Probing QED and fundamental constants through laser spectroscopy of vibrational transitions in HD$^+$

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The simplest molecules in nature, molecular hydrogen ions in the form of H$_2^+$ and HD$^+$, provide an important benchmark system for tests of quantum electrodynamics in complex forms of matter. Here, we report on such a test based on a frequency measurement of a vibrational overtone transition in HD$^+$ by laser spectroscopy. We find that the theoretical and experimental frequencies are equal to within 0.6(1.1) parts per billion, which represents the most stringent test of molecular theory so far. Our measurement not only confirms the validity of high-order quantum electrodynamics in molecules, but also enables the long predicted determination of the proton-to-electron mass ratio from a molecular system, as well as improved constraints on hypothetical fifth forces and compactified higher dimensions at the molecular scale. With the perspective of comparisons between theory and experiment at the 0.01 part-per-billion level, our work demonstrates the potential of molecular hydrogen ions as a probe of fundamental physical constants and laws.
The possibility of accurate quantum electrodynamics (QED) calculations and the presence of narrow optical transitions between long-lived vibrational levels make laser spectroscopy of H$_2^+$ and HD$^+$ a sensitive tool to test fundamental physics at the molecular scale. Examples include tests of relativistic quantum mechanics and QED$^{1-4}$, and searches for physics beyond the Standard Model at the molecular scale$^{5,6}$ and beyond General Relativity$^{7,8}$. Furthermore, spectroscopy of the molecular hydrogen ion has long been proposed as a means to determine the value of fundamental physical constants$^{1,2,4,9}$, and to realise precise molecular clocks$^{8,10}$. Naturally all the above applications involve a comparison of state-of-the-art molecular theory with accurate results from (most often laser) spectroscopy. The most accurate results so far have been obtained using HD$^+$ ions stored in radiofrequency (r.f.) traps, sympathetically cooled by laser-cooled Be$^+$ ions$^{3,11}$, allowing tests at a relative uncertainty of a few parts per billion (p.p.b.). However, the most precise experimental result$^3$, a frequency measurement of the ($\nu_L$): (0,0)–(1,1) rovibrational line at 5.1 µm in HD$^+$ with a relative uncertainty of 1.1 p.p.b., was found to disagree by 2.7 p.p.b. with a more accurate theoretical value obtained from state-of-the-art ab initio molecular theory$^{1,2}$. This disagreement has thus far been unresolved, and additional high-precision experimental data are needed to draw conclusions about the validity of the theoretical framework, and to open up the wide range of applications of molecular hydrogen ion spectroscopy mentioned above.

Here, we report on an optical frequency measurement of the ($\nu_L$): (0,2)–(8,3) vibrational overtone transition in HD$^+$ at 782 nm. Our experimental result is found to be in agreement with the theoretical prediction to within 0.6(1.1) p.p.b., thereby confirming the validity of relativistic quantum mechanics and QED in a vibrating molecular system at an unprecedented level. We subsequently exploit the agreement between theory and experiment for the first determination of the proton–electron mass ratio from a molecular system, and to put tighter constraints on the strength and range of ‘fifth forces’ at the molecular scale.

### Results

#### Experimental procedure

Our experimental apparatus and procedure for HD$^+$ spectroscopy are described in detail in the Methods section. In brief, trapped HD$^+$ molecular ions are cooled to ~10 mK by storing them together with laser-cooled Be$^+$ ions, and we excite and detect the ($\nu_L$): (0,2)–(8,3) transition by resonance-enhanced (1$^+$) multiphoton dissociation (REMPD) spectroscopy, see Fig. 1a. We acquire a spectrum by observing the loss of HD$^+$ because of REMPD, inferred from the change in the monitored Be$^+$ fluorescence induced by r.f. excitation of the HD$^+$ secular motion, for different values of the 782 nm spectroscopy laser frequency (Methods and Fig. 2a). The latter is stabilized and counted using an optical frequency comb laser (Methods).

**Line shape model for nonlinear least-squares fitting.** Hyperfine interactions lead to a manifold of 83 lines (Fig. 1b,c), the ~25 strongest of which are located within the range (~110 MHz, 140 MHz) around the hyperfine-less rovibrational frequency, $\nu_0$. Each hyperfine component is Doppler broadened to ~16 MHz, and the hyperfine structure is only partially resolved. Using a realistic spectral line shape function (Methods), we employ nonlinear least squares fitting to extract not only the transition frequency $\nu_{0,\text{fit}}$ but also the intensity of the 782 nm laser, $I_L$, the motional temperature of the HD$^+$ ion, $T_{\text{HD}^+}$, and the temperature of the Be$^+$ ions during secular excitation, $T_s$, which are relevant parameters for the spectral analysis (see Methods for details). The 782-nm intensity we find agrees (within the fit error) with the intensity estimated from the laser beam waist and beam alignment uncertainty. Likewise, the fitted temperature agrees well with the results of molecular dynamics (MD) simulations.

The relevance of the additional fit parameters is illustrated by the correlation matrix, $\Omega$, of the estimated parameters, which reveals significant correlations between $\nu_{0,\text{fit}}$ and $T_{\text{HD}^+}$, and $\nu_{0,\text{fit}}$ and $I_L$ (Fig. 2c). Adding fit parameters results in an increased error in the fitted value $\nu_{0,\text{fit}}$, which rises from 0.25 MHz (0.65 p.p.b. relative to $\nu_{0,\text{fit}}$) to 0.33 MHz (0.85 p.p.b.) when $T_s$, $T_{\text{HD}^+}$ and $I_L$ are added as free fit parameters. Even so, the spectral fit presented here marks the first time that a sub-p.p.b. resolution is achieved in molecular-ion spectroscopy.

**Systematic effects and frequency value.** The fit result $\nu_{0,\text{fit}}$ is corrected for various systematic frequency offsets because of electric and magnetic fields. We calculate the a.c. and d.c. Stark shifts ab initio with high accuracy following the approach of Karst$^{10}$ to find the frequency shift because of blackbody radiation (BBR), the r.f. trap field and the electric fields of the lasers. The total Stark shift of ~1.3(1) kHz is dominated by the shifts due to the 313, 532 and 782 nm lasers (which are all on during excitation), with individual contributions of 0.008(1) kHz, –0.45(7) kHz and –0.87(13) kHz, respectively. The uncertainty of the Stark shift is caused almost entirely by the uncertainties of the laser beam intensities. We also evaluate the Zeeman effect, which stems from the static quantization field of 0.19 mT directed along the z axis of the trap (Methods). The polarization of the 782 nm laser is such that it induces $\sigma^-$ and $\sigma^+$ transitions at equal rates. The Zeeman effect leads to a shift to $\nu_{0,\text{fit}}$ by ~16.9(3.2) kHz, the uncertainty of which is due to a possible 2% imbalance between the $\sigma^-$ and $\sigma^+$ rates caused by imperfect polarization optics and depolarization because of the windows of the vacuum chamber. Another uncertainty stems from the accuracy of the theoretical hyperfine structure$^{21}$, which enters through our spectral line shape function. We repeated the fit procedure with a spectral line shape function based on the hyperfine structure obtained with slightly altered spin coefficients (within their uncertainty range), for which we observe essentially no shift of $\nu_{0,\text{fit}}$. Compared with the 0.33 MHz statistical fit uncertainty of $\nu_{0,\text{fit}}$, the contribution of the above line shifts to the total frequency value and uncertainty is negligible, as are the frequency shifts due to the second-order Doppler effect (~5 Hz) and the electric-quadrupole shift (~0.1 kHz).

During REMPD, the motional dynamics in the laser-cooled Coulomb crystal are significantly influenced by several (laser-induced) chemical processes. For example, REMPD of an HD$^+$ ion leads to the formation of energetic fragments, and previously it was observed that the two reactions, HD$^+$ + $h\nu_1 + h\nu_2 \rightarrow$H(1s) + D$^+$ + k.e. and HD$^+$ + $h\nu_1 + h\nu_2 \rightarrow$D(1s) + H$^+$ + k.e., occur with about equal probability (here k.e. stands for kinetic energy, and $\nu_1$ and $\nu_2$ for the frequencies of the 782 and 532 nm lasers, respectively)$^{15}$. Owing to their relatively high charge-to-mass ratio, the produced protons are not stably trapped in our apparatus. Indeed, we observe only cold, trapped deuterons after REMPD, indicating that each deuteron transferred most of its 0.41 eV kinetic energy to the ions in the Coulomb crystal (which itself contains only 2 meV of thermal energy at 10 mK), causing (at least transiently) significant heating of the crystal. Other reactions with energetic ionic products are the result of collisions with H$_2$ molecules in the background vapour, and we also take the reactions Be$^+$ + (P$_2$,H$_2$) $\rightarrow$ BeH$^+$ + H(1s) + k.e., HD$^+$ + H$_2$ $\rightarrow$H$_2$D$^+$ + H(1s) + k.e. and HD$^+$ + H$_2$ $\rightarrow$H$_2^+$ + D(1s) + k.e. (with ionic product kinetic...
energies of 0.25, 0.36 and 0.66 eV, respectively) into account here. We determine reaction rates from measured loss rates of Be\(^+\) and HD\(^+\), which are in agreement with expected Langevin reaction rates given the pressure of \(1 \times 10^{-8}\) Pa in our vacuum apparatus. We include these processes in realistic MD simulations (Methods) employing leapfrog integration with an
adaptive time step, to ensure that collisions between energetic ions are correctly handled. Under these conditions, our MD simulations reveal average HD\textsuperscript{+} z-velocity distributions, which deviate significantly from thermal (Gaussian) distributions, an effect that has hitherto been neglected by the widespread assumption that laser-cooled ion ensembles exhibit thermal velocity distributions. As shown in Fig. 3, we empirically find that the velocity distributions are better represented by q-Gaussians\textsuperscript{17}, which have the additional advantage that the effect of a given chemical reaction can be parameterized by a corresponding q-value (with q = 1 corresponding to a Gaussian distribution). Taking all reactions and reaction rates into account, we find that the velocity distribution is best characterized by a q-Gaussian with q ranging between 1.00 and 1.07, depending on the assumed thermalization rate and the REMPD rate. We therefore include q-Gaussians in our spectral line shape function (Methods). Comparing scenarios with minimum and maximum expected thermalization rates (corresponding to q = 1.07 and q = 1.00, respectively), we find a mean shift of −0.25(25) MHz with respect to the case of q = 1.00. The origin of this shift lies in the overlap and saturation of Doppler-broadened hyperfine components in the spectrum (Fig. 2d). A similar frequency shift may occur when micromotion sidebands are present. Here we make a distinction between excess radial micromotion caused by radial static offset fields, and axial micromotion that could arise from an axial r.f. field because of geometrical imperfections of our ion trap. A finite-element analysis of the trap’s electric field reveals that such an axial field will be approximately constant over the extent of the Coulomb crystal, which implies that the corresponding micromotion contribution to the line shape will be homogeneous. We use the fluorescence correlation method of Berkeland et al.\textsuperscript{13} to find a small micromotion amplitude of 11(4) nm amplitude along the 782-nm laser beam as follows. Measurements of the r.f. field amplitude are performed on the Be\textsuperscript{+} ions using the 313-nm laser beam (which co-propagates with the 782 nm laser beam). Repeating such measurements for various values of the trap r.f. voltage allows separating the axial and the radial component (the latter being due to the residual projection of the laser beam onto the radial direction). We find that the axial micromotion component is dominant, which is explained as follows. First, the 782-nm laser is aligned parallel to the trap axis, so that the radial micromotion amplitude is suppressed by the near-zero angle between the 782-nm laser and the radial directions. Second, as the surrounding Be\textsuperscript{+} ions shield the HD\textsuperscript{+} from static radial offset fields, the HD\textsuperscript{+} ions are trapped symmetrically about (and close to) the nodal line of the r.f. field. These two conditions limit the contribution of the radial micromotion to well below the measured axial amplitude of 11(4) nm. The resulting sidebands are included in the spectral line shape function, leading to an additional frequency shift of −55(20) kHz with respect to the case of zero micromotion.

After correcting for all systematic frequency shifts (Table 1), we finally obtain v\textsubscript{0} = 383,407,177.38(41) MHz.

**Discussion**

Our frequency value v\textsubscript{0} of the (ν, L): (0,2)–(8,3) transition is in good agreement with the more accurate theoretical value\textsuperscript{2} v\textsubscript{0, theo} = 383,407,177.15(15) MHz. The contribution of the QED terms\textsuperscript{1,2,18} to this frequency amounts to −1547.225(15) MHz (−4035.46(4) p.p.b.), and our measurement therefore confirms the validity of QED in a molecular system at an unprecedented level of 2.7 × 10\textsuperscript{−4}. We furthermore note that our measurement is sensitive to (and in agreement with) QED terms up to order m\textsubscript{e} x\textsuperscript{2}, given that the m\textsubscript{e} x\textsuperscript{2} term contributes 780(15) kHz (that is, 2.03(4) p.p.b.) to the transition frequency.

Salumbides et al.\textsuperscript{5} showed that spectroscopic tests of molecular QED can be used to set upper bounds on a hypothetical ‘fifth force’, acting between hadrons at separations of the order of 1 Å, and arising from the exchange of unknown, massive virtual particles. Modelling such a hadron–hadron interaction with a

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**Table 1 | Systematic shifts and uncertainty budget.**

| Origin | Shift (MHz) | Uncertainty (MHz) | Uncertainty (p.p.b) |
| --- | --- | --- | --- |
| Resolution (statistical fit error) | 0 | 0.33 | 0.85 |
| Doppler effect due to chemistry | −0.25\textsuperscript{*} | 0.25 | 0.66 |
| Ignoring population L = 6 in rate equations | 0.032 | 0.020 | 0.052 |
| Doppler effect due to micromotion | −0.055\textsuperscript{*} | 0.020 | 0.052 |
| Frequency measurement | 0 | 0.010 | 0.026 |
| BBR temperature | 0 | 0.005 | 0.013 |
| Zeeman effect | −0.0169 | 0.003 | 0.008 |
| Stark effect | −0.0013 | 0.0001 | 0.0004 |
| Electric-quadrupole shift | 0\textsuperscript{†} | 0.0001 | 0.0003 |
| 2nd-Order Doppler effect | 0\textsuperscript{†} | 0.000005 | 0.00001 |
| Total | −0.0182 | 0.41 | 1.1 |

BBR, blackbody radiation; p.p.b., parts per billion.

\*These frequency shifts are accounted for by the spectral fit function, rather than being subtracted from v\textsubscript{0, fit}.

\†These values are non-zero, but negligibly small and therefore ignored here.
Yukawa-type potential of the form $\frac{\hbar c}{\alpha} \frac{s}{r^{1/2}/r}$ and computing the resulting frequency shift to $\nu_0$, we can exploit the 1 p.p.b. agreement between theory and experiment to rule out (at the 90% confidence level) interactions at a range $\lambda = 1 - 2 \, \text{Å}$ (corresponding to force-carrying particles with mass $m_V = 1 - 2 \, \text{keV} \, \text{c}^{-2}$) with an interaction strength relative to the fine-structure constant, $|s/\alpha|$, larger than $5 - 8 \times 10^{-10}$ (Fig. 4). In a similar way, applying the Arkani-Hamed–Dimopoulos–Dvali formulation to probe the effect of compactified higher dimensions on energy levels in molecules, we place an improved upper bound of 0.5 μm on the compactification radius of higher dimensions in 11-dimensional M-theory.

Four decades ago, Wing et al. suggested that molecular theory could one day be used to translate measured vibrational frequencies of HD$^+$ to a new value of the proton–electron mass ratio, $\mu$. The high accuracy of our result and the good agreement with theory, which assumes the 2010 Committee on Data for Science and Technology (CODATA) recommended value $\mu_{\text{CODATA}}$, now allow the first determination of $\mu$ from molecular vibrations. Previously we had derived the sensitivity relation $\delta \mu/ \mu = -2.66 \, \delta \nu_0/ \nu_0$, which we employ to adjust $\mu_{\text{CODATA}}$ to a new value, $\mu_{\text{HD}^+}$, such that the theoretical frequency matches our experimental value. We thus find $\mu_{\text{HD}^+} = 1,836.1526695(53)$, with a relative uncertainty of 2.9 p.p.b., which approaches that of the values taken into account in the 2010 CODATA adjustment. For example, the value reported by Farnham et al. is only a factor of 1.3 more precise than our result. Although the precision of a very recent determination by Sturm et al. is still 31 times higher, we point out that our method yields $\mu$ as a single parameter from molecular vibrations, whereas most other $\mu$ values are ratios of individual determinations of the electron and proton relative atomic masses (exceptions are $\mu$ determinations from atomic laser spectroscopy). Therefore, the agreement of $\mu_{\text{HD}^+}$ with all other values of $\mu$ forms an additional consistency check of the various (and vastly different) methods used (Fig. 5b). In particular, it implies that relativistic quantum mechanics and QED consistently describe at the few p.p.b. level such diverse systems as the bound electron in antiprotonic helium and the molecular hydrogen ion. Furthermore, all of the methods that produce $\mu$ as a single parameter, our approach is surpassed only by spectroscopy of antiprotonic helium, which is 2.3 times more precise but additionally requires charge, parity and time reversal invariance (Fig. 5a).

In principle, the transition frequency $\nu_0$ depends on the value of other fundamental constants as well, such as the deuteron–proton mass ratio, $m_d/m_p$, the fine structure constant, and the proton charge radius. However, the sensitivity of $\nu_0$ to changes in $\mu$ is known to be three times larger than the second largest one, the $m_d/m_p$ sensitivity. Moreover, if we propagate the uncertainties of the 2010 CODATA values of the fundamental constants through the sensitivity relations, we find that the relative contributions by $\mu$, $m_d/m_p$, $\alpha$ and the proton radius to the theoretical uncertainty of $\nu_0$ are 154, 11.6, 0.004 and 5.13 parts per trillion, respectively. We therefore conclude that $\mu$ is the correct parameter to constrain.

The error budget in Table 1 reveals that the experimental uncertainty is limited by Doppler broadening. To overcome this, more involved Doppler-free two-photon spectroscopy of HD$^+$ has been proposed, which should reduce the uncertainty to below $1 \times 10^{-12}$. This should enable a comparison between theory and experiment that would not only test the QED description of chemically bonded particles at an unprecedentedly high accuracy but also probe the 11-dimensional M-theory framework.
level, but also produce a new value of $\mu$ with an uncertainty below 0.1 p.p.b., surpassing the most precise determination of $\mu$ obtained from independent electron and proton relative atomic mass measurements$^{2,7}$, which represent a completely different method (Fig. 5c). Our work demonstrates the potential of molecular hydrogen ions for the determination of mass ratios of fundamental particles, as well as stringent tests of QED, and searches for new physics.

**Methods**

**Experimental procedure.** We typically store 40–85 HD$^+$ ions in a linear r.f. trap, together with $\sim$750 Be$^+$ ions, which are laser cooled to a temperature of 5–10 mK using a continuous-wave (CW) 313-nm laser beam propagating along the symmetry (z) axis of the trap. As a consequence, only the axial motion of the Be$^+$ ions is laser-cooled directly. However, the three-dimensional extent of the Coulomb crystal ensures good coupling of the axial motion to the radial motion of the Be$^+$ and HD$^+$ ions, so that both Be$^+$ and HD$^+$ ions are efficiently cooled in all three dimensions. Although larger numbers of ions may be trapped, smaller ion numbers ensure better reproducibility of the experimental conditions. The stronger confinement of HD$^+$ by the pseudopotential leads to the formation of a string or zig-zag structure of HD$^+$ ions along the nodal line of the r.f. field, which coincides with the z axis. Be$^+$ ions arrange themselves in a three-dimensional ellipsoidal structure of HD$^+$ ions. At temperatures below 0.1 K, the two-species ion ensemble solidifies into a Coulomb crystal. 313 nm fluorescence photons emitted by Be$^+$ are imaged onto an electron multiplied charge-coupled device camera and a photomultiplier tube. We obtain a measure of the number of trapped HD$^+$ ions by resonantly driving their radial secular motion (~800 kHz) using an ac electric field$^{28}$. This ‘sweep’ increases the number of HD$^+$ ions in the ensemble, heating the Be$^+$ ions to an average temperature (in the z-direction) $T_{\text{Be},z}$ proportional to the number of HD$^+$, $N_{\text{HD}}$. Typically, $T_{\text{Be},z}$ is 2–4 K. For a fixed cooling-laser detuning $\Delta = -18$ GHz (with $\Delta = 2\times 19.4$ MHz, the natural linewidth of the 313 nm cooling transition), this temperature rise leads to Doppler-limited laser-cooling of the HD$^+$ ions in the 313-nm cooling laser direction with an average value $\bar{F}$. Whereas previous work approximated the fluorescence rise $F$ observed in the experiment, and allows us to determine five-dimensional functions $G(T,H_{\text{rep}},T_{\text{HD}},T_{\text{Be}},\bar{F})$, whereas the possible 5 K error in the BBR temperature estimate (which takes into account day-to-day temperature variations and the possibility that the trap electrodes may be at a slightly higher temperature due to r.f. dissipation) translates to a 5 kHz effect.

**Spectral line shape function for fitting.** Hyperfine rate equations allow computing the evolution of a sample of HD$^+$ ions, with an initial thermal rotational distribution$^{29}$ corresponding to $T = 300(5)$ K, under the influence of REMPD lasers, BBR and losses due to chemical reactions with background-gas molecules (Fig. 1b,d). Population in rotational states with $J = 0–5$ is included, thus ignoring the 2.4% population in $J = 6$ an higher. Accurate hyperfine line strength at the magnetic sub-state level are obtained by extending the approach of Koelmeijer$^{30}$ so as to include hyperfine structure and the Zeeman effect. The response to the 782-nm laser of each hyperfine level is modelled using a Doppler-broadened profile based on $g$-factors. For the assessment of the Zeeman effect, the hyperfine rate equation is adapted to include Zeeman splittings, which results in circular frequency shifts and broadening due to hyperfine line splitting (which remains much smaller than the 16-MHz Doppler width). The $q$ parameter is determined from realistic MD simulations (which take into account the time-dependent trap potential and momentum changes by scattering of photons from the cooling laser) with an interference limited by the minimum distance between ion impacts.

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Author contributions
J.B. and J.C.J.K built the apparatus, and acquired and analysed data. K.S.E.E. provided the optical frequency measurement system. J.-Ph.K., L.H., J.B. and J.C.J.K. evaluated systematic frequency shifts and performed simulations. W.U. and J.C.J.K. conceived and supervised the experiment. J.B. and J.C.J.K. wrote the manuscript, which was edited and approved by all co-authors.

Additional information
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