We present a high precision frequency measurement of the vibrational overtone transition \((v,L):(0,2) \rightarrow (8,3)\) in the deuterated molecular hydrogen ion \(HD^+\). This measurement has a resolution of 0.85 parts-per-billion (p.p.b.) and is in agreement with molecular theory within 0.6(1.1) p.p.b. We here provide the details of the experimental procedures and spectral analysis. A model is devised to obtain a spectral lineshape function which is subsequently fitted to the recorded spectrum. This model, which is generally applicable to any form of Doppler-broadened, destructive spectroscopy of finite samples of trapped ions, is sensitive to the shape of the velocity distribution. In particular we find that deviations from a thermal (Gaussian) distribution, due to laser-induced chemistry, leads to a lineshift. We perform realistic molecular dynamics simulations to obtain an estimate of the relative frequency correction, which is found to be -0.6(6) p.p.b.
4. High-precision spectroscopy of the HD$^+$ molecule

4.1 Introduction

Because of their relative simplicity, molecular hydrogen ions such as H$_2^+$ and HD$^+$ can be used as probes to test fundamental physics. Already four decades ago, Wing et al. [57] performed measurements of the ro-vibrational transitions in HD$^+$ and proposed that such measurements could be used to test quantum electrodynamics (QED) theory in molecules, and improve on the existing value of the proton-to-electron mass ratio $\mu$. With the assumption that the precision of theoretical calculations and measurements would increase in the upcoming years, precision tests of theory would increase in stringency.

Nowadays, values of ro-vibrational transition frequencies in H$_2^+$ and HD$^+$ have been calculated up to the order $m_e\alpha^8$, with $m_e$ the electron mass, and $\alpha$ the fine-structure constant, leading to relative uncertainties at the level of $10^{-11}$ [1, 2]. The frequencies of these transitions are typically in the (near-) infrared with linewidths below 10 Hz, which makes them amenable to high-resolution laser spectroscopy. Optical clocks based on trapped ions have shown that laser spectroscopy at very high accuracy (below one part in $10^{17}$) is possible [4]. Recent theoretical studies point out that for molecular hydrogen ions experimental uncertainties in the $10^{-16}$ range should be possible [14, 15]. High-precision measurements on molecular hydrogen ions can also be used to probe physics beyond the standard model, which could manifest itself in the form of hypothetical fifth forces between hadrons [69, 70] or gravitational effects from compactified higher dimensions [72]. If present, such effects might result in a discrepancy between molecular theory and experiment.

The most precise measurement of a ro-vibrational transition in HD$^+$ so far resulted in a 2.4$\sigma$ discrepancy with more accurate theoretical data [64]. The question whether this offset is a statistical outlier, or is caused by an experimental systematic effect or by possible new physics has remained unanswered. Therefore, additional experimental data on HD$^+$ are needed. In this article we present a high-precision frequency measurement of the ro-vibrational transition $(v,L):(0,2)\rightarrow(8,3)$ in the HD$^+$ molecule, and compare it with state-of-the-art molecular theory. From this comparison one can derive new constraints on possible new physics in HD$^+$ and determine a value of $\mu$ for the first time from a molecular system [76].

This article is organized as follows. In Sec. 4.2 we briefly review the theory of HD$^+$ relevant to this experiment. In Sec. 4.3 we describe a setup where HD$^+$ is trapped in a Paul trap and sympathetically cooled with beryllium ions. A non-destructive detection scheme is presented which is used as a diagnostic tool for spectroscopy. The analysis of the data based on a line-shape fit model is described in Sec. 4.4. Here a significant effect of chemical processes in a Coulomb crystal is discussed for the first time.
4.2 Theory

4.2.1 Calculation of ro-vibrational frequency transitions in HD$^+$

The calculation of ro-vibrational energies in quantum mechanical three-body systems can be split into two main parts: the non-relativistic energies and the other contributions, i.e. relativistic and radiative energies and finite nuclear size effects. The non-relativistic part is calculated through solving the three-body Schrödinger equation, which can be done with practically infinite precision [44] (up to relative precision of $\sim 10^{-30}$ [48]). The resulting wavefunctions allow an analytical evaluation of the Breit-Pauli Hamiltonian and the leading-order radiative corrections.

The precision of relativistic and radiative energy corrections to the non-relativistic energies was recently strongly improved. With the inclusion of the full set of contributions of order $m\alpha^7$ and leading-order terms of order $m\alpha^8$, the relative uncertainty is now below $4 \times 10^{-11}$. For example, the theoretically determined value of the ro-vibrationial ($v, L$):$(0,2)\rightarrow (8,3)$ transition frequency in HD$^+$, $\nu_{th}$, is $383,407,177.150(15)$ MHz, and has a relative uncertainty of $4 \times 10^{-11}$ [1,2]. Note that the specified error (within parentheses) does not include the uncertainty of the fundamental constants used. By far the largest contribution is due to the $4.1 \times 10^{-10}$ uncertainty of $\mu$ (2010 CODATA table), which translates to a frequency uncertainty of 59 kHz.

4.2.2 Hyperfine structure and rotational states

Since the HD$^+$ constituents possess nonzero spin, the ro-vibrational transition spectra contain hyperfine structure due to spin-spin and spin-orbit couplings. In [109] the hyperfine energy levels and eigenstates in HD$^+$ are calculated by diagonalization of the effective spin Hamiltonian:

$$H_{\text{eff}} = E_1(L \cdot s_e) + E_2(L \cdot I_p) + E_3(L \cdot I_d) + E_4(I_p \cdot s_e)$$
$$+ E_5(I_d \cdot s_e) + E_6 K_d(L,I_p,s_e) + E_7 K_d(L,I_d,s_e)$$
$$+ E_8 K_d(L,I_p,I_d) + E_9 K_Q(L,I_d), \quad (4.1)$$

where the spin coefficients, $E_i$, are obtained by averaging the Breit-Pauli Hamiltonian over the nonrelativistic wavefunctions, $L$ is the rotational angular momentum operator, and $s_e, I_p$ and $I_d$ are the electron, proton and deuteron spin operators. $K_d$ and $K_Q$ are spherical tensors composed of angular momenta, whose explicit form is given in [109]. The strongest coupling is the proton-electron spin-spin interaction (the term in $E_4$ in Eq. (4.1)), which is the Fermi contact term on the proton, and the preferred angular momentum coupling
4. High-precision spectroscopy of the HD$^+$ molecule

scheme is

\[ \mathbf{F} = \mathbf{I}_p + \mathbf{s}_e \quad \mathbf{S} = \mathbf{F} + \mathbf{I}_d \quad \mathbf{J} = \mathbf{L} + \mathbf{S}. \]  

(4.2)

This leads to hyperfine levels spread out over an energy range of $\sim 1$ GHz, as schematically depicted in Fig. 4.1. Diagonalization produces eigenstates $\phi_{\tilde{F}\tilde{S}JM_J}$, with the magnetic quantum number $M_J$ corresponding to the projection of $J$ onto the laboratory-fixed $z$-axis. Note that after diagonalization the quantum numbers $(\tilde{F}\tilde{S})$ are only approximately good (which is why they are labeled with a tilde), and a hyperfine eigenstate can be expressed in the ‘pure’ basis states $|FSJM_J\rangle$ as follows:

\[ \phi_{\tilde{F}\tilde{S}JM_J} = \sum_{F,S} \beta_{FSJ} |FSJM_J\rangle, \]  

(4.3)

with real-valued coefficients $\beta_{FSJ}$. In [109] the hyperfine levels in vibrationally excited states in HD$^+$ are calculated with an uncertainty of $\sim 50$ kHz, but the uncertainty effects on the $(v,L):(0,2)\rightarrow(8,3)$ transition are much smaller due to a large common mode cancellation (see Sec. 4.4.6).
4.2. Theory

4.2.3 Determination of transition rates

Because of the hyperfine structure, the spectrum of the \((0,2) \rightarrow (8,3)\) electric dipole transition consists of a large number of hyperfine components. Together with Doppler broadening, this leads to an irregular lineshape function. In addition, the excitation laser may address multiple hyperfine states simultaneously, which are furthermore coupled to other rotational states by the ambient 300 K blackbody radiation (BBR) field. Therefore, for the analysis of the \((0,2) \rightarrow (8,3)\) signal we develop a model based on Einstein rate equations which take all resonant molecule-electric field interactions into account. We note that at 300 K, states with \(v = 0\) and \(L = 1–6\) are significantly populated, with 27\% in \(L = 2\) (see Fig. 4.2). Below, we calculate the Einstein rate coefficients at the level of individual hyperfine states for transitions driven by the laser and BBR fields.

Following the approach of Koelemeij [93], we first ignore hyperfine structure and solve the radial Schrödinger equation which gives the radial wave function of nuclear motion \(\chi_{v,L}^{\prime}\):

\[
\frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2} \chi_{v,L}(R) + \left[ V(R) + \frac{\hbar^2 L(L + 1)}{2\mu_{\text{red}} R^2} \right] \chi_{v,L}(R) = E_{v,L} \chi_{v,L}(R) \tag{4.4}
\]

where \(R\) is the nuclear separation, \(\mu_{\text{red}}\) stands for the reduced mass of the molecule, \(v\) labels vibrational state, \(L\) is the angular momentum and \(E_{v,L}\) is the ro-vibrational energy. \(V(R)\) is the potential energy curve belonging to the \(1s\sigma\) electronic ground state of HD\(^{+}\) which is shown in Fig. 4.4a. The transition dipole moment is then given by

\[
\mu_{vL' L} = \int_{0}^{\infty} \chi_{v',L'}(R) D_1(R) \chi_{v,L}(R) dR \tag{4.5}
\]
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where \(D_1(R)\) denotes the permanent electric dipole moment of the 1s\(\sigma\) state which is calculated along with the potential energy curve in [42].

To take hyperfine structure into account we write the dipole transition matrix elements between the states \(\phi_{F\tilde{S}JM_J\chi v,L}\) and \(\phi_{F'\tilde{S}'J'M'_J\chi v',L'}\) as [93, 110, 111]:

\[
\langle \phi_{F\tilde{S}JM_J\chi v,L} | \vec{E} \cdot \vec{\mu} | \phi_{F'\tilde{S}'J'M'_J\chi v',L'} \rangle = \sum_{F'S'} \beta_{FSJ} \beta_{F'S'J'}^* E_p (-1)^{J+J'+S-M_J+1+L'+L} \\
\times \left[ (2J+1)(2J'+1)(2L+1)(2L'+1) \right]^{1/2} \\
\times \left( \begin{array}{ccc} L & 1 & L' \\ M_J & p & M_J - p \end{array} \right) \left( \begin{array}{ccc} L & 1 & L' \\ 0 & 0 & 0 \end{array} \right) \left\{ \begin{array}{ccc} L' & J' & S \\ J & L & 1 \end{array} \right\} \\
\times \mu_{vv'LL'}. \tag{4.6}
\]

Here we have used a transformation from the molecule fixed frame to the laboratory frame with \(p = -1, 0, 1\) denoting the polarization state of the electric field with respect to the laboratory frame [110].

The linestrength is subsequently calculated by squaring and summing over the \(M_J\) states [112]:

\[
S_{\alpha\alpha'} = \sum_{M_J} |\langle \phi_{F\tilde{S}JM_J\chi v,L} | \vec{E} \cdot \vec{\mu} | \phi_{F'\tilde{S}'J'M'_J\chi v',L'} \rangle|^2, \tag{4.7}
\]

with \(\alpha \equiv vLFSJ\). The Einstein rate coefficients for spontaneous emission, absorption and stimulated emission \((A_{\alpha\alpha'}, \bar{B}_{\alpha\alpha'}\;\text{and}\;B_{\alpha\alpha'})\) are obtained through the relations

\[
A_{\alpha\alpha'} = \frac{2\omega_{vv'LL'}^3}{3\hbar c^3} S_{\alpha\alpha'} \tag{4.8}
\]

\[
B_{\alpha\alpha'} = \frac{\pi^2 c^3}{\hbar \omega_{vv'LL'}^3} A_{\alpha\alpha'} \tag{4.9}
\]

\[
\bar{B}_{\alpha\alpha'} = \frac{2J'+1}{2J+1} B_{\alpha\alpha'}. \tag{4.10}
\]

Note that we use the hyperfineless transition frequency \(\omega_{vv'LL'}\) rather than \(\omega_{\alpha\alpha'}\), which has a negligible effect on the value of the rate coefficients. These results are used in Sec. 4.4.1 to calculate the expected \((0,2)\rightarrow(8,3)\) signal, which is incorporated into a model describing the dynamics during the spectroscopic measurement.

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4.3 Experiment

4.3.1 Trapping and cooling Be$^+$ and HD$^+$

To achieve narrow linewidths and small systematic shifts, we choose to perform spectroscopy on small samples of HD$^+$ molecules in a radiofrequency (rf) ion trap. We reduce the motional temperature of the HD$^+$ ions by storing them together with HD$^+$ ions which are Doppler-cooled by a continuous-wave (cw) 313 nm laser beam (see [75,93] and [113] for details). The rf trap is placed inside an ultra-high vacuum chamber with a background pressure of $1 \times 10^{-10}$ mbar. The rf trap operates at a frequency of 13.2 MHz, leading to Be$^+$ radial trap frequencies of $\omega_r = 2\pi \times 290$ kHz. The trap geometry and rf circuitry are designed so as to minimize unwanted rf fields and phase differences between the rf electrodes. The two dc electrodes are segmented into two endcaps and a center electrode (Fig. 4.3). The dc voltages of the center electrodes, rf electrodes and endcap pairs can be individually adjusted to compensate stray electric fields. Be$^+$ and HD$^+$ are loaded by electron-impact ionization as done by Blythe et al., and monitored with a photomultiplier tube (PMT) and an electron-multiplied charge-coupled-device (EMCCD) camera [114]. EMCCD images show ellipsoidal mixed-species Coulomb crystals, with a dark core of molecular hydrogen ions surrounded by several shells of fluorescing Be$^+$ ions. The apparatus and procedures for loading and compensation of stray electric fields is described in more detail in [93].

4.3.2 Spectroscopy of HD$^+$

The (0,2)→(8,3) transition in HD$^+$ is detected destructively through resonance enhanced multi-photon dissociation (REMPD), see Fig. 4.4a. A 782 nm cw titanium:sapphire laser is used to excite HD$^+$ from its vibrational ground state to the $v=8$ state, which is efficiently dissociated by the field of a co-propagating 532 nm cw laser beam. Both lasers are directed along the trap axis and counterpropagate the 313 nm laser (see Fig. 4.3). Since all HD$^+$ are initially in the vibrational ground state, dissociation via the $v=8$ level only takes place if the 782 nm laser is resonant with the (0,2)→(8,3) transition. We used 90 mW of 532 nm radiation, focused to a beam waist of 140 µm, which is sufficient to dissociate an HD$^+$ molecule from this level within a few ms, much faster than the spontaneous decay of the $v=8$ state (lifetime 12 ms).

A single REMPD cycle lasts 10 seconds. During the first seconds of REMPD the majority of the HD$^+$ in $L=2$ is dissociated, leading to depletion of the $L=2$ state (Fig. 4.4). During the remainder of the cycle, BBR repopulates the $L=2$ state from other rotational levels, and this enhances the number of dissociated HD$^+$ ions by approximately a factor of 2.
4. High-precision spectroscopy of the HD$^+$ molecule

Figure 4.3: Schematic view of the trap setup. An ultrahigh vacuum (UHV) chamber houses a linear rf trap in which Be$^+$ ions and deuterated molecular hydrogen ions are loaded by electron-impact ionization. Be$^+$ ions are Doppler-cooled by the 313 nm laser, which is directed in parallel to the trap axis and B field direction. The 313 nm Be$^+$ fluorescence is imaged onto and detected with a PMT and an EMCCD camera. The 782 nm and 532 nm cw REMPD lasers are overlapped with the 313 nm laser and the ions, but propagate in the opposite direction.
4.3. Experiment

Figure 4.4: (a) Potential energy curves of the 1s\(\sigma\) and 2p\(\sigma\) electronic states are plotted together with the radial nuclear wave functions for \(v=0\), \(v=8\) and for the dissociative wave function in the 2p\(\sigma\) state. The REMPD scheme is also shown, with the red arrow indicating the \((v,L):(0,2)\rightarrow(8,3)\) transition by the 782 nm laser and the green arrow corresponding to the 532 nm photon which photodissociates the molecule. (b) Detailed partial level scheme showing the \((0,2)\rightarrow(8,3)\) transition including hyperfine levels together with the BBR interaction which couples the rotational levels \(L=1,2,3\). Coupling to \(L=0\) and \(L=4,5,6\) also occurs, but is not shown here. (c) A schematic view of the HD\(^+\) molecule showing the angular momenta responsible for the hyperfine structure and rotational motion.
The 782 nm laser has a linewidth of ∼0.5 MHz and is frequency-stabilized by locking its frequency to a nearby mode of a self-referenced optical frequency comb laser. To this end, a 63.5 MHz beat note is created by mixing the light of the 782 nm laser and the frequency comb. The frequency comb itself is locked onto a rubidium atomic clock for short-term stability, which is disciplined to the 1-pps signal of a GPS receiver for long-term accuracy and traceability to the SI second. The resulting relative accuracy of the frequency measurement system is $2 \times 10^{-12}$.

The ∼25 strongest hyperfine components of the $(0, 2) \rightarrow (8, 3)$ transition are located in the range ($-110$ MHz, $140$ MHz) around the hyperfine-less frequency. As we expect Doppler broadening to ∼16 MHz, we divide this range into a set of 140 evenly spaced frequencies at which REMPD spectroscopy is performed. To convert possible time-varying systematic effects into random noise, we randomize the ordering of the frequency list. For each frequency point, six to seven REMPD measurements are made, which gives us a set of ∼900 REMPD measurements in total.

During REMPD, about 300 mW of 782 nm light is used with a beam waist of ∼120 µm at the location of the ions. The 313 nm cooling laser is detuned to $-80$ MHz from the cooling resonance and reduced in power to ∼70 µW, which results into an intensity of two times the saturation intensity of the 313 nm cooling transition, and leads to an ion temperature of about 10 mK.

To obtain a measure of the fraction of HD+ ions lost during REMPD, we employ so-called secular excitation [115]. This procedure is based on the indirect heating of the Be+ which occurs when the motion of HD+ ions is resonantly excited by an additional radial rf field. The heating of Be+ leads to a change of the 313 nm fluorescence, which is connected to the number of HD+ ions. Before and after each REMPD cycle an rf frequency scan is scanned over the secular motional resonance of HD+ at ∼830 kHz. This induces a temporal rise of temperature in the Coulomb crystal up to a few Kelvin. At a detuning of the 313 nm cooling laser of $-300$ MHz and using a few mW of laser power, such a ‘secular scan’ shows up as a peak of the 313 nm beryllium fluorescence yield (see Fig. 4.5). In Appendix B we show that the area under this peak, $A$, scales with the number of HD+ ions, although not linearly. A single measurement cycle consists of a secular scan (10 s), followed by 10 s of REMPD and another 10-s secular scan (see Fig. 4.5). We define our spectroscopic signal as the relative difference between the areas of the initial and final secular scan peaks:

$$S = \frac{A_i - A_f}{A_i} \quad (4.11)$$

Repeating this procedure for all frequencies $\nu$ of the 782 nm laser while recording fluorescence traces with both the PMT and EMCCD camera, we obtain a total set of 1772 of data points ($\nu, S$).
4.4 Results and Discussion

4.4.1 A spectral lineshape model

In order to determine the spinless ro-vibrational \((0,2)\rightarrow(8,3)\) transition in HD\(^+\), having frequency \(\nu_0\), we need a realistic lineshape model which includes the relevant physics present during REMPD. Here the aim is to obtain a spectral lineshape function which parametrizes all effects. Parameters are estimated by independent means where possible, or included as a fit parameter otherwise. Importantly, the fit function will contain \(\nu - \nu_{0,\text{fit}}\), where \(\nu_{0,\text{fit}}\) is a fit parameter from which we later deduce the value of \(\nu_0\). Before fitting, the \((\nu, S)\) data is corrected for reactions with background gas (primarily \(\text{H}_2\)). This procedure is described below in Sec. 4.4.5.

We start with building a state vector \(\rho(t)\) which contains the population in all 62 hyperfine levels in the rotational states ranging from \(L=0\) to \(L=5\) in the \(v=0\) level. This includes 97.6% of the total internal states of \(v=0\) given a blackbody-radiation temperature of 300 K. We neglect the Zeeman splitting.

Figure 4.5: The secular scan - REMPD - secular scan detection scheme. Each cycle starts with loading a new sample of HD\(^+\) ions in the ion trap. During loading the Be\(^+\) ions are exposed to neutral HD gas, leading to the formation of a small number of BeH\(^+\) and BeD\(^+\) ions (see also Table 4.1). These are expunged from the trap by applying a dc quadrupole potential of \(\sim 0.9\) V, which reduces the trap depth such that only ions with mass \(\leq 9\) amu remain trapped (see Sec. 2.2). Five seconds after loading, the HD\(^+\) is motionally excited by scanning an rf electric field over the secular motional resonance frequency at 830 kHz. A 313 nm laser detuning of \(-300\) MHz is used, in which case the secular excitation results in a rise in the Be\(^+\) fluorescence. Ten seconds later, the 313 nm laser is detuned to \(-80\) MHz from the Be\(^+\) resonance and its intensity reduced to \(I \sim 2I_{\text{sat}}\). After 10 s of REMPD, the 313 nm laser settings are restored to their values as used for the first secular scan, and a second secular scan is executed. A smaller 313 nm fluorescence peak indicates loss of HD\(^+\).
4. High-precision spectroscopy of the HD\(^+\) molecule
due to 0.19 mT B-field at the location of the trapped ions, as this splitting is
negligibly small compared to the Doppler linewidth and the width of the BBR
spectrum. The lineshift due to the Zeeman effect is considered separately in
Sec. 4.4.6. Also the Stark effect, the electric-quadrupole shift and 2\(^{nd}\) order
Doppler shift are not included in this model, but addressed in Sec. 4.4.6.

During the 10 s of REMPD the hyperfine levels in the \(L=2\) initial state
interact with the 782 nm laser and BBR. We here make the simplifying as-
sumption that any population in the \(v=8\) target state will be dissociated by
the 532 nm laser. The interaction with the 782 nm laser is therefore modeled
as a simple loss process. The evolution of the state vector \(\rho(t)\) is obtained by
solving the set of coupled rate equations:

\[
\frac{d\rho(t)}{dt} = M_R \rho(t) + M_{BBR} \rho(t),
\]

where \(M_R\) and \(M_{BBR}\) are the matrices describing the interaction with the
REMPD lasers and BBR field. The matrix elements of \(M_R\) are given by

\[
M_{R,ij} = B_{ij} D_z (\omega, T_{HD^+}) I_{\text{laser}} / c,
\]

where \(B_{ij}\) denotes the Einstein coefficient belonging to a particular transition
between hyperfine levels in \(v=0\) and \(v=8\). \(I_{\text{laser}}\) is the intensity of the 782
nm laser and \(D_z\) represents a normalized response function averaged over the
distribution of \(z\)-velocities of the HD\(^+\) ions. This involves an integration over all
frequencies \(\omega = \omega' - k_z v_z\), where \(\omega'\) is the (fixed) angular frequency of the
782 nm laser in the laboratory frame, \(k_z\) the wavevector of the laser and \(v_z\) the
velocity in the \(z\)-direction. If the HD\(^+\) velocity distribution is thermal (Gaus-
sian), \(D_z\) depends only on the temperature in the \(z\)-direction, \(T_{HD^+}\). However,
the effects of micromotion and chemistry during REMPD in the Coulomb crys-
tal lead to deviations from a thermal distribution. This implies that \(D_z\) cannot
be described by a single Gaussian lineshape. In Secs. 4.4.3 and 4.4.4 those pro-
cesses are explained in detail and the precise shapes of \(D_z\) are determined.

\(M_{BBR}\) is given by

\[
M_{BBR} = A_{ij} + (\tilde{B}_{ij} + B_{ji}) W(\omega, T_{BBR})
\]

with \(A_{ij}\), \(\tilde{B}_{ji}\) and \(B_{ij}\) the Einstein coefficients of spontaneous emission, ab-
sorption and stimulated emission by BBR, respectively. \(W(\omega, T_{BBR})\) denotes
the BBR energy distribution function, which is given by:

\[
W(\omega, T_{BBR}) = \frac{h \omega^3}{\pi^2 c^3} \left( e^{\frac{\hbar \omega}{k_B T_{BBR}}} - 1 \right)^{-1}.
\]

Since the typical frequency of the internal degrees of freedom (> 1 THz) differs
from that of the external degrees of freedom (< 1 MHz) by many orders of
4.4. Results and Discussion

Any energy transfer mechanism between them must be of extremely high order and consequently negligibly small. Laser cooling of the external degrees of freedom may therefore be expected to have no significant effect on the temperature of the internal degrees of freedom, which are coupled strongly to (and in equilibrium with) the BBR field [116].

We use Mathematica to solve Eq. (4.12) in order to obtain $\rho(t)$. We subsequently find the relative HD$^+$ loss, $\epsilon$, by summing over the hyperfine state populations (62 hyperfine states in $v, L=(0,2)$) before ($t = 0$) and after ($t = 10$) REMPD and computing:

$$
\epsilon = \frac{N_i - N_f}{N_i} = \frac{\sum_{j}^{62} \rho_j(0) - \rho_j(10)}{\sum_{j}^{62} \rho_j(0)}.
$$

(4.16)

Here $N_i$ and $N_f$ are the numbers of HD$^+$ ions present in the trap directly before and after REMPD, respectively. Note that for a thermal ensemble of HD$^+$ ions, $\epsilon \equiv \epsilon(\nu - \nu_{0,\text{fit}}, T_{\text{HD}^+}, I_{\text{laser}})$, which is furthermore assuming an blackbody radiation field at $T = 300$ K.

The question arises what the relation is between the signal $S$ defined in Eq. (4.11) and the fractional loss $\epsilon$ defined above. In previous work it was assumed that $S$ and $\epsilon$ are interchangeable [63, 93, 115, 117]. In Appendix B we study the dependence of the signal $S$ on the initial number of ions $N_i$ and the dissociated fraction $\epsilon$ in detail using realistic molecular dynamics (MD) simulations. We find that the fraction $\epsilon$ (which is a theoretical construct) can be mapped to the ‘signal domain’ $S$ by use of a slightly nonlinear function,

$$
S_{\text{fit}} = f_{\text{NL}}(\bar{T}_0, \epsilon)
$$

(4.17)

where $\bar{T}_0$ is defined as the average Be$^+$ temperature along the $z$-axis during the initial secular scan of the REMPD cycle. This means we have to use a five-dimensional fit function

$$
S_{\text{fit}}(\bar{T}_0, \epsilon(\nu - \nu_{0,\text{fit}}, T_{\text{HD}^+}, I_{\text{laser}})) = S_{\text{fit}}(\nu - \nu_{0,\text{fit}}, T_{\text{HD}^+}, I_{\text{laser}}, \bar{T}_0).
$$

(4.18)

An analytical solution of the fit function proves difficult to find, whereas a numerical implementation of the fit function takes excessively long to compute. Therefore we compute values of $S_{\text{fit}}$ on a dense grid of values ($\nu - \nu_{0,\text{fit}}, T_{\text{HD}^+}, I_{\text{laser}}, \bar{T}_0$), which we interpolate (again using Mathematica) to find a fast, continuous and smooth approximation to the function $S_{\text{fit}}$, which is suitable for nonlinear least squares fitting. A 3D projection of this interpolated function (assuming fixed values of $I_{\text{laser}}, \bar{T}_0$ and $\nu_{0,\text{fit}}$) is plotted in Fig. 4.6. The reason for treating $I_{\text{laser}}$ as a fit parameter instead of inserting a single fixed value is the following. The entire spectroscopy measurement is divided into 15 sessions each taken at a different day. To ensure reproducible laser
4. High-precision spectroscopy of the HD$^+$ molecule

![Figure 4.6](image)

**Figure 4.6:** A plot of the fit function $S_{\text{fit}}$ with $I_{\text{laser}}=1.0 \times 10^7 \text{ Wm}^{-2}$, $\bar{T}_0=4 \text{ K}$ and $\nu_{0,\text{fit}} = \nu_{\text{th}}$. On the frequency axis, the theoretical values of transitions between the particular hyperfine levels are depicted as sticks. The height of the sticks corresponds to their linestrengths. The colors of the sticks are the same colors used in Fig. 4.4 and distinguish different groups of transitions with similar $F$ and $S$ quantum numbers. For decreasing HD$^+$ temperature, Doppler broadening is reduced and the hyperfine structure becomes more resolved. Effects of saturation are also visible in the spectrum.

Beam intensities from session to session, we used diaphragms to overlap all laser beams with the 313 nm cooling laser, which itself is aligned with the Be$^+$ Coulomb crystal visually using the EMCCD camera. Using a mock version of this setup, we verified that this procedure leads to beam pointing errors up to 40 $\mu$m. Assuming a Gaussian distribution of beam pointing errors, we find an intensity at the location of the HD$^+$ ions which varies from the intensity in the center of the beam by a factor of 0.6 to 1. Since the spectral line shape is strongly saturated, these variations of the intensity only lead to small signal changes. It is therefore allowed to treat $I_{\text{laser}}$ as a free fit parameter which represents the average 782 nm laser intensity for all data points. Similarly, the variables $T_{\text{HD}^+}$ and $\bar{T}_0$ cannot be determined accurately a priori and are treated as free fit parameters as well.

4.4.2 Estimation of absolute trapped ion numbers

As explained in Sec. 4.4.4, effects of chemistry in the Coulomb crystal significantly influence the measured lineshape of the $(0,2)\rightarrow(8,3)$ transition. The impact of such effects depends on (and can be estimated from) the absolute numbers of beryllium ions and molecular hydrogen ions. In order to estimate absolute numbers we combine results from MD simulations and spectroscopy. Similar as observed by Blythe *et al.* [114], our mixed-species ion ensembles...
contain not only Be\(^+\) and HD\(^+\), but also BeH\(^+\), BeD\(^+\), H\(_2\)D\(^+\), and HD\(_2\)^{+}. In this paragraph we focus on the latter two species which are created during the HD\(^+\) loading procedure through the exothermic reactions

\[
\text{HD} + \text{HD}^+ \rightarrow \text{H}_2\text{D}^+ + \text{D} \quad (4.19)
\]

and

\[
\text{HD} + \text{HD}^+ \rightarrow \text{HD}_2^+ + \text{H}. \quad (4.20)
\]

Triatomic hydrogen ions can be detected by secular excitation. An example is shown in Fig. 4.7, where the peak in the PMT signal at the left is attributed to the overlapping peaks belonging to species with charge-to-mass ratios 1:4 and 1:5, corresponding to H\(_2\)D\(^+\) and HD\(_2\)^{+}, respectively. In rf traps, lighter species experience stronger confinement (Sec. 2.2). This is evident from EM-CCD camera images which exhibit fluorescing Be\(^+\) ions surrounding a dark core of lighter species (Fig. 4.8). The size of the core reflects the total number of light ions. We analyze this by means of MD simulations (Appendix A), from which a relation is obtained between the size of the dark core and the number of trapped ions. By comparing simulated and real EMCCD images, an average number of \(\sim 750\) Be\(^+\) ions is obtained. From the analysis of the intensity profiles, we cannot distinguish the HD\(^+\) from the triatomic molecular species. To solve this we use a collection of 140 EMCCD images taken before and after REMPD while the 782 nm laser was tuned at the same fixed frequency near the maximum of the \((0,2)\rightarrow(8,3)\) spectrum. From the lineshape model we estimate that the average relative HD\(^+\) loss is 0.57 at this frequency. By comparing the
4. High-precision spectroscopy of the HD$^+$ molecule

Figure 4.8: (a) An EMCCD image of the Be$^+$ fluorescence just before a secular scan. (b) An image of ions obtained from a MD simulation based on 750 Be$^+$ ions and 50 ions with masses 3, 4 and 5 amu.

EMCCD images taken before and after REMPD with the simulated images, we also determine the total initial and final numbers of light ions. Combining this with the expected loss of 57% of the HD$^+$ ions, we infer the ratio of HD$^+$ numbers to heavier molecular species (H$_2$D$^+$, HD$_3^+$). An average number of 43 HD$^+$ ions is obtained together with 60 ions of heavier species. We cannot determine the relative abundance of H$_2$D$^+$ and HD$_3^+$, but previous observations indicate a branching ratio between Eqs. (4.19) and (4.20) of 1:1 and, thus, equal abundances [53,118]. The set of EMCCD images shows an appreciable spread in the size of the dark core and, in particular, the ratio of HD$^+$ to heavier triatomic hydrogen ions. Variations in both are due to uncontrolled shot-to-shot fluctuations of the HD background pressure during HD$^+$ loading. The resulting standard deviation of the number of HD$^+$ is 41 ions. This also indicates that analysis of EMCCD images (under the present conditions) is not suitable to replace the signal obtained by mass-selective secular excitation (Eq. (4.11)).

For the treatment of effects of chemistry on the lineshape below, we consider two scenarios:

- Scenario a: $N_{\text{HD}^+} = 43$, $N_{\text{H}_2\text{D}^+} = N_{\text{HD}_2^+} = 30$
- Scenario b: $N_{\text{HD}^+} = 84$, $N_{\text{H}_2\text{D}^+} = N_{\text{HD}_2^+} = 60$,

where scenario b reflects the one sigma upper variation.

4.4.3 Effect of micromotion

The rf quadrupole field of the ion trap inevitably leads to micromotion of ions with non-zero displacement from the trap z-axis. In addition, excess micromotion may be caused by unwanted rf fields arising from geometrical
imperfections of the trap electrode structure or phase differences between the rf electrodes [87]. In an ideal linear rf trap, micromotion is strictly radially oriented, but small imperfections in the trap geometry can cause excess micromotion with a component along the trap axis and laser direction, thus adding sidebands to each hyperfine component in the (0,2)→(8,3) spectrum. Due to the combination of an asymmetric and saturated lineshape of the (0,2)→(8,3) spectrum, these sidebands can lead to a shift of ν₀. Therefore the micromotion amplitude along the 782 nm laser needs to be determined. As the laser propagates virtually parallel to the trap axis, and since the HD⁺ ions are always located near the trap axis, we are primarily concerned with the possible axial micromotion component.

The HD⁺ axial micromotion amplitude x_{HD⁺}, can be determined through fluorescence measurements of a trapped string of beryllium ions by using a modified version of the photon-rf field correlation technique [87]. The idea here is to displace a string of about 10 Be⁺ ions by ~100 µm by applying a static offset field. This will induce significant radial micromotion, in addition to the axial micromotion. The 313 nm cooling laser propagates at an unknown but small angle θ (θ <10 mrad) with respect to the trap axis, and may therefore have a nonnegligible projection along the radial direction. In Appendix C we show that if the rf voltage, V₀, is varied, the axial micromotion amplitude scales linearly with V₀, while the radial one varies as θ/V₀². The latter behavior stems from the V₀-dependent confinement and the concomitant variation of the Be⁺ radial displacement with V₀. Thus, measuring the micromotion amplitude for various values of V₀ allows separating the radial and axial contributions.

To determine the micromotion amplitude, we use a similar setup as described in [87]. Photons detected with the PMT are converted to electrical pulses and amplified by an amplifier-discriminator, which generates a START pulse at time tᵢ. Subsequently, a STOP pulse is generated at time tᵢ through another amplifier-discriminator at the first downward zero crossing of the rf signal. A time-to-amplitude converter (TAC) converts the duration between the START and STOP pulses to a voltage. We record the TAC output voltage with a digital phosphor oscilloscope for 400 ms. We subsequently process the stored voltage trace with a computer algorithm to obtain a histogram of START-STOP time delays, employing 1-ns bins in a range 0-76 ns (i.e. one rf cycle). The bin heights thus reflect the scattering rate as a function of the rf phase, and micromotion will lead to a modulation of the scattering rate about its mean value (Fig. 4.9). The Be⁺ scattering rate (indicated as R^{MB}, where
MB stands for Maxwell-Boltzmann) is given by:

\[
R^{MB} = \frac{\Gamma}{2} \sqrt{\frac{m_{\text{Be}}}{2\pi k_B T}} \int \frac{I/I_{\text{sat}}}{I/I_{\text{sat}} + 1 + (2(\Delta - \mathbf{k} \cdot (\mathbf{v}_\mu - \mathbf{v}))/\Gamma)^2} \exp \left( -\frac{m_{\text{Be}} v^2}{2k_B T} \right) dv
\]

(4.21)

where \(m_{\text{Be}}\) is the Be\(^+\) mass, \(T\) is the Be\(^+\) temperature, \(I\) and \(I_{\text{sat}}\) the laser intensity and saturation intensity respectively, \(\Delta = 2\pi \times -25\) MHz is the detuning of the 313 nm laser light, \(\mathbf{k}\) the wavevector of the 313 nm laser, and \(\mathbf{v}\) and \(\mathbf{v}_\mu\) the secular and micromotion velocities of the Be\(^+\) ions. While the rf voltage is being varied, the 313 nm laser is displaced so that the ions always are at the maximum of the Gaussian laser intensity profile. The \(\mathbf{k} \cdot \mathbf{v}_\mu\) term can be written as

\[
\mathbf{k} \cdot \mathbf{v}_\mu = k x_{0,k} \Omega \sin(\Omega(t - t_0)),
\]

(4.22)

where \(x_{0,k}\) is the amplitude of Be\(^+\) micromotion along the direction of the laser wavevector and \(t_0\) is a time offset. We extract \(x_{0,k}\) by fitting Eq. (4.21) to the acquired fluorescence histogram. Repeating this procedure for various values of \(V_0\), a list of data points of the form \((V_0, x_{0,k})\) is obtained. We subsequently extract the radial and axial micromotion components by fitting a model function to these data. The model function is derived in Appendix C.

The procedure of displacing a string of Be\(^+\) ions and varying \(V_0\) is carried out for both the horizontal and vertical directions. The data and fit functions are shown in Fig. 4.10 and an average axial micromotion amplitude \(x_{\text{HD}}\) of 11(4) nm is found. As explained in Appendix C, the radial micromotion contribution (due to a possible small angle of the 782 nm laser with the trap axis) averages to zero.
4.4. Results and Discussion

Figure 4.10: Be\textsuperscript{+} micromotion amplitude along the 313 nm wavevector versus rf voltage amplitude for an offset in the horizontal (Fig. 4.10a) and vertical (Fig. 4.10b) direction. The red solid curve is the model fit function [Eq. (C.8)] which includes $x_{\text{HD}^+}$ as a fit parameter. For comparison the fitted curve with $x_{\text{HD}^+} = 0$ is also shown (dashed curve).

We incorporate the micromotion effect by extending the lineshape function $D_z$ in Eq. (4.13) with sidebands at frequencies $m\Omega$ with amplitudes $J_m^2(k_7\text{82}^\pm x_{\text{HD}^+})$. Here, the $J_m$ are Bessel functions of the first kind, with $m$ an integer in the range $[-3, 3]$.

4.4.4 Effects of chemistry in the Coulomb crystal

During REMPD, H\textsubscript{2} molecules from the background gas can react with the ions in the Coulomb crystal. Those reactions can be divided into two classes: (i) elastic collisions, and (ii) inelastic collisions, during which a chemical reaction or charge exchange occurs, and chemical energy is converted to kinetic energy. In general, the kinetic energy transfer to the ion from elastic collisions with room-temperature particles is much lower than the chemical energy released from inelastic collisions.
At close range \( r \), the electric field of the ion polarizes the neutral molecule which results in an attractive interaction potential \( U(r) = -\alpha Q^2/(8\pi\epsilon_0 r)^4 \). Here \( \alpha \) denotes the polarizability volume (in m\(^3\)) of the molecule, \( \epsilon_0 \) is the electric constant, and \( Q \) is the elementary charge. If we integrate the interaction force over the trajectory of the neutral near the ion (assuming a relatively large impact parameter \( b > b_{\text{crit}} \); see below), we obtain a change of momentum which corresponds to a velocity kick of tens of meters per second for most species.

If a neutral atom or molecule and an ion approach each other within a critical impact parameter \( b_{\text{crit}} = (\alpha q^2/\pi\epsilon_0 \mu_{\text{red}} v)^{1/4} \), where \( \mu_{\text{red}} \) and \( v \) are the reduced mass and relative velocity of the pair, a so called Langevin collision occurs, during which particles spiral towards each other and a chemical reaction can occur at very short range [119]. The chemical reaction products contain hundreds of meV of kinetic energy, which is dissipated into the ion crystal which itself only contains about 2 meV of kinetic energy (at 10 mK). A possible adverse side effect is that such collisions may lead to time-averaged velocity distributions which deviate from thermal distributions. Table 4.1 shows the relevant reactions during REMPD along with the released chemical energy and their reaction rates. Reaction (1) corresponds to the REMPD process itself. From observations reported in [42] we infer that the ratio of \( \text{HD}^+ \rightarrow \text{D}^+ + \text{H} \) and \( \text{HD}^+ \rightarrow \text{H}^+ + \text{D} \) is approximately 1:1. The charge-to-mass ratio of \( \text{H}^+ \) is too large for this product to be stably trapped, but the \( \text{D}^+ \) ions can stay

<table>
<thead>
<tr>
<th>Nr</th>
<th>Reaction</th>
<th>Energy of ionic product (eV)</th>
<th>Rate(s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HD(^+) + h(\nu) + h(\nu)′ (\rightarrow) D(^+) + H</td>
<td>0.41</td>
<td>0-10(^2)</td>
</tr>
<tr>
<td>2</td>
<td>HD(^+) + H(_2) (\rightarrow) H(_2)D(^+) + H</td>
<td>0.36</td>
<td>0.0042</td>
</tr>
<tr>
<td>3</td>
<td>HD(^+) + H(_2) (\rightarrow) H(_3)^+ + D</td>
<td>0.66</td>
<td>0.0014</td>
</tr>
<tr>
<td>4</td>
<td>H(_2)D(^+) + H(_2) (\rightarrow) HD + H(_3)^+</td>
<td>0.016</td>
<td>0.0019</td>
</tr>
<tr>
<td>5</td>
<td>HD(_2)^+ + H(_2) (\rightarrow) D(_2) + H(_3)^+</td>
<td>0.017</td>
<td>0.0004</td>
</tr>
<tr>
<td>6</td>
<td>HD(_2)^+ + H(_2) (\rightarrow) HD + H(_2)D(^+)</td>
<td>0.022</td>
<td>0.0015</td>
</tr>
<tr>
<td>7</td>
<td>Be(^+)(2P(_{3/2})) + H(_2) (\rightarrow) BeH(^+) + H</td>
<td>0.25</td>
<td>0.0019/0.005(^3)</td>
</tr>
</tbody>
</table>

\(^2\)The rate (in s\(^{-1}\) per molecule) of D\(^+\) production is dependent on time and frequency in the (0,2)\(\rightarrow\)(8,3) spectrum.

\(^3\)The rate is dependent on the fraction of time a Be\(^+\) ion spends in the excited \(^2\)P\(_{3/2}\) state, which is dependent on the 313 nm laser intensity and detuning (−80 MHz or −300 MHz, respectively).

\(^1\)The polarizability volume and the polarizability in SI units are related through \( \alpha = \alpha_{\text{SI}}/(4\pi\epsilon_0) \)
4.4. Results and Discussion

trapped and can orbit the Coulomb crystal for many seconds. The reaction rate of (1) is calculated from the REMPD model described in Sec. 4.4.1, and is dependent on the frequency of the 782 nm laser.

Reaction (7) occurs most frequently due to the large number of Be$^+$ ions present in the trap. The reaction rate is obtained from a decay measurement of the 313 nm fluorescence from a loaded Be$^+$ crystal, and is in good agreement with the rate estimated from the Langevin cross section given the background pressure of $1 \times 10^{-8}$ Pa in our apparatus [120]. The different rate constants of reactions (2) and (3) illustrate the fact that HD$^+$ can react with H$_2$ in two ways: either the H$_2$ breaks apart, donating an H atom to the HD$^+$ molecule, or the HD$^+$ breaks apart, after which an H$^+$ or D$^+$ is added to the neutral molecule. According to [53] and [118] the probability of each scenario is approximately 50%. In case the ion breaks apart, the probability that either a H$^+$ or a D$^+$ is donated to the H$_2$ molecule is also 50%. This leads to a ratio of reaction (2) to (3) of 3:1. The rate of reaction (2) can be measured (keeping in mind that HD$^+$ and H$_3^+$ in reaction (3) have the same charge-to-mass ratio and therefore cannot be distinguished) by applying the measurement scheme depicted in Fig. 4.5 without 782 nm laser, which is further described in Sec. 4.4.5. The rates of reactions (4), (5) and (6) are obtained from [121]. The kinetic energies of the chemical products are calculated by using the binding energies and energy and momentum conservation laws.

Realistic MD simulations show that the fast ionic chemical products may heat up the Coulomb crystal by 1–2 mK (depending on the REMPD rate), and that the HD$^+$ velocity distribution becomes slightly non-thermal. A MD simulation of a Coulomb crystal containing 750 laser-cooled Be$^+$ ions, 40 sympathetically cooled HD$^+$ ions and 14 fast D$^+$ ions produces the HD$^+$ z-velocity distribution shown in Fig. 4.11. A detailed explanation of the MD code is given in Appendix A. It turns out that the z-velocity distribution deviates clearly from a Gaussian curve and is better described by a $q$-Gaussian [122], which is a Gaussian curve with higher wings parameterized by a parameter $q$:

$$Q(\omega, \beta, q) = \frac{\sqrt{q - 1} \left(1 + \frac{(q-1)(\omega - \omega_0)^2}{2\beta^2}\right)^{-\frac{1}{2q}} \Gamma \left(\frac{1}{q-1}\right)}{\sqrt{2\pi} \beta \Gamma \left(-\frac{q-3}{2(q-1)}\right)} \quad 1 < q < 3 \quad (4.23)$$

where $\omega$ and $\omega_0$ are the frequency and center frequency, $\Gamma$ is the gamma function, and $\beta$ is analogous to the standard deviation of a Gaussian distribution, and which is related to the Doppler width. For $q = 1$, the function reduces to a regular Gaussian distribution. This function is merely used as a mathematical tool to describe the simulated data and we have not derived this velocity distribution based on a particular physical model. Since the value $\nu_0$, fit turns out to be sensitive to the shape of the velocity distribution, it is important that
we insert the lineshape based on the correct velocity distribution in Eq. (4.13), and specify the bounds to within this distribution is valid. An initial analysis reveals that $\nu_{0, \text{fit}}$ may shift several hundreds of kHz by implementing a $q$-Gaussian with a $q$ varying between 1.0 and 1.1. Note that recently, another study of MD simulations independently confirmed the non-thermal character of velocity distributions of laser-cooled ion crystals due to collisions with background gas molecules [123].

In the remainder of this section, we determine the $q$-values applicable to our REMPD measurement with the help of MD simulations. The value of $q$ is dependent on the number of trapped fast ions, $N_{\text{fast}}$. The more fast ions, the higher the $q$-value. We note that $N_{\text{fast}}$ is frequency dependent (more D$^+$ produced near the peak of the REMPD spectrum) as well as time dependent (the production rate of D$^+$ is governed by the rate equations, Eq. (4.12)).

When a fast ion collides with a cold ion, each particle may undergo a nonadiabatic transition to a different solution of the Mathieu equation which governs its motion in the trap [124]. This implies that a fast ion can either lose or gain energy during such a collision. Since the energy change per collision is relatively small, fast ions can retain their high speeds in the trap for many seconds. Values for $N_{\text{fast}}$ can be obtained by solving the rate equation:

$$\frac{\partial N_{\text{fast}}}{\partial t} = \alpha_{\text{prod}} N_{\text{source}} - \alpha_{\text{relax}} N_{\text{fast}} - \alpha_{\text{esc}} N_{\text{fast}}$$  \hspace{1cm} (4.24)$$

The term $\alpha_{\text{prod}}$ is the production rate from a number of $N_{\text{source}}$ particles, such as Be$^+$ or HD$^+$. In Sec. 4.4.2 we determined $N_{\text{source, Be}^+} = 750$ and $N_{\text{source, HD}^+} = 43$ or $N_{\text{source, HD}^+} = 84$. $\alpha_{\text{relax}}$ is the rate at which fast ions are cooled and become embedded within the Coulomb crystal, while $\alpha_{\text{esc}}$ is the rate at which
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Figure 4.12: The (secular) speed distribution of approximately 100 BeH$^+$ ions after a simulated time of 100 ms. All BeH$^+$ ions had an initial velocity of 2200 ms$^{-1}$ in random directions. Comparing such histograms for various initial velocities points out that there is a tendency for faster ions to acquire ever larger velocities (presumably by micromotion heating), which will ultimately lead to the loss of these ions. Likewise, ions which happen to slow down have an ever increasing chance to be cooled down to the 10 mK temperature of the Coulomb crystal.

ions escape from the trap. The values of $\alpha_{\text{prod}}$ correspond to the reaction rates in Table 4.1. However, obtaining such rates requires a multitude of individual MD simulations, with simulation periods of several seconds each. Even with current academic supercomputers, the total time to perform such simulations is prohibitively long. Nevertheless, boundaries on $\alpha_{\text{relax}}$ and $\alpha_{\text{esc}}$ can be inferred from many short simulations which can be run in parallel. We use a set of 10 simulations per fast ion species, each containing approximately 10 fast ions together with a trapped and laser-cooled Coulomb crystal of 750 Be$^+$ and 40 HD$^+$ ions. Each simulation lasts 100 ms, and at the start of each simulation the initial velocities of the ions have the same magnitude but a different, randomly chosen direction.

We here outline the procedure followed to obtain the relaxation rate for BeH$^+$. Starting with 10 fast ions with an initial velocity of 2200 ms$^{-1}$ (see Table 4.1), and running the simulations 10 times, we obtain the histogram of velocities (averaged over one cycle of the rf trap potential) after 100 ms shown in Fig. 4.12. None of the simulated 100 fast ions have escaped or relaxed, and it is clear that both heating and cooling occurs. Running a similar set of 10 simulations, but this time with an initial velocity of 1200 ms$^{-1}$, we find that all 100 ions are sympathetically cooled and embedded within the Coulomb crystal after 100 ms.
4. High-precision spectroscopy of the HD\(^+\) molecule

We obtain an estimate of the average relaxation time of BeH\(^+\) by running similar sets of simulations for 2200, 2000, 1800, 1600, and 1200 ms\(^{-1}\). From each set of simulations we collect the percentage of fast ions that decelerate during 100 ms to below the initial velocity of the next set of simulations. The results are shown in Table 4.2. Obviously, sympathetic cooling starts to become efficient at the 100-ms time scale for velocities below 1600 ms\(^{-1}\). The percentages (see column 3 of Table 4.2) are treated as probabilities, which we denote as \(p_i\), from which the time constant, \(\alpha_i\), of the ‘decay’ from speed category \(v_i\) to speed category \(v_{i+1}\) is calculated through

\[
\alpha_i = -\frac{100 \text{ ms}^{-1}}{\ln(1 - p_i)}.
\]

Next, the coupled differential equations

\[
\begin{align*}
N'_0(t) &= -\alpha_0 N_0(t) \\
N'_1(t) &= -\alpha_1 N_1(t) + \alpha_0 N_0(t) \\
N'_2(t) &= -\alpha_2 N_2(t) + \alpha_1 N_1(t) \\
N'_3(t) &= -\alpha_3 N_3(t) + \alpha_2 N_2(t) \\
N'_4(t) &= -\alpha_4 N_4(t) + \alpha_3 N_3(t)
\end{align*}
\] (4.25)

are solved, where \(N_i\) stands for the number of fast ions in the \(i^{th}\) velocity category. The category index \(i\) corresponds to the row of Table 4.2, \(i.e. \ i=0\) for 2200 m/s and \(i=4\) for 1200 m/s. We omit level \(i=5\) for 0 m/s because a particle that reaches 1200 m/s certainly relaxes within tens of milliseconds. From the solutions of Eq. (4.25) we obtain an effective relaxation time for BeH\(^+\) of 1.5 s. The relaxation times for the products of reactions (1), (2) and (3) are too long to determine within reasonable computation time because of their higher initial velocities and smaller cooling efficiencies (due to the larger mass

<table>
<thead>
<tr>
<th>(v_i)</th>
<th>(v_{i+1})</th>
<th>percentage of ions ending at (v &lt; v_{i+1}) within 100 ms</th>
<th>percentage of ions that relaxes within 100 ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>2000</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>2000</td>
<td>1800</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>1800</td>
<td>1600</td>
<td>35</td>
<td>6</td>
</tr>
<tr>
<td>1600</td>
<td>1200</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>1200</td>
<td>800</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of simulations performed to obtain the relaxation time of BeH\(^+\). The third column shows the percentage of ions having a speed lower than \(v_{i+1}\) after 100 ms simulated time. The fourth column shows the percentage of ions which relax (\(i.e.\) become fully embedded within the Coulomb crystal) within 100 ms.
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difference with Be$^+\). The same holds for the time it takes a fast ion to escape the trap. Histograms as in Fig. 4.12 are produced for the other species as well, but only for a few initial speeds. Since those histograms are fairly symmetric in shape (with respect to the initial velocity) we assume that the ratio of escaping and relaxing is approximately 50:50. The chemical products of reactions (4), (5) and (6) have relatively low velocities. They are found to relax within tens of milliseconds with zero probability of escaping from the trap. The MD simulations point out that their influence on the HD$^+$ z-velocity distribution is negligible.

Based on the results described above, we set $\alpha_{\text{relax,BeH}^+}$ at $0.67\text{ s}^{-1}$. Concerning the relaxation and escape rates of the reactions (1)–(3), we consider two extreme scenarios:

- **Scenario 1:** A minimum number of fast ions is present in the trap. $\alpha_{\text{relax}}$ and $\alpha_{\text{esc}}$ are set to their maximum value of one per second for all species, which is based on the observation that no ion loss and no relaxation are observed over simulated times up to 800 ms. This scenario will produce the smallest value of $q$.

- **Scenario 2:** A maximum number of fast ions is present in the trap, which means $\alpha_{\text{relax}}$ and $\alpha_{\text{esc}}$ are set to their minimum value of zero. All fast ions remain in the trap at high speed for the entire 10 seconds of REMPD. This scenario leads to the largest value of $q$.

We assume that fast ions do not mutually interact when present in numbers of ten or less, so that the observations based on MD simulations with ten fast ions are also valid for smaller numbers of fast ions. Note that BeH$^+$ ions are already created during the first secular scan before the REMPD phase starts. The fast specimen of the species of fast H$_2$D$^+$ and H$_3^+$ occur less frequently in the trap, and in line with the concept of extreme scenarios we assume zero H$_2$D$^+$ and H$_3^+$ for scenario 1, and 3 H$_2$D$^+$ and 1 H$_3^+$ for scenario 2. Together with scenarios a and b described in Sec. 4.4.2 this gives us four scenarios in total, and therefore four different spectral fit functions and four different $\nu_0$ results.

For all possible combinations of fast ions present during REMPD (e.g. 1 D$^+$, 2 BeH$^+$ and 1 H$_2$D$^+$ or 3 D$^+$, 3 BeH$^+$ and 3 H$_2$D$^+$) an MD simulation is carried out. From these simulations, the HD$^+$ z-velocity distribution is determined and a $q$-Gaussian is fitted which results in one $q$ value for each simulated case. As mentioned before, the production rate of fast D$^+$ depends on the REMPD rate (and thus on the 782 nm laser frequency $\nu$), which itself depends on the time-dependent number of available HD$^+$ ions in the target state. To take this properly into account we introduce a time and frequency dependent parameter $q(t, \nu)$ as follows. For each of the four scenarios, the number of fast
4. HIGH-PRECISION SPECTROSCOPY OF THE HD$^+$ MOLECULE

Figure 4.13: 3D $q(t, \nu)$ plots for scenario 1a (a) and 2b (b). Note that scenario 1a nearly corresponds to the case $q = 1$, i.e. the case in which all chemistry-induced effects can be ignored. See text for further details.

D$^+$ is simulated on a grid of different REMPD durations, $t_j$, and of different frequencies, $\nu_j$ of the 782 nm laser. On each point of this two-dimensional grid, the number of fast D$^+$ is combined with the number of other fast ions, and the corresponding value of $q(t_j, \nu_j)$ is looked up in a library of $q$ values, obtained from many MD simulations performed with various combinations and abundances of fast ion species. Interpolation of the grid $q(t_j, \nu_j)$ leads to a smooth continuous function $q(t, \nu)$, which is subsequently inserted into the lineshape function $D_z$ used in Eqs. (4.12) and (4.13). Figure 4.13 shows the 3D plots of $q(t, \nu)$ for the different scenarios.

Besides the $q$ value, also the ion temperature $T_{HD}$ is frequency and time dependent. Due to a larger number of D$^+$ ions at the top of the spectrum than
at the wings, the temperature differences between top and wings can reach a few mK. We note that the increase of \( q \) and \( T_{\text{HD}} \) share the same origin (namely collisions with fast ions), and in Fig. 4.14 we show the relation between \( q \) and \( T_{\text{HD}} \), obtained from fitting \( q \)-Gaussians to simulated velocity distributions. In scenario 1, the temperature difference between top and wings is found to be 0.5 mK. For scenario 2, the estimated temperature difference is 2.5(5) mK, where the uncertainty of 0.5 mK is treated as one standard deviation. The \( t \) and \( \nu \) dependent temperature is also included in \( D_z \).

### 4.4.5 Background gas reactions

During the REMPD phase the number of HD\(^+\) is not only reduced through photodissociation by the lasers. As described in Sec. 4.4.4, trapped ions can react with H\(_2\) molecules of the background gas in the vacuum setup. In order to correct the spectroscopic signal for these so-called background losses, the rates of reactions (2) and (3) in Table 4.1 are measured and included into the rate equations, Eq. (4.12), as an additional loss channel.

The spectral data were acquired over the course of several months during 15 independent measurement sessions lasting several hours each (Fig. 4.15). During this period the background pressure varied from session to session. For each session, the HD\(^+\) background signal is obtained by using the measurement scheme depicted in Fig. 4.5, but with a shutter blocking the 782 nm laser, thus preventing REMPD. Typically, a few HD\(^+\) ions react with H\(_2\) which is detected as a small difference between the secular scan peak areas \( A_{\text{bg},i} \) and \( A_{\text{bg},f} \). During each measurement session, a background loss measurement is carried out approximately three times, providing a data set of about 20 background measurement per session. From the average background loss signal per session a
4. High-precision spectroscopy of the HD$^+$ molecule

Figure 4.15: Signals corresponding to background gas losses per measurement session. During some sessions the background pressure of the vacuum was high, which results in a higher signal. The dots are the averages of a set of measurements, the error bars represent a ±1σ standard deviation.

The reaction rate $\gamma_{bg}$ is extracted from the relation

$$1 - e^{-\gamma_{bg} t} = \frac{N_{bg,i} - N_{bg,f}}{N_{bg,i}} = f_{NL}^{-1} \left( \bar{T}_0, \frac{A_{bg,i} - A_{bg,f}}{A_{bg,i}} \right)$$

(4.26)

with $t = 10$ s and $f_{NL}^{-1}$ mapping $(A_{bg,i} - A_{bg,f})/A_{bg,i}$ onto $(N_{bg,i} - N_{bg,f})/N_{bg,i}$ (see Appendix B). The values of $\gamma_{bg}$ are inserted into a modified set of rate equations, which include the process of background loss reactions:

$$\frac{d\rho_{bg}(t)}{dt} = (M_{\text{rempd}} + M_{\text{BBR}} + M_{bg}) \rho_{bg}(t).$$

(4.27)

Here $\rho_{bg}$ is $\rho$ from Eq. (4.12) including two additional rows which describe the occurrence of ions in the form of H$_2$D$^+$ or H$_3^+$. $M_{bg}$ is a diagonal matrix containing $\gamma_{bg}$ which describes the HD$^+$ losses. We take into account the fact that conversion of HD$^+$ to H$_3^+$ in reaction (3) in Table 4.1 is not detected by the method of detection through secular excitation because HD$^+$ and H$_3^+$ have the same mass-to-charge ratio. This means that the measured values of $\gamma_{bg}$ only represent the rates for reaction (2). As explained in Sec. 4.4.4, the reaction rate of (3) is a factor of three lower, which is taken into account.

We correct the data set of each session individually for the background signal following an iterative procedure. During the first step we insert an estimated $\bar{T}_0$ value in Eq. (4.26), and we simply subtract the signal predicted by the model without background losses (based on Eq. (4.12)) from the signal prediction including background losses (based on Eq. (4.27)). In this way an estimate of the background signal is obtained which is subsequently subtracted from the raw measurement data. Then the spectral fit function $S_{fit}$ (see Sec. 4.4.1) is
fitted to the corrected data points with free fit parameters $\bar{T}_0$, $T_{HD^+}$, $I_{laser}$ and $\nu_{0,fit}$. The first three parameters are reinserted into equations 4.12 and 4.27 and after a few iterations, convergence is achieved.

Reactions (4) and (5) in Table 4.1 result in the production of $H_3^+$ during REMPD, which is falsely detected as extra HD$^+$ during the secular scans. To correct for these processes we insert correction factors in front of $N_i$ and $N_f$ (see Eq. (4.16)) based on the reaction rates of (4) and (5). From the rate equations corresponding to these reactions, a time-dependent multiplication factor which accounts for the excess signal due to $H_3^+$, $R(t) \equiv 1 + N_{H_3^+}(t)/N_{HD^+}(t)$, can be derived, which modifies $\epsilon$ in the following way:

$$\epsilon' = \frac{N_f R(t_f) - N_i (R(t_i))}{N_f R(t_f)},$$

(4.28)

where $t_i = 10$ s is the duration from the time of loading of HD$^+$ ($t_0 = 0$ s) until halfway the first secular scan, and $t_f = 26$ s is the duration between halfway the first and halfway the second secular scans (see Fig. 4.5). This results in a REMPD signal that is corrected by approximately 2% (with respect to the unmodified signal strength) due to the increased fraction of $H_3^+$.

Another correction we include is the amount of HD$^+$ reacting with the background gas during the secular scans themselves (see reactions (2) and (3) in Table 4.1) and during tuning of the 313 nm laser directly before and after REMPD (see Fig 4.5). This yields the following modifications of $N_i$ and $N_f$:

$$N_i \rightarrow N'_i(t_a, t_c) \equiv N_i e^{\gamma_2 t_a} e^{\gamma_3 t_c} \approx N_i (1 + \gamma_2 t_a + \gamma_3 t_c)$$

(4.29)

$$N_f \rightarrow N'_f(t_b) \equiv N_f e^{-\gamma_2 t_b} \approx N_f (1 - \gamma_2 t_b),$$

(4.30)

where $\gamma_2 (= \gamma_{bg})$ and $\gamma_3$ are the rates of reactions (2) and (3), respectively. The last step in both equations is justified given the slow rate constants (about $1/500$ s$^{-1}$ or slower, see Table 4.1) compared to the secular scan duration (10 s), thus $\gamma_2 t_a \ll 1$, $\gamma_2 t_b \ll 1$ and $\gamma_3 t_c \ll 1$. Note the positive signs in the exponents of Eq. (4.29), which correspond to a measured $N'_i$ larger than the number of trapped HD$^+$ ions during REMPD.

The choices for $t_a$, $t_b$ and $t_c$ are made as follows: we assume that reaction (3) does not affect the secular scan fluorescence signals because the change of charge-to-mass ratio of the ion is negligible in this case. Therefore, $t_c$ is the full period between creation of HD$^+$ and REMPD, i.e. $t_c = 18$ s (see Fig. 4.5). After REMPD, there is no need to distinguish between HD$^+$ and $H_3^+$, and therefore $t_c$ is absent in Eq. (4.30).

Concerning reaction (2), HD$^+$ losses at the beginning of a secular scan result in lower integrated fluorescence signals than losses at the end of a secular scan. In our analysis, we use the average time (mean value) of the distribution
4. High-precision spectroscopy of the HD$^+$ molecule

Figure 4.16: $N'_i(t_a) = 1 + \gamma_2 t_a$ is represented by the blue line (in this example we can ignore the $\gamma_3 t_a$ term which is in fact a constant factor). The average of $N'_i$ is its integrated value (grey area) divided by the secular scan duration of 10 seconds. This is equal to $N'_i(t_a = 5)$.

Expressed numerically, for the loss rates in our experiment, the modifications are:

\[ N_i \rightarrow 1.06 N_i \]  
\[ N_f \rightarrow 0.97 N_f \]  

4.4.6 Spectrum, systematic effects and final result

The function $S_{\text{fit}}$ is fitted to the REMPD data set after correction for the background signal. Figure 4.17 shows the REMPD data set and fit function for scenario 1a. The noise in the spectrum has several origins. Firstly, the number of trapped ions is relatively small and varies from shot to shot. Secondly, the population in the various hyperfine states of the $L = 2$ state varies from shot to shot, as expected for hyperfine states with a mean occupancy of order unity. The (stochastic) BBR interaction, which couples the states with $L = 2$ with other rotational states, adds another factor of noise. Furthermore, the variation of the number of reactions of HD$^+$ with the background gas is in the order of a few per shot, which dominates the noise for low REMPD signals. Finally, part of the noise originates from intensity variations due to spatial alignment variations of the 313 nm, 782 nm and 532 nm lasers.

For each of the four scenarios we obtain a particular set of fit parameters, which are listed in Table 4.3. The correlation coefficients of the fit parameters...
4.4. Results and Discussion

Figure 4.17: Upper panel: Measured spectrum (dots), least-squares fit (solid curve); lower panel: fit residuals. All 1772 data points are plotted together with the fit function corresponding to scenario 1a. The fitted functions corresponding to the different scenarios are visually indistinguishable from the result shown here. The colored sticks represent the theoretical lines at represent the positions and linestrengths of the individual hyperfine components, shown schematically in Fig. 4.4b.

are presented in Table 4.4 and the values for $\nu_{0,\text{fit}} - \nu_{\text{th}}$ are graphically shown in Fig. 4.18. The error bars represent the $1\sigma$ statistical fit uncertainty which can be considered as the precision of the spectroscopy measurement. We remark that the sensitivity to the chemistry processes (scenario 1 and 2) is much stronger than the sensitivity to the numbers of HD$^+$ ions in the trap (scenario a and b). We note that the values $\nu_{0,\text{fit}}$ for 1a and 2a represent extreme upper and lower limits (with respect to the line shift due to chemistry) for the average number of HD$^+$ ions. We therefore chose to obtain our final result for $\nu_{0,\text{fit}}$ by taking the mean of these two values, while interpreting the mean single-fit error of (which is virtually the same for all four results) as the statistical uncertainty of the final result. We subsequently quantify the 'which-scenario' uncertainty as follows. For scenarios 1a and 1b (and similarly for 2a and 2b) the differ-
4. HIGH-PRECISION SPECTROSCOPY OF THE HD\textsuperscript{+} MOLECULE

Figure 4.18: Values of $\nu_{0,\text{fit}} - \nu_{\text{th}}$ found for the four different scenarios 1a, 1b, 2a and 2b. Error bars indicate the 1\sigma fit uncertainty. All values are plotted with respect to the theoretical frequency (blue horizontal line) \cite{2}.

ence is due to a 1\sigma variation in the number of HD\textsuperscript{+} ions. Therefore, we treat the frequency interval between the two values corresponding to scenario a and b as the corresponding 1\sigma interval, which amounts to 80 kHz when averaged over the two scenario’s 1 and 2. To find the error corresponding to scenarios 1 and 2, we take frequency interval between the values found for scenarios 1a and 2a (which are essentially extreme limits) and conservatively equate the interval to a 68 \% confidence interval. The interval thus corresponds to 2\sigma, with $\sigma = 0.23$ MHz. The uncertainty of 0.5 mK in the temperature difference between top and wings of the spectrum (see Sec. 4.4.4) results in 0.028 MHz difference in $\nu_{0,\text{fit}}$, which is treated as 1\sigma variation. The frequency shifts due to these systematic effects together with their uncertainties are listed in Table 4.5.

Table 4.3: The fit results of the free fit parameters per scenario. Scenario 1 and 2 give a clear difference in $\nu_{0,\text{fit}}$ results. Scenario a and b give give different results for $T_0$. This can be explained by the different amount of trapped molecular species, which result in different Be\textsuperscript{+} temperatures during a secular scan.

<table>
<thead>
<tr>
<th>fit parameter</th>
<th>Scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1a</td>
</tr>
<tr>
<td>$\nu_{0,\text{fit}} - \nu_{\text{th}}$ (MHz)</td>
<td>0.46(33)</td>
</tr>
<tr>
<td>$T_{\text{HD}^+}$ (mK)</td>
<td>10.9(8)</td>
</tr>
<tr>
<td>$I_{\text{laser}} \times 10^{7}$ Wm\textsuperscript{-2}</td>
<td>0.99(14)</td>
</tr>
<tr>
<td>$T_0$ (K)</td>
<td>2.79(3)</td>
</tr>
</tbody>
</table>

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4.4. Results and Discussion

Frequency uncertainty of the 782 nm laser

The beat note of the frequency-locked 782 nm laser with the optical frequency comb is counted during REMPD. We use the beat-note frequencies to compute the Allan deviation, which is of the order of 0.1 MHz after 10 s averaging. The uncertainty of the 782 nm laser frequency can be transferred to an uncertainty in the \((0,2) \rightarrow (8,3)\) fit result \(\nu_{0,\text{fit}}\) by taking the Allan deviation as a measure of the standard deviation of a Gaussian noise distribution, describing the laser frequency offset from the set frequency during each REMPD cycle. We perform a Monte Carlo simulation in which each of the 140 measurement frequencies is assigned a frequency offset, selected at random from the Gaussian distribution. Repeating this 100 times generates 100 different spectral data sets. Fitting \(S_{\text{fit}}\) to each of the data sets gives 100 different values of \(\nu_{0,\text{fit}}\). A histogram of the resulting distribution of \(\nu_{0,\text{fit}}\) values is shown in Fig. 4.19, where the \(x\)-axis denotes the difference between \(\nu_{0,\text{fit}}\) and the fit value of scenario 1a, \(\nu_{0,\text{fit,s1a}}\).

The mean and standard deviation of this list of fit values are 0.5 kHz and 8 kHz, respectively. Based on these simulations we set the frequency uncertainty due to the frequency lock at 0.01 MHz.

The 782 nm laser has a Gaussian linewidth of \(\sim 0.5\) MHz. The convolution of this lineshape with the (Gaussian) Doppler-broadened line (16 MHz) will give rise to another Gaussian lineshape. Since the linewidths add up quadratically, the increase in linewidth is smaller then the uncertainty of the linewidth due to the fit uncertainty of the temperatures, which is \(\sim 0.8\) mK. Therefore, we consider the laser linewidth to be completely absorbed into the fitted temperature \(T_{\text{HD}^+}\) with no significant effect on its value.

Zeeman and Stark and other shifts

So far we have neglected the Zeeman splitting of the lines in the spectrum. Incorporating the Zeeman effect makes the hyperfine transition matrices very large and MATHEMATICA is only able to solve the rate equations [Eq. (4.12)] effectively if lineshapes are not too complicated. We circumvent these issues as

\[
\begin{array}{cccc}
\nu_{0,\text{fit}} - \nu_{\text{th}} & T_{\text{HD}^+} & I_{\text{laser}} & T_0 \\
1 & -0.609 & 0.483 & 0.049 \\
-0.609 & 1 & -0.690 & 0.038 \\
0.483 & -0.690 & 1 & 0.579 \\
0.049 & 0.038 & 0.579 & 1 \\
\end{array}
\]

Table 4.4: The correlation coefficients for the fit of scenario 1a to the data.
follows. First, we calculate the lineshifts and linestrengths of the magnetic subcomponents of individual hyperfine lines. This is done by diagonalizing the sum of the hyperfine and Zeeman Hamiltonians, after which the eigenvectors and energy values are used to compute the stick spectrum of the \((v, L):(0,2)\rightarrow(8,3)\) transition. This procedure is similar to that followed in Refs. [63, 125]. As the Zeeman splitting is small compared to the Doppler width, the magnetic subcomponents belonging to the same hyperfine component overlap well within the profile of the lineshape function \(D_z\), forming a new composite (and Zeeman-shifted) lineshape function \(D'_z\). This new lineshape function is subsequently used in Eq. (4.13). For simplicity, we do not implement effects of micromotion and chemistry in this analysis, and we compare \(\nu_{0,\text{fit}}\) fit results based on versions with \(B=0.19\) mT with a version with zero \(B\) field. It is important to note that during the \((0,2)\rightarrow(8,3)\) excitation only \(\sigma^+\) and \(\sigma^-\) transitions are driven as the 782 nm laser and \(B\)-field directions are parallel. The practically linear polarization of the laser can be decomposed into two circularly polarized components with an estimated maximum intensity imbalance of 2%. Figure 4.20 shows the \(\nu_{0,\text{fit}}\) fit results of several \(\sigma^+/\sigma^-\) ratios with respect to a fit performed for the case of zero magnetic field. For the 0.19 mT field in our experiment, a shift of -0.017(3) MHz is obtained, with the uncertainty due to the possible polarization imbalance.

The ac Stark shifts due to the 782 nm, 532 nm and 313 nm lasers are \(-869\) Hz, \(-452\) Hz and \(8\) Hz respectively. These values represent the shift of the center of gravity of the spectral line and thus can be considered as weighted means of all the shifts of the single hyperfine components. The calculations of the Stark shifts are shortly explained in Appendix D. Stark shifts due to the BBR and trap rf field are calculated in [111] and are smaller than 1 Hz.
4.4. Results and Discussion

Figure 4.20: Zeeman shift of $\nu_{0,\text{fit}}$ found with a spectral fit function including the Zeeman effect due to a 0.19 mT magnetic field, for different ratios of $\sigma^+/\sigma^-$ transitions. The horizontal line at 0 MHz corresponds to the value obtained using a fit function assuming zero magnetic field.

Together, this gives us a total Stark shift of 1.3(1) kHz. The uncertainty in this value stems almost exclusively from the accuracy to which the laser beam intensities are known.

A conservative upper limit of 100 Hz to the electric-quadrupole shift for the $(v,L):(0,2)\rightarrow(8,3)$ transition is obtained from [16]. The 2nd order Doppler effect is calculated from the average micromotion velocity of the HD$^+$ ions, and is found to be less than 5 Hz. The values of the mentioned shifts and their uncertainties are listed in Table 4.5.

If we compare $\nu_{0,\text{fit}}$ from scenario 1a based on the model containing rotational states $L \leq 5$ with a version containing $L \leq 6$ states we find a shift of $\nu_{0,\text{fit}}$ of 28 kHz which we use as uncertainty due to the neglect of population in $L = 6$. By comparing the $\nu_{0,\text{fit}}$ value from scenario 1a that includes micromotion with a the result of a version with zero micromotion, a shift of 0.055(20) MHz is obtained. The estimated uncertainty of the BBR temperature is about 5 K, and caused by day-to-day variations of the temperature in the laboratory, and to a possible elevated temperature of the trap electrodes due to rf current dissipation. If we compare the $\nu_{0,\text{fit}}$ values after inserting BBR temperature of 300 K and 305 K, we obtain a difference of 5 kHz. The uncertainty of spin coefficient $E_4$ (see Eq. (4.1)), which is estimated at a value of 50 kHz [109] has an effect of $\sim$1 Hz on the $\nu_0$ result.
4. High-precision spectroscopy of the HD\textsuperscript{+} molecule

Table 4.5: Systematic shifts and uncertainty budget.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Shift (MHz)</th>
<th>Uncertainty (MHz)</th>
<th>(ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution (statistical fit error)</td>
<td>0</td>
<td>0.33</td>
<td>0.85</td>
</tr>
<tr>
<td>Uncertainty (q) value</td>
<td>-0.25\textsuperscript{1}</td>
<td>0.23</td>
<td>0.61</td>
</tr>
<tr>
<td>Uncertainty (N_{\text{HD}^+})</td>
<td>0</td>
<td>0.080</td>
<td>0.21</td>
</tr>
<tr>
<td>Ignoring population (L=6) in rate equations</td>
<td>0</td>
<td>0.032</td>
<td>0.083</td>
</tr>
<tr>
<td>(T_{\text{HD}^+}) variation in spectrum</td>
<td>0</td>
<td>0.028</td>
<td>0.072</td>
</tr>
<tr>
<td>Doppler effect due to micromotion</td>
<td>-0.055\textsuperscript{1}</td>
<td>0.020</td>
<td>0.052</td>
</tr>
<tr>
<td>Frequency measurement</td>
<td>0</td>
<td>0.010</td>
<td>0.026</td>
</tr>
<tr>
<td>BBR temperature</td>
<td>0</td>
<td>0.005</td>
<td>0.013</td>
</tr>
<tr>
<td>Zeeman effect</td>
<td>-0.0169</td>
<td>0.003</td>
<td>0.008</td>
</tr>
<tr>
<td>Stark effect</td>
<td>-0.0013</td>
<td>0.0001</td>
<td>0.0004</td>
</tr>
<tr>
<td>Electric-quadrupole shift</td>
<td>0\textsuperscript{2}</td>
<td>0.0001</td>
<td>0.0003</td>
</tr>
<tr>
<td>2\textsuperscript{nd} order Doppler effect</td>
<td>0\textsuperscript{2}</td>
<td>0.000005</td>
<td>0.00001</td>
</tr>
<tr>
<td>Uncertainty (E_4)</td>
<td>0\textsuperscript{2}</td>
<td>0.000001</td>
<td>0.000003</td>
</tr>
</tbody>
</table>

\textsuperscript{1} This is a shift with respect to a scenario with a zero effect of \(q\) or micromotion, and serve to illustrate the size of the effect. The shift itself, however, is absorbed in the value of \(\nu_{0,\text{fit}}\).

\textsuperscript{2} The value of these shifts is actually nonzero but negligibly small, and therefore ignored here.

Result of \(\nu_0\)

We take average of the fit values obtained from scenarios 1a and 2a as the \((v,L):(0,2)\rightarrow(8,3)\) frequency result, which yields 383,407,177.38 MHz. Table 4.5 shows the error budget, with a total uncertainty of 0.41 MHz that corresponds to 1.1 ppb. This result differs 0.21 MHz (0.6 ppb) from the more accurate theoretical value of the \((v,L):(0,2)\rightarrow(8,3)\) frequency, \(\nu_{\text{th}}=383,407,177.150(15)\) MHz \textsuperscript{[2]}. The two main uncertainty contributions are the statistical fit error of 0.33 MHz and the uncertainty in the \(q\)-factor scenario of 0.23 MHz.

4.5 Conclusion

We have measured the \((v,L):(0,2)\rightarrow(8,3)\) transition in the HD\textsuperscript{+} molecule with 0.85 p.p.b (0.33 MHz) precision, which is the first sub-p.p.b. resolution achieved in molecular spectroscopy. The result differs by only 0.6 p.p.b. from the theoretically predicted value, and a thorough analysis of systematic effects...
points out that the total uncertainty is 1.1 p.p.b. A large contribution to the systematics is the effect of chemical reactions in the Coulomb crystal, of which the $1\sigma$ uncertainty is 0.61 p.p.b (0.23 MHz). This effect, which had not been recognized before, causes a nonthermal velocity distribution that can be approximated by a $q$-Gaussian function, and which significantly influences the final value of $\nu_0$.

The agreement between experimental and theoretical data allows us to put new bounds on the existence of hypothetical fifth forces, and put new limits on the compactification radius of higher dimensions, which is explained in [69, 72, 76]. Furthermore, for the first time, a new value the proton-to-electron mass ratio based on molecular spectroscopy can be found [76].

Our analysis clearly demonstrates that the first-order Doppler effect is responsible for the largest contribution to the uncertainty. In fact, a measurement that is first-order Doppler-free can improve the precision by a factor of 100 to 1000. In [126] an experiment was proposed in which the $(v, L) = (0, 3) \rightarrow (9, 3)$ line in HD$^+$ is addressed through a two-photon transition with nearly degenerate photons. Using counter-propagating laser beams with a narrow linewidth, the Lamb-Dicke regime may be reached in which first-order Doppler broadening is virtually eliminated.
Figure 5.4: Constraint on fifth forces between hadrons at the Ångstrom scale. The high accuracy of our result and the good agreement with theory allow constraining the strength of hypothetical hadron-hadron interactions \cite{69} with a characteristic range of the order of 1 Å, mediated through virtual particles with a mass of order 1 keV\(c^{-2}\). The present result (solid curve) improves several times on the previous best constraints obtained from HD\(^+\) (dashed curve) and neutral molecular hydrogen \((\text{D}_2\), dotted curve) \cite{69}, ruling out interactions with strengths \(|\alpha_5/\alpha| \geq 5 \times 10^{-10}\) (90\% confidence level). The yellow region remains unexplored by this experiment.

fine-structure constant, \(|\alpha/\alpha_5|\), larger than 5-8\times10^{-10} (Fig. 5.4). In a similar way, applying the Arkani-Hamed-Dimopoulos-Dvali formulation to probe the effect of compactified higher dimensions on energy levels in molecules \cite{71,72}, we place an improved upper bound of 0.5 \(\mu\)m on the compactification radius of higher dimensions in eleven-dimensional M-theory.

Four decades ago, Wing et al. \cite{57} 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 \(\mu_{\text{CODATA10}}\), now allow the first determination of \(\mu\) from molecular vibrations. Previously \cite{93} we had derived the sensitivity relation \(\delta \mu/\mu = -2.66 \delta \nu/\nu\), which we employ to adjust \(\mu_{\text{CODATA10}}\) 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 \cite{128}. For example, the value
reported by Farnham et al. is only a factor of 1.3 more precise than our result [129]. While the precision of a very recent determination by Sturm et al. is still 31 times higher [130], 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 [131, 132]). 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. 5.5b). 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 [130, 133, 134] antiprotonic helium [131], and the molecular hydrogen ion. Furthermore, of all the methods which 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 [131] (Fig. 5.5a).

In principle, the transition frequency $\nu_0$ depends on the value of other fundamental constants as well, such as the deuteron-proton mass ratio [46], $m_d/m_p$, the fine structure constant, and the proton charge radius [1, 2]. 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 [46]. 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 5.1 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 [126], which should reduce the uncertainty to below $1 \times 10^{-12}$. This should enable a comparison between theory and experiment which would not only test the QED description of chemically bonded particles at an unprecedented 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 [130], which represent a completely different method (Fig. 5.5c). 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.
5.3 Supplementary methods informations

5.3.1 Experimental procedure

We typically store 40 to 85 HD$^+$ ions in a linear rf trap, together with about 750 Be$^+$ ions, which are laser cooled to a temperature of $5\text{–}10$ 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$^+$ 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 surrounding the HD$^+$. 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 (EMCCD) camera and a photomultiplier tube. We obtain a measure of the number of trapped HD$^+$ ions by resonantly driving their radial secular motion ($800 \text{ kHz}$) using an a.c. electric field [93]. MD simulations indicate that this secular excitation heats up and melts the ion ensemble, heating the Be$^+$ ions to an average temperature (in the $z$-direction) $\bar{T}_0$ proportional to the number of HD$^+$, $N_{\text{HD}^+}$. Typically, $\bar{T}_0 = 2–4 \text{ K}$. For a fixed cooling-laser detuning $\Delta = -18 \Gamma$ (with $\Gamma = 2\pi \times 19.4 \text{ MHz}$ the natural linewidth of the 313 nm cooling transition), this temperature rise leads to Doppler broadening and, thus, to a significant rise in the 313 nm fluorescence rate with average value $F$. Whereas previous work approximated the fluorescence rise versus $N_{\text{HD}^+}$ by a linear dependence [117], we realistically model the (nonlinear) dependence of $F$ on $N_{\text{HD}^+}$, and take this into account in our analysis (see Spectral line shape function for fitting).

To excite the $(v,L): (0,2) \rightarrow (8,3)$ rovibrational transition at 782 nm, we send a CW 782 nm laser beam along the $z$-axis, counter-propagating the 313 nm laser beam. The 782 nm radiation is obtained from a titanium:sapphire laser with a linewidth of 0.5 MHz, which is frequency locked to an optical frequency comb laser as follows. The frequency of the optical beat note of the 782 nm laser with a nearby mode of the comb is measured by a counter every 30 ms. From the measured beat-note frequency, the comb repetition rate, comb carrier-envelope offset frequency, and the comb mode number we determine the lasers optical frequency. The counter output is fed into a digital feedback loop, which controls the 782 nm laser so as to stabilise the beat-note frequency to a preset value. The comb is fully referenced to a GPS-disciplined rubidium atomic clock (providing long-term relative accuracy at the level of $2 \times 10^{-12}$), and the frequency uncertainty of our optical frequency measurement system (10 kHz) is limited solely by the frequency instability of the locked 782 nm laser averaged over the 10 s of REMPD. To detect excitation to the $v=8$ state by the 782 nm laser, we overlap this beam with a CW 532 nm laser beam, leading to REMPD of HD$^+$ (Fig. 5.1a). An experimental cycle looks as follows. We first load a fresh sample of HD$^+$ and find a measure, $F_i$, of the initial ion number, $N_i$, by secular excitation. We subsequently lower the 313 nm cooling laser intensity and detuning to reduce the ion temperature to $\sim 10 \text{ mK}$, and expose the ions to the 313 nm, 782 nm and 532 nm lasers for 10 s. Afterwards, we apply secular excitation to determine the fluorescence level $F_f$ corresponding to the remaining ion number, $N_f$, and we define a signal $S = (F_i - F_f) / F_i$. Repeating this cycle for different values of the 782 nm laser frequency, $\nu$, we obtain a spectrum consisting of 1772 points (Fig. 5.2a). Noise in the spectrum is primarily due to the stochastic nature of REMPD of small HD$^+$ ensembles with a mean rotational-hyperfine occupancy of the order of one ion per state.
5.3. Supplementary methods informations

5.3.2 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 \([116]\) corresponding to \(T = 300(5) \text{ K}\), under the influence of REMPD lasers, BBR and losses due to chemical reactions with background-gas molecules (Figs. 1b,d). Population in rotational states with \(L = 0 - 5\) is included, thus ignoring the 2.4% population in \(L = 6\) and higher. Accurate hyperfine line strengths at the magnetic sub-state level are obtained by extending the approach of Koelemeij \([111]\) 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 \(q\)-Gaussians. For the assessment of the Zeeman effect, the hyperfine rate equations are adapted to include Zeeman line 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 uncertainty limited by the minimum and maximum expected rates of heating events. Solving the rate equations allows predicting the fractional loss of HD\(^+\), \(\epsilon\), as a function of the 782 nm laser frequency relative to the hyperfine-less frequency, \(\nu - \nu_0\), the intensity, \(I_{\text{laser}}\), of the 782 nm laser, and the HD\(^+\) motional temperature, \(T_{\text{HD}^+}\). We obtain a smooth, continuous spectral line shape function for fitting as follows. First, we compute \(\epsilon\) on a dense three-dimensional grid of values \((\nu, I_{\text{laser}}, T_{\text{HD}^+})\), which we subsequently interpolate to obtain a four-dimensional function \(\epsilon(\nu - \nu_{0,\text{fit}}, I_{\text{laser}}, T_{\text{HD}^+})\). Using the shorthand notation \(\epsilon(\nu - \nu_{0,\text{fit}}, I_{\text{laser}}, T_{\text{HD}^+}) = \epsilon\), and making use of the linear dependence of \(\bar{T}_0\) on \(N_{\text{HD}^+}\) found from MD simulations, the average Be\(^+\) temperatures during secular excitation of HD\(^+\) before and after REMPD are given by \(T_i = \bar{T}_0(N_i)\) and \(T_f = \bar{T}_0((1 - \epsilon)N_f)\), respectively. We consecutively insert these temperature values in the scattering rate function \(R_{\text{MB}}\), defined as

\[
R_{\text{MB}}(T) = \frac{\Gamma}{2} \sqrt{\frac{m_{\text{Be}}}{2\pi k_B T}} \int \frac{I/I_{\text{sat}}}{I/I_{\text{sat}} + 1 + (2(\Delta - kv_k)/\Gamma)^2} \exp \left(-\frac{m_{\text{Be}}v_k^2}{2k_B T}\right) dv_k,
\]

which includes the beryllium mass, \(m_{\text{Be}}\), and the fixed 313 nm laser detuning, wave vector, \(k\), and saturation parameter, \(I/I_{\text{sat}}\). The integration is performed over the distribution of Be\(^+\) velocities \(v\) along \(k\), i.e. \(v_k \equiv k \cdot v / |k|\). This function is used to model the fluorescence rise \(F\) observed in the experiment, and allows us to construct a five-dimensional fit function \(S_{\text{fit}}(\nu - \nu_{0,\text{fit}}, I_{\text{laser}}, T_{\text{HD}^+}) = [R_{\text{MB}}(T_i) - R_{\text{MB}}(T_f)]/[R_{\text{MB}}(T_i)R_{0_{\text{MB}}}]\), with \(R_{0_{\text{MB}}}\) the steady-state scattering rate before secular excitation. The function \(S_{\text{fit}}\) realistically models the signal \(S\) (Fig. 5.2c), and is used for fitting.

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5. Probing QED and fundamental constants

We employ the above model also to estimate the uncertainties due to several systematic effects. For example, MD simulations predict a slight increase of $T_{\text{HD}^+}$ and $q$ with increased REMPD rates in the scenario of inefficient thermalisation of fast $D^+$. We can estimate the frequency shift due to this effect by making both $T_{\text{HD}^+}$ and $q$ REMPD-rate dependent. This leads to an additional frequency uncertainty of 61 kHz, which is included in the error associated with Doppler effects due to chemistry (Table 5.1). From our model we furthermore deduce that ignoring states with $L \geq 6$ introduces an uncertainty of 32 kHz, while 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 Hz effect [135].
5.3. Supplementary methods informations

Table 5.1: Systematic shifts and uncertainty budget.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Shift (MHz)</th>
<th>Uncertainty (MHz)</th>
<th>Uncertainty (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution (statistical fit error)</td>
<td>0</td>
<td>0.33</td>
<td>0.85</td>
</tr>
<tr>
<td>Doppler effect due to chemistry</td>
<td>-0.25(^1)</td>
<td>0.25</td>
<td>0.66</td>
</tr>
<tr>
<td>Ignoring population (L=6) in rate equations</td>
<td>0</td>
<td>0.032</td>
<td>0.083</td>
</tr>
<tr>
<td>(T_{\text{HD}^+}) variation in spectrum</td>
<td>0</td>
<td>0.028</td>
<td>0.072</td>
</tr>
<tr>
<td>Doppler effect due to micromotion</td>
<td>-0.055(^1)</td>
<td>0.020</td>
<td>0.052</td>
</tr>
<tr>
<td>Frequency measurement</td>
<td>0</td>
<td>0.010</td>
<td>0.026</td>
</tr>
<tr>
<td>BBR temperature</td>
<td>0</td>
<td>0.005</td>
<td>0.013</td>
</tr>
<tr>
<td>Zeeman effect</td>
<td>-0.0169</td>
<td>0.003</td>
<td>0.008</td>
</tr>
<tr>
<td>Stark effect</td>
<td>-0.0013</td>
<td>0.0001</td>
<td>0.0004</td>
</tr>
<tr>
<td>Electric-quadrupole shift</td>
<td>0(^2)</td>
<td>0.0001</td>
<td>0.0003</td>
</tr>
<tr>
<td>2(^{nd}) order Doppler effect</td>
<td>0(^2)</td>
<td>0.000005</td>
<td>0.00001</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>-0.0182</td>
<td>0.41</td>
<td>1.1</td>
</tr>
</tbody>
</table>

\(^1\) This is a shift with respect to a scenario with a zero effect of \(q\) or micromotion, and serves to illustrate the size of the effect. The shift itself, however, is absorbed in the value of \(\nu_0,\text{fit}\).

\(^2\) The value of these shifts is actually nonzero but negligibly small, and therefore ignored here.
Appendix A

Molecular dynamics simulations

MD simulations are implemented in Fortran code in order to realistically describe the dynamics of trapped and laser-cooled ions in the presence of the time-dependent trap field, 313 nm photon scattering by the Be$^+$ ions, and fast ionic products from chemical reactions. A cycle of one time step starts by computing the sum of the forces acting on each ion, which consists of the Coulomb force, $\vec{F}_C$, the time-dependent force from the trapping field field, $F_{\text{trap}}$, and an optional rf electric field, $F_{\text{SS}}$ which drives the secular motion:

$$\vec{F}_{\text{tot}} = \sum \vec{F} = \vec{F}_C + \vec{F}_{\text{trap}} + \vec{F}_{\text{SS}}.$$  \hspace{1cm} (A.1)

Note that we here use arrow symbols to indicate vectors, instead of bold symbols as used elsewhere in this thesis. The radial and axial part of $\vec{F}_{\text{trap}}$ are given by

$$F_{\text{trap},x,y} = -\frac{QV_0}{R^2} (x\hat{x} - y\hat{y}) \cos(\Omega t) + \frac{1}{2} m\omega_z^2(x\hat{x} + y\hat{y})$$  \hspace{1cm} (A.2)

and

$$F_{\text{trap},z} = az + bz^3 + cz^5,$$  \hspace{1cm} (A.3)

where $\omega_z$ is the secular angular frequency in the $z$-direction. The constants $a$, $b$ and $c$ depend on the trap geometry, which are determined through a finite-element analysis performed with the software package SIMION. The forces exerted on each ion are calculated, and leapfrog integration [136] provides the new velocities $\vec{v}_{i+1}$ and positions $\vec{x}_{i+1}$ at the $i$th time step $\Delta t$:

$$\vec{v}_{i+1} = \vec{v}_i + (\vec{F}_{\text{tot},i}/m_j)\Delta t$$

$$\vec{x}_{i+1} = \vec{x}_i + \vec{v}_{i+1}\Delta t$$  \hspace{1cm} (A.4)
where $m_j$ is the mass of the $j$th ion. The new positions, $\vec{x}_{i+1}$, are inserted into A.1, after which the next cycle starts.

Doppler-cooling is included at the level of single-photon scattering. Photon momentum kicks are simulated as velocity changes where absorption only takes place in the laser direction. In order to include ion motional heating which occurs in the trap, we implemented additional stochastic velocity kicks with a size of the recoil momentum of a single 313 nm photon with random directions. If an average kick rate of 75 MHz is used, realistic ion temperatures of around 10 mK are obtained.

The processes of elastic and inelastic neutral-ion collisions are simulated as velocity kicks in random directions. For example, simulating reaction (7) in Table 4.1, a BeH$^+$ is created at 10 mK and then its speed is modified.

Simulation of particles which in some cases have high velocities requires the use of a variable time step size. (If the proper step size is not observed, two particles with a high velocity difference at close distance could skip each other within one time step instead of colliding). The default step size is $\Delta t = 0.2$ ns. However, if for any of the trapped particles the condition $v_j \Delta t > 10 \times \min\{\Delta x_{jk}\}$ is met, where $\min\{\Delta x_{jk}\}$ is the distance between particle $j$ with velocity $v_j$ and the nearest particle $k$, the time step $\Delta t$ is reduced by a factor of 10 and vice versa.

To simulate EMCCD images, we made use of a simpler MD implementation, which treats the motion of the ions in the pseudopotential approximation and which does not include high-energy ions. This allows for a larger time integration step (10 ns) and, thus, faster MD simulations.
Appendix B

Derivation of the non-linear fluorescence function

The relative HD$^+$ loss during REMPD, $\epsilon$, is related to the spectroscopic signal $S$ through the non-linear function $f_{NL}$, which we derive here. The fluorescence yield during a secular scan depends on the Be$^+$ temperature, $T$, and is described by the scattering rate formula integrated over a Maxwell-Boltzmann velocity distribution. If we neglect micromotion effects, we find the overall scattering rate $R_{MB}$:

$$R_{MB}(T) = \frac{\Gamma}{2} \sqrt{\frac{m_{Be}}{2 \pi k_B T}} \int \frac{I/I_{sat}}{I/I_{sat} + 1 + (2(\Delta - k v_k)/\Gamma)^2} \exp \left( - \frac{m_{Be} v_k^2}{2 k_B T} \right) dv_k,$$  

(B.1)

where $v$ along $k$, i.e. $v_k \equiv k \cdot v / |k|$ is integrated over the distribution of Be$^+$ velocities. During the experiment we used the values $\Delta = 2\pi \times -300$ MHz and $I/I_{sat} = 67$.

During a secular scan, the temperature $T$ varies, which leads to a fluorescence peak as described by Eq. (B.1). The spectroscopic signal $S$ is the relative difference between the areas under the fluorescence peaks (see equation 4.11). We may rewrite the area, $A$, as

$$A = C \left( \frac{R_{MB}(\bar{T})}{\Delta t} - \frac{R_{MB}(\bar{T}_{bl})}{\Delta t} \right),$$  

(B.2)

where $C$ is a constant taking into account the collection and quantum efficiencies of the PMT or EMCCD imaging system, $\Delta t$ denotes the duration of the secular scan (10 s), $\bar{T}$ stands for the average value of $T$ during a secular scan, and $\bar{T}_{bl}$ is the average baseline temperature during $\Delta t$. In the experiment, the
B. Derivation of the non-linear fluorescence function

![Figure B.1: A simulated (yellow) and a real (blue) secular scan peak plotted in the same window.](image)

baseline may have a slope corresponding to the wing of the secular resonance of particles with mass 4 and 5 amu (see for example, Fig. 4.7). This slope is detected and removed by the Mathematica code we use to analyze the PMT signal traces. Inserting equation B.2 into Eq. (4.11), we obtain

\[ S = \frac{R^{MB}(\bar{T}_i) - R^{MB}(\bar{T}_f)}{R^{MB}(\bar{T}_i) - R^{MB}(\bar{T}_{bl})}, \]  

(B.3)

which is a relationship between the spectroscopic signal \( S \) and the average ion temperatures during the initial and final secular scan, \( \bar{T}_i \) and \( \bar{T}_f \) respectively.

The relationship between the number of trapped HD\(^+\) molecules and \( \bar{T} \) can be obtained from MD simulations. A realistic Coulomb crystal is simulated containing 750 trapped Doppler-cooled Be\(^+\) ions and with HD\(^+\) numbers varying from 0 to 100 (for details see appendix A). Concerning the number of particles with mass 4 and 5 amu (\( \text{H}_2\text{D}^+ \) and HD\(^+\)), we take the two scenarios a and b into account that are introduced in 4.4.2. The simulated secular scans over the HD\(^+\) secular resonance frequency produce fluorescence peaks which agree qualitatively with those obtained in the laboratory as shown in Fig. B.1.

The simulated duration of a secular scan is approximately 100 ms, which is much shorter than the ten seconds of a real secular scan. The time scale at which temperature and fluorescence changes take place in the simulation is 1 ms or longer, which is much longer than the time scale of fluorescence dynamics during laser cooling, which takes place at time scales of the order of \( 10 \mu s \) \[137\]. Therefore, we can rely on results of the simulated secular scan peaks.

The MD simulations reveal a linear relationship between the number of trapped HD\(^+\) ions and \( \bar{T} \). This confirms the intuitive picture in which the Be\(^+\) temperature rise during secular excitation is directly proportional to the
Figure B.2: Results from MD simulations that give the average ion temperature during a secular scan $\bar{T}$ versus the number of HD$^+$ ions $N_{\text{HD}^+}$ for both the scenarios a (blue dots) and b (yellow dots). The blue and yellow lines represent least-squares fits, showing a linear relationship between $\bar{T}$ and $N_{\text{HD}^+}$.

number of HD$^+$ ions. Figure B.2 shows the $(N_{\text{HD}^+}, \bar{T})$ relationship for the two scenarios a and b. Having established that $\bar{T}$ is a measure of the number of trapped HD$^+$ molecules, we now combine the relations $\epsilon = (N_i - N_f)/N_i$, $\bar{T}_i = c_1 N_i + c_2$ and $\bar{T}_f = c_1 N_f + c_2$, where $c_1$ and $c_2$ are constants derived from MD simulations (Fig. B.2), to obtain

$$\bar{T}_f(\epsilon) = \bar{T}_i(1 - \epsilon) + c_2 \epsilon. \quad (B.4)$$

$\bar{T}_i$ can also be defined as the average temperature with zero HD$^+$ loss ($\bar{T}_i = \bar{T}_f(\epsilon = 0) \equiv \bar{T}_0$), and the term $c_2$ can be considered as the average baseline temperature ($c_2 = \bar{T}_f(\epsilon = 1) = \bar{T}_{\text{bl}}$). Inserting Eq. (B.4) into Eq. (B.3) results in the nonlinear function

$$f_{\text{NL}}(\bar{T}_0, \epsilon) \equiv \frac{R^{MB}(\bar{T}_0) - R^{MB}(\bar{T}_{\text{bl}})\epsilon + \bar{T}_0}{R^{MB}(\bar{T}_0) - R^{MB}(\bar{T}_{\text{bl}})}, \quad (B.5)$$

which is plotted for scenario a in Fig. B.3.

In the analysis $\bar{T}_0$ is treated as a free fit parameter. $\bar{T}_{\text{bl}}$ is kept at a fixed value which is obtained from MD simulations. From Fig. B.2 it can be seen that $\bar{T}_{\text{bl}} \simeq 0.5$ K for scenarios a and b. This indicates that the rf field used for secular excitation already induces heating of Be$^+$ while the field is still off resonance. This effect is also seen in the experiment.

The nonlinear function $f_{\text{NL}}$ is used to map the relative HD$^+$ loss $\epsilon$ onto the spectroscopic signal $S$. In Sec. 4.4.5 we need to map $S$ to $\epsilon$, which requires the inverse non-linear function $f_{\text{NL}}^{-1}$. This inverse function is obtained by use of MATHEMATICA.
B. Derivation of the non-linear fluorescence function

Figure B.3: 3D plot of the function $f_{NL}(\bar{T}_0, \epsilon)$ (here plotted for scenario a) which connects the raw measurement signal $S$ to the actual fractional loss of HD$^+$, $\epsilon$. 

**Figure B.3:** 3D plot of the function $f_{NL}(\bar{T}_0, \epsilon)$ (here plotted for scenario a) which connects the raw measurement signal $S$ to the actual fractional loss of HD$^+$, $\epsilon$. 

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The Be\textsuperscript{+} micromotion amplitude can be written as
\[ x_0 = \frac{Q}{m_{\text{Be}} \Omega^2} E_t(x, y, z, t) \]  
(C.1)
where \( Q \) is the elementary charge. The measured micromotion amplitude can be written as
\[ x_{0,k} = \frac{k \cdot x_0}{\|k\|}, \]  
(C.2)
which is the projection of the 313 nm laser direction onto \( x_0 \). \( E_t \) in Eq. (C.1) is the E-field in the ion trap, which can be expressed as [87]
\[ E_t(x, y, z, t) \cong - \frac{V_0}{R^2} (x\hat{x} - y\hat{y}) \cos(\Omega t) - \frac{\kappa U_0}{Z_0^2} \times (2z\hat{z} - x\hat{x} - y\hat{y}), \]  
(C.3)
where \( R \) is half the distance between two diagonally opposing electrodes, \( U_0 \) is the endcap voltage, \( Z_0 \) stands for half the endcap-to-endcap distance and \( \kappa \) is a shielding factor. From simulations of the rf trap circuitry with the simulation software Spice, we find a very small phase difference \( \phi_{ac} \) of 4 mrad in between the rf electrodes, which has a negligible effect on the ion micromotion and is ignored here. With the program SIMION, we have calculated the shielding factor \( \kappa \) and the static electric fields \( E_{dc} \) as a function of the dc voltages applied to the trap electrodes. From the static electric fields, the radial ion displacement \( r_d \) is obtained by balancing the ponderemotive force and static E-field in the radial direction:
\[ m_{\text{Be}} \omega_r^2 r_d = -qE_{dc} \]  
(C.4)
where $\omega_r$ is the radial secular trap frequency. By inserting the $x$- and $y$-components of $r_d$ in Eq. (C.3), the value of $E_t$ at the location of the ions is obtained.

A geometric imperfection of the trap could lead to an axial rf field, which can be written as (here we ignore the small modification of the radial rf field of the trap due to the same imperfection):

$$E_{ax,HD}(V_0,t) = \frac{1}{Q} \frac{V_0}{V_{0,e}} m_{HD} x_{HD} \Omega^2 \cos \Omega t$$

where $x_{HD}$ is the HD$^+$ micromotion amplitude along the trap $z$-axis, $m_{HD}$ is the mass of HD$^+$, and $V_{0,e}$ is the rf voltage used during the spectroscopy measurement, which is 270 V.

Now, we turn to the case of a linear string of Be$^+$ ions, which is the configuration used to determine the axial rf field amplitude. Adding $E_{ax,HD}$ to the $z$-component of $E_t$ gives a new expression for $E_t$ which is inserted into Eq. (C.1). We then obtain the following expression for $x_0$:

$$x_0 = \left( \frac{2E_{t,x} q R^2 V_0 Z_0^2}{q V_0^2 Z_0^2 - 2 m_{Be} R^4 U_0 \kappa \Omega^2}, \frac{2E_{t,y} q R^2 V_0 Z_0^2}{q V_0^2 Z_0^2 - 2 m_{Be} R^4 U_0 \kappa \Omega^2}, \frac{m_{HD} V_0 x_{HD}}{m_{Be} V_{0,e}} \right).$$

which is subsequently inserted into Eq. (C.2), together with the wavevector, which is written as

$$k = \frac{2\pi}{\lambda} (\sin(\theta) \cos(\phi), \sin(\theta) \sin(\phi), \cos(\theta)).$$

Here $\theta$ is the angle between $k$, and the trap $z$-axis and $\phi$ is the angle between $k$ and the trap $y$-axis, which is very close to $\pi/4$ in our setup. The value of $\theta$ lies between $\pm 10$ mrad and is treated as a free fit parameter. We insert Eqs. (C.7) and (C.6) into Eq. (C.2) and then expand the expression in powers of $\theta$. This gives us the following fit function:

$$x_{0,k}(V_0) = \frac{m_{HD} V_0 x_{HD}}{m_{Be} V_{cal}} - \frac{8(E_{h,offs} - E_{v,offs} + \delta E_h - \delta E_v) Q^2 V_0}{m_{Be} R^2 \Omega^4 (2a_M + q^2_M)} \theta + O(\theta^2).$$

where $\omega_r$ is the radial secular trap frequency. By inserting the $x$- and $y$-components of $r_d$ in Eq. (C.3), the value of $E_t$ at the location of the ions is obtained.
Here $E_{h,\text{offs}}, E_{v,\text{offs}}$ are the applied static electric fields, and $\delta E_h, \delta E_v$ the unknown offset electric fields in the horizontal and vertical directions (due to e.g. charging of electrodes). The Mathieu parameters $a_M$ and $q_M$ are defined as:

$$a_M = -\frac{4Q\kappa U_0}{m_{\text{Be}}Z_0^2\Omega^2}, \quad q_M = \frac{2QV_0}{m_{\text{Be}}R^2\Omega^2}. \quad (C.9)$$

The displacement of the Be\(^+\) string in the vertical direction can be accurately determined with images of the EMCCD camera, and therefore $\delta E_h$ can be zeroed (for example by minimizing the displacement of the Be\(^+\) string while the radial confinement of the trap is modulated by varying the rf amplitude). However, the displacement in the horizontal direction is not accurately known and therefore we treat $\delta E_h$ as another free fit parameter. In summary, we use Eq. (C.8) as a fit function with $x_{\text{HD}^+}, \theta$ and $\delta E_h$ as free fit parameters while neglecting higher orders of $\theta$. The fitted curves and the result for $x_{0,k}$ are shown in Sec. 4.4.3.

The question arises what happens if the 782 nm laser propagates at a small angle with respect to the trap axis, while the HD\(^+\) ions form a shell structure around the trap axis. In this case a small fraction of the radial micromotion is projected onto the wavevector. However, from Eqs. (C.1-C.3) it follows that the sign of this additional micromotion alternates for each quadrant in the $(x, y)$ plane. As long as the radial micromotion component does not exceed the axial micromotion amplitude (which is the case here), the former averages out to zero given the radial symmetry of the HD\(^+\) crystal.
Appendix D

Stark shift calculations

Here we summarize the formulas that are used to calculate the ac Stark shift of a ro-vibrational transition \((v, L) \rightarrow (v', L')\) in the HD\(^+\) molecule induced by a laser with intensity \(I\) and polarization state \(p\). A general expression for the second-order energy shift depending on the angle \(\theta\) between the polarization direction and the quantization axis is:

\[
\Delta E = -\frac{I}{2c} \left[ \alpha^{(0)}_{vL}(\omega) + P_2(\cos \theta) \frac{3M^2 - L(L + 1)}{L(2L - 1)} - \alpha^{(2)}_{vL}(\omega) \right],
\]

where \(P_2(x) = \frac{1}{2}(3x^2 - 1)\) is a Legendre polynomial. This expression contains the scalar and tensor polarizabilities

\[
\begin{align*}
\alpha^{(0)}_{vL}(\omega) &= 4\pi a_0^3 Q_s, \\
\alpha^{(2)}_{vL}(\omega) &= 4\pi a_0^3 \sqrt{\frac{L(2L - 1)}{(L + 1)(2L + 3)}} Q_t,
\end{align*}
\]

where \(a_0\) is the Bohr radius and \(Q_s\) and \(Q_t\) stand for the two-photon scalar and tensor matrix elements:

\[
\begin{align*}
Q_s &= \frac{\langle vL \| Q^{(0)} \| v'L \rangle}{\sqrt{2L + 1}}, \\
Q_t &= \frac{\langle vL \| Q^{(2)} \| v'L \rangle}{\sqrt{2L + 1}}.
\end{align*}
\]

Here \(Q^{(0)}\) and \(Q^{(2)}\) are the irreducible scalar and tensor components that belong to the two-photon operator (in atomic units):

\[
Q_{pp}(E) = d \cdot \epsilon_p \frac{1}{H - E} d \cdot \epsilon_p,
\]

\[(D.4)\]

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D. Stark shift calculations

with Hamiltonian $H$, dipole moment operator, $d$ and polarization vector $\epsilon_p$. The matrix elements $Q_s$ and $Q_t$ were calculated numerically by J.-Ph. Karr using the three-body variational wave functions described in [14].

Since the hyperfine structure is partially resolved in this spectrum, we also have to consider the contribution of the Stark shifts to off-resonant coupling to hyperfine levels in $v = 0$ and $v = 8$ by the 782 nm laser during spectroscopy. Here, the situation is more complicated as the 782 nm laser also non-resonantly couples $v = 8$ states to continuum states above the dissociation limit of the $1s\sigma$ electronic ground state. The 782-nm contribution to the Stark shift was calculated by J.-Ph. Karr at the hyperfine level. The corresponding shifts turn out to be negligible for our experiment, contributing only at the level of a few Hertz.