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Rovibrational spectroscopy of trapped molecular hydrogen ions at millikelvin temperatures

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We report a high-resolution spectroscopic study of molecular ions at millikelvin temperatures. We measured several rovibrational infrared transitions in HD^+ molecular ions, stored in a radio-frequency trap and sympathetically cooled to ≈20 mK by laser-cooled Be^+ ions. We observed hyperfine splitting of the lines, in good agreement with theoretical predictions. The transitions were detected by monitoring the decrease in ion number after selective photodissociation of HD^+ ions in the upper vibrational state. The method described here is expected to be generally applicable.

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In recent years, a number of novel techniques have been developed to cool the translational energy of gas-phase molecules to the millikelvin regime, where conventional cryogenic techniques are not applicable [1]. With the availability of stored ensembles of subkelvin neutral and charged molecules, sometimes also internally cold, their use for a variety of applications is moving into focus. One wide-ranging application is high-resolution spectroscopy, which is possible because the usual line-shifting and broadening effects due to collisions, high thermal velocities, and finite transit time are strongly suppressed. Spectroscopy of rovibrational transitions in the electronic ground state can take advantage of these special conditions because the lifetime of vibrational levels of molecules is typically long (~ milliseconds or longer), and thus lifetime broadening is not an important limitation. The low translational temperature also increases the absorption rate significantly, and efficient excitation is possible even on weak overtone transitions.

Subkelvin molecular ions can be obtained by sympathetic cooling [2,3]—the molecular species and a laser-coolable atomic species, with the same sign of charge, are simultaneously stored in a radio-frequency trap. Laser cooling the atoms then also efficiently cools the molecular ions via the long-range Coulomb interaction. Temperatures below 20 mK can be reliably reached. We have recently shown that using Be^+ ions as coolant permits to cool sympathetically ions from mass 1 to mass 200 amu [4–6]. A heavier atomic coolant species can be used to extend the mass range. For example, using $^{138}Ba^+$ as coolant, molecular ions up to mass 410 amu have recently been cooled [7].

Here we demonstrate high-resolution spectroscopy of vibrational transitions in a localized sample of molecular ions at millikelvin temperature. We show that high spectral resolution can be achieved even with small molecular samples and standard laser systems. We apply the technique to HD^+ ions, but it could be used in the same way to significantly improve the precision of (ground-state) level energies of a large variety of molecular ions, which have traditionally been measured in discharges [8] or in ion beams [9] and in traps equipped with buffer gas cooling (>10 K) [10].

Our application to HD^+ is motivated by the fact that it is the simplest molecule after $H_2{}^+$, and as such is of interest as a fundamental three-body quantum system. HD^+ is also important for astrochemistry [11]. In particular, a comparison between measured vibrational transition frequencies and high-precision *ab initio* calculations [12–16] could lead to the first identification of QED effects in a molecular system and to a spectroscopic measurement of the fundamental constant m_e/m_p [17] and of the deuteron quadrupole moment [18]. Previous spectroscopic studies of HD^+ and other isotopomers were performed on warm ensembles or on ion beams [9,19–21].

Vibrational spectroscopy in the electronic ground state in absence of collisions is faced with the difficulty that molecules excited to a vibrational level decay only slowly, implying very low fluorescence rates. As the fluorescence wavelengths are in the mid to far infrared, photon counting would require a sophisticated detection system. We circumvent this difficulty by applying the technique of $(1+1')$ resonance-enhanced multiphoton dissociation (REMPD): the molecules are excited by an infrared (ir) laser and then selectively photodissociated from the upper vibrational state by a second, fixed-wavelength ultraviolet (uv) laser (Fig. 1). The remaining number of molecular ions is the quantity mea-

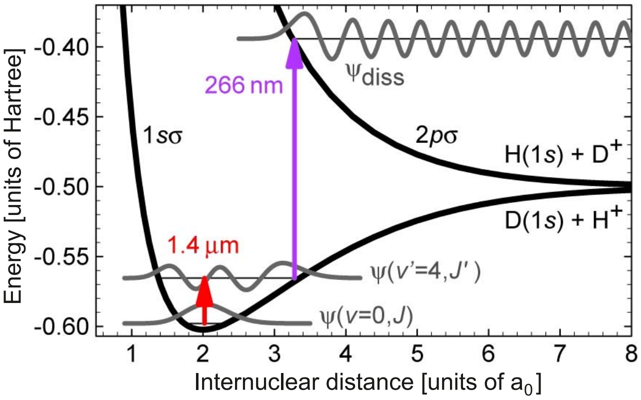

FIG. 1. (Color online) Principle of $(1+1')$ REMPD spectroscopy of HD^+ ions. A tunable ir diode laser excites a rovibrational overtone transition $(v'=4,J')\leftarrow(v=0,J)$. The HD^+ ions excited to the $v'=4$ vibrational level are dissociated using cw 266 nm laser radiation: $HD^+(v'=4)+h\nu\rightarrow H+D^+$ or H^++D. Due to different Franck-Condon wave function overlap, the calculated uv absorption cross section from the $v'=4$ level $(\sim 2.4\times10^{-17}\ \mathrm{cm}^2)$ is about seven orders of magnitude larger than from $v=0$ [25]. Energy values represent total binding energies of the molecule.

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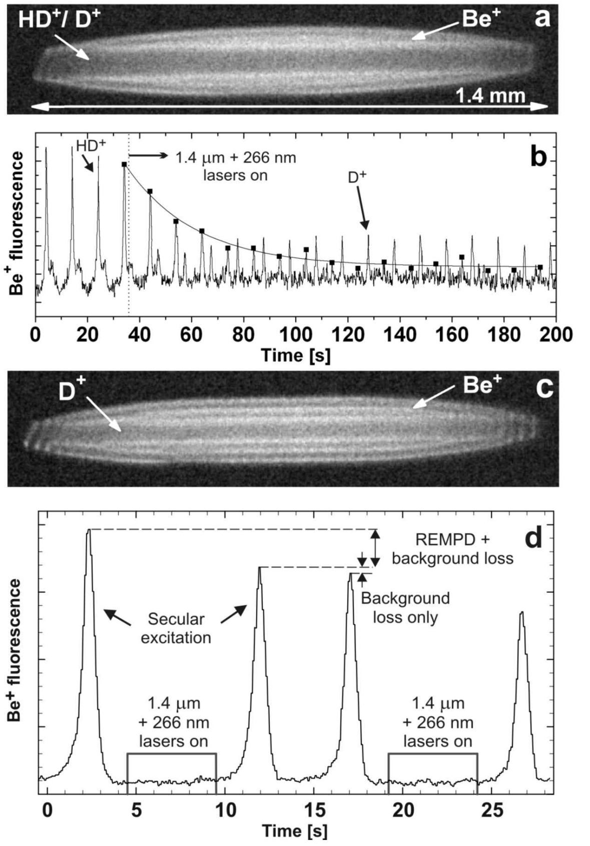

FIG. 2. (a) Initial ion crystal: $\approx$1100 Be^+, $\approx$100 HD^+, and $\approx$20 D^+ ions at $\approx$20 mK. The presence of cold HD^+ ions is obvious from the dark crystal core. (b) Repeated secular excitation of the crystal in (a) at 3 V amplitude. The excitation frequency was swept between 500 and 1500 kHz. The ir laser is tuned to the maximum of the $(v'=4,J'=1)\leftarrow(v=0,J=2)$ line. The curve is an exponential fit with a decay constant of 0.04 s^{-1}. (c) Ion crystal after dissociation of all HD^+ ions: $\approx$1100 Be^+ and $\approx$50 D^+ ions at $\approx$20 mK. (d) Measurement cycle consisting of repeated probing of the number of HD^+ ions before and after exposure to the spectroscopy lasers.

sured as a function of the frequency of the ir laser. As the molecular sample is small (typically 40–100 ions) the spectroscopy requires the spectra to be obtained by repeated molecular ion production and interrogation cycles.

For sympathetic cooling of HD^+ ions, we store both Be^+ and molecular ions in a linear radio-frequency trap [4]. The Be^+ ions are laser cooled and form a cluster structure around the trap center [22]. Due to the long-range electrostatic interaction between atomic coolants and molecular ions, the latter are efficiently cooled and embedded in the vicinity of the axis of the Be^+ ion crystals [see Fig. 2(a)]. Small numbers of D^+ ions, formed during loading by dissociation of neutral HD, are also present, but do not influence the subsequent measurements. The crystal in Fig. 2(a) contains $\approx$1100 Be^+, $\approx$100 HD^+, and $\approx$20 D^+ ions at a translational temperature of $\approx$20 mK. The HD^+ clusters formed have lifetimes of several minutes, limited by chemical reactions with residual gas. Inside the clusters, the ions perform a diffusive motion due to the residual thermal energy. Since the particles repel each other, the long-range collisions do not lead to significant line shifts or line broadening.

The trapped species are identified and the time evolution of their numbers is monitored by excitation of their mass-dependent radial (secular) modes, using a spatially homogenous and temporally oscillating electric field. We use molecular dynamics simulations to deduce ion numbers, spatial distributions, and upper limits for the translational temperature of the ions [4]. We excite HD^+ at an electric field frequency around 840 kHz. As a consequence, the atomic coolants are heated by the molecular ions, which changes the scattering rate of 313 nm cooling light by the Be^+ ions. The secular resonance becomes visible in the Be^+ fluorescence [see Fig. 2(b)], and its height is proportional to the amount of HD^+ in the ion crystal. Typically we use a 3 V peak-to-peak potential amplitude, applied to an electrode outside the trap, with the frequency being swept linearly from 500 to 1000 kHz at a rate of 0.2 Hz. Excitation amplitude, sweep rate, and covered frequency range were chosen so that the ion crystal had sufficient time to cool back to its initial temperature between individual excitation cycles.

Rovibrational spectroscopy is performed by continuous-wave (cw) excitation by a single-frequency, widely tunable diode laser, followed by photodissociation from the upper level by a cw ultraviolet laser (Fig. 1). The loss of HD^+ ions from the trap is measured. Due to the weak coupling between external and internal degrees of freedom, the internal (rotational) temperature of the HD^+ ions is expected to be at 300 K, in thermal equilibrium with the vacuum chamber [23], with a significant ($>5\%$) population for rotational levels up to $J=6$. Indeed, we have observed 12 transitions between 1391 and 1471 nm, from lower rotational levels $J=0$ to 6. The linewidth of the ir laser was ~5 MHz on a 1 s time scale, and its frequency was calibrated with an accuracy of 40 MHz by absorption spectroscopy in a water vapor cell.

The loss of HD^+ ions depends not only on the REMPD process, but also on transitions induced by blackbody radiation (BBR). We modeled the loss of HD^+ by solving the rate equations for the populations of all (v,J) levels interacting with the ir and uv lasers, as well as with the BBR radiation at 300 K. The theoretically obtained excitation spectrum (see Fig. 3 and text below) of the levels probed by the ir laser is included, but for the remainder of the calculation hyperfine structure, due to electron, nuclear, and rotational spins, is ignored. The rovibrational transition moments involved are taken from [24]. The rate of dissociation by uv light is obtained using cross sections from [25]. For typical uv intensities, dissociation rates of 10^2–10^3 s^{-1} are found. The rate equation model reveals two different time scales at which the HD^+ number declines during a typical experiment. A first, fast (<1 s) decay occurs when the ir laser selectively promotes HD^+ ions from a specific $(v=0,J)$ level to a rotational level in $v'=4$, from which they are efficiently photodissociated. This process rapidly dissociates those $(v=0,J)$ HD^+ ions which are in the hyperfine states probed by the ir laser. The remaining molecular ions (a significant fraction of the total initial number) are dissociated significantly slower, essentially at the rate at which the hyperfine levels of $(v=0,J)$ are repopulated by BBR and spontaneous emission. For example, for the $(v'=4,J'=1)\leftarrow(v=0,J=2)$ transition, and for typical intensities of 6 W/cm^2 for the ir and

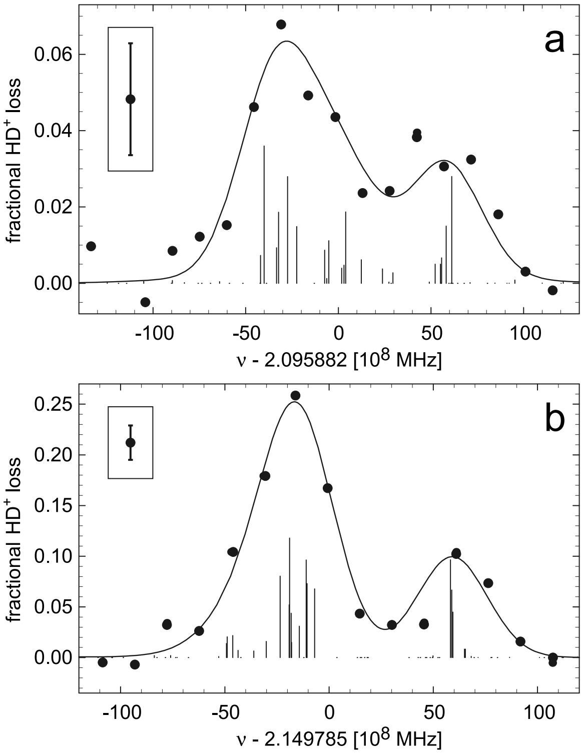

FIG. 3. Rovibrational transition spectra with partially resolved hyperfine splitting: (a) $(v'=4,J'=1)\leftarrow(v=0,J=2)$ at 1430 nm, (b) $(v'=4,J'=3)\leftarrow(v=0,J=2)$ at 1394 nm. The curves are fits to the data (●), where the theoretical stick spectra were broadened by ≈40 MHz. The theoretical spectrum exhibits a large number of very weak transitions, due to weak mixing of pure coupled angular momentum states by H_{eff}. The ordinate values are the molecular ion dissociation probability for a 5 s irradiation of 0.65 W/cm^2 ir and 10 W/cm^2 uv light. The insets show typical error bars.

10 W/cm^2 for the uv laser, the fast HD$^+$ decay takes place at a rate ~10 s^{-1} (which is not resolved experimentally), whereas the decay due to BBR-induced repopulation occurs at a rate of ~0.04 s^{-1}. The latter rate is fairly consistent with the measured decay depicted in Fig. 2(b), but observed decay rates depend strongly on which part of the hyperfine spectrum is interrogated. This points at a shortcoming of the simple rate equation model used here, and our observations can probably be explained precisely only by a rate equation model that takes the full hyperfine structure of all involved (v,J) levels into account.

As an example, Fig. 2(b) shows the time evolution of the HD$^+$ secular excitation resonance while the HD$^+$ ions are excited on the maximum of the rovibrational line $(v'=4,J'=1)\leftarrow(v=0,J=2)$ at 1430.3883 nm. The decrease of the HD$^+$ resonance in the secular excitation spectrum, induced by the REMPD process, is accompanied by a decrease of the dark crystal core containing the hydrogen molecular ions. The secular excitation spectrum also shows an increase of the number of D$^+$ ions, which result from the dissociation of excited HD$^+$ ions. These ions are sympathetically cooled and remain in the crystal core. Figure 2(c) shows the mixed-species ion crystal after all HD$^+$ was dissociated. The dark crystal core has shrunk significantly, and the crystal now contains ≈1100 Be$^+$ and ≈50 D$^+$ ions. Assuming equal probability for photodissociation to D$^+$ and H$^+$, this number indicates that most generated D$^+$ ions are sympathetically cooled and trapped. Loss rates are obtained by exponential fitting to the maxima of the HD$^+$ resonances in the secular excitation spectrum [solid line in Fig. 2(b)]. In this way, a 0.01 s^{-1} background loss rate of HD$^+$ ions from the trap is obtained when both the ir and uv lasers are turned off. This loss is due to chemical reactions between HD$^+$ ions and background gases. The observed background loss rate is fitted well by a single-exponential decay, which rules out strong nonlinear dependence of the Be$^+$ fluorescence during secular excitation on the number of HD$^+$ ions.

The spectroscopic signal used to produce the spectra in Figs. 3(a) and 3(b) is the molecular ion dissociation probability, obtained as the relative change of the heights of the HD$^+$ secular resonances in the Be$^+$ fluorescence before and after the REMPD excitation [Fig. 2(d)]. For each transition, the HD$^+$ dissociation probability was measured as a function of the frequency of the ir laser, in steps of 15 MHz. Each data point was obtained by averaging over several individual measurements of the HD$^+$ dissociation probability occurring over ~5 s. Each data point requires a new loading of HD$^+$ ions in the Be$^+$ crystal. For all measurements, comparable HD$^+$ ion numbers were used, as deduced from the size of the crystal core after loading. However, during each HD$^+$ loading cycle a small fraction of the Be$^+$ is lost from the trap, due to chemical reactions with neutral HD gas [6]. The same Be$^+$ ion crystal can be used for up to 40 HD$^+$ loadings, sufficient for obtaining the spectra in Figs. 3(a) and 3(b). A typical spectrum is taken within 1–2 h.

Detailed measurements for two transitions $(v'=4,J'=1,3)\leftarrow(v=0,J=2)$ are shown in Figs. 3(a) and 3(b). Both spectra reveal a partly resolved hyperfine structure, which can be compared with the prediction from an effective spin Hamiltonian, written as $H_{\mathrm{eff}}=b_1\mathbf{I}_p\cdot\mathbf{S}+c_1I_{pz}S_z+b_2\mathbf{I}_d\cdot\mathbf{S}+c_2I_{dz}S_z+\gamma\mathbf{S}\cdot\mathbf{J}$ [15,21]. Here, $\mathbf{I}_p$, $\mathbf{I}_d$, and $\mathbf{S}$ denote the spin of the proton, deuteron, and electron, respectively; the subscript z indicates the projection on the internuclear axis. The hyperfine coefficients b_1, b_2, c_1, c_2, and γ have been recently calculated to high accuracy [13]. The hyperfine level energies and eigenfunctions are found by diagonalization of the matrix representation of H_{eff} in a suitable angular momentum coupling scheme. Terms arising from the nuclear spin-rotation and deuteron quadrupole interactions are neglected as they contribute ≪1 MHz to the hyperfine level energies [13]. The results of the diagonalization were subsequently used to calculate line strengths of the individual hyperfine components within a given rovibrational transition, leading to "stick spectra," as shown in Figs. 3(a) and 3(b). Inhomogeneous broadening of the spectra may be accounted for by convolving each line with a Gaussian line shape of a given width.

The broadened stick spectra are fitted to the experimental spectra using the linewidth, the vertical scale and the frequency offset as fit parameters [Figs. 3(a) and 3(b)]. The frequency offset corresponds to the deperturbed rovibrational transition frequency, which is thus determined to within the accuracy of the wavelength calibration of the ir laser (40 MHz) and the fit uncertainty (3 MHz). The measured deperturbed rovibrational transition frequency is in good agreement with the *ab initio* results from [14]. The partly resolved hyperfine structure in the measured spectra agrees well with the theoretical results obtained from [13,15]. We find both theoretically and experimentally that the hyperfine structure for other transitions in the *P* and *R* branches is similar to that in Figs. 3(a) and 3(b).

We observe a typical line broadening of 40 MHz. This is remarkable, as the kinetic energy in the secular motion (as inferred from molecular dynamics simulations) of the HD^+ ions can give rise to broadening of about 10 MHz only [4]. Saturation broadening also does not play a significant role, as confirmed by comparing spectra taken at different ir and uv intensities. Using the polarization-dependent 313 nm fluorescence of the Be^+ ions as a magnetic field probe, the magnetic field (which is along the direction of propagation of the 313 nm laser beam) has been adjusted and verified to be 50 mT and to vary by no more than 40 mT over the extent of the crystal, which implies Zeeman broadening <1 MHz. This leaves Doppler broadening due to micromotion as the most probable cause for the observed line broadening. For our trap, in which the HD^+ ions are located at least 10 μm away from the trap axis, the (radial) micromotion energy exceeds $k_B \times (0.5 \text{ K})$. Through the Coulomb interaction, this radial motion couples to the axial motion, which is along the ir laser beam direction. A linewidth of 40 MHz would be explained by $k_B \times (0.2 \text{ K})$ of energy in the axial motion, and we therefore attribute the excess broadening to the Doppler effect associated with micromotion.

The results described are of significance in several respects. They demonstrate the possibility of high-resolution spectroscopy of small, trapped molecular ion samples, sympathetically cooled well into the millikelvin range. We have achieved a spectral resolution ten times higher than with any previous cold molecular ion method, and the same enhancement was obtained for the excitation rate. The observed population dynamics demonstrated the weakness of collisions. The methods used for trapping, cooling, and detection are quite general, and are applicable to a host of other molecular ion species. This includes other ions of astrophysical and cosmological interest such as H_3^+ and its isotopomers, which have been trapped in our setup [4,5]. Also, the spectral resolution achieved here may be further improved: for instance, first-order Doppler broadening may be circumvented by use of a tightly confining trap which holds the ions in the Lamb-Dicke regime, or by two-photon spectroscopy. Furthermore, the presence of the atomic coolant ions offers an *in situ* tool to detect possible perturbing fields. In the absence of first-order Doppler shifts, a spectroscopic accuracy well below the megahertz level should be attainable. For few-electron molecular ions, HD^+ in particular, this offers a realistic perspective for testing *ab initio* theoretical descriptions [12]. Finally, the present method will enable studies of internal coherence in molecules on time scales orders of magnitude longer than with conventional methods and measurements of all rovibrational levels in small ions by multistep ir excitation.

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