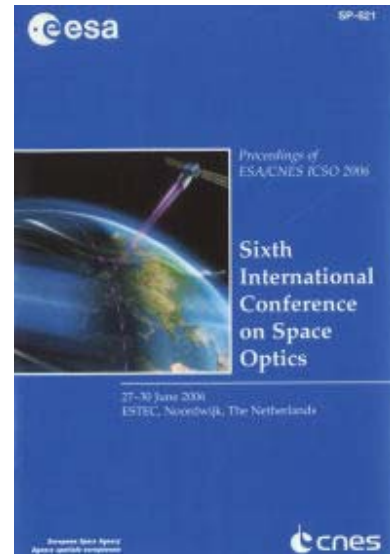


# International Conference on Space Optics—ICSO 2006

Noordwijk, Netherlands

27–30 June 2006

*Edited by Errico Armandillo, Josiane Costeraste, and Nikos Karafolas*



## *Trapped ultracold molecular ions: candidates for an optical molecular clock for a fundamental physics mission in space*

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## TRAPPED ULTRACOLD MOLECULAR IONS: CANDIDATES FOR AN OPTICAL MOLECULAR CLOCK FOR A FUNDAMENTAL PHYSICS MISSION IN SPACE

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Narrow ro-vibrational transitions in ultracold molecules are excellent candidates for frequency references in the near-IR to visible spectral domain and interesting systems for fundamental tests of physics, in particular for a satellite test of the gravitational redshift of clocks. We have performed laser spectroscopy of several ro-vibrational overtone transitions  $v = 0 \rightarrow v = 4$  in  $\text{HD}^+$  ions at around  $1.4 \mu\text{m}$ . 1+1 REMPD was used as a detection method, followed by measurement of the number of remaining molecules. The molecular ions were stored in a linear radiofrequency trap and cooled to millikelvin temperatures, by sympathetic cooling using laser-cooled  $\text{Be}^+$  ions simultaneously stored in the same trap.

For more than a century, spectroscopy of atoms and molecules has given insight into many aspects of nature, ranging from the very small (nuclear, atomic and particle physics) to the very large (astronomy and cosmology). Ongoing developments in precision spectroscopy are partly motivated by the possibility to perform stringent tests of fundamental laws and postulates of physics, which form the framework of contemporary theoretical models such as the standard model and general relativity. Alternatively, precision spectroscopy may be used to determine the value of fundamental constants of nature. Predictions by theoretical models need to be combined with spectroscopic data to achieve both of these goals.

Precision spectroscopy has been used once in a space experiment, the 1976 Gravity Probe A rocket mission, which carried a hydrogen maser into space. The hyperfine transition frequency of the maser (1.4 GHz) was compared with ground clocks as a function of the rocket height. The results were analyzed in the framework of General Relativity (GR) and it was found that the gravitational redshift agreed with the GR prediction at a level of 70 ppm [1].

Present state-of-the-art precision spectroscopy is performed with ultrastable lasers which probe narrow, optical transitions between energy levels in atoms and molecules. The most accurate spectroscopic results to date have been achieved with laser spectroscopy of single, ultracold trapped atomic ions [2, 3, 4]. The strong suppression of Doppler shifts, their good isolation from the environment and their long storage times make single trapped ions ideally suited for prolonged interrogation of narrow transitions. Very recently, it has been shown that the ratio of the transition frequencies of two dissimilar trapped atomic ions can be measured with a precision exceeding 1 part in  $10^{16}$  [5]. For similar reasons as for atomic ions, the hitherto unexplored option of precision spectroscopy of trapped ultracold *molecular* ions is of great interest. The more complex structure of the molecules offers unique possibilities to test additional theoretical models and/or to determine the value

of fundamental constants.

Based on the outstanding progress in precision spectroscopy in the optical domain, it is expected that a satellite test of General Relativity using optical clocks could search for deviations from the gravitational redshift result of GR at a level at least 10 000 times more precise than the Gravity Probe A mission [6]. By flying both atomic and molecular clocks, the scope of the test would be significantly widened, since these two clock types are dissimilar: the frequency of an atomic clock depends on the fine structure constant, and that of a molecular clock on the ratio of electron to nuclear mass. Thus, two types of tests can be performed: a test of redshift universality (Local Position Invariance) by comparing the two dissimilar clock types directly on-board, and an absolute redshift measurement by comparing the two satellite clocks with ground clocks.

Promising candidates for precision molecular spectroscopy are the molecular hydrogen ion ( $\text{H}_2^+$ ) and its isotopomers ( $\text{HD}^+$ ,  $\text{D}_2^+$ , etc.), which are the simplest of all molecules. As such, they represent the ultimate quantum-mechanical model for ab-initio molecular structure calculations, including higher order corrections, such as non-adiabatic, relativistic, and QED contributions [7, 8, 9, 10, 11, 12, 13, 14]. The relative inaccuracy of such calculations is currently at the level of  $10^{-8}$  [8], and efforts are underway towards  $10^{-10}$ – $10^{-11}$  inaccuracy [11]. Precise measurements on these systems can therefore test quantum chemical calculations at their current state of accuracy or better and stimulate the development of more advanced theoretical models [15, 16].

Apart from being a candidate for a test of the universality of the gravitational redshift, another interesting possibility offered by the molecular hydrogen ion is the search for a temporal variation of  $m_e/m_p$  [9, 17, 18]. Theories which have recently been developed in an attempt to unify the standard model with general relativity allow for or even predict such a variation. In case that  $m_e/m_p$  varies in time, repeated spectroscopic measurements on a limited set of lines in the molecular hydrogen

ion should eventually reveal a change of the transition frequencies with time [9]. Furthermore, even when an experimental result consistent with zero variation is found it still provides an upper limit on the possible variation (given by the uncertainty of the measurement), and it may serve as input for theory.

In particular, comparison of frequencies of two vibrational transitions of  $\text{HD}^+$  would allow setting limits on the time dependence of both the electron-to-proton ( $m_e/m_p$ ) and the proton-to-deuteron mass ratio ( $m_p/m_d$ ). A comparison between transition frequencies in  $\text{HD}^+$  and  $\text{H}_2^+$  could be used to determine the individual contributions [9]. Apart from such measurements, high-precision spectroscopy on ultracold  $\text{HD}^+$  ions could allow determining molecular physics effects such as (i) the dependence of the hyperfine coupling constants on the rotational quantum number [12, 19, 20], (ii) identification of the nuclear spin rotation interaction effect [21], (iii) measurement of the electric quadrupole interaction contribution [22], and (iv) identification of the effects of the anapole magnetic moment of the molecule [23, 24].

The molecular hydrogen cation has been subject of several experimental studies in the past. The main work has been on the hyperfine structure in several low-lying vibrational states, by Dehmelt and others [25, 26, 27], and on vibrational transitions between states close to the dissociation limit [28]. There has been only a single study of laser-induced transitions of low-lying vibrational levels, performed by Wing and coworkers almost thirty years ago [29]. All studies were performed on warm samples or on ion beams.

The extension of such measurements to the ultracold temperature regime offers the potential to increase the spectroscopic accuracy, possibly by several orders of magnitude, due to the reduction of first-order Doppler broadening and of systematic effects. Molecular hydrogen ion ensembles at  $< 20$  mK translational energy were recently produced by sympathetic cooling using laser-cooled atomic ions stored in a linear radiofrequency trap [30]. In this environment, the molecular ions are well-localized inside ordered structures, denoted as Coulomb crystals, where they can be stored on the time scale of several minutes, favorable for long interrogation times in spectroscopic measurements. Within such crystals, the particles are in an isolated, nearly collision-less regime. Typical interparticle distances are in the range of several tens of micrometers, hence collisional or pressure broadening of the transition lines is insignificant.

We have demonstrated high-resolution laser spectroscopy on ultracold molecular hydrogen ions,  $\text{HD}^+$ , in traps. Using the method developed, we have performed a first measurement of the ro-vibrational transitions ( $v = 0, J = 0, 1, 2 \rightarrow v = 4, J = 1, 0, 1$ ), respectively, where  $v$  and  $J$  are the vibrational and rotational quantum numbers in the  $\text{HD}^+$  electronic ground state. The above transitions span the frequency range

6991.1091 to 7122.486  $\text{cm}^{-1}$ , corresponding to wavelengths between 1.430 and 1.404  $\mu\text{m}$ . The method developed can be applied to a huge number of other molecular ion systems.

We simultaneously store both  $\text{Be}^+$  ions and molecular ions in a linear radiofrequency trap, enclosed in a UHV chamber, kept below  $10^{-10}$  mbar. The trap is driven at 14.2 MHz, with a peak-to-peak amplitude of 380 V. This leads to a radial Mathieu stability parameter  $q_r \simeq 0.04$ , [31], and a (single-particle) radial secular oscillation frequency of 280 kHz for the  $\text{Be}^+$ . For the deuterium hydride ions ( $\text{HD}^+$ )  $q_r \simeq 0.12$  and the (single-particle) radial oscillation frequency is at 840 kHz.

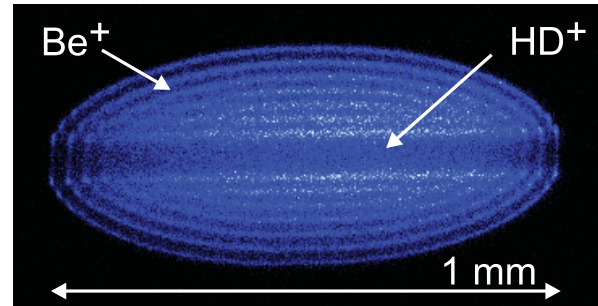


FIG. 1: Two-species ion crystal used for 1+1 REMPD spectroscopy of  $\text{HD}^+$ . The crystal contains  $\approx 3150$   $\text{Be}^+$  and  $\approx 95$   $\text{HD}^+$  ions at a translational temperature of  $\approx 12$  mK. Crystal structure, ion numbers and upper limits for the translational temperature were deduced via MD simulations.

The  $\text{Be}^+$  ions are laser-cooled to millikelvin temperatures using a 313 nm UV laser [32]. For strong cooling, the ions are nearly localized in ordered structures (Coulomb crystals) [33]. Due to the long-range electrostatic interaction between atomic coolants and molecular ions, the latter are efficiently cooled to translational temperatures  $< 20$  mK and embedded around the axis of the  $\text{Be}^+$  ion crystals, which is energetically more favorable. Fig.1 shows a typical two-species ion crystal containing  $\approx 95$  ultracold  $\text{HD}^+$  ions used for our measurements. The presence of the  $\text{HD}^+$  ions is obvious from the dark core of the ion crystal. Due to the weak coupling between external and internal degrees of freedom, the internal temperature of the  $\text{HD}^+$  ions is expected to be at 300 K [34], in thermal equilibrium with the vacuum chamber. We use molecular dynamics (MD) simulations to deduce ion numbers, three-dimensional spatial distributions, and upper limits for the translational temperature of each species contained in the crystal. The simulations include full Coulomb interaction, light pressure forces, anisotropies of the effective trap potential, and species-dependent heating rates. We identify the trapped species by excitation of their mass-dependent motional (secular) frequencies. For individual ions in a radiofrequency trap, the motional frequencies are inversely proportional to their mass (see [30, 35, 36, 37] for a detailed

description of our procedure).

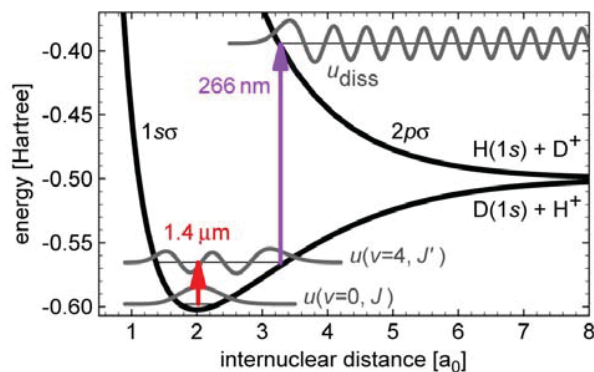


FIG. 2: Scheme of 1+1 REMPd of  $\text{HD}^+$  molecular ions.

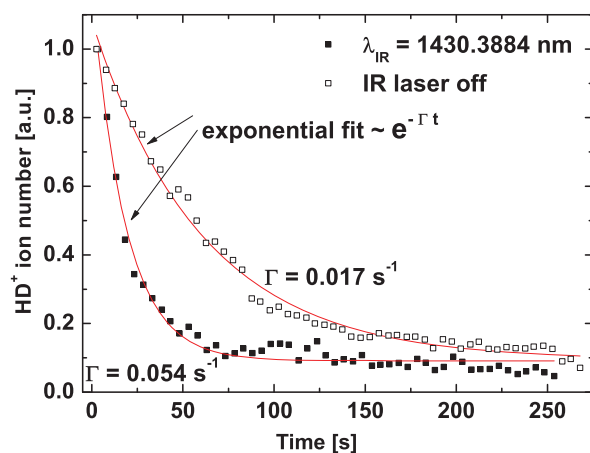


FIG. 3: Observed decrease of the number of  $\text{HD}^+$  ions when the IR laser is tuned close to the  $(v=0, J=2) \rightarrow (v=4, J=1)$  transition (solid squares). Background  $\text{HD}^+$  losses when both lasers are off (open squares) are mainly due to chemical reactions with residual nitrogen gas present in the trap.

We perform 1+1 resonance enhanced multiphoton dissociations (REMPd) spectroscopy using a tunable infrared (IR) diode laser with a maximum output power of 4 mW to excite the ro-vibrational overtone transitions at around  $1.4 \mu\text{m}$ . The diode laser has a jitter limited linewidth  $< 5 \text{ MHz}$ . The excited  $\text{HD}^+$  ions in the  $v=4$  vibrational level are state-selectively dissociated, [38], using a continuous wave 266 nm UV laser source:  $\text{HD}^+(v=4) + h\nu \rightarrow \text{H} + \text{D}^+$  or  $\text{H}^+ + \text{D}$ . Fig.2 shows a schematic of the spectroscopic technique used.

For detection, we observe the loss rate of ultracold  $\text{HD}^+$  ions from the trap, while scanning the frequency of the IR excitation laser in a range of several 100 MHz around the (calculated) ro-vibrational transition frequency [7]. The above loss rate is determined by repeated excitation of the  $\text{HD}^+$  secular motion in the trap, after turning on the excitation and dissociation lasers,

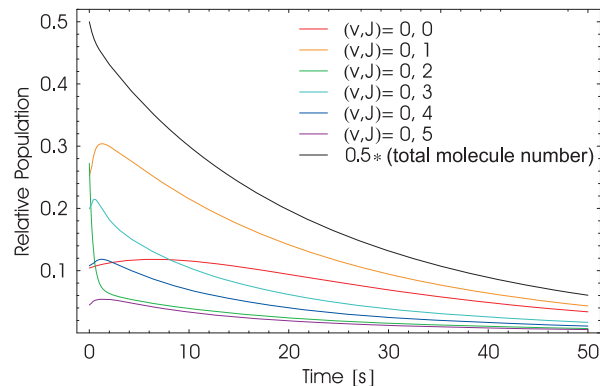


FIG. 4: Simulated population dynamics for a translationally ultracold (20 mK) collision-free ensemble of  $\text{HD}^+$  ions, with the IR laser set to the maximum of the  $(v=0, J=2) \rightarrow (v=4, J=1)$  transition. The intensities of the lasers are  $I(\nu_{IR}) = 0.32 \text{ W/cm}^2$ ,  $I(266 \text{ nm}) = 0.57 \text{ W/cm}^2$ .

and observation of the change induced in the  $\text{Be}^+$  fluorescence, due to heating of the atomic coolants by the molecular ions. This change in the atomic fluorescence is proportional to the number of  $\text{HD}^+$  ions contained in the crystal.

The  $\text{HD}^+$  decay rate was measured as a function of the frequency of the IR laser, by scanning the latter in discrete 15 MHz steps, Fig.3. Prior to each measurement, the frequency of the IR laser was calibrated, via absorption spectroscopy in a water vapor cell. The accuracy of the calibration is  $\pm 30 \text{ MHz}$ . We have fitted a Gaussian to the lines obtained, in order to determine the line center. We find good agreement of the value for the line center measured with the calculated transition frequencies from [7]. The width of the lines is in the range of 100 MHz.

The observed time evolution of the  $\text{HD}^+$  ion number under laser irradiation is well described by a rate equation model, see Fig.4. The model takes into account spontaneous emission and absorption of black-body radiation as well as absorption of the IR and UV light, and stimulated emission by the IR light. Transition moments are taken from [39]. The lifetimes for the excited ro-vibrational states are from [40].

As an example, Fig.4 shows the evolution when the  $(v=0, J=2) \rightarrow (v=4, J=1)$  transition is driven. For the intensities shown, there is a rapid decrease of the population of the initial state due to prompt photo dissociation and, dominantly, decay from the upper vibrational state to other rotational levels of the ground vibrational state.

Due to coupling between neighboring levels via black-body radiation absorption or spontaneous emission, the  $J=2$  level population remains significant so that photo dissociation continues. On a time scale of several tens of seconds, all  $\text{HD}^+$  ions contained in the crystal are photo dissociated. This time scale is in good agreement with

the experimental observation. Furthermore, the time evolution of the total population can be reasonably well described by a single exponential.

Several effects contribute to the observed line widths, e.g., hyperfine splitting of the ro-vibrational transitions [20], residual Doppler broadening, saturation broadening, and Zeeman splitting by the 10 G bias magnetic field used for  $\text{Be}^+$  cooling.

In summary, we have observed a total of 12 ro-vibrational overtone transitions between 1391 nm and 1471 nm, on ultracold trapped  $\text{HD}^+$  molecular ions, cooled to approximately 20 mK via laser-cooled  $\text{Be}^+$  ions [41]. After excitation to the  $v = 4$  vibrational level, using a tunable diode laser at 1.4  $\mu\text{m}$ , the molecules were state-selectively dissociated via a 266 nm UV laser. We used secular excitation mass-spectroscopy to monitor the  $\text{HD}^+$  loss rate from the trap, as a function of the frequency of the IR laser, calibrated using water absorption spectroscopy. A first measurement of the transition frequencies using a femtosecond frequency comb has been performed, and will be reported elsewhere.

The method demonstrated represents a promising route towards the application of ultracold, trapped molecules for high-precision measurements of ro-vibrational transitions, possibly leading to an improvement of the spectroscopic accuracy by several orders of magnitude. Furthermore, narrow ro-vibrational transitions in ultracold molecules are candidates for frequency references in the near-IR to visible spectral domain. They are especially interesting for fundamental tests of physics, such as a test of the time-independence of the electron-to-nuclear mass ratio, a test of Local Position Invariance, and a test of isotropy of space. Such tests could advantageously be performed in space [6].

Large ion crystals containing several hundred ultracold  $\text{HD}^+$  ions may limit the spectroscopic accuracy, due to spatially varying Doppler shifts of the transition frequency. The spatial extent also introduces a sensitivity to field gradients, and the resulting spread of frequency shifts might limit the spectral resolution. Finally, even at a temperature of 10 mK, first-order Doppler shifts will limit the achievable accuracy of the 1.4  $\mu\text{m}$  spectroscopy to about  $10^{-9}$ .

Most of the problems anticipated for trapped clouds of  $\text{HD}^+$  will be virtually absent, or may be substantially alleviated otherwise, by turning to quantum-logic-enabled spectroscopy (QLES) as proposed [42] and recently demonstrated by the Wineland and coworkers for atomic ions [43]. The method would involve using a single ultracold  $\text{HD}^+$  molecular ion in the Lamb-Dicke regime, coupled to a single  $\text{Be}^+$  atomic ion, which is used for both cooling the translational energy of the  $\text{HD}^+$  and state-selective detection of the molecular state.

**Acknowledgements** We thank the Deutsche Forschungsgemeinschaft (DFG) and the EC network HPRN-CT-2002-00290 for support. We thank C.B. Zhang for helpful as-

sistance with the MD simulations.

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