P H Y S I C A L   R E V I E W   L E T T E R S

High-Resolution Rotational Spectroscopy in a Cold Ion Trap: H_2D^+ and D_2H^+

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The lowest-lying $1_{01} \leftarrow 0_{00}$ transition of $para$-H_2D^+ and $1_{11} \leftarrow 0_{00}$ of $ortho$-D_2H^+ has been detected by the enhancement of the D/H isotope exchange reaction in collisions with p-H_2 upon rotational excitation. These are the first pure rotational spectra of molecular ions by action spectroscopy. For this purpose, a cryogenic multipole ion trap has been combined with narrow-band tunable radiation sources operating in the 1.25 to 1.53 THz range. The low temperature of the ions allows us to determine the astronomically important transitions with a relative precision of $\Delta\nu/\nu = 10^{-8}$. While the $1\,476\,605.708(15)$ MHz line center frequency for the o-D_2H^+ transition agrees very well with previous unpublished work, the $1\,370\,084.880(20)$ MHz line center frequency for the p-H_2D^+ transition deviates by 61 MHz. Potential future applications of this new approach to rotational spectroscopy are discussed.
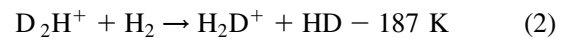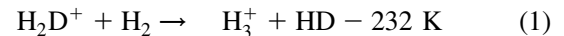
H_3^+ plays an important role in hydrogen dominated plasmas, in astronomical environments [1,2], and as a testbed for *ab initio* calculations [3]. Its deuterated versions H_2D^+ and D_2H^+ have gained special interest for astronomers in recent years as they are known to be responsible for a very strong enrichment of deuterium containing molecules (isotopic fractionation) in cold interstellar regions, and because their dipole moments permit a radioastronomical detection and thus a quantitative characterization of the chemistry of cold clouds. For that purpose, accurate line positions of the rotational transition are mandatory. Only the lowest rotational transition of these two key molecules can be detected in the interstellar medium, and in recent years o-H_2D^+ [4] and p-D_2H^+ [5] have been observed based on earlier laboratory work [6–8]. Since then, the 372 GHz 1_{10}–1_{11} emission line of o-H_2D^+ has been used routinely as a probe for cold clouds, while the 692 GHz 1_{10}–1_{01} detection of p-D_2H^+ is the only one thus far. Concerning the complementary nuclear spin families (*ortho-para*), only one tentative detection of p-H_2D^+ exists [9].

Rotational and vibrational spectroscopy of ions is usually performed by measuring the absorption of narrow-band electromagnetic radiation traversing a discharge tube in which these transient species are generated [6–8,10,11]. This method has been very successful for a large number of species. However, it suffers from a number of problems. Namely, (i) many different ions are usually produced in a discharge, and assigning the measured lines can be a difficult task. (ii) Rather high column densities are needed to record an absorption spectrum. (iii) The ions are comparably hot, leading to a further complication of the spectrum and to unfavorable partition functions. Velocity modulation is sometimes used to separate ions from neutrals. However, (iv) applying electrical fields for this separation also induces Doppler shifts which have to be taken into account to obtain accurate rest frequencies.

In the present work, a rather different approach has been applied, which largely overcomes these limitations. Mass selected molecular ions, here H_2D^+ or D_2H^+, are stored in a low-temperature 22-pole ion trap where they interact with ambient, cold H_2 gas. The endothermic hydrogenation reactions (with the given calculated enthalpies taken from [12])

$$H_2D^+ + H_2 \rightarrow \quad H_3^+ + HD - 232 \text{ K} \qquad (1)$$

$$D_2H^+ + H_2 \rightarrow H_2D^+ + HD - 187 \text{ K} \qquad (2)$$

$$\rightarrow \quad H_3^+ + D_2 - 340 \text{ K} \qquad (3)$$

are enhanced by the additional rotational energy of the parent ion when excited by the radiation from a THz source. A spectrum can thus be recorded by detecting the number of product ions as a function of excitation frequency. This method of action spectroscopy allows to record high-resolution spectra of mass-selected, cold molecular ions with only a few hundred ions per trap filling. This technique has been used quite extensively over the last years to record vibrational and ro-vibrational spectra of small ions such as CH_5^+ [13] and $C_2H_2^+$ [14,15], and recently also the fundamental bands [16], overtone, and combination bands [17] of H_2D^+ and D_2H^+ have been investigated. In this Letter, we demonstrate the first application of this technique to pure rotational spectroscopy. The results lead to new molecular parameters for the important H_2D^+ ion.

The experimental setup is depicted in Fig. 1 and will be briefly described in the following. The parent ions are generated by electron bombardment of hydrogen gas containing D_2 admixtures of $5-20\%$ and subsequent ion-molecule reactions in a ~350 K storage ion source (left in Fig. 1). A pulse of ions is mass selected in a quadrupole mass spectrometer and injected into the 22-pole ion trap held at 13 K (center in Fig. 1). This multipole trap, devel-
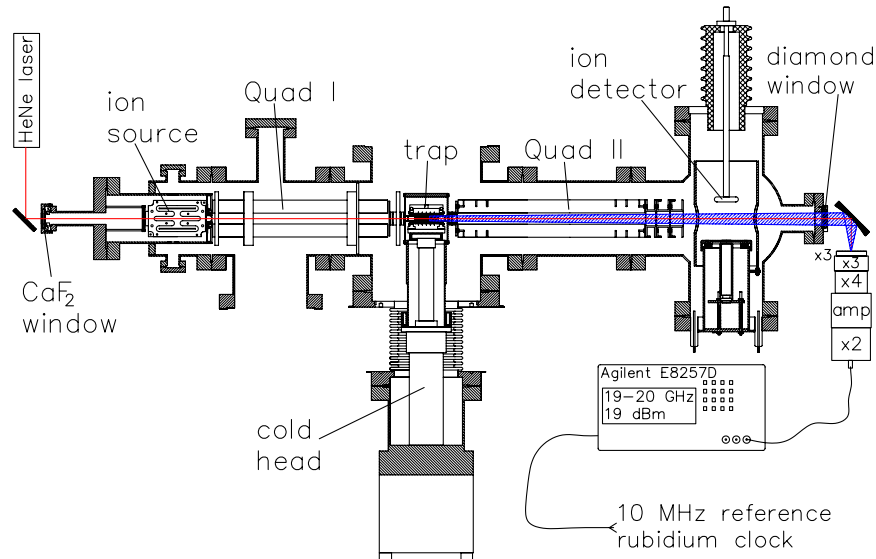
FIG. 1 (color online).   Experimental setup consisting of the ion trapping machine and the THz source. The unit consisting of THz source and elliptical mirror (on the right) is placed on a common support, which can be moved between the trapping machine and a test setup on a nearby optical bench (not shown). In both setups, a HeNe laser defines the beam path, to which the THz source is adjusted by a *xyz*-stage.

oped by Gerlich [18], features a wide field-free region and thus allows for cooling ions kinetically as well as internally by a buffer gas to low temperatures. A pulse of helium gas is applied on entrance of the ions. The trap is filled with a constant number density (10^{10} to 10^{12} cm^{-3}) of p-H_2 produced in an external catalytic p-H_2-generator. p-H_2 is used as reaction partner instead of n-H_2 due to its lower rotational energy content, leading to fewer background counts, and, in the case of H_2D^+, the investigated p-H_2D^+ is enriched by collisions in the ion trap. During storage, the ions are irradiated by the cw THz-beam and collide with p-H_2. After a trapping time of 870 ms, the ions are again mass selected and parent or product ions are detected in a high-efficiency detector counting the number of ions at a given charge to mass ratio (right side in Fig. 1).

The THz-radiation is generated by two sets of multiplier chains (Virginia Diodes, Inc.) covering the frequency ranges 1.25–1.40 and 1.42–1.53 THz, respectively. The chains, usually applied as local oscillators in heterodyne receivers [19], consist consecutively of a doubler, an intermediate amplifier, a quadrupler, and two triplers, giving a total frequency multiplication factor of 72 by which the output-frequency of the rubidium-clock referenced synthesizer (Agilent E8257D) operating at some 20 GHz is multiplied. The resulting total output power of the chains is frequency dependent and varying between 1 and 3 μW. The divergent radiation emerging from the last stage of the multiplier chain is redirected and focused by an elliptical mirror ($f = 43.7$ mm), entering the vacuum chamber via a 0.8 mm thick CVD diamond window (Diamond Materials GmbH), into the 0.6 m distant 22-pole ion trap, see Fig. 1. For alignment and calibration purposes, the optical setup consisting of source and mirror was placed on a common

support and first tested separately on an optical bench. Using a Golay-cell detector, it is estimated that a maximum of about 0.5 μW is reaching the trap, taking into account 70% transmission of the diamond window in the trap configuration. With this power estimate and literature *ab initio* Einstein *A* coefficients [12], an on-resonance excitation rate of 88 s^{-1} is calculated for the H_2D^+ $1_{01} \leftarrow 0_{00}$ transition and 60 s^{-1} for D_2H^+ $1_{11} \leftarrow 0_{00}$. As a result, a substantial fraction of the molecular ions are excited when they collide with the ambient p-H_2 and are ready for reactions (1)–(3).

The search for the p-H_2D^+ $1_{01} \leftarrow 0_{00}$ and o-D_2H^+ $1_{11} \leftarrow 0_{00}$ transitions was guided by unpublished data [20] cited in [10,11,21] and by *ab initio* values [12], which are listed in Table I. The action spectra obtained for the two species are shown in Figs. 2 and 3. A similar search for the weak fine-structure transition of N$^+$ [22] failed. The signals have been observed on all parent and product ions as suggested by reactions (1)–(3). The traces of the product ions have been recorded with relatively large frequency steps of 144 kHz (72×2 kHz) between the trapping cycles, and p-H_2 number densities below 10^{11} cm^{-3}. In

TABLE I.   Frequencies for the H_2D^+ $1_{01} \leftarrow 0_{00}$ and D_2H^+ $1_{11} \leftarrow 0_{00}$ rotational lines in MHz. The numbers in parentheses give the experimental uncertainty of the last digit.

	H_2D^+ $1_{01} \leftarrow 0_{00}$	D_2H^+ $1_{11} \leftarrow 0_{00}$
this work	1370084.880(20)	1476605.708(15)
ab initio[a]	1369991.8	1476628.0
unpublished value[b]	1370146.0(3)	1476605.5(3)

[a]Reference [12]
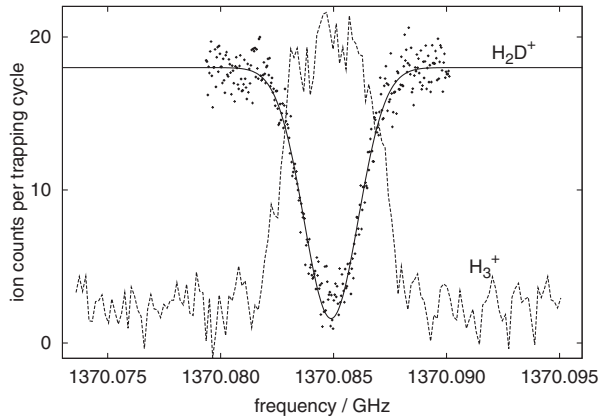[b]Unpublished values [20] cited in [10,11,21]

FIG. 2. Action spectrum of the H_2D^+ rotational transition $1_{01} \leftarrow 0_{00}$, observed as a decrease of the H_2D^+ parent species and as an increase of the product ion counts H_3^+ when the excitation frequency is in resonance. The baseline of background counts of a few hundred ions has been subtracted in both cases and only relative ion count changes are shown. Both traces have been recorded under different experimental conditions. The H_2D^+ trace has been obtained at a higher p-H_2 number density of about 4×10^{11} cm^{-3}. The Doppler width of $\sigma_D \approx 1$ MHz corresponds to a kinetic ion temperature of 23 K.

contrast, the reduction of the corresponding parent ion counts were recorded at a p-H_2 number density of about 4×10^{11} cm^{-3}, leading to the low temperature of the ions and a Doppler width around $\sigma_D \approx 1$ MHz. These measurements were chosen for the determination of accurate line center positions. Doing small frequency steps of
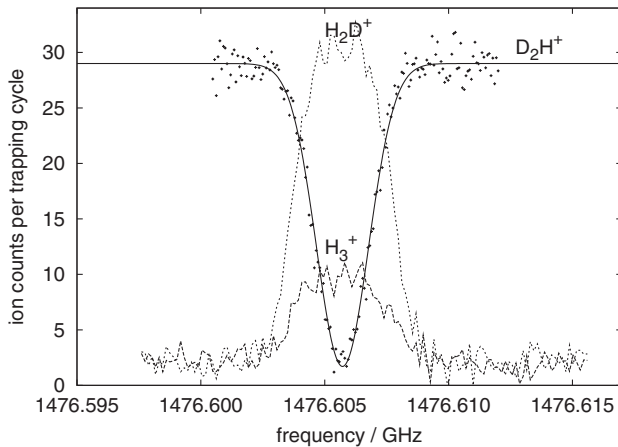

FIG. 3. The rotational transition $1_{11} \leftarrow 0_{00}$ of D_2H^+ has been detected by counting the number of parent ions (D_2H^+) or product ions (H_3^+ and H_2D^+) after a trapping time of 870 ms. The H_3^+ and H_2D^+ traces were recorded under similar experimental conditions, showing that reaction to H_2D^+ is more probable than H_3^+, while the D_2H^+ trace has been recorded at a p-H_2 number density of about 5×10^{11} cm^{-3}. The Doppler width of this signal is $\sigma_D \approx 1$ MHz, yielding an ion temperature of about 25 K. Applying small frequency steps of 72 kHz and sufficient iterations, the center frequency of the D_2H^+ trace is obtained with an accuracy of 15 kHz, see Table I.

72 kHz and about 100 iterations for the D_2H^+ trace (Fig. 3), the line center has been determined within an uncertainty of about 15 kHz, giving an overall precision of $\Delta\nu/\nu = 10^{-8}$. There is still room for further improvement in accuracy, as the present investigation suffered from temporal trap imperfections leading to increased noise in the ion signal as well as heating of the ion temperature about 10 K higher than the nominal trap temperature as derived from the Doppler line profiles. Probably for this reason, or due to the application of exceeding radiation power leading to saturation effects, the shapes of the product ion signals in Figs. 2 and 3 deviate a bit from Gaussian Doppler profiles when using low number densities of p-H_2. Nevertheless, the line profiles are perfectly symmetric. Therefore, frequency shifts induced by ion drifts or other difficulties in determining an accurate center frequency can be excluded in the low-temperature bath of the 22-pole ion trap.

The transition frequency for D_2H^+, see Table I, agrees very well within the given uncertainties to the value given in [11]. In sharp contrast, a difference of 61 MHz is found for the H_2D^+ transition as compared to the value given in the same reference [11]. Interestingly, a frequency in good agreement with ours is cited in [9] although the same origin of the experimental data has been used [20]. In the present investigation, the mass-selection capability of the ion trapping machine and the possibility of observing all parent and product ions gives us confidence about the identity of the target ions. In summary, the reproduction of the D_2H^+ transition to a precision of some 15–20 kHz and the new and accurate determination of the H_2D^+ transition clearly demonstrates the high-resolution possibilities of action spectroscopy in cold ion traps. As a result, new rotational constants A, B, C have to be calculated for H_2D^+ even though only the lowest rotational transition of p-H_2D^+ has changed. A sufficiently accurate Hamiltonian model describing the molecular rotation of this asymmetric rotor requires more spectroscopic parameters than can be determined with significance from the available laboratory data. Therefore, results from high-level *ab initio* theoretical work have been used to derive starting values for the molecular parameters. Details of these new calculations will be given elsewhere [23].

Besides the spectroscopic studies presented here, trap experiments can be used to determine state-specific reaction processes leading finally to state-specific rate coefficients which are most relevant for interstellar species populating only a few quantum levels. In the case of H_3^+ and its isotopic variants, state-specific information will lead to a largely improved understanding of interstellar deuterium chemistry which is one focus of current astrophysics. First experiments along these lines have already been performed using IR lasers [15–17]. In the present experiment, quantitative data require a better knowledge of the THz power reaching the ion trap. Moreover, caution is required when analyzing the product branching ratios of

the excited D_2H^+ in Fig. 3, reactions (2) and (3). For statistical and energetic reasons, a direct production of H_3^+ seems quite unlikely. Instead, the majority of the measured H_3^+ signal is thought to be produced in a two-step process, in which the excited D_2H^+ first forms H_2D^+, which subsequently forms H_3^+ in collision with H_2. As pointed out by Gerlich [24], even small impurities of o-H_2 contained in the p-H_2 environment can enhance this process.

The combination of a low-temperature multipole ion trap with a tunable narrow-band THz-source demonstrates that pure rotational spectroscopy on a few hundred stored ions is feasible using this type of action spectroscopy. The precisely determined frequencies for the lowest lying H_2D^+ $1_{01} \leftarrow 0_{00}$ and D_2H^+ $1_{11} \leftarrow 0_{00}$ transitions will enable a dedicated search for the p-H_2D^+ and o-D_2H^+ spin modification in interstellar space using current and future ground-based, airborne, or space THz telescopes, such as APEX, SOFIA, or the Herschel satellite.

The current accuracy of the determination of rotational line centers is limited by the Doppler width. Applying sympathetic cooling of molecular ions [25,26], the technique presented here opens up the way for unprecedented high precision rotational spectroscopy. It will be interesting to apply this new method of rotational spectroscopy to other molecular ions, like H_5^+ or CH_5^+. For such cases, H/D exchange reactions are slightly endoergic in one direction, and therefore action spectroscopy will work. It might even be feasible to consider thermoneutral reactions, e.g., proton transfer between AH^+ and the molecule A, combining traps with molecular beam methods. However, these tasks will pose some specific challenges to the experiment. The rotational constants for the heavier species are substantially smaller than those for H_2D^+. On the one hand, much more powerful radiation sources are available at lower frequencies. But on the other hand, the smaller rotational spacings lead to less favorable partition functions and limitations due to the finite number of parent ions in the trap. Therefore, it is most important to cool the ions to temperatures even below 10 K. Another complication arises from the fact that the energy of the photon for the rotational excitation will not lead to a significant enhancement of product formation. Double resonance experiments including ro-vibrational or even electronic transition could serve as a solution to this problem.

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