational transition $\{I\rightarrow J:(0,2)\rightarrow(3,3)\}$. The normalized sensitivities are $s^{ep}_{IJ}=0.45413$ $s^{pd}_{IJ}=0.15146$. According to Eqs. (2) and (3), a comparison of the $I\rightarrow J$ transition in HD^+ with the $C\rightarrow D$ transition in H_2^+ leads to a near-cancellation of the sensitivity to m_e/m_p,

$$\frac{d\ln\left(\frac{\Delta E_{IJ}}{\Delta E_{CD}}\right)}{dt}=-0.0008\frac{d\ln(m_e/m_p)}{dt}+0.151\frac{d\ln(m_p/m_d)}{dt}. \tag{13}$$

This frequency comparison can thus be used to test the time independence of m_p/m_d.

For transitions with higher vibrational quantum number, the normalized sensitivities differ considerably, even changing sign: for example, the $\{K\rightarrow L:(10,0)\rightarrow(18,1)\}$ transition has $s^{ep}_{KL}=-0.40229$, and $s^{pd}_{KL}=-0.13412$. For the comparison of the above two transition frequencies of HD^+ we have

$$\frac{d\ln\left(\frac{\Delta E_{IJ}}{\Delta E_{KL}}\right)}{dt}=0.856\frac{d\ln(m_e/m_p)}{dt}+0.286\frac{d\ln(m_p/m_d)}{dt}. \tag{14}$$

Thus the HD^+ molecule is a useful system to test whether any of the two constants m_e/m_p, m_p/m_d is time dependent. It is unlikely that the time dependencies are such that their effect cancels.

We now consider two frequency ratios in order to verify the possibility of setting of limits for both m_e/m_p and m_p/m_d with a single molecular species. As a concrete example, we choose the transitions $\{P\rightarrow Q:(0,0)\rightarrow(0,1)\}$, $\{R\rightarrow S:(4,1)\rightarrow(10,0)\}$, $\{T\rightarrow U:(3,1)\rightarrow(4,0)\}$, $\{V\rightarrow W:(10,0)\rightarrow(18,1)\}$. Solving Eq. (2) for the time rates of change of m_e/m_p and m_p/m_d, we obtain

TABLE III. Derivatives $\eta^{pd}\partial E/\partial\eta^{pd}\times 10^2$ of nonrelativistic energies of the HD^+ hydrogen molecular ion with respect to the proton-deuteron mass ratio (in atomic units).

	$\nu=0$	$\nu=1$	$\nu=2$	$\nu=3$	$\nu=4$	$\nu=10$	$\nu=18$
$N=0$	0.081468	0.219284	0.342846	0.452749	0.549475	0.866431	
$N=1$	0.088045	0.225410	0.348538	0.458023	0.554342		0.508453
$N=2$	0.101120	0.237586	0.359851	0.468501	0.564010		
$N=3$	0.120536	0.255664	0.376642	0.484049	0.578350		
$N=4$	0.146066	0.279425	0.398703	0.504466	0.597170		

$$\frac{d\ln(m_e/m_p)}{dt} = -8111.7\frac{d\ln\left(\frac{\Delta E_{PQ}}{\Delta E_{RS}}\right)}{dt} + 7579.7\frac{d\ln\left(\frac{\Delta E_{TU}}{\Delta E_{VW}}\right)}{dt}, \tag{15}$$

$$\frac{d\ln(m_p/m_d)}{dt} = 24326.9\frac{d\ln\left(\frac{\Delta E_{PQ}}{\Delta E_{RS}}\right)}{dt} - 22727.7\frac{d\ln\left(\frac{\Delta E_{TU}}{\Delta E_{VW}}\right)}{dt}. \tag{16}$$

The coefficients are rather large, so the discrimination between the time dependencies of m_e/m_p and m_p/m_d is very weak. The reason lies in the fact that the ratio of the normalized energy derivatives $\eta^{ep}(\partial E/\partial\eta^{ep})/\eta^{pd}(\partial E/\partial\eta^{pd})$ is about constant ($\simeq 3$) for all transitions. This constant ratio can be explained as follows. If we restrict ourselves to the states of the same adiabatic potential then the essential part of the energy is defined by the two-body adiabatic model with $H_{ad}=-P^2/2\mu+V_{ad}$, where $\mu^{-1}=\eta^{ep}(1+\eta^{pd})$ [33]. From this consideration one immediately obtains that the ratio of normalized energy derivatives is $(1+\eta^{pd})/\eta^{pd}=2.99$, no matter which level is considered and how far it is from the bottom of the potential well. Thus, also the normalized sensitivities exhibit the ratio $s_k^{ep}/s_k^{pd}\simeq 3$, independent of the transition k.

IV. EXPERIMENTAL CONSIDERATIONS

Above we have discussed a few examples on how to use molecular transitions to extract information about mass ratios. With the single species HD^+ it is in principle possible to search for the time dependence of both m_e/m_p and m_p/m_d. If a time dependence of a transition frequency ratio such as in Eq. (14) is found, a comparison between HD^+ and H_2^+ can be used to determine the individual contributions.

Apart from the sensitivities, many other aspects play a role for an experimental implementation, such as the experimentally achievable transition linewidths, the required laser wavelengths, the hyperfine structure of the transitions, the ability to measure and calculate systematic frequency shifts, etc.

The measurement of frequency ratios as required for time dependence tests [see Eq. (2)] can today be performed with exceptional accuracy using the femtosecond frequency comb method [30], and poses no experimental limitation at present.

While the basic concept proposed here may be applied to an ultracold neutral molecule ensemble (e.g., produced by photoassociation [31] and stored in an optical lattice), charged molecules are particularly suited for precision molecular studies because they can be easily trapped and cooled.

Trapping of charged particles allows long observation times since trap loss can be made very small under ultrahigh vacuum conditions. The use of a radiofrequency trap rather than a Penning trap is advantageous because of the magnetic fields involved are typically much smaller, with correspondingly smaller influence on the spectra. The low density of the trapped ensemble and of the UHV environment implies absence of pressure broadening [32]. In a trap, molecular ion ensembles can be sympathetically cooled to low temperatures ($\sim$10 mK) by laser-cooling simultaneously trapped atomic ions [24,34–36]. By sympathetic cooling with Be^+ ions, we have recently produced ensembles of cold molecular hydrogen ions, including H_2^+, D_2^+, HD^+, and H_3^+ [22].

The simplest effect of the resulting low velocity of the cold molecules is the reduction of Doppler broadening of transitions. For few-ion ensembles, sophisticated techniques of cooling close to the trap motional ground state and quantum state measurement techniques can be applied in order to achieve even higher resolution (see below). With sufficiently cold molecules and use of a narrow-linewidth laser, the spectral linewidth will be limited by the natural linewidth. For vibrational transitions of isotopically asymmetrized homonuclear ions these are of the order 0.01 to 10 Hz, roughly 1 part in 10^{14} [38]. With lasers of ultranarrow linewidth [39], a determination of the center of the molecular transition line well below the natural linewidth, in the 10^{-15} range, is in principle possible.

The excellent frequency stabilities and accuracies (at the level of 1×10^{-14} [11]) achieved with single-ion optical frequency standards point to the potential of achieving similar levels also with molecular ions. As stated above, control of the systematic frequency shifts of the molecular transitions will be the central open issue to be solved in order to achieve this.

A. Spectroscopy on a single isolated molecule

Measurements of the transition frequencies of ultracold trapped molecular ions are most easily performed on an ensemble, perhaps crystallized into a Coulomb crystal. The detection of a vibrational excitation by detection of subsequent fluorescence will not be practical, because of the relatively small ion numbers ($\sim$1000) and long (tens of milliseconds to seconds) vibrational level lifetimes, implying weak fluorescence. As an alternative, destructive detection of excited state population has been proposed, whereby a laser pulse of suitable wavelength selectively photodissociates molecules from the upper vibrational state [37]. The products of the photodissociation are then detected with ion counters and provide a signal proportional to the number of previously excited molecules. However, a destructive detection method is not optimum, because of the need to reload the trap in order to take a complete spectrum of a transition and the uncertainties associated with not being able to reestablish a sufficiently similar initial state of the molecular ion ensemble.

Preferably, the initial state is one in which the systematic effects perturbing the molecular levels can be most accurately measured and controlled. A single isolated molecule, a configuration similar to the single atomic ions used in optical atomic clocks, is one suitable solution. Considering the difficulty to perform fluorescence detection and the need to keep the molecule cold, an atomic ion must be added to the system, which can act both as a coolant ion and as monitor of the molecular excitation. Recently, sympathetic cooling of an atomic ion by a second coolant atomic ion of another species to Doppler and sub-Doppler temperatures has been experi-

mentally demonstrated [40,41]. A symmetrical arrangement of two atomic ions with the molecule in between may also be of interest.

A method to detect the molecular excitation analogous to a certain implementation of quantum gates [42] can be employed. This has already been proposed for high resolution spectroscopy of atomic ions that do not have cooling transitions [43]. The two-ion system ("crystal") is first laser cooled to the motional ground state of, e.g., the axial crystal mode [44,45]. The atomic ion is then laser excited to a metastable state. A molecular transition is now driven, with the laser tuned to the blue motional sideband. The ion crystal motional oscillation is thereby simultaneously excited.

The next step is the readout of the crystal motional state. To this end, the atomic ion is transferred from the metastable state to, say, one of the levels of the cooling transition, using red-detuned light. This ensures that the atomic ion is only transferred when a crystal phonon is present.

Finally, the cooling laser is turned on, and strong atomic fluorescence occurs, signaling that the molecule had absorbed a photon. Thus, the molecular quantum jump is detected by detecting the atomic fluorescence. Eventually the molecule will decay back to the ground state. As in the usual electron shelving technique, the whole sequence must be repeated sufficiently often so as to be able to determine the excitation probability. To obtain a complete spectrum, the outlined procedure is repeated for different values of the molecular excitation frequency.

This method would allow us to perform spectroscopy on narrow molecular transitions with similar sensitivity as in the electron shelving method of single atomic ion spectroscopy. The advantage is thus a good signal-to-noise ratio, allowing a precise determination of line center and study of systematics. Time-domain Ramsey spectroscopy is a further possibility.

V. CONCLUSION

The aim of this work was to propose ultracold molecules as suitable systems for tests of time independence of fundamental masses, as a natural extension of the atomic systems currently under investigation. This proposal opens up the possibility of laboratory tests of the time independence of nuclear mass ratios and of the electron-to-nuclear mass ratio using the highly succesful techniques of quantum optics. Thanks to the narrow linewidths of vibrational transitions and the possibility to control systematic effects it appears feasible to reach limits at the level of 10^{-15}/yr or better.

Molecular ions appear to be a suitable choice for such tests, and molecular hydrogen ions in particular offer the advantage of allowing *ab initio* calculations of their properties, which will be very helpful in understanding systematic effects. As a concrete example, the dependencies of a number of vibrational transition frequencies of the HD^+ molecule to the particle masses were calculated.

We have shown that a single frequency ratio measurement on HD^+ allows us to test for a time dependence of any of the two mass ratios m_e/m_p and m_p/m_d, provided there is no accidental cancellation. It is, however, not possible to obtain stringent limits for the *individual* time dependencies; this was explained by noting the near-adiabaticity of the molecular potential. A comparison of frequencies of the two isotopomers HD^+, H_2^+, on the other hand, allows us to determine the individual time dependencies. Inclusion of HT^+ in the comparison would yield a limit also on the proton-to-triton mass m_p/m_t. Generalizing the above observations, we can state that a comparison of two transitions in a molecule with three different nuclei, e.g., HDT^+, would allow a simultaneous test for the time independence of any of the three mass ratios m_e/m_p, m_p/m_d, and m_p/m_t, again assuming absence of cancellations.

Quantum jump spectroscopy on a single trapped ultracold molecular ion was proposed as a favorable implementation, allowing lifetime-limited spectral resolution, good signal-to-noise ratio, and study and control of systematics. This approach may also be useful for measurements of parity violation [46], tests of the symmetrization postulate, and of the electron dipole moment [47]. Other molecular implementations of mass-ratio time independence tests have not been discussed in detail, but are also of interest. For example, the idea of optical lattice clocks [48] could be extended from ultracold neutral atoms to ultracold neutral molecules. The progress in the generation of ultracold neutral molecules by photoassociation makes this possibility not unrealistic.

The large variety of molecular species and the methods for cooling and manipulating molecules currently under development offer many possibilities to optimize the measurement approach. Here theoretical calculations can serve as a guide, with experiments being required to test various approaches. A central issue will be the sensitivity of the transition frequency to external perturbations and the ability of the experimental configuration to control these sufficiently well.

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