

# **PFI-ZEKE photoelectron spectroscopy of metastable He<sub>2</sub>: ionization potential and rovibrational structure of He<sub>2</sub><sup>+</sup>**

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## Introduction: the helium dimer

${}^4\text{He}_2 \times {}^1\Sigma_g^+$ : extremely weakly bound, only one quantum state ( $v = 0, J = 0$ )  
( $D_e = 7.650(3) \text{ cm}^{-1}$ ,  $r_e = 2.968(6) \text{ \AA}$ ,  $D_0 = 0.00120(3) \text{ cm}^{-1}$ )

F. Luo, G. C. McBane, G. Kim, C. F. Giese, W. R. Gentry, J. Chem. Phys. **98**, 3564 (1993)

R. E. Grisenti, W. Schöllkopf, J. P. Toennies, G. C. Hegerfeldt, T. Köhler, M. Stoll, Phys. Rev. Lett. **85**, 2284 (2000)

M. Jeziorska, W. Cencek, K. Patkowski, B. Jeziorski, K. Szalewicz, J. Chem. Phys. **127** 124303 (2007)

and many more theoretical papers...

${}^4\text{He}_2 [(1\sigma_g)^2(1\sigma_u)]2s\sigma_g \text{ a } {}^3\Sigma_u^+$ :  $T_e = 17.86 \text{ eV}$ , long lifetime (18 s)  
( $\omega_e = 1808.500(84) \text{ cm}^{-1}$ ,  $B_e = 7.707364(67) \text{ cm}^{-1}$ ,  $r_e = 1.0454158(45) \text{ \AA}$ ,  
theory:  $D_e = 15848 \text{ cm}^{-1}$  with barrier of  $505 \text{ cm}^{-1}$  at  $r = 2.71 \text{ \AA}$ )

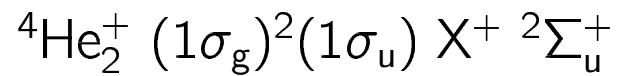
C. M. Brown, M. L. Ginter, J. Mol. Spectrosc. **40**, 302 (1971)

C. Focsa, P. F. Bernath, R. Colin, J. Mol. Spectrosc. **191**, 209 (1998)

R. M. Jordan, H. R. Siddiqui, P. E. Siska, J. Chem. Phys. **84**, 6719 (1986)

N. Bierre, A. O. Mitrushenkov, P. Palmieri, P. Rosmus, Theor. Chem. Acc. **100**, 51 (1998)

${}^4\text{He} (1s)(2s) 2 {}^3S_1$ :  $T = 159855.9726(15) \text{ cm}^{-1}$  (19.820 eV), rad. lifetime 8000 s



early calculations:  $r_e = 1.085 \text{ \AA}$ ,  $D_e = 2.47 \text{ eV}$

L. Pauling, J. Chem. Phys. **1**, 56 (1933)

extrapolation from  $\text{He}_2$  Rydberg states ( $v^+ = 0$ :  $N^+ \leq 21$ ,  $v^+ = 1$ :  $N^+ \leq 15$ ):

$\omega_e = 1698.6 \text{ cm}^{-1}$ ,  $B_e = 7.211 \text{ cm}^{-1}$ ,  $r_e = 1.0806 \text{ \AA}$ ;

$T_0 = 34302.3(10) \text{ cm}^{-1}$  (wrt  $\text{He}_2$  a  ${}^3\Sigma_u^+$ )

M. L. Ginter, D. S. Ginter, J. Chem. Phys. **48**, 2284 (1968)

D. S. Ginter, M. L. Ginter, J. Mol. Spectrosc. **82**, 152 (1980)

$v^+ = 1 - 0$  infrared spectrum of  ${}^3\text{He} {}^4\text{He}^+$

$\omega_e = 1832.7598(50) \text{ cm}^{-1}$ ,  $B_e = 8.3906(40) \text{ cm}^{-1}$ , [ $r_e = 1.08096(26) \text{ \AA}$ ]

N. Yu, W. H. Wing, Phys. Rev. Lett. **59**, 2055 (1987), **60**, 2445 (1988)

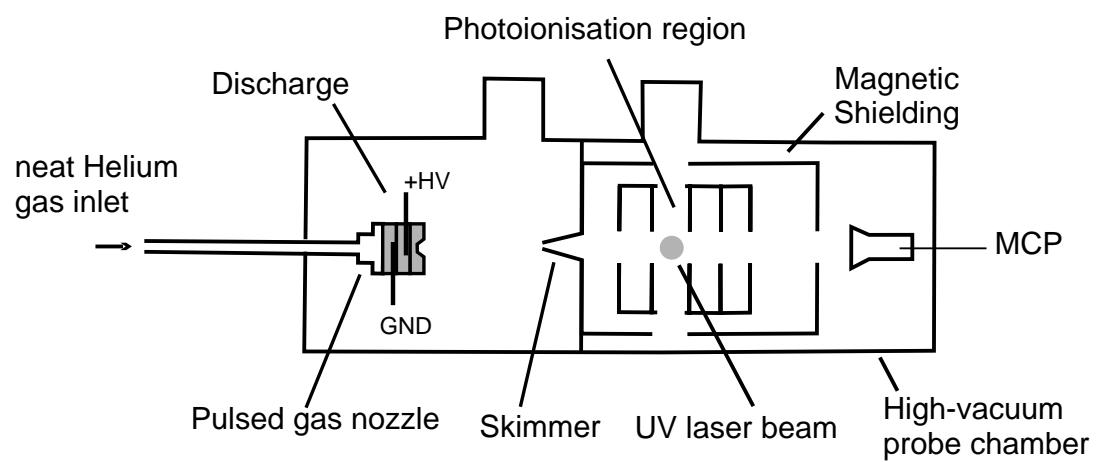
$A^+ \ ^2\Sigma_g^+ \ (v' = 0, 1) \leftarrow X^+ \ ^2\Sigma_u^+ \ (v'' = 22, 23)$  microwave spectrum of  ${}^4\text{He}_2^+$

A. Carrington, C. H. Pyne, P. J. Knowles, J. Chem. Phys. **102** 5979 (1995)

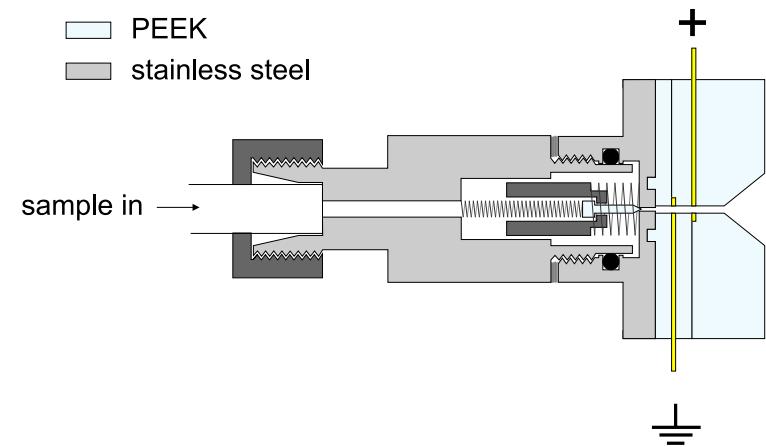
theory:  $D_e = 19945.82 \text{ cm}^{-1}$ ,  $r_e = 1.0811(3) \text{ \AA}$

J. Xie, B. Poirier, G. I. Gellene, J. Chem. Phys. **122**, 184310 (2005)

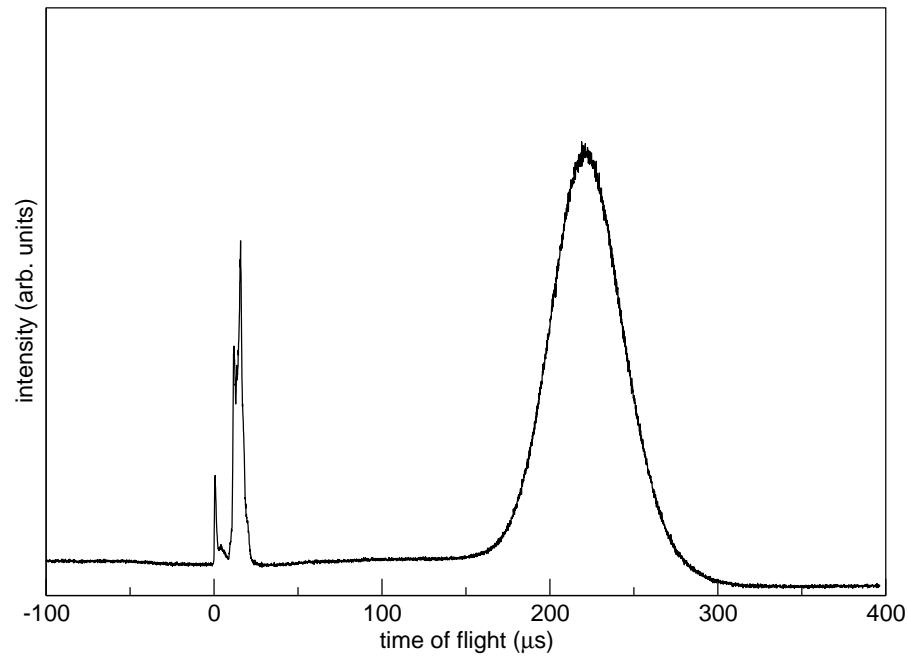
## Experimental setup



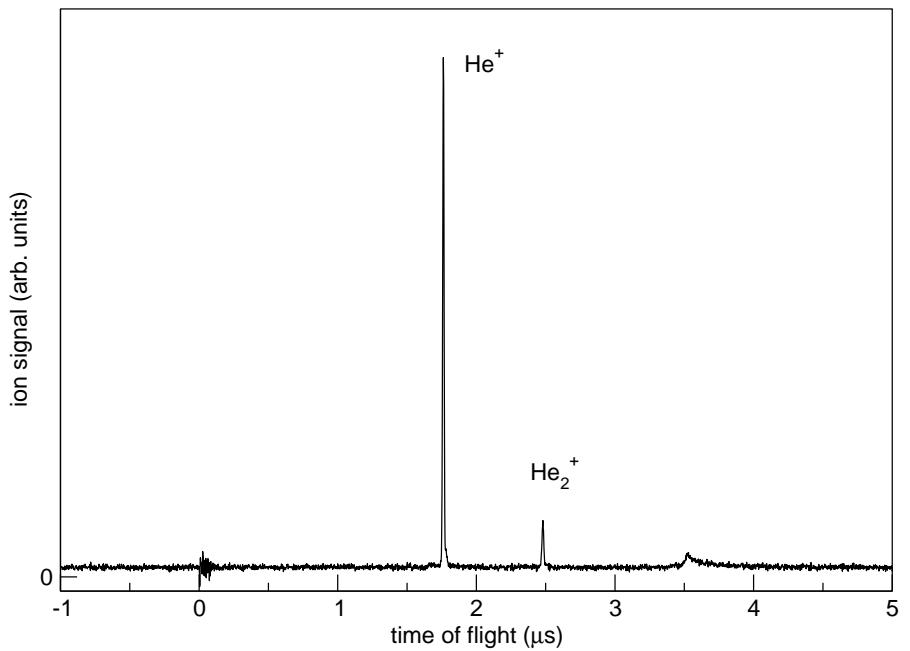
— electrode  
— PEEK  
— stainless steel



## Performance of the pulsed discharge



TOF of metastable  $\text{He}^*$  and  $\text{He}_2^*$   
[ $t = 0$ : discharge pulse]  
 $T_{\text{vib}} \approx 1000 \text{ K}$ ,  $T_{\text{rot}} \approx 300 \text{ K}$ ,  $T_{||} \approx 10 \text{ K}$



TOF of metastable  $\text{He}^*$  and  $\text{He}_2^*$  ionized by UV laser (252.5 nm)  
[ $t = 0$ : extraction field pulse]

# Pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy

1 Laser excitation to high- $n$

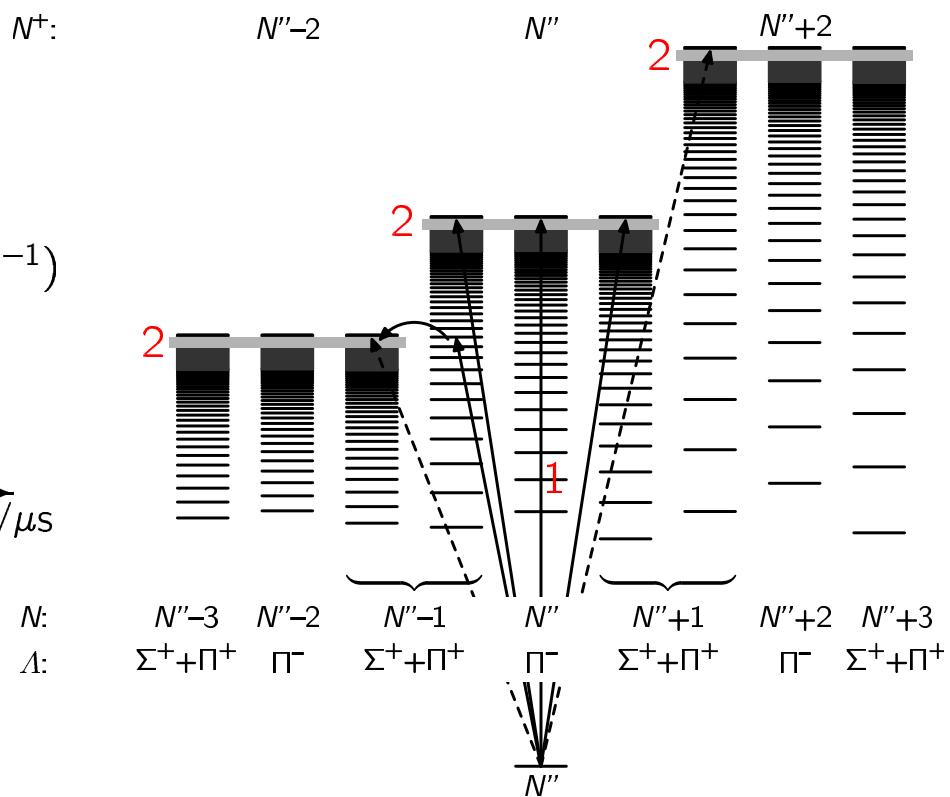
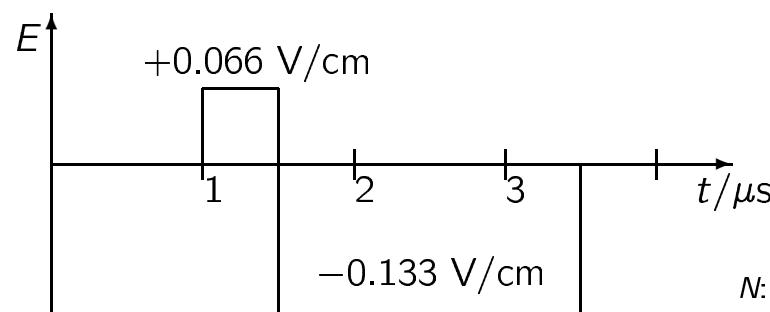
$np$  Rydberg states

$^3\Pi_g^-$  ( $N = N''$ )

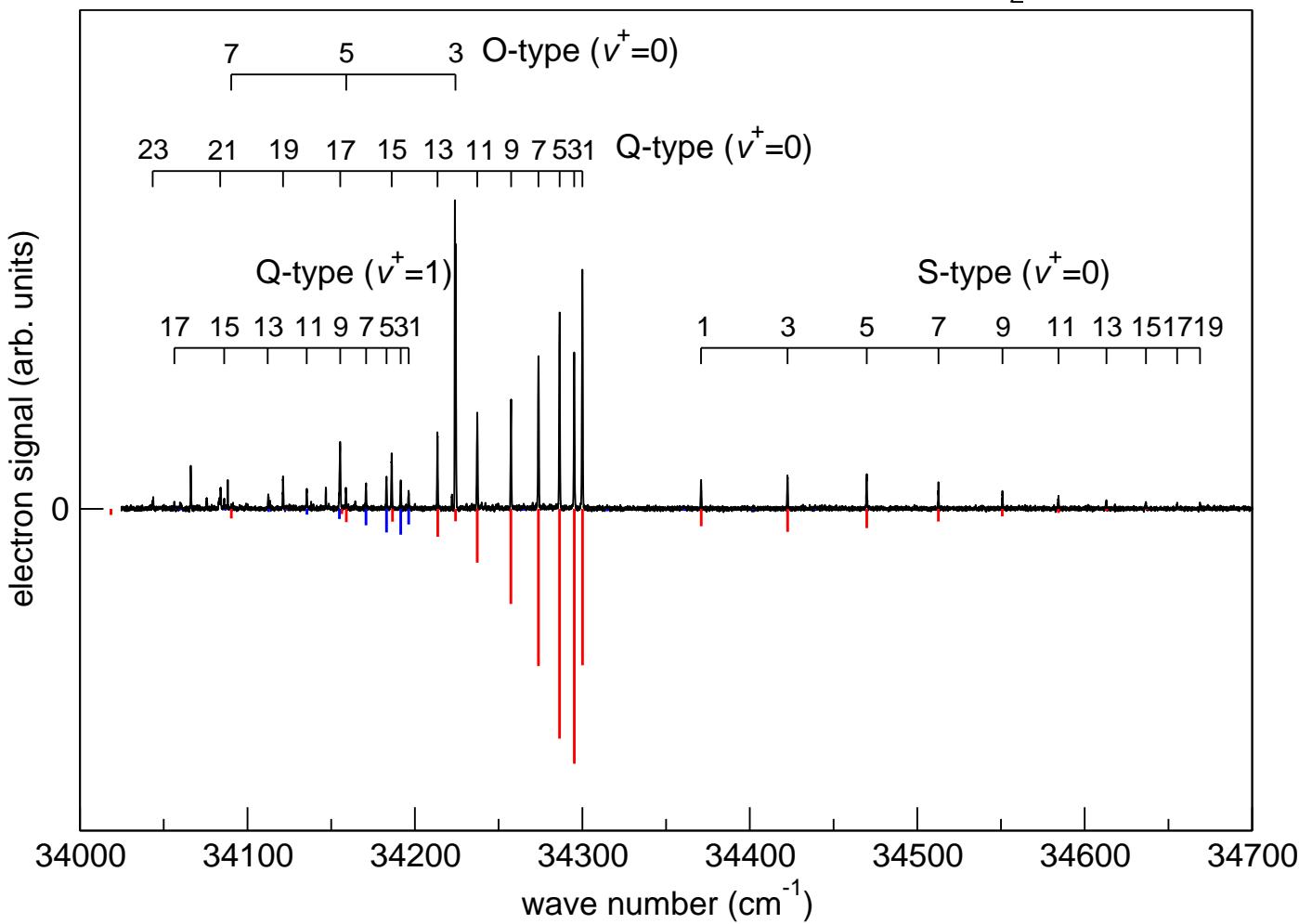
$^3\Sigma_g^+$ ,  $^3\Pi_g^+$  ( $N = N'' \pm 1$ )

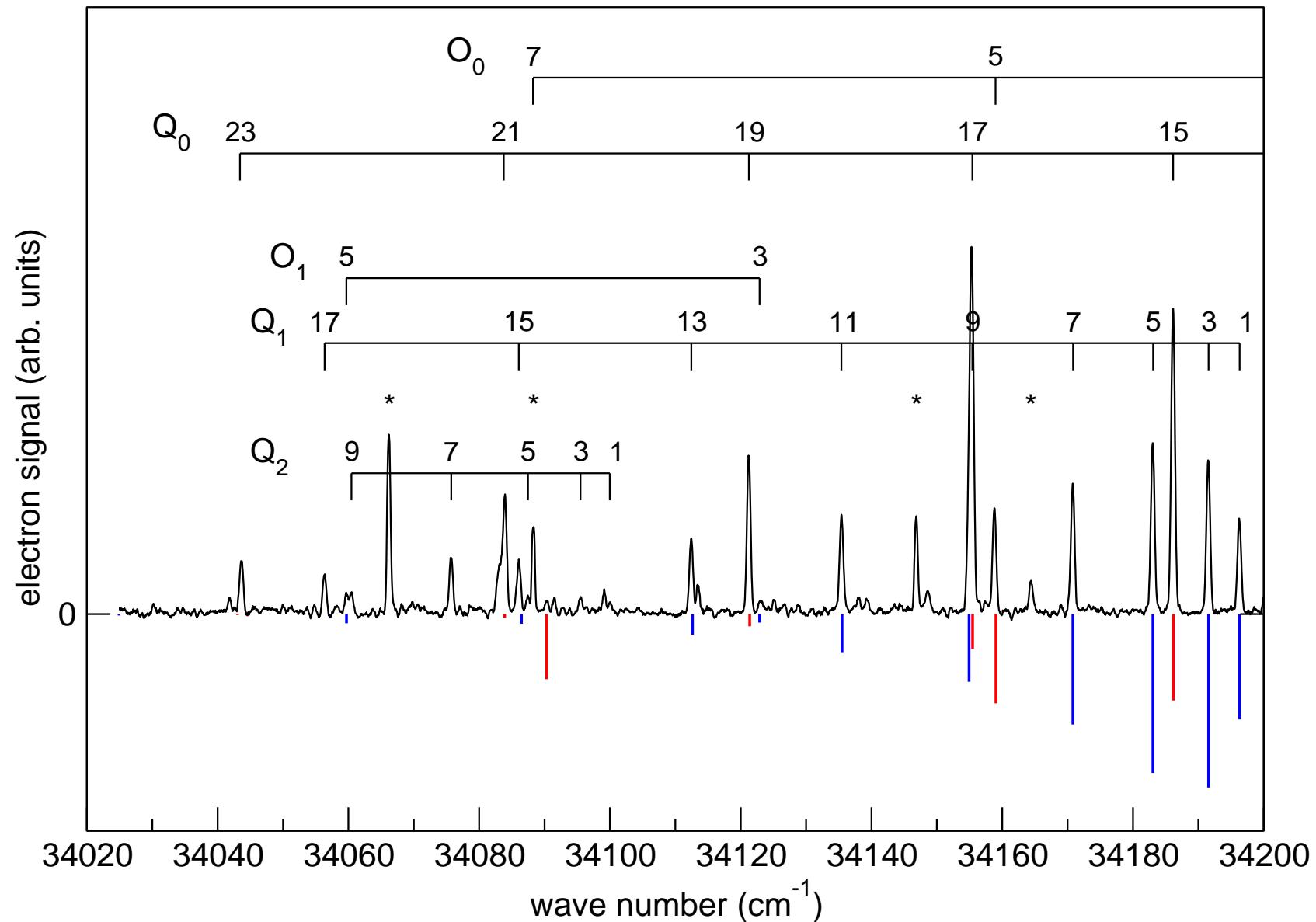
2 Pulsed field ionization

( $\Gamma_{\text{FWHM}} = 0.5 \text{ cm}^{-1}$ , shift  $-1.20 \text{ cm}^{-1}$ )

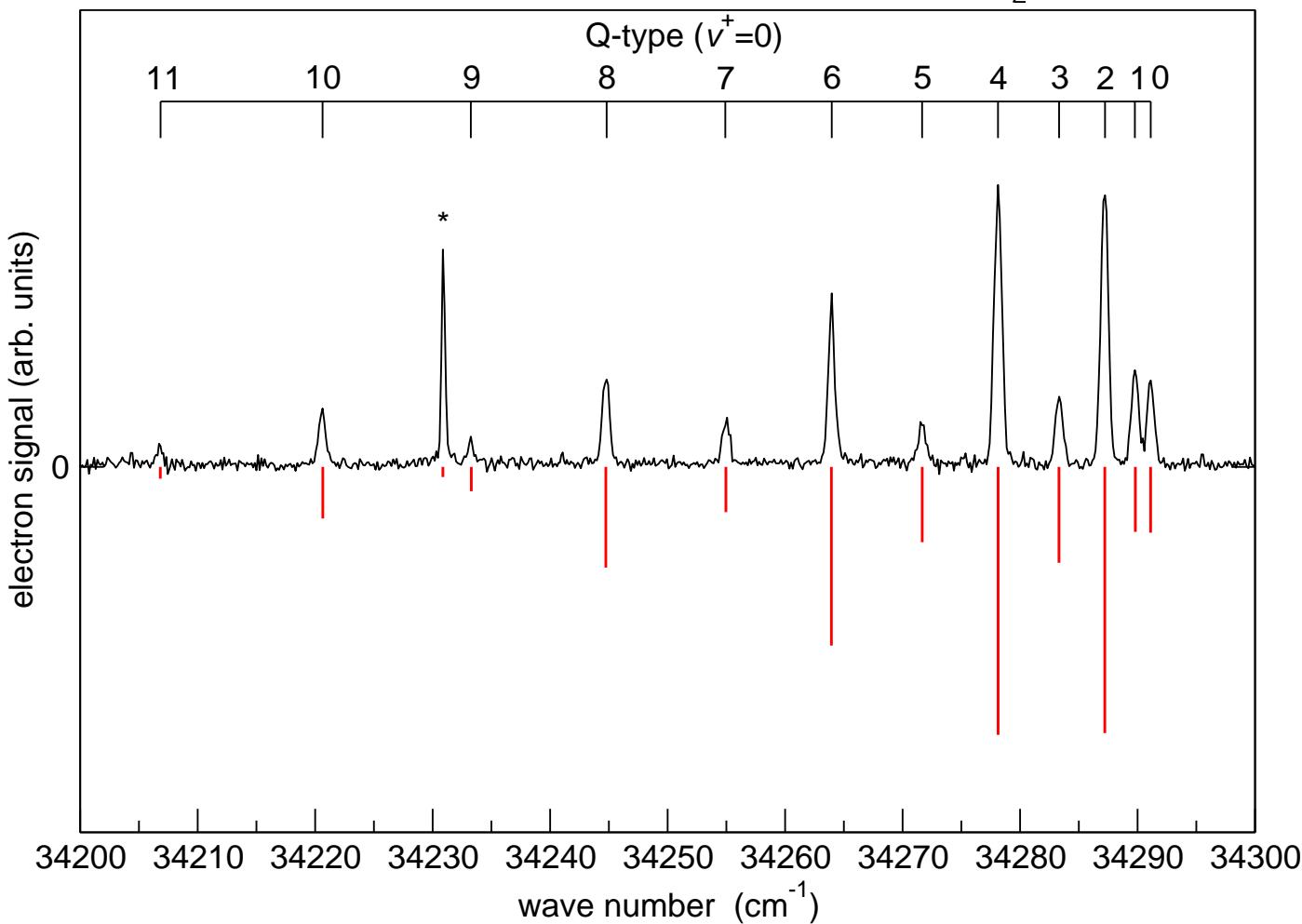


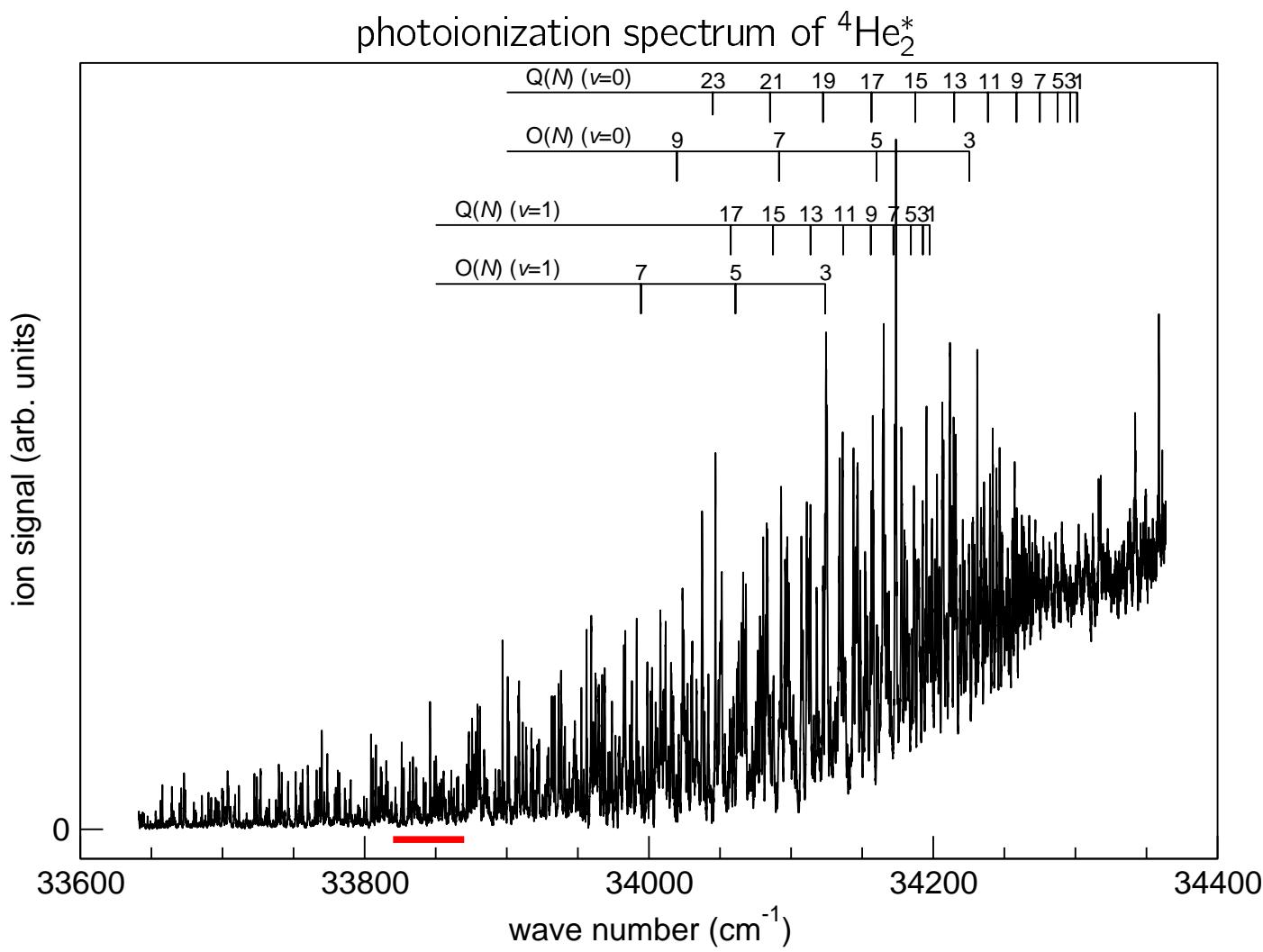
PFI-ZEKE photoelectron spectrum of  ${}^4\text{He}_2^*$

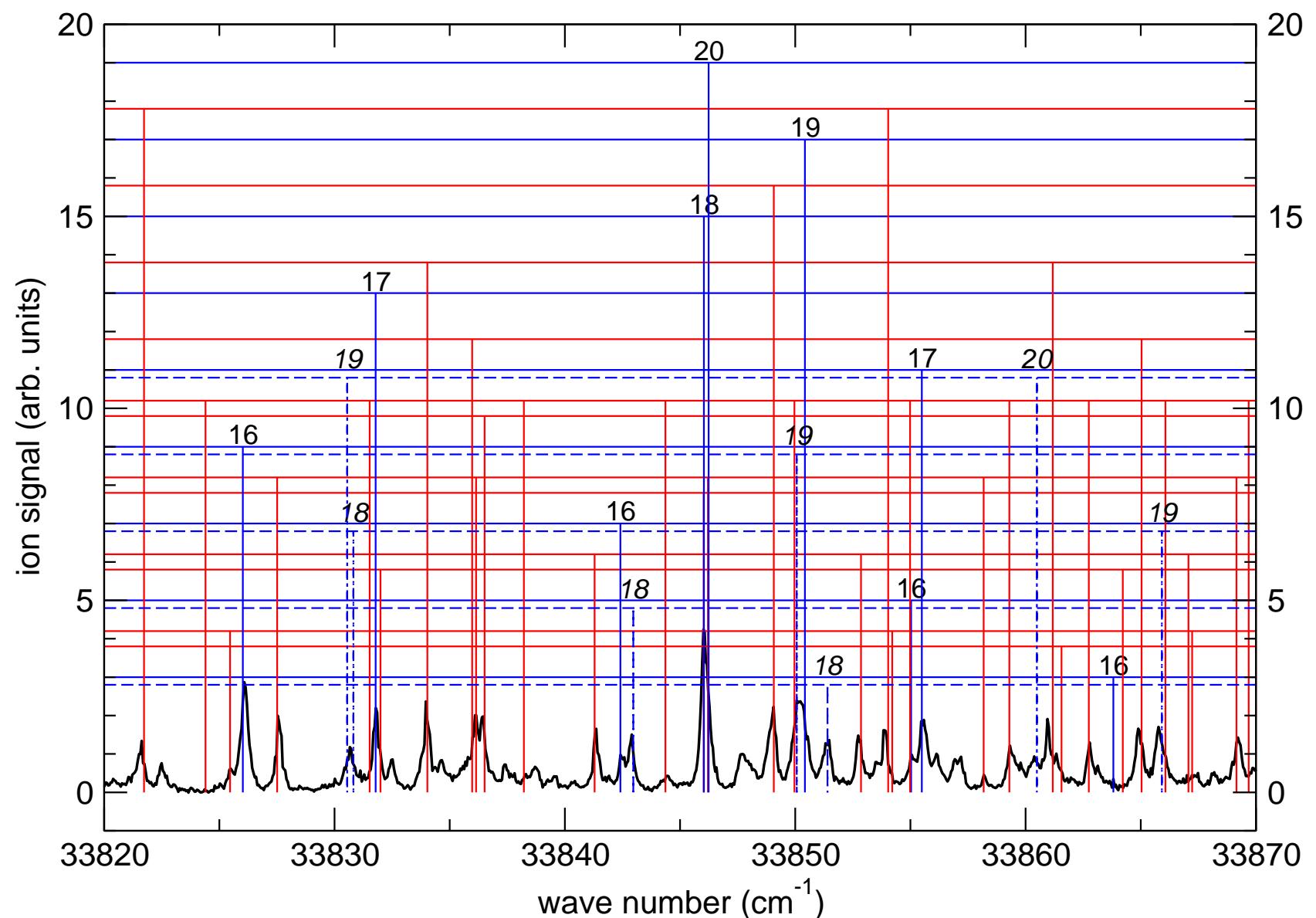




PFI-ZEKE photoelectron spectrum of  ${}^3\text{He}_2^*$







|                                    | $\nu, \nu^+ = 0$     | ${}^4\text{He}_2$      | $\nu, \nu^+ = 2$       | ${}^3\text{He}_2$ |
|------------------------------------|----------------------|------------------------|------------------------|-------------------|
|                                    | $\nu, \nu^+ = 0$     |                        | $\nu, \nu^+ = 0$       |                   |
| $T_\nu$ (cm $^{-1}$ )              | 0.0                  | 1732.1615 <sup>a</sup> | 3386.5024 <sup>a</sup> | 0.0               |
| $B_\nu$ (cm $^{-1}$ )              | 7.58914 <sup>a</sup> | 7.34874 <sup>a</sup>   | 7.10175 <sup>a</sup>   | 10.0386(95)       |
| $D_\nu$ (10 $^{-4}$ cm $^{-1}$ )   | 5.6153 <sup>a</sup>  | 5.6538 <sup>a</sup>    | 5.7439 <sup>a</sup>    | 9.90 <sup>b</sup> |
| $H_\nu$ (10 $^{-8}$ cm $^{-1}$ )   | 3.22 <sup>a</sup>    | 2.84 <sup>a</sup>      | 3.31 <sup>a</sup>      |                   |
| $T_\nu^+ - T_\nu$ (cm $^{-1}$ )    | 34302.236(20)        | 34198.390(24)          | 34102.102(46)          | 34292.298(27)     |
| $T_\nu^+ - T_0^+$ (cm $^{-1}$ )    | 0.0                  | 1628.416               | 3186.469               | 0.0               |
| $B_\nu^+$ (cm $^{-1}$ )            | 7.09796(25)          | 6.87394(52)            | 6.6528(27)             | 9.3884(91)        |
| $D_\nu^+$ (10 $^{-4}$ cm $^{-1}$ ) | 5.012(5)             | 5.094(18)              | 5.79(28)               | 9.051(94)         |

<sup>a</sup> Fixed to the values of C. Focsa, P.F. Bernath, R. Colin, J. Mol. Spectrosc. **191**, 209 (1998).

<sup>b</sup> Derived from the value of  ${}^4\text{He}_2$ .

$$\begin{aligned}
 {}^4\text{He}_2^+: & \quad B_e = 7.20997(46) \text{ cm}^{-1}, r_e = 1.08102(3) \text{ \AA} & [\text{H}_2^+: r_e = 1.052 \text{ \AA}] \\
 & \quad \omega_e = 1698.578(106) \text{ cm}^{-1}, \omega_e x_e = 35.131(40) \text{ cm}^{-1}, k = 340 \text{ N m}^{-1} & [\text{H}_2^+: k = 160 \text{ N m}^{-1}] \\
 \text{Lit.:} & \quad B_e = 7.211 \text{ cm}^{-1}, r_e = 1.0806 \text{ \AA} \text{ (theor.: } 1.0811(3) \text{ \AA}) \\
 & \quad \omega_e = 1698.6 \text{ cm}^{-1}, \omega_e x_e = 35.25 \text{ cm}^{-1}; T_0^+ - T_0 = 34302.3(10) \text{ cm}^{-1}
 \end{aligned}$$

## Conclusion

- Improved molecular constants for  $X^+ \ ^2\Sigma_u^+$  state of  ${}^4\text{He}_2^+$  (incl.  $v^+ = 2$ )
- First spectroscopic data for  ${}^3\text{He}_2$  a  ${}^3\Sigma_u^+$  and  ${}^3\text{He}_2^+$   $X^+ \ ^2\Sigma_u^+$  states
- PFI-ZEKE data consistent with results from MQDT analysis of photoionization spectrum

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## Symmetries and selection rules

| $D_{\infty h}(M)$                      | E  | (12)                        | $E^*$ | $(12)^*$ |
|--|----|-----------------------------|-------|----------|
| $\Lambda_g^+$                          | +s | 1                           | 1     | 1        |
| $\Lambda_u^+$                          | +a | 1                           | -1    | 1        |
| $\Lambda_g^-$                          | -a | 1                           | -1    | -1       |
| $\Lambda_u^-$                          | -s | 1                           | 1     | -1       |
| $\Lambda = \Sigma, \Pi, \Delta, \dots$ |    | $(\Gamma^* = \sum_u^-, -s)$ |       |          |

|                         |         |                      |
|-------------------------|---------|----------------------|
| $\Gamma_{\text{Ryd}}$   | +s      | $\ell$ even          |
|                         | -s      | $\ell$ odd           |
| $\Gamma_{\text{rot}}$   | +s      | $N$ even             |
|                         | -a      | $N$ odd              |
| $\Gamma_{\text{nspin}}$ | +s      | $w = (2I+1)(I+1)$    |
|                         | +a      | $w = (2I+1)I$        |
| $\Gamma_{\text{int}}$   | $\pm s$ | for bosonic nuclei   |
|                         | $\pm a$ | for fermionic nuclei |

statistical weights:

$$\Gamma_{\text{rve}} \otimes \Gamma_{\text{nspin}} \supset \Gamma_{\text{int}}$$

$$\Gamma_{\text{Ryd}} \otimes \Gamma_{\text{rve}}^+ \otimes \Gamma_{\text{nspin}} \supset \Gamma_{\text{int}}$$

|                      |                  | ${}^4\text{He}_2$ | ${}^3\text{He}_2$ |   |   |
|----------------------|------------------|-------------------|-------------------|---|---|
|                      | $N^{(+)}$ :      | e                 | o                 | e | o |
| $X^+ {}^2\Sigma_u^+$ | $N^+$            | 0                 | 1                 | 3 | 1 |
| high Ryd             | $N^+$            | 0                 | 1                 | 3 | 1 |
| $n p \sigma$         | ${}^3\Sigma_g^+$ | $N$               | 1                 | 0 | 1 |
| $n p \pi$            | ${}^3\Pi_g^+$    | $N$               | 1                 | 0 | 1 |
| $n p \pi$            | ${}^3\Pi_g^-$    | $N$               | 0                 | 1 | 3 |
| $2s$ a               | ${}^3\Sigma_u^+$ | $N$               | 0                 | 1 | 3 |

## Symmetries and selection rules

| $D_{\infty h}(M)$ | $E$  | $(12)$ | $E^*$ | $(12)^*$ |
|-------------------|------|--------|-------|----------|
| $\Lambda_g^+$     | $+s$ | 1      | 1     | 1        |
| $\Lambda_u^+$     | $+a$ | 1      | -1    | 1        |
| $\Lambda_g^-$     | $-a$ | 1      | -1    | -1       |
| $\Lambda_u^-$     | $-s$ | 1      | 1     | -1       |

$$\Lambda = \Sigma, \Pi, \Delta, \dots \quad (\Gamma^* = \Sigma_u^-, -s)$$

|                         |         |                      |
|-------------------------|---------|----------------------|
| $\Gamma_{\text{Ryd}}$   | $+s$    | $\ell$ even          |
|                         | $-s$    | $\ell$ odd           |
| $\Gamma_{\text{rot}}$   | $+s$    | $N$ even             |
|                         | $-a$    | $N$ odd              |
| $\Gamma_{\text{nspin}}$ | $+s$    | $w = (2I+1)(I+1)$    |
|                         | $+a$    | $w = (2I+1)I$        |
| $\Gamma_{\text{int}}$   | $\pm s$ | for bosonic nuclei   |
|                         | $\pm a$ | for fermionic nuclei |

electric dipole transitions: ( $\Gamma'_{\text{nspin}} = \Gamma''_{\text{nspin}}$ )

$$\Gamma'_{\text{rve}} \otimes \Gamma''_{\text{rve}} \supset -s$$

photoionization:

$$\Gamma'_{\text{rve}} \otimes \Gamma''_{\text{rve}} \supset -s \text{ for } \ell \text{ even}$$

$$\Gamma'_{\text{rve}} \otimes \Gamma''_{\text{rve}} \supset +s \text{ for } \ell \text{ odd}$$

$$+ \leftrightarrow - \quad + \leftrightarrow + \quad - \leftrightarrow - \quad \ell \text{ even}$$

$$+ \leftrightarrow + \quad - \leftrightarrow - \quad + \leftrightarrow - \quad \ell \text{ odd}$$

$$s \leftrightarrow s \quad a \leftrightarrow a \quad s \leftrightarrow a$$

$$g \leftrightarrow u \quad g \leftrightarrow g \quad u \leftrightarrow u \quad \ell \text{ even}$$

$$g \leftrightarrow g \quad u \leftrightarrow u \quad g \leftrightarrow u \quad \ell \text{ odd}$$

$$2s \text{ a } {}^3\Sigma_u^+ \rightarrow np \text{ } {}^3\Pi_g^- \quad N' - N'' = 0$$

$$2s \text{ a } {}^3\Sigma_u^+ \rightarrow np \text{ } {}^3\Sigma_g^+, {}^3\Pi_g^+ \quad N' - N'' = \pm 1$$

$$2s \text{ a } {}^3\Sigma_u^+ \rightarrow X^+ \text{ } {}^2\Sigma_u^+ \quad N^+ - N'' \text{ even}$$

$$(p \text{ photoelectron: } N^+ - N'' = 0, \pm 2)$$

Ionization from  $2s\sigma_g$  orbital with dominant s character ( $N^+ - N'' = 0$  strong) and small d contribution ( $N^+ - N'' = \pm 2$  weak)

