

Precision spectroscopy of the molecular ion HD⁺: Control of Zeeman shifts

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Precision spectroscopy on cold molecules can potentially enable novel tests of fundamental laws of physics and alternative determination of some fundamental constants. Realizing this potential requires a thorough understanding of the systematic effects that shift the energy levels of molecules. We have performed a complete *ab initio* calculation of the magnetic field effects for a particular system, the molecular hydrogen ion HD⁺. Different spectroscopic schemes have been considered, and several transitions, all accessible by modern radiation sources and exhibiting well controllable or negligible Zeeman shift, have been identified. Thus, HD⁺ is a candidate for the determination of the ratio of electron-to-nuclear reduced mass, and for tests of its time independence.

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Cold molecules have recently been proposed as novel systems for precision measurements related to fundamental aspects of physics, such as the measurement of the electron-to-nuclear mass ratio, its possible time variability, tests of Lorentz invariance, tests of quantum electrodynamics (QED), and parity violation.

Several of these are based on precision spectroscopy [1–8], where frequencies of ro-vibrational transitions exhibiting high-quality factors must be measured. As the tests mentioned previously have already been performed with very high precision using various atomic systems, studies on molecular systems must be conceived in ways that have the potential of surpassing atomic tests. This implies that molecular systems must be experimentally accessible and that systematic shifts of the transition frequencies must be sufficiently small so as to guarantee the desired spectroscopic accuracy.

We focus on a particular diatomic molecule, HD⁺. Because of its relative simplicity it can be analyzed with high-precision *ab initio* methods. QED calculations of ro-vibrational frequencies have reached a relative accuracy of a few parts in 10⁻¹⁰ [9], and the influence of external perturbing and exciting electromagnetic fields (i.e., all systematics) can also be treated accurately *ab initio*. Comparison of theoretical and experimental transition frequencies in HD⁺ can potentially lead to determining the electron-to-proton or -deuteron mass ratio and the Rydberg constant in an alternative way. For these purposes, an experimental transition frequency accuracy in the range 1 × 10⁻¹⁰ to 1 × 10⁻¹⁴ must be attained. The requirement is even more stringent, at the 10⁻¹⁶ level, if the system is to be used to test the time independence of the mass ratio or Lorentz invariance.

Experimentally, HD⁺ can be cooled to tens of mK by sympathetic cooling in an ion trap [10] and rotationally cooled [11]. One-photon laser spectroscopy of rovibrational transitions has been performed and one transition frequency has been determined with a relative uncertainty at the 2 × 10⁻⁹ level [3], in agreement with the QED calculation [9].

Here we present the results of a thorough study of the magnetic field effects on the radiofrequency, rotational (THz) and ro-vibrational transitions in HD⁺. Both one- and two-photon transitions are of interest for precision spectroscopy. Earlier, Karr *et al.* [12] had evaluated the two-photon transition strengths in HD⁺ in the spinless particle approximation.

An analysis of a particular rovibrational transition at moderate spectral resolution has been reported in Ref. [3].

Theoretical approach. The Hamiltonian H of the HD⁺ ion in an external magnetic field has the form $H = H^{\text{NR}} + V^{\text{diag}} + V^{\text{spin}} + V^{\text{mag}}$, where H^{NR} is the nonrelativistic three-body Hamiltonian and the correction terms collect the spin-independent interactions, the spin interactions (cf. Ref. [13,14]), and the external magnetic field interaction terms, respectively. In the leading order approximation $V^{\text{mag}} = -\mathbf{B} \cdot \sum_i (eZ_i/2M_i c)[\mathbf{L}_i + (\mu_i/s_i)\mathbf{S}_i]$, where the summation is over the constituents of HD⁺ ($i = p, d, e$), M_i , Z_i , and μ_i are the mass, the electric charge (in units e), and the magnetic moment (in units $e\hbar/2M_i c$) of particle “ i ,” s_i is the size of its spin (1/2 for $i = p, e$ and 1 for $i = d$), \mathbf{L}_i and \mathbf{S}_i are the orbital and spin angular momentum operators in the center-of-mass-frame, and \mathbf{B} is the external magnetic field.

Neglecting the higher order corrections to V^{mag} (cf. Ref. [16]) is justified for magnetic fields B below the threshold $B_{\text{thr}} \sim 10^2$ G for which the contribution of V^{mag} , increasing with B , reaches the order of magnitude of the hyperfine energy, since the relativistic corrections to V^{mag} are smaller than the theoretical uncertainty of the hyperfine energy levels of Ref. [13].

The spin structure of the rovibrational state (v, L) , where v and L are the vibrational and total orbital momentum quantum numbers, is calculated in first order of perturbation theory using an effective Hamiltonian V^{eff} that is obtained by averaging $V^{\text{spin}} + V^{\text{mag}}$ over the spatial degrees of freedom.

Compared to H_{eff} (the HD⁺ effective spin Hamiltonian of Ref. [13]), V^{eff} includes four additional terms, originating

from V^{mag} :

$$V^{\text{eff}} = H_{\text{eff}} + E_{10}(\mathbf{L} \cdot \mathbf{B}) + E_{11}(\mathbf{S}_p \cdot \mathbf{B}) \\ + E_{12}(\mathbf{S}_d \cdot \mathbf{B}) + E_{13}(\mathbf{S}_e \cdot \mathbf{B}).$$

In the adopted leading order approximation $E_{11} = -4.2577$ kHz/G, $E_{12} = -0.6536$ kHz/G, and $E_{13} = 2.8025$ MHz/G are expressed only in terms of the mass and magnetic moments of the particles.

The values of E_{10} were calculated using the variational nonrelativistic wave functions of HD⁺ of Ref. [17], thus improving on the accuracy of the first such calculations [16].

The matrix of V^{eff} is evaluated in the basis set of vectors with definite values of the squared angular momenta $\mathbf{F} = \mathbf{S}_p + \mathbf{S}_e$, $\mathbf{S} = \mathbf{F} + \mathbf{S}_d$, $\mathbf{J} = \mathbf{S} + \mathbf{L}$ and z -axis projection J_z of \mathbf{J} .

Except for the “stretched” states with the “extreme” values $F=1$, $S=2$, $J=L+2$, and $J_z=\pm J$, J_z is the only exact quantum number; labeling the eigenstates of V^{eff} requires an additional index n .

The corresponding eigenvalues ΔE^{vLnJ_z} represent the energy levels of HD⁺, defined relative to the “spinless” energies E^{vL} , calculated as eigenvalues of $H^{\text{NR}} + V^{\text{diag}}$.

Since the hyperfine spectrum is only deformed but not rearranged by magnetic fields B below a few G, we take for n the set of quantum numbers (F, S, J) labeling the hyperfine states at $B=0$.

The hyperfine states of HD⁺ are split into sublevels distinguished with the quantum number J_z . The Zeeman shift may be approximated with the quadratic form,

$$\Delta E^{vLnJ_z}(B) - \Delta E^{vLnJ_z}(0) \approx h^{vLn} J_z B + q^{vLnJ_z} B^2. \quad (1)$$

The numerical values of h^{vLn} and q^{vLn0} , calculated by the least square method and providing relative uncertainty below 10^{-6} for $B < 1$ G are given in [15]. Equation (1) may be used to evaluate the Zeeman shift of transition frequencies and choose the less sensitive ones as candidates for precision spectroscopy. Stretched states are a special case: the Zeeman shift is *strictly* linear, with $h^{vLn} = [L E_{10} + E_{12} + (E_{11} + E_{13})/2]/(L+2)$.

Transitions. The probability per unit time for an electric dipole transition between lower $|i\rangle \equiv |vLnJ_z\rangle$ and upper $|f\rangle \equiv \langle v'L'n'J'_z|$ states, stimulated by an oscillating electric field $\mathbf{E}(t) = \mathbf{E} \cos 2\pi \nu t$ of frequency ν , is (in units $h=1$) $\pi^2 \delta(\nu - \nu_{fi}) |\langle f|W|i\rangle|^2$, where $\nu_{fi} = \nu_0 + \Delta E^{v'L'n'J'_z} - \Delta E^{vLnJ_z}$, $\nu_0 = E^{v'L'} - E^{vL}$ is referred to as “central frequency,” $W = -\mathbf{E} \cdot \mathbf{d}$ is the interaction with the electric field, and \mathbf{d} is the electric dipole moment operator. The matrix elements $\langle f|W|i\rangle$ are expressed in terms of the reduced matrix elements of \mathbf{d} which, in the nonrelativistic approximation, do not depend on the spin quantum numbers: $d_{fi} \equiv d_{v'L',vL}$. Accurate numerical values of $d_{v'L',vL}$ have been calculated with the variational Coulomb wave functions of Ref. [17]; they agree with earlier results of Ref. [18] at the 10^{-3} level.

Assuming statistical population of the hyperfine states, the observable spectrum of the transition $(v, L) \rightarrow (v', L')$ can be put in the form $|\mathbf{E}|^2 \sum_{f,i} \delta(\nu - \nu_{fi}) T_{fi}^{(1)}(\theta)$, where θ is the angle between \mathbf{B} and \mathbf{E} , the sum is over all pairs of states (i, f) belonging to the hyperfine structure of the initial and final rovibrational states.

The number of hyperfine lines may exceed 10^3 , but most of them are weak. For magnetic fields B below a few G

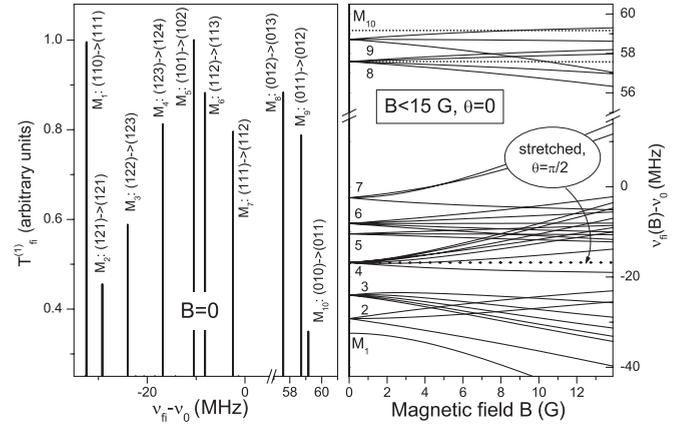


FIG. 1. (Left) Strength $T_{fi}^{(1)}$ of 10 favored hyperfine components M_1, \dots, M_{10} of the $(0, 1) \rightarrow (4, 2)$ one-photon transition line at $B=0$ (no θ dependence), labeled with the quantum numbers (F, S, J) of the initial and final states. (Right) Frequencies of the $\Delta J_z=0$ components of M_1, \dots, M_{10} as function of the magnetic field B for $\theta=0$. The $J_z=0 \rightarrow J'_z=0$ components of M_8 and M_{10} (short dotted lines) undergo a very small quadratic shift. The frequencies of the transitions between stretched states in transversal field (dotted line) have a very small linear shift; their mean is independent of B .

the spectrum is dominated by the “favored” components corresponding to transitions between states that satisfy $\Delta S = \Delta F = 0$; the frequencies of the favored transitions lie in a band of width ~ 100 MHz around ν_0 .

Figure 1 illustrates the Zeeman structure of an overtone rovibrational transition $[(0, 1) \rightarrow (4, 2)]$, to be discussed further in the following.

Of interest also are the radio-frequency (RF) magnetic dipole (M1) transitions between spin substates of the same (vL) state, stimulated by an oscillating magnetic field $\mathbf{B}' \cos 2\pi \nu t$. The frequencies ν_{fi} of the transitions with $\Delta F = \pm 1$ are in the range $700 < \nu_{fi} < 1100$ MHz, while $\nu_{fi} < 200$ MHz for $\Delta F = 0$. The explicit expressions of the RF transition probabilities show that they are mainly due to the $(\mathbf{B}' \cdot \mathbf{S}_e)$ term in V^{mag} .

The two-photon spectrum may similarly be put in the form $|\mathbf{E}|^4 \sum_{f,i} \delta(\nu - \nu_{fi}/2) T_{fi}^{(2)}(\theta)$. In transverse polarization ($\theta = \pi/2$) each favored hyperfine component splits into three components with $\Delta J_z = J'_z - J_z = -2, 0, 2$ with a typical separation of the order of $\sim 10^2$ kHz at $B = 0.5$ G; each of these components acquires an additional superfine structure with separations in the 10^1 kHz range. In a longitudinal magnetic field ($\theta = 0$) $\Delta J_z = 0$, and the lines are “superfine” split only.

Transitions between stretched states are allowed by selection rules, both as one-photon pure rotational ($v = v'$) or rovibrational as well as two-photon transitions.

Discussion. At low B , the Zeeman shift of the frequency of a single Zeeman component may be estimated using Eq. (1): $\delta \nu_{fi}(B) \approx (h' J'_z - h J_z) B + (q' - q) B^2$. The systematic uncertainty due to the external magnetic field may be minimized by selecting transitions with minimal $\delta \nu_{fi}(B)$. We describe a few concrete transitions, for different cases of assumed experimental spectral resolution.

1. *Resolved hyperfine structure, unresolved Zeeman sub-components.* The level of spectroscopic resolution needed

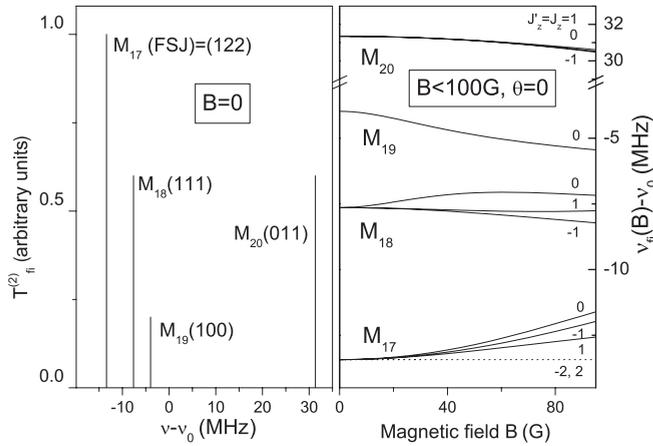


FIG. 2. (Left) Strength $T_{fi}^{(2)}$ of the favored components of the $(0,0) \rightarrow (2,0)$ two-photon transition line at $B=0$, labeled with the quantum numbers $(FSJ)=(F'S'J')$. (Right) Zeeman shift of the $\Delta J_z=0$ components. The spectrum is independent of θ . The transition frequencies between stretched states ($J_z = \pm 2$ components of M_{17} ; dotted line) are independent of B .

for improved measurements of mass ratios is about 10 kHz for an overtone vibrational transition and therefore requires experimental resolution of the hyperfine structure (with typical spacing of several MHz; see Fig. 1), but not necessarily of the Zeeman sublevels.

Among the one-photon transitions, a favorable case is the triplet of magnetic subcomponents $|vL(FSJ)J_z\rangle = |01(010)0\rangle \rightarrow |42(011)J'_z\rangle$. The $J_z=0 \rightarrow J'_z=0$ subcomponent (parallel polarization) has a very small quadratic Zeeman shift (-18 Hz at 1 G), while the $J_z=0 \rightarrow J'_z=\pm 1$ subcomponents (observable in perpendicular polarization) have dominant linear Zeeman shifts of 34.3 and -36.3 kHz, respectively, with an intensity-weighted shift of only 290 Hz at 1 G (1.3×10^{-12} in relative units). If the magnetic field direction is not optimal, the latter value sets the scale of the Zeeman systematic effect. A two-photon transition candidate is the θ -insensitive $|00(011)J_z\rangle \rightarrow |20(011)J_z\rangle$ triplet (line M_{20} in Fig. 2) with a weighed shift of -95 Hz at 1 G (-8×10^{-13}). As fields below 1 G are feasible, such shift values will be well below the current and near-future theoretical uncertainties and thus will not be a limitation in comparisons of theoretical and experimental results.

2. Resolved Zeeman subcomponents. The preferred experimental situation, in which the transition frequencies of individual subcomponents can be measured.

Examples of one-photon transitions with very low magnetic field sensitivity include transitions with $J'_z=J_z=0$ with eliminated linear and suppressed quadratic dependence on B : $|vL(FSJ)J_z\rangle = |01(011)0\rangle \rightarrow |02(012)0\rangle$ (pure rotational), $|01(112)0\rangle \rightarrow |32(113)0\rangle$, $|01(010)0\rangle \rightarrow |42(011)0\rangle$, $|01(012)0\rangle \rightarrow |42(013)0\rangle$, $|02(012)0\rangle \rightarrow |43(013)0\rangle$, with sensitivities $\delta\nu(1\text{G})/\nu_0 \approx (3, 0.1, -0.08, -0.2, -0.2) \times 10^{-12}$, respectively. The sensitivity may also be weak in transitions with $\Delta J_z \neq 0$ [e.g., in $|02(011)-1\rangle \rightarrow |43(012)-2\rangle$] with $|\delta\nu(B)/\nu_0| < 8 \times 10^{-13}$ for $B < 1$ G.

One-photon pure rotational or rovibrational transitions between stretched states occur as a doublet with purely

linear magnetic shift: $\delta\nu_{fi}(B) = \pm(L'E'_{10} - LE_{10})B$ for $J_z = \pm(L+2) \rightarrow J'_z = \pm(L'+2)$, where L, E_{10} (L', E'_{10}) refer to the initial (final) state, and $|L-L'| = 1$. This is about ± 0.5 kHz for $B = 1$ G. The mean of the frequencies is strictly independent of B in the adopted approximation.

It should be possible to measure each component of the doublet independently and then compute the average, as in atomic optical clocks.

Figure 1 gives an example of a one-photon transition, $(0,1) \rightarrow (4,2)$ at $\lambda \approx 1.4 \mu\text{m}$. The hyperfine spectrum includes 18 favored lines of which 10 are plotted. While most of them are quite sensitive to the external magnetic field strength, the $J_z=0 \rightarrow J'_z=0$ subcomponents of M_8 and M_{10} are weakly sensitive to B . Line M_{10} also contains the moderately sensitive doublet mentioned previously, and M_4 contains the stretched state transitions observable at perpendicular polarization only.

Two-photon transitions between stretched states are of metrological interest. In transitions with $L' = L \pm 2$ the doublet splitting is of the order ± 10 Hz/G, since E_{01} varies weakly with the vibrational quantum number, and the mean shift is zero. Again, it should be possible to measure each doublet component independently and then compute the mean. For two-photon transitions with $L' = L = 0$ there is no splitting and no shift. Favorable two-photon transitions are $(0,0) \rightarrow (2,0)$ at $2 \times 5.362 \mu\text{m}$ and $(0,1) \rightarrow (2,1)$ at $2 \times 5.368 \mu\text{m}$, which have intermediate states whose detuning is not too large and therefore allow a reasonable excitation strength for realistic laser power from quantum cascade lasers. In addition, the $(0,0) \rightarrow (2,0)$ transition has a particularly simple spectrum (see Fig. 2), since the $L=0$ states have only four levels and the two-photon transition selection rules [19] allow only $\Delta J = \Delta J_z = 0$ transitions. This gives a relatively strong weight to the stretched-state transition relative to the sum over all transitions (which are all equally strong). Its frequency is given by a simple expression (see the following).

Kajita and Moriwaki [20] have discussed the possibility of exciting the light-induced $(0,0) \rightarrow (1,0)$ one-photon transition at high intensity in diatomic molecules. Also for the present molecule HD^+ , the two stretched state components are free of Zeeman shift.

3. Comparison of ab-initio theory and experiment. When spectroscopy of HD^+ is pursued with the goal of comparison with QED calculations and for a determination of the particle mass ratio, it may be important to determine the central frequency ν_0 since in the adopted approximation, unlike the spin corrections, ν_0 includes the contribution of QED corrections of order $O(m\alpha^5)$ and $O(m\alpha^5 \log \alpha)$. We propose to combine the results of optical spectroscopy between vibrational levels (v, L) and (v', L') with the results of RF spectroscopy within each of these levels to extract ν_0 .

Indeed, the coefficients of the effective spin Hamiltonian E_i and the spin corrections to E^{vL} , can be expressed in terms of the frequencies of RF transitions within the hyperfine structure of the (v, L) state [and similar for the (v', L') state].

Since the number n_h of linearly independent hyperfine transition frequencies exceeds the number N_e of nonvanishing E_i , the previously mentioned relations can be resolved for E_i only if the radio frequencies satisfy $N_h - N_e$ compatibility relations that may serve to test the experimental accuracy.

The value of ν_0 is then expressed in terms of spectroscopic data and may be used to test the predictions of few-body bound state QED in next-to-leading orders in α .

This approach is particularly simple in states with $L=0$, since the only nonvanishing coefficients are E_4 and E_5 . Denote the frequencies of the $J_z=0 \rightarrow J'_z=0$ components at $B=0$ of three RF transitions in the $(v, L=0)$ state as follows: $\nu_1 = \nu_{v0(111)0, v0(100)0}$, $\nu_2 = \nu_{v0(122)0, v0(111)0}$, $\nu_3 = \nu_{v0(100)0, v0(011)0}$, and similarly, by ν'_1, \dots, ν'_3 , the corresponding frequencies in the $(v', 0)$ state. Diagonalizing the hyperfine Hamiltonian, we obtain $E_4 = \nu_2 + \nu_3$, $E_5 = 2(\nu_1 + \nu_2)/3$, with compatibility relation $\nu_2(\nu_1 + \nu_2 + \nu_3) = 2\nu_1\nu_3$ [and similar for the $(v', 0)$ state].

The spin energy of the stretched states is $\Delta E^{v0(122)2} = E_4/4 + E_5/2 = \nu_1/3 + 7\nu_2/12 + \nu_3/4$. The transition frequency between stretched states is $\nu_{v0(122)2, v'0(122)2} = \nu_0 + \Delta\nu$, $\Delta\nu = 1/3(\nu'_1 - \nu_1) + 7/12(\nu'_2 - \nu_2) + (\nu'_3 - \nu_3)/4$. Thus, ν_0 could be obtained by measuring one vibrational transition, and six RF transitions. The sensitivity to the magnetic field comes only from $\Delta\nu$, since the Zeeman shift of $\nu_{v0(122)2, v'0(122)2}$ is strictly zero in the adopted approximation. For example, $\Delta\nu$ is shifted by only 55 Hz (5×10^{-13}) in the case $v=0, v'=2$ at $B=1$ G. This shift value could be taken as a conservative Zeeman uncertainty for ν_0 , but it could be further reduced by correcting for the magnetic field in the trap; the field could be determined (e.g., from a measurement of the Zeeman splitting of an appropriate magnetic-sensitive transition and using the theoretical magnetic sensitivities).

4. *Spectroscopic techniques.* In order to achieve the spectroscopic resolutions discussed, a Doppler-free technique is required, and two methods appear suitable. Two-photon spectroscopy with counterpropagating beams of an ensemble of cooled, but not strongly confined molecular ions strongly suppresses the first-order Doppler broadening [21]. The second method is quantum logic spectroscopy [22] on a single HD^+

ion. For both methods, techniques for strongly populating the lower spectroscopic state will be helpful [11].

Summary. By evaluating the Zeeman effect for all experimentally relevant spectroscopies of HD^+ we have shown that it will not be a limiting factor for the experimental accuracy if appropriate transitions and spectroscopic technique are selected. This is of particular relevance to the possible use of HD^+ for setting limits to a hypothetical time dependence of particle mass ratios, where a relative accuracy of 10^{-16} is desired. For the determination of the ratio of electron to reduced nuclear mass by comparison of *ab initio* QED calculations and experimental frequencies, it is advantageous to determine the central transition frequencies ν_0 since the uncertainties related to particle magnetic moments and nuclear electromagnetic structure will be significantly suppressed. We have shown how this can be achieved by combining two-photon and RF spectroscopy of states with low magnetic sensitivity, the latter feature not being affected by the higher-order relativistic mass and anisotropy corrections.

Other systematic shifts, such as light, black-body radiation and Stark shifts are currently being analyzed.

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