Hyperfine structure of the spectrum of ultracold HD^+ ions

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A series of high precision laser spectroscopy experiments with ultracold hydrogen molecular ions has been proposed recently, aimed at improving the present value of the electron-to-proton mass ratio and the limits of its time-independence. To enable the interpretation of the spectroscopical data which requires the accurate knowledge of the spin structure of the transition lines, we calculate the hyperfine structure of the lower ro-vibrational excited states of HD^+, and investigate the laser-frequency, laser pulse duration and initial state population dependence of the one- and two-photon transition spectra.

1 Introduction

The high precision laser-spectroscopy measurement of the absorbtion spectrum of the hydrogen molecular ion HD^+ was proposed recently at the Düsseldorf University [1, 2]. In order to improve the present experimental results on the electron-to-proton mass ratio [3], the uncertainty of the spectroscopical data (as well as of the theoretical calculations of the spectra to compare to) should not exceed 1 ppb. To meet these requirements, an experimental method has been developed in the recent years [4]. The HD^+ ions are trapped in a linear radio frequency trap and sympathetically cooled by laser-cooled Be^+ atomic ions; subsequently the Be^+ ions undergo a phase transition to an ordered structure, and the HD^+ ions are embedded in the Be^+ ionic crystal. The transitions of the ultra-cold HD^+ molecular ions are then studied by means of high-resolution laser spectroscopy.

In the theoretical calculations of the hyperfine structure of the energy spectrum of HD^+ traditionally a Breit-type spin interaction Hamiltonian is used. The uncertainty of the results is determined by the magnitude of the contribution of the interaction operators that are *not* included in the spin Hamiltonian V. Similar to the approach of [5], we take V

in the form of a sum of pairwise interaction terms which account for one-photon exchange contributions of relative order $O(\alpha^2)$. In the perturbative calculations of this work we use as an initial approximation the variational solution of the three-body Coulomb problem which produces energy levels accurate to 10^{-14} or better [2]. Typically the spin corrections to the energy levels do not exceed 1 GHz and, therefore, the uncertainty of the hyperfine splitting is smaller than 100 kHz, that is equivalent to a relative accuracy of $\sim 0.5 \cdot 10^{-9}$ of the theoretical predictions for the resonant transition wave length. As long as the consideration is restricted to spin effects, however, and the spin-independent shift of the energy levels is not taken into account, the results of this work cannot be directly used for extracting improved values of the m_e/m_p mass ratio from experimental data. Instead, they are needed for the interpretation of the experimental spectra and, in particular, for the accurate experimental determination of the center of the hyperfine multiplet of transition lines ω_0.

2 Hyperfine structure of the HD^+ ion

Only the ro-vibrational excitations of the ground electronic state of HD^+ are of interest for the spectroscopy of ultra-cold ions. In the non-relativistic approximation, the ro-vibrational excited states are labelled with the quantum number of the total orbital momentum L, its projection on the z-axis of the lab frame L_z, and the vibrational quantum number v. In the present work we restrict ourselves to the evaluation of the effects of the spin interactions which split each of the ro-vibrational states of HD^+ into a multiplet of hyperfine states (while the spin-independent effects shift the multiplet as a whole). This is true in first order of perturbation theory only, but the corrections of second order are expected to have the same magnitude as the first order contribution of the unknown interaction terms of next-to-leading order, and will not be discussed here. A basis set in the space of the spin interaction Hamiltonian V is needed for the calculations; since the coupling of the different ro-vibrational or electronic excitations through V is weak, in a good approximation we use only the basis subset of states with definite L and v. By adopting the angular momentum coupling scheme $\mathbf{F} = \mathbf{S}_d + \mathbf{S}_e$, $\mathbf{S} = \mathbf{F} + \mathbf{S}_p$, $\mathbf{J} = \mathbf{L} + \mathbf{S}$ (where $\mathbf{S}_i, i = e, p, d$ denote the spin operators of the electron, proton and deuteron), we define the basis $|vLFSJ, J_z\rangle$ by means of

$$|vLFSJ, J_z\rangle = \sum_{\zeta_e,\zeta_p,\zeta_d,S_z,F_z,L_z} C^{FF_z}_{S_d\zeta_d,S_e\zeta_e} C^{SS_z}_{FF_z,S_p\zeta_p} C^{JJ_z}_{LL_z,SS_z} |vLL_z\rangle |S_p\zeta_p\rangle |S_d\zeta_d\rangle |S_e\zeta_e\rangle. \quad (1)$$

Here $C^{JJ_z}_{LL_z,SS_z}$ are Clebsch-Gordan coefficients, $|vLL_z\rangle$ is the non-relativistic three-body state vector, and $|S_i\zeta_i\rangle$, i=e, p, d, are constant spinors of definite values of S_i and ζ_i, satisfying $(\mathbf{S}_i^2 - S_i(S_i+1))|S_i\zeta_i\rangle = 0$, $(S_{iz} - \zeta_i)|S_i\zeta_i\rangle = 0$. The spin corrections to the Coulomb energy levels ΔE^{vLNJ} are then calculated from the secular equations

$$\sum_{F'S'} (\langle vLFSJ, J_z|V|vLF'S'J, J_z\rangle - \delta_{FF'}\delta_{SS'}\Delta E^{vLNJ})\beta^{vLNJ}_{F'S'} = 0 \quad (2)$$

Instead of L and L_z, in the spin case the classification of the rovibrational states is done with the quantum numbers of the total angular momentum J and of its z-axis projection

J_z, together with the integer N which labels the eigenstates of the matrix of V in the subspace of definite J. In first order of perturbation theory the energies E^{vLNJ} are represented as the sum of the Coulomb energy E^{vL}, the spin-independent shift ΔE^{vL}, and the spin correction ΔE^{vLNJ}: $E^{vLNJ} = E^{vL} + \Delta E^{vL} + \Delta E^{vLNJ}$. The sum $E^{vL} + \Delta E^{vL}$ of the Coulomb energy and the spin-independent shift is also referred to as "center of the multiplet" of hyperfine levels E^{vLNJ}. The expansion of the hyperfine state vectors in the basis (1) has the form $|vLNJ, J_z\rangle = \sum_{FS} \beta_{FS}^{vLNJ} |vLFSJ, J_z\rangle$ The hyperfine structure of the states with $L = 0$ consists of 4 substates, for $L = 1$ – of 10, and for $L > 1$ – of 12 hyperfine substates.

3 Hyperfine structure of LASER stimulated one- and two-photon transitions in HD^+

Consider the E1-transitions stimulated by an external monochromatic electric field $\mathbf{E} \sin \omega t$ between the initial state of the HD^+ ion $|i\rangle = |vLNJ, J_z\rangle$ and the final one $\langle f| = \langle v'L'N'J', J'_z|$. Since the "selective photo-dissociation" registration method [1, 6] cannot distinguish the contribution from the different pairs of initial and final hyperfine states, the observable spectrum is the sum of the probabilities for the individual transitions weighed with the population w_i of the hyperfine components of the initial state:

$$\mathcal{P}^{(1)}(\Delta t, \omega) = \frac{2\pi\alpha}{3} \overline{G} \sum_{i,f} \frac{w_i}{2J+1} \left(\frac{\omega_{fi}}{\omega}\right)^2 (T_{fi})^2 F(\Delta t, \omega - \omega_{fi}). \tag{3}$$

Here $\omega_{fi} = (E^{v'L'} + \Delta E^{v'L'N'J'}) - (E^{vL} + \Delta E^{vLNJ})$, $F(t, \Delta\omega) = (\sin(t\,\Delta\omega/2)/(\Delta\omega/2))^2$, $\overline{G} = e^2\mathbf{E}^2/8\pi\alpha\hbar$ is the density of the energy flux of the laser beam, T_{fi} stands for

$$T_{fi} = d_{fi} \sqrt{(2J+1)(2J'+1)} \sum_{FS} (-1)^{S+J+L'} \left\{ \begin{array}{ccc} L & 1 & L' \\ J' & S & J \end{array} \right\} \beta_{FS}^f \beta_{FS}^i, \tag{4}$$

and $d_{fi} = \langle v'L'||\mathbf{d}||vL\rangle$ is the reduced matrix element of the electric dipole moment of HD^+ which, in the approximation adopted, depends only on the non-relativistic quantum numbers v and L. The shape of the spectrum is sensitive to the laser pulse duration Δt. At pulse lengths $\Delta t < 4\pi/\Delta\omega$ hyperfine transition lines separated by a frequency gap of $\Delta\omega$ mix up, while in the opposite limit $\Delta t \gg 4\pi/\Delta\omega$ the individual lines are clearly distinguished and the golden rule of Fermi may be applied. The typical values for which the shape of the HD^+ hyperfine spectrum changes are $\Delta t \sim 1$ μs. Note that for laser frequencies ω in a sufficiently broad neighborhood of the resonance frequency ω_{fi}, the ratio (ω_{fi}/ω) in (3) can be safely replaced by 1.

The two-photon transition spectrum is expressed in a similar form, but involves a double sum over the intermediate states $|k\rangle = |v_1 L_1 N_1 J_1 J_{1z}\rangle$ and $|k'\rangle = |v'_1 L'_1 N'_1 J'_1 J'_{1z}\rangle$:

$$\begin{aligned} \mathcal{P}^{(2)}(\Delta t, \omega) = \sum_{f,i} w_i \mathcal{P}_{fi}^{(2)}(\Delta t, \omega) = \frac{4\pi^2\alpha^2}{3} \overline{G}^2 \sum_{f,i} \frac{w_i}{2J+1} \sum_{k'k} T_{fk} T_{fk'} T_{ki} T_{k'i} \\ \times g_{fk'i}(\Delta t, \omega)^* \, g_{fki}(\Delta t, \omega) \left(\left\{ \begin{array}{ccc} J & 1 & J_1 \\ 1 & 0 & 1 \\ J'_1 & 1 & J' \end{array} \right\} + 2 \left\{ \begin{array}{ccc} J & 1 & J_1 \\ 1 & 2 & 1 \\ J'_1 & 1 & J' \end{array} \right\} \right), \end{aligned} \tag{5}$$

$$g_{fki}(t,\omega) = \frac{1}{\omega_{ki}-\omega}\left(\frac{1-e^{it(\omega_{fk}-\omega)}}{\omega_{fk}-\omega} + \frac{1-e^{it(\omega_{fk}+\omega)}}{\omega_{fk}+\omega} - \frac{1-e^{it(\omega_{fi}-2\omega)}}{\omega_{fi}-2\omega}\right) + \tag{6}$$
$$\frac{1}{\omega_{ki}+\omega}\left(\frac{1-e^{it(\omega_{fk}-\omega)}}{\omega_{fk}-\omega} + \frac{1-e^{it(\omega_{fk}+\omega)}}{\omega_{fk}+\omega} - \frac{1-e^{it(\omega_{fi}+2\omega)}}{\omega_{fi}+2\omega}\right) - \frac{1-e^{it\omega_{fi}}}{\omega_{fi}}\frac{2\omega_{ki}}{\omega_{ki}^2-\omega^2};$$

$9j$-symbols appear in the second line of Eq. (5). For a given value of ω, the dominant contribution to $\mathcal{P}^{(2)}(\Delta t,\omega)$ comes from the intermediate states with energy levels such that the denominator of some of the terms in Eq. (6) becomes small. The fact that the energy level of the $(2,3)$ state is (accidentally) close to the mid-point of the energy interval between the $(0,4)$ and $(4,4)$ states makes the $(0,4)\to(4,4)$ transition the most appropriate for precision two-photon spectroscopy of the HD^+ ion. The double sum in (5) for this transition may be truncated to the intermediate states $(2,3)$, $(2,5)$, $(3,3)$ and $(1,3)$ since the contribution of the remaining states does not exceed 0.1%. Because of the complex hyperfine structure of the initial, intermediate and final states, the shape of the spectrum $\mathcal{P}^{(2)}(\Delta t,\omega)$ proves to be very sensitive to the value of Δt. Whether the contributions from two intermediate hyperfine states $|vLNJ\rangle$ and $|vLN'J'\rangle$ can be distinguished or not depends on the duration of the perturbation Δt, i.e. on the laser pulse length. For $\Delta t \gg 2/|\Delta E^{vLN'J'} - \Delta E^{vLNJ}| \sim 1\ \mu$s the two peaks appear separately, while for smaller values of Δt they fuse. Figure 1 shows the spectra $\mathcal{P}^{(2)}(\Delta t,\omega)$ for Δt varying between 100 ns and 10 μs and equilibrium temperatures 1 K and 0.01 K. Plotted is the peak region of the spectra, with ω varying in the neighborhood of the "central" frequency $\omega_0 = (E^{44}+\Delta E^{44}) - (E^{04}+\Delta E^{04})$. The spectra $\mathcal{P}^{(1)}(\Delta t,\omega)$ of the one-photon transition $(0,4)\to(2,3)$ on Fig. 1 have a similar dependence on the initial state populations w_i. This makes possible the model-independent determination of w_i by comparing the theoretical results on $\mathcal{P}^{(1)}(\Delta t,\omega)$ with experimental data from highly efficient one-photon spectroscopy of HD^+.

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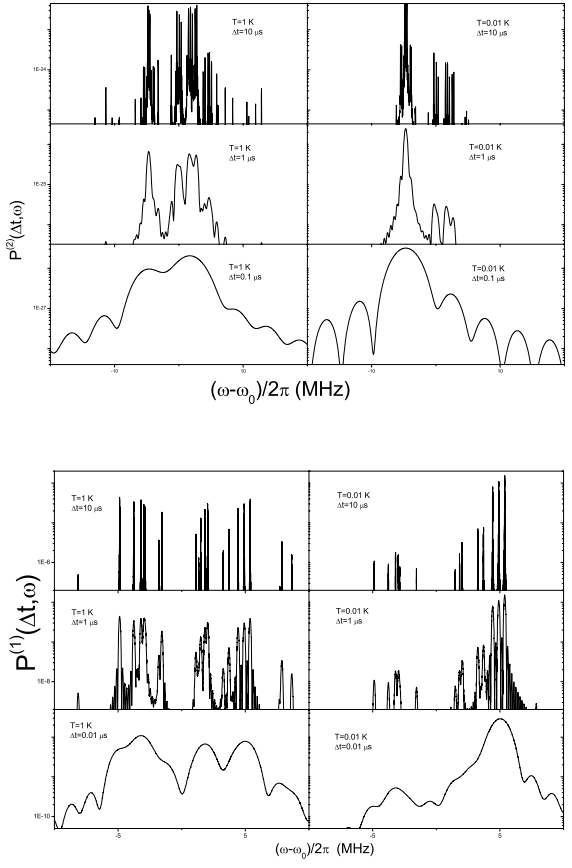

Figure 1: Probabilities for the two-photon transition $(0,4) \rightarrow (4,4)$ ($\mathcal{P}^{(2)}(\Delta t, \omega)$, upper graph) and for the $E1$-transition $(0,4) \rightarrow (2,3)$ ($\mathcal{P}^{(1)}(\Delta t, \omega)$, lower graph), stimulated by an electromagnetic plane wave of circular frequency ω, normalized to unit energy flux density $\overline{G}$=1 W.m^{-2}, for perturbation durations Δt=0.1, 1, and 10 μs, and initial equilibrium populations w_i for 1 K and 0.01 K.