Measurement of rotational levels of the homonuclear helium dimer cation by extrapolation of Rydberg series

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Introduction: the $\text{He}_2^+$ molecule

- three-electron system, candidate for highly accurate \textit{ab initio} calculations
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- not much experimental data available:
  - 9 rovibrational $v=0\rightarrow1$ transitions in $^3\text{He}^4\text{He}^+$ (uncertainty 18 MHz) [1]
  - 7 rovibronic $X\rightarrow A$ ($v=22,23\rightarrow0,1$) transitions in $^4\text{He}_2^+$ (uncer. 0.2-2 MHz) [2]

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- many studies on the Rydberg states of $\text{He}_2$ [M.L. Ginter et al. 1965-89]
- $\text{He}_2$ is a Rydberg molecule according to G. Herzberg [3]:

A molecule which has an essentially repulsive ground state and all excited states are Rydberg states


Picture taken from: [Buchenua et al. JCP 95, 8134 (1991)]
Rydberg states of atoms and molecules

H

other atoms

<table>
<thead>
<tr>
<th>n+2</th>
<th>n+1</th>
<th>n</th>
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Ionization energy $E_i$

Rydberg formula:

$$E_{n,\ell} = E_i - \frac{\hbar c R_M}{(n - \delta_\ell)^2}$$

Quantum defect
Rydberg states of atoms and molecules

H other atoms

He$_2$ molecule

Energy

\( n \)
\( n+1 \)
\( n+2 \)

\( \ell = 0 \)
\( \ell = 1 \)
\( \ell = 2 \)

Rydberg formula:

\[ E_{n,\ell} = E_i - \frac{\hbar c R_M}{(n - \delta_{\ell})^2} \]

quantum defect

ionization energy \( E_i \)
Experimental
Experimental

chamber

detector

pump

N^+ = N^- - 2

N^+ = N^- 

a^3Σ_u^+ 

N^-
Experimental

Nozzle and discharge

Experimental chamber

\[ N^+ = N'' - 2 \]

\[ a^3\Sigma_u^+ \]

\[ N'' \]
Experimental Glass fiber

Nozzle and discharge

Solid-state laser system

HeNe-cw-laser
Etalon, FSR=149.966 MHz
Etalon, FSR=161.653 MHz
Wavemeter
l_0 calibration
Nd:YVO_4; cw-pump 532 nm
699 Ti:Sa-cw-ringlaser 875 nm
Nd:YAG
532 nm

AOM

\( \nu_{\text{ex}} + 1 \text{ GHz} \)

Fresnel rhomb
Faraday isolator
Filter for \( \lambda < 850 \text{ nm} \)

Nd:YAG
532 nm

Photo diode
Telescope

KDP
BBO

3 (\( \nu_{\text{ex}} + 1 \text{ GHz} \))
to the experimental chamber

N_p = N'' - 2
\( a^3 \Sigma_u^+ \)
Experimental
Nozzle and discharge

Solid-state laser system

- pulse length ~ 40 ns
- bandwidth ~ 20 MHz
- pulse energies
  - @875nm: ~ 15 mJ
  - @438nm: ~ 2 mJ
  - @292nm: ~ 150 μJ
Experimental

Nozzle and discharge

- electrode
- PEEK
- stainless steel

Solid-state laser system

- HeNe-cw-laser
- Etalon, FSR=149.966 MHz
- Etalon, FSR=161.653 MHz
- Wavemeter
- I\textsubscript{2} calibration
- Nd:YVO\textsubscript{4}; cw-pump 532 nm
- 699 Ti:Sa-cw-ring laser 875 nm

Experimental chamber

- detector
- pump

- field delay: 2 \mu s
- field strength: 12.8 V/cm

- pulse length \sim 40 ns
- bandwidth \sim 20 MHz
- pulse energies
  - @875nm: \sim 15 mJ
  - @438nm: \sim 2 mJ
  - @292nm: \sim 150 \mu J
Overview Q-region

$N^- = 7 \rightarrow N^+ = 7$

[Graph showing electron signal in arbitrary units against wave number in cm$^{-1}$ with significant peaks at 34275, 34280, 34285, 34290, 34295, and 34300 with labels 5→5, 3→3, and 1→1]
Resolved fine structure of the triplet a state
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[Focsa et al. JMS 191, 209 (1998)]
Resolved fine structure of the triplet $a$ state

$1 \rightarrow 92p \ (N^+=1)$  
$3 \rightarrow 38p \ (N^+=3)$  
$5 \rightarrow 110p \ (N^+=5)$

[Ref: Focsa et al. JMS 191, 209 (1998)]
The $N^+ = 5$ Rydberg series

notation: $N'' \rightarrow n \ell N^+_N$
The $N^+ = 1,3$ Rydberg series

notation: $N'' \rightarrow n \ell N^+_N$
Overview over all observed states

Quantum number $N$ associated with the total angular momentum excluding spins
Extrapolation of Rydberg series with multichannel quantum defect theory (MQDT)

\[ E_{n,\ell} = E_i - \frac{hcR_M}{(n - \delta_\ell)^2} \]

quantum defects from MQDT (adjusted to reproduce positions of 600 \( n<25 \) states)

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Results of the extrapolation

\[ N^+ = 5 \quad 198.3666(4) \text{ cm}^{-1} \]

\[ N^+ = 3 \quad 70.9395(4) \text{ cm}^{-1} \]

This work

\[ N'' = 5 \]

Focsa et al.
Results of the extrapolation

\[ \begin{array}{|c|c|c|c|}
\hline
N^+ & \text{Exp.} & \text{Calc. [1]} & \Delta \\
\hline
5 & 198.3666(4) & 198.39 & -0.02 \\
3 & 70.9395(4) & 70.95 & -0.01 \\
\hline
\end{array} \]


All values in cm\(^{-1}\).
Conclusions

- Transitions to triplet np Rydberg states (n up to 150) of He$_2$ have been resolved.
- The ionization energy of the $a \ ^3\Sigma_u^+$ state of He$_2$ was determined with an uncertainty of 0.006 cm$^{-1}$ (180 MHz).
- The energy spacing between the first three rotational states of He$_2^+$ could be extracted with an accuracy of 0.0004 cm$^{-1}$ (12 MHz).

Results of the extrapolation

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Merk group
ETH Zurich
Switzerland
(March 2009)
Molecular Rydberg states and MQDT

Eigen quantum defect $\mu_{\ell,\ell'}^{S,\Lambda}$

Quantization condition:

$$\det \left| U_{i\alpha} \sin[\pi(\mu_\alpha + \nu_i)] \right| = 0$$

with $\nu_i = n - \delta_i$

Triplett pp eigen quantum defects have been adjusted to reproduce positions of almost 600 $n<25$ states:

[D.S. Ginter et al. JCP 81, 6013 (1984)]
[M. Raunhardt et al. JCP 128, 164310 (2008)]

$E_n = E_i - \frac{\hbar c R_M}{(n - \delta)}$
HeNe stabilized etalon