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High-Resolution Spectroscopy of He_2^+ Using Rydberg-Series Extrapolation and Zeeman-Decelerated Supersonic Beams of He_2

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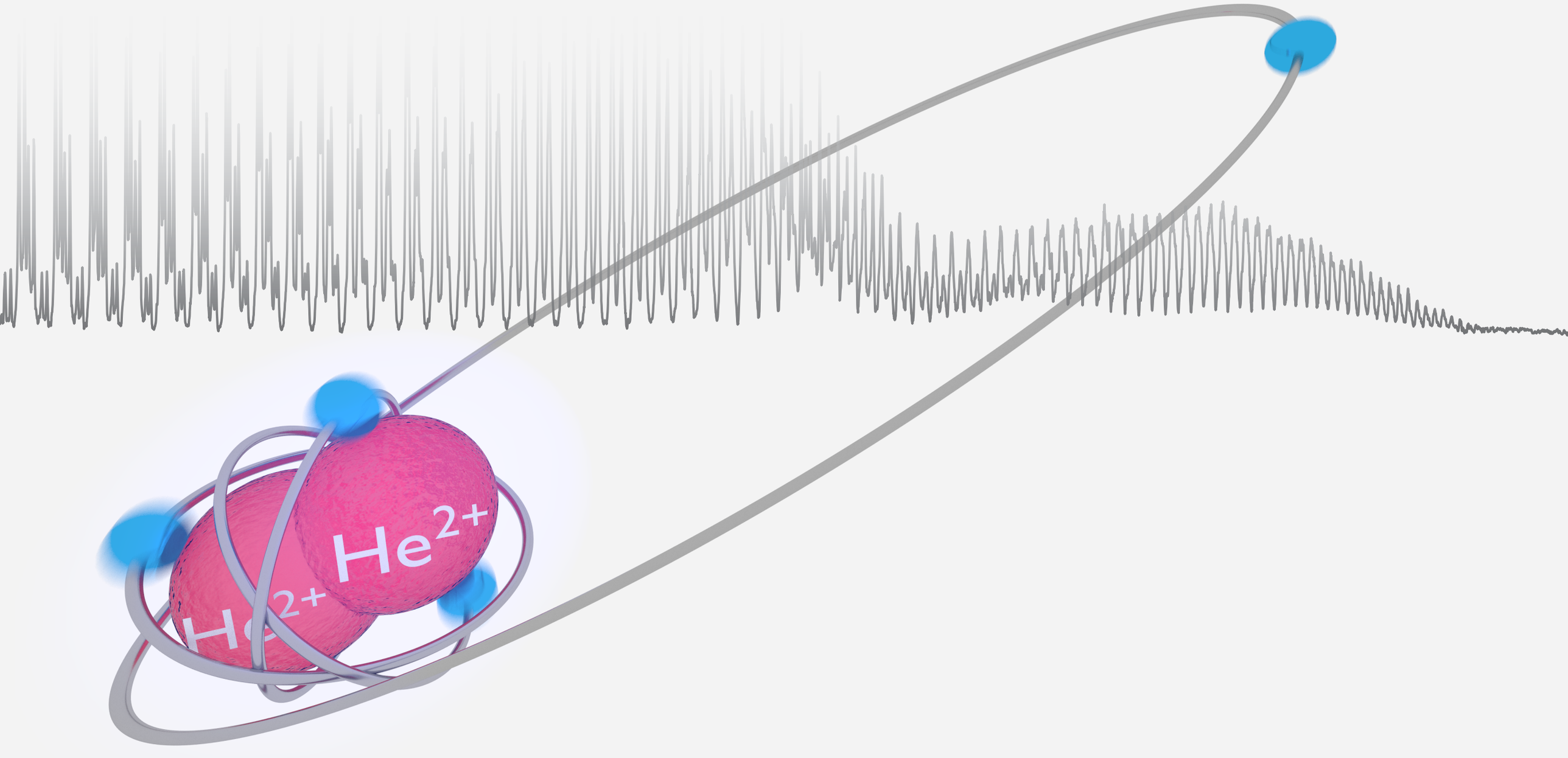
Laboratorium für Physikalische Chemie, ETH Zurich Switzerland



A familiar molecule

Volume 74, number 2 CHEMICAL PHYSICS LETTERS 1 September 1980

OBSERVATION OF LASER DRIVEN TRANSITIONS TO HIGH RYDBERG STATES OF He_2

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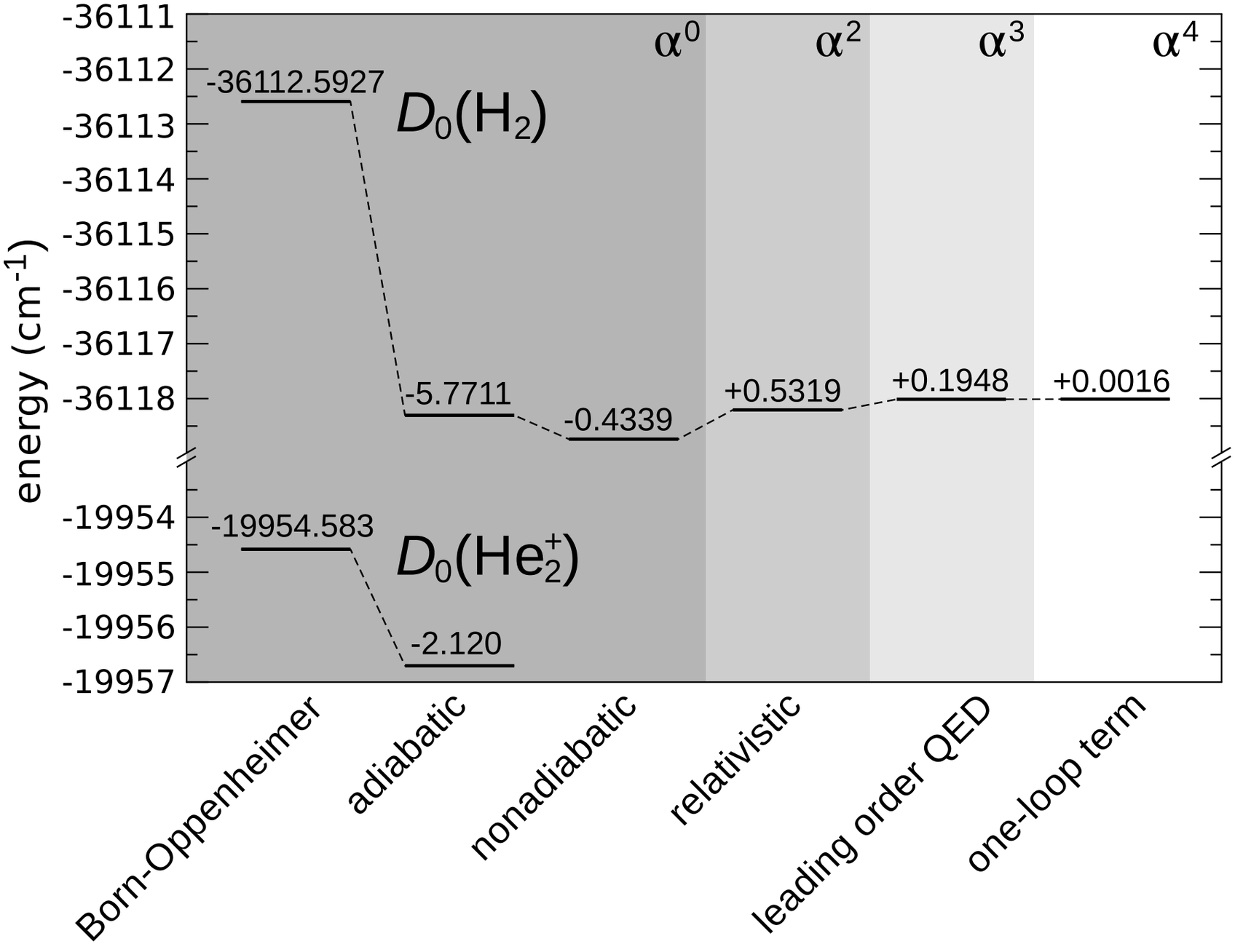
Received 19 July 1980

We report the excitation and detection of Rydberg states of He_2 with principal quantum numbers $\lesssim 25$. The transitions were driven from the metastable $(2s\sigma)\, a\,^3\Sigma_u^+$ He_2 state, and the excited states were detected using ionization techniques. Q branch transitions terminating on $np\pi\,^3\Pi_g$ $(v = 0)$ states up to $n = 25$ have been identified and assigned.

Precision spectroscopy and calculations of few electron molecules

$$E(\alpha) = \alpha^0 \mathcal{E}^{(0)} + \alpha^2 \mathcal{E}^{(2)} + \alpha^3 \mathcal{E}^{(3)} + \alpha^4 \mathcal{E}^{(4)} + \mathcal{O}(\alpha^5)$$



experiment [1]:
36118.06962(37) cm^{-1}

total theory [2]:
36118.0695(10) cm^{-1}

[1] Liu *et al.*, *J. Chem. Phys.* **130**, 174306 (2009).

[2] Piszczatowski *et al.*, *J. Chem. Theory Comput.* **5**, 3039 (2009).

[3] Tung *et al.*, *J. Chem. Phys.* **136**, 104309 (2012).

THE JOURNAL OF CHEMICAL PHYSICS **136**, 104309 (2012)

Very accurate potential energy curve of the He_2^+ ion

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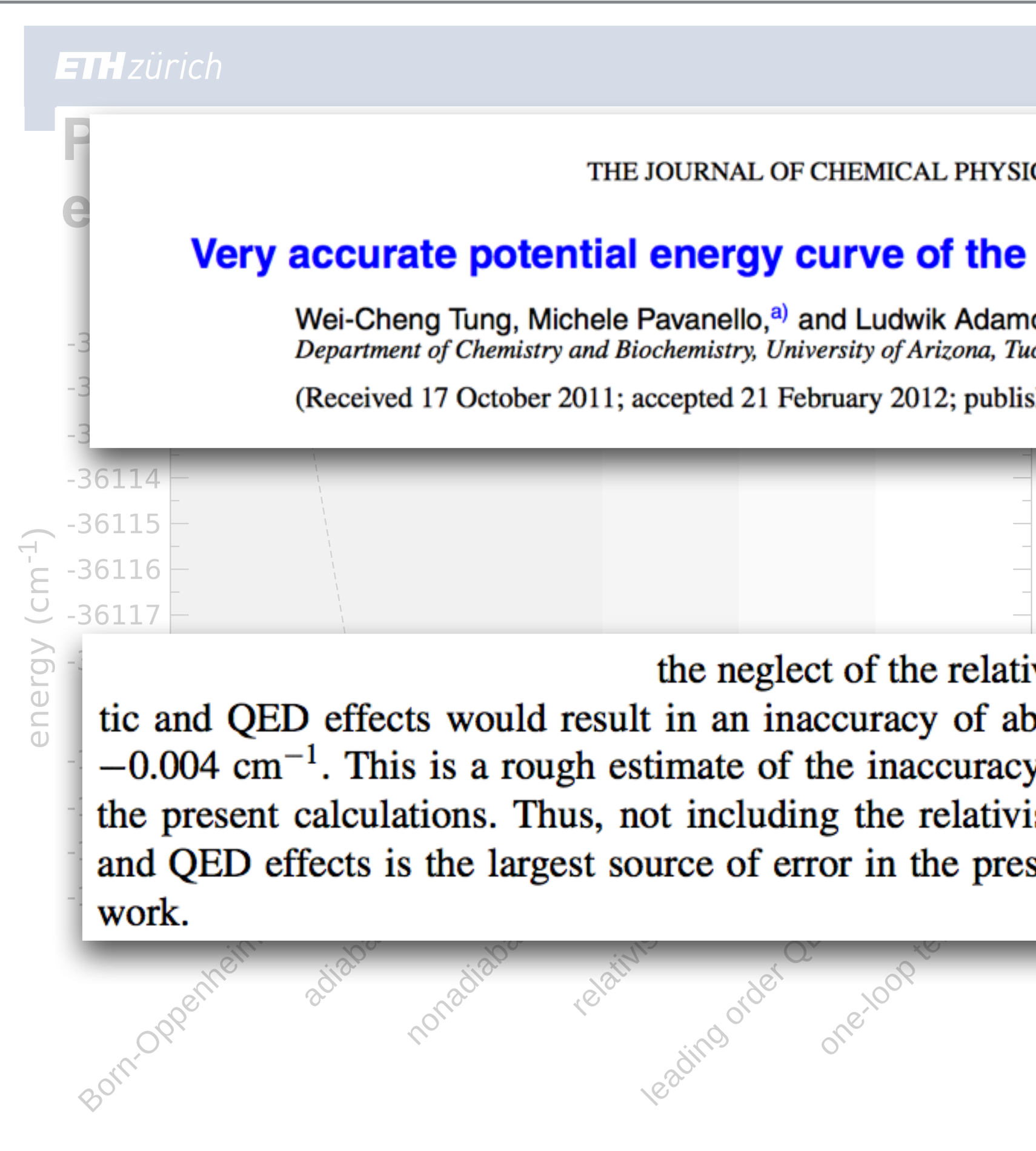
(Received 17 October 2011; accepted 21 February 2012; published online 14 March 2012)

the neglect of the relativistic and QED effects would result in an inaccuracy of about -0.004 cm^{-1}. This is a rough estimate of the inaccuracy of the present calculations. Thus, not including the relativistic and QED effects is the largest source of error in the present work.



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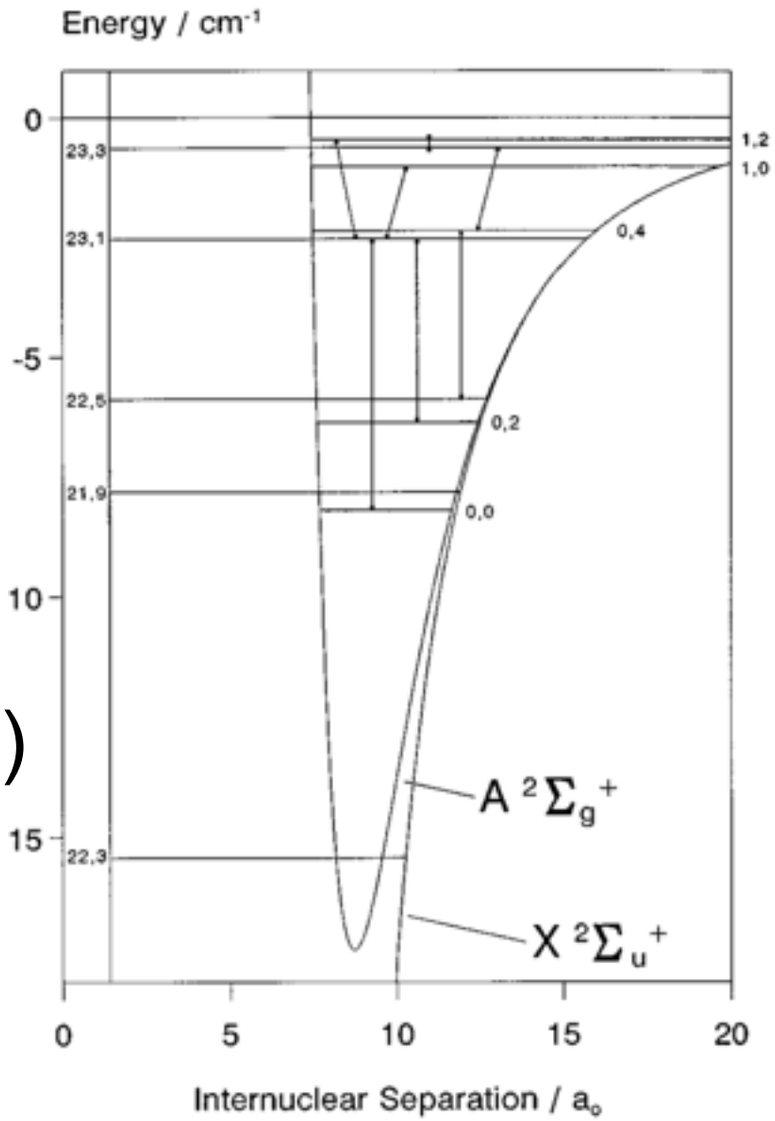
Previous studies of He_2^+

- He_2^+ has no electric dipole moment or easily accessible electronic states.
- Only a few transitions have been observed experimentally:
  - 9 robivrational ($v^+ = 0$) transitions in $^3He^4He^+$ (uncertainty ~ 18 MHz) [1]
  - 7 rovibronic $X^+ \rightarrow A^+$ ($v^+ = 22, 23 \rightarrow 0,1$) in $^4He_2^+$ (uncertainty ~ 2 MHz) [2]



[1] Yu and Wing, *Phys. Rev. Lett.* **59**, 2055 (1987).
[2] Carrington *et al.*, *J. Chem. Phys.* **102**, 5979 (1995).

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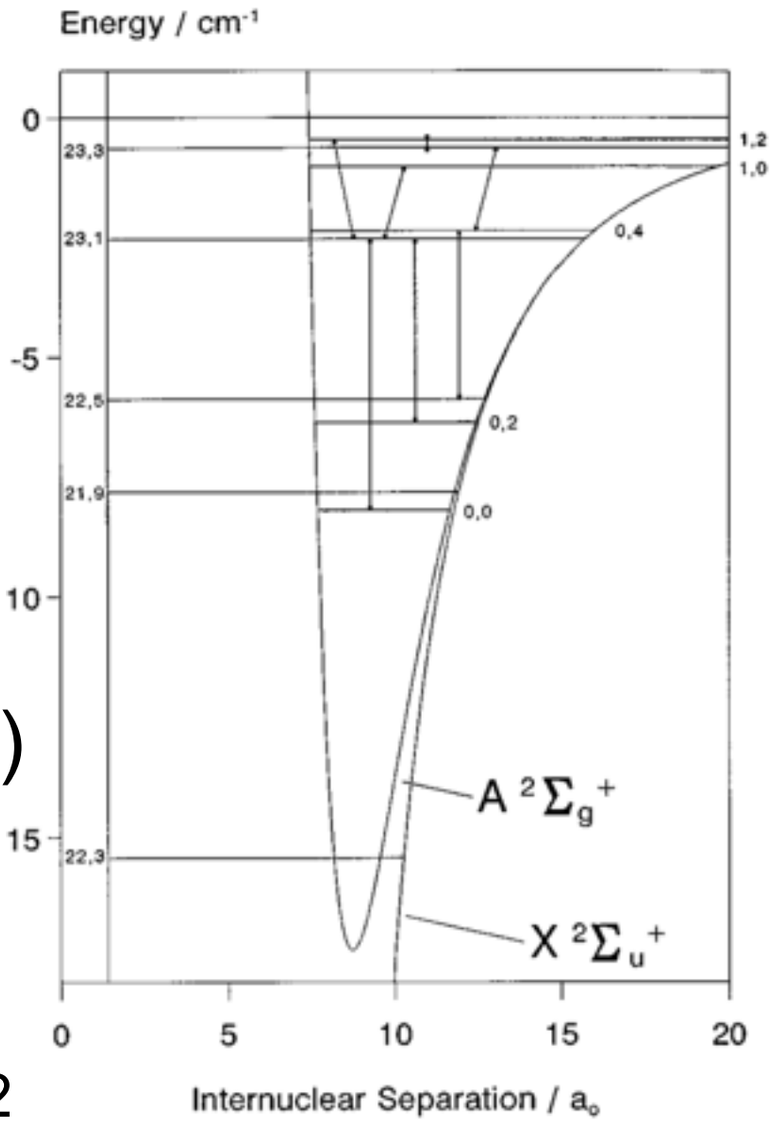


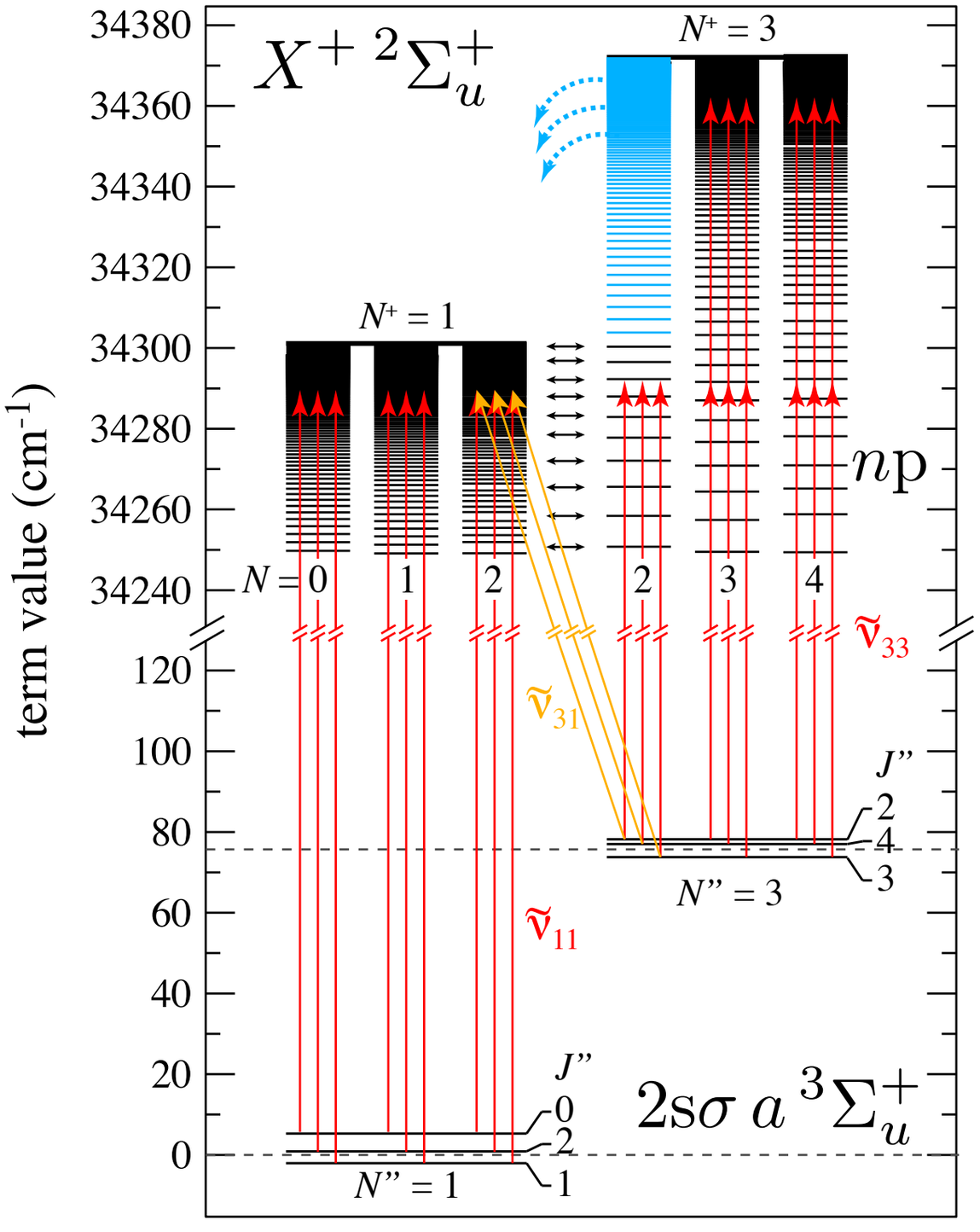
Alternative: Rydberg spectroscopy of He_2

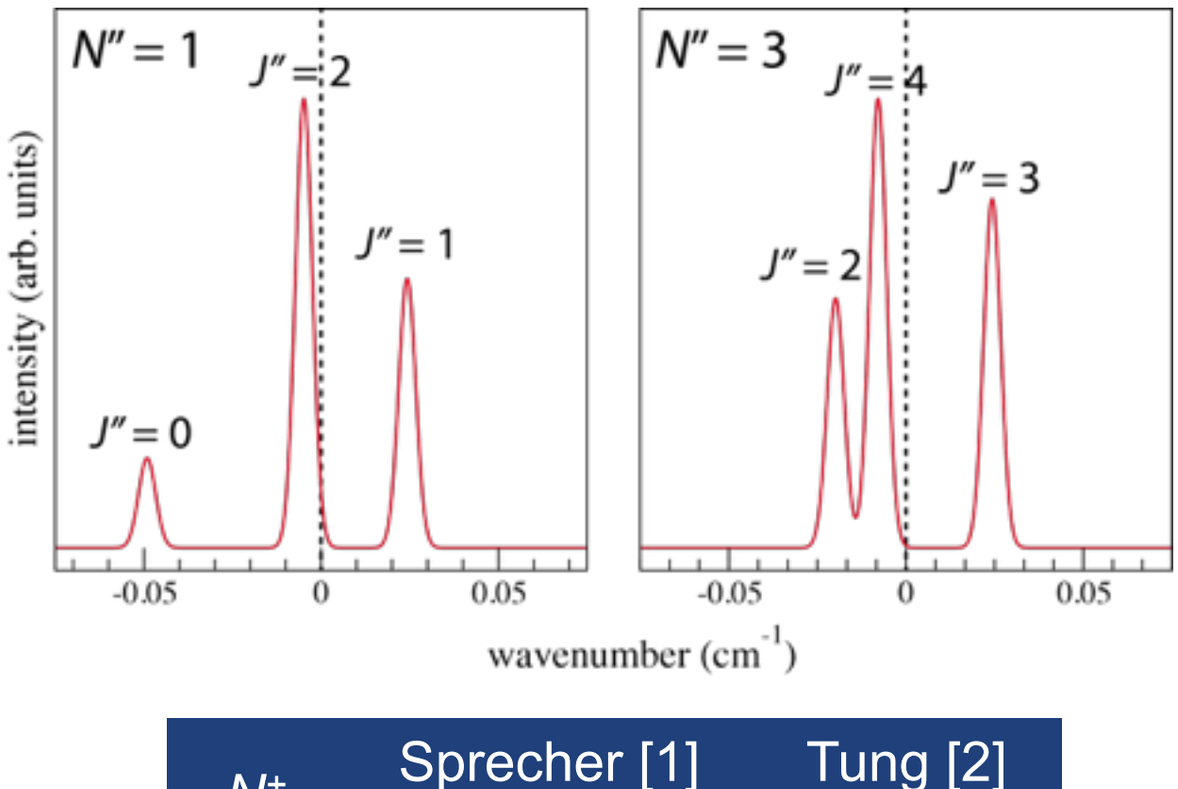
[1] Yu and Wing, *Phys. Rev. Lett.* **59**, 2055 (1987).
[2] Carrington *et al.*, *J. Chem. Phys.* **102**, 5979 (1995).

He_2^+ by Rydberg-series extrapolation

- Ginter and coworkers (1966-1989):
  Rydberg series (n<25) extrapolation to He_2^+
  (v^+ = 0,1, N^+ = 1-25) series limits (resolution ~6 GHz)

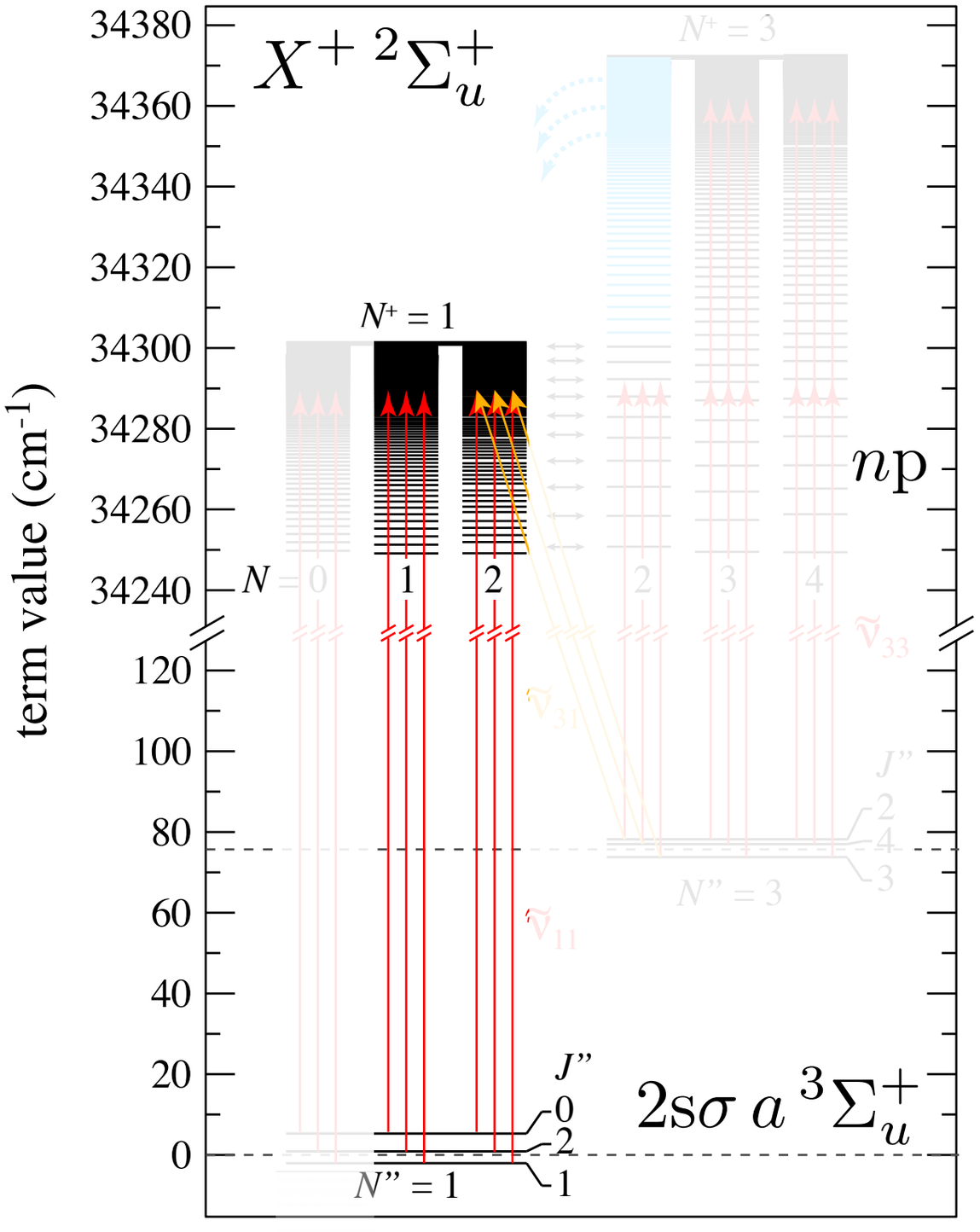
- Merkt and coworkers (2008-2014):
  Rydberg series (n~100) extrapolation to lowest rotational levels of He_2^+ (resolution ~0.3 GHz)

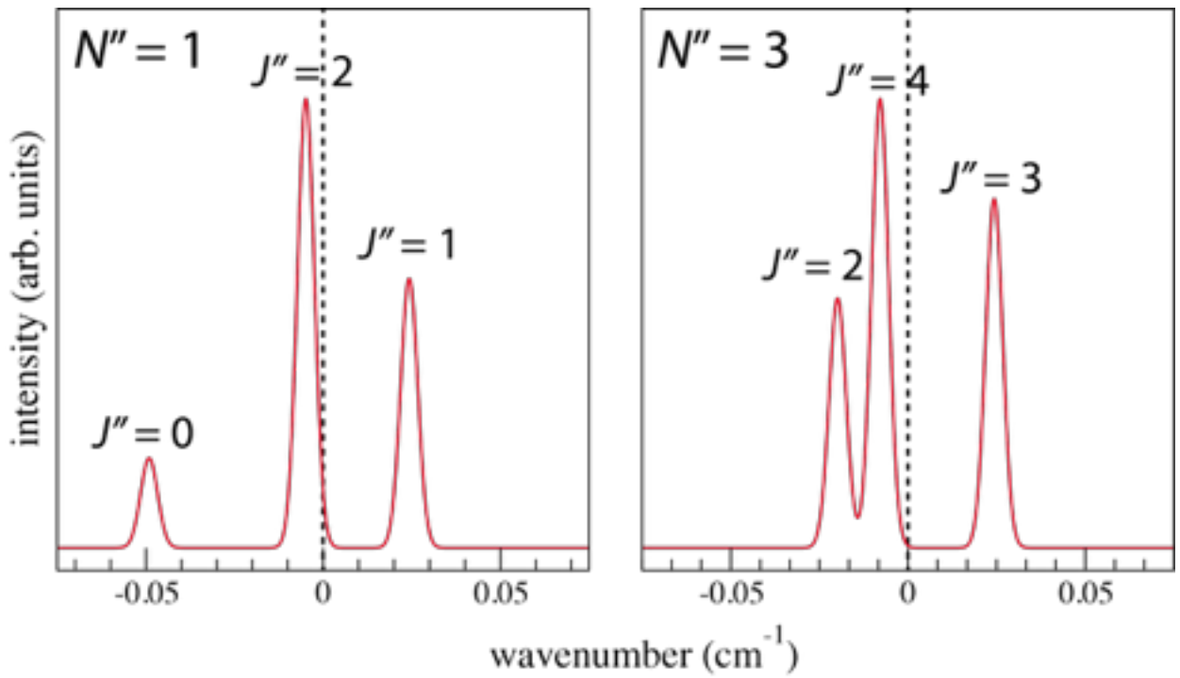




N^+	Sprecher [1] (MQDT fit)	Tung [2] (*ab initio*)
1	0	0
3	70.937(3)	70.936(4)
5	198.369(6)	198.359(4)

[1] Sprecher *et al.*, *J. Chem. Phys.* **140**, 064304 (2014).
[2] Tung *et al.*, *J. Chem. Phys.* J. Chem. **136**, 104309 (2012).





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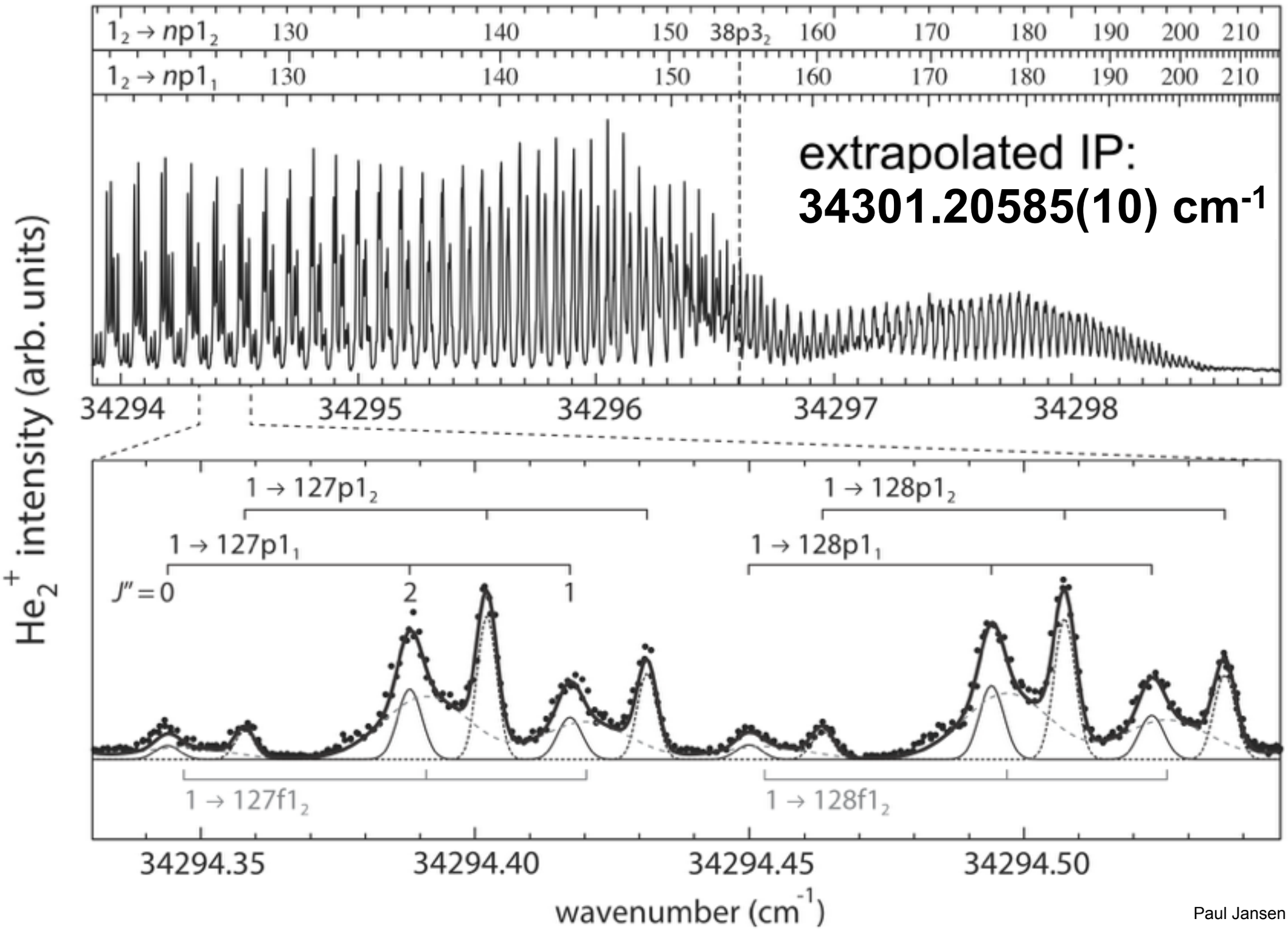
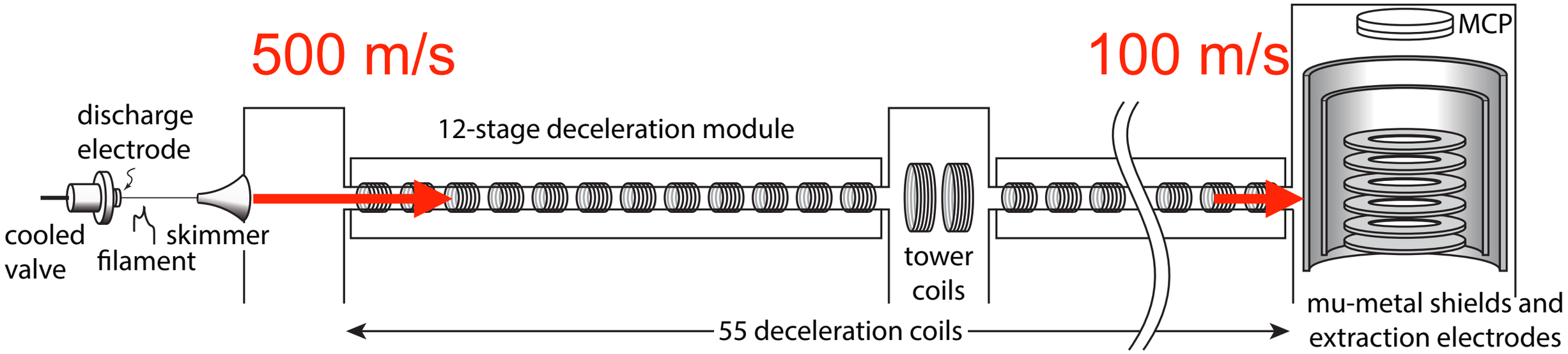
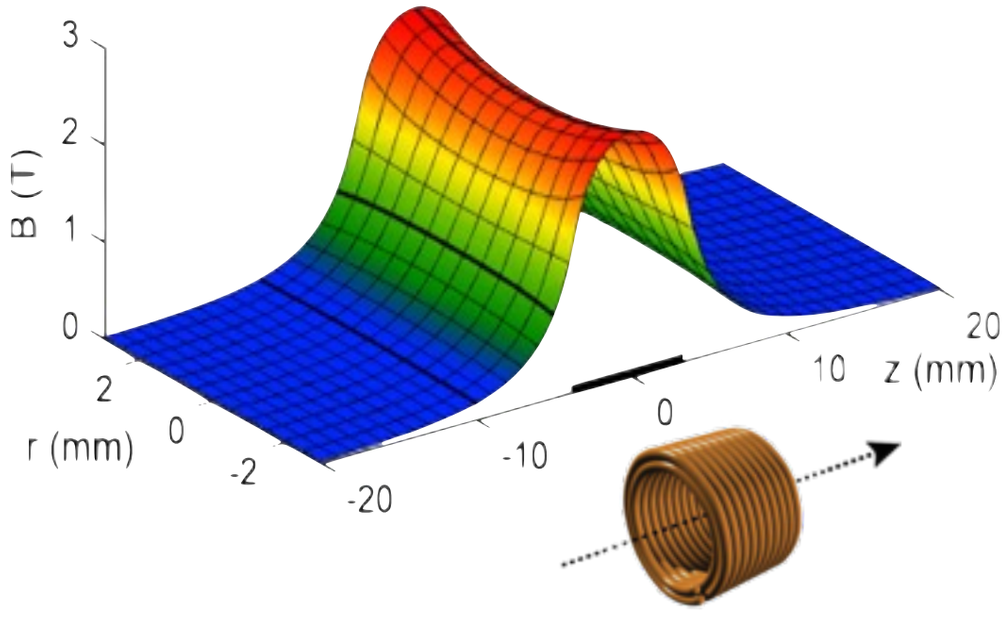
Rydberg spectrum of He_2^* at high *n* values



Zeeman deceleration

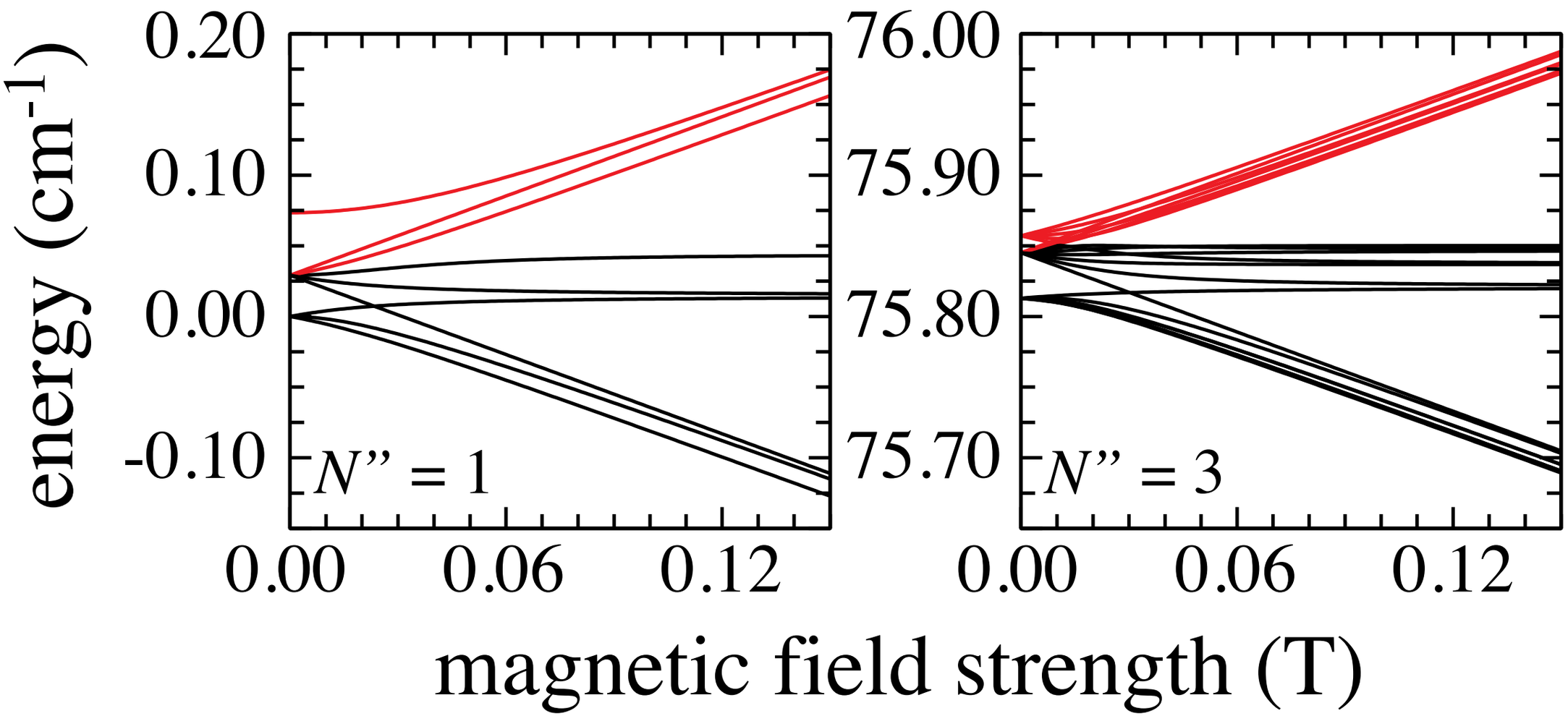




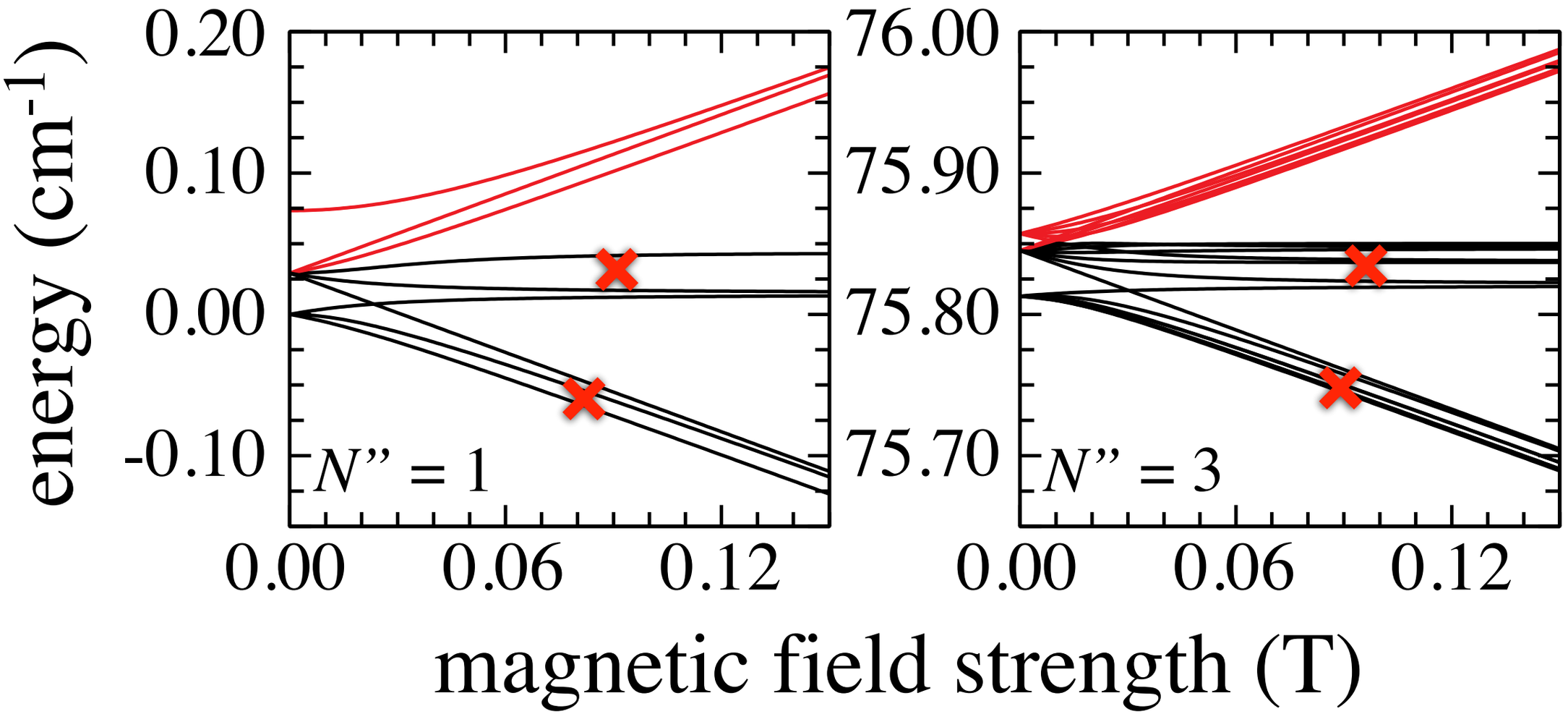
coil properties:	
wire diameter	0.4 mm
solenoid length	7.2 mm
current	300 A
maximal field strength	2.2 T
number of windings	62
number of layers	4

Motsch *et al.*, *Phys. Rev. A* **89**, 043240 (2014).

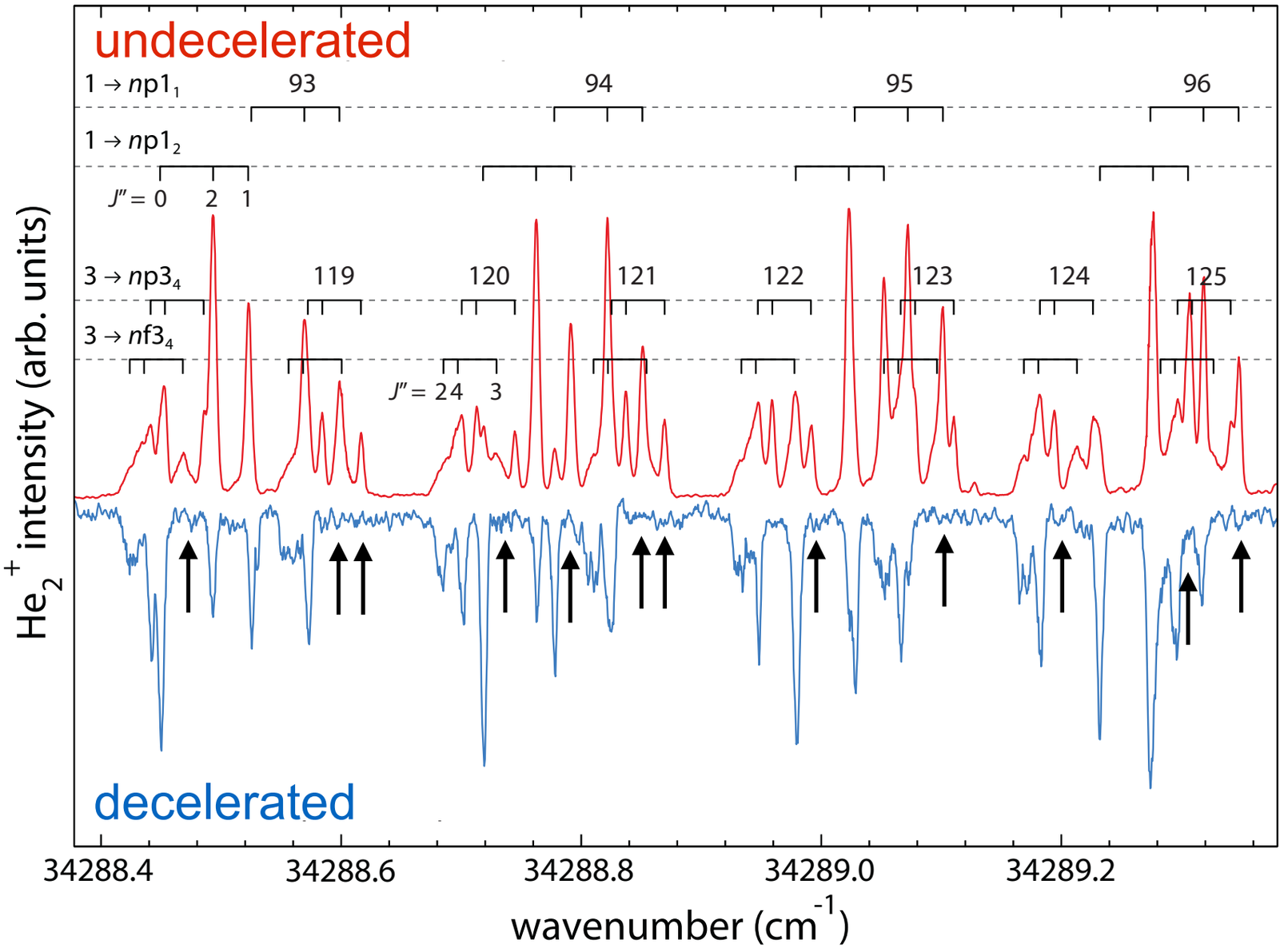
He_2^* in an inhomogeneous magnetic field



He_2^* in an inhomogeneous magnetic field

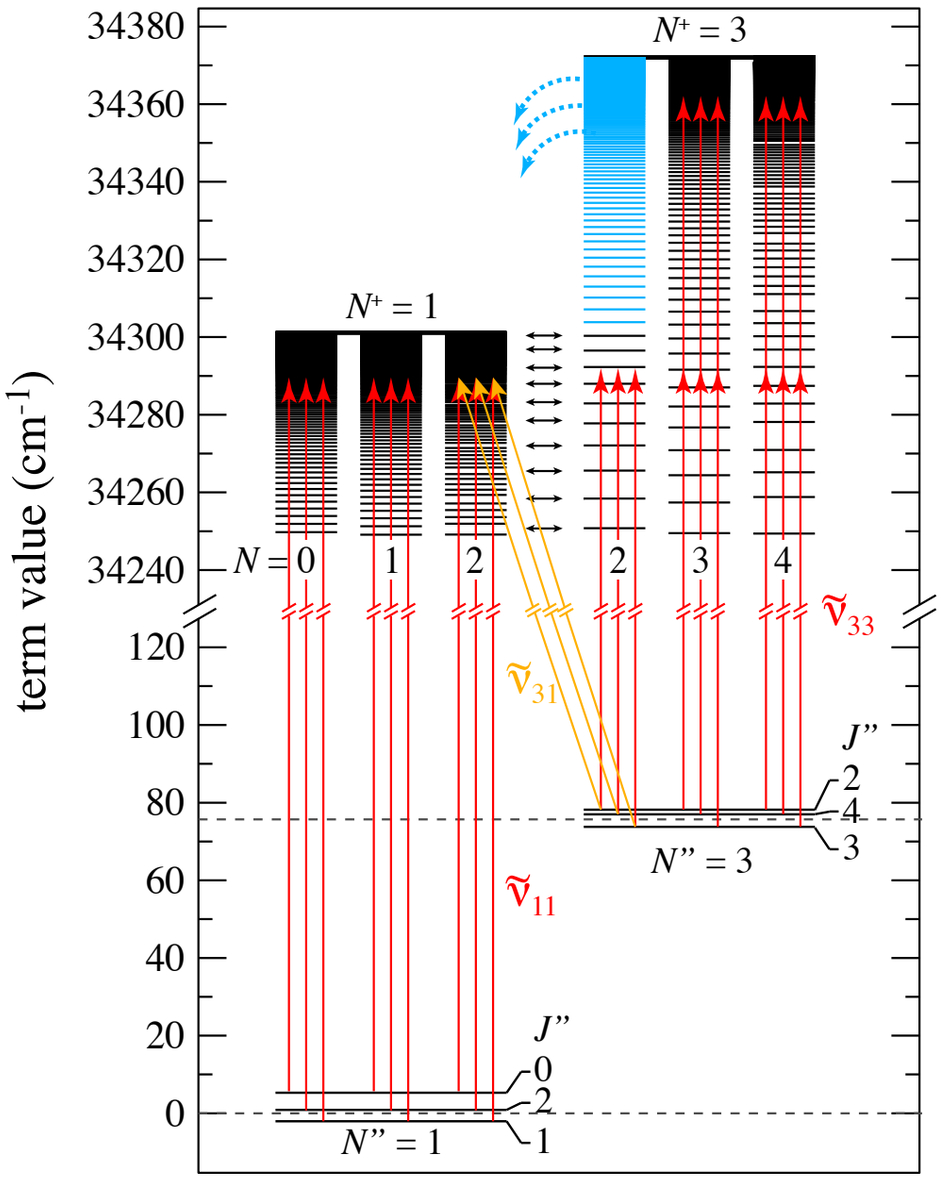


Comparing spectra of decelerated and undecelerated beams



- Reduction of spectral congestion
- Easy assignment
- No residual Doppler shift
- Width limited by linewidth laser (180 MHz)

The lowest rotational interval of He_2^+

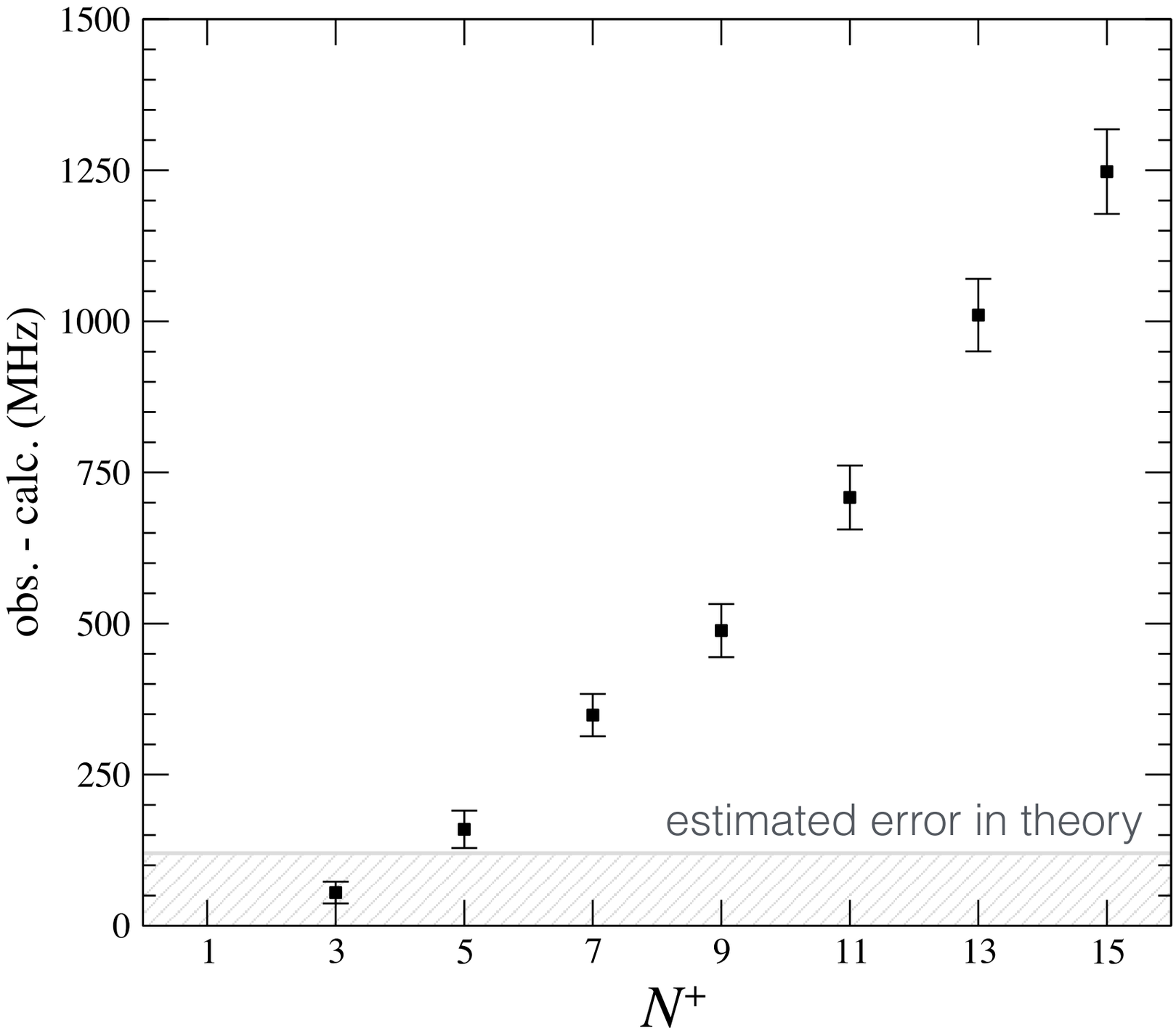


	This work [1] (MQDT fit)	Focsa [2] (FTIR)	Tung [3] (ab initio)
Q(1)	34301.20585(10)		
Q(3)	34296.33037(7)		
E_{13}''	75.8137(4)	75.8129(3)	
E_{13}^+	70.9380(6)		70.936(4)

Error budget	IP	Interval
Statistical		
Wavemeter calibration	0.0013	-
Uncertainty in line centers	0.0003	0.0003
MQDT fit	0.0001	0.0002
Systematic		
AC-Stark shift	0.0002	-
DC-Stark shift	0.00005	-
Zeeman shift	0.00003	-
Residual Doppler	0.0002	-

[1] Jansen *et al.*, *Phys. Rev. Lett.* **115**, 133202 (2015).
[2] Focsa *et al.*, *J. Mol. Spectrosc.* **191**, 209 (1998).
[3] Tung *et al.*, *J. Chem. Phys.* **136**, 104309 (2012).

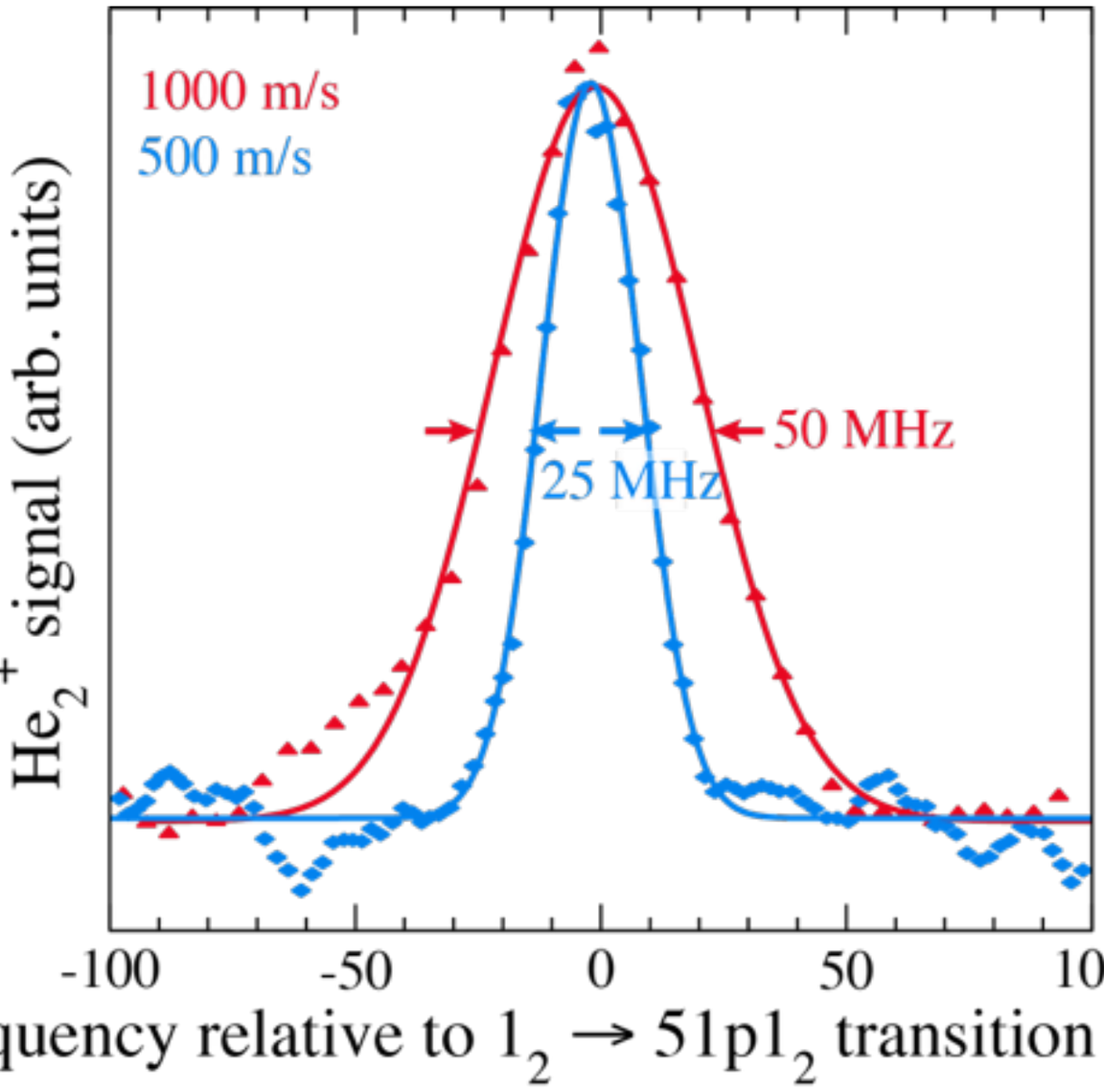
Level energies of higher rotational states of He_2^+



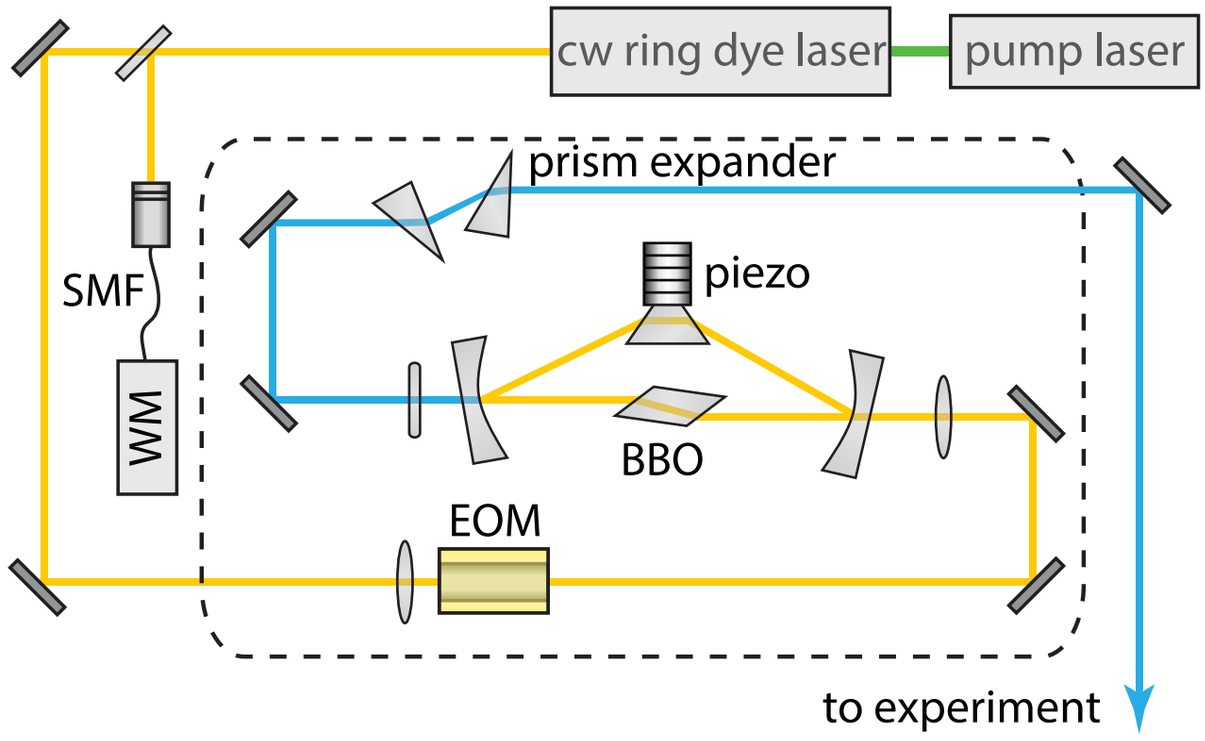
- Measure of nonadiabatic, relativistic, and QED effects.
- Requires inclusion of higher-order terms in *ab initio* calculations [1]

[1] Tung *et al.*, *J. Chem. Phys.* J. Chem. **136**, 104309 (2012).

Continuous-wave excitation



$$\Gamma_\nu = 1.5\,\mathrm{MHz}$$



Observed linewidth equals Doppler width

Jansen *et al.*, *J. Mol. Spectrosc.* **322**, 9 (2016).

Conclusions & Outlook

- In small molecules, relativistic and QED effects make significant contributions to the level structure.

- We have determined the rotational level energies of He_2^+ ($N^+ \leq 15$) to an accuracy ranging from 18 to 60 MHz

- These data indicate a need to improve *ab initio* calculations in 3-electron molecules.

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Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

QSIT Quantum Science and Technology
National Centre of Competence in Research

FNSNF