

Vibrational Spectroscopy of HD^+ with 2-ppb Accuracy

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By measurement of the frequency of a vibrational overtone transition in the molecular hydrogen ion HD^+ , we demonstrate the first optical spectroscopy of trapped molecular ions with submegahertz accuracy. We use a diode laser, locked to a stable frequency comb, to perform resonance-enhanced multiphoton dissociation spectroscopy on sympathetically cooled HD^+ ions at 50 mK. The achieved 2-ppb relative accuracy is a factor of 150 higher than previous results for HD^+ , and the measured transition frequency agrees well with recent high-accuracy *ab initio* calculations, which include high-order quantum electrodynamic effects. We also show that our method bears potential for achieving considerably higher accuracy and may, if combined with slightly improved theoretical calculations, lead to a new and improved determination of the electron-proton mass ratio.

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The molecular hydrogen ion and its isotopomers play a fundamental role in molecular physics because of their simple three-body nature, making them a benchmark system for quantum theoretical calculations [1]. Past precision spectroscopic measurements of molecular hydrogen ions and theoretical results have been, in general, in agreement at the level of the dominant (of third order in the fine-structure constant α) quantum electrodynamic contributions [2–4]. Recently, the accuracy of *ab initio* calculations of the energy levels of the molecular hydrogen ion has been strongly improved [5,6] and is now approaching the limits set by the uncertainty in the values of the fundamental constants which enter the calculations. The largest contributor to this type of uncertainty is the electron-proton mass ratio m_e/m_p , which is known to within 0.46 ppb [7]. Wing *et al.* pointed out that if the uncertainty due to the theoretical formalism becomes smaller than that caused by m_e/m_p , the theoretical functional dependence of the energy levels on m_e/m_p may be combined with results from high-resolution spectroscopy to infer an improved value for m_e/m_p [2]. Both this perspective and the theoretical advances call for improved measurements of the energy levels of HD^+ . In view of the recently found indication of a variation of m_e/m_p over \sim Gyr time scales [8], which would signify a violation of the Einstein equivalence principle [9], it is also important to develop high-precision molecular spectroscopic techniques allowing laboratory spectroscopic searches for a present temporal variation of m_e/m_p [10]. Molecular hydrogen ions appear as promising systems because their accurate theoretical description is possible.

High-accuracy spectroscopy is best implemented using cold and confined particles. This has been achieved at a very high level with laser-cooled, trapped atomic ions, as exemplified by single-ion atomic clocks; see, for example, Ref. [11] and references to other work therein. Molecular ions, however, have not seen such a development, which is primarily due to a lack of transitions that can be used for

laser cooling and for internal-state detection, as required for the spectroscopy. Several schemes to overcome this limitation have been proposed [12] and, as far as it concerns cooling, realized [13,14]. Recently, we have demonstrated a general method for molecular ion spectroscopy, which relies on sympathetic cooling of the molecular ions by storing them together with laser-cooled atomic ions. Detection of a laser-induced transition is done by selective dissociation of the excited molecules and mass-spectroscopic measurement of the number of remaining molecular ions. This method enabled the first observation of several vibrational overtone transitions in the $X^2\Sigma^+$ electronic ground state of HD^+ [15]. In this Letter, we report a precision frequency measurement of the $(v, N): (4, 3) \leftarrow (0, 2)$ rovibrational transition in ground-state HD^+ , which represents, to our knowledge, the most accurate optical frequency measurement performed on any molecular ion to date. We also present a comprehensive theoretical analysis of the systematic effects that contribute to the frequency uncertainty, showing that our method can potentially lead to a new and improved determination of m_e/m_p .

The experimental procedure has been described in detail in Ref. [15]. In brief, we load ~ 2000 Be^+ ions and ~ 150 HD^+ ions in a linear rf trap by *in situ* electron impact ionization of their neutral counterparts [14]. The ions are kept under ultrahigh vacuum conditions to virtually eliminate the effect of collisions with background gas constituents. The Be^+ ions are cooled by a single 313 nm laser beam, leading to the formation of a so-called ellipsoidal Coulomb crystal, in which the ions have a translational (secular) temperature of ~ 50 mK in all three dimensions [16]. A measure for the number of trapped HD^+ ions is obtained by applying an ac electric field which drives the motion of the HD^+ ions. For a specific mass-dependent frequency, driving takes place resonantly and causes heating of the entire Coulomb crystal, which manifests itself as a change in the 313 nm fluorescence emitted by the Be^+ ions. Using this mass-spectroscopic detection method, the

molecular spectroscopy is performed by $(1 + 1')$ resonance-enhanced multiphoton dissociation (REMPD) of the HD^+ ions as follows: The first photon at $1.4 \mu\text{m}$ populates the $v = 4$ level (which is otherwise unpopulated under the conditions in our apparatus, as spontaneous decay is possible through the HD^+ permanent dipole moment), from which the HD^+ ions are selectively dissociated by an additional 266 nm photon [Fig. 1(a)]. The consequent loss of HD^+ ions is interpreted as a signature of resonance of the first photon. We note that the long upper-state lifetimes ($\sim 20 \text{ ms}$) would make spectroscopy by infrared fluorescence detection a challenging task. The $1.4 \mu\text{m}$ laser system used is referenced to a GPS-disciplined hydrogen maser. It is based on a grating-enhanced diode laser with resonant optical feedback, which combines the good tunability of regular grating diode lasers with the good short-term stability of diode lasers with resonant optical feedback [17]. This laser is frequency-locked to a titanium:sapphire-based, self-referenced fs-frequency comb, which itself is phase-locked to the hydrogen maser. To frequency-lock the diode laser to the frequency comb, we preprocess the beat note signal between the diode laser and the comb by a tracking oscillator. We subsequently use a frequency-to-voltage scheme [18] to derive an error signal for the diode laser frequency stabilization from the tracking oscillator output signal. This locking scheme limits the diode laser frequency inaccuracy to a few kilohertz over the 6 s duration of one measurement cycle and to less than 25 kHz on longer time

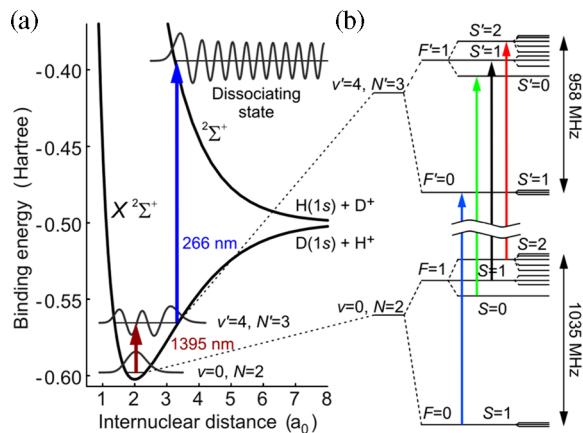


FIG. 1 (color online). (a) Potential energy curves and rovibrational wave functions for the states involved in the $(1 + 1')$ REMPD scheme (see text). Franck-Condon overlap prevents dissociation of $v = 0$ population by the 266 nm laser but ensures efficient dissociation of any population in $v' = 4$. (b) Hyperfine levels of the $(v, N): (0, 2)$ and rovibrational states. The quantum numbers refer to the following coupling scheme for the electron spin s_e , proton spin \mathbf{I}_p , deuteron spin \mathbf{I}_d , and molecular rotation \mathbf{N} : $\mathbf{J} = \mathbf{S} + \mathbf{N}$, where $\mathbf{S} = \mathbf{F} + \mathbf{I}_d$, and $\mathbf{F} = s_e + \mathbf{I}_p$. The labels for the quantum number J are not shown. As the 1395 nm radiation does not couple to the various spins, the strongest transitions can be grouped by their spin configurations, as indicated by the different colors used in the graph.

scales ($\sim \text{days}$). The resolution of the laser system is currently limited to $\sim 300 \text{ kHz}$, which is primarily due to the short-term instability of the frequency comb.

The spectrum of the $(v, N): (4, 3) \leftarrow (0, 2)$ transition at 1395 nm measured with this laser system is displayed in Fig. 2. Each data point shown in the graph is the average of seven individual points, each of which equals the fractional loss of HD^+ ions induced by a 6 s period of REMPD. The signal due to loss of HD^+ by processes other than the REMPD process (e.g., chemical reactions during collisions with background gas molecules) is independently measured and eliminated from the data. The spectrum shown in Fig. 2 was taken in three runs lasting $5\text{--}8 \text{ hours}$ each. Care was taken to reproduce the same conditions (most importantly, the HD^+ ion number and temperature [19], the intensities of all lasers involved, and the magnetic field settings) during each run. The spectrum in Fig. 2 shows two resolved hyperfine components around the deperturbed frequency ν_d of the $(v, N): (4, 3) \leftarrow (0, 2)$ rovibrational transition. The value of ν_d is of interest as it contains

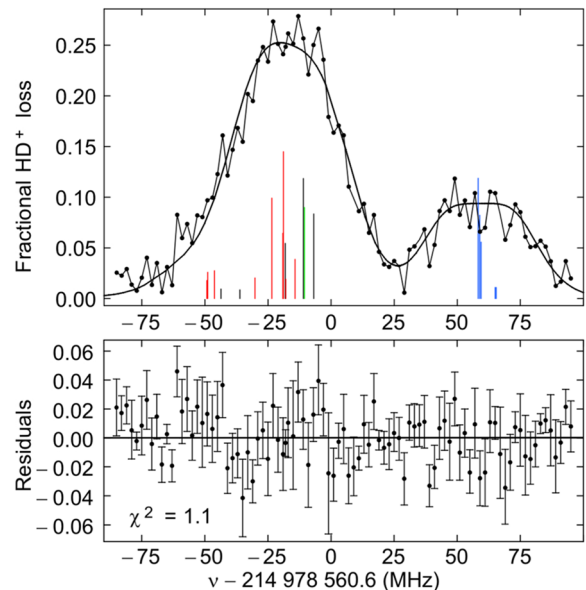


FIG. 2 (color online). Spectrum of the $(v, N): (4, 3) \leftarrow (0, 2)$ transition in the $X^2\Sigma^+$ electronic ground state of HD^+ , obtained by $(1 + 1')$ REMPD spectroscopy. The offset frequency in the abscissa label is our measured result for the deperturbed frequency ν_d and is accurate to within 0.5 MHz . The smooth curve in the upper panel represents a fit with a reduced χ^2 value of 1.1 of the model line function to the data. Underneath the data and the fit, the theoretical hyperfine line spectrum, calculated using the hyperfine Hamiltonian given in Ref. [20], is shown. The same color coding as in Fig. 1(b) is used to classify the individual hyperfine transitions. For clarity, the data points in the upper panel are joined by line segments; the lower panel shows the differences between the individual data points (black dots) and the fitted curve. Each data point is an average of seven individual measurements of the fractional loss of trapped HD^+ ions induced by a 6 s period of REMPD. Frequency error bars are not shown as they are smaller than the dots representing the data points.

the dependence on m_e/m_p . To separate off the hyperfine contribution to the spectrum, we fit the spectrum to a model line function obtained using the theoretical effective hyperfine Hamiltonian given by Bakalov *et al.* [20]. We neglect contributions arising from nucleon-rotation interactions, the deuteron quadrupole moment, and finite-size effects of the proton and deuteron. The omitted terms contribute less than 100 kHz to the hyperfine level energies. A schematic of the hyperfine levels in the upper and lower rovibrational states, as well as the strongest electric dipole transitions between them, are shown in Fig. 1(b). The theoretical spectrum in the absence of any broadening or micromotion effects is represented by the stick spectrum in Fig. 2. The model line function includes Doppler broadening, as well as the sidebands of each line in the spectrum due to excess micromotion of the HD⁺ ions at the 14.2 MHz drive frequency of the trap. This micromotion is driven by electric fields that stem from imperfections in the ion trap design and has an amplitude of 0.3 μm along the propagation direction of the infrared laser beam. We independently confirmed the presence of micromotion by means of a time-to-amplitude correlation measurement on the 313 nm fluorescence [21]. As Doppler broadening gives a width of $\Gamma \sim 20$ MHz to each spectral component, the carrier and sidebands of each feature merge together to yield an overall broadening to ~ 40 MHz. Several of the model parameters (ν_d , Γ , and a vertical scaling factor) of the spectrum are fitted to all individual data points simultaneously. The fitted spectrum is indicated by the smooth continuous curve through the data in Fig. 2. A fit to the averaged data points gives the same result. From the fitted value for the Doppler width $\Gamma = 20.3(1.4)$ MHz, we deduce an HD⁺ temperature of 53(8) mK, which agrees with results from molecular dynamics simulations of the crystal images observed with a CCD camera [14]. The most important of all fitted parameters, the value for ν_d , is sensitive to changes in the other parameters of the model. Uncertainties in parameters of the model line function which are not fitted but determined independently are translated to an additional uncertainty in ν_d , yielding a total 1σ statistical uncertainty of 0.45 MHz. We note that the measurement of the laser frequency does not contribute significantly to this uncertainty. The fit also indicates that the hyperfine structure observed in our experiment agrees with the calculated hyperfine structure at the same level of uncertainty.

Besides the statistical uncertainty, the value of ν_d has an uncertainty due to systematic shifts. An overview of systematic shifts and their uncertainties is shown in Table I. The largest contribution to the inaccuracy comes from the terms which were omitted from the hyperfine Hamiltonian. The second largest uncertainty stems from the Zeeman effect, which we evaluate as follows. First, we determine the magnetic field in our ion trap from the spatial intensity distribution of the 313 nm fluorescence, as seen on a camera image of the Be⁺ ion crystal. From the behavior of this distribution as a function of the magnetic field

TABLE I. Uncertainty budget. All values are in megahertz.

Origin	Shift	Uncertainty
Measurement uncertainty	0	0.45
Hyperfine Hamiltonian	0	0.14
Zeeman effect	0	0.06
ac Stark shifts	0 ^a	0.017
2nd-order Doppler shift	0 ^a	0.01
Collisional shift	0 ^a	0.001
Final result for ν_d	214978560.6	0.5
Theory [5,6]	214978560.88	0.07

^aShift does not contribute significantly and is set to zero here.

vector, which can be controlled through three mutually perpendicular sets of Helmholtz coils, we retrieve the magnetic field and its gradient. Next, we theoretically investigate the effect of the measured magnetic field (which varies between 0 and 1 G over the trap volume) on the observed spectrum using the Zeeman Hamiltonian given by Hegstrom [22]; see [16]. Our analysis yields a zero Zeeman shift with a statistical uncertainty margin of 60 kHz. This value is taken as an upper limit on the uncertainty of the Zeeman shift to ν_d and should be compared with the expected magnitude of rotational Zeeman shifts of $\nu_d \sim g_R \mu_n \times (1 \text{ G}) \approx 500 \text{ Hz}$, where g_R is the g value for the rotation of the molecule, and μ_n stands for the nuclear magneton (in units of Hz/G).

Other systematic shifts include ac Stark shifts due to the various optical fields at the position of the ions. The infrared laser itself causes a shift as it probes a multilevel system, consisting of various transitions at different frequencies which are all addressed by the infrared laser. Taking three mutually connected levels at a time, we solve the optical Bloch equations to obtain an upper bound to the shift. The 266 nm dissociation laser and the 313 nm cooling laser also cause a shift as they couple bound states to the dissociation continuum. We obtain the strength of the bound-continuum state coupling from the wavelength-dependent dissociation rate given in Ref. [23] and use Fano theory to estimate the total shift caused by the 266 and 313 nm lasers [24]. Both ultraviolet lasers have an intensity corresponding to about 1 mW focused to a 100 μm spot size at the position of the ions, whereas the infrared laser has 170 μW of power focused to a 200 μm spot size. We estimate that each of these lasers causes an ac Stark shift of much less than 10 kHz to ν_d . Other ac Stark shifts are due to the presence of blackbody radiation (BBR) and the rf trap potential. To estimate the magnitude of these shifts, we use the electric dipole polarizability $\alpha(\omega)$ for the levels probed by our laser. $\alpha(\omega)$ is found employing the HD⁺ rovibrational wave functions and the dipole moment function for the $X^2\Sigma^+$ state obtained using the *ab initio* data from Ref. [25]. We find that both the BBR shift and the shift by the trap potential are smaller than 1 kHz. Other small systematic shifts are due to collisions with background gas constituents and the second-order Doppler

effect, for which we take into account both the trap (secular) motion and the (excess) micromotion. We estimate that these shifts affect ν_d by less than 1 and 10 kHz, respectively.

Our final result for ν_d is 214 978 560.6(5) MHz. The 2.3-ppb relative uncertainty in our result represents an improvement over previous spectroscopic results for HD^+ by a factor of 150 [3,26]. Our value agrees well with the most recent theoretical value of 214 978 560.88(7) MHz by Korobov, who considered relativistic and radiative corrections up to order $m_e\alpha^6$ [5,6]. Thus, our value for ν_d is consistent with the 2002 Committee on Data for Science and Technology recommended value for m_e/m_p , which was used in the calculations, to within 5 ppb. To obtain this margin, we used the partial derivatives with respect to m_e/m_p of the energies of the (ν, N) : (0, 2) and (4, 3) levels, given in Ref. [10].

The uncertainty budget in Table I shows that there are no obvious limitations for improvement of the experimental accuracy by 1 order of magnitude, other than the statistical uncertainty and the uncertainty in the hyperfine Hamiltonian. The former is closely related to the width of the lines which constitute the spectrum. With relatively straightforward modifications to the apparatus, it will be possible to eliminate the micromotion sidebands. Furthermore, resolution in the kilohertz range (and possibly lower) will result if the confinement by the trap is increased so that Doppler-free spectroscopy in the Lamb-Dicke regime becomes possible, thereby removing the Doppler broadening [27]. In addition, the hyperfine Hamiltonian and the Zeeman effect may be determined experimentally with sufficient accuracy by rf spin flip spectroscopy in combination with the REMP method used here [3]. If the experimental accuracy improves by 1 order of magnitude, and provided the uncertainty in the theoretical level energies improves by a factor of 2, a competitive new value for m_e/m_p could be inferred already. In addition, the combined theoretical and experimental results for the HD^+ energy levels would establish an accurate link between the value of m_e/m_p and that of other fundamental constants, such as α and the proton-deuteron mass ratio.

Finally, we point out that the relative accuracy achieved in the spectroscopy here is considerably better than obtained with methods based on buffer gas-cooled trapped molecular ions [28] and obtained with ion beams, buffer gas-cooled by a supersonic jet [29], where Doppler broadening due to ≥ 10 K temperatures limits the resolution achievable with single-photon spectroscopy. The main ingredients of the method, sympathetic cooling by laser-cooled ions and a destructive spectroscopic scheme in combination with mass-specific detection, lend themselves for extension of this form of high-resolution spectroscopy to other ionic species such as, for example, the astronomically relevant H_3^+ ion [30] and complex molecules [31]. Therefore, it could lead to a vast improvement of the accuracy of spectroscopic constants for many molecular ions and give an impetus to developments in molecular theory.

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