Precision measurement of the ionization and dissociation energies of H_2, HD, and D_2

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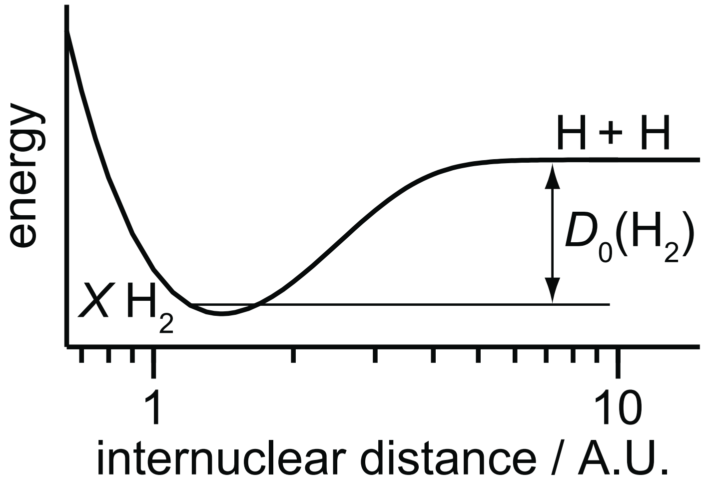
Ohio State University, June 21-25, 2010
RD08, June 24, 11:04am, 1015 McPherson Lab

Dissociation energy of the hydrogen molecule



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- the dissociation energy is a benchmark quantity for any *ab initio* calculation in molecular systems

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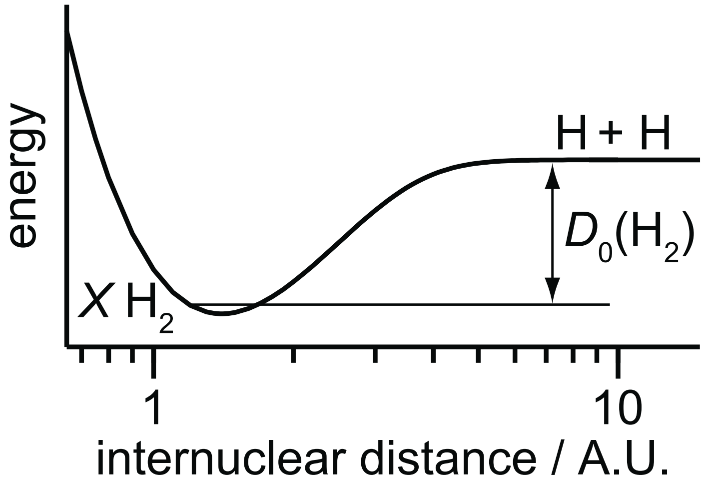

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$D_0(H_2)$	Year	Experiment	Theory
Witmer	1926	4.15 eV	
Heitler and London	1927		2.9 eV
Richardson and Davidson	1929		
James and Coolidge	1933		
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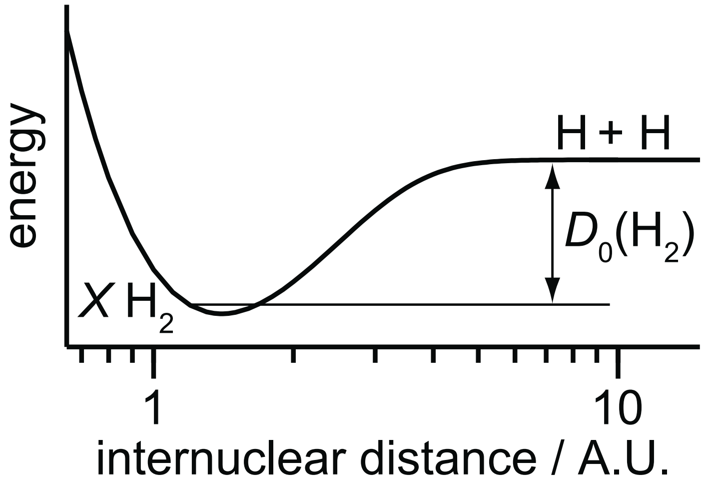

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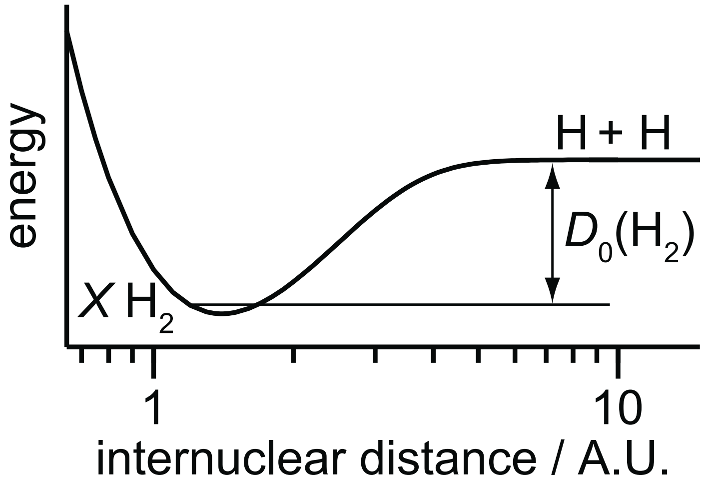

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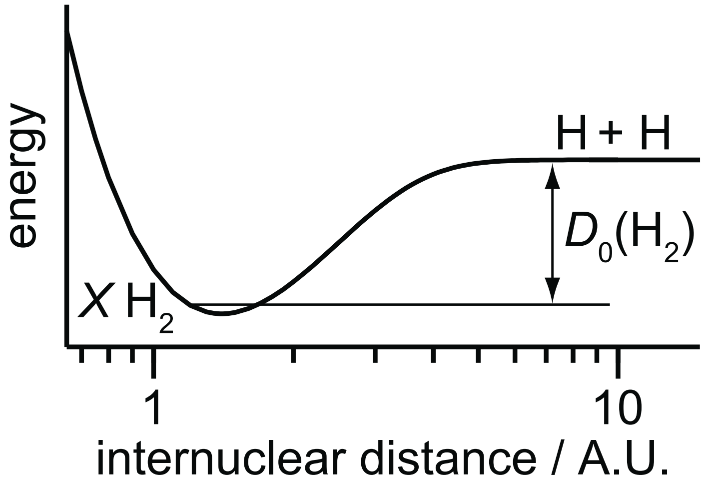

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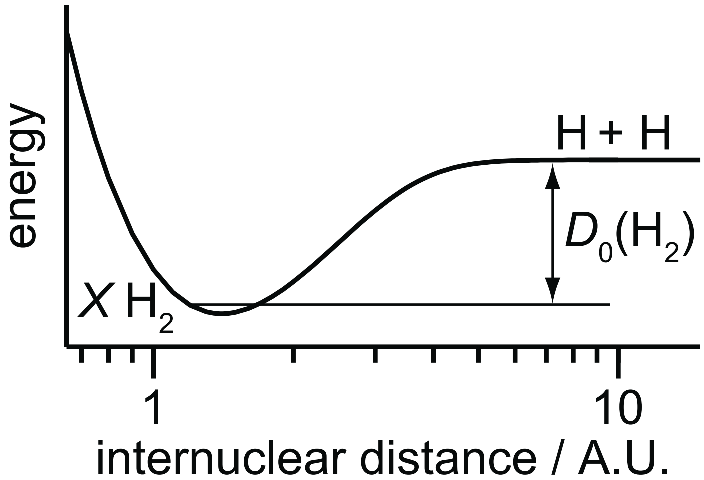

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$D_0(H_2)$ / cm^{-1}	Year	Experiment	Theory
James and Coolidge	1933		35924(105)
Beutler	1935	36116(6)	
Kolos and Roothaan	1960		
Herzberg and Monfils	1960		
Kolos and Wolniewicz	1965		
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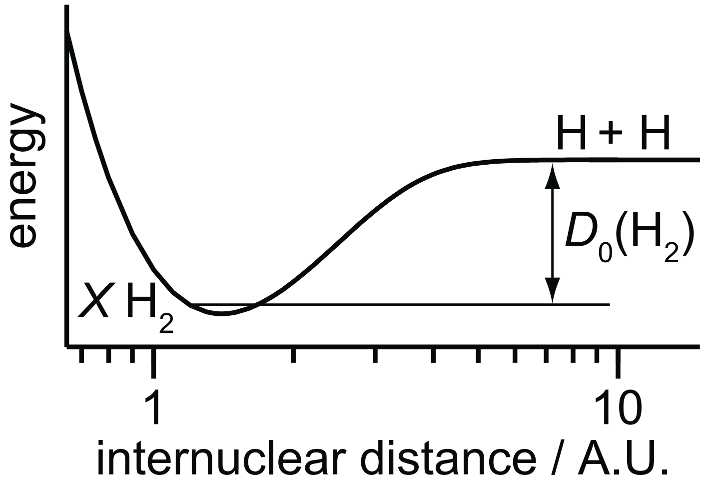

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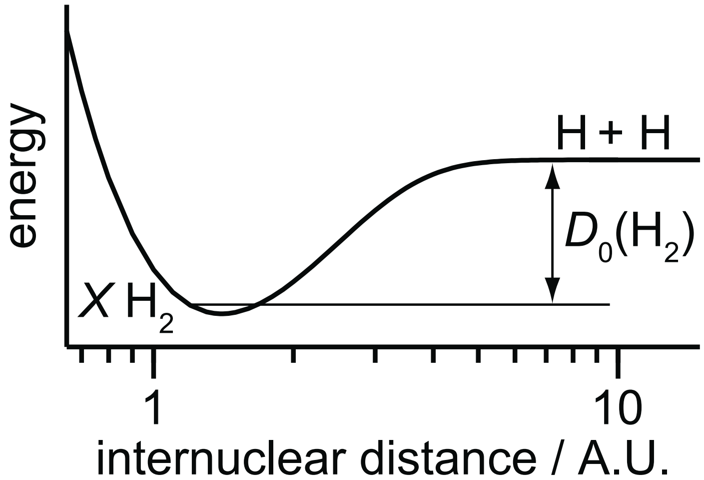

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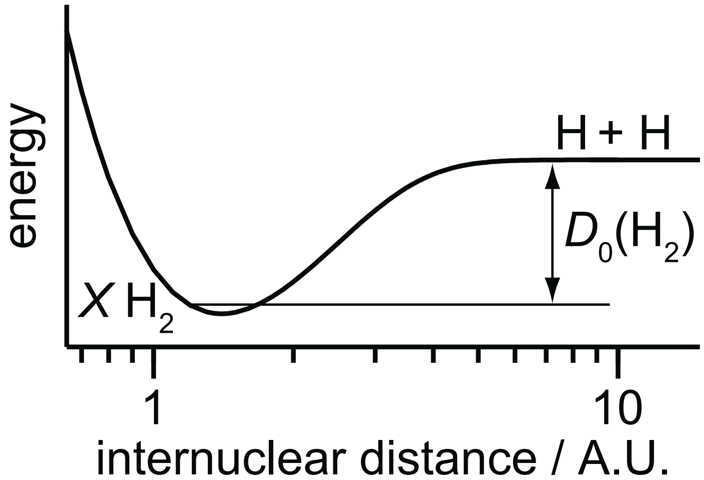

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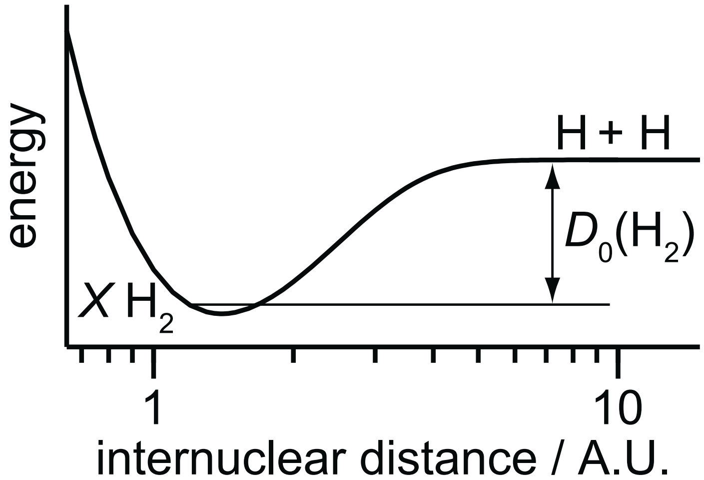

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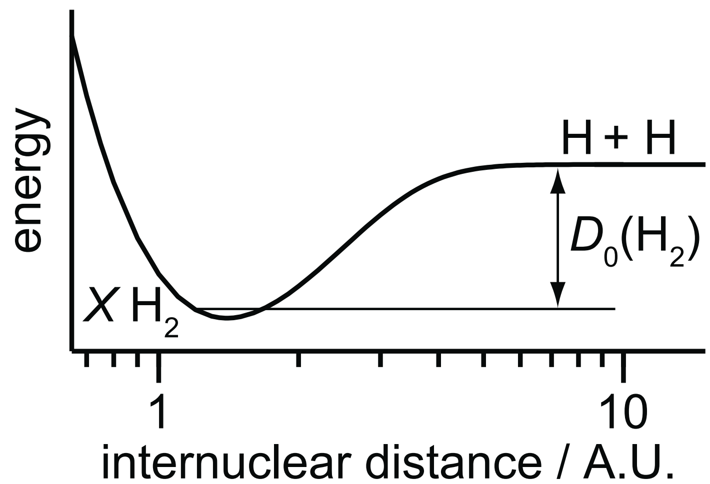

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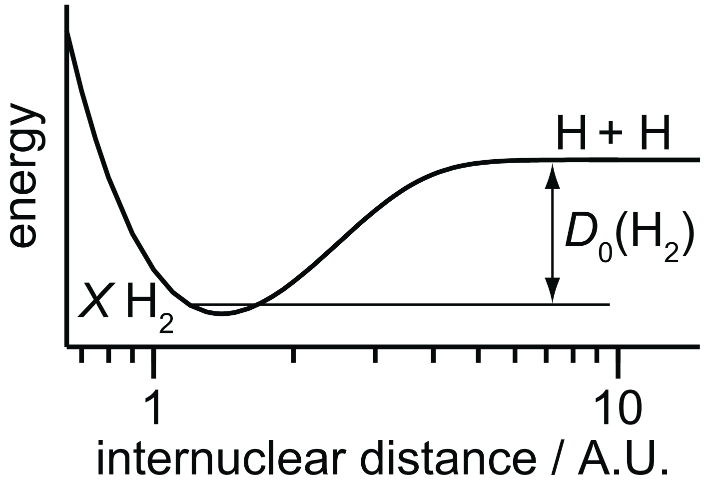

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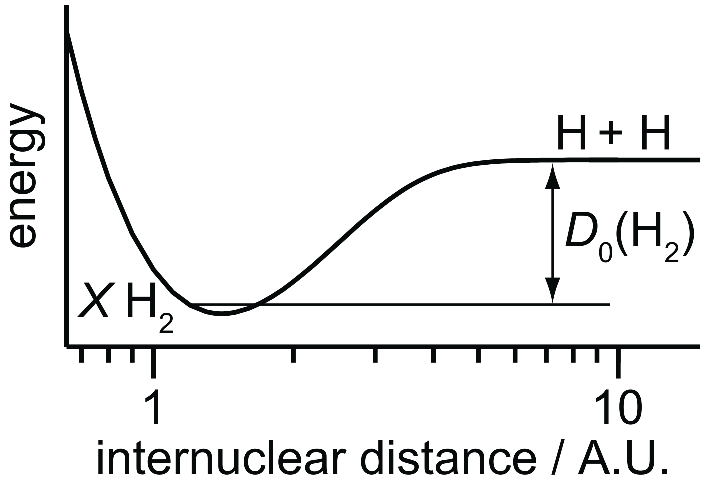

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Eyler and coworkers	2004	36118.062(10)	

Dissociation energy of the hydrogen molecule

$D_0(H_2)$:	Experiment [1]	36118.0696(4) cm^{-1}
	Theory [2]:	
	Born–Oppenheimer	36112.5927(1) cm^{-1}
	adiabatic	
	nonadiabatic	
	total α^0	
	α^2 all relativistic	
	α^3 all QED	
	α^4 one-loop term	
	Total theory	

[1] Liu *et al.* JCP **130**, 174306 (2009)
[2] Piszczatowski *et al.* JCTC **5**, 3039 (2009)

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$D_0(H_2)$:	Experiment [1]	36118.0696(4) cm^{-1}
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	α^2 all relativistic	– 0.5319(5) cm^{-1}
	α^3 all QED	– 0.1948(3) cm^{-1}
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	Total theory	36118.0695(10) cm^{-1}

$D_0(D_2)$:

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$D_0(D_2)$:	Total theory [2]	36748.3633(9) cm^{-1}
	Experiment [3]	36748.343(10) cm^{-1}

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	Experiment [3]	36748.343(10) cm^{-1}
	Experiment [4]	36748.3629(7) cm^{-1}

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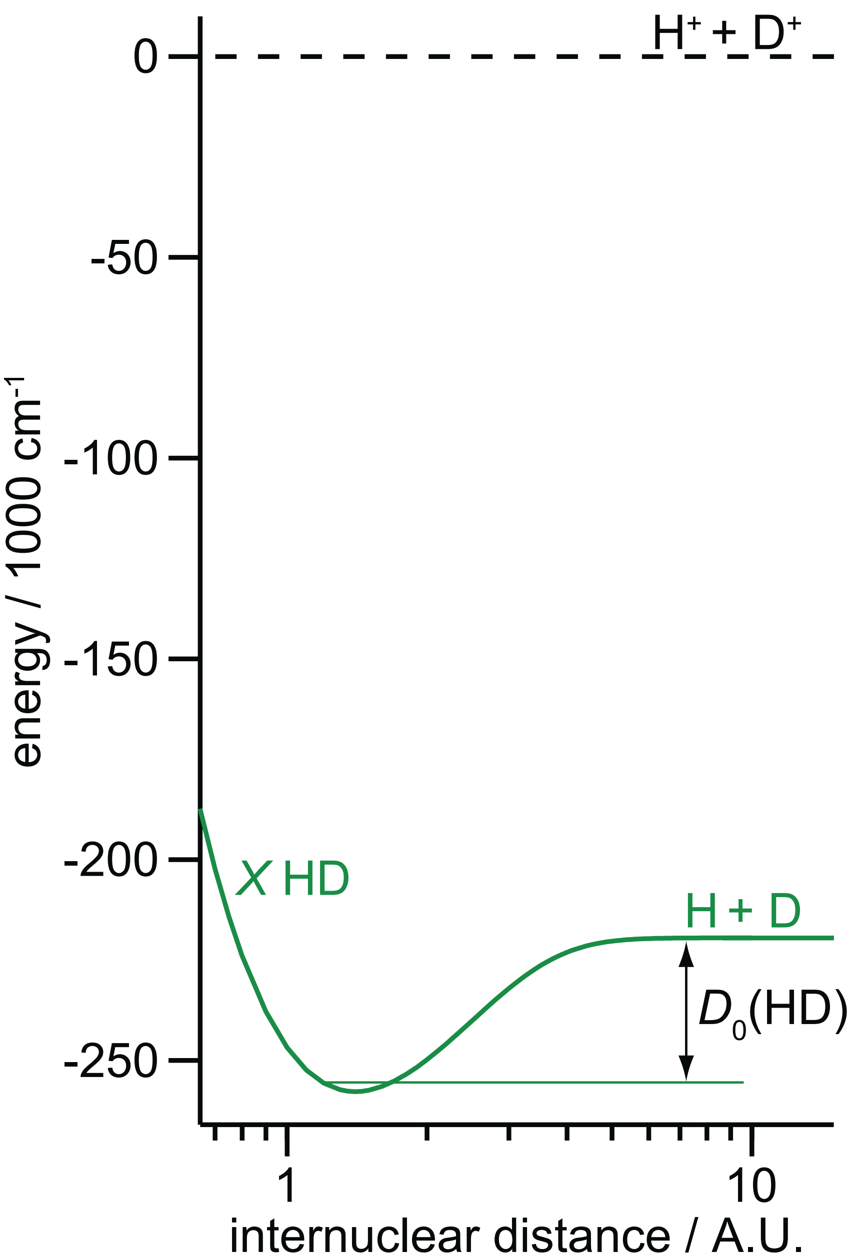
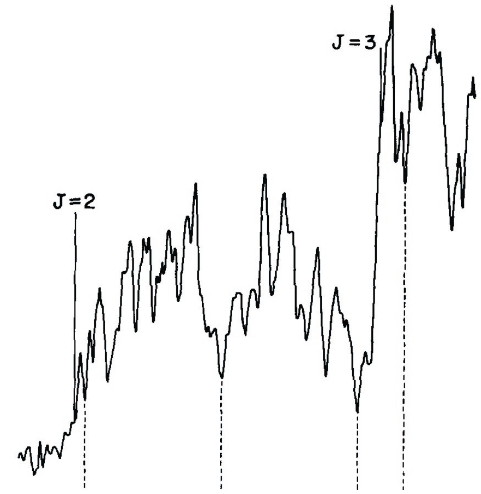
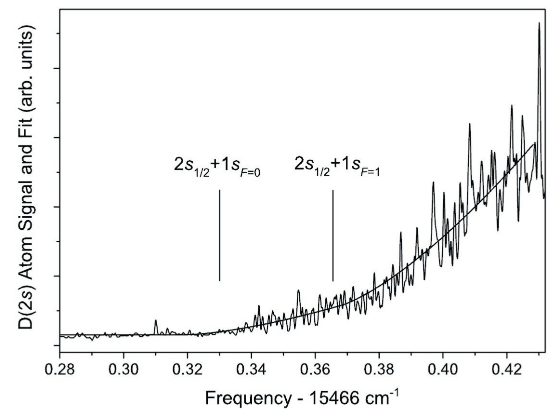
[4] Liu *et al.* JCP **132**, 154301 (2010)

Principle of the measurement





from [Herzberg and Monfils JMS **5**, 482 (1960)]



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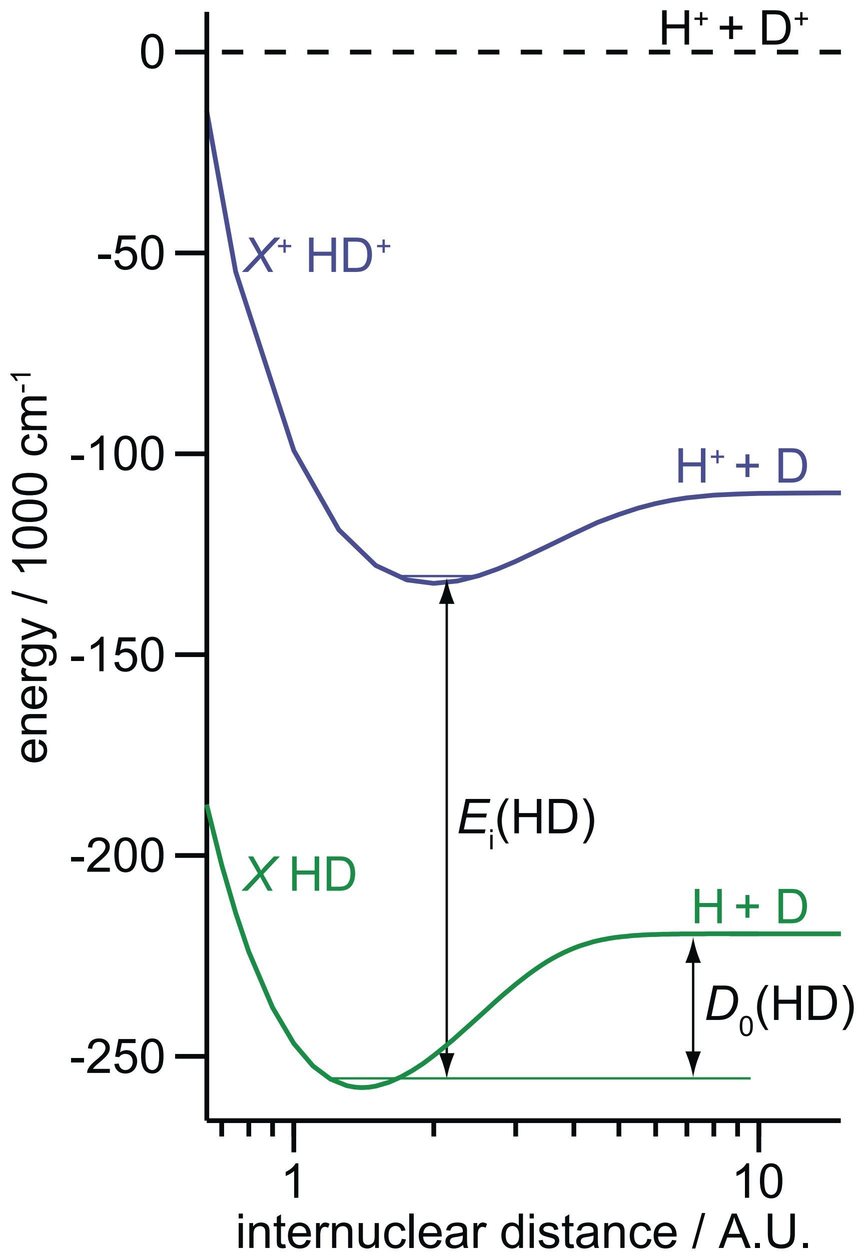

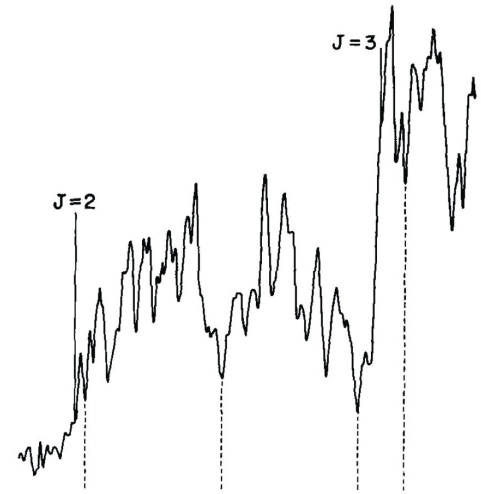

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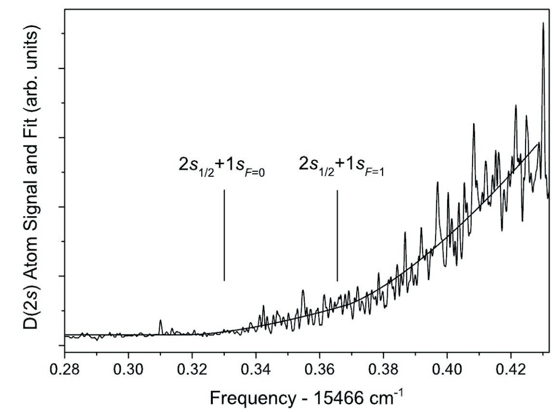

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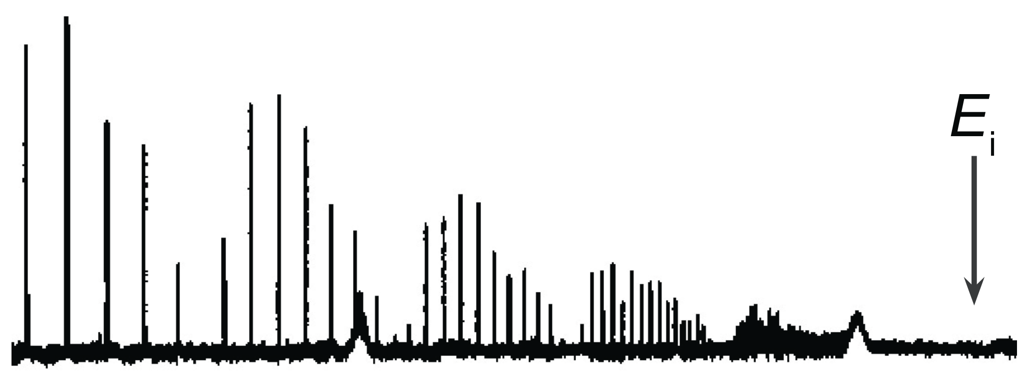

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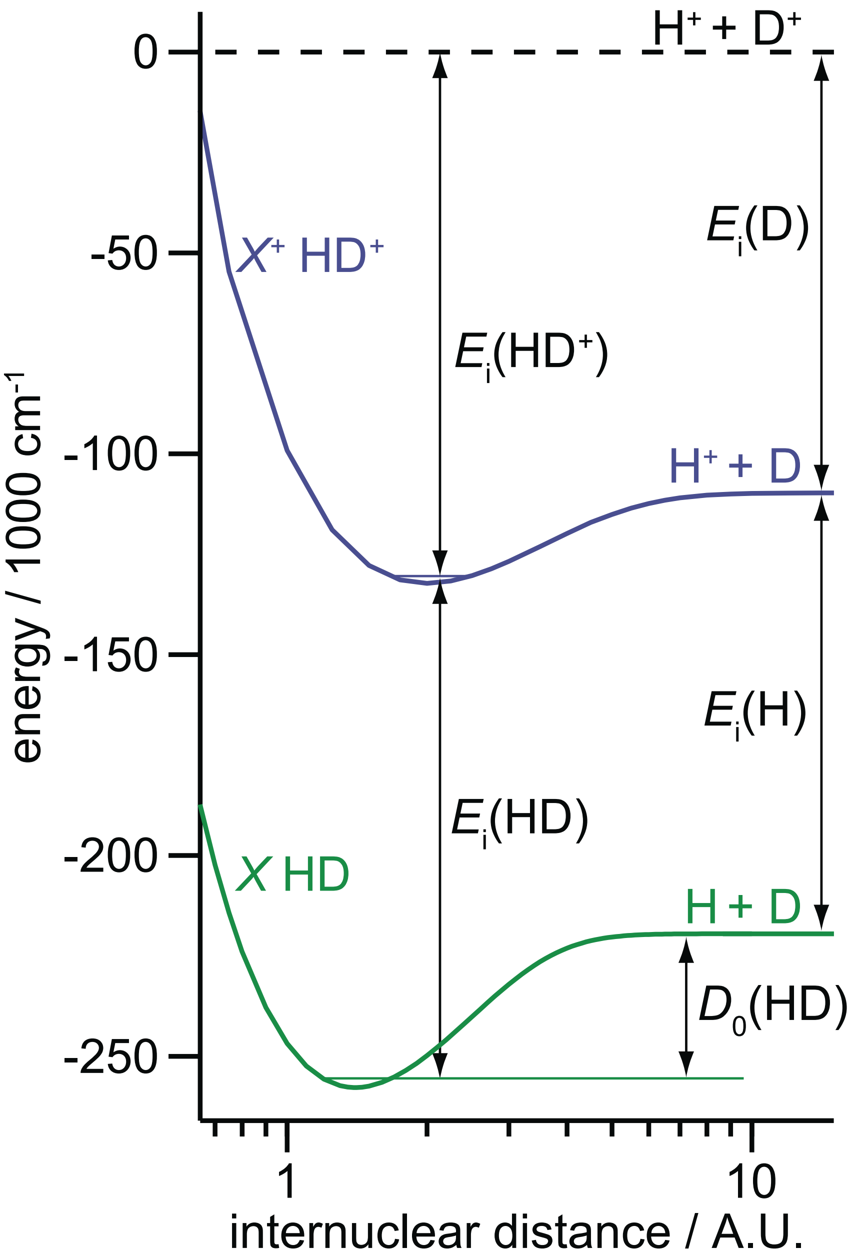

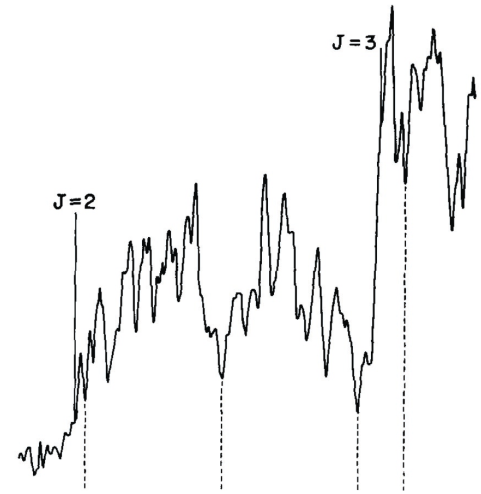

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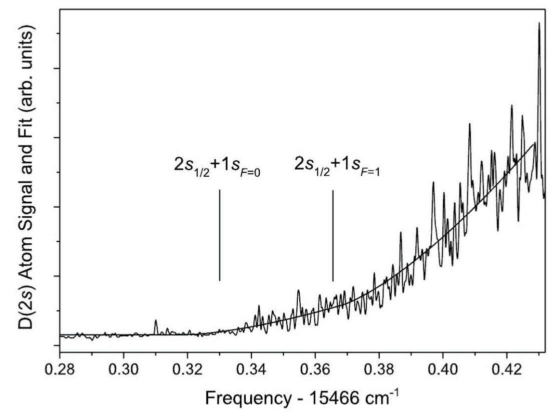

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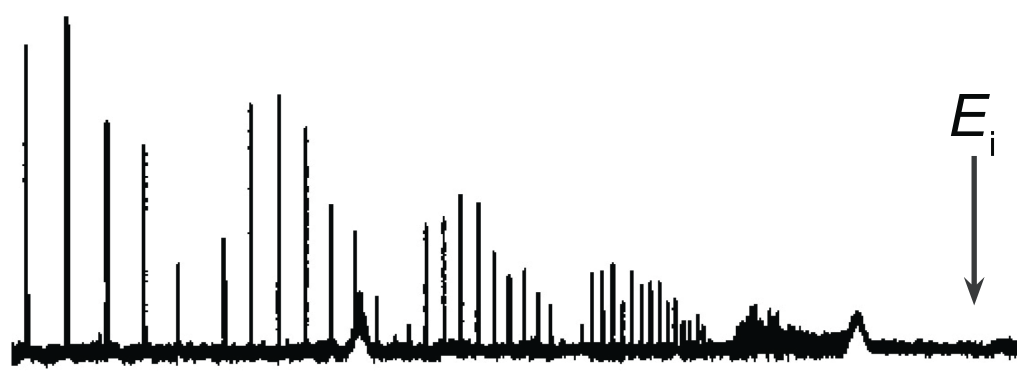

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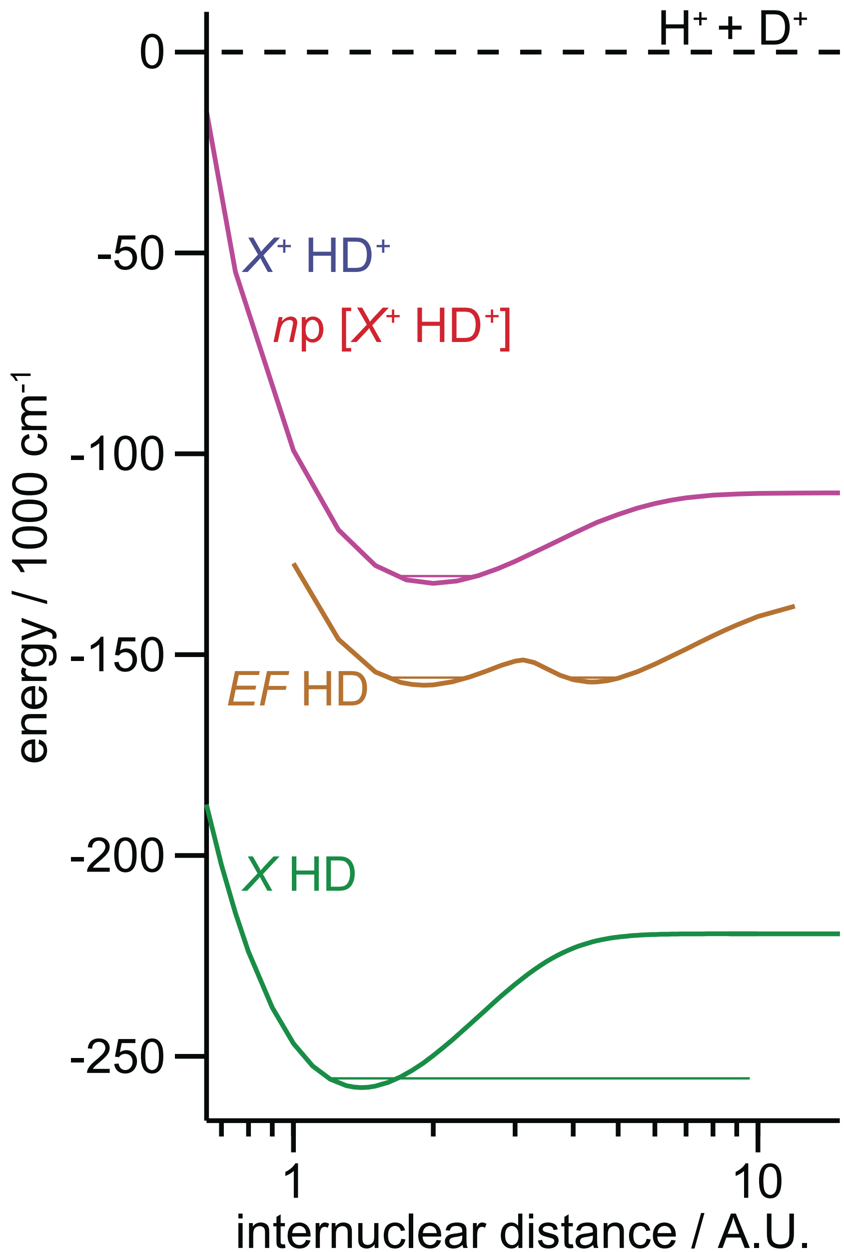

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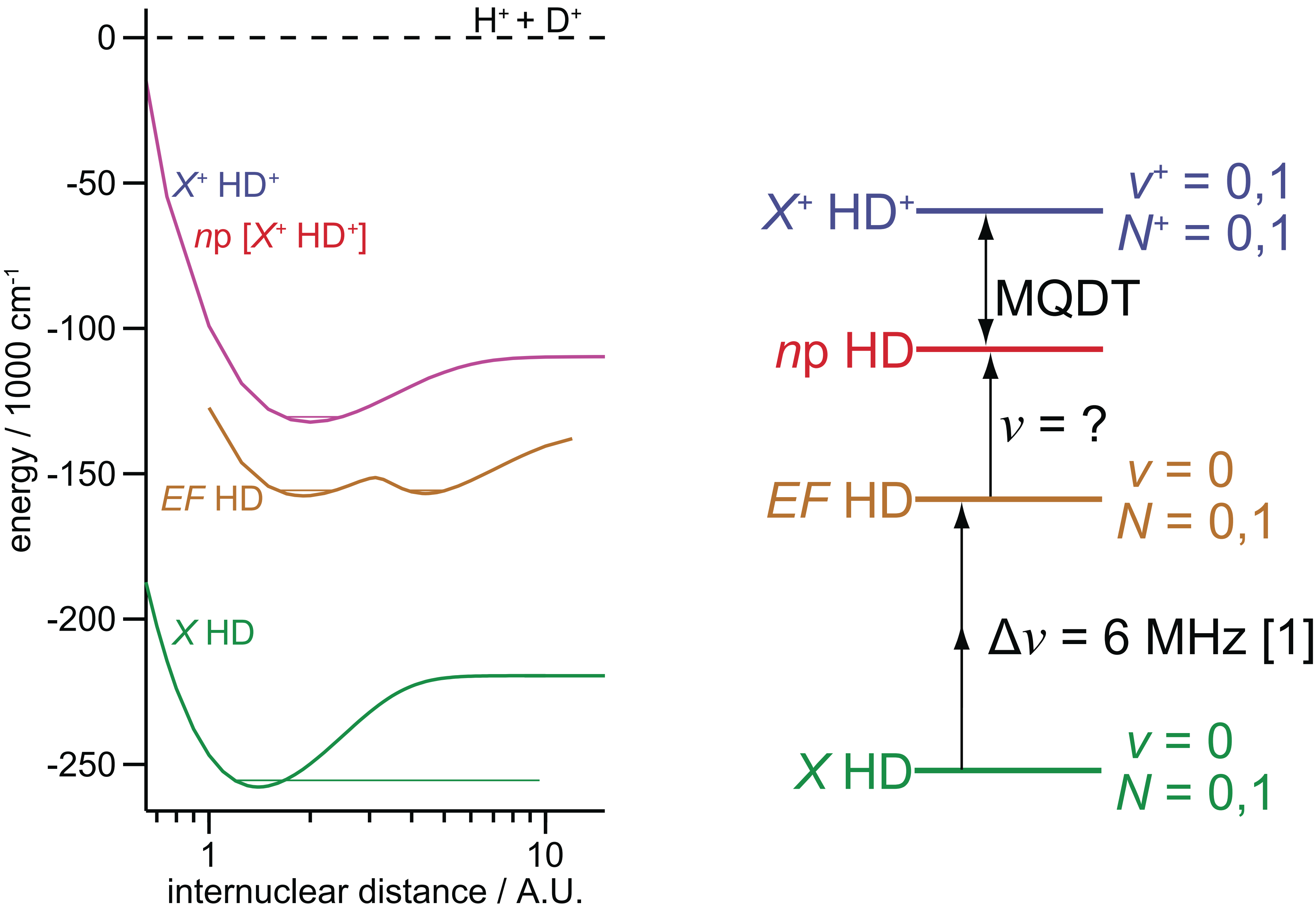
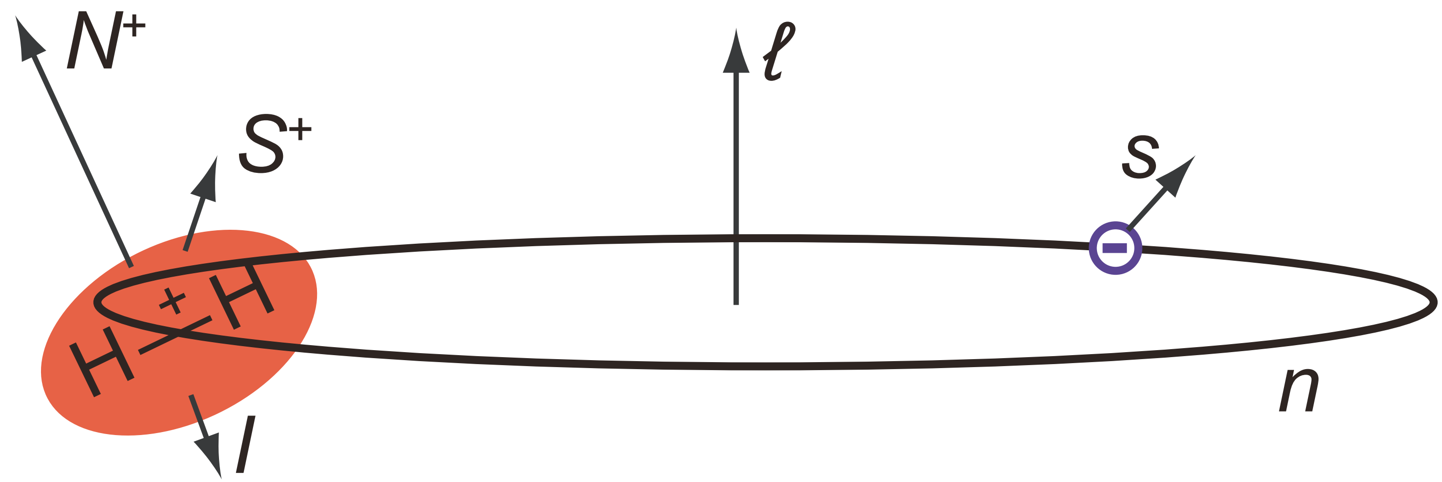


[1] Hannemann *et al.* PRA **74**, 062514 (2006)

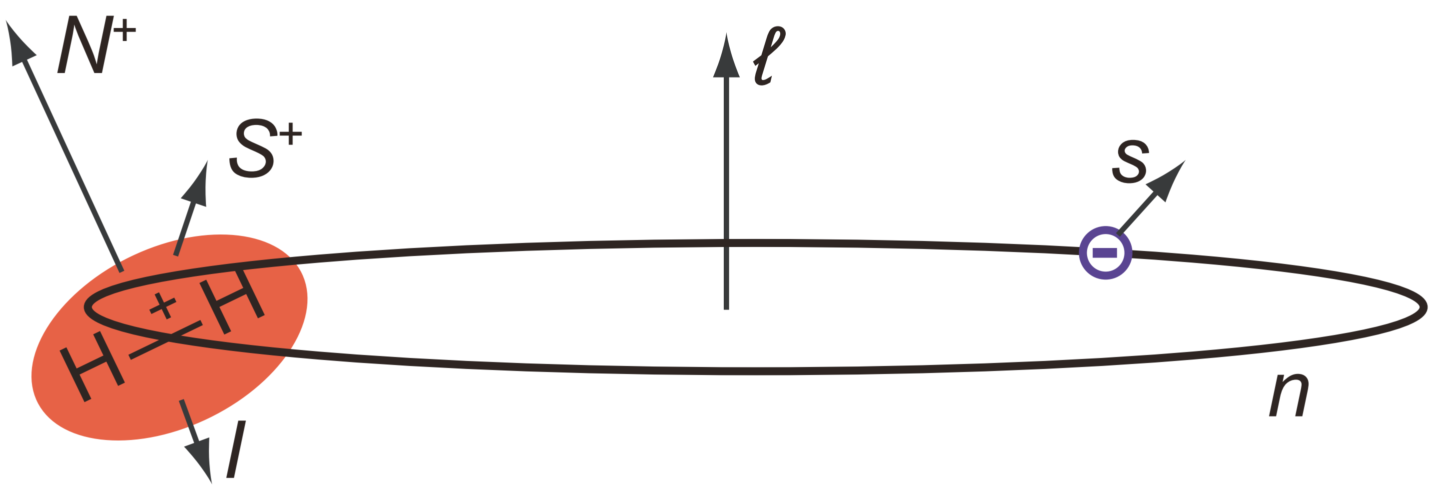
Rydberg states

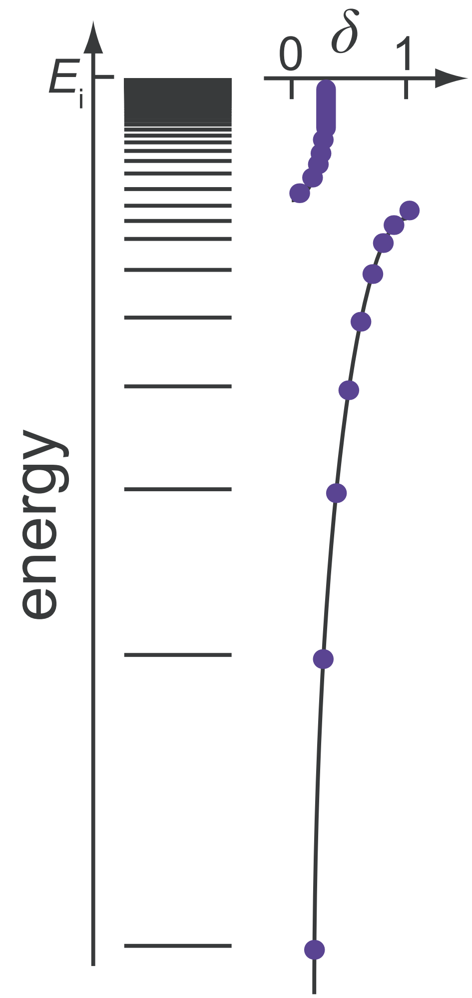


Properties of Rydberg states:

- highly excited electronic states

Rydberg states





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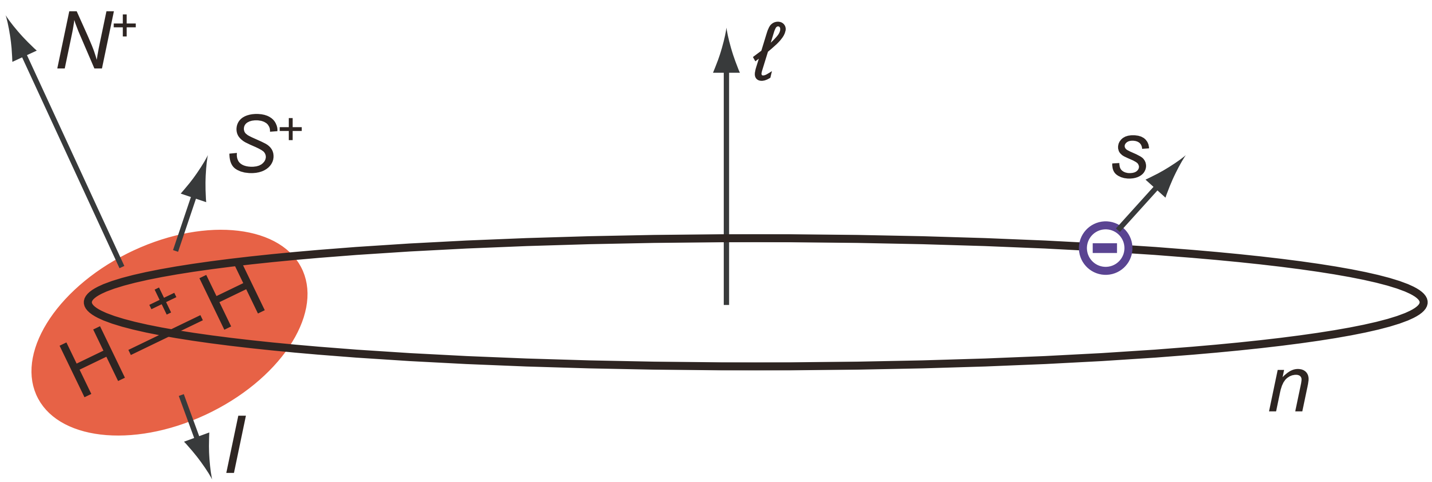
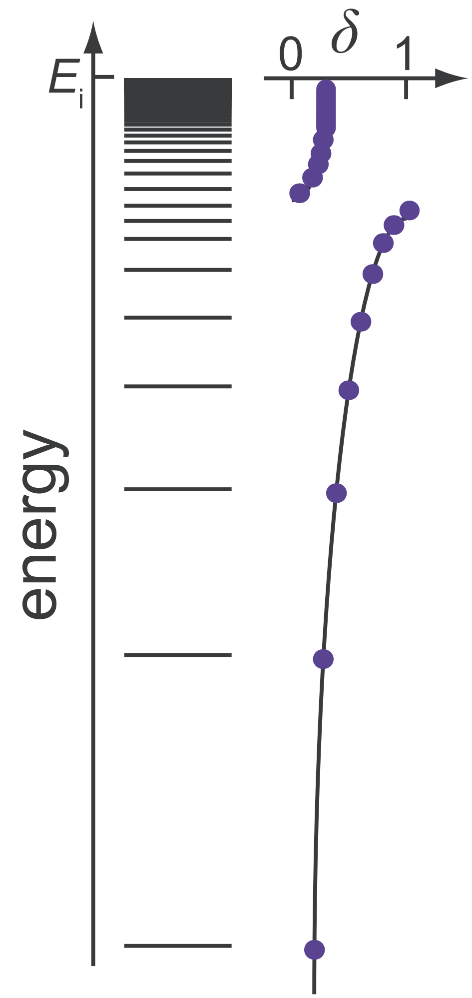
- energies described by the Rydberg formula

$$E_n = E_{\mathrm{i}} - \frac{hcR_M}{(n-\delta)^2}$$

Rydberg states





Properties of Rydberg states:

- highly excited electronic states
- energies described by the Rydberg formula
- radiative lifetimes ~ μs (n ≈ 50)
- sensitive to electric fields
- electron binding energies ~ 40 cm^{-1} (n ≈ 50)

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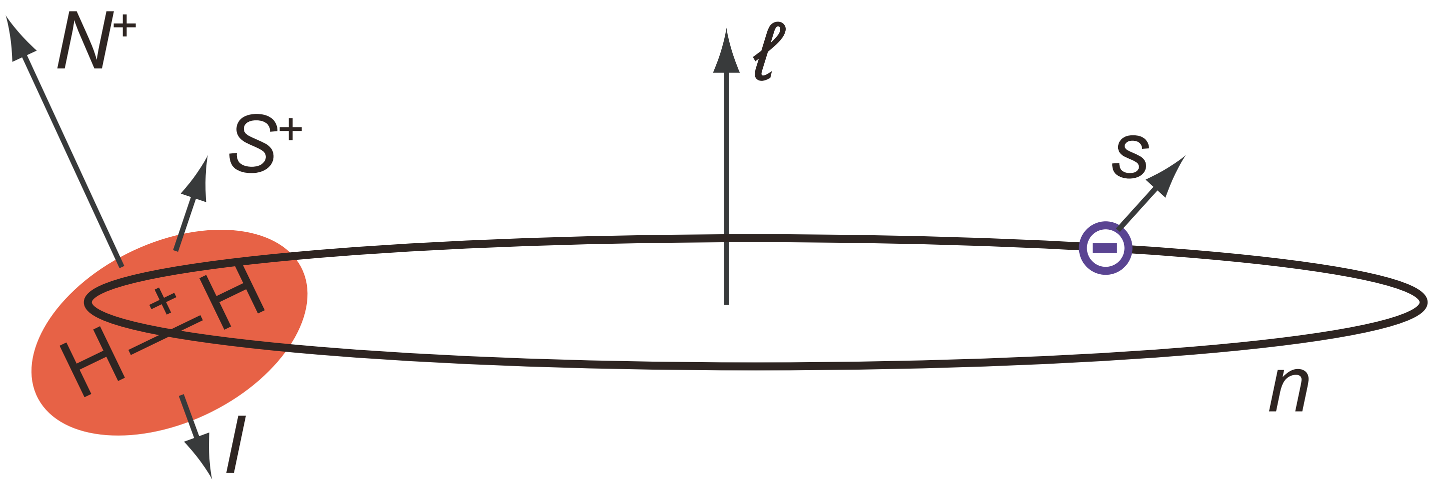
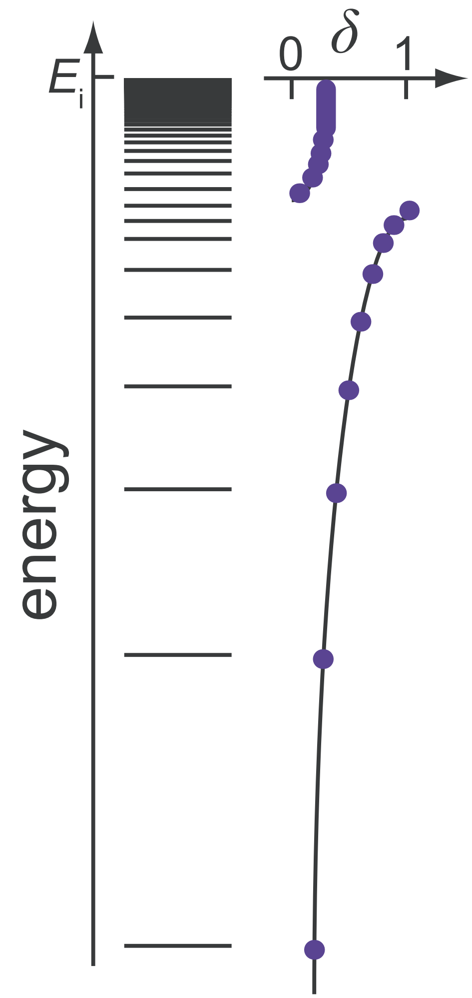
Rydberg states





multichannel quantum
defect theory

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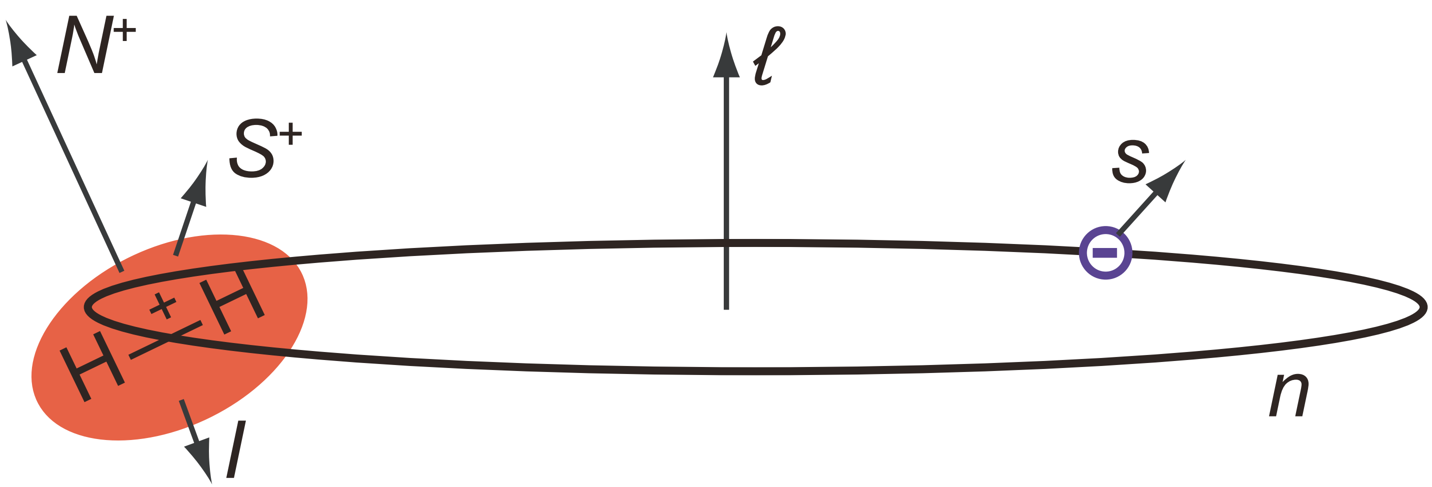

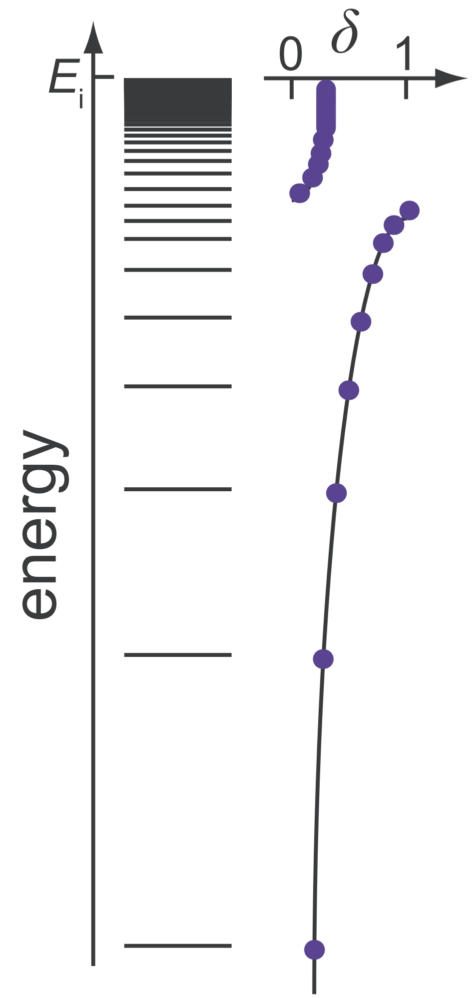

eigen quantum defects

multichannel quantum defect theory

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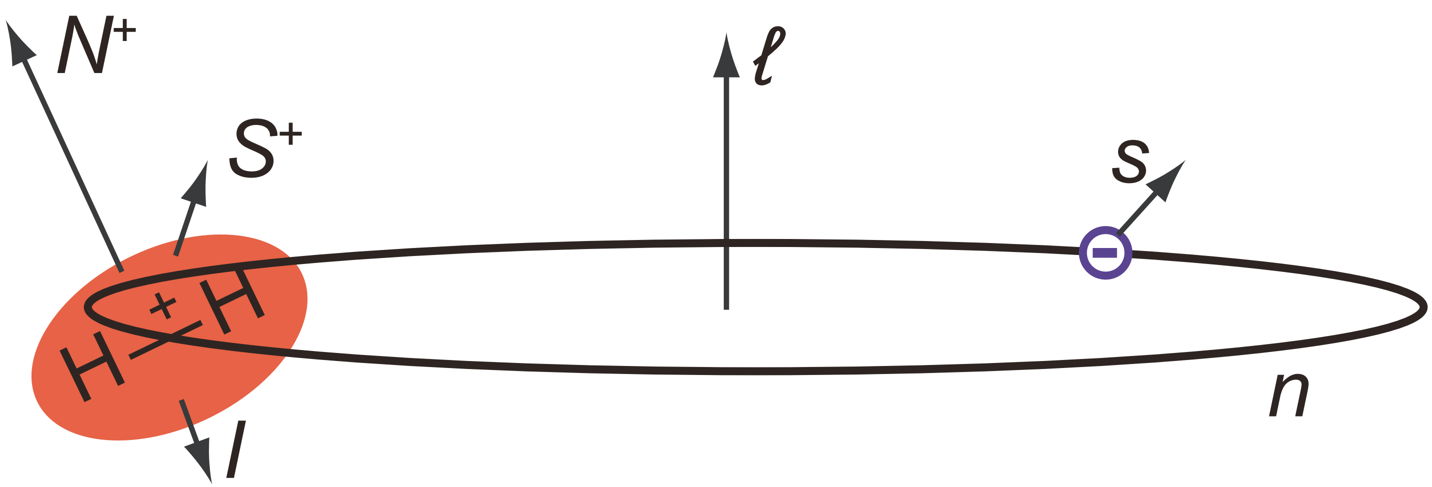
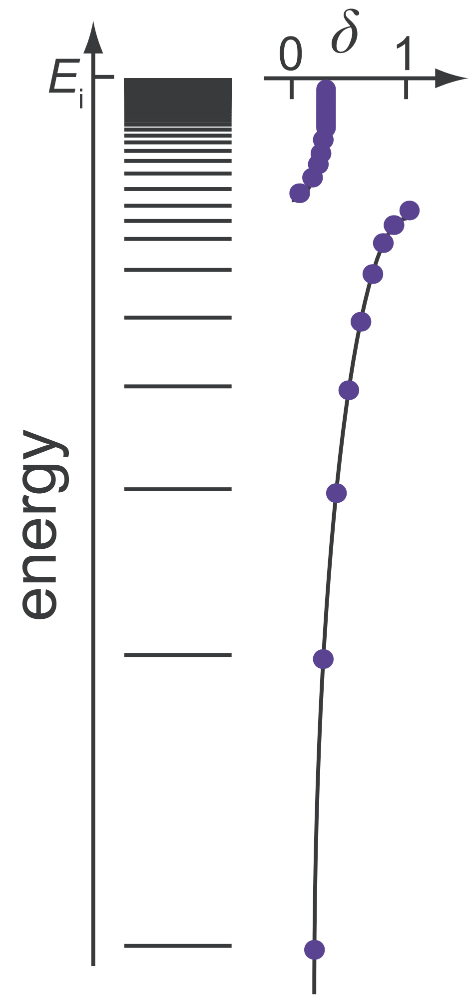




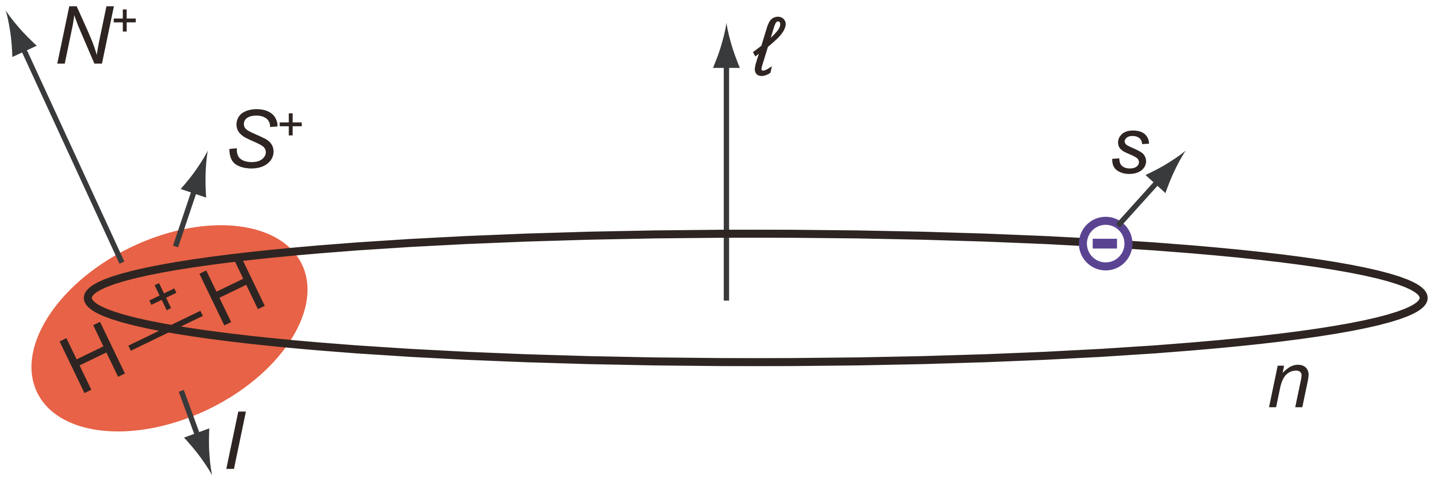
eigen quantum defects

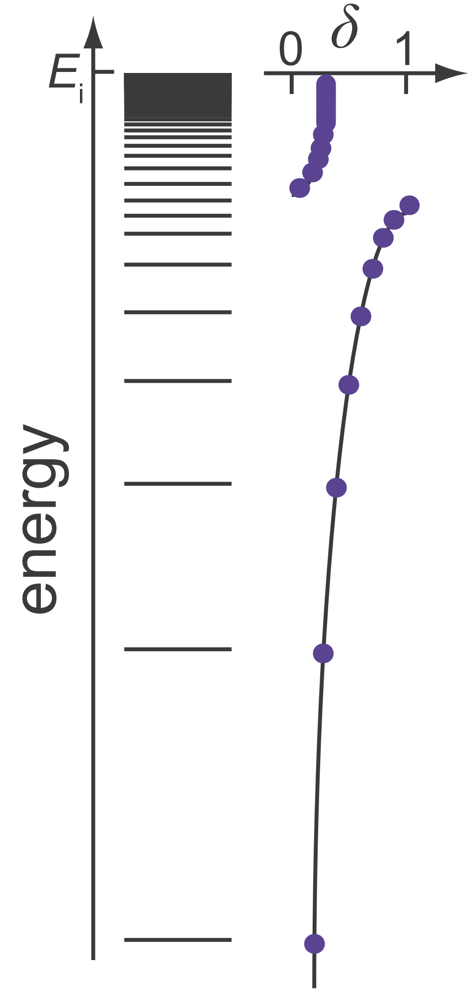
ab initio data of HD+

multichannel quantum defect theory

$$E_n = E_{\mathrm{i}} - \frac{hcR_M}{(n-\delta)^2}$$

Rydberg states





eigen quantum defects

ab initio data of HD^+

multichannel quantum defect theory

frame transformation
Hund's cases (b)↔(e)
including nuclear spins

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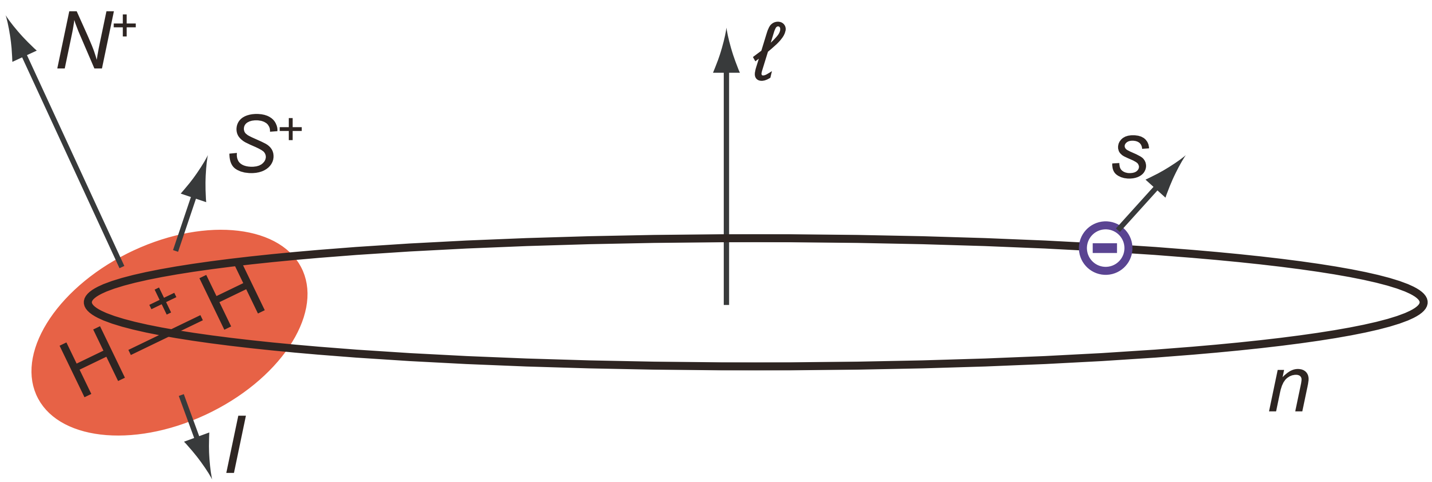
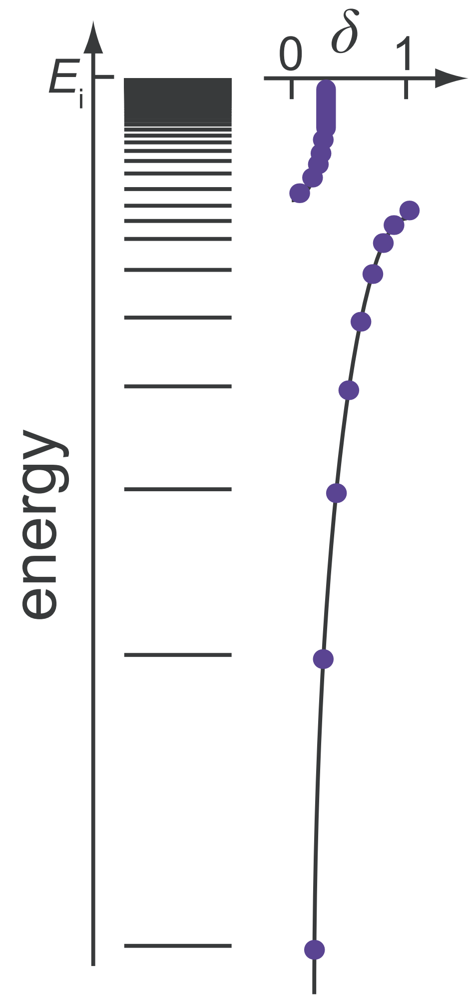
Rydberg states





eigen quantum defects

ab initio data of HD⁺

multichannel quantum defect theory

frame transformation
Hund's cases (b)↔(e)
including nuclear spins

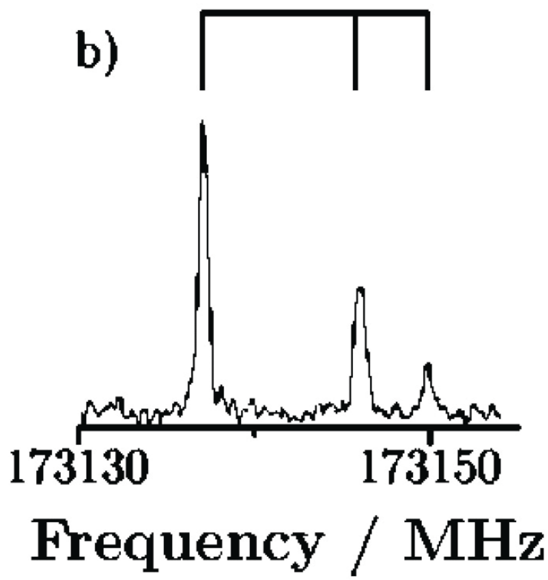
$$E_n = E_\mathrm{i} - \frac{hcR_M}{(n-\delta)^2}$$

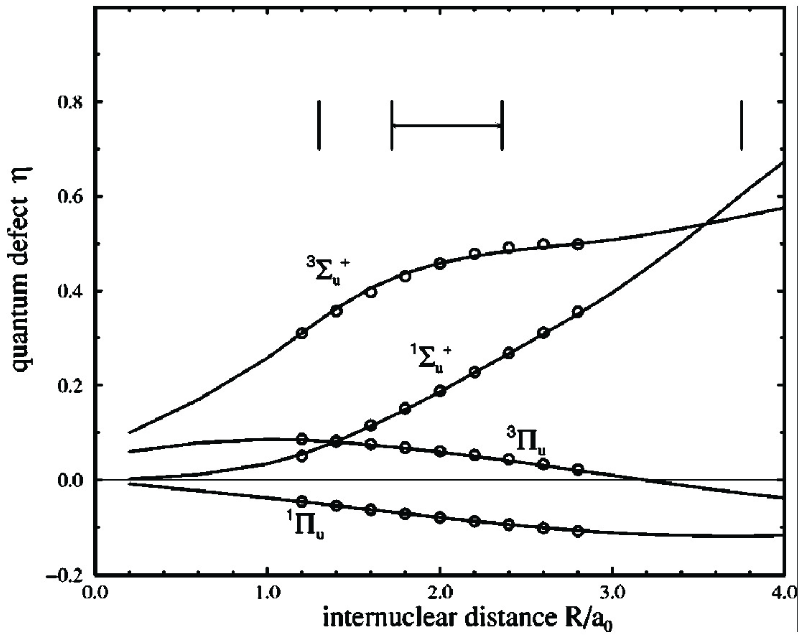
Origin of the eigen quantum defects

Fitted to very-high resolution data of H_2

[Osterwalder *et al.* JCP **121**, 11810 (2004)]

51d → 55p (S=0)





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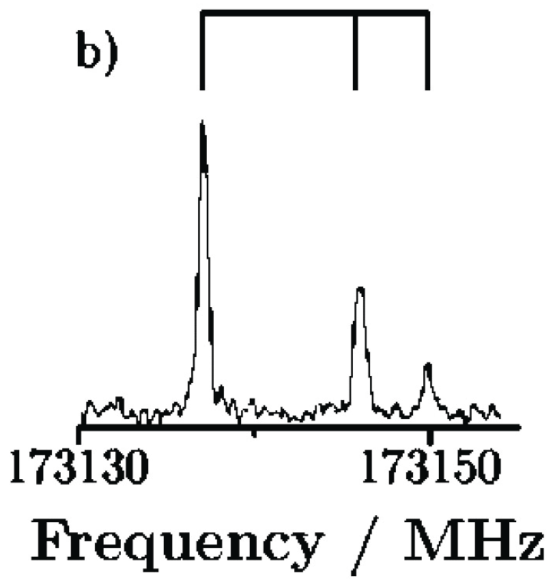

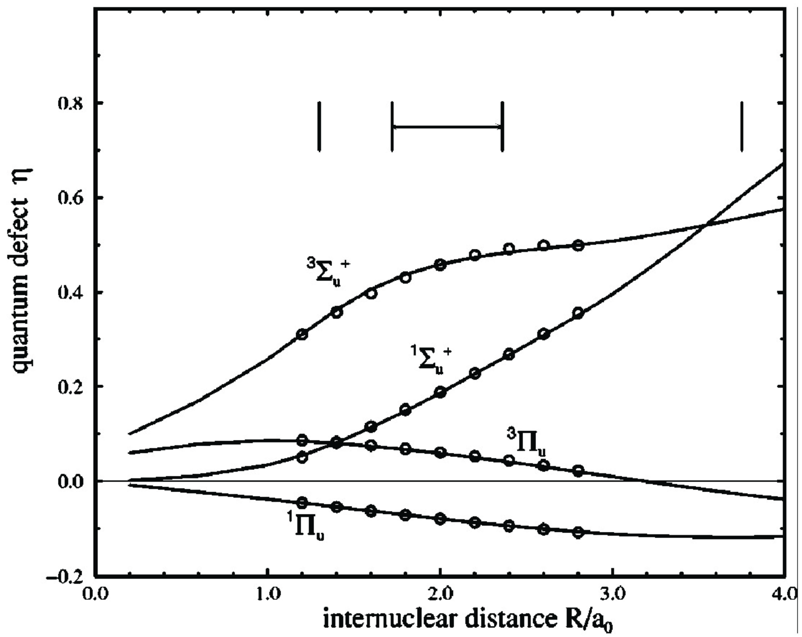

- line width < 1 MHz
- 140 *n*p and *n*f states with 54≤*n*≤64 observed and assigned
- rms deviation after adjustment: 0.6 MHz
- uncertainty of E_i is 0.3 MHz

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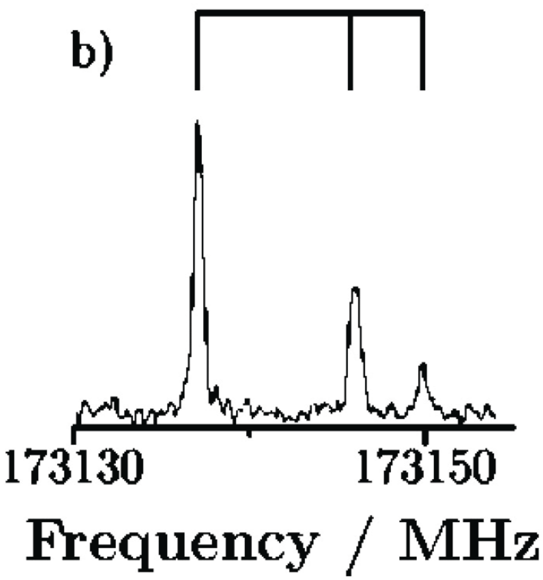
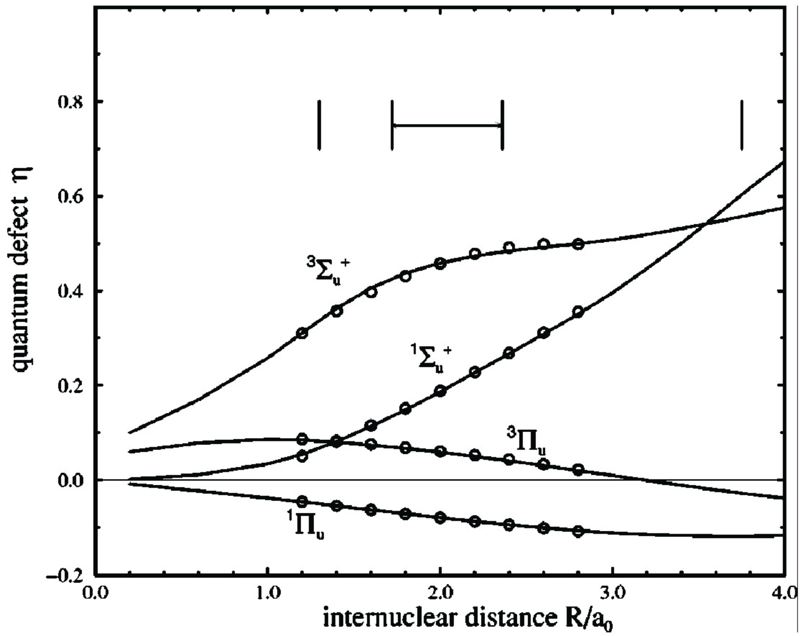
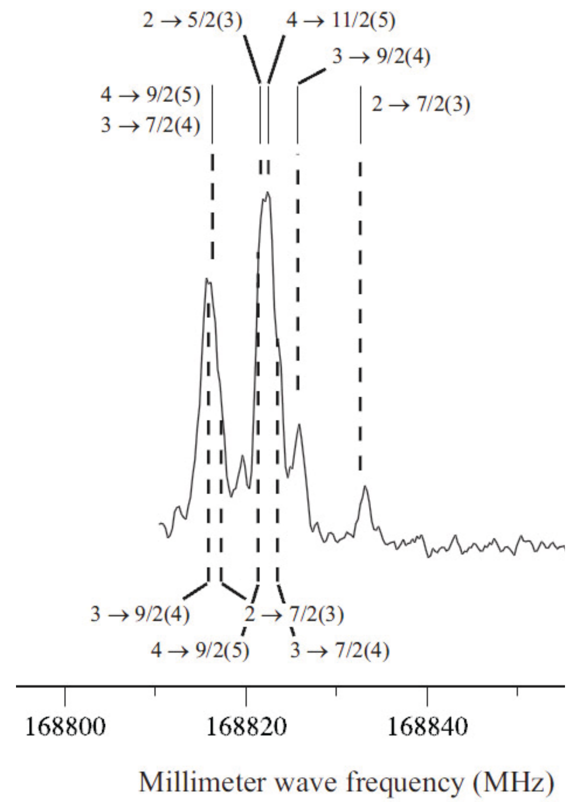




Independent of isotopic substitution

52d → 56f in D_2



- line width < 1 MHz
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- rms deviation after adjustment: 0.6 MHz
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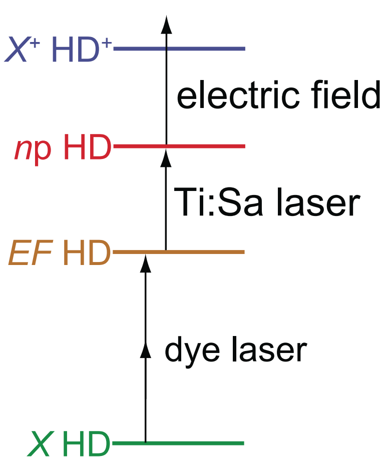
[Cruse *et al.* PRA **77**, 042502 (2008)]

Experimental setup



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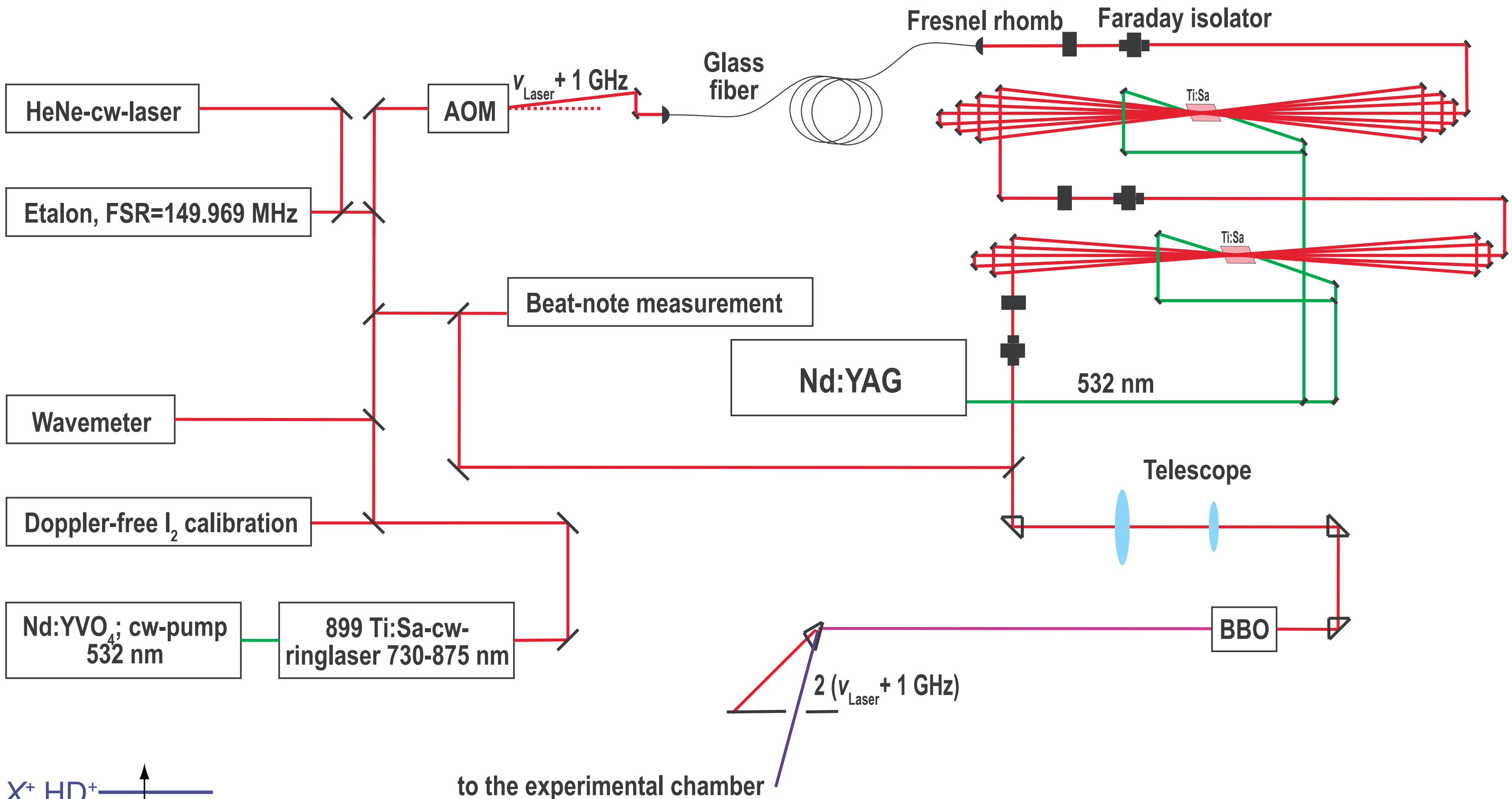
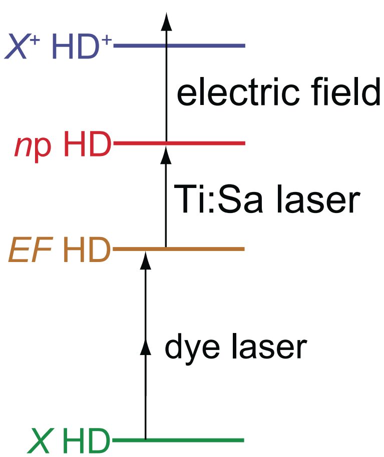


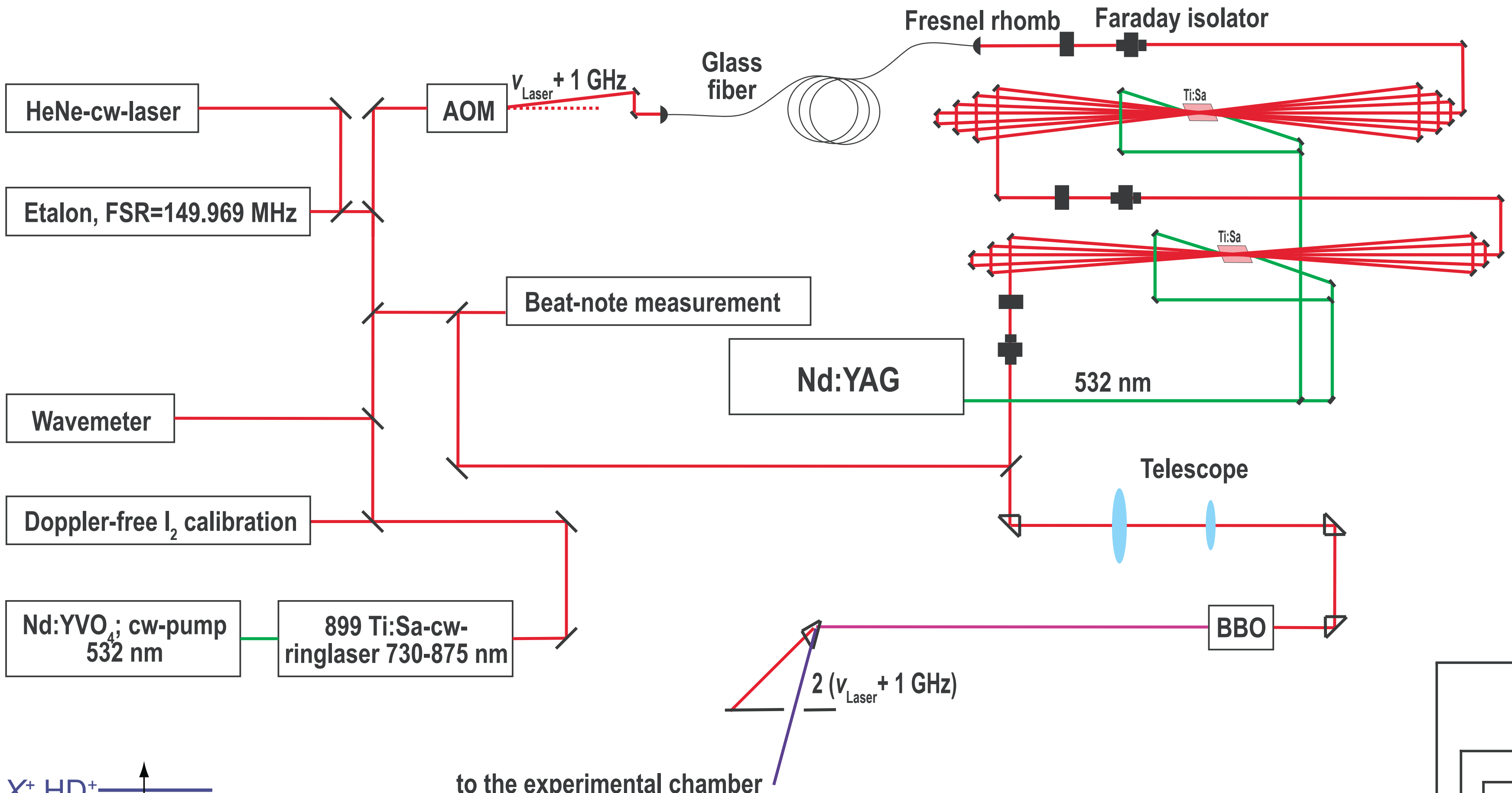


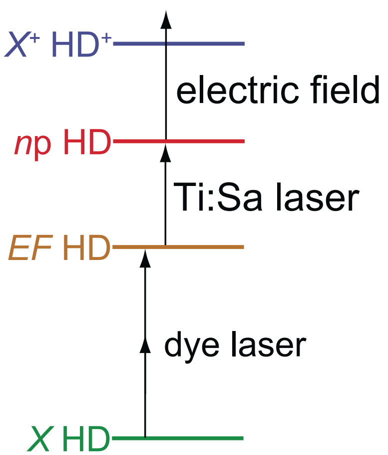
pulse length ~ 40 ns

bandwidth ~ 20 MHz

pulse energy ~ 50 μs

Experimental setup

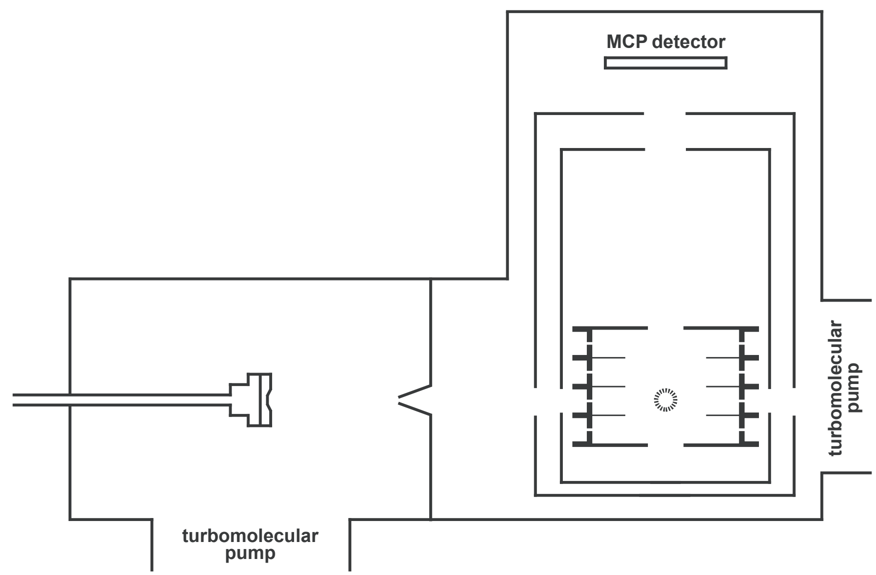




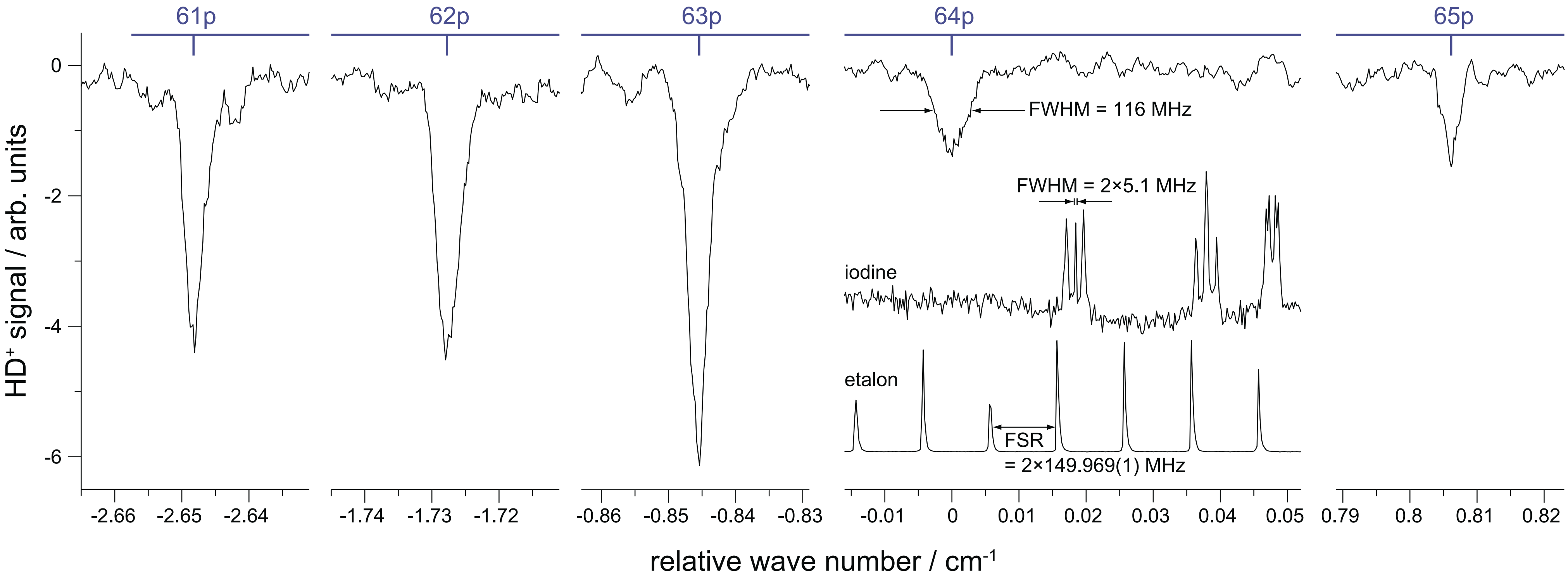
pulse length ~ 40 ns

bandwidth ~ 20 MHz

pulse energy ~ 50 μJ



Survey scans for HD

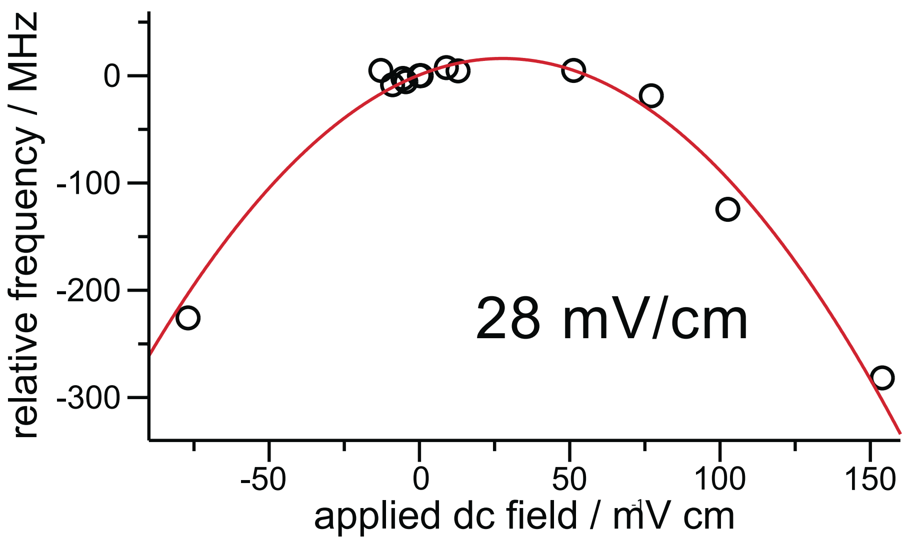


- Doppler-free $^{127}I_2$ absorption peaks have been measured with a frequency comb to an accuracy of 100 kHz.
- relative frequency measurement using a high-finesse etalon locked to a polarization-stabilized He-Ne laser

Absolute wave number measurements in HD

Sources of experimental errors

- dc Stark shift (15.4±2.4 MHz)



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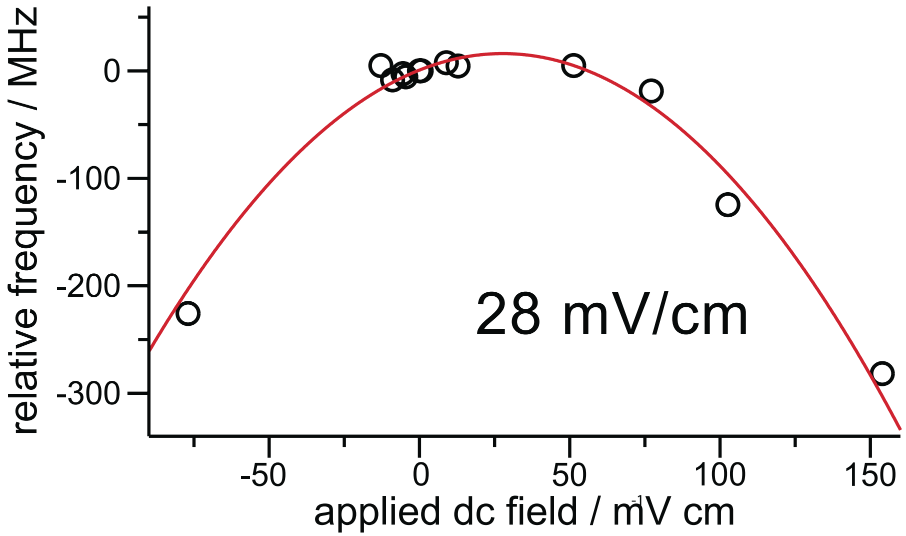

- ac Stark shift (0.0±4.4 MHz)
- shift induced by HD^+ ions (0.0±5.2 MHz)
- frequency shift in the Ti:Sa amplifier (typically -8±1 MHz)

Absolute wave number measurements in HD

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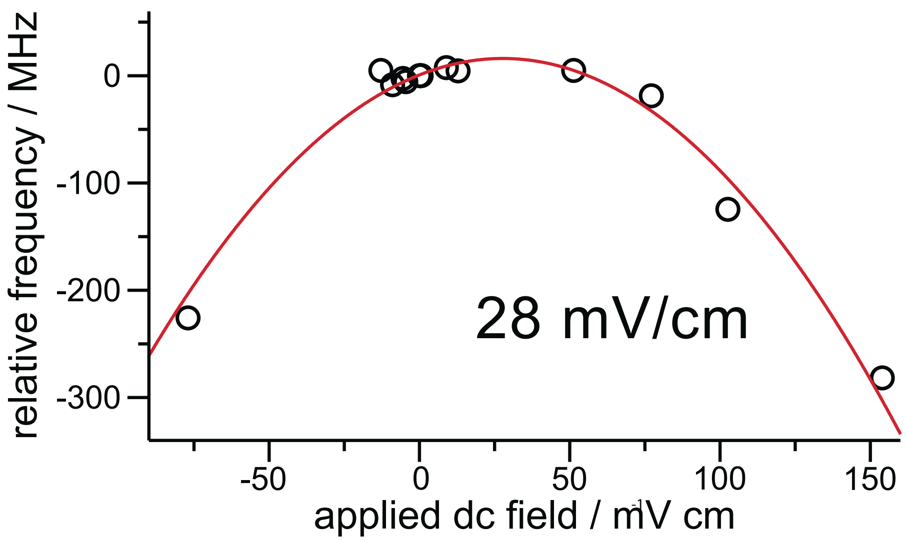
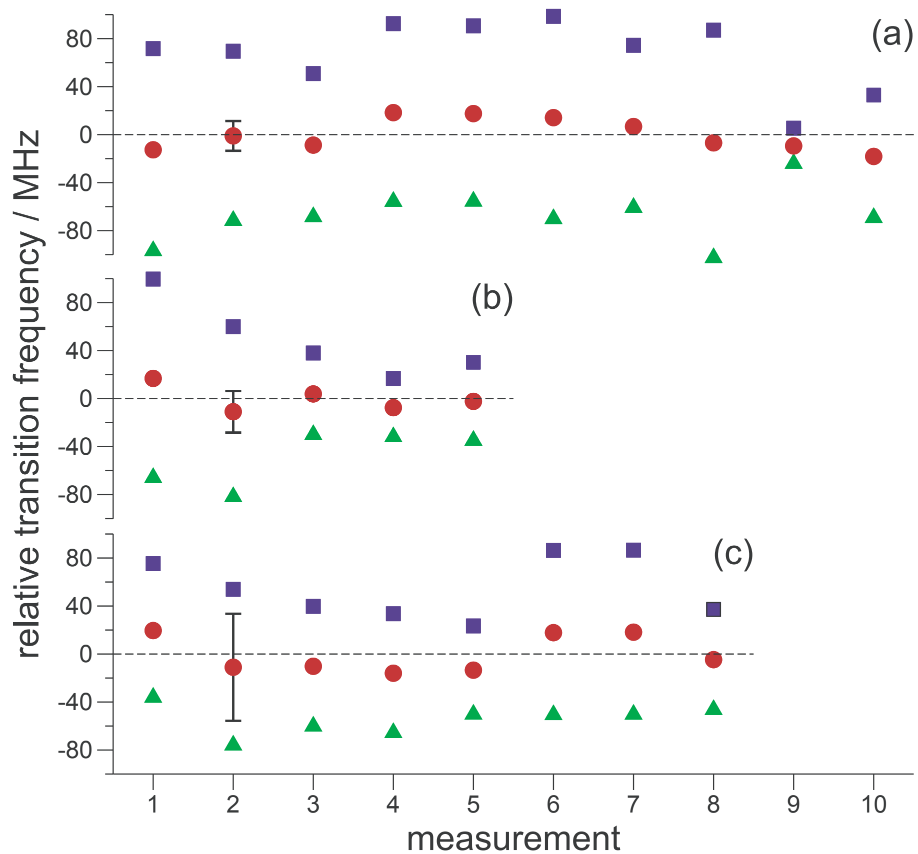


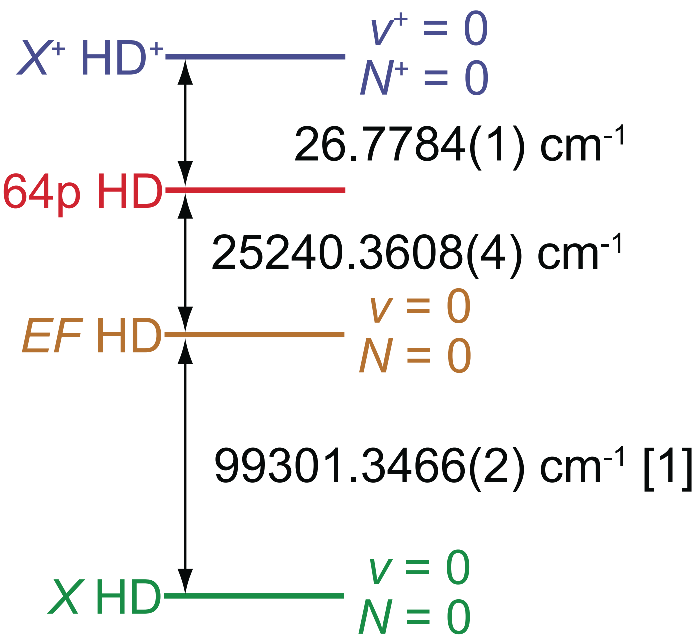
- ac Stark shift (0.0±4.4 MHz)
- shift induced by HD^+ ions (0.0±5.2 MHz)
- frequency shift in the Ti:Sa amplifier (typically -8±1 MHz)

- elimiminate Doppler shift by taking pairs of measurements with counterpropagating laser beams:



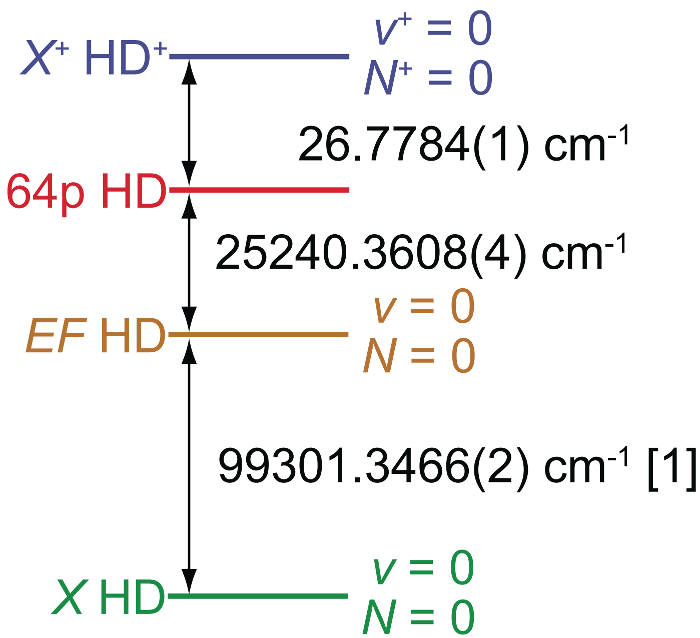
(a) *EF* (v=0,N=0) → 64p (v^+=0,N^+=0)
(b) *EF* (v=0,N=1) → 69p (v^+=0,N^+=1)
(c) *EF* (v=0,N=0) → 55p (v^+=1,N^+=0)

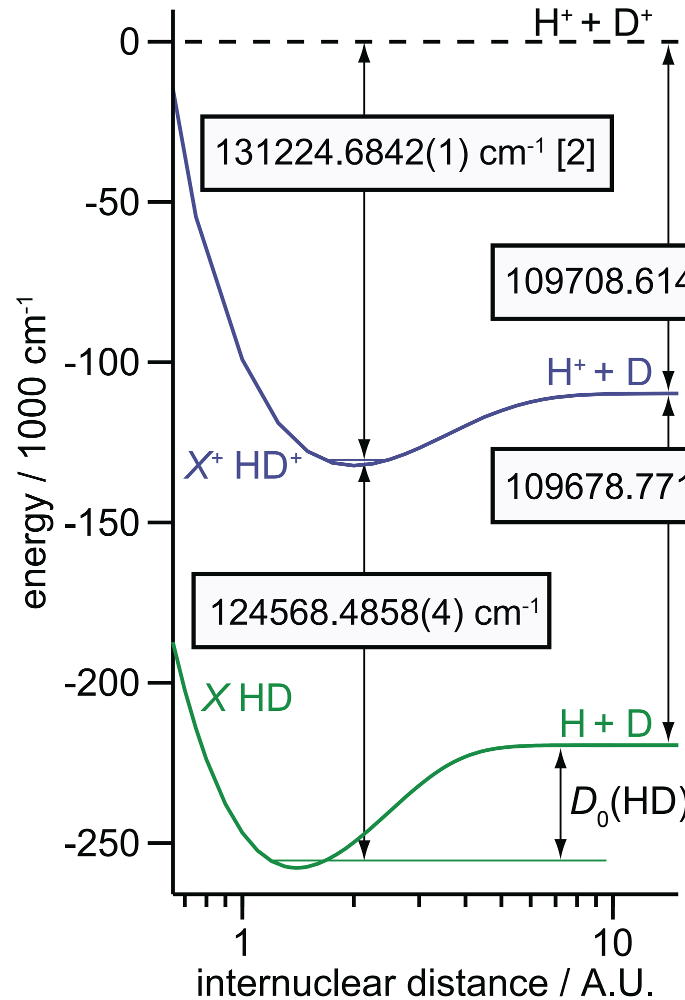
Results



[1] Hannemann *et al.* PRA **74**, 062514 (2006)

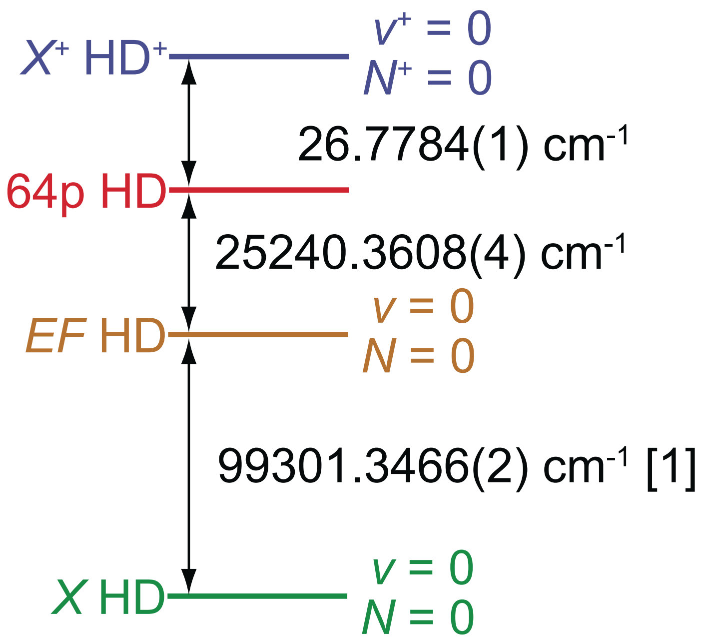
Results

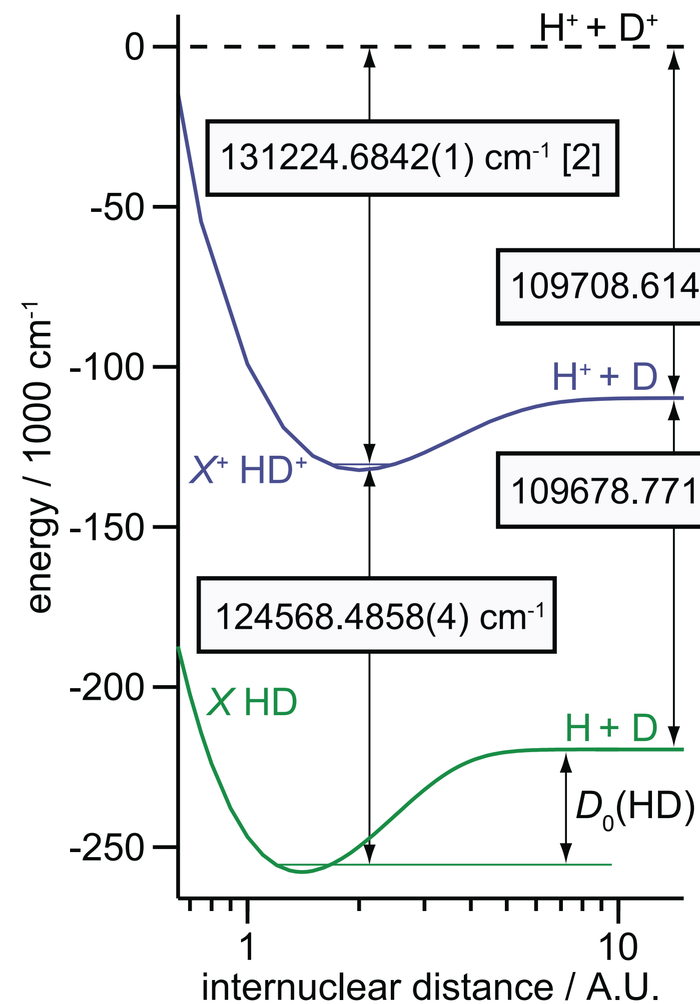




[1] Hannemann *et al.* PRA **74**, 062514 (2006)
[2] Korobov, PRA **77**, 022509 (2008)
[3] Mohr *et al.* Rev. Mod. Phys. **80**, 633 (2008)

Results





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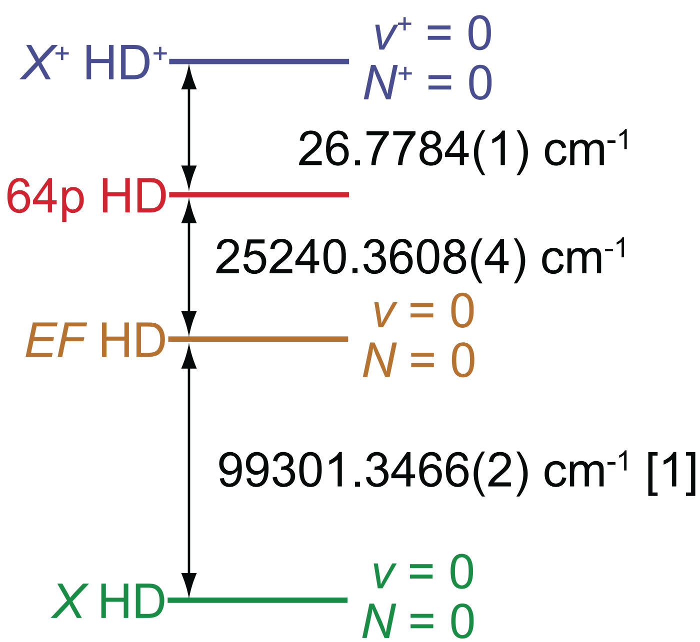
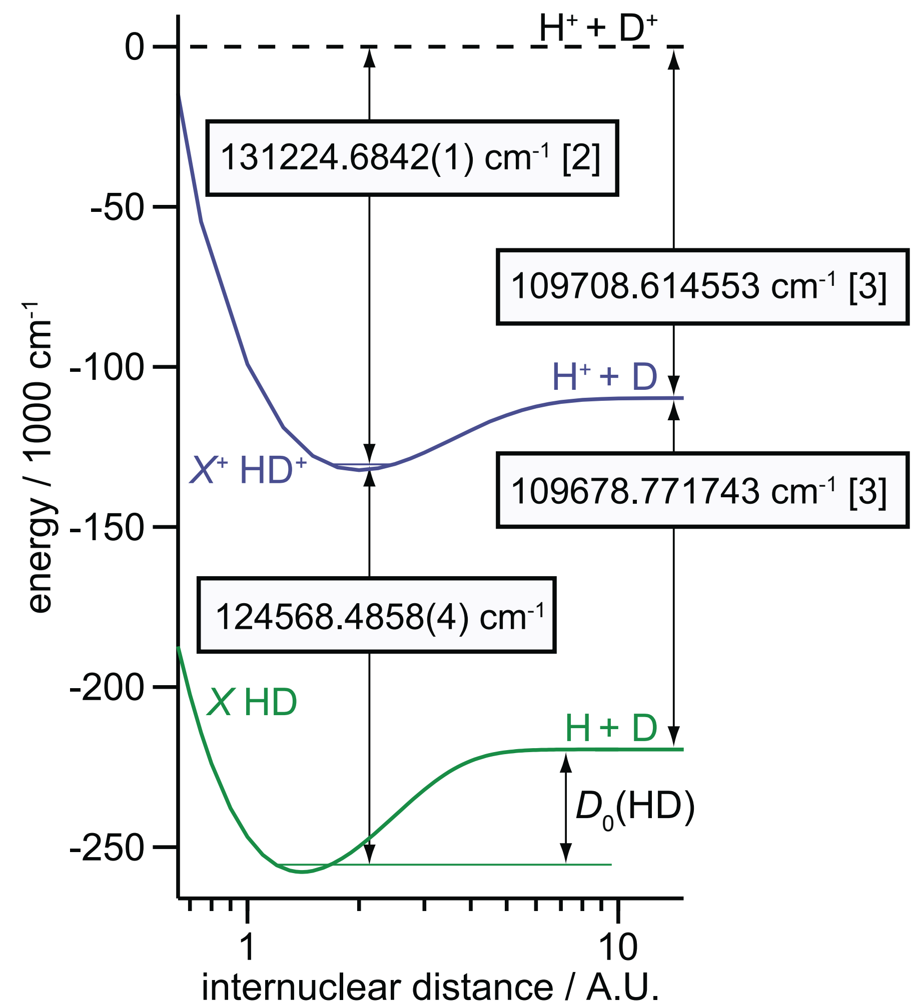
D_0(HD) / cm^{-1}	Year	Experiment	Theory
Wolniewicz	1995		36405.787
Eyler and coworkers	2004	36405.828(16)	
This work	2010		

Results





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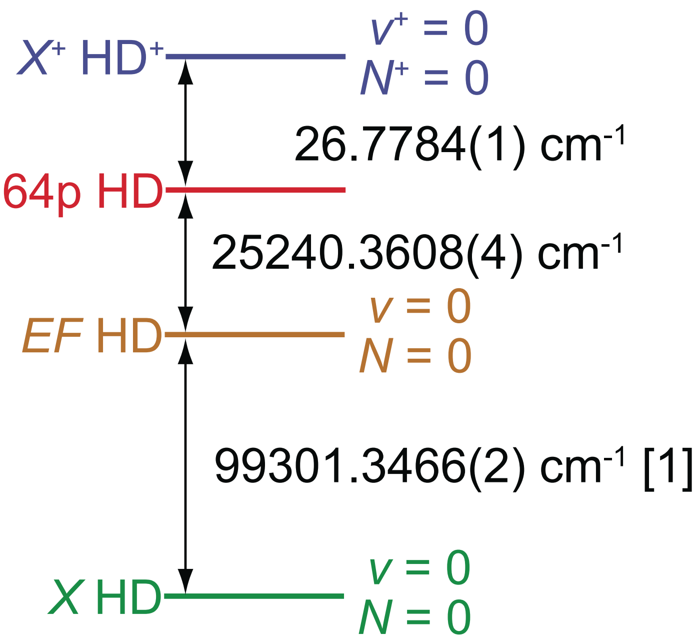

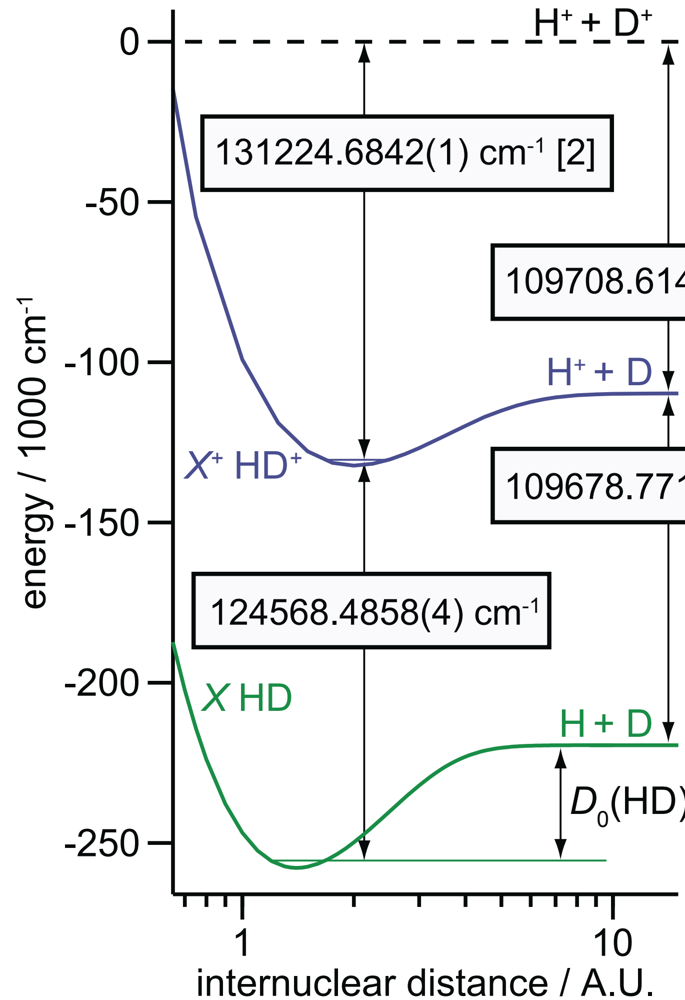

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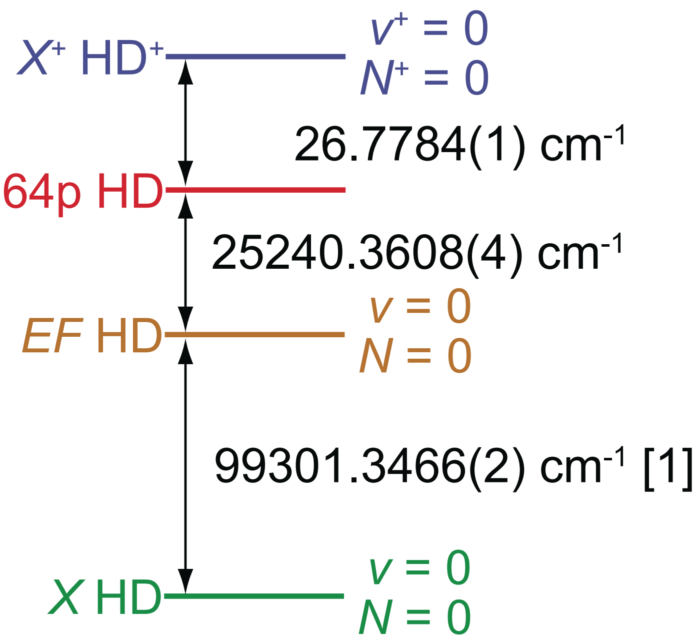
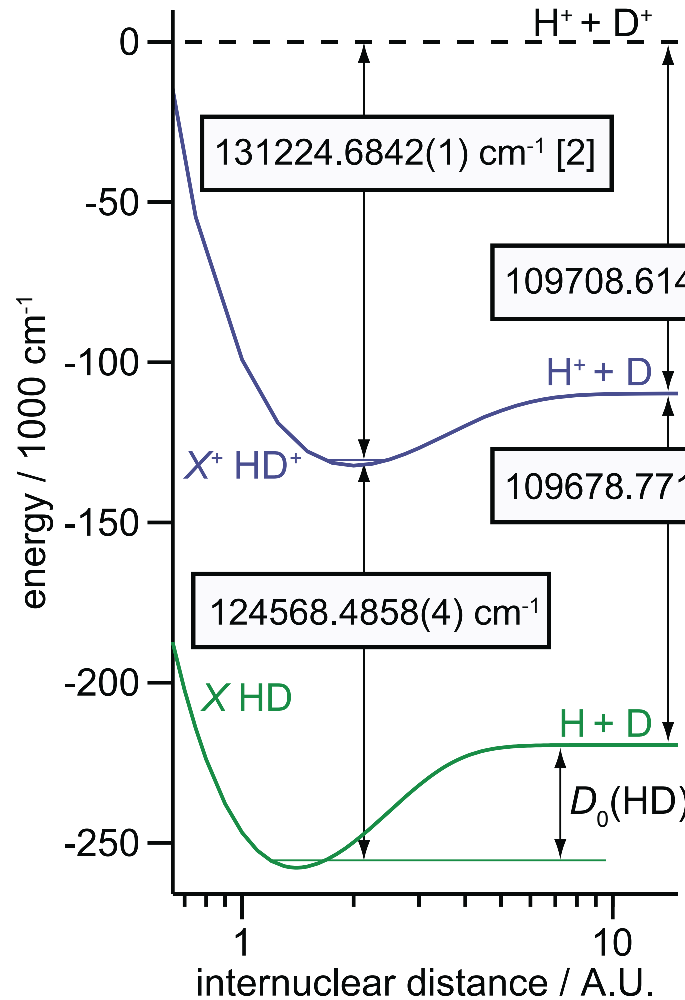
Results





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This work	2010	36405.7837(4)	
Pachucki and coworkers	2010		36405.7828(10)[a]

[a] private communication, with permission

Conclusions

- Transition wave numbers from the *EF* (v=0, N=0,1) to np Rydberg states (n ≈ 60) were measured in H_2, HD and D_2 with an uncertainty of less than 20 MHz.
- Electron binding energies of these Rydberg states could be determined with MQDT (eigen quantum defects adjusted to experimental data).
- Adding the transition energies, the electron binding energies and previously reported term energies of the *EF* state led to a determination of the adiabatic ionization energy.
- Combining these measurements with highly accurate theoretical values of the ionization energies of the one-electron systems H, D, and HD^+ further enabled a new determination of the dissociation energy.
- Our values and the results of an *ab intio* investigation by Packuchi and coworkers agree within 0.001 cm^{-1} (30 MHz) for H_2, HD, and D_2.

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ETH Zurich
Switzerland
(March 2009)

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Comparison between survey spectra and MQDT

Rydberg state $n\,\ell\,N^+_N(v^+)$	Relative exp. wave number	MQDT binding energy	Sum rel. to mean value
$(v^+, N^+) = (0,0)$			
$56p0_1(0)$	-8.30825	35.08548	-0.00045
$57p0_1(0)$	-7.17062	33.94850	0.00021
$58p0_1(0)$	-6.20710	32.98551	0.00073
$26p2_1(0)$	-5.42239	32.20084	0.00077
$60p0_1(0)$	-3.59805	30.37518	-0.00055
$61p0_1(0)$	-2.64818	29.42491	-0.00096
$62p0_1(0)$	-1.72758	28.50535	0.00010
$63p0_1(0)$	-0.84556	27.62288	-0.00036
$64p0_1(0)$	0	26.77844	0.00076
$65p0_1(0)$	0.80612	25.97130	-0.00026
$66p0_1(0)$	1.57971	25.20021	0.00224
$67p0_1(0)$	2.31081	24.46389	-0.00297
$68p0_1(0)$	3.01434	23.76127	-0.00207
$(v^+, N^+) = (0,1)$			
$64p1_2(0)$	-3.70730	26.75416	-0.00049
$64p1_1(0)$	-3.67078	26.71723	-0.00090
$65p1_2(0)$	-2.89882	25.94695	0.00079
$65p1_1(0)$	-2.85518	25.90240	-0.00013
$66p1_2(0)$	-2.12693	25.17429	0.00002
$66p1_1(0)$	-2.07799	25.12428	-0.00106
$69p1_2(0)$	0	23.04834	0.00100
$69p1_1(0)$	0.05796	22.98922	-0.00016
$70p1_2(0)$	0.64966	22.39845	0.00077
$70p1_1(0)$	0.70867	22.33772	-0.00096
$71p1_2(0)$	1.27293	21.77547	0.00105
$71p1_1(0)$	1.33390	21.71353	0.00008
$(v^+, N^+) = (1,0)$			
$42p0_1(1)$	-25.92414	62.07063	0.00089
$47p0_1(1)$	-13.30965	49.45468	-0.00057
$48p0_1(1)$	-11.38886	47.53320	-0.00125
$49p0_1(1)$	-9.53819	45.68277	-0.00101
$54p0_1(1)$	-1.23751	37.38408	0.00098
$55p0_1(1)$	0	36.14565	0.00005
$56p0_1(1)$	1.22532	34.92033	0.00005
$57p0_1(1)$	2.40493	33.74074	0.00008
$58p0_1(1)$	3.53122	32.61487	0.00050
$66p0_1(1)$	11.05893	25.08584	-0.00082
$69p0_1(1)$	13.13060	23.01540	0.00041
$72p0_1(1)$	14.98039	21.16590	0.00070

Standard deviation < 24 MHz (experimental uncertainty)

Comparison between survey spectra and MQDT

Rydberg state $n\,\ell\,N_N^+(v^+)$	Relative exp. wave number	MQDT binding energy	Sum rel. to mean value
$(v^+, N^+) = (0, 0)$			
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$(v^+, N^+) = (0, 1)$			
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$64p1_1(0)$	-3.67078	26.71723	-0.00090
$65p1_2(0)$	-2.89882	25.94695	0.00079
$65p1_1(0)$	-2.85518	25.90240	-0.00013
$66p1_2(0)$	-2.12693	25.17429	0.00002
$66p1_1(0)$	-2.07799	25.12428	-0.00106
$69p1_2(0)$	0	23.04834	0.00100
$69p1_1(0)$	0.05796	22.98922	-0.00016
$70p1_2(0)$	0.64966	22.39845	0.00077
$70p1_1(0)$	0.70867	22.33772	-0.00096
$71p1_2(0)$	1.27293	21.77547	0.00105
$71p1_1(0)$	1.33390	21.71353	0.00008
$(v^+, N^+) = (1, 0)$			
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$49p0_1(1)$	-9.53819	45.68277	-0.00101
$54p0_1(1)$	-1.23751	37.38408	0.00098
$55p0_1(1)$	0	36.14565	0.00005
$56p0_1(1)$	1.22532	34.92033	0.00005
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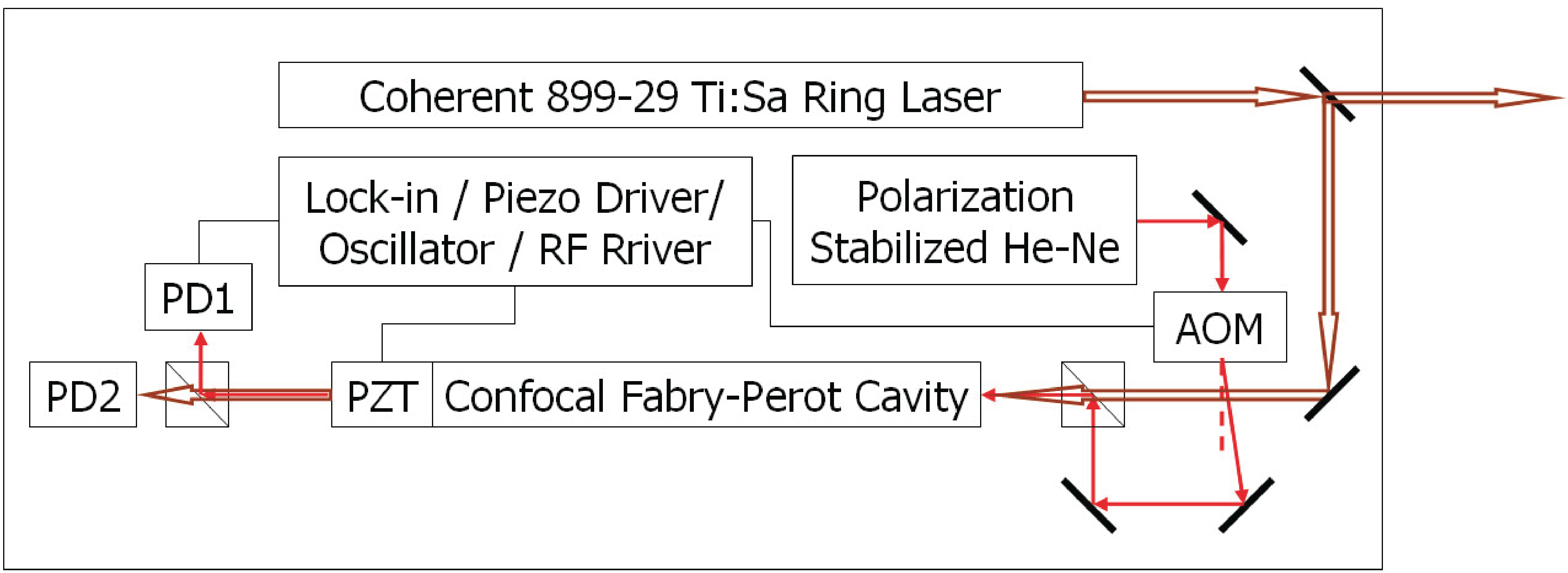
$72p0_1(1)$	14.98039	21.16590	0.00070

Standard deviation < 24 MHz (experimental uncertainty)

Error budget

Rydberg state $n\,\ell\,N_N^+(v^+)$	$64p0_1(0)$		$69p1_2(0)$		$55p0_1(1)$	
Standard deviation of the individual measurements	13.3		11.0		15.7	
Statistical uncertainties						
Uncertainty in the determination of the I_2 line centers	$\pm$ 0.30	$\times 2$	$\pm$ 0.42	$\times 2$	$\pm$ 0.35	$\times 2$
Uncertainty in the determination of the HD line centers	$\pm$ 2.5	$\times 2$	$\pm$ 3.7	$\times 2$	$\pm$ 6.7	$\times 2$
Nonlinearity of the $EF \rightarrow n$ laser scans	$< \pm$ 1.1	$\times 2$	$< \pm$ 1.1	$\times 2$	$< \pm$ 1.1	$\times 2$
Residual Doppler shift	$< \pm$ 0.26		$< \pm$ 0.26		$< \pm$ 0.28	
Sum in quadrature	$\pm$ 5.5		$\pm$ 7.8		$\pm$13.6	
Systematic shifts and uncertainties						
Uncertainty caused by the uncertainty of the etalon FSR[a]	$\pm$ 0.004	$\times 2$	$\pm$ 0.046	$\times 2$	$\pm$ 0.027	$\times 2$
Uncertainty in the positions of the I_2 reference lines	$\pm$ 0.1	$\times 2$	$\pm$ 0.1	$\times 2$	$\pm$15	$\times 2$
Frequency shift in the Ti:Sa amplifier	$\pm$ 0.29	$\times 2$	$\pm$ 0.16	$\times 2$	$\pm$ 0.31	$\times 2$
Frequency shift in the doubling crystal	$< \pm$ 0.35		$< \pm$ 0.35		$< \pm$ 0.35	
ac Stark shift by the $EF \rightarrow n$ laser	$< \pm$ 1.8	$\times 2$	$< \pm$ 3.0	$\times 2$	$\pm$ 2.2	$\times 2$
Frequency shift by the $X \rightarrow EF$ laser	$< \pm$ 2.9	$\times 2$	$< \pm$ 3.3	$\times 2$	$< \pm$ 2.6	$\times 2$
dc Stark shift by the stray electric fields	($-$2.8$\pm$ 0.6)	$\times 2$	($-$7.7$\pm$ 1.7)	$\times 2$	(+7.7$\pm$ 1.2)	$\times 2$
Pressure shift	+0.10$\pm$ 0.05		+0.10$\pm$ 0.05		+0.10$\pm$ 0.05	
Sum and uncertainty in quadrature	$-$5.5$\pm$ 7.0		$-$15.3$\pm$ 9.6		+15.5$\pm$30.9	
Total shift and uncertainty	$-$5.5$\pm$12.5		$-$15.3$\pm$17.4		+15.5$\pm$44.5	

HeNe stabilized etalon



Extrapolation of the ionization energy

Label	Energy interval	Wave number / cm^{-1}	Reference
(1)	$X\,^1\Sigma_g^+\,(v=0,N=0)$ — $EF\,^1\Sigma_g^+\,(v=0,N=0)$	99301.34662(20)	[1]
(2)	$EF\,^1\Sigma_g^+\,(v=0,N=0)$ — $64\mathrm{p}0_1\,(v^+=0,S=0)$	25240.36096(42)	This work
(3)	$64\mathrm{p}0_1\,(v^+=0,S=0)$ — $X^+\,^2\Sigma_g^+\,(v^+=0,N^+=0)$	26.77844(3)	This work
$E_\mathrm{i}^{(0,0)}$ = (1)+(2)+(3)	$X\,^1\Sigma_g^+\,(v=0,N=0)$ — $X^+\,^2\Sigma_g^+\,(v^+=0,N^+=0)$	124568.48602(47)	This work
(4)	$X\,^1\Sigma_g^+\,(v=0,N=0)$ — $X\,^1\Sigma_g^+\,(v=0,N=1)$	89.227950(5)	[2]
(5)	$X\,^1\Sigma_g^+\,(v=0,N=1)$ — $EF\,^1\Sigma_g^+\,(v=0,N=1)$	99259.91793(20)	[1]
(6)	$EF\,^1\Sigma_g^+\,(v=0,N=1)$ — $69\mathrm{p}1_2\,(v^+=0,S=0)$	25240.15251(58)	This work
(7)	$69\mathrm{p}1_2\,(v^+=0,S=0)$ — $X^+\,^2\Sigma_g^+\,(v^+=0,N^+=1)$	23.04834(3)	This work
$E_\mathrm{i}^{(0,1)}$ = (4)+(5)+(6)+(7)	$X\,^1\Sigma_g^+\,(v=0,N=0)$ — $X^+\,^2\Sigma_g^+\,(v^+=0,N^+=1)$	124612.34673(61)	This work
(8)	$EF\,^1\Sigma_g^+\,(v=0,N=0)$ — $55\mathrm{p}0_1\,(v^+=1,S=0)$	27143.98830(148)	This work
(9)	$55\mathrm{p}0_1\,(v^+=1,S=0)$ — $X^+\,^2\Sigma_g^+\,(v^+=1,N^+=0)$	36.14565(3)	This work
$E_\mathrm{i}^{(1,0)}$ = (1)+(8)+(9)	$X\,^1\Sigma_g^+\,(v=0,N=0)$ — $X^+\,^2\Sigma_g^+\,(v^+=1,N^+=0)$	126481.48057(149)	This work

[1] S. Hannemann *et al.* PRA **74**, 062514 (2006)

[2] K.M. Evanson *et al.* Astrophys. J. **330**, L135 (1988)

Extrapolation of the ionization energy

Label	Wave number / cm^{-1}	Reference
Rotational separation $(v^+, N^+) : (0,0)$—$(0,1)$		
$E_i^{(0,1)} - E_i^{(0,0)}$	43.86071(77)	This work.
(10)	43.86120186(2)	[1]
Vibrational separation $(v^+, N^+) : (0,0)$—$(1,0)$		
$E_i^{(1,0)} - E_i^{(0,0)}$	1912.99455(154)	This work
(11)	1912.9952347(7)	[1]
Adiabatic ionization energy		
$E_i^{(0,0)}$	124568.48602(47)	This work
$E_i^{(0,1)} - (10)$	124568.48553(61)	This work
$E_i^{(1,0)} - (11)$	124568.48534(149)	This work
combined E_i(HD)	124568.48581(36)	This work

Relative uncertainty $4 \cdot 10^{-9}$

	H_2	HD	D_2
Most recent exp.	124417.476(12) [2]	124568.491(17) [3]	124745.353(24) [4]
This work	124417.49113(37)	124568.48581(36)	124745.39407(58)

[1] V.I. Korobov, PRA **77**, 022509 (2008)
[2] A. de Lange *et al.* PRA **65**, 064501 (2002)
[3] G.M. Greetham *et al.* PCCP **5**, 2528 (2003)
[4] D. Shiner *et al.* PRA **47**, 4042 (1993)

Dissociation energy of the hydrogen molecule

	Year	Experiment	Theory
James and Coolidge	1933		35924(105)
Beutler	1935	36116(6)	
Kolos and Roothaan	1960		
Herzberg and Monfils	1960	36113.0(3)	
Kolos and Wolniewicz	1965		36117.3 cm^{-1}
Kolos and Wolniewicz	1968		36117.4 cm^{-1}
Herzberg	1970	36117.3(10)	
Stwalley	1970	36118.6(5)	
Kolos and coworkers	1986		
Stoicheff and coworkers	1992	36118.11(8)	
Eyler and Melikechi	1993	36118.06(4)	
Kolos and Rychlewski	1993		36118.049
Wolniewicz	1995		36118.069
Eyler and coworkers	2004	36118.062(10)	
Liu *et al.*	2009	36118.06962(37)	
Pachucki and coworkers	2009		36118.0695(10)

	H_2	HD	D_2
Ref. [1] (Exp.)	36118.062(10)	36405.828(16)	36748.343(10)
Refs. [2,3] (Theory)	36118.0695(10)	36405.7828(10)	36748.3633(09)
This work (hybrid)	36118.06962(37)	36405.78366(36)	36748.36286(68)