High-Precision Calculation of the Hyperfine Structure of the HD^+ Ion

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(Received 7 May 2006; published 11 December 2006)

High-precision laser spectroscopy of ultracold hydrogen molecular ions has the potential of improving the precision of the electron-to-proton mass ratio. An accurate knowledge of the spin structure of the transition is required in order to permit precise comparison with experimental transition frequencies. We calculate with a relative accuracy of the order of $O(\alpha^2)$ the hyperfine splitting of the rovibrational states of HD^+ with orbital momentum $L \le 4$ and vibrational quantum numbers up to $v = 17$, using the Breit-Pauli spin interaction Hamiltonian. These are the first complete *ab initio* calculations at this order of accuracy. A discrepancy between experiment and previous theory is resolved.

DOI: 10.1103/PhysRevLett.97.243001 PACS numbers: 33.15.Pw, 31.15.Ar, 31.15.Pf

It has been recognized that high-precision spectroscopy of rovibrational transitions in molecules opens up interesting possibilities for the metrology of the fundamental constants (electron-to-nucleus mass ratios) and for tests of few-body bound state QED [1,2]. Assuming the validity of QED, and using high-precision calculations for one-electron molecules, the masses of the particles constituting the molecules may be determined [3], possibly with higher accuracy than using present methods [4].

The possibility of a time variation of the electron-to-nuclear mass ratio, m_e/m_p, revealed by astronomical molecular spectra is presently under discussion [5]. A measurement of vibrational transition frequencies over time could lead to significantly improved laboratory tests of the time independence of m_e/m_p [3].

The molecular hydrogen ion isotopomers (H_2^+, HD^+, etc.) are stable one-electron molecules of fundamental interest. Since the birth of quantum theory their spectrum has been the subject of calculations of steadily increasing precision, including relativistic, QED, and nuclear effects [6].

On the experimental side, laser spectroscopy of a large variety of molecules and with a significant increase of resolution is currently underway, thanks to the development of methods of molecular cooling. In particular, molecular ions can be sympathetically cooled by atomic ions to temperatures of ~10 mK [7,8]. High-resolution spectroscopy of cold HD^+ at a level of ~2 parts in 10^7 has recently been demonstrated [9] and is being further developed towards higher precision. Because of the long lifetimes (~ 10 ms) of vibrational excitations of molecules in the ground electronic state it is expected that the spectroscopic resolution of rovibrational transitions (of typical frequencies 100 THz) can be pushed to the relative level of 10^{-15} in ultracold molecules by eliminating the 1st order Doppler effect, via one-photon spectroscopy in the Lamb-Dicke regime or via two-photon spectroscopy [10]. There is thus an important need to improve the accuracy of the theoretical spectrum by several orders of magnitude.

For the range of states with $L \le 4$ and $v \le 4$ the precision of ~10 Hz has been achieved in the nonrelativistic calculations [3]. For these states the leading relativistic [11] and radiative [12] corrections have been obtained recently with a *numerical uncertainty* below 1 kHz. The yet unevaluated QED corrections of order $m\alpha^6$ would contribute to the transition energy at the level of about 50 kHz.

The next important contribution is the hyperfine energy. The calculations performed so far used adiabatic [13] and two-state adiabatic [14,15] approximations and included the electron-nuclear spin-spin and the electron-spin-rotation interactions. The theoretical predictions were in agreement with the laser spectroscopic studies on HD^+ ion beams performed by Wing *et al.* [16] and Carrington *et al.* [17] within the experimental accuracy. However, a comparison with precise radio frequency measurements [15] disclosed a slight disagreement with the approximate theory.

In the present consideration of HD^+ a complete set of spin-dependent terms of the Breit-Pauli Hamiltonian is used; i.e., we include for the first time the nuclear spin-orbit couplings and the deuteron electric quadrupole moment. Furthermore, we use the essentially exact nonrelativistic variational wave functions. The uncertainty of the results is determined by the magnitude of the contribution of the interactions that are *not* included in the spin Hamiltonian and, from the known results for the H atom, are estimated to about 50 kHz.

In the nonrelativistic approximation, the rovibrational excited states are labeled with the quantum numbers of the total orbital momentum L and vibrational quantum number v. The variational bound state wave functions were calculated by solving the three-body Schrödinger equation with Coulomb interaction using the variational approach based on the exponential expansion with randomly chosen exponents [18]. The high precision of the solutions allows to say that the numerical uncertainty in the mean values of the Breit-Pauli Hamiltonian may be neglected compared to the uncalculated contributions of higher order in α.

The following notation is used throughout this Letter. $\mathbf{P}_d$, $\mathbf{P}_p$, and $\mathbf{p}_e$ are the momenta and $\mathbf{R}_d$, $\mathbf{R}_p$, $\mathbf{r}_e$ are the coordinates of deuteron, proton, and electron with respect to the center of mass of a molecule, and $\mathbf{r}_d = \mathbf{r}_e - \mathbf{R}_d$, $\mathbf{r}_p = \mathbf{r}_e - \mathbf{R}_p$, $\mathbf{R} = \mathbf{R}_p - \mathbf{R}_d$. $\mathbf{I}_d$, $\mathbf{I}_p$, and $\mathbf{s}_e$ are the spins of nuclei and electron, and $\mu_e = -(1+\kappa_e)$ is the magnetic moment of an electron in Bohr magnetons, while $\mu_{p,d}$ are the magnetic moments of proton and deuteron in nuclear magnetons. We use the CODATA02 recommended values of the fundamental constants [19]. The deuteron quadrupole moment, Q_d, that is the most accurate to date is taken from [20,21].

The spin interaction Hamiltonian is the sum of pairwise interactions: $V = V_{ep} + V_{ed} + V_{pd}$. The electron-proton and electron-deuteron interactions are expressed (in units $e = \hbar = 1$) by:

$$\begin{aligned}
V_{ep} = \alpha^2\Big\{ & \frac{1+2\kappa_e}{2m_e^2}\frac{(\mathbf{r}_p\times\mathbf{p}_e)\mathbf{s}_e}{r_p^3} - \frac{1+\kappa_e}{m_e m_p}\frac{(\mathbf{r}_p\times\mathbf{P}_p)\mathbf{s}_e}{r_p^3} \\
& - \frac{2\mu_p - 1}{2m_p^2}\frac{(\mathbf{r}_p\times\mathbf{P}_p)\mathbf{I}_p}{r_p^3} + \frac{\mu_p}{m_e m_p}\frac{(\mathbf{r}_p\times\mathbf{p}_e)\mathbf{I}_p}{r_p^3} \\
& - \frac{8\pi}{3}\frac{\mu_e\mu_p}{m_e m_p}\delta(\mathbf{r}_p)(\mathbf{s}_e\cdot\mathbf{I}_p) \\
& + \frac{\mu_e\mu_p}{m_e m_p}\frac{r_p^2(\mathbf{s}_e\cdot\mathbf{I}_p) - 3(\mathbf{r}_p\cdot\mathbf{s}_e)(\mathbf{r}_p\cdot\mathbf{I}_p)}{r_p^5}\Big\}. \\
V_{ed} = \alpha^2\Big\{ & \frac{1+2\kappa_e}{2m_e^2}\frac{(\mathbf{r}_d\times\mathbf{p}_e)\mathbf{s}_e}{r_d^3} - \frac{1+\kappa_e}{m_e m_d}\frac{(\mathbf{r}_d\times\mathbf{P}_d)\mathbf{s}_e}{r_d^3} \\
& - \frac{1}{m_d}\Big[\frac{\mu_d}{2m_p} - \frac{1}{2m_d}\Big]\frac{(\mathbf{r}_d\times\mathbf{P}_d)\mathbf{I}_d}{r_d^3} + \frac{\mu_d}{2m_e m_p}\frac{(\mathbf{r}_d\times\mathbf{p}_e)\mathbf{I}_d}{r_d^3} \\
& - \frac{4\pi}{3}\frac{\mu_e\mu_d}{m_e m_p}\delta(\mathbf{r}_d)(\mathbf{s}_e\cdot\mathbf{I}_d) \\
& + \frac{\mu_e\mu_d}{2m_e m_p}\frac{r_d^2(\mathbf{s}_e\cdot\mathbf{I}_d) - 3(\mathbf{r}_d\cdot\mathbf{s}_e)(\mathbf{r}_d\cdot\mathbf{I}_d)}{r_d^5}\Big\} \\
& + \frac{Q_d}{2}\frac{r_d^2\mathbf{I}_d^2 - 3(\mathbf{r}_d\cdot\mathbf{I}_d)^2}{r_d^5}. \qquad (1)
\end{aligned}$$

It is worthy to note here that the third term in the electron-deuteron interaction should be derived from the relativistic charge-current density; however, it has an analog in the classical electrodynamics and can be obtained for an arbitrary nonzero nuclear spin with account of the Thomas precession [22].

The proton-deuteron interaction is

$$\begin{aligned}
V_{pd} = \alpha^2\Big\{ & -\frac{2\mu_p - 1}{2m_p^2}\frac{[\mathbf{R}\times\mathbf{P}_p]\mathbf{I}_p}{R^3} + \frac{\mu_p}{m_p m_d}\frac{[\mathbf{R}\times\mathbf{P}_d]\mathbf{I}_p}{R^3} \\
& + \frac{1}{m_d}\Big[\frac{\mu_d}{2m_p} - \frac{1}{2m_d}\Big]\frac{[\mathbf{R}\times\mathbf{P}_d]\mathbf{I}_d}{R^3} \\
& - \frac{\mu_d}{2m_p^2}\frac{[\mathbf{R}\times\mathbf{P}_p]\mathbf{I}_d}{R^3} - \frac{4\pi}{3}\frac{\mu_p\mu_d}{m_p^2}\delta(\mathbf{R})(\mathbf{I}_d\cdot\mathbf{I}_p) \\
& + \frac{\mu_p\mu_d}{2m_p^2}\frac{R^2(\mathbf{I}_d\cdot\mathbf{I}_p) - 3(\mathbf{R}\cdot\mathbf{I}_d)(\mathbf{R}\cdot\mathbf{I}_p)}{R^5}\Big\} \\
& - \frac{Q_d}{2}\frac{R^2\mathbf{I}_d^2 - 3(\mathbf{R}\cdot\mathbf{I}_d)^2}{R^5}. \qquad (2)
\end{aligned}$$

Nuclear spin-spin contact interaction is negligibly small and will be omitted from the consideration.

Averaging (1) and (2) over the spatial degrees of freedom one arrives to the effective spin Hamiltonian,

$$\begin{aligned}
H_{\rm eff} = {} & E_1(\mathbf{L}\cdot\mathbf{s}_e) + E_2(\mathbf{L}\cdot\mathbf{I}_p) + E_3(\mathbf{L}\cdot\mathbf{I}_d) + E_4(\mathbf{I}_p\cdot\mathbf{s}_e) \\
& + E_5(\mathbf{I}_d\cdot\mathbf{s}_e) + E_6\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{s}_e) \\
& - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_p)]\} \\
& + E_7\{2\mathbf{L}^2(\mathbf{I}_d\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{s}_e) \\
& + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_d)]\} + E_8\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{I}_d) \\
& - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d) + (\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{I}_p)]\} \\
& + E_9[\mathbf{L}^2\mathbf{I}_d^2 - \tfrac{3}{2}(\mathbf{L}\cdot\mathbf{I}_d) - 3(\mathbf{L}\cdot\mathbf{I}_d)^2]. \qquad (3)
\end{aligned}$$

References [13,14,17] considered the simplified effective spin Hamiltonian:

$$H_{\rm eff} = b_1\mathbf{I}_p\cdot\mathbf{s}_e + c_1 I_{pz}s_{ez} + b_2\mathbf{I}_d\cdot\mathbf{s}_e + c_2 I_{dz}s_{ez} + \gamma\mathbf{s}_e\cdot\mathbf{L}, \qquad (4)$$

where the coefficients are related to the ones in (3) as follows (for $L \neq 0$):

$$b_1 = E_4 - c_1/3, \qquad c_1 = 3(2L-1)(2L+3)E_6, \qquad \gamma = E_1.$$

TABLE I. Comparison of calculated and experimental constants b_1, c_1, and γ of the effective spin Hamiltonian (4), in MHz.

	b_1		c_1		γ	
(v, L)	[13]	this work	[13]	this work	[13]	this work
(0,1)	882.54	881.574	128.91	129.167	31.98	31.984
(0,2)	881.04	880.079	128.47	128.718	31.84	31.841
(1,1)	863.72	862.743	121.76	122.050	30.28	30.280
(2,1)	846.20	845.197	115.11	115.239	28.64	28.645
(2,2)	844.88	843.868	114.70	114.831	28.51	28.513

	experiment [15]		theory [15]		this work	
	b_1	γ	b_1	γ	b_1	γ
(17,1)	711.90(1)	7.41(3)	713.14	8.09	712.083	7.45
(17,2)	711.6(2)	7.6(3)	712.64	8.00	711.579	7.40

TABLE II. Coefficients E_i of the effective spin Hamiltonian (3) (in MHz), $a[b] = a \times 10^b$.

L	v	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9
0	0				925.456	142.273				
0	1				904.207	139.016				
0	2				884.348	135.973				
0	3				865.798	133.133				
0	4				848.490	130.485				
1	0	31.9846	−3.134[−02]	−4.809[−03]	924.629	142.146	8.6111	1.3218	−3.057[−03]	5.666[−03]
1	1	30.2800	−3.046[−02]	−4.664[−03]	903.427	138.896	8.1367	1.2489	−2.945[−03]	5.659[−03]
1	2	28.6445	−2.953[−02]	−4.513[−03]	883.611	135.860	7.6826	1.1792	−2.832[−03]	5.621[−03]
1	3	27.0705	−2.856[−02]	−4.356[−03]	865.103	133.026	7.2467	1.1123	−2.719[−03]	5.555[−03]
1	4	25.5503	−2.753[−02]	−4.193[−03]	847.834	130.385	6.8269	1.0479	−2.604[−03]	5.463[−03]
2	0	31.8409	−3.114[−02]	−4.779[−03]	922.985	141.894	2.0431	0.3136	−7.236[−04]	1.334[−03]
2	1	30.1428	−3.026[−02]	−4.634[−03]	901.874	138.658	1.9305	0.2963	−6.970[−04]	1.333[−03]
2	2	28.5134	−2.933[−02]	−4.483[−03]	882.145	135.635	1.8227	0.2798	−6.702[−04]	1.324[−03]
2	3	26.9450	−2.836[−02]	−4.326[−03]	863.720	132.814	1.7192	0.2639	−6.431[−04]	1.308[−03]
2	4	25.4301	−2.734[−02]	−4.164[−03]	846.532	130.185	1.6195	0.2486	−6.159[−04]	1.286[−03]
3	0	31.6274	−3.083[−02]	−4.733[−03]	920.542	141.518	0.9485	0.1456	−3.346[−04]	6.127[−04]
3	1	29.9389	−2.995[−02]	−4.589[−03]	899.566	138.303	0.8962	0.1376	−3.223[−04]	6.118[−04]
3	2	28.3185	−2.903[−02]	−4.438[−03]	879.966	135.301	0.8461	0.1299	−3.098[−04]	6.077[−04]
3	3	26.7585	−2.806[−02]	−4.282[−03]	861.666	132.499	0.7980	0.1225	−2.973[−04]	6.005[−04]
3	4	25.2515	−2.704[−02]	−4.121[−03]	844.596	129.888	0.7517	0.1154	−2.846[−04]	5.905[−04]
4	0	31.3464	−3.043[−02]	−4.674[−03]	917.324	141.024	0.5505	0.0845	−1.933[−04]	3.504[−04]
4	1	29.6706	−2.956[−02]	−4.530[−03]	896.527	137.837	0.5201	0.0798	−1.861[−04]	3.499[−04]
4	2	28.0621	−2.864[−02]	−4.380[−03]	877.099	134.861	0.4910	0.0754	−1.788[−04]	3.475[−04]
4	3	26.5132	−2.767[−02]	−4.225[−03]	858.962	132.084	0.4630	0.0711	−1.716[−04]	3.434[−04]
4	4	25.0165	−2.666[−02]	−4.064[−03]	842.049	129.498	0.4361	0.0669	−1.642[−04]	3.376[−04]

Table I contains a comparison of coefficients of the effective spin Hamiltonian (4) obtained in [13] with our computed values. For small v we have a complete coincidence in values for γ, the spin-orbit term. However, the spin-spin coefficient, b_1, differs already in the third significant digit. In our calculations the estimated relative accuracy of the expectation value $\langle \delta(\mathbf{r}_{d,p}) \rangle$ is about 10^{-7}. The discrepancy can be attributed to the adiabatic approximation of [13,17]. The most advanced calculation of Carrington *et al.* [15] involved the two-state approximation. Since second-order effects were not included, discrepancies in b_1 and γ were observed by them for high vibrational states using rf spectroscopy. As seen from Table I, our calculations represent a significant improvement. The measured frequencies of individual transitions [15] agree with our calculation to within the experimental accuracy of ±0.3 MHz. The importance of nonadiabatic effects for the spin-spin coupling has been shown for the case of H_2^+ by Babb and Dalgarno [23].

The numerical results of our calculation of the coefficients of the effective spin Hamiltonian are presented in Table II. The strongest coupling is due to the spin-spin electron-proton interaction. The spin-spin interaction between electron and deuteron is a factor of 5 smaller. These

TABLE III. Hyperfine splitting (in MHz) of rovibrational levels of the HD^+ molecular ion.

		$(F, S) = (0, 1)$			$(1, 0)$		$(1, 1)$						
									$(1, 2)$				
L	v	$J = L + 1$	L	$L - 1$	L	$L + 1$	L	$L - 1$	$L + 2$	$L + 1$	L	$L - 1$	$L - 2$
0	0	−705.779			89.091	171.914			302.500				
0	1	−689.576			87.036	167.964			295.560				
0	2	−674.432			85.114	164.271			289.073				
1	0	−707.913	−704.061	−699.728	80.016	183.702	153.513	165.299	312.575	314.236	269.293		
1	1	−691.587	−687.925	−683.827	78.822	179.118	150.497	161.653	305.108	306.628	263.816		
1	2	−676.326	−672.847	−668.974	77.701	174.818	147.709	158.255	298.115	299.503	258.748		
2	0	−709.970	−703.821	−697.855	71.732	194.426	165.229	139.786	325.483	318.834	291.745	257.152	225.955
2	1	−693.512	−687.671	−682.018	71.115	189.265	161.299	137.813	317.331	310.966	285.154	252.321	223.150
2	2	−678.124	−672.581	−667.227	70.552	184.412	157.640	136.002	309.682	303.594	279.012	247.877	220.627

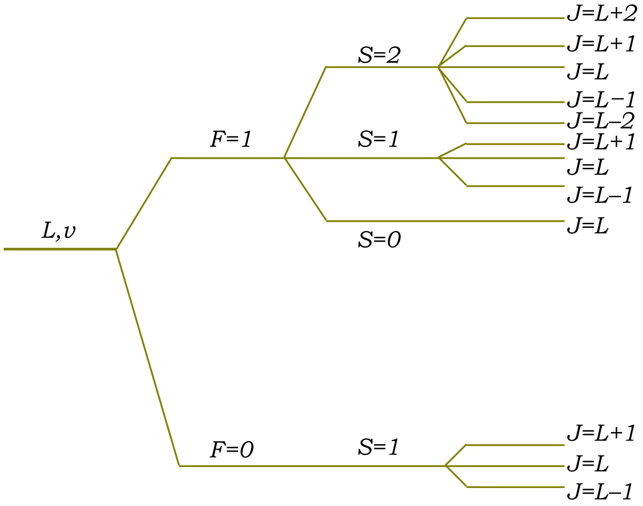

FIG. 1 (color online). Hyperfine structure of the lower rovibrational energy levels of HD$^+$ with $L \geq 2$.

two interactions determine the principal splitting of the rovibrational levels of HD$^+$ as is seen from Table III. With this consideration in mind, the preferable coupling scheme of angular momentum operators is

$$\mathbf{F} = \mathbf{I}_p + \mathbf{s}_e, \qquad \mathbf{S} = \mathbf{F} + \mathbf{I}_d, \qquad \mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{5}$$

The schematic diagram of the hyperfine states is shown in Fig. 1. The separation of the states with $F = 0$ and $F = 1$ is typically 700–1000 MHz; the separation in S is of the order of 200 MHz [that justifies the choice of the coupling scheme of (5)]. It is worthy to note that with increase of L the electron-spin-orbit coupling becomes more and more important. That leads to breaking of the LS coupling scheme for high L.

The hyperfine splitting of the lower rovibrational levels of HD$^+$ is presented in Table III. The results were obtained by diagonalization of the effective spin Hamiltonian. The deuteron quadrupole moment interaction contributes at the level of only 10 kHz; therefore, an improved determination of the deuteron quadrupole moment by optical spectroscopy will be difficult.

In conclusion, we present the first *ab initio* calculation of the hyperfine structure in the rovibrational states of the HD$^+$ molecular ion, which is essentially exact within the assumptions of the Breit-Pauli interaction. We expect the comparison between the obtained theoretical results with data from oncoming experiments [9] for the lower rovibrational transition frequencies to be possible at a level of $\approx$50 kHz, i.e., a relative level of $\sim 5 \times 10^{-10}$. Such a comparison would allow a test of the current value of the electron-to-proton mass ratio at the level of 1 ppb. For a measurement of this mass ratio at the sub-ppb level, the calculations will require consideration of the $O(m\alpha^6)$ order relativistic and radiative corrections as well as the finite size effects like the Zemach electromagnetic radii [24] of proton and deuteron or deuteron polarizability. In case of the atomic hydrogen hyperfine structure, these three effects are of about the same significance [25]. This program is in progress now, including evaluation of systematic line shifts under experimentally relevant conditions; we expect to reduce the theoretical uncertainty below 10 kHz.

The work was supported in part by the RFBR, Grant No. 05-02-16618 (V. I. K.), Joint Research grant of JINR (Dubna) and INRNE (Sofia) (V. I. K. and D. B.), the DFG, and the EC network "Cold Molecules" No. HPRN-CT-2002-00290.

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