



Spectroscopy of hydrogen molecular ions

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Hydrogen molecular ions (HMI)



- Simple (one-electron, three-body) quantum systems Energy levels and other properties calculable with high accuracy.
- Many ultra-narrow ro-vibrational transitions natural lifetimes from tens of ms (HD⁺) to weeks (H₂⁺)
- High-accuracy techniques as in optical ion clocks: ion traps, laser cooling, Hz-linewidth laser, femtosecond comb...



- Experiments : recent developments, ongoing projects
- Theory : hyperfine structure, energy levels
- Comparing theory with experiments
 - determination of fundamental constants
 - constraints on "new physics"

Progress in HD⁺ spectroscopy

Precision of "Spin-averaged" rovibrational transition frequencies

LKB





- Ensembles of $\sim 50-100~\text{HD}^{\scriptscriptstyle +}$ ions sympathetically cooled by laser-cooled $\text{Be}^{\scriptscriptstyle +}$



- HD⁺ ion creation by electron-impact ionization
 - relax to v = 0, but distributed in many rotational/hyperfine sates
 - rotational cooling (T. Schneider et al., Nature Phys. 2010)
 - rf fields to transfer population between hyperfine levels
- Detection by selective photodissociation of excited state (REMPD)
 signal = ion loss, measured from Be⁺ fluorescence change after secular excitation of HD⁺

Trapped ion spectroscopy in the Lamb-Dicke regime

- Lamb-Dicke regime : $\delta x < \lambda/2\pi$
- Easy in the microwave domain (even at 300 K) Ex: Hg⁺ ion clock ($\nu = 40.5$ GHz, $\lambda = 7.4$ mm) @JPL
- More challenging in the optical domain (requires tightly confining trap)



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J.D. Prestage et al., IEEE 1990
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• Easier for rotational/vibrational transitions in molecular ions (MIR/THz domain)

Sympathetic cooling (T ~ 10 mK), weakly confining trap: $\delta x \sim 1-10~\mu{\rm m}$

HD⁺ rotational transition (v = 0, L = 0) \rightarrow (v' = 0, L' = 1): $\lambda = 228 \ \mu m$



S. Alighanbari et al., Nature Phys. 2018

HD⁺ high-precision measurements (~ $10^{-11} - 10^{-12}$)

LKB



S. Alighanbari et al., Nature 2020 S. Patra et al., Science 2020 I. Kortunov et al., Nature Phys. 2021



Results, ongoing projects

 $v = 0 \rightarrow 9$ transition (one hyperfine component)



- 2 hyperfine components measured
- Theoretical hyperfine structure required to extract spin-averaged transition frequency

Outlook

- H_2^+ two-photon spectroscopy (LKB) \rightarrow see next slides
- Quantum-logic spectroscopy

Be⁺/HD⁺ Ch. Wellers et al., Mol. Phys. 2021

 Be^+/H_2^+ D. Kienzler, ETH Zürich

Spectroscopy of a single molecular ion in a Penning trap

Proposal for H_2^+ /anti- H_2^+ E.G. Myers, PRA 2018 ; J.-Ph. Karr, PRA 2018 and 2021 Ongoing experiment: HD⁺ (hfs) S. Sturm, MPIK Heidelberg 8

H₂⁺ two-photon spectroscopy (LKB)

Abdessamad Mbardi, Bérangère Argence, Laurent Hilico

Complications with respect to HD⁺

Ro-vibrational transitions are not dipole-allowed, thus...

- Worse population problem
 - long-lived excited vibrational states (~ 1 week)
 - Our solution : state-selective production of H₂⁺ by multiphoton (3+1) ionization (REMPI) from a pulsed H₂ molecular beam J. Schmidt et al., PR Appl. 2020

Weaker transitions

- Doppler-free two-photon transition : $(v = 0, L = 2) \rightarrow (v' = 1, L' = 2), \lambda = 9.17 \,\mu\text{m}$
- No enhancement from quasi-resonant intermediate states
- In-vacuum enhancement cavity required
- ✓ Trapped, sympathetically cooled, state-selected H₂⁺
- ✓ Selective photodissociation (213 nm) + ion counting for REMPD spectroscopy
- ✓ Ultrastable laser source @ 9.17 µm : QCL phase-locked to singlemode CO₂ laser, injected in-vacuum cavity
- Lastly: absolute frequency measurements in the mid-infrared



- Frequency comb centered at 1.56 μm, locked on ultrastable signal T-REFIMEVE from SYRTE at 1.542 μm
- \checkmark Extension around 1.89 μm
- ✓ SFG in AgGaSe₂ : 1.89 μ m + 9.17 μ m → 1.56 μ m
- ✓ Beat note SFG signal/comb used to lock CO_2 laser
- ✓ QCL locked to CO_2 laser with tunable frequency offset (+/- 2 GHz)

Characterization : spectroscopy of formic acid (HCOOH)

Intracavity saturated absorption, 3rd harmonic detection



Repeatability of line center : ± 37 Hz (~ 10^{-12})

See B. Argence et al.,

Nature Photon. 2015



- Nonrelativistic Quantum Electrodynamics (NRQED)
 - effective Hamiltonian approach
 - expansion of corrections in powers of α , $Z\alpha$, m/M.
- Resolution of the three-body Schrödinger equation by a variational method

Separation of radial and angular variables:

$$\psi_{LM}^{\Pi}(\mathbf{R},\mathbf{r}_{1}) = \sum_{l_{1}+l_{2}=L \text{ or } L+1} \Upsilon_{LM}^{l_{1}l_{2}}(\hat{\mathbf{R}},\hat{\mathbf{r}}_{1}) F_{l_{1}}(R,r_{1},r_{2})$$

C. Schwartz, Phys. Rev. 123, 1700 (1961)

Radial wavefunctions:



$$F(R,r_1,r_2) = \sum_{n=1}^{N} \left(C_n \operatorname{Re}\left(e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2} \right) + D_n \operatorname{Im}\left(e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2} \right) \right)$$

V.I. Korobov, Phys. Rev. A 61, 064503 (2000)

✓ Extremely accurate energy levels (10⁻¹⁵-10⁻²⁰ or better) and wavefunctions



Some higher-order corrections are evaluated in the adiabatic approximation

 $\Psi^{\rm BO} = \phi_{\rm el}({\bf r};R) \chi_{\rm BO}(R)$

Variational expansion:

$$\phi_{\rm el}(r_1, r_2) = \sum_{i=1}^N C_i \Big(e^{-\alpha_i r_1 - \beta_i r_2} + e^{-\beta_i r_1 - \alpha_i r_2} \Big)$$

Ts. Tsogbayar and V.I. Korobov, J. Chem. Phys. 125, 024308 (2006)

LCAO approximation :

$$\phi_{\text{LCAO}}(r_1, r_2) = \frac{1}{\sqrt{2(1+S)}} \left[\phi_{1s}(r_1) + \phi_{1s}(r_2) \right]$$



Effective spin Hamiltonian: HD⁺ \boldsymbol{I}_d $\sim E_1 \sim 30$ MHz ; E_6 , $E_7 \sim$ MHz = 1 + 1*S* = 2 = L - 1 d J = L - 2 $I \sim E_5 \sim 150 \text{ MHz}$ F = 1J = L + 1S = 1= 1 *l* = L - 1 $\bigvee S = 0$ J = Lv,L $\sim E_{\Lambda} \sim 1 \text{ GHz}$ $\mathbf{F} = \mathbf{s}_e + \mathbf{I}_p$ $\mathbf{S} = \mathbf{F} + \mathbf{I}_d$ / = L - 1 $\mathbf{J} = \mathbf{S} + \mathbf{L}$ F = 0S = 1J = L + 1Nuclear spin-rotation Electronic spin-orbit $H_{\text{eff}} = E_1(\mathbf{L} \cdot \mathbf{s}_e) + E_2(\mathbf{L} \cdot \mathbf{I}_p) + E_3(\mathbf{L} \cdot \mathbf{I}_d) + E_4(\mathbf{I}_p \cdot \mathbf{s}_e) + E_5(\mathbf{I}_d \cdot \mathbf{s}_e)$ "Fermi" interaction + E_6 {2 $\mathbf{L}^2(\mathbf{I}_p, \mathbf{s}_e) - 3[(\mathbf{L} \cdot \mathbf{I}_p)(\mathbf{L} \cdot \mathbf{s}_e) + (\mathbf{L} \cdot \mathbf{s}_e)(\mathbf{L} \cdot \mathbf{I}_p)]$ } Spin-spin tensor + E_7 {2 \mathbf{L}^2 ($\mathbf{I}_d \cdot \mathbf{s}_e$) - 3[($\mathbf{L} \cdot \mathbf{I}_d$)($\mathbf{L} \cdot \mathbf{s}_e$) + ($\mathbf{L} \cdot \mathbf{s}_e$)($\mathbf{L} \cdot \mathbf{I}_d$)]} interactions + E_8 {2 \mathbf{L}^2 ($\mathbf{I}_p \cdot \mathbf{I}_d$)-3[($\mathbf{L} \cdot \mathbf{I}_p$)($\mathbf{L} \cdot \mathbf{I}_d$)+($\mathbf{L} \cdot \mathbf{I}_d$)($\mathbf{L} \cdot \mathbf{I}_p$)]} + $E_{o}\left\{\mathbf{L}^{2}\mathbf{I}_{d}^{2} - (3/2)(\mathbf{L}\cdot\mathbf{I}_{d}) - 3(\mathbf{L}\cdot\mathbf{I}_{d})^{2}\right\}$ Deuteron Quadrupole moment 13

D. Bakalov, V.I. Korobov, S. Schiller, PRL 97, 243001 (2006)



V.I. Korobov, L. Hilico, J.-Ph. Karr, PRA 74, 040502(R) (2006)



- All coefficients calculated within Breit-Pauli approximation, taking into account electron anomalous magnetic moment All terms of order $m\alpha^4$ and $m\alpha^5$ included \Rightarrow relative uncertainty $\sim \alpha^2$ D. Bakalov et al., PRL 2006
- > Sufficient for small coefficients (E_2 , E_3 , E_8 , E_9) at present level of exp. accuracy
- For the largest coefficients, higher-order corrections need to be considered $E_4, E_5 \rightarrow \text{see next slide}$ E_1, E_6, E_7 : V.I. Korobov et al., PRA 2020; M. Haidar et al., arXiv:2209.02382, to appear in PRA



Spin-spin contact interactions

H atom HD⁺ molecule Type of contribution $\Delta E_{hfs}(1S)$ $E_4(v = 0, L = 0)$ 1 418 840.093 924 383.973 Fermi splitting E_F [$m\alpha^4$ order] Breit-Pauli 1 645.361 1 071.964 Anomalous magnetic moment [αE_F] Relativistic ("Breit") correction $[(Z\alpha)^2 E_F]$ 66.936(61) 113.333 One-loop radiative correction $[\alpha(Z\alpha)E_F]$ -136.517-88.942Stateindependent -7.381 One-loop radiative correction $[\alpha(Z\alpha)^2 E_F]$ -11.330Higher-order nonrecoil QED 1.089(1)-2.241(432) Nuclear correction $= E_{hfs}^{exp} - E_{hfs}^{QED}$ -46.276(1) -30.150(424 TOTAL 925 394.159(860) 1 420 405.752 0.93 ppm (exp.)

J.-Ph. Karr et al., PRA 102, 052827 (2020)

- \succ $(Z\alpha^2)E_F$ relativistic correction calculated in the adiabatic approximation.
- Nuclear correction in H atom determined from the difference between experimental value and total nonrecoil QED prediction.
- Higher-order QED & nuclear correction added in HD⁺ theory under the approximation that they are entirely described by a **delta function**.

Comparison with experiments : H₂+

- Complete measurements of the hyperfine splitting
 K. B. Jefferts, PRL 23, 1476 (1969)
- \Rightarrow spin-spin contact interaction coefficient $b_F \iff E_4$ in HD⁺)
- ✓ Good agreement at ~ 1 ppm level

Unit: MHz		L = 1	
v	b_F (theory)	b_F (experiment)	
4	836.7287(8)	836.7292(8)	
5	819.2267(8)	819.2273(8)	
6	803.1745(7)	803.1751(8)	
7	788.5075(7)	788.5079(8)	
8	775.1712(7)	775.1720(8)	

J.-Ph. Karr et al., PRA 102, 052827 (2020)

High-precision measurements (~ 10⁻⁷) for a few hyperfine intervals
 S. C. Menasian and H. G. Dehmelt, Bull. Am. Phys. Soc. 18, 408 (1973)

Sensitive to $c_e, d_1 \iff E_1, E_6$ in HD⁺)

✓ Small deviations of 60-80 Hz (3-5 ppm) \sim 1.2-1.6 σ_c



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(L, v)	f (theory)	f (experiment)		
(1,4)	15.371 316(56)	15.371 407(2)		
(1,5)	14.381 453(52)	14.381 513(2)		
(1,6)	13.413 397(48)	13.413 460(2)		

M. Haidar et al., PRA 106, 022816 (2022)

Unit: kHz

Transition	f_{hfs}^{exp}	f_{hfs}^{theor}	Δf	$\Delta f/\sigma_c$	
$(v = 0, L = 0) \rightarrow (v' = 1, L' = 1)$	41 294.06(32)	41 293.66(12)	0.40	1.2	E_{1}, E_{6}
$(v = 0, L = 0) \rightarrow (v' = 5, L' = 1)$	126 092.6(1.2)	126 092.02(10)	0.58	0.5	E_{4}, E_{5}
$(v = 0, L = 3) \rightarrow (v' = 9, L' = 3)$	178 254.4(9)	178 245.89(28)	8.5	9.0	E_{4}, E_{5}

▶ Rotational transition : 6 hyperfine components measured → extract E_1 , E_6 , E_7

$\operatorname{coefficient}$	E_k^{exp}	E_k^{theor} (this work)	ΔE_k	$\Delta E_k / \sigma_c$
E_1	31 984.9(1)	$31 \ 985.41(12)$	-0.5	-3.3
E_6	$8\ 611.17(5)$	$8\ 611.299(18)$	-0.13	-2.4
E_7	$1 \ 321.72(4)$	$1\ 321.7960(28)$	-0.08	-2.0

- No contribution(s) identified that could have the required order of magnitude to explain discrepancies
- Take discrepancies into account by expanding error bars

HD⁺ energy levels: overview and comparison with H atom



- <u>Unit</u>: kHz, CODATA 2018 values of FC
- Only theoretical uncertainties are shown

Type of contribution	H atom $\Delta E(1S)$	HD ⁺ molecule $\Delta E(v = 0, L = 0)$
1. Relativistic energy	-3 288 095 029 857.92	-3 934 027 681 033.9 <mark>(1.1)</mark>
2. Relativistic-recoil	2 402.35	2 229.6 <mark>(0.6)</mark>
3. One-loop self-energy	8 383 339.47	10 891 032.6 <mark>(17.4)</mark>
4. One-loop vacuum polarization Muonic VP Hadronic VP	- 214 816.61 -5.07 -3.40 <mark>(8)</mark>	-280 113.6 -6.6 -4.4 <mark>(0.1)</mark>
5. Two-loop radiative corrections	727.19 <mark>(66)</mark>	944.6(11.8)
6. Three-loop radiative corrections	1.72 <mark>(34)</mark>	2.4 <mark>(0.6)</mark>
 Nuclear finite size and polarizability (+ rad. corr.) 	1 107.98 <mark>(39)</mark>	5 330.2 <mark>(0.5)</mark>
8. Radiative-recoil corrections	-12.32 <mark>(74)</mark>	-13.5 <mark>(2.2)</mark>
9. Nuclear self-energy	4.62 <mark>(16)</mark>	3.8 <mark>(0.1)</mark>
TOTAL	-3 288 086 857 111.4 <mark>(1.1)</mark>	-3 934 017 061 629 <mark>(21)</mark>
E. Tiesinga et al., Rev. Mod. Phys. 93	$3,025010(2021)$ 3.5×10	-13 5.3×10^{-12}

S. Karshenboim et al., Phys. Lett. B 795, 432 (2019)



$$E_{se} = m\alpha^{5} \Big[(A_{41}\ln(\alpha^{-2}) + A_{40}) \langle Z_{1}\delta(\mathbf{r_{1}}) + Z_{2}\delta(\mathbf{r_{2}}) \rangle + A_{50}\alpha \langle Z_{1}^{2}\delta(\mathbf{r_{1}}) + Z_{2}^{2}\delta(\mathbf{r_{2}}) \rangle + (A_{62}\ln^{2}(\alpha^{-2}) + A_{61}\ln(\alpha^{-2}) + A_{60})\alpha^{2} \langle Z_{1}^{3}\delta(\mathbf{r_{1}}) + Z_{2}^{3}\delta(\mathbf{r_{2}}) \rangle + (A_{71}\ln(\alpha^{-2}) + A_{70})\alpha^{3} \langle Z_{1}^{4}\delta(\mathbf{r_{1}}) + Z_{2}^{4}\delta(\mathbf{r_{2}}) \rangle + \cdots \Big]$$

- Some coefficients $(A_{41}, A_{50}, A_{62}, A_{71})$ are state-independent and can be taken from H-like atom theory.
- mα⁵ order: Bethe logarithm calculated with 8-9 significant digits
 V.I. Korobov, PRA 85, 042514 (2012) ; V.I. Korobov and Z.-X. Zhong, PRA 86, 044501 (2012)
- mα⁷ order: calculated in the adiabatic approximation
 V.I. Korobov, L. Hilico, J.-Ph. Karr, PRL **112**, 103003 and PRA **89**, 032511 (2014)
- → Higher-order remainder ($m\alpha^8$ and above): estimated from H(1S) results using the LCAO approximation $E_{se}^{(8+)} = m\alpha^7 (G_{SE}(1S) - A_{60}(1S)) \langle Z_1^3 \delta(\mathbf{r_1}) + Z_2^3 \delta(\mathbf{r_2}) \rangle$ V.I. Korobov and J.-Ph. Karr, PRA **104**, 032806 (2021)



$(L,v) \to (L',v')$	Theory			Experiment		
$(0, 0) \rightarrow (1, 0)$ $(0, 0) \rightarrow (1, 1)$ $(3, 0) \rightarrow (3, 9)$	1 314 925 7 58 605 052 415 264 925	752.932(<u>19</u> 163.9(<u>0.5</u>) 5 502.8(<u>3.3</u>)(<u>61</u>) (<u>1.3</u>))(<u>6.7</u>)	1 314 92 58 605 0 415 264	5 752.91 52 164.2 925 501	10(17) 24(86) .8(1.3)
V.I. Korobov and JPh. Karr, PRA 104 , 032806 (2021)	- Tl ui	heoretical ncertainties	Uncerta from FC	iinties C (CODATA 2018	3)	
Uncertainty contr Example : $v = 0 \rightarrow 9$ S. Patra et al., Science 369 ,	ibutions transition 1238 (2020)	Contributed uncertainty (kHz)			V _{SA,exp}	21



- Theoretical uncertainty \sim 7.5 10⁻¹² (1.5 10⁻¹¹) for vibrational (rotational) transitions
- Satisfactory agreement with experimental data
- Next step : nonperturbative calculation of the one-loop self-energy using highly precise solutions of two-center Dirac equation:

 H.D. Nogueira, V.I. Korobov, J.-Ph. Karr, PRA 105, L060801 (2022)
 Mullie, S. Schiller, PRA 105, 052801 (2022)
 Teduce uncertainty by a factor of ~ 2.

Applications

- Determination of fundamental constants
- Constraining "new physics"

Determination of the proton-electron mass ratio



• From HD⁺ data alone:

 $m_p/m_e = 1836.152\ 673\ 466(61)\ [3.3 \times 10^{-11}]$ Good agreement with CODATA 2018 and recent mass spectrometry results.

• From HD⁺ and mass spectrometry combined: $m_p/m_e = 1836.152\ 673\ 454(33)\ [1.8 \times 10^{-11}]$

V.I. Korobov and J.-Ph. Karr, PRA 104, 032806 (2021)

Example : $(v = 0, L = 3) \rightarrow (v' = 9, L' = 3)$ transition



- r_p , r_d , R_∞ are strongly correlated (H/D 1S-2S)
- With measurements at 10^{-12} precision level, theory improvement to $3 \ 10^{-12} : u(r_p) < 0.01$ fm

J.-Ph. Karr et al., PRA 94, 050501(R) (2016)

Constraint on "fifth force" between hadrons

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M. Germann et al., Phys. Rev. Research 3, L022028 (2021)

Self-consistent approach to constrain new physics (NP)

- C. Delaunay, JPK, T. Kitahara, J. Koelemeij, Y. Soreq, J. Zupan (soon on arXiv)
- Precision measurements (e.g. spectroscopy of simple atoms/molecules) can be used for NP searches by comparing with Standard Model (SM) prediction.
- SM predictions use accepted (CODATA) values of fundamental constants, which are obtained <u>under the assumption that no NP exists</u>. The presence of NP would affect the extraction of fundamental constants !
- Self-consistent approach: <u>global fit of precision data in the presence of NP</u>, simultaneously extracting fundamental constants and NP parameters.

Datasets

- 1) "Control" dataset = subset of CODATA 2018
 - H, D, μ H, μ D spectroscopy (R_{∞}, r_p, r_d)
 - a_e , h/m_X , bound electron g-factors, mass spectrometry (α , m_e , m_p , m_d)
 - 78 observational equations, 44 adjusted constants (CODATA 2018: 105/62 without G and d_{220})
- 2) 2022 dataset: with most recent data and theory improvements and HD⁺, \bar{p} He spectroscopy (more sensitive to some NP models) ²⁶



NP model favored over SM

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- Tensions related to the proton radius favor nonzero e-p coupling
- "Up-Lepto-Darko-philic" scalar model statistically favored at $\sim 5\sigma$ level, not excluded by other constraints



- Several HD⁺ rovibrational transitions measured with 10⁻¹¹/10⁻¹² precision More - and more precise - data to come.
- Improved hyperfine structure theory
 - \succ Good agreement in H₂⁺
 - HD⁺: good agreement or big discrepancy, depending on transition
 - > Affects the precision of extracted spin-averaged transition frequencies, but no big impact on m_p/m_e determination.
- Theoretical precision : 7.5 10⁻¹² (1.5 10⁻¹¹) for vibrational (rotational) transitions Next step: nonperturbative calculation of the one-loop self-energy, using accurate solutions of the two-center Dirac equation.
- Final data for CODATA 2022 adjustment under study Preliminary estimate : m_p/m_e uncertainty reduced to ~ 2 10^{-11} , combining HD⁺ spectroscopy with mass spectrometry.
- Self-consistent bounds on NP : check arXiv !

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