Higher-order corrections to the spin-orbit and spin-spin tensor interactions in HD^+

Mohammad Haidar,[1,*] Vladimir I. Korobov,[2] Laurent Hilico,[1,3] and Jean-Philippe Karr[1,3]

[1]*Laboratoire Kastler Brossel, Sorbonne Université, CNRS, ENS-Université PSL, Collège de France, 4 place Jussieu, F-75005 Paris, France*

[2]*Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia*

[3]*Université d'Evry-Val d'Essonne, Université Paris-Saclay, Boulevard François Mitterrand, F-91000 Evry, France*

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Improved values of hyperfine coefficients related to the electronic spin-orbit and electron-nucleus spin-spin tensor interactions in the HD^+ molecular ion are obtained through numerical calculation of relativistic corrections at the $m\alpha^6$ order and radiative corrections at the $m\alpha^7 \ln(\alpha)$ order. The theoretical accuracy is improved by more than one order of magnitude. Some deviations with recent high-precision rovibrational spectroscopy experiments are observed, in contrast with the good agreement obtained in H_2^+.

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I. INTRODUCTION

Laser spectroscopy of HD^+ has recently made a significant leap in precision, as a rotational transition [1] and two vibrational transitions [2,3] were probed in the Lamb-Dicke regime on ensembles of trapped and sympathetically cooled molecular ions. Transition frequencies were measured with relative uncertainties in the 10^{-11}–10^{-12} range, and comparison with theoretical predictions [4,5] was used to get improved determinations of the proton-electron mass ratio and constraints on a "fifth force" between the nuclei [6].

The hyperfine splitting of HD^+ rovibrational levels gives rise to 4, 10, or 12 sublevels for $L = 0$, $L = 1$, and $L \geqslant 2$ states, respectively, where L is the rotational quantum number [7]. In the above-mentioned experiments, a few hyperfine components of the rovibrational transitions (between 2 and 6) were measured with sub-kHz uncertainties, from which a "spin-averaged" transition frequency was extracted using theoretical predictions of the hyperfine structure. A discrepancy between theory and experiment was evidenced in the hyperfine slitting of the $(v = 0, L = 3) \rightarrow (v' = 9, L' = 3)$ transition [8], which affects the uncertainty of the extracted spin-averaged transition frequency [2,9]. Beyond that, constant progress in experimental accuracy opens the way to highly precise tests of the hyperfine structure theory. It is also worth noting that the HD^+ hyperfine structure is sensitive to the deuteron's electric quadrupole moment Q_d. A value of Q_d was extracted from the rotational transition measurement [1], although it is significantly less precise than that obtained from magnetic resonance measurements in D_2 [10,11]. For all these reasons, it is highly desirable to improve further the hyperfine structure theory in HD^+.

On the theoretical side, all the coefficients of the effective spin Hamiltonian introduced by the authors of Ref. [7] were calculated in the framework of the Breit-Pauli Hamiltonian with an account of the electron's anomalous magnetic moment, which yielded a relative accuracy on the order of α^2. We recently improved the precision of the largest hyperfine coefficients, i.e., the electron-proton and electron-deuteron spin-spin scalar interactions, to slightly below 1 ppm [8]. The next largest coefficients are those related to the electron spin-orbit (denoted by E_1 in Ref. [7]) and the electron-proton (E_6) and electron-deuteron (E_7) spin-spin tensor interactions. The effective Hamiltonian describing $m\alpha^6$-order relativistic corrections to these interactions was derived in Ref. [12] in the framework of nonrelativistic quantum electrodynamics (NRQED) and preliminary numerical results were given. In Ref. [13], the theory was further refined by including logarithmic radiative corrections at the following order. The spin-orbit and spin-spin interaction coefficients were calculated numerically in the H_2^+ ion for a range of rovibrational states, and good agreement with available rf spectroscopy data was observed. In the present work, we report on the numerical calculation of these corrections in HD^+, which improves the theoretical accuracy of the E_1, E_6, and E_7 coefficients by almost one order of magnitude with respect to Ref. [7]. We then compare our theoretical predictions of the hyperfine splitting with available experimental data [1–3]. Significant deviations are evidenced, possible causes of which are discussed in the last section.

II. NUMERICAL RESULTS

Higher-order corrections to the spin-orbit and spin-spin tensor interaction coefficients in the hydrogen molecular ions were studied in our previous works [12,13]. The expressions of relativistic corrections at orders $m\alpha^6$ can be found in Ref. [13], Eqs. (17) to (24), and radiative corrections at the $m\alpha^7 \ln(\alpha)$ order are given in Eqs. (27) and (29) to (35). In Tables I, II, and III, we report the results of numerical calculations of these correction terms for a few rovibrational states of HD^+ of direct interest for experiments [1–3,14]. Complete

*Present addresses: Sorbonne Université, Laboratoire de Chimie Théorique (LCT), 4 place Jussieu, F-75005 Paris, France; Sorbonne Université, CNRS, Université Paris Cité, Laboratoire Jacques-Louis Lions (LJLL), 4 place Jussieu, F-75005 Paris, France; and TotalEnergies, Tour Coupole, 2 Pl. Jean Millier, F-92078 Paris la Défense, France.

TABLE I. Corrections to the spin-orbit interaction coefficient E_1 for a few rovibrational states of HD^+ (in kHz). The leading-order (Breit-Pauli) value $E_1^{(\mathrm{BP})}$ (Ref. [7]) is given in column 2. Columns 3 to 5 and 6 to 8 are, respectively, the first-order and second-order contributions (Eqs. (18) and (19) of Ref. [13]) at the $m\alpha^6$ order, and the total correction at this order $\Delta E_1^{(6)}$ is given in column 9. Columns 10 and 11 are the first-order contributions at the $m\alpha^7 \ln(\alpha)$ order (Eqs. (27) and (29) of Ref. [13]) whereas column 12 is the second-order term [Eq. (32)] of Ref. [13]. The total correction at this order, $\Delta E_1^{(7\,\mathrm{ln})}$, is given in column 13. The last column is our value of E_1. Its estimated uncertainty (equal to one third of $\Delta E_1^{(7\,\mathrm{ln})}$) is indicated between parentheses.

(L, v)	$E_1^{(\mathrm{BP})}$	$\mathcal{U}_{Y_1}$	$\mathcal{U}_W$	$\mathcal{U}_{CM}$	$\Delta E_{\mathrm{so}\text{-}H_B}$	$\Delta E^{(1)}_{so\text{-}so}$	$\Delta E_{\mathrm{so\text{-}ret}}$	$\Delta E_1^{(6)}$	$\mathcal{U}_{Y_1}$	$\mathcal{U}_{q^2}$	$\Delta E_{\mathrm{so}\text{-}H_{(5\,\mathrm{ln})}}$	$\Delta E_1^{(7\,\mathrm{ln})}$	E_1 (this work)
(1,0)	31 984.645	1.170	−2.736	0.021	2.088	0.312	0.257	1.112	−0.026	0.045	−0.367	−0.348	31 985.41(12)
(1,1)	30 280.027	1.110	−2.631	0.027	1.986	0.299	0.243	1.035	−0.025	0.044	−0.345	−0.326	30 280.74(11)
(1,5)	24 076.867	0.893	−2.205	0.042	1.592	0.233	0.193	0.747	−0.020	0.036	−0.268	−0.252	24077.36(8)
(1,6)	22 643.449	0.834	−2.097	0.044	1.498	0.219	0.181	0.679	−0.019	0.035	−0.251	−0.235	22643.89(8)
(3,0)	31 627.353	1.156	−2.694	0.019	2.042	0.308	0.255	1.086	−0.026	0.045	−0.360	−0.341	31 628.10(11)
(3,9)	18 270.560	0.680	−1.732	0.043	1.158	0.182	0.146	0.478	−0.015	0.028	−0.198	−0.185	18 270.85(6)

results for the rovibrational states ($1 \leqslant L \leqslant 4, 0 \leqslant v \leqslant 9$) are given in the Supplemental Material [15]. These numerical calculations are performed following the methods presented in Refs. [12,13] relying on a variational expansion of the three-body wave function in terms of exponentials of interparticle distances, with pseudorandomly chosen exponents [16,17].

The numerical and theoretical uncertainties were discussed in Ref. [13] in the context of the H_2^+ ion, and the main conclusions remain valid for the results presented here. Briefly, the numerical uncertainty of E_1 (or E_6, E_7) is estimated to be smaller than 10 Hz (or 1 Hz), see Ref. [13] from a study of convergence of a few terms. The overall uncertainty is dominated by the as-yet unevaluated nonlogarithmic $m\alpha^7$-order contribution, and is estimated to about one third of the total contribution of order $m\alpha^7 \ln(\alpha)$. The resulting uncertainties amount to 3 to 4 ppm for the electronic spin-orbit interaction and 2 ppm for tensor interactions, respectively. This represents an improvement by factors of about 15 for E_1, and 25 for E_6 and E_7, over the results of Ref. [7].

III. COMPARISON WITH EXPERIMENTS AND DISCUSSION

A. Theoretical hyperfine splitting of rovibrational transitions

These results allow us to improve theoretical predictions of the hyperfine splitting of rovibrational transitions that were recently measured with high accuracy. These are obtained by diagonalizing the effective spin Hamiltonian of Ref. [7], which comprises nine coefficients $E_1 \ldots E_9$. The values of E_1, E_6, and E_7 are taken from the present work. For the largest coefficients, i.e., the electron-proton and electron-deuteron spin-spin scalar interaction coefficients ("Fermi" contact interaction), E_4 and E_5, we use the very precise values computed in Ref. [8]. Finally, the smaller coefficients E_2, E_3, E_8, and E_9 are calculated in the framework of the Breit-Pauli Hamiltonian [7]. We updated the E_9 coefficient, which corresponds to the effect of the deuteron's quadrupole moment Q_d, with the latest and most precise determination of Q_d [11]. The values of all the coefficients used here can be found in Appendix A. The fractional uncertainties of E_4 and E_5 are estimated to 0.93 and 0.57 ppm, respectively [8]. Those of the smaller coefficients (E_2, E_3, E_8, E_9) were taken as equal to $\alpha^2 \simeq 53$ ppm in previous works (see, e.g., Refs. [1,13]), which corresponds to the expected accuracy level of the Breit-Pauli Hamiltonian. However, in this specific case, crossed second-order contributions (in the sense of perturbation theory) involving larger hyperfine interaction terms can be significantly larger than this limit [18]. For example, the second-order perturbation term induced by spin-orbit (E_1) and electron-proton spin-spin (E_4) interactions contributes to the proton spin-orbit interaction (E_2). From numerical evaluation of these second-order terms, we estimate the fractional uncertainty of E_k to $5\alpha^2 \simeq 270$ ppm for $k = 2, 3, 8$. In the case of E_9, crossed second-order terms are smaller than $\alpha^2 E_9$, and we thus confirm our previous uncertainty estimate. However, the 82 ppm uncertainty of Q_d [11] should be taken into account. Adding it quadratically to the α^2

TABLE II. Corrections to the electron-proton spin-spin tensor interaction coefficient E_6 for a few rovibrational states of HD^+ (in kHz). The leading-order (Breit-Pauli) value $E_6^{(\mathrm{BP})}$ (Ref. [7]) is given in column 2. Columns 3 to 4 and 5 are, respectively, the first-order and second-order contributions (Eqs. (22) and (23) of Ref. [13]) at the $m\alpha^6$ order. The total correction at this order, $\Delta E_6^{(6)}$, is given in column 6. Column 7 is the second-order contribution at the $m\alpha^7 \ln(\alpha)$ order (Eq. (35) of Ref. [13]). The last column is our value for E_6. Its estimated uncertainty (equal to one-third of $\Delta E_6^{(7\,\mathrm{ln})}$) is indicated between parentheses.

(L, v)	$E_6^{(\mathrm{BP})}$	$\mathcal{U}_W^{(2)}$	$\mathcal{U}_{CM}^{(2)}$	$\Delta E^{(2)}_{ss\text{-}H_B}$	$\Delta E_6^{(6)}$	$\Delta E_6^{(7\,\mathrm{ln})}$	E_6 (this work)
(1,0)	8611.112	−0.806	0.093	0.955	0.242	−0.055	8611.299(18)
(1,1)	8136.686	−0.770	0.090	0.905	0.225	−0.052	8136.859(17)
(1,5)	6421.232	−0.632	0.079	0.726	0.172	−0.041	6421.364(14)
(1,6)	6027.810	−0.599	0.076	0.678	0.154	−0.039	6027.925(13)
(3,0)	948.5222	−0.0883	0.0101	0.1042	0.0260	−0.0060	948.5421(20)
(3,9)	538.9906	−0.0544	0.0070	0.0593	0.0119	−0.0035	538.9991(12)

TABLE III. Same as Table II, for the electron-deuteron spin-spin tensor coefficient E_7.

(L, v)	$E_7^{(\mathrm{BP})}$	$\mathcal{U}_W^{(2)}$	$\mathcal{U}_{CM}^{(2)}$	$\Delta E_{ss\text{-}H_B}^{(2)}$	$\Delta E_7^{(6)}$	$\Delta E_7^{(7\,\ln)}$	E_7 (this work)
(1,0)	1321.7673	−0.1237	0.0142	0.1467	0.0371	−0.0085	1321.7960(28)
(1,1)	1248.9359	−0.1182	0.0138	0.1390	0.0346	−0.0080	1248.9624(27)
(1,5)	985.5868	−0.0971	0.0121	0.1115	0.0264	−0.0063	985.6069(21)
(1,6)	925.1895	−0.0919	0.0115	0.1040	0.0237	−0.0060	925.2072(20)
(3,0)	145.5938	−0.0136	0.0016	0.0160	0.0040	−0.0009	145.5969(3)
(3,9)	82.7237	−0.0083	0.0010	0.0091	0.0018	−0.0005	82.7250(2)

theoretical uncertainty yields a total fractional uncertainty of 98 ppm. It should be stressed that the reevaluated error bars for small coefficients have negligibly small influence on the total theoretical uncertainty of the hyperfine splitting and do not question uncertainty estimates made in previous works [1,13].

The theoretical uncertainties of hyperfine intervals $f_{ij} = f_j - f_i$, where i (j) denotes the lower (upper) hyperfine states and f_i, f_j their respective hyperfine shifts are then calculated by propagating the uncertainties of the hyperfine coefficients, using the derivatives

$$\gamma_{i,k} = \frac{\partial f_i}{\partial E_k}, \qquad 1 \leqslant k \leqslant 9. \tag{1}$$

The values of these derivatives for the hyperfine states involved in the $v = 0 \to 9$ transition [2] are given in Appendix B. For the states relevant to the rotational transition and to the $v = 0 \to 1$ transition, they can be found in Ref. [1] and the Supplementary Material [3], respectively.

It is important to take correlations into account to get reliable uncertainty estimates. There are strong correlations between theoretical errors of a given coefficient E_k in different rovibrational states, which can be understood as follows. First, these errors are dominated by yet uncalculated QED contributions (numerical uncertainties being negligibly small), which are given by expectation values of the same effective operators, evaluated with different wave functions. Second, the uncalculated terms are corrections to the bound electron and essentially depend on the electronic part of the wave function, which varies only slowly with the rovibrational state. Correlations may also exist between errors of different coefficients E_k, E_l for the same rovibrational state if they originate from similar QED terms. The hypotheses we adopted for our uncertainty estimates are presented in Appendix C.

B. Comparison with experimental data

A comparison between experiment and theory is shown in Table IV. Regarding the hyperfine splitting of the $(v = 0, L = 0) \to (v' = 1, L' = 1)$ transition [3] and of the $(v = 0, L' = 3) \to (v = 9, L' = 3)$ transition [2], the theoretical precision is significantly improved and previous conclusions remain essentially valid: reasonable agreement between theory and experiment is observed in the first case, whereas a clear discrepancy appears in the second case, becoming even more significant (nine combined standard deviations) due to the reduced theoretical error bar. The cause of this discrepancy is currently unknown, but it is clear that it has no relationship with the corrections calculated in the present work that shift the theoretical prediction by only −0.3 kHz with respect to the previous evaluation [8].

We now discuss the rotational transition [1], which represents the most stringent test of our improved values of the E_1, E_6, and E_7 coefficients, in view of the higher absolute precision of the measurements and of their much lower sensitivity to the Fermi coefficients E_4 and E_5 (due to strong cancellation between the lower and upper states). Comparison between theory and experiment is more involved in this case, as six hyperfine components of this transition were measured, from which 15 hyperfine intervals can be deduced (the values of which are, of course, partially redundant). A detailed comparison for these 15 intervals is shown in Appendix D, revealing significant discrepancies for several lines. These data are, however, difficult to interpret, and a useful overview of the results can be obtained by extracting experimental values of E_1, E_6, and E_7 from a least-squares adjustment of the experimental data whose results are shown in the last line of Table IV. The difference between experimental and theoretical values is above 3 σ_c for the spin-orbit coefficient and 2 σ_c for spin-spin tensor coefficients. Details of the least-squares adjustment procedure can be found in Appendix E.

C. Discussion

The observed deviations could be due to a problem in the theory, in the experiment, or both; let us discuss here the first of these possibilities.

The largest discrepancy in terms of absolute magnitude (8.5 kHz, or a fractional difference of 4.8×10^{-5}) is in the hyperfine splitting of the $v = 0 \to 9$ transition. As discussed in Ref. [8] it points towards the largest hyperfine coefficients E_4 and/or E_5 because the error that would be required in the other coefficients to explain the discrepancy is much larger than the expected order of magnitude of any corrections beyond the Breit-Pauli Hamiltonian. However, a mistake in the calculation of the electron-proton spin-spin coefficient E_4 would also affect at a similar level the corresponding coefficient (denoted by b_F) in H_2^+, where agreement with experiments at a sub-kHz level is observed [8]. This suggests that the problem might come from the electron-deuteron interaction coefficient E_5 (note that this hypothesis is not contradictory with the reasonably good agreement obtained for the $v = 0 \to 1$ transition frequency because the latter only weakly depends on E_5).

What could then be missing in the theory of the electron-deuteron spin-spin interaction? The difference between proton and deuteron cases resides in the nuclear structure and recoil corrections. The first include the Zemach correction [19] that

TABLE IV. Comparison between experimental and theoretical hyperfine intervals (unit: kHz). In parts (a) and (b), hyperfine components are identified by their label (following the notations of the original publications [2,3]) and by the hyperfine states in the lower and upper rovibrational states (columns 1 to 4). Experimental values and previous theoretical predictions of the hyperfine intervals are given in columns 5 and 6. Our predictions are shown in column 7. The deviations $\Delta_{ij} = f_{ij}^{\rm exp} - \Delta_{ij}^{\rm theor}$ are given in kHz in column 8 and in units of the combined uncertainty $\sigma_c = ([u(f_{ij}^{\rm exp})]^2 + [u(f_{ij}^{\rm theor})]^2)^{1/2}$ in the last column. In part (c), column 2 contains the values of the E_1, E_6, and E_7 hyperfine coefficients extracted from the experimental data of Ref. [1] using a least-squares adjustment described in Appendix E. Previous theoretical predictions are given in column 3. Our predictions are shown in column 4. Deviations $\Delta E_k = E_k^{\rm exp} - E_k^{\rm theor}$ are given in kHz in column 5, and in units of the combined uncertainty in the last column.

(a) $(v = 0, L = 0) \rightarrow (v' = 1, L' = 1)$

i	$FSJ \rightarrow F'S'J'$	j	$FSJ \rightarrow F'S'J'$	$f_{ij}^{\rm exp}$ [3]	$f_{ij}^{\rm theor}$ [3]	$f_{ij}^{\rm theor}$ (this work)	Δ_{ij}	Δ_{ij}/σ_c
12	$122 \rightarrow 121$	16	$122 \rightarrow 123$	41 294.06(32)	41 293.81(44)	41 293.66(12)	0.40	1.2

(b) $(v = 0, L = 3) \rightarrow (v' = 9, L' = 3)$

i	$FSJ \rightarrow F'S'J'$	j	$FSJ \rightarrow F'S'J'$	$f_{ij}^{\rm exp}$ [2]	$f_{ij}^{\rm theor}$ [8]	$f_{ij}^{\rm theor}$ (this work)	Δ_{ij}	Δ_{ij}/σ_c
$F = 0$	$014 \rightarrow 014$	$F = 1$	$125 \rightarrow 125$	178 254.4(9)	178 246.2(1.8)	178 245.89(28)	8.5	9.0

(c) $(v = 0, L = 0) \rightarrow (v' = 0, L' = 1)$

Coefficient	$E_k^{\rm exp}$	$E_k^{\rm theor}$	$E_k^{\rm theor}$ (this work)	ΔE_k	$\Delta E_k/\sigma_c$
E_1	31 984.9(1)	31 985.76(35) [12]	31 985.41(12)	−0.5	−3.3
E_6	8 611.17(5)	8 611.1(5) [7]	8 611.299(18)	−0.13	−2.4
E_7	1 321.72(4)	1 321.77(7) [7]	1 321.7960(28)	−0.08	−2.0

is the leading-order contribution to the Bohr-Weisskopf effect [20], as well as the nuclear polarizability correction. The sum of all these corrections was determined phenomenologically from the experimental ground-state hyperfine splitting of the hydrogen and deuterium atoms [8] under the assumption that they are state independent, i.e., they can be described by a contact (delta-function) term. Possible errors induced by this approximation are linked to the existence of state-dependent corrections. The largest such term is a recoil correction of order $(Z\alpha)^2(m/M)E_F$ [21], which contributes to the ground-state hyperfine splitting of the deuterium atom at a level of only 39 Hz. An error on the electron-deuteron spin-spin interaction at a level of ∼10 kHz thus seems extremely unlikely.

Regarding the rotational transition, the deviations between theory and experiment could be explained by errors in the spin-orbit (E_1) and spin-spin tensor coefficients (E_6, E_7) coefficients, as revealed by the adjustment described in the previous section (see last line of Table IV). However, any error in the calculation of E_1 for the $(L = 1, v = 0)$ would affect the $(L = 1, v = 1)$ level at a similar level. If one assumes, for example, that E_1 is shifted by −0.5 kHz for both states with respect to our present theoretical value, this would improve the agreement for the rotational transition, but increase the deviation from 0.4 kHz to about 0.9 kHz for the $v = 0 \rightarrow 1$ transition. Moreover, it would affect the value of the corresponding coefficient (denoted by c_e) in H_2^+, which we calculated in our previous work [13], and cause significant tension with rf spectroscopy data. Overall, it appears that available measurements are not fully consistent with each other.

Apart from errors or missed contributions in theoretical hyperfine coefficients, another possible cause of deviations between theory and experiment is the incompleteness of the effective spin Hamiltonian introduced in Ref. [7]. Only the terms that appear at the leading order (Breit-Pauli Hamiltonian) were included so far, but other spin couplings appear at the order $m\alpha^6$ and higher. The largest one is the spin-spin contact interaction between proton and deuteron ($\mathbf{I}_p \cdot \mathbf{I}_d$). This term is already present in the Breit-Pauli Hamiltonian, but was not included in the effective spin Hamiltonian because the associated coupling coefficient is proportional to the proton-deuteron delta function expectation value, which is negligibly small due to the strong Coulomb repulsion. However, a larger coupling appears at the $m\alpha^6$ order due to the second-order contribution mediated by the electron. This contribution was studied in Ref. [22], where it was shown that the coupling constant is on the order of 100 Hz, but shifts the hyperfine

TABLE V. Hyperfine coefficients for a few rovibrational states of HD^+ (in kHz). The values of E_4, E_5 (or E_2, E_3, E_8) are taken from Ref. [8] (or Ref. [7]). The value of E_9 has been updated with the latest determination of the deuteron's quadrupole moment [11]. Uncertainties are discussed in Sec. III A of the main text.

(v, L)	E_2	E_3	E_4	E_5	E_8	E_9
(0,0)			925 394.159(860)	142 287.556(84)		
(0,1)	−31.345(8)	−4.809(1)	924 567.718(859)	142 160.670(84)	−3.057(1)	5.660(1)
(1,1)	−30.463(8)	−4.664(1)	903 366.501(839)	138 910.266(82)	−2.945(1)	5.653(1)
(0,3)	−30.832(8)	−4.733(1)	920 479.981(855)	141 533.075(83)	−0.335	0.612
(9,3)	−21.304(6)	−3.225(1)	775 706.122(721)	119 431.933(73)	−0.219	0.501

TABLE VI. Sensitivity coefficients for the hyperfine states involved in the $v = 0$–9 transition in HD^+. Here $\gamma_{n,v} = \partial E_{hfs}(v, L, F, S, J)/\partial E_n$. Note that for the $F = 1$ level, the sensitivities are the same in $v = 0$ and $v = 9$, which is due to $(F = 1, S = 2, J = 5)$ being a "pure" state.

(L, v, F, S, J)	$\gamma_{1,v}$	$\gamma_{2,v}$	$\gamma_{3,v}$	$\gamma_{4,v}$	$\gamma_{5,v}$	$\gamma_{6,v}$	$\gamma_{7,v}$	$\gamma_{8,v}$	$\gamma_{9,v}$
(3,0,0,1,4)	−0.414	0.424	2.986	−0.726	−0.215	0.274	3.079	−3.328	−7.400
(3,9,0,1,4)	−0.359	0.372	2.984	−0.730	−0.201	0.193	2.474	−2.722	−7.385
(3,0,1,2,5)	1.50	1.50	3.00	0.250	0.500	−7.50	−15.00	−15.00	−7.50
(3,9,1,2,5)	1.50	1.50	3.00	0.250	0.500	−7.50	−15.00	−15.00	−7.50

components of the rotational transition by less than 2 Hz due to cancellation between the lower and upper levels.

In conclusion, we did not identify any contribution that could potentially have the required order of magnitude to explain the observed discrepancies and there is a strong need for additional measurements of the HD^+ hyperfine structure to give new insight on this problem.

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APPENDIX A: OTHER COEFFICIENTS OF THE EFFECTIVE SPIN HAMILTONIAN

We give in Table V the values of all the coefficients of the HD^+ effective spin Hamiltonian (see Eq. (3) of Ref. [7]) in the rovibrational states considered in Sec. III (see Table IV).

APPENDIX B: DEPENDENCE OF HYPERFINE SHIFTS ON THE HYPERFINE COEFFICIENTS

The values of the derivatives $\gamma_{i,k}$ [as defined in Eq. (1)], for the hyperfine states probed in spectroscopy of the $(L = 3, v = 0) \rightarrow (L = 3, v = 9)$ transition [2], are given in Table VI. These quantities are required to estimate the uncertainty of the theoretical hyperfine interval.

APPENDIX C: CORRELATIONS BETWEEN THE HYPERFINE COEFFICIENTS

In this Appendix, we present and justify our hypotheses regarding correlations between theoretical errors in the hyperfine coefficients, which are summarized in Table VII.

Let us first discuss the correlations between errors on a given coefficient E_k in different rovibrational states. In the case of the largest hyperfine coefficients E_4 and E_5, related to the Fermi contact interaction between the electron and both nuclei, uncertainties and correlations can be controlled very well thanks to the fact that these interactions were studied in great depth in the context of the hydrogen and deuterium ground-state hyperfine splitting. This allowed us to estimate the unevaluated QED terms from their value in the hydrogen (deuterium) atom ground state using the LCAO approximation. The uncertainties of E_4 and E_5 are conservatively taken as equal to the full estimated term [8]. Then, for the evaluation of uncertainties of hyperfine shifts in rovibrational transitions, we assume perfect correlations between different rovibrational states, i.e., the uncertainty of a transition frequency is obtained by subtracting the uncertainties due to the upper and lower states. We tested this assumption by applying it to lower-order terms that were actually calculated by us, and found that the uncertainty estimated in this way matches well the magnitude of the actual correction.

For other hyperfine coefficients, we used cruder uncertainty estimates based on the expected order of magnitude of the largest unevaluated QED terms. For example, for coefficients calculated at the Breit-Pauli, we estimate the relative uncertainty to be α^2. In this case, it is harder to correctly evaluate the degree of correlation between theory errors, but all correlations are expected to be positive. In this work, we assumed that the theory errors of the lower and upper levels are uncorrelated, which provides an upper limit of uncertainties on transition frequencies.

Let us now discuss correlations between errors in different coefficients E_k, E_l for the same rovibrational state. Such correlations occur if the uncalculated QED terms that limit the theoretical precision are of the same nature. This is the case for the E_2 and E_3 coefficients that correspond to the proton (E_2) and deuteron (E_3) spin-orbit interactions. Both coefficients were calculated in the framework of the Breit-Pauli Hamiltonien [7], and their theoretical errors are associated with $(Z\alpha^2)$-order relativistic corrections. These corrections will be described by the same effective potentials, the only difference being the substitution between proton and deuteron. Similarly, errors in the E_6 and E_7 coefficients that correspond to the electron-proton (E_6) and electron-deuteron (E_7) spin-spin tensor interactions are caused by the same QED term, that

TABLE VII. Summary of our assumptions on correlations between errors in the theoretical hyperfine coefficients.

First coefficient	Second coefficient	Correlation coefficient
$E_k(v, L)$	$E_k(v', L')$	1 if $k = 4$ or 5; 0 otherwise.
$E_k(v, L)$	$E_l(v, L)$	1 if $(k, l) = (2, 3), (3,2), (6,7)$, or $(7,6)$; 0.4016 if $(k, l) = (4, 5)$ or $(5,4)$; 0 otherwise.
$E_k(v, L)$	$E_l(v', L')$	0.4016 if $(k, l) = (4, 5)$ or $(5,4)$; 0 otherwise.

TABLE VIII. Comparison between experimental and theoretical hyperfine intervals (unit: kHz). All definitions are identical to those of Table IV.

				$(v=0, L=0) \to (v'=0, L'=1)$				
i	$FSJ \to F'S'J'$	j	$FSJ \to F'S'J'$	$f_{ij}^{\rm exp}$ [1]	$f_{ij}^{\rm theor}$ [1]	$f_{ij}^{\rm theor}$ (this work)	Δ_{ij}	Δ_{ij}/σ_c
12	122 → 121	14	100 → 101	24 134.211(75)	24 134.5(1.1)	24 134.465(23)	−0.254	−3.2
12	122 → 121	16	011 → 012	31 073.752(43)	31 073.7(1.2)	31 074.102(56)	−0.350	−4.9
12	122 → 121	19	122 → 123	43 283.419(54)	43 283.4(2.2)	43 284.10(12)	−0.677	−5.0
12	122 → 121	20	122 → 122	44 944.338(72)	44 944.6(1.9)	44 945.289(64)	−0.951	−9.8
12	122 → 121	21	111 → 112	44 996.486(61)	44 996.4(1.9)	44 997.14(11)	−0.652	−5.3
14	100 → 101	16	011 → 012	6 939.541(66)	6 939.2(1.2)	6 939.636(42)	−0.095	−1.2
14	100 → 101	19	122 → 123	19 149.208(74)	19 148.8(2.0)	19 149.63(11)	−0.423	−3.2
14	100 → 101	20	122 → 122	20 810.127(88)	20 810.1(1.8)	20 810.823(62)	−0.696	−6.5
14	100 → 101	21	111 → 112	20 862.275(79)	20 861.9(2.0)	20 862.673(91)	−0.398	−3.3
16	011 → 012	19	122 → 123	12 209.667(41)	12 209.7(1.5)	12 209.994(72)	−0.327	−4.0
16	011 → 012	20	122 → 122	13 870.586(62)	13 870.9(1.4)	13 871.187(43)	−0.601	−7.9
16	011 → 012	21	111 → 112	13 922.734(49)	13 922.7(1.0)	13 923.037(51)	−0.303	−4.3
19	122 → 123	20	122 → 122	1 660.919(70)	1 661.2(2.6)	1 661.19(10)	−0.274	−2.2
19	122 → 123	21	111 → 112	1 713.067(59)	1 713.0(0.7)	1 713.042(25)	0.025	0.4
20	122 → 122	21	111 → 112	52.148(76)	51.8(1.9)	51.850(75)	0.298	2.8

is, the nonlogarithmic $m\alpha^7$-order radiative corrections (see Sec. II). We thus assume perfect correlations between theory errors of E_2 and E_3, as well as between E_6 and E_7.

The case of the electron-proton (E_4) and electron-deuteron (E_5) Fermi contact interactions is slightly more involved. Indeed, errors in these coefficients originate from both nonrecoil QED corrections, which will have the same expressions apart from substitution of proton and deuteron, and from recoil corrections, which depend on the nucleus [8]. We assume that errors associated with nonrecoil (or recoil) terms are fully correlated (or uncorrelated), which yields a correlation coefficient.

$$r(E_4, E_5) = \frac{u_{\rm non-rec}(E_4) u_{\rm non-rec}(E_5)}{u_{\rm tot}(E_4) u_{\rm tot}(E_5)} = 0.4016. \qquad \text{(C1)}$$

Here, $u_{\rm non-rec}(E_k)$ is the uncertainty of E_k due to nonrecoil QED corrections and $u_{\rm tot}(E_k)$ its total uncertainty. These uncertainties are estimated to $u_{\rm non-rec}(E_k) = 0.47 \times 10^{-6} E_k^{(F)}$, $u_{\rm tot}(E_4) = 0.93 \times 10^{-6} E_4^{(F)}$, and $u_{\rm tot}(E_5) = 0.59 \times 10^{-6} E_4^{(F)}$ (see Ref. [8] for details).

APPENDIX D: DETAILED COMPARISON BETWEEN THEORY AND EXPERIMENT FOR THE HYPERFINE SPLITTING OF THE ROTATIONAL TRANSITION

A full comparison between the experimental results of Ref. [1] and our theoretical predictions is shown in Table VIII.

APPENDIX E: LEAST-SQUARES ADJUSTMENT OF THE SPIN-ORBIT AND SPIN-SPIN TENSOR COEFFICIENTS IN THE $(v=0, L=1)$ STATE FROM EXPERIMENTAL DATA

The frequencies of the hyperfine components of the rotational transition (measured in Ref. [1]) can be written as a sum of the "spin-averaged" transition frequency, $f_{\rm SA}$ and a hyperfine shift. In Ref. [1] (see also Ref. [9]), a value of $f_{\rm SA}$ is extracted from the experimental data. Here, our goal is instead to extract experimental values of three hyperfine coefficients, E_1, E_6, and E_7. We do this in a way that is completely independent of the value of $f_{\rm SA}$, which we describe in the following.

From the six measured transition frequencies, we deduce five independent hyperfine intervals by choosing one of the lines f_i as reference and computing the differences $f_{ij} = f_j - f_i$ for $j \neq i$. We then perform a least-square adjustment taking into account experimental and theoretical uncertainties. The latter are due to uncertainties in hyperfine coefficients (other than E_1, E_6, E_7), and are accounted for by additive corrections $\delta[E_k(v, L)]$ that are treated as additional adjusted parameters, as done in the CODATA adjustments [23]. Correlations between theoretical errors are taken as described in the Appendix C. Experimental uncertainties are assumed to be uncorrelated. For illustration, the input data used in the adjustment are shown in Table IX for the case where the line labeled 12 is chosen as reference line.

We repeated this procedure for all possible choices of a reference line and found that the adjusted values slightly depend on the chosen line. In our final results (reported in Table IV), we increased the error bars to make the values compatible with

TABLE IX. Input data for the least-squares adjustment of the E_1, E_6, and E_7 coefficients, where the line 12 is chosen as reference line.

$f_{14} - f_{12} = 24\,134.211(75)$ kHz
$f_{16} - f_{12} = 31\,073.752(43)$ kHz
$f_{19} - f_{12} = 43\,283.419(54)$ kHz
$f_{20} - f_{12} = 44\,944.338(72)$ kHz
$f_{21} - f_{12} = 44\,996.486(61)$ kHz
$\delta[E_4(v=0, L=0)] = 0.000(860)$ kHz
$\delta[E_5(v=0, L=0)] = 0.000(84)$ kHz
$\delta[E_2(v=0, L=1)] = 0.0000(17)$ kHz
$\delta[E_8(v=0, L=1)] = 0.00000(16)$ kHz
$\delta[E_9(v=0, L=1)] = 0.00000(55)$ kHz

all possible choices. We also checked that the dependence of our results on the hypotheses made on correlations between theoretical errors (see Appendix C) is negligibly small.

It is worth stressing that the adjustments give satisfactory results (with residuals below 1σ), indicating that experimental data are well explained by the effective spin Hamiltonian introduced in Ref. [7] and in good agreement with the theoretical values of the six other coefficients. The only exception is the hyperfine interval involving line 16 (such as $f_{16} - f_{12}$ in Table IX), which has $2 - 3\sigma$ residuals in all cases. This might be an indication of some experimental problem for this specific line.

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