Manipulation of Individual Hyperfine States in Cold Trapped Molecular Ions and Application to HD^+ Frequency Metrology

U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, and S. Schiller
Institut für Experimentalphysik, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany

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Advanced techniques for manipulation of internal states, standard in atomic physics, are demonstrated for a charged molecular species for the first time. We address individual hyperfine states of rovibrational levels of a diatomic ion by optical excitation of individual hyperfine transitions, and achieve controlled transfer of population into a selected hyperfine state. We use molecular hydrogen ions (HD^+) as a model system and employ a novel frequency-comb-based, continuous-wave 5 μm laser spectrometer. The achieved spectral resolution is the highest obtained so far in the optical domain on a molecular ion species. As a consequence, we are also able to perform the most precise test yet of the *ab initio* theory of a molecule.

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Cold trapped molecules [1,2] currently represent an intense field of activity relying on sophisticated methods of molecule production, translational and internal cooling, spectroscopy and sensitive detection. Many applications, such as chemical reaction studies [3,4], tests of molecular quantum theory [5], fundamental physics [6,7] and quantum computing [8] would benefit strongly from the availability of advanced manipulation techniques, already standard in atomic physics. These are not straightforward for molecules, and for charged molecules have not been demonstrated yet. Production methods for molecular ions (usually, e.g., by electron impact ionization) and, if heteronuclear, their interaction with the blackbody radiation of the surrounding vacuum chamber, usually lead to significant population of a substantial number of internal states. A first, important step in the manipulation of internal states of molecular ions is population transfer between rotational states (heteronuclear molecules usually being cold vibrationally, i.e., are all in the $v = 0$ ground vibrational state). It has been demonstrated that a significant fraction (ca. 75%) of an ensemble of diatomic molecular ions can be pumped into the vibrational and rotational ground level ($v = 0$, $N = 0$) [9,10]; see Fig. 1.

For a general diatomic molecule, however, this pumping is usually not capable of preparing molecules in a single quantum state, because spin interactions generate a hyperfine structure with several states in each rovibrational level. For example, a diatomic molecule with one unpaired electron ($s_e = 1/2$), and nuclei with nuclear spins $I_1 = 1/2$ and $I_2 = 1$ (such as HD^+) has 4 hyperfine states in zero magnetic field if the rotational angular momentum is $N = 0$, but 10 if $N = 1$, and 12 if $N \geq 2$; see Fig. 2(a). The ability to address selectively molecules in one particular hyperfine state (or even in a single quantum state with a particular magnetic quantum number J_z) and to transfer molecules from one hyperfine state to another are clearly important tools of a molecular quantum toolbox that can be part of a full quantum state preparation procedure.

Complicating the addressing, the number of strong transitions between two given rovibrational levels (v, N), (v', N') is equal to the larger of the two numbers of hyperfine states, i.e., potentially high, and with only small differences in transition frequency. Figure 2(b) shows as an example the case of the fundamental vibrational transition $(v = 0, N = 0) \rightarrow (v' = 1, N' = 1)$ in HD^+, where 10 strong transitions occur over a range of about 60 MHz ([11,12]). Addressing a single hyperfine state in a multispin molecule thus requires a spectroscopy that can resolve individual hyperfine lines in the spectrum.

In this work, our approach is based on one-photon laser excitation of the fundamental vibrational transition $(0, 0) \rightarrow (1, 1)$ at the wavelength λ_f, see Fig. 1. The relatively low transition frequency, $\lambda_f > 2.5$ μm for diatomics, in combination with the low secular kinetic energy $k_B T_{\rm sec}$ achievable by sympathetic cooling, yields a Doppler broadening $\Delta\nu_D$ of the transitions that is smaller than many line spacings. This provides the desired quantum state selectivity for addressing some of the hyperfine states, using strong transitions. For our test case HD^+, $\lambda_f = 5.1$ μm, $T_{\rm sec} \simeq 10$ mK, $\Delta\nu_D \simeq 3$ MHz. Additionally, excitation of weak transitions [which violate the approximate selection rules $\Delta F = 0$, $\Delta S = 0$, see Fig. 2(b)], provides selectivity for all hyperfine states, since for these transitions the frequency spacings are larger. Compared to the use of a pure rotational excitation $(0, 0) \rightarrow (0, 1)$ [13] or a microwave transition within a rovibrational level, the use of a vibrational transition has the advantage that the excitation may be followed by a much faster spontaneous decay from (1,1), either back into the ground rovibrational level (rate approx. 6 s^{-1}) or into the relatively long-lived rotational level ($v'' = 0$, $N'' = 2$) (rate approx. 12 s^{-1}). This allows reasonably rapid pumping of the molecule (possibly after repeated absorption and spontaneous emission events) into

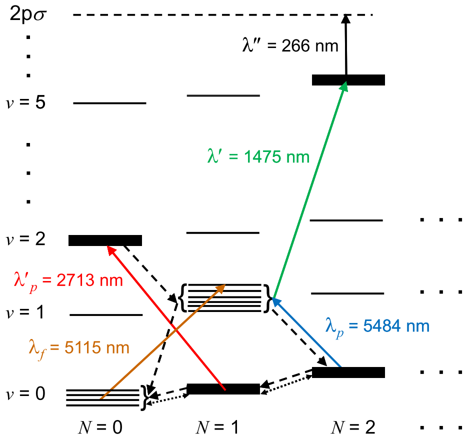

FIG. 1 (color online). Schematic energy level scheme of HD$^+$ with transitions relevant to this work. Hyperfine structure is shown schematically only for the ($v = 0$, $N = 0$) and (1,1) levels as lines, but is implied for all other levels as well (thick bars). Full lines: laser-induced transitions, dashed lines: some relevant spontaneous emission transitions; dotted lines: some blackbody induced transitions. The spectrally narrow wave λ_f selectively excites molecules from a particular hyperfine state ($v = 0, N = 0, F, S, J$) to a single hyperfine state ($1,1, F', S', J'$) Quantum state preparation is performed by irradiating alternatly the appropriately tuned waves λ_f and λ_p, in conjunction with spontaneous emission from the level (1,1). Resonant laser radiation at λ' and nonresonant radiation at λ'' is used to detect that hyperfine-state-selective excitation to the (1,1) level has occurred, by transferring the excited molecules to the electronically excited molecular state $2p\sigma$ from which they dissociate. Initially, rotational cooling is performed by radiation at λ_p and λ'_p. The level energy differences are not to scale. The waves at λ', λ'', λ_p, λ'_p, have large spectral linewidths and do not excite hyperfine state selectively.

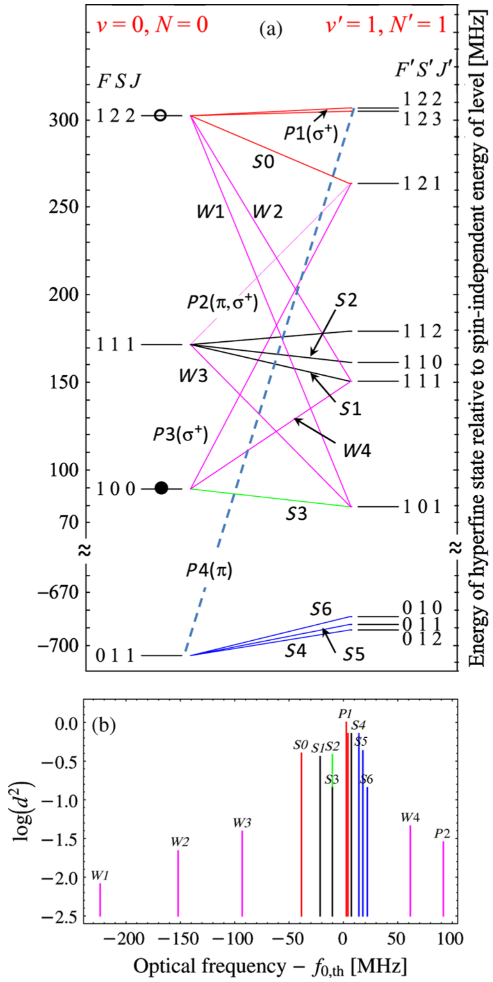

FIG. 2 (color online). (a) Energy diagram of the hyperfine states and main electric-dipole transitions in zero magnetic field. (b) Stick spectrum of the transitions (in zero magnetic field; values of the squared transition moment d^2 are normalized to the strongest transition). The states are labeled by the quantum numbers (F, S, J). Weak transitions are shown in pink [12]. Very weak transitions are not shown, except for $P4$ (dashed). The "spin-independent" transition frequency $f_{0,\mathrm{th}}$ is the value if nuclear and electron spin were zero. $S0$, $S1$, $S2$, $S3$, $S4$, $S5$, $S6$, $W1$, $W2$, $W3$, $W4$, $P2$ are transitions studied here ("W, S, P" mean "weak", "strong", and "pumping", respectively). All were observed except $S4$. $W1$, $W3$ are the transitions used here to achieve population transfer from the hyperfine states ($v = 0$, $N = 0$, $F = 1$, $S = 2$, $J = 2$, J_z) (empty circle) and ($0,0,1,1,1,J'_z$) into the hyperfine state ($0,0,1,0,0,J''_z$) (filled circle). $P1$, $P2$, $P3$, and $P4$ are proposed optical pumping transitions (with indicated polarizations) for preparation of the molecule in the single quantum state (0, 0, 1, 2, 2, $J_z = +2$) (one of the Zeeman states in the open circled hyperfine state).

another long-lived state, a necessary condition for efficient quantum state preparation, as shown below.

The experiment is performed on ensembles of HD$^+$ ions trapped in a linear quadrupole radio-frequency trap (14.2 MHz), sympathetically translationally cooled by co-trapped, laser-cooled Beryllium atomic ions [14] and rotationally cooled by lasers. The HD$^+$ molecule is of interest since it is a fundamental quantum system that allows precision measurements of QED effects and fundamental constants [5]. Our laser system consists of four subsystems: a $\lambda_f = 5.1\ \mu$m laser spectrometer referenced to an atomic frequency standard [15] (see Supplemental Materials [16]), a reliable, frequency-stabilized fiber-laser-based 313 nm laser for cooling of Beryllium ions [17], a rotational cooling laser system (a $\lambda_p = 5.5\ \mu$m quantum cascade laser and, for part of the measurements, a $\lambda'_p = 2.7\ \mu$m diode laser), and a pair of lasers (λ, λ') for resonance-enhanced multiphoton dissociation (REMPD); see Fig. 1. Rotational cooling [9] is a crucial tool here, as it significantly increases the fractional population of molecules in the lower rovibrational level ($v = 0$, $N = 0$), from ca. 10% to 60%–75%. The possibility provided by our laser system to measure the HD$^+$ fundamental vibrational transition frequency $f = c/\lambda_f$ also allows us to perform a precise comparison with the *ab initio* theory of the molecular hydrogen ion.

Hyperfine-resolved rovibrational transitions are induced by the $\lambda_f = 5.1\ \mu$m radiation tuned precisely to individual transitions. We then detect (without hyperfine-state selectivity) the population of the goal vibrational level ($v' = 1, N' = 1$), by $1 + 1'$ resonance-enhanced multiphoton dissociation (REMPD) [18]; see Fig. 1. Together, this represents a three-photon ($1 + 1' + 1$") REMPD process. The reduction of the HD$^+$ number by the REMPD process is our spectroscopic signal [18].

Figure 3 shows the obtained hyperfine-state resolved spectrum. All theoretically predicted and addressed hyperfine transitions were observed; only the (nominally strong) transition $S4$ is barely detected, for unknown reason. Transition $W4$, which originates from a lower hyperfine state with only a small fractional population ($J = 0$, thus statistically containing only 5%–6% of all molecules), could only be made clearly evident using a preceding hyperfine pumping step (see below). Each of the 4 hyperfine states of the lower level was selectively addressed, and 5 of the 12 upper level hyperfine states were selectively populated. We also observed the line at -10.2 MHz, which contains two nearly coinciding transitions $S2$ and $S3$, but originating from different ground hyperfine states. The remaining strong transitions (including the line marked $P1$ in Fig. 2) were also observed, but their small spacing prevents complete resolution, and they are not reported in the Fig. 3.

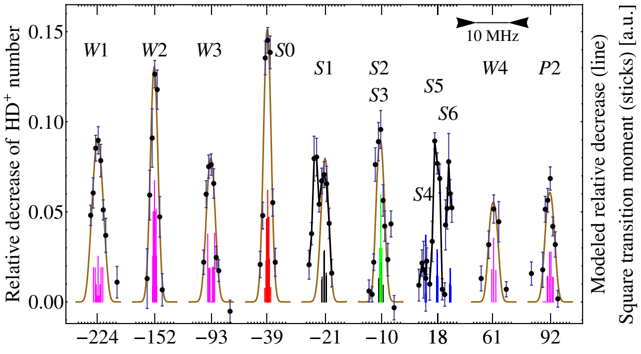

FIG. 3 (color online). Observed hyperfine spectrum of the $(v = 0, N = 0) \rightarrow (1, 1)$ fundamental rovibrational transition in cold trapped HD$^+$ ions. The effective intensity times irradiation duration product of the 5.1 μm radiation varied from line to line, and was adapted to avoid saturation. Brown lines are the result of fitting $f_{0,\mathrm{exp}}$, the individual line amplitudes, the Doppler temperature (9.5 mK) and the average magnetic field (0.8 G). The sticks are for illustration purpose and show the theoretical squared transition dipole moments for the Zeeman components at 0.8 G, assuming exciting radiation polarized at 45° to the magnetic field. They are scaled by different factors for presentation purpose. Color coding is as in Fig. 2. $S4$, $S6$ were taken at high intensity-irradiation time product, $S5$ at a lower value. The side peak of $S1$ is probably due to an ion micromotion sideband of $S2/S3$. The $W4$ line required hyperfine-state optical pumping for its detection (see Fig. 4).

We demonstrate hyperfine-state manipulation by optical pumping of individual hyperfine-state populations into a goal state. As a goal state we choose ($v = 0$, $N = 0$, $F = 1$, $S = 0$, $J = 0$, $J_z = 0$) which is nondegenerate ($J = 0$) and thus a single quantum state (filled circle in Fig. 2). After rotational cooling, we apply the following sequence twice: $W1$ line (3 s), rotational repumping (λ_p and λ'_p simultaneously for 5 s), $W3$ line (3 s). A final 10 s of rotational repumping is performed before the spectroscopic excitation. The $W1$ and $W3$ transitions excite population from two initial hyperfine states (0, 0, 1, 2, 2, J_z), (0, 0, 1, 1, 1, J'_z) (without J_z selectivity) into the state (1, 1, 1, 0, 1, J''_z). This state has dominant spontaneous decay to the goal state (green line $S3$ in Fig. 2). We find clear evidence that this hyperfine-state preparation is taking place by observing the transition $W4$ starting from the goal state by REMPD; see Fig. 4. This transition is not observable in our experiment without the preparation procedure, since then the population in the lower hyperfine state is too low.

Our hyperfine-state resolved spectrum represents the highest-resolution optical spectrum of any molecular ion so far [5,19,20]. This enables an accurate comparison of experimental frequencies with *ab initio* theory. We

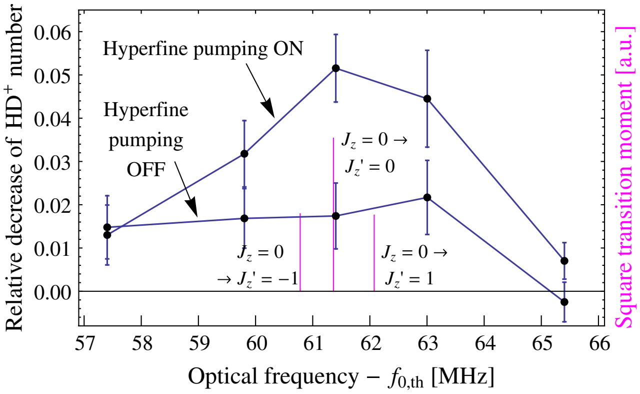

FIG. 4 (color online). Demonstration of hyperfine-state manipulation. The transition $W4$ shown here is observed only when hyperfine optical pumping is implemented. This transition represents the excitation from a single quantum state, (0,0,1,0,0,$J_z = 0$). Data shown were taken alternating measurements preceded by hyperfine optical pumping (upper data points joined by line) and not (lower data points). The intensity of the 5.1 μm laser radiation was set to its maximum both during hyperfine pumping on the $W1$ and $W3$ transitions and subsequent detection of the $W4$ transition. Irradiation time on the $W4$ transition was 3 s. Rotational cooling by the 2.7 μm and 5.5 μm laser was used. The zero level corresponds to the relative decrease measured when the 5.1 μm spectroscopy laser was blocked. The three sticks show, for illustration purposes, the theoretical transition frequencies and strengths in a 0.8 G magnetic field and radiation polarized at 45° to the magnetic field. The shift of the central component is -0.05 MHz relative to the zero-field frequency.

obtain two hyperfine-state separations in the ground state, $\Delta f_{0,0,a} = (E(0,0,1,2,2) - E(0,0,1,1,1))/h$ and $\Delta f_{0,0,b} = (E(0,0,1,1,1) - E(0,0,1,0,0))/h$, from the measured transition frequency combinations $f(S1) - f(W2)$, $f(W3) - f(W1)$, $f(P2) - f(S0)$, and from $f(W4) - f(S1)$, $f(P3) - f(P2)$, respectively. In addition, two excited state splittings, $\Delta f_{1,1,c} = (E(1,1,1,2,1) - E(1,1,1,1,1))/h$ and $\Delta f_{1,1,d} = (E(1,1,1,1,1) - E(1,1,1,0,1))/h$ are similarly obtainable by suitable frequency combinations. A fit of these hyperfine-state separations to the data (fitting also the spin-independent frequency) yields agreement with the *ab initio* results $(\Delta f_{0,0,a}, \Delta f_{0,0,b}, \Delta f_{1,1,c}, \Delta f_{1,1,d}) = (130.60(1), 82.83(1), 113.33(1), 71.68(1))$ MHz [11,21], with deviations (experimental minus theoretical) of $(-0.22(0.13), 0.28(0.38), -0.13(0.15), 0.27(0.19))$ MHz. The values in inner parentheses being the experimental uncertainties. The two measured hyperfine separations of the ground state also allow determining the two hyperfine constants $E_4(0,0)$, $E_5(0,0)$ [11] which fully describe the hyperfine structure of the ground state [12]. Our fit yields $(E_4(0,0), E_5(0,0)) = (906(17), 142.33(25))$ MHz, whereas the theory values are $(925.38(1), 142.29(1))$ MHz [11,21].

Assuming instead that the hyperfine energies are given by the theoretical values (this assumption being strengthened by the agreement of hyperfine theory and experiment for large-v levels [11,22]), we can fit an overall frequency correction to the spectra $W1$, $W2$, $W3$, $S0$, $S1$, $S2 + S3$, $W4$, $P2$. We obtain the spin-independent frequency $f_{0,\mathrm{exp}} = 586\,050\,52.00$ MHz, with combined statistical and systematic error of 0.064 MHz (see Supplemental Material [16]). The theoretical value is $f_{0,\mathrm{th}} = 586\,050\,52.139(11)(21)$ MHz, where the first error is due to the uncertainty of the fundamental constants and the second is the theoretical error in the evaluation of the QED contributions [21,23,24]. The difference between experimental and theoretical results is -2.0 times the combined theoretical plus experimental error. The relative experimental uncertainty of 1.1×10^{-9} represents the most accurate test of molecular theory to date. In particular, our measurement is the first molecular measurement sufficiently accurate to be explicitly sensitive to the QED contributions of order α^5 (relative to the nonrelativistic contribution to the transition frequency), calculated as 0.109(21) MHz for the transition studied here [21,24].

Based on the technique demonstrated here, we can propose a realistic optical pumping procedure for preparing most of the population in a single quantum state (v, N, F, S, J_z), i.e., with well-defined projection of the total angular momentum. Under typical conditions, the relative statistical occupation of any individual quantum state in $(v = 0, N = 0)$ is only $\simeq (1/12) \times (60\%–75\%) \simeq 5\%–6\%$ under rotational cooling by a single laser (λ_p) or two lasers (λ_p, λ'_p). Exciting sequentially the four transitions $P4[(0,0,0,1,1) \rightarrow (1,1,1,2,2)]$, $P3$, $P2$, $P1[(0,0,1,2,2) \rightarrow (1,1,1,2,3)]$ in a weak magnetic field and with polarizations chosen as indicated in Fig. 2(a) will cause transfer of the population of all Zeeman quantum states of (0, 0) to the single Zeeman quantum state $(0, 0, 1, 2, 2, J_z = +2)$, via spontaneous emission processes from $(1, 1, 1, 2, J' = \{1, 2\}, J'_z)$, which dominantly occur on strong transitions [red lines in Fig. 2(a)]. These excitations should be interleaved with rotational cooling (lasers λ_p, λ'_p), which also serves as repumper following spontaneous decay into $(v'' = 0, N'' = 2)$. The optical pumping procedure should take a few ten seconds and lead to 60%–70% fractional population in the goal state.

In summary, we have shown that it is possible to address and prepare individual hyperfine states in cold, trapped diatomic molecular ions even in presence of a complex spin structure. A midinfrared laser spectrometer controlled by an atomic standard-referenced frequency comb, and sufficiently low ion kinetic energies were two important aspects. The observed, Doppler-limited, transition linewidths (3 MHz) are the lowest obtained to date on a molecular ion species in the optical domain [note that they scale as $(\text{molecule mass})^{-1/2}$]. We also observed, for the first time to our knowledge, weakly allowed hyperfine transitions using optical excitation. As one application, we were able to directly determine the population fraction of molecules, in particular, hyperfine states. The largest value we found was 19%, clearly indicating the effectiveness of our rotational cooling. We also demonstrated excitation of a transition from a single quantum state. Since our test molecule HD^+ is the simplest heteronuclear molecule and is excited from the rovibrational ground state, this study represents the first precision measurement of the most fundamental electric-dipole allowed rovibrational transition of any molecule [19]. A comparison of theory with experiment showed that (i) the hyperfine energies of small-v, N rovibrational levels agree within deviations of less than 0.3 MHz and (ii) the spin-independent energy agrees within 2 times the relative error of 1.1×10^{-9}.

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