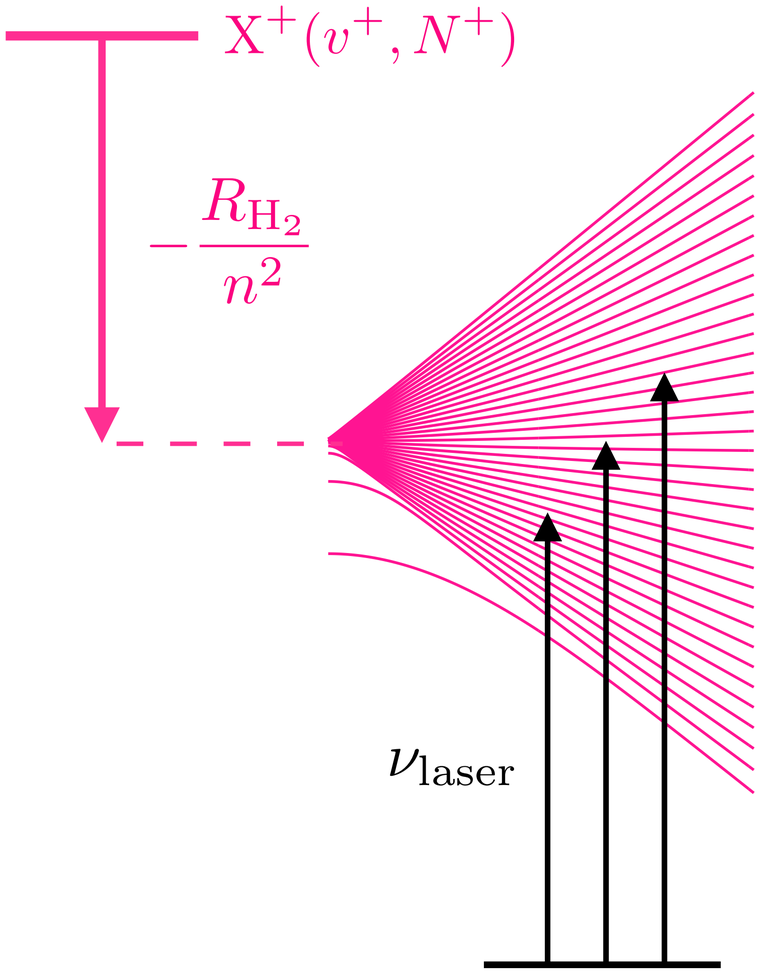

Spin-Rovibrational Structure of the Molecular Hydrogen Ion from Spectroscopy of Rydberg States

Ioana Doran[a], Maximilian Beyer[b], Frédéric Merkt[a]

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[b] Laboratory of Physics and Astronomy, Vrije Universiteit, Amsterdam, The Netherlands

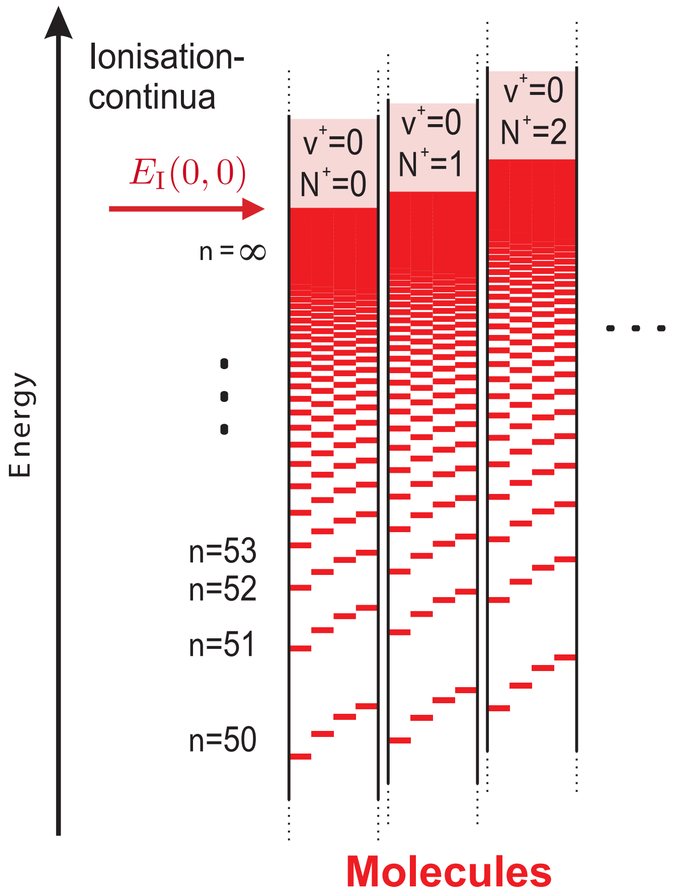
PSAS 2024, 12.06.2024

Precision measurements in H_2^+ for benchmarking *ab-initio* calculations

- **H_2^+: Simplest molecular three-body system: determination of physical constants (μ_p [1], r_p [2])**

- No permanent electric dipole moment => no pure rotational / vibrational spectra (within electric-dipole approximation)

- Alternatively: **drive transitions to Rydberg series converging to different rovibrational / hyperfine levels of the ion & extrapolate to their ionization limits**: => energy intervals in the molecular ion.



n: principal quantum number

[1] Karr et al., Phys. Rev. A **94**, 050501 (R) (2016)

[2] Puchalski et al., Phys. Rev. Lett. **122**, 103003 (2019)

The fundamental vibrational interval of H_2^+ — ab-initio calculations

PRL **118,** 233001 (2017) PHYSICAL REVIEW LETTERS week ending 9 JUNE 2017

Fundamental Transitions and Ionization Energies of the Hydrogen Molecular Ions with Few ppt Uncertainty

Vladimir I. Korobov
Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia

L. Hilico and J.-Ph. Karr
Laboratoire Kastler Brossel, UPMC-Université Paris 6, ENS, CNRS, Collège de France 4 place Jussieu, F-75005 Paris, France
and Université d'Evry-Val d'Essonne, Boulevard François Mitterrand, F-91000 Evry, France
(Received 23 March 2017; published 8 June 2017)

We calculate ionization energies and fundamental vibrational transitions for H_2^+, D_2^+, and HD^+ molecular ions. The nonrelativistic quantum electrodynamics expansion for the energy in terms of the fine structure constant α is used. Previous calculations of orders $m\alpha^6$ and $m\alpha^7$ are improved by including second-order contributions due to the vibrational motion of nuclei. Furthermore, we evaluate the largest corrections at the order $m\alpha^8$. That allows us to reduce the fractional uncertainty to the level of 7.6×10^{-12} for fundamental transitions and to 4.5×10^{-12} for the ionization energies.

DOI: 10.1103/PhysRevLett.118.233001

dependence of transition lines on the masses and on the proton and deuteron charge radii

$$\nu(H_2^+) = \nu_0(H_2^+) + \frac{\Delta R_\infty}{R_\infty}\nu_0(H_2^+) + 2(R_\infty c) \times [-2.55528 \times 10^{-6}\Delta\mu_p - 8.117 \times 10^{-12}\Delta r_p],$$

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \ldots$$

TABLE IV. Fundamental transition frequencies ν_{01} for H_2^+, D_2^+, and HD^+ molecular ions (in kHz). CODATA14 recommended values of constants. The first error is the theoretical uncertainty, the second error is due to the uncertainty in mass ratios.

	H_2^+	D_2^+	HD^+
ν_{nr}	65 687 511 047.0	47 279 387 818.4	57 349 439 952.4
ν_{α^2}	1 091 040.5	795 376.3	958 151.7
ν_{α^3}	−276 545.1	−200 278.0	−242 126.3
ν_{α^4}	−1952.0(1)	−1413.4(1)	−1708.9(1)
ν_{α^5}	121.8(1)	88.1(1)	106.4(1)
ν_{α^6}	−2.3(5)	−1.7(4)	−2.0(5)
ν_{tot}	65 688 323 710.1(5)(2.9)	47 279 981 589.8(4)(8)	57 350 154 373.4(5)(1.7)

3 kHz uncertainty for H_2^+ dominated by uncertainty in μ_p

Last experimental determination: Herzberg & Jungen (1972)

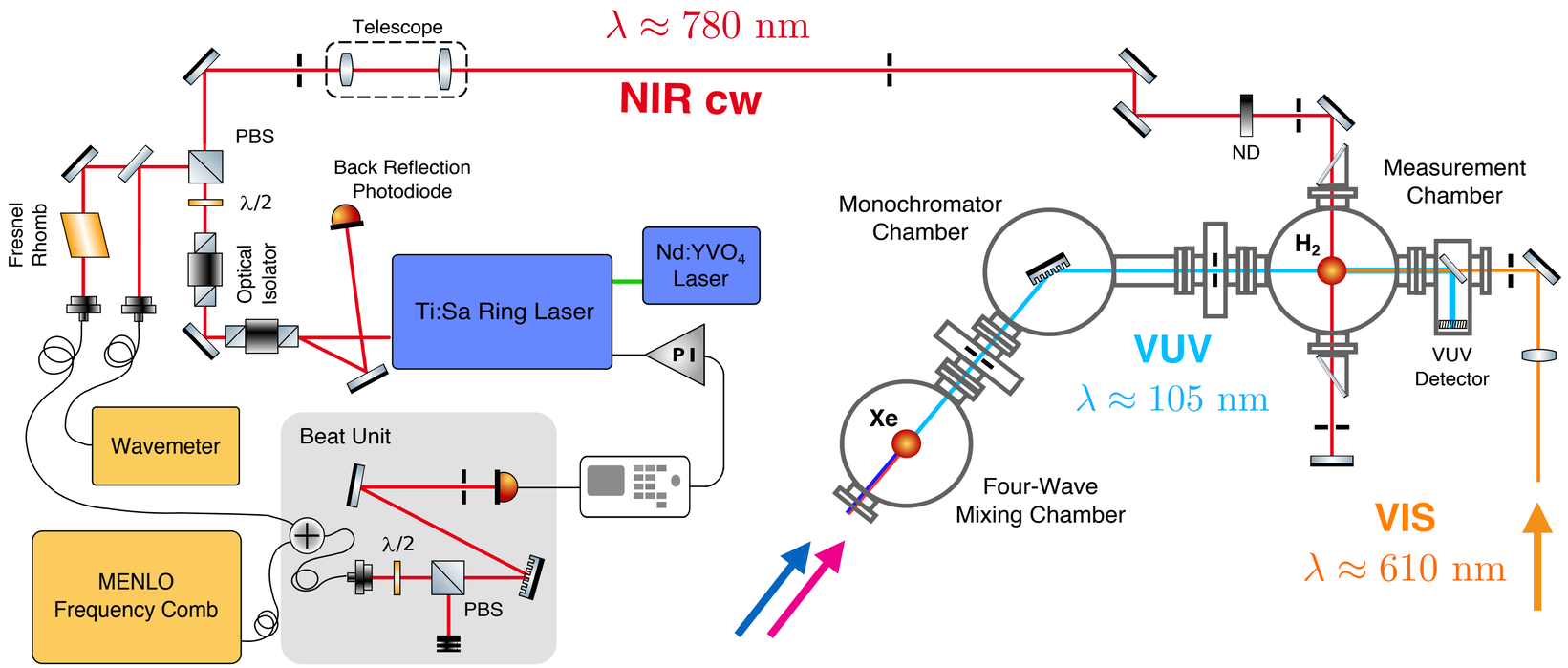
0.2 cm^{-1} (6 GHz) uncertainty

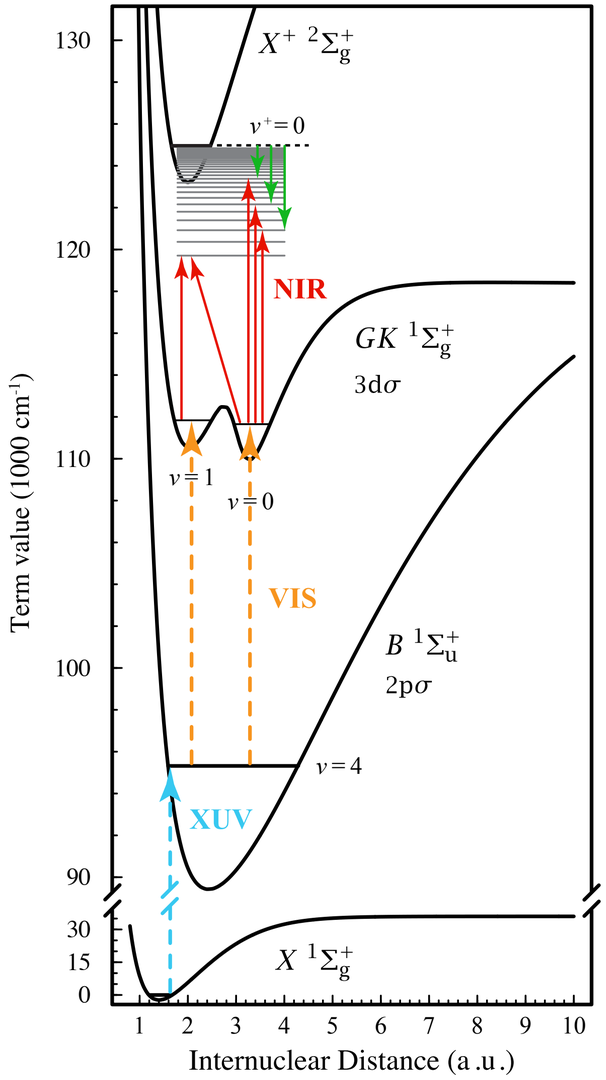
* S. Alighanbari, 12.06.2024, 2 pm
* D. Holzapfel, 12.06.2024, 2.50 pm

Excitation scheme & experimental setup

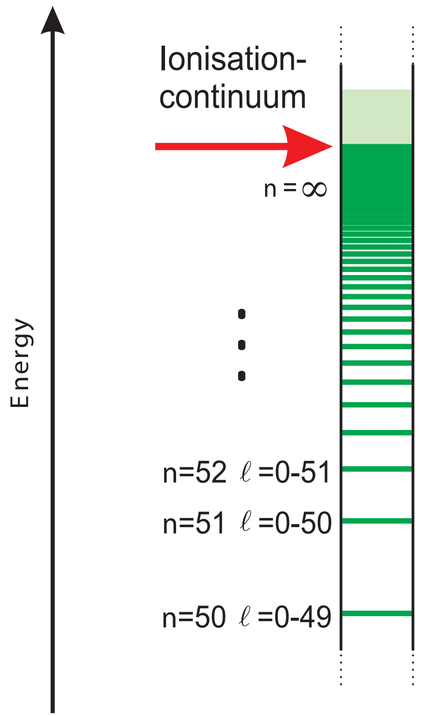
Driving transitions to Rydberg states:

<u>Multiphoton excitation scheme:</u> $\mathrm{X}(0,0) \longrightarrow \mathrm{B}(4,1) \longrightarrow \mathrm{GK}(v,2) \longrightarrow n\ell$ (Rydberg states) $(\Delta\ell = \pm 1)$



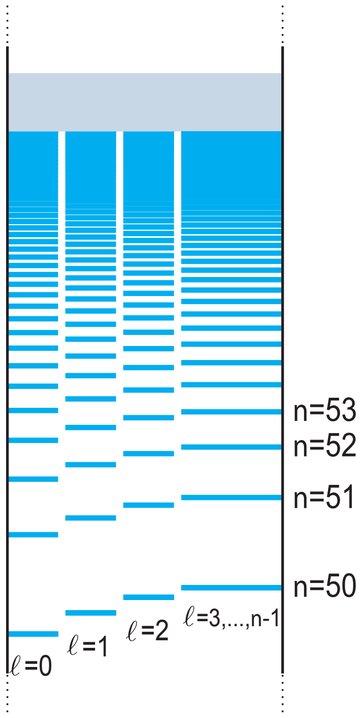


Theoretical description of Rydberg states in atoms and molecules



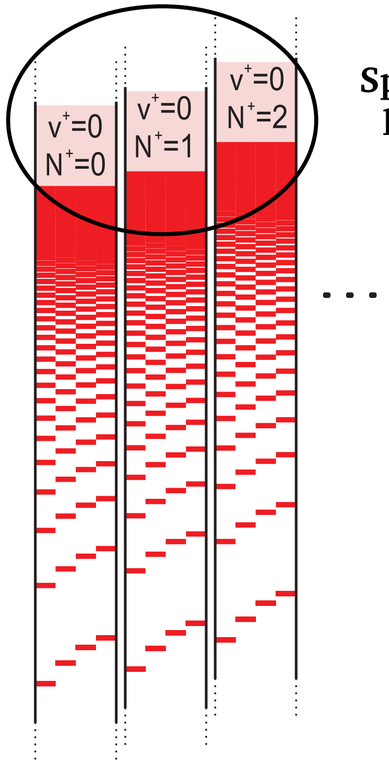
H-Atom

$$E_n = E_\mathrm{I} - \frac{hcR_\mathrm{H}}{n^2}$$



Other atoms

$$E_n = E_\mathrm{I} - \frac{hcR_\mathrm{M}}{(n-\mu_l)^2}$$

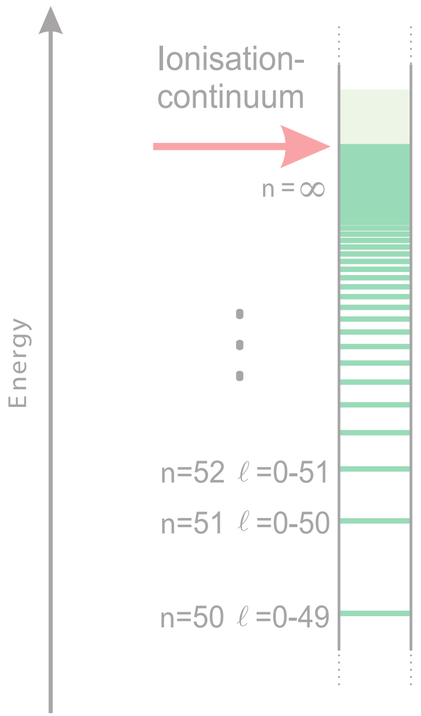


Spin-Rovibrational levels of the ion

Molecules

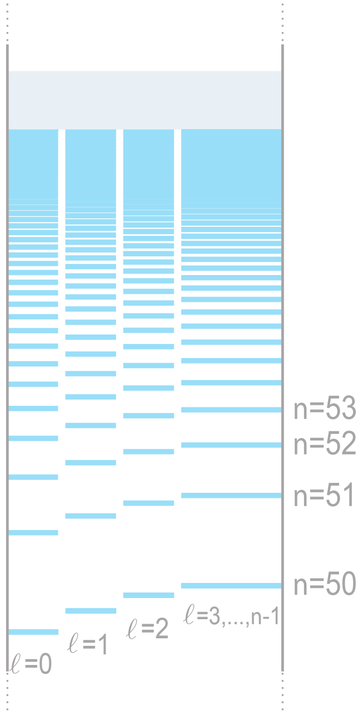
$$E_n = E_\mathrm{I} - \frac{hcR_{\mathrm{H}_2}}{(n-\mu_{l,N^+,v^+,\ldots})^2}$$

Theoretical description of Rydberg states in atoms and molecules



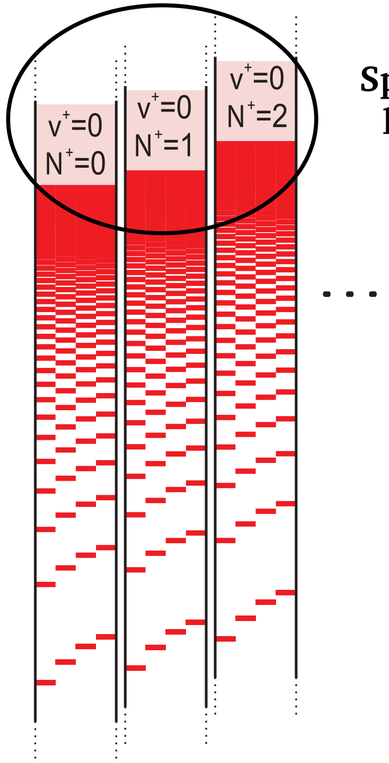
H-Atom

$$E_n = E_\mathrm{I} - \frac{hcR_\mathrm{H}}{n^2}$$



Other atoms

$$E_n = E_\mathrm{I} - \frac{hcR_\mathrm{M}}{(n-\mu_l)^2}$$



Spin-Rovibrational levels of the ion

Molecules

$$E_n = E_\mathrm{I} - \frac{hcR_{\mathrm{H}_2}}{(n-\mu_{l,N^+,v^+,\ldots})^2}$$

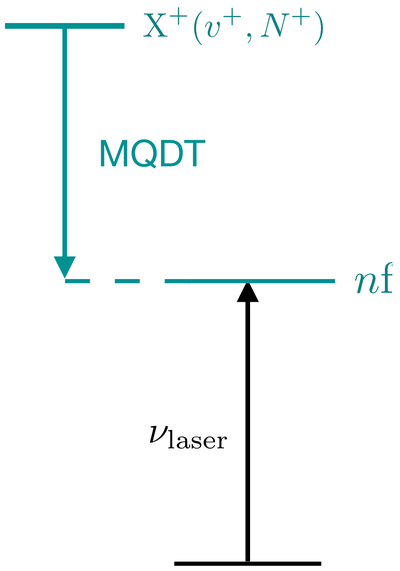
Challenging theoretical description
of low-*l* states
because of ion core penetration,
channel interactions!

(Multichannel-quantum-defect theory)

Ch. Jungen in "Handbook of High-Resolution Spectroscopy"
(Eds. M. Quack and F. Merkt, 2011)

ZQD Method

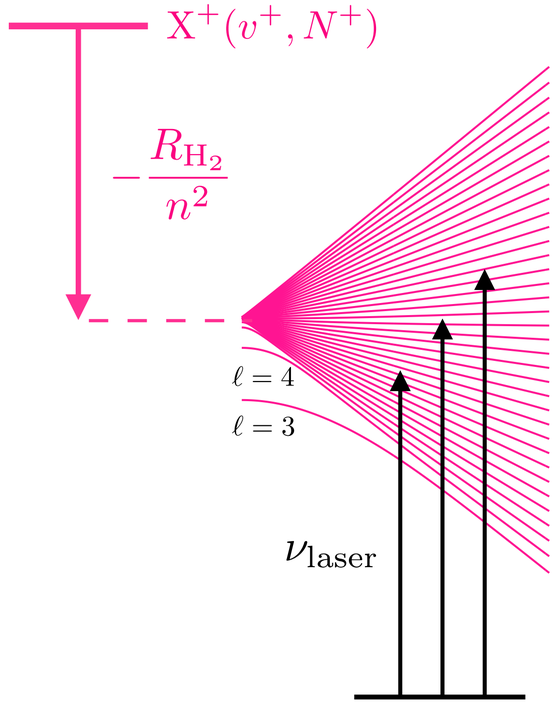
MQDT Extrapolation: low-*l* Rydberg series



External dc field

$\Delta\ell = \pm 1$

Zero-Quantum-Defect (ZQD) Method: Stark maps

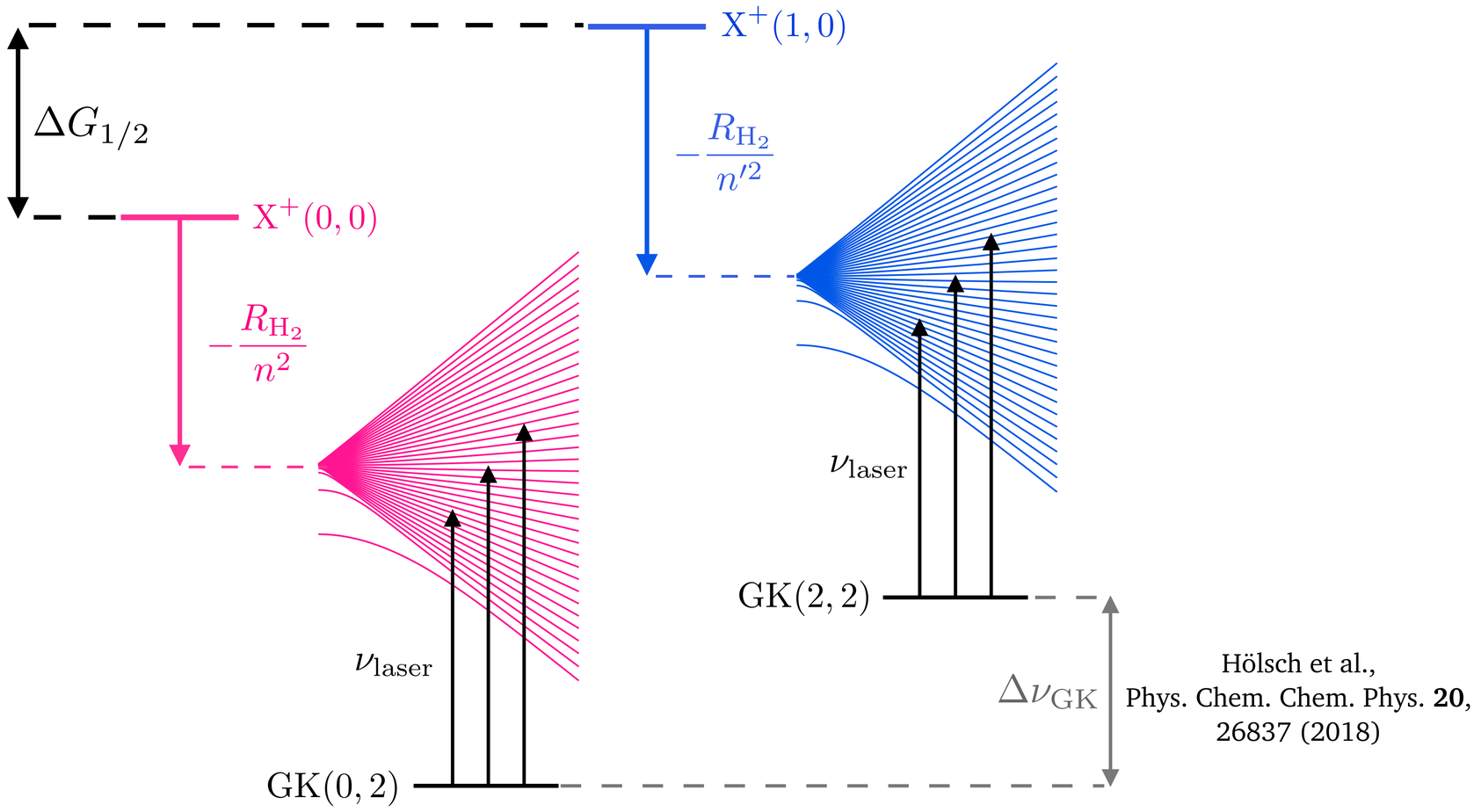


- Relies on the theoretical description of the optically accessible low-*l* Rydberg states

- Precise minimization of residual electric fields not necessary
- Uncertainties of the low-*l* quantum defects: smaller, indirect effect on manifold positions

Hölsch et al., J. Mol. Spectrosc. **387**, 111648 (2022)

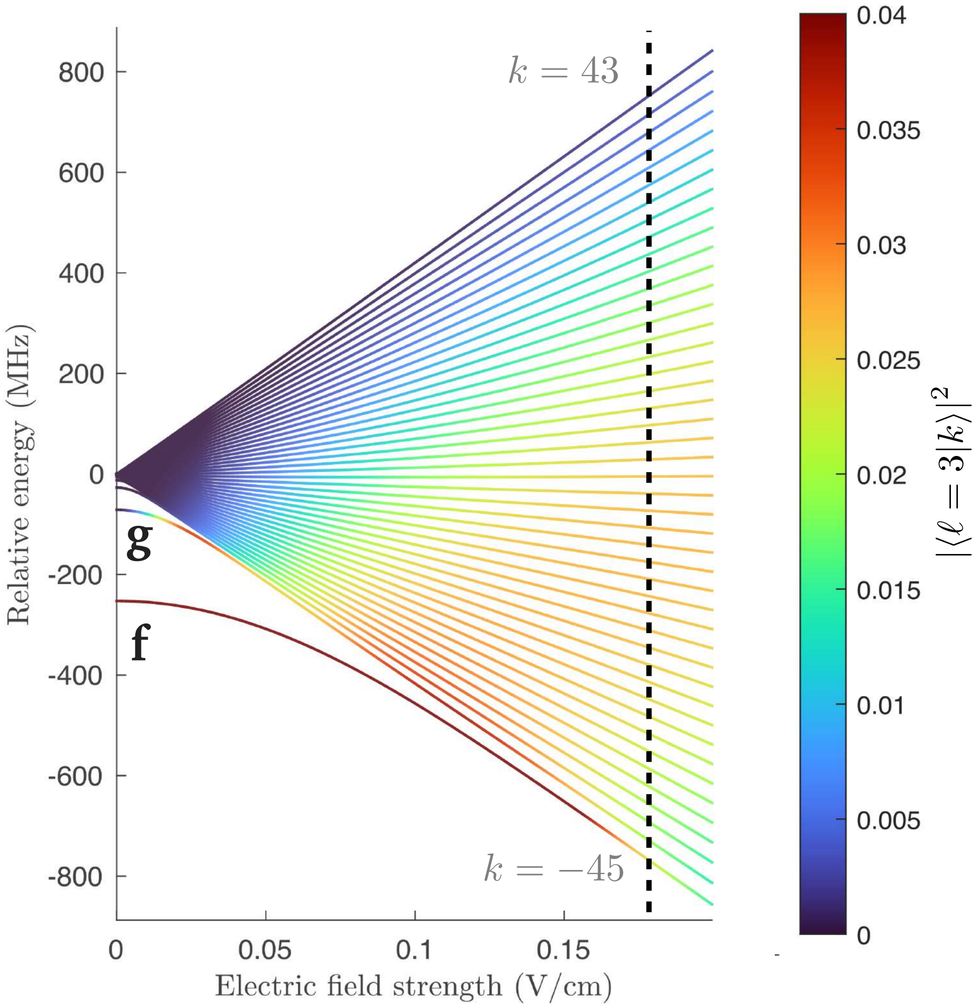
ZQD Method for the fundamental vibrational interval of H_2^+



Hölsch et al.,
Phys. Chem. Chem. Phys. **20**,
26837 (2018)

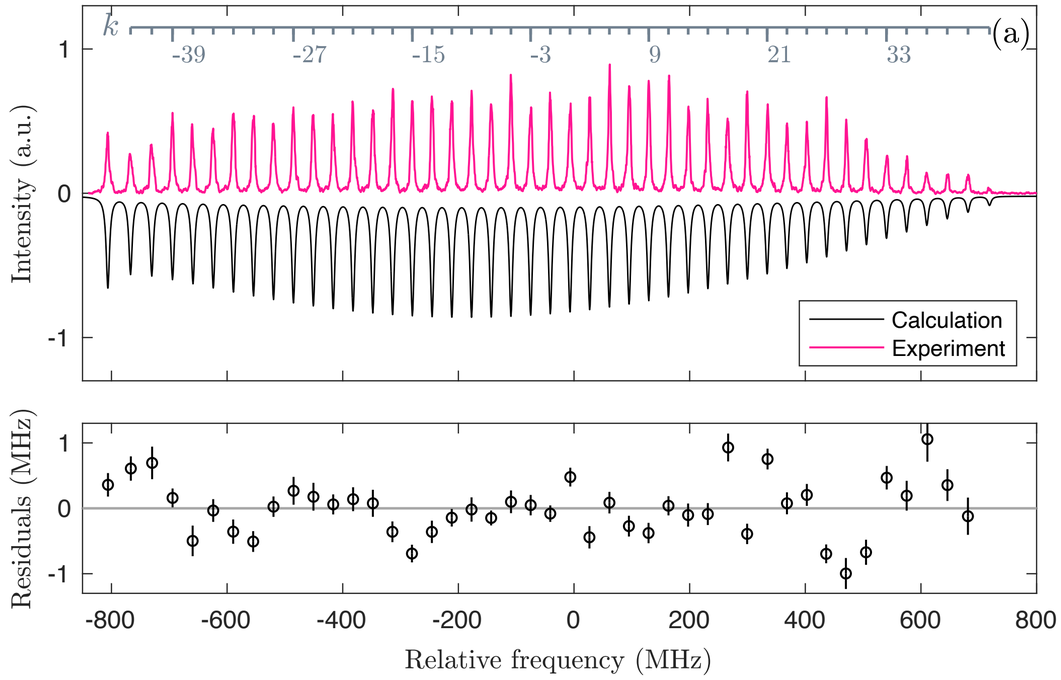
Stark spectra (v^+=0)

$$\hat{H} = \hat{H}_0 + eF\hat{z}$$



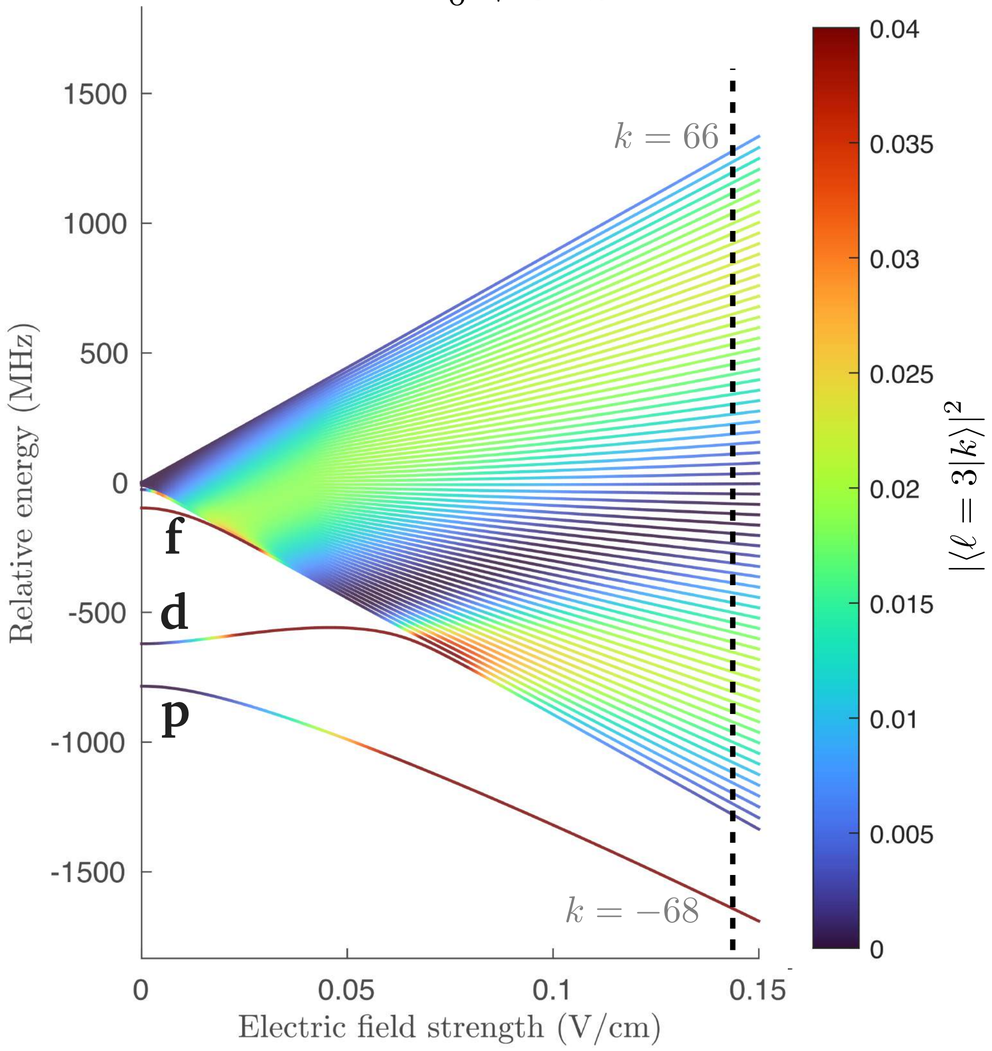
$$k = -(n-1-|m_\ell|) : 2 : (n-1-|m_\ell|)$$

$n = 48$ ($v^+ = 0$)



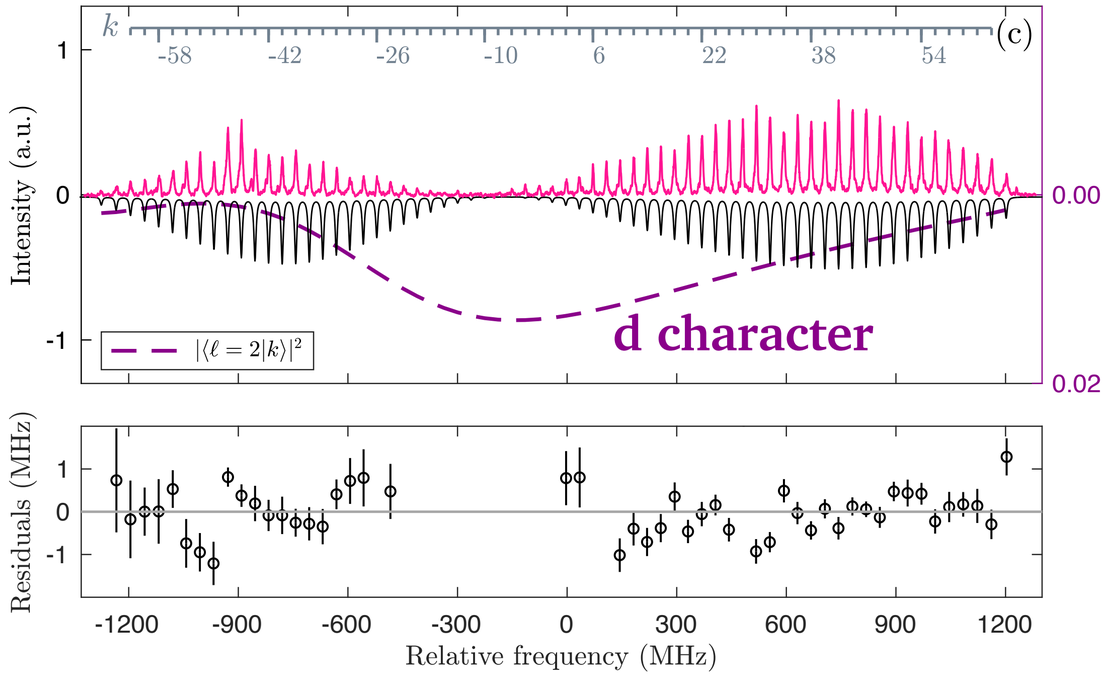
Stark spectra (ν^+=0)

$$\hat{H} = \hat{H}_0 + eF\hat{z}$$



$$k = -(n-1-|m_\ell|) : 2 : (n-1-|m_\ell|)$$

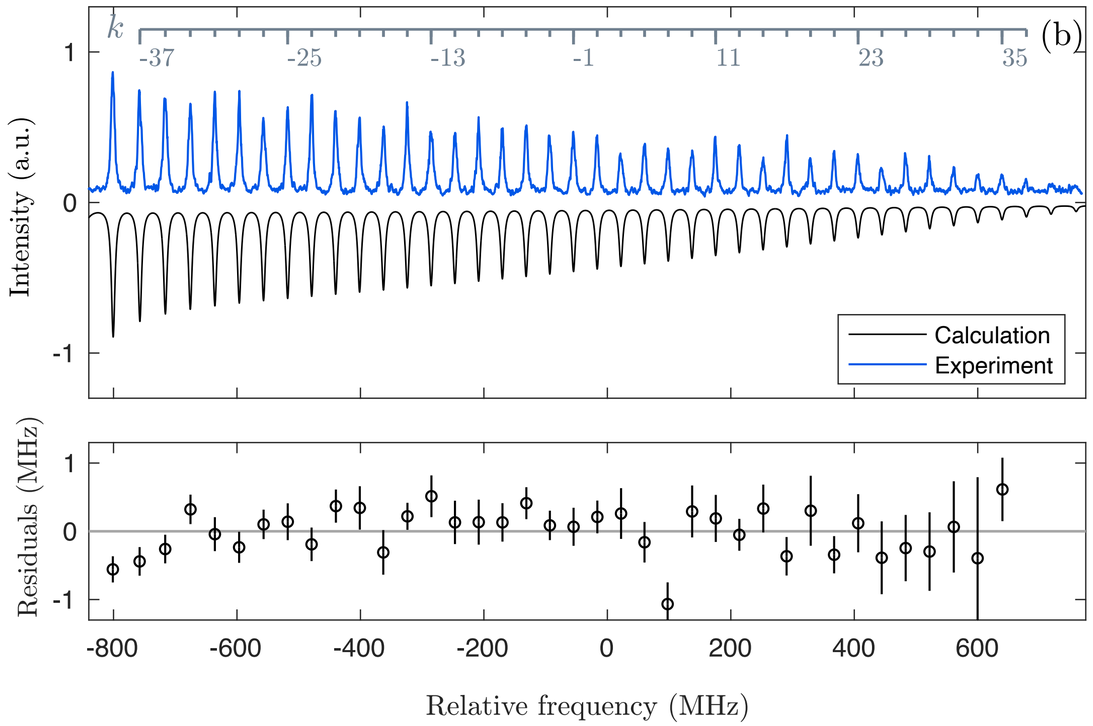
$n = 69$ ($\nu^+ = 0$)



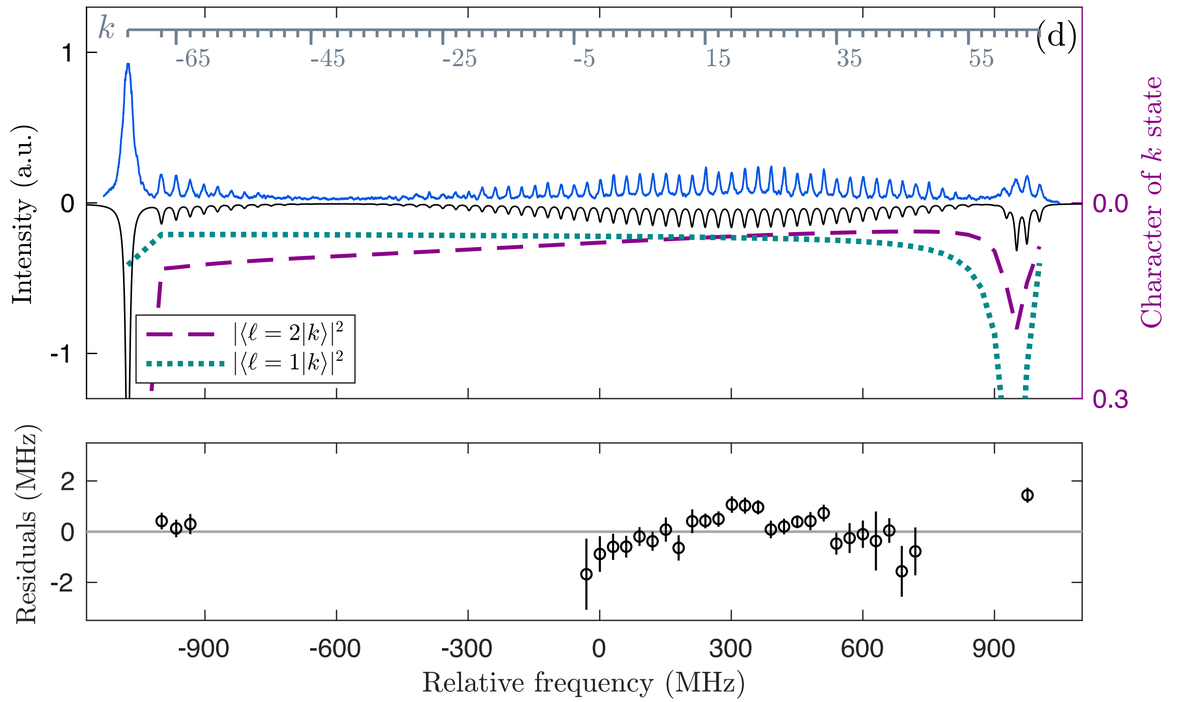
Stark spectra ($v^+=1$)

- Autoionization suppressed by mixing into the manifold of the high-l, non-penetrating states
- Linewidths of 7-8 MHz

$n = 46$ ($v^+ = 1$)

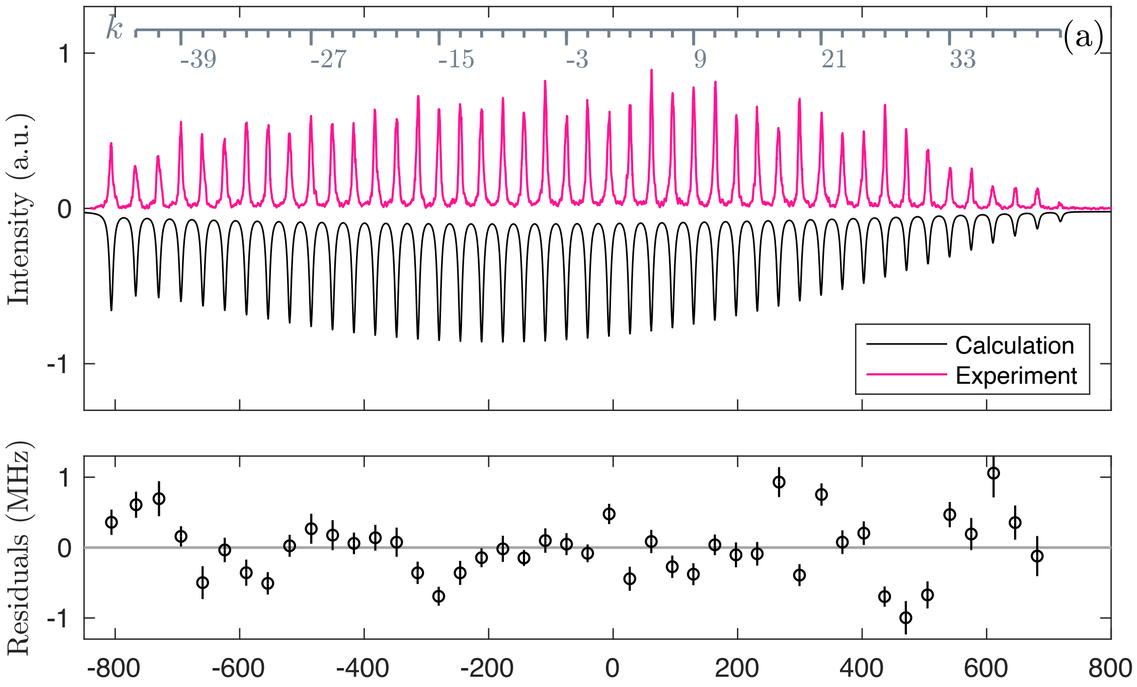


$n = 70$ ($v^+ = 1$)

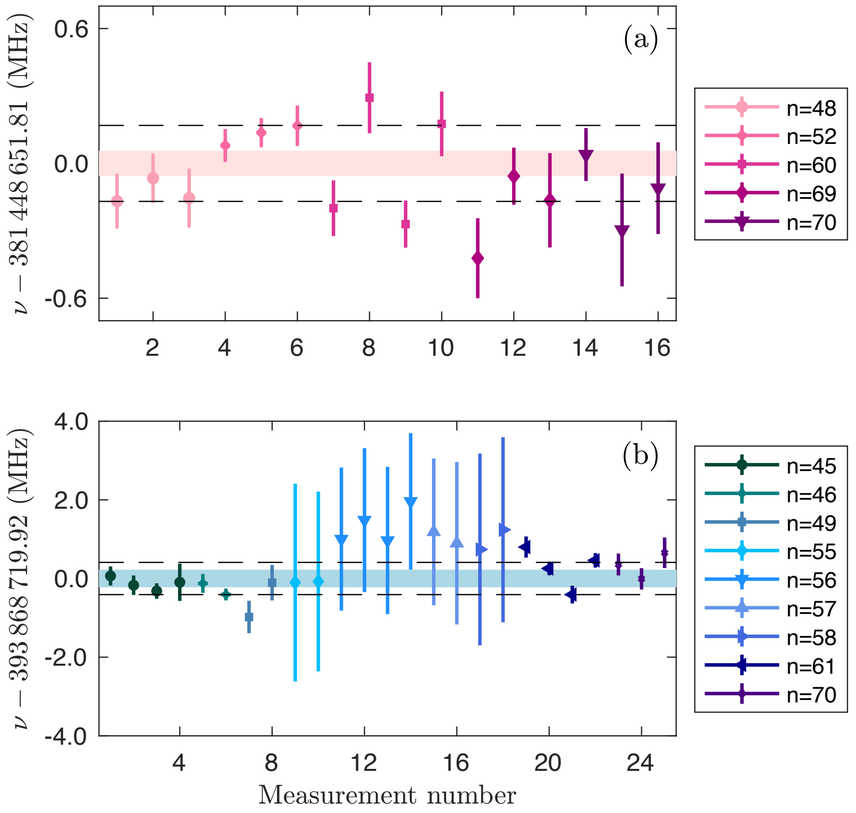


Determination of $E_{\mathrm{I}}(0,0)$ and $E_{\mathrm{I}}(1,0)$

Stark spectra: fit of line positions with 2 parameters:
E_{I} (ν^{+},0) and F_{z}



$\sigma_{\mathrm{ZQD}} < 500$ kHz



$(\nu^{+} = 0)$

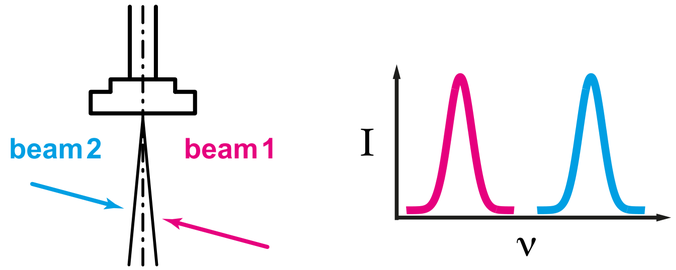
$(\nu^{+} = 1)$

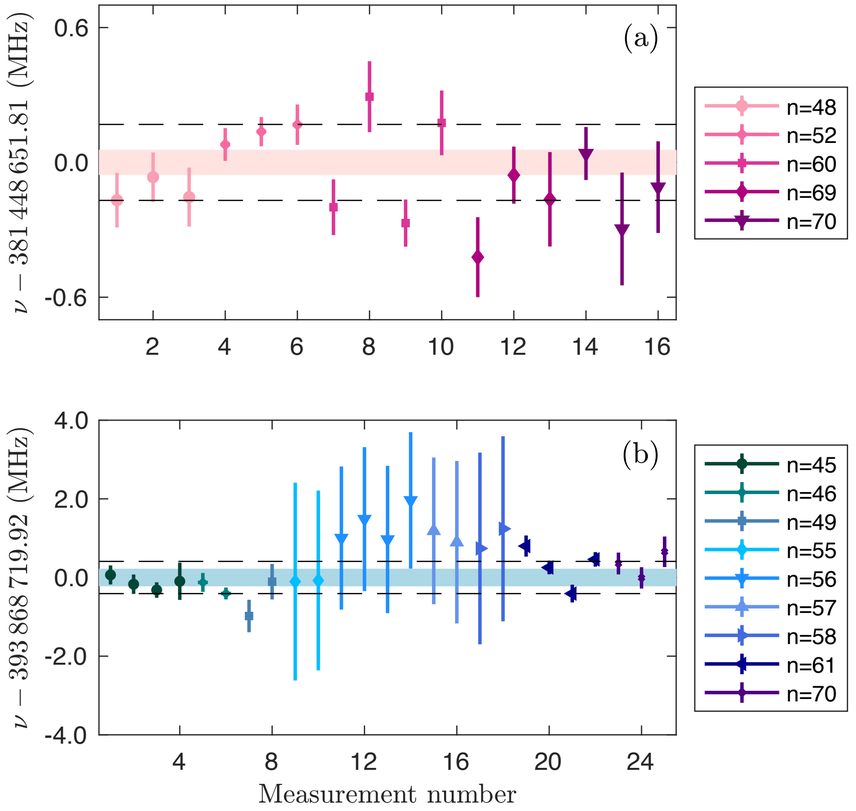
Determination of the fundamental vibrational interval in H_2^+

TABLE I. Error budget and frequency corrections for the determination of the binding energy of the GK(0,2) [GK(2,2)] state from the measurement of transitions to the Rydberg-Stark manifold for one value of n and one value of the electric field strength. All values and uncertainties are reported in kHz.

	$\Delta\nu$	σ_{stat}	σ_{sys}
Least-squares fit of ZQD method		<500[a]	
Residual 1st order Doppler shift			250[b]
Line-shape model			100(200)[c]
2nd order Doppler shift	+2		0.5
ac Stark shift			~5
Zeeman shift			~10
Pressure shift			~1
Photon-recoil shift	−160[d]		

[a]Dependent on the measurement.
[b]Averages out upon multiple realignments.
[c]For $v^+ = 0$ ($v^+ = 1$).
[d]Corresponds to $\tilde{\nu}_{\text{laser}} = 12\,701.365\ \text{cm}^{-1}$.

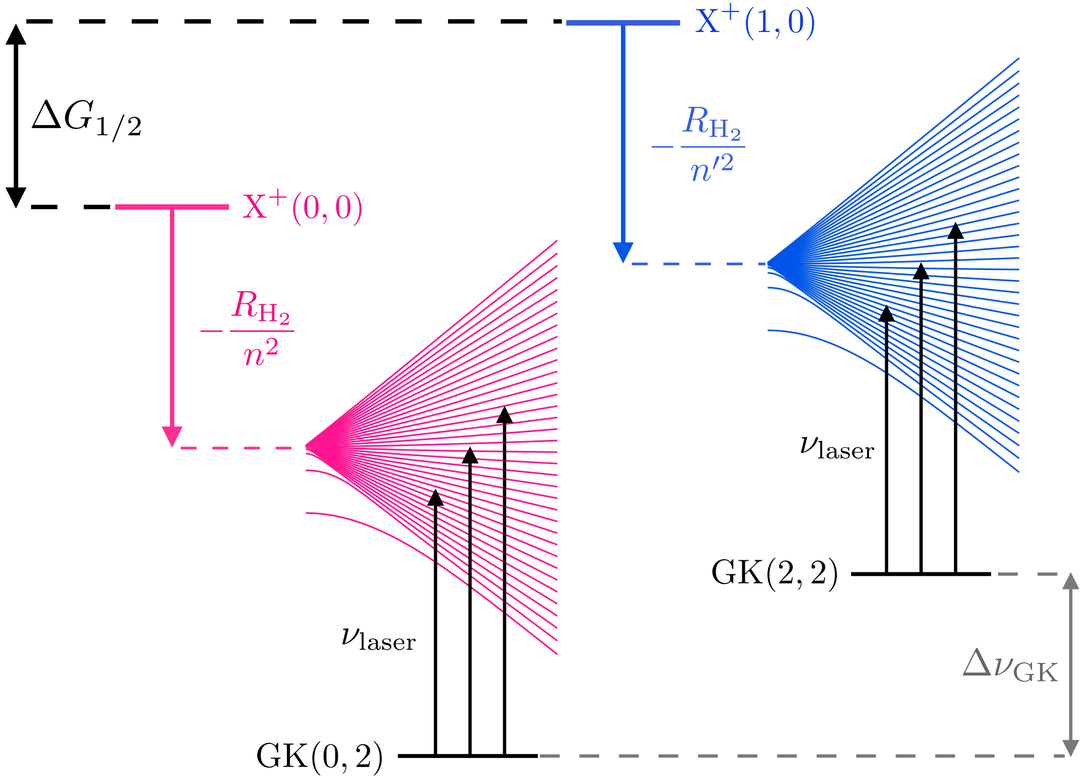




$(v^+ = 0)$

$(v^+ = 1)$

Determination of the fundamental vibrational interval in H_2^+



Doran et al., Phys. Rev. Lett. **132**, 073001 (2024)

Energy interval	Value (cm^{-1})	Ref.
$X^+(0,0) - GK(0,2)$	$12\,723.757\,440\,7(18)_{stat}(40)_{sys}$	This Letter
$X^+(0,0) - GK(0,2)$	$12\,723.757\,461(23)$	[1]
$X^+(1,0) - GK(2,2)$	$13\,138.046\,319(5)_{stat}(8)_{sys}$	This Letter
$GK(2,2) - GK(0,2)$	$1776.837\,736\,1(14)$	[2]
$X^+(1,0) - X^+(0,0)$	$2191.126\,614(5)_{stat}(12)_{sys}$	This Letter
$X^+(1,0) - X^+(0,0)$	$2191.2(2)$	[3]
$X^+(1,0) - X^+(0,0)$	$2191.126\,626\,344(17)(100)^a$	[4]

[1] Beyer et al., Phys. Rev. Lett. **123**, 163002 (2019)

[2] Hölsch et al., Phys. Chem. Chem. Phys. **20**, 26837 (2018)

[3] Herzberg and Jungen, J. Mol. Spectrosc. **41**, 425 (1972)

[4] Korobov et al., Phys. Rev. Lett. **118**, 233001 (2017)

Determination of the fundamental vibrational interval in H_2^+

nature physics

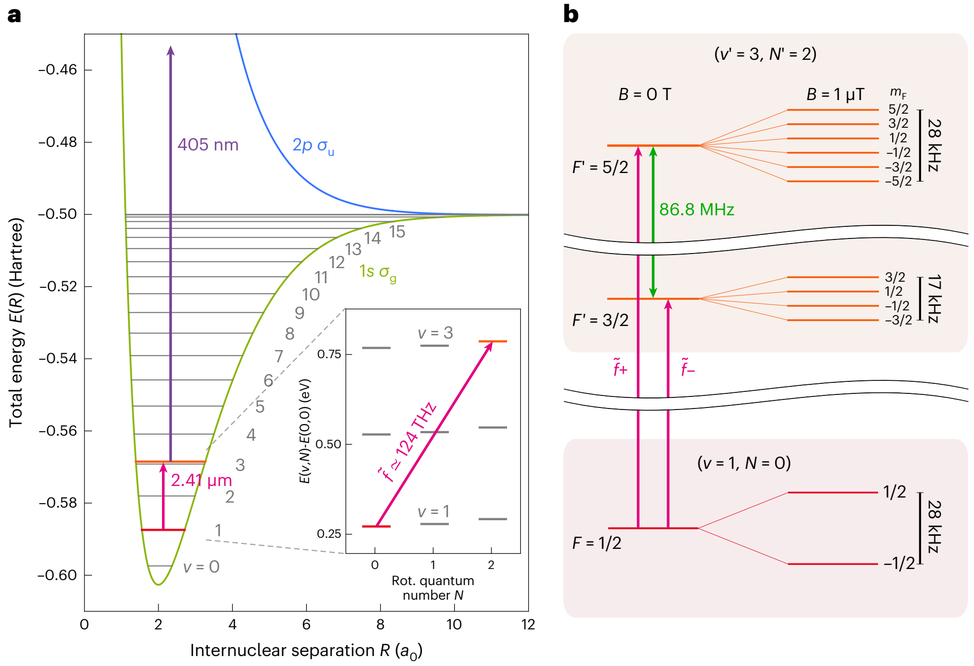
Article

https://doi.org/10.1038/s41567-023-02320-z

Laser spectroscopy of a rovibrational transition in the molecular hydrogen ion H_2^+

M. Schenkel, S. Alighanbari and S. Schiller

Nature Physics **20**, 383-388 (2024)

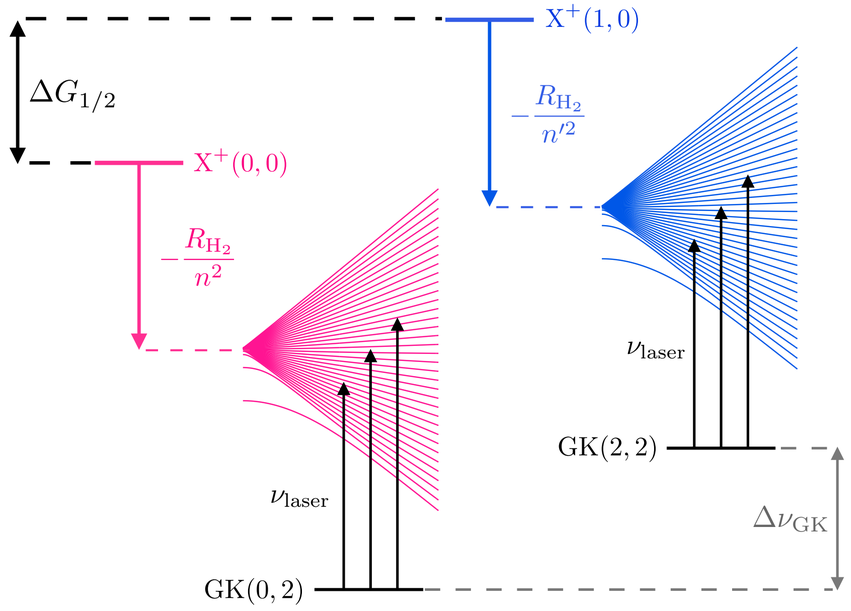


Exp.: 124’487’032.7(1.5) MHz

Th.: 124’487’032.45(6) MHz (Korobov et al., PRL **118**, 233001 (2017))

Zero-Quantum-Defect Method and the Fundamental Vibrational Interval of H_2^+

I. Doran,[1] N. Hölsch,[1] M. Beyer,[2] and F. Merkt[1,3,4,*]

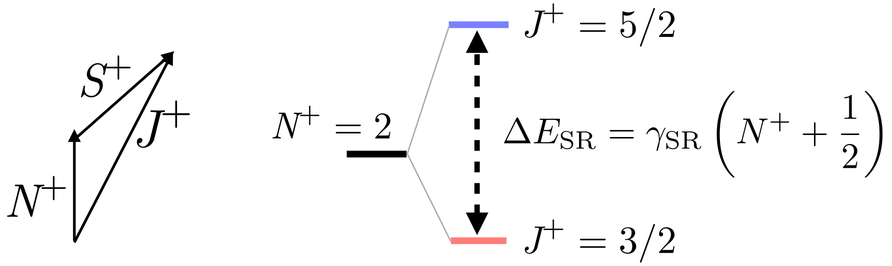


Exp.: 65’688’323.3(0.5) MHz

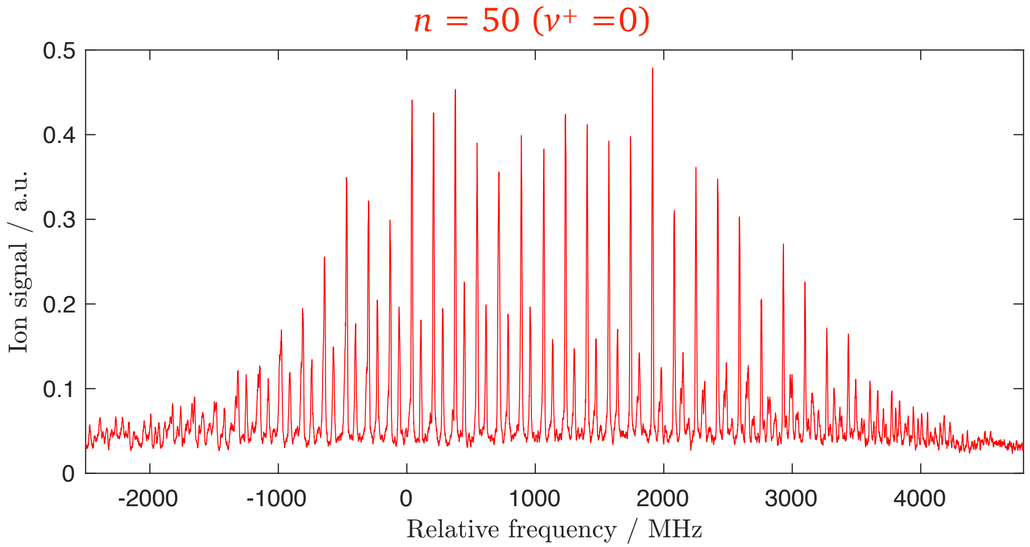
Th.: 65’688’323.7101(5)(29) MHz (Korobov et al., PRL **118**, 233001 (2017))

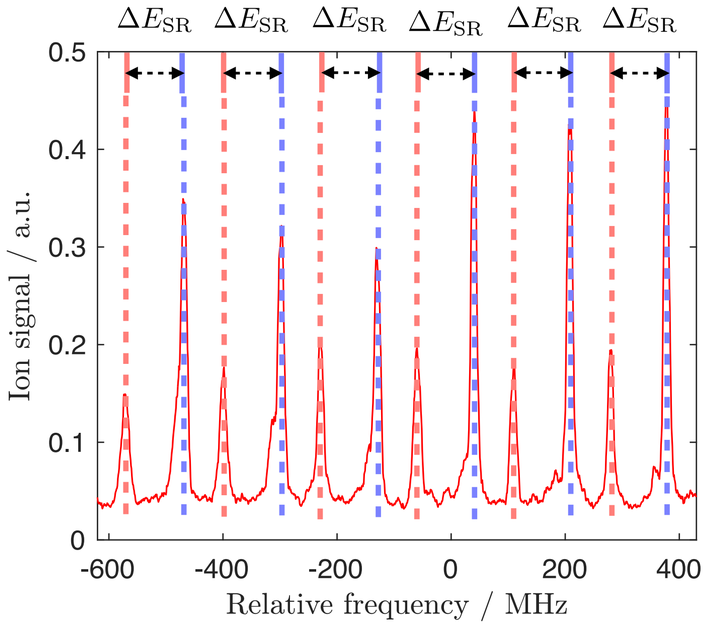
ZQD Method: Further applications

The spin-rotational interval of para-H_2^+:



Th.:Korobov et al., Phys. Rev. A 74, 040502 (R) (2006)





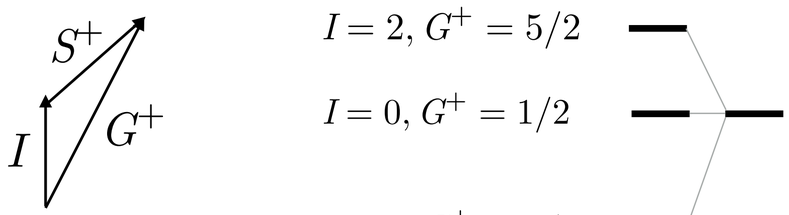
Current status — MQDT Extrapolation f series

N^+	γ_{SR} (MHz) (This work)	γ_{SR} (MHz) (Korobov et al., 2006)
2	42.21(4)	42.1625 ✓
4	41.26(8)	41.2942 ✓
6	40.04(8)	39.99 * ✓

I. Doran, M. Beyer, F. Merkt, unpublished

**using McEachran et al., 1978*

The hyperfine structure of ortho-D_2^+:

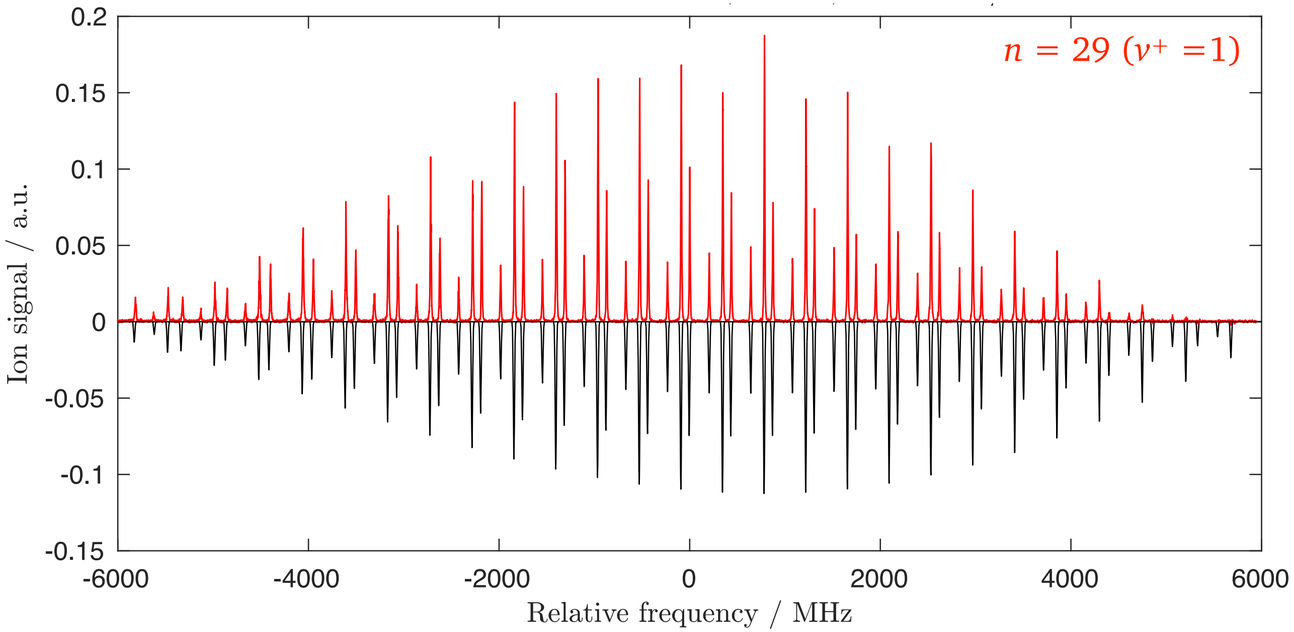


$I = 2, G^+ = 5/2$

$I = 0, G^+ = 1/2$

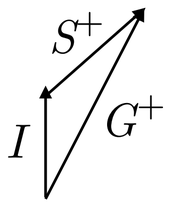
$I = 2, G^+ = 3/2$

Th.:Danev et al., Phys. Rev. A 103, 012805 (2021)



Work done together with Leon Jeckel

The hyperfine structure of ortho-D_2^+:

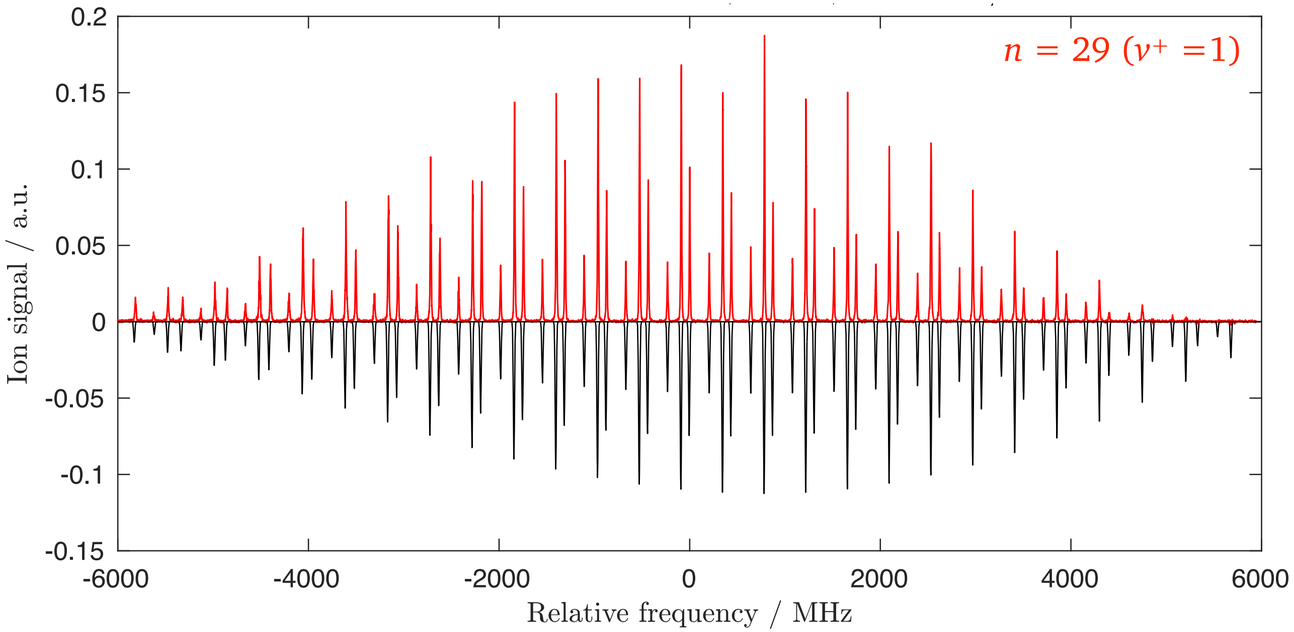


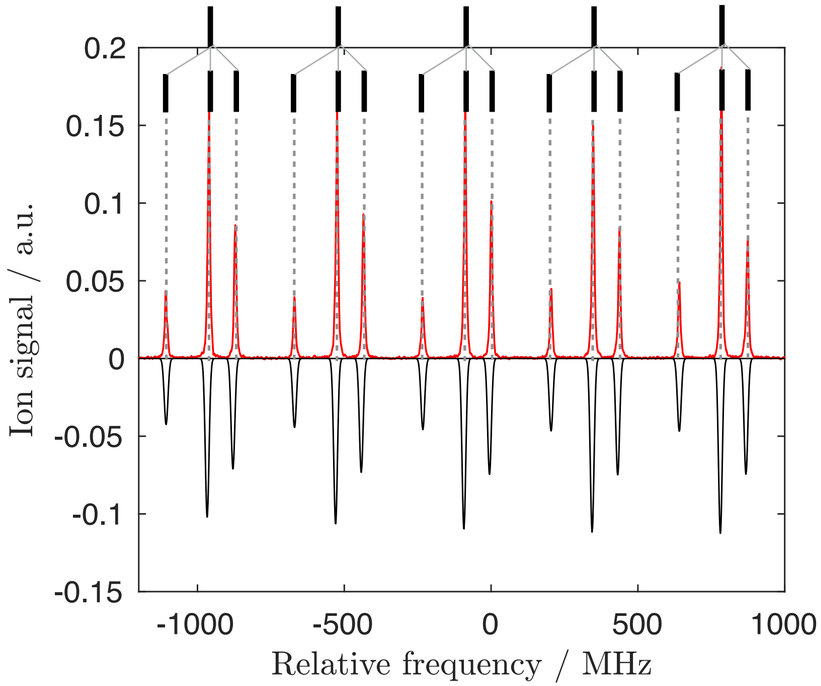
$I = 2, G^+ = 5/2$

$I = 0, G^+ = 1/2$

$I = 2, G^+ = 3/2$

Th.:Danev et al., Phys. Rev. A 103, 012805 (2021)





Work done together with Leon Jeckel

Thank you for your attention!

The Merkt group

Special thanks:

- Dr. Nicolas Hölsch
- Leon Jeckel
- Josef Agner
- Hansjürg Schmutz

Calculation of Stark Maps without Spins: Summary

para-H_2:

$I = 0$ (no nuclear spin)

$S = 0$ (only access singlet states)

Summary: para-H_2, $N^+ = 0$

$$\hat{H} = \hat{H}_0 + eFz$$

1) Build Hamiltonian matrix in a basis set of choice *here, Hund's case (d): $|nlN^+_{N,M_N}\rangle$

2) Diagonal elements ($\hat{H}_0$) $\Longrightarrow$
- low-l states: MQDT (l up to 5)
- high-l states: polarization model (ab initio, no channel interactions)

3) Off-diagonal elements (eFz)

$$\langle nlN^+_{N,M_N}|eFz|n'l'N'^+_{N'M_{N'}}\rangle = eF(-1)^{N-M_N+l+N^++N'+1}\sqrt{(2N+1)(2N'+1)} \times \begin{pmatrix} N & 1 & N' \\ -M_N & 0 & M_N \end{pmatrix} \begin{Bmatrix} l & N & N^+ \\ N' & l' & 1 \end{Bmatrix} \langle nl||r||n'l'\rangle\, \delta_{N^+N^{+\prime}}$$

$\langle nl||r||n'l'\rangle$

↕ (Wigner-Eckart theorem)

$\langle nl|r|n'l'\rangle$ (Numerov algorithm)

4) Diagonalize the Hamiltonian matrix at each value of electric field

$$\mathbf{N} = \mathbf{N}^+ + \ell$$

$\mathbf{N}^+$: Rotational angular momentum of ion core

ℓ : Orbital angular momentum of Rydberg electron

$\mathbf{N}$: Total angular momentum excluding spin

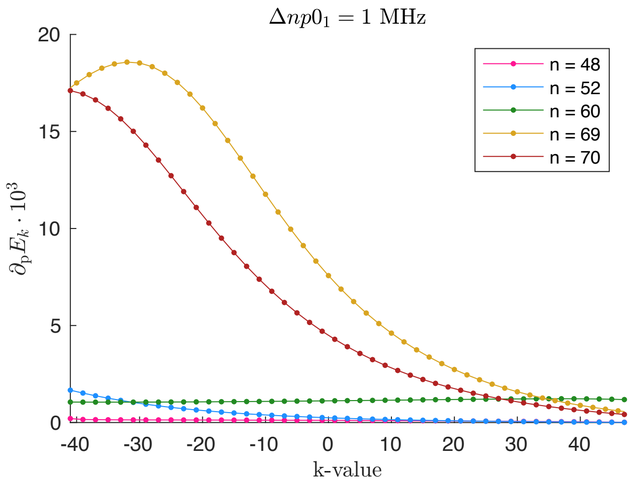
Laser Stark maps at $\nu^+ = 0$ (para-H_2)

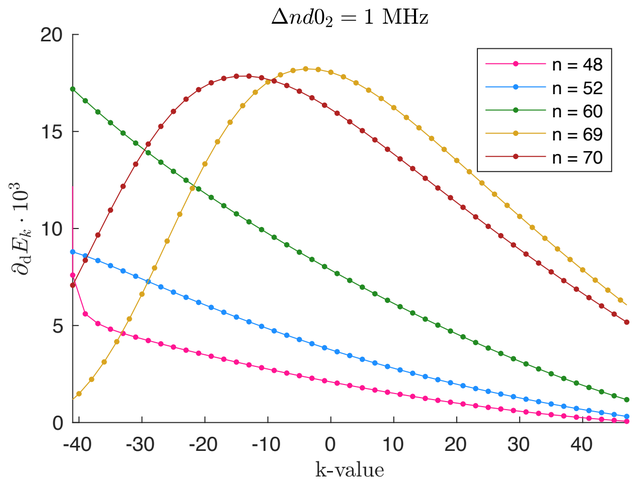
$n = n_1 + n_2 + |m| + 1$

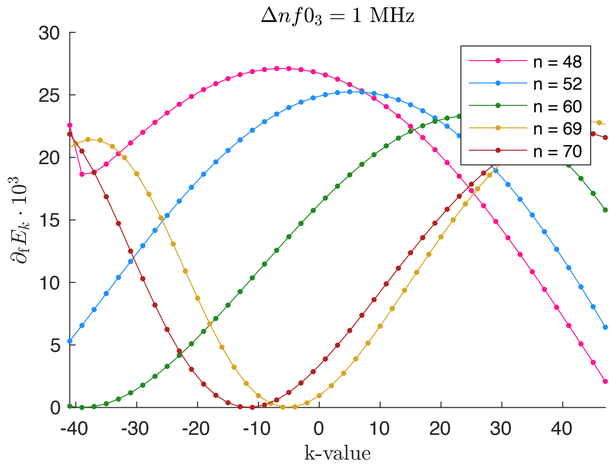
$k = n_1 - n_2$

Sensitivity analysis: Effect on manifold of shifting the low-l states positions by 1 MHz w.r.t. MQDT-predicted values

$$E_{nn_1n_2m} = -\frac{E_\mathrm{h}}{2n^2} + \frac{3}{2}nkFea_0 \text{ => } \Delta E_{n,|\Delta k|=1} \propto nF$$





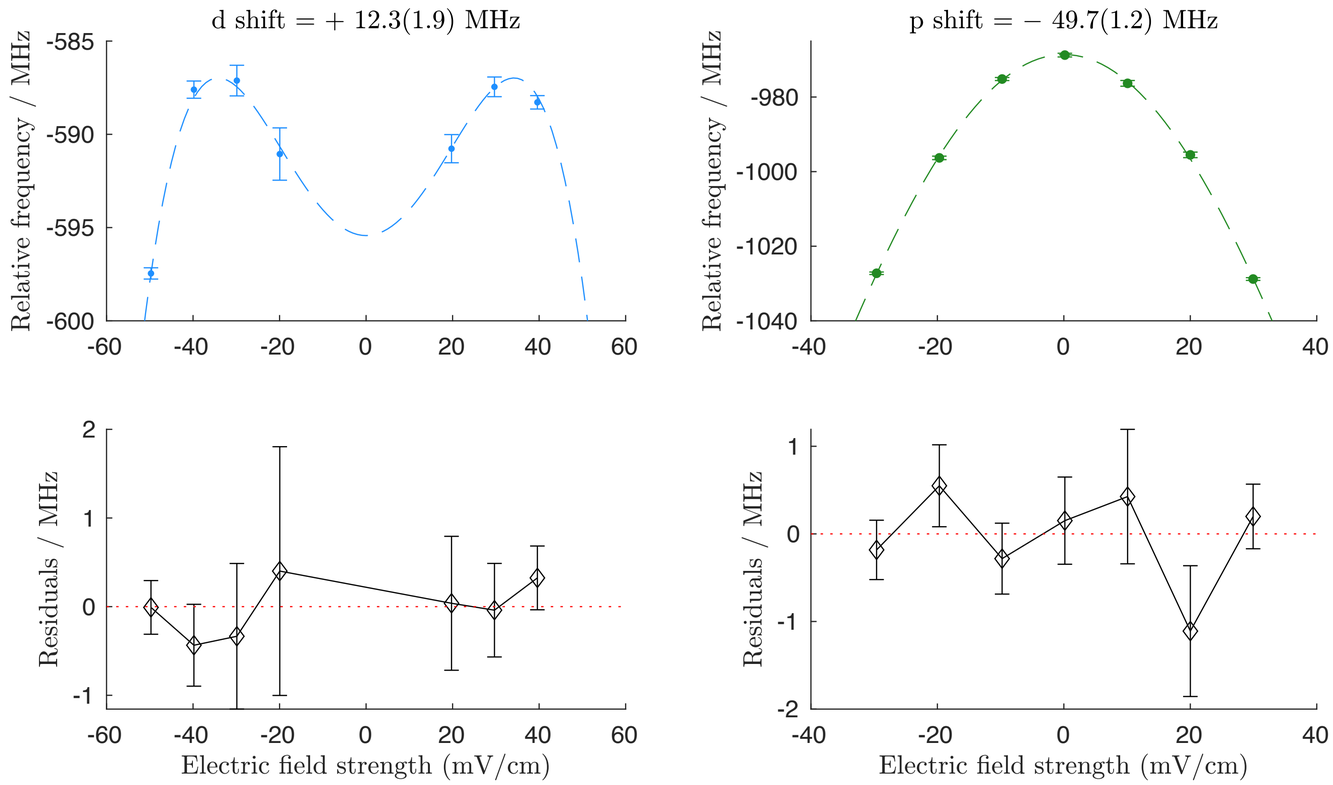


$n'\ell N_N^+(M_N)$	$\Delta_{\text{e-c}}$(MHz)	
$n\mathrm{p}0_1(0)$	5 MHz	✓
$n\mathrm{d}0_2(0)$	5 MHz	Estimated MQDT precision worse!
$n\mathrm{f}0_3(0)$	3 MHz	✓

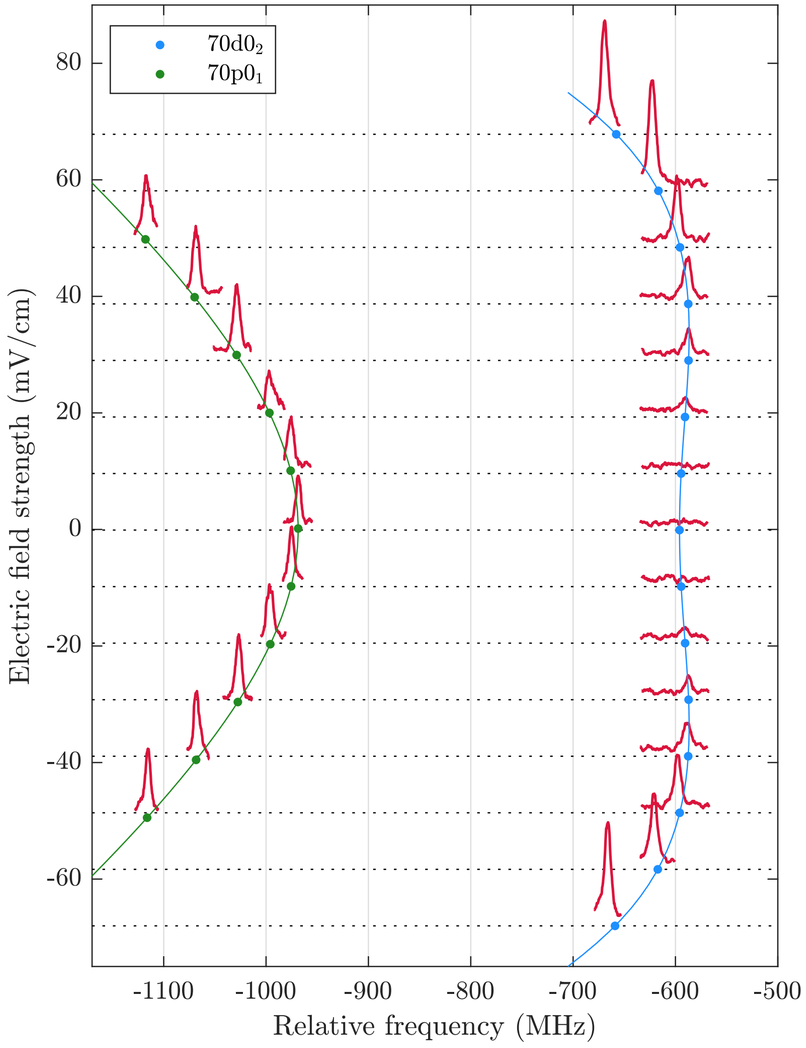
Need to determine binding energies of $nd0_2$ (and $70p0_1$) states experimentally!

Laser Stark maps at $v^+ = 0$ (para-H_2)

$$\Delta\nu(F) = a_0 + a_2\,F^2 + a_4\,F^4$$

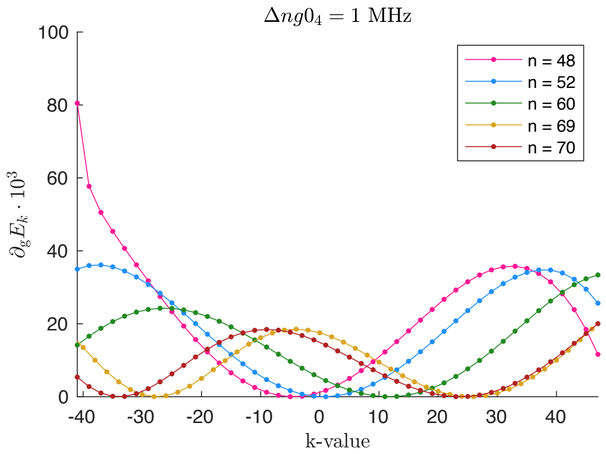


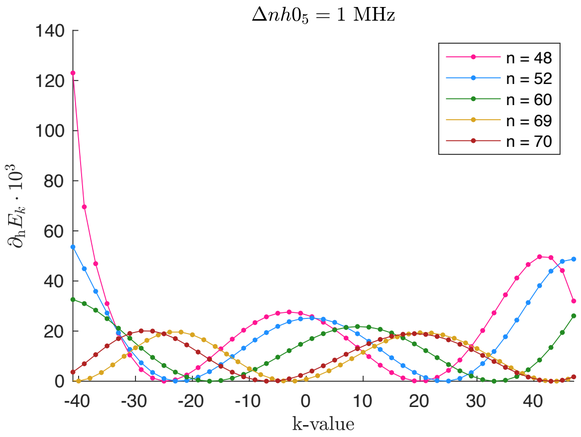
$n'\ell N_N^+(M_N)$	$\Delta E^0/h$ (MHz)	$\Delta_{\text{e-c}}$(MHz)	a_2 (MHz mV^{-2} cm^2)	a_4 (MHz mV^{-4} cm^4)
70d0_2(0)	−596.0(1.9)	+12.3	$+1.4(3)\times10^{-2}$	$-6.2(8)\times10^{-6}$
70p0_1(0)	−968.6(1.3)	−49.7	$-7.2(8)\times10^{-2}$	$6(8)\times10^{-6}$



Laser Stark maps at $\nu^+ = 0$ (para-H_2)

Sensitivity analysis: Effect on manifold of shifting the low-l states positions by 1 MHz w.r.t. MQDT-predicted values





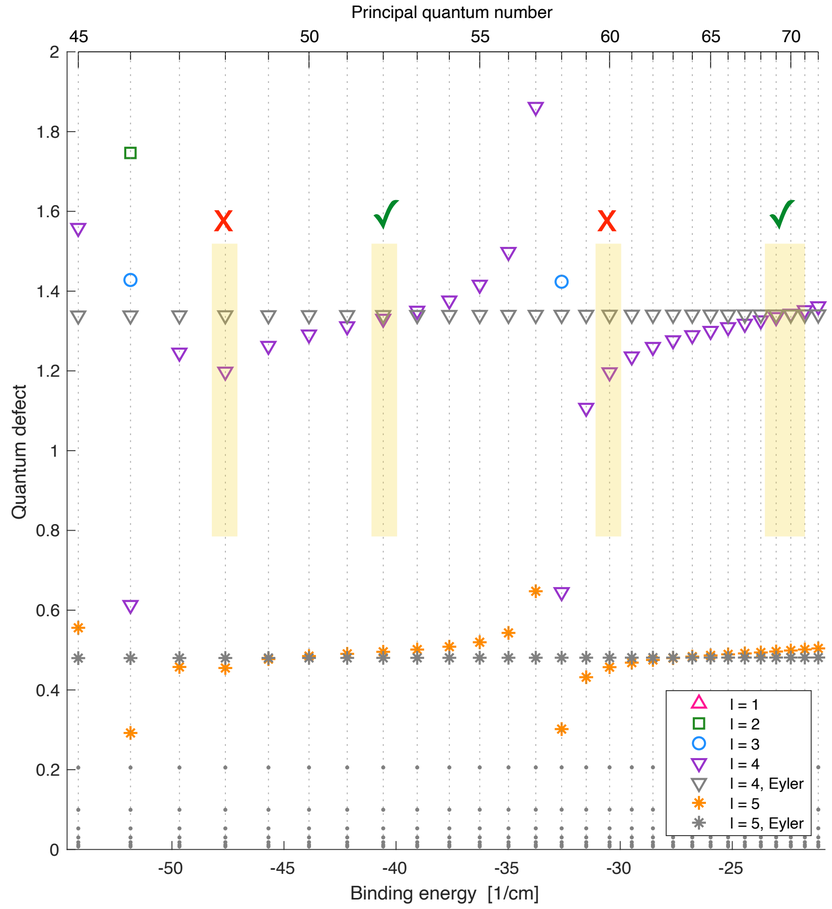
n	$\delta\mu_g/\mu_g$	$\delta\mu_h/\mu_h$
48	0.03	0.07
52	0.03	0.09
60	0.05	0.14
69	0.07	0.20
70	0.08	0.21

✓

Estimated error of quantum defects < 10%

$$\delta\varepsilon_{\mathrm{bind}}/(hc) \approx \frac{2R}{n^3}\delta\mu$$

=> Expect more significant effect at n = 48 — to be quantified



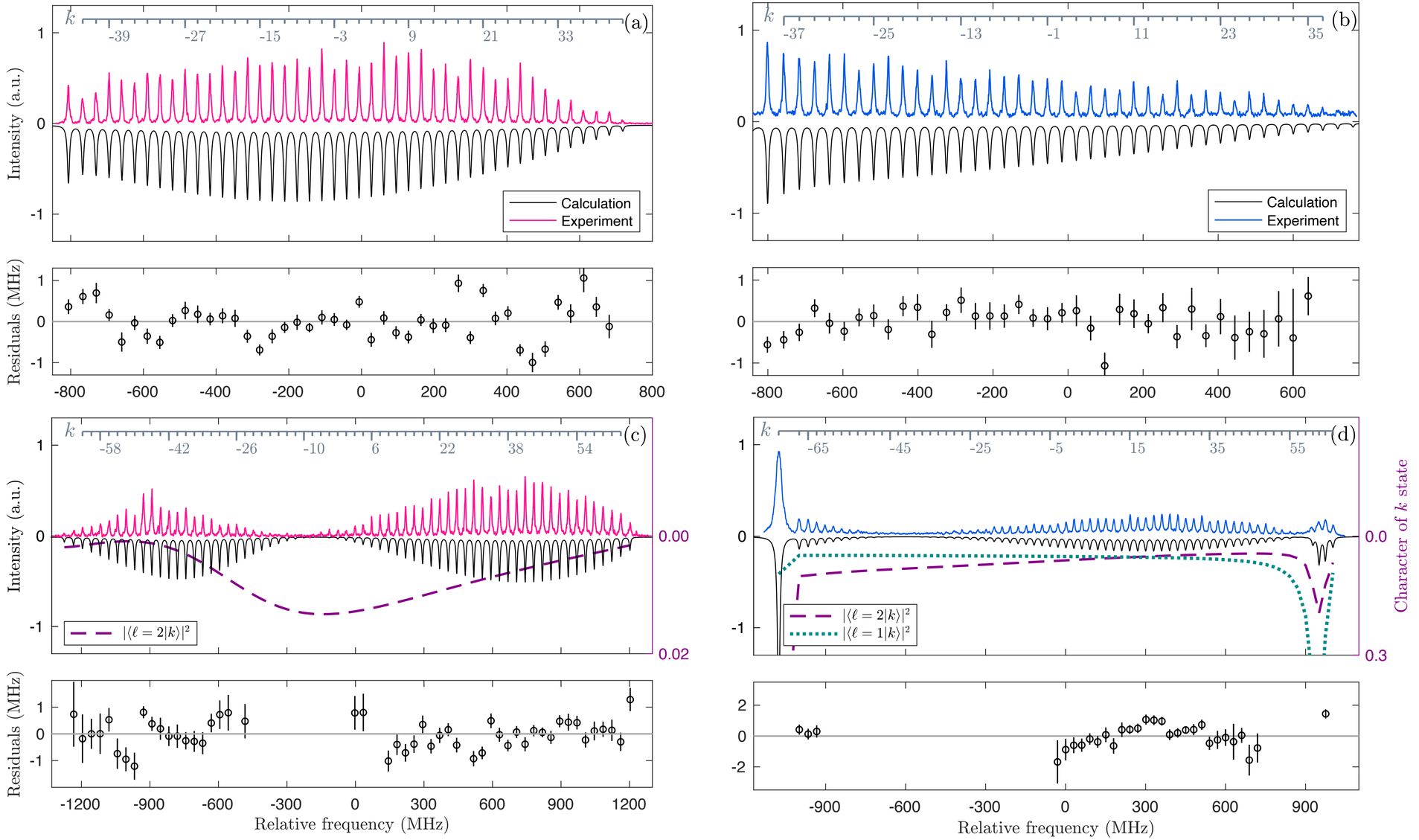
Stark spectra

$n = 48$
$(v^+ = 0)$

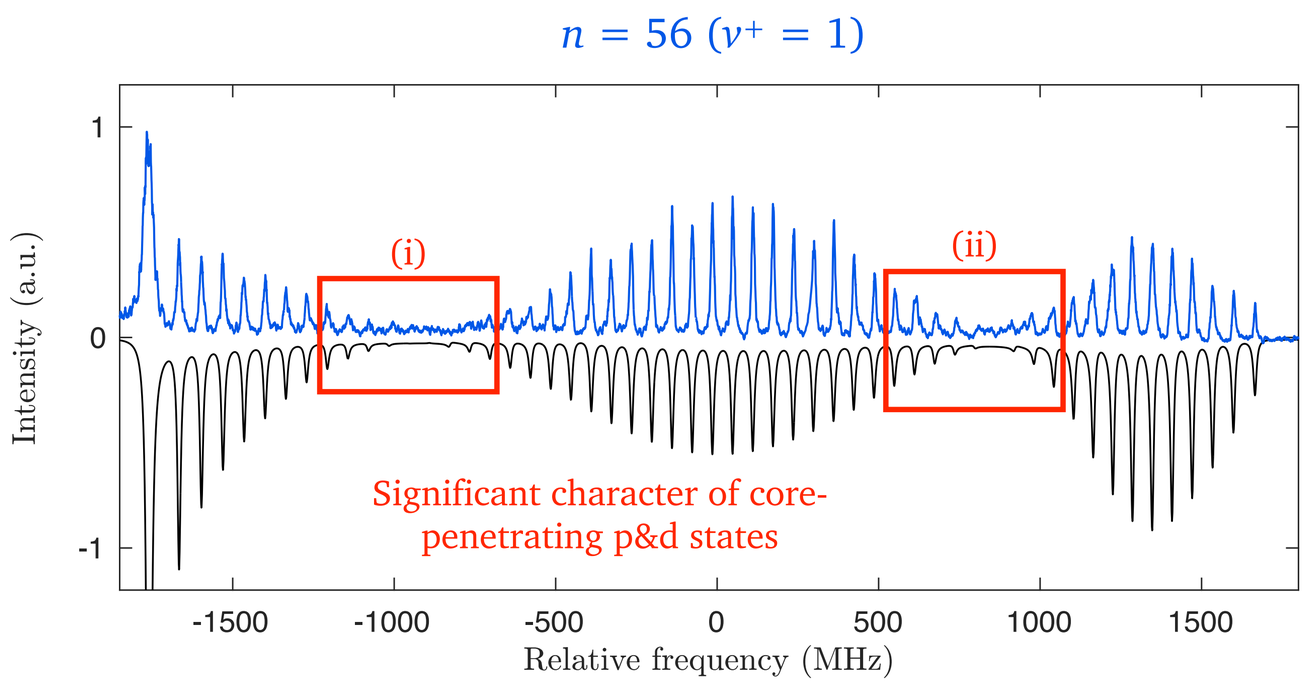
$n = 46$
$(v^+ = 1)$

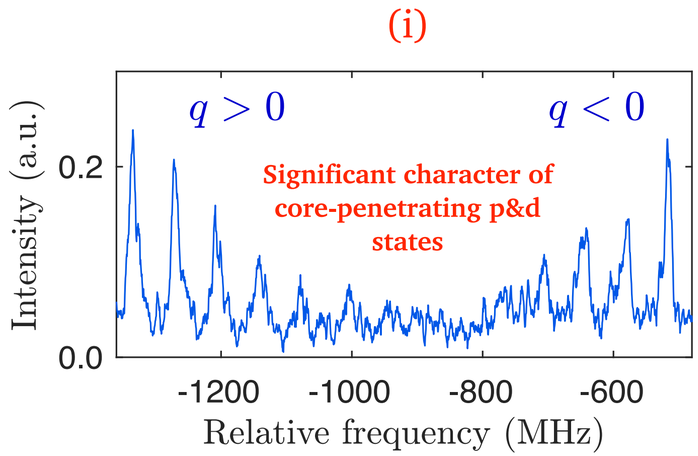
$n = 69$
$(v^+ = 0)$

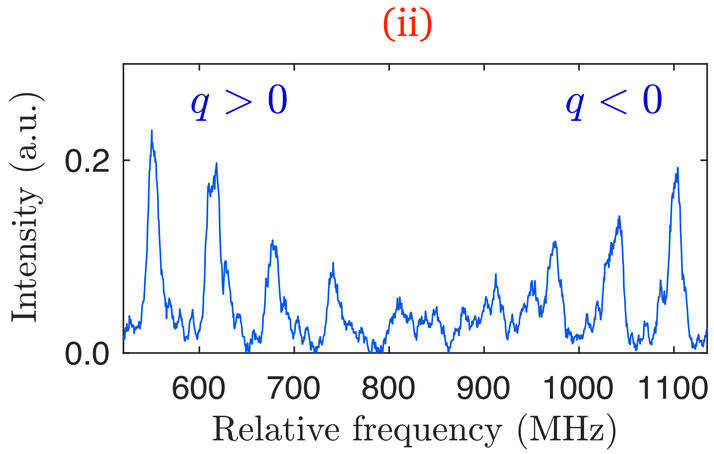
$n = 70$
$(v^+ = 1)$



Fano profiles ($v^+=1$) & q-reversal







- Line broadening (core-penetrating, autoionizing character)
- Fano lineshapes (interaction with continuum)
- q-reversal

Fano lineshape: one closed + one open channel

Effects of Configuration Interaction on Intensities and Phase Shifts*

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(Received July 14, 1961)

The interference of a discrete autoionized state with a continuum gives rise to characteristically asymmetric peaks in excitation spectra. The earlier qualitative interpretation of this phenomenon is extended and revised. A theoretical formula is fitted to the shape of the $2s2p\ ^1P$ resonance of He observed in the inelastic scattering of electrons. The fitting determines the parameters of the $2s2p\ ^1P$ resonance as follows: $E=60.1$ ev, $\Gamma\sim0.04$ ev, $f\sim2$ to 4×10^{-3}. The theory is extended to the interaction of one discrete level with two or more continua and of a set of discrete levels with one continuum. The theory can also give the position and intensity shifts produced in a Rydberg series of discrete levels by interaction with a level of another configuration. The connection with the nuclear theory of resonance scattering is indicated.

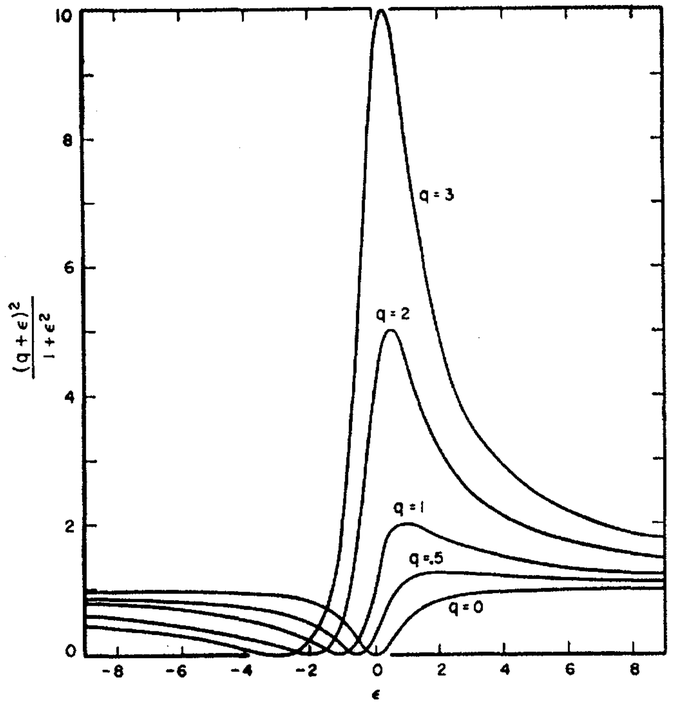


FIG. 1. Natural line shapes for different values of q. (Reverse the scale of abscissas for negative q.)

Cause of asymmetry:

Destructive interference between transition moments from the initial state to i) the **discrete contribution** to the final state
ii) the **continuum contribution** to the final state

=> transition probability vanishes on one side of the resonance.

Fano profiles ($v^+=1$) & q-reversal

***q*-reversal:** at least two closed + one open channel

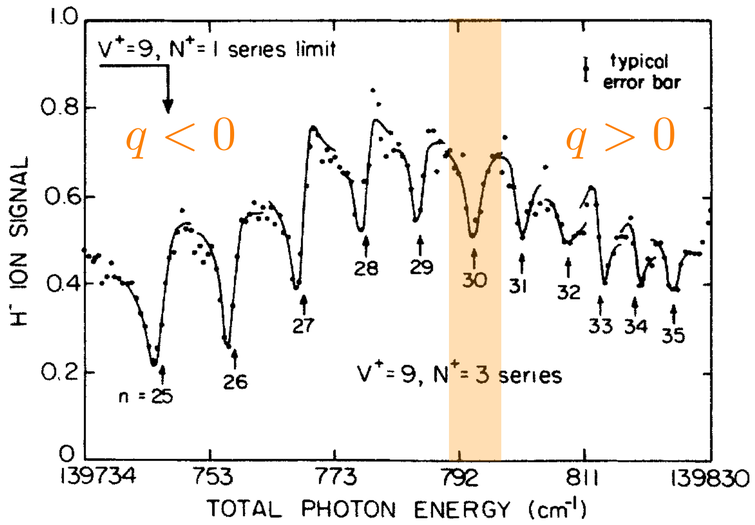
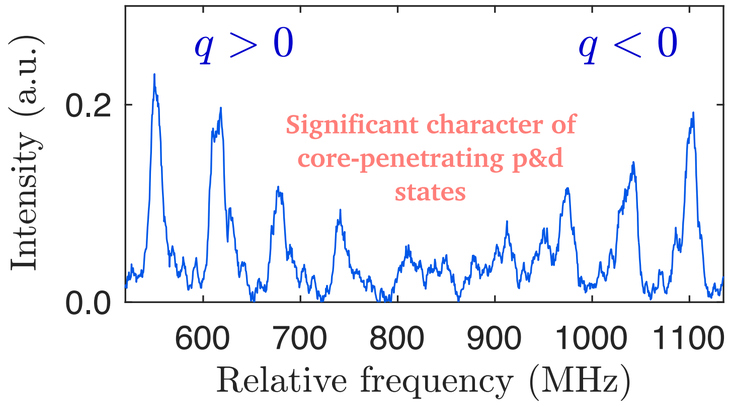


FIG. 3. Expanded ion-pair-production spectrum of H_2 between the $N^+=1$ and $N^+=3$ series limits showing the fitted Fano line profiles: Solid curves, calculated profile; circles, experimental points; and arrows, fitted line center positions.

Kung et al., 1986: First observation of q-reversal in H_2

<u>In our case:</u>



<u>Interacting channels:</u>

(i) the Rydberg-Stark states with predominantly high- ℓ character that are only very weakly coupled to the $v^+=0$ continua,

(ii) the low-ℓ states that are strongly coupled to both the high-ℓ Rydberg-Stark states and the $v^+=0$ continua, and

(iii) the $v^+=0$ continua

Doppler shift compensation

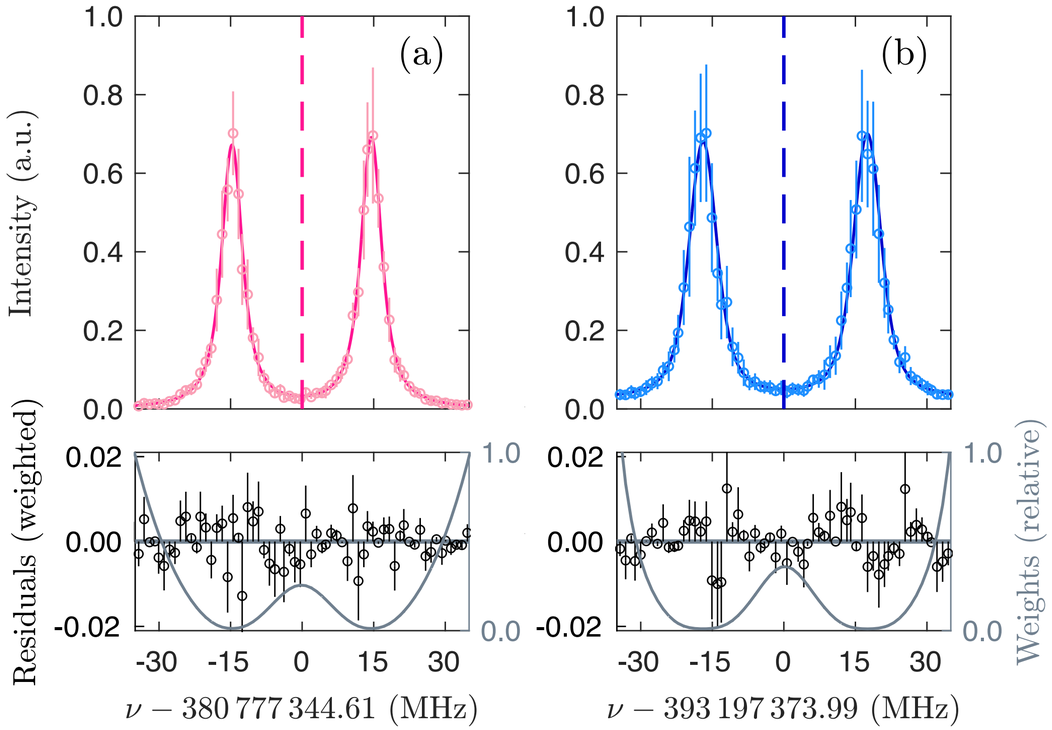


Figure 2. Upper panels: spectra of the $70f0_3$ (v^+=0) ← GK(0,2) (a) and $70f0_3$ (v^+=1) ← GK(2,2) (b) transitions (dots) and fits using a Voigt line-shape model (solid lines). The vertical dashed lines indicate the Doppler-free transition frequencies. Lower panels: weighted residuals and their corresponding relative weights (gray traces).