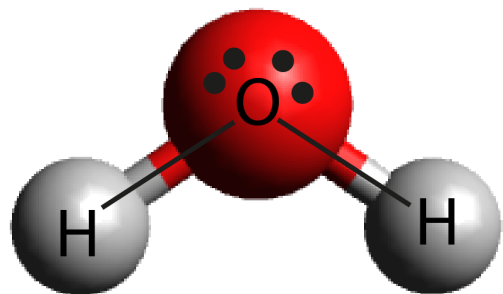


Rotationally resolved photoelectron spectroscopic study of the \tilde{A}^+ state of H_2O^+ .

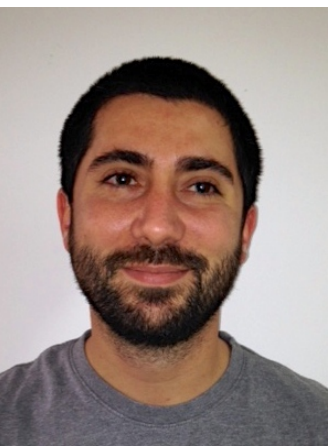


photoelectron spectroscopy

Introduction to water

The experimental set-up

B. GANS



The Results

The Conclusions

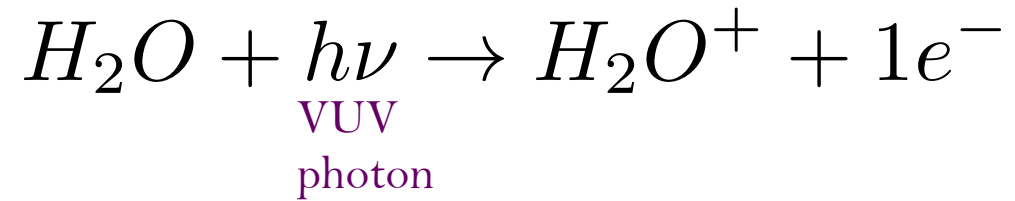
U. JACOVELLA



F. MERKT



Photoelectron spectroscopy



Photoelectron spectroscopy

Two different approaches

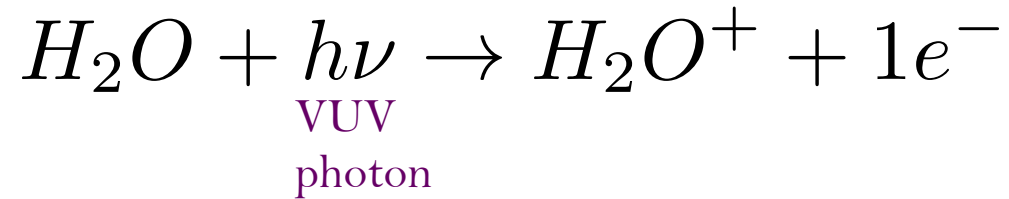
The frequency of the
light source is:

①

Fixed

②

Tunable



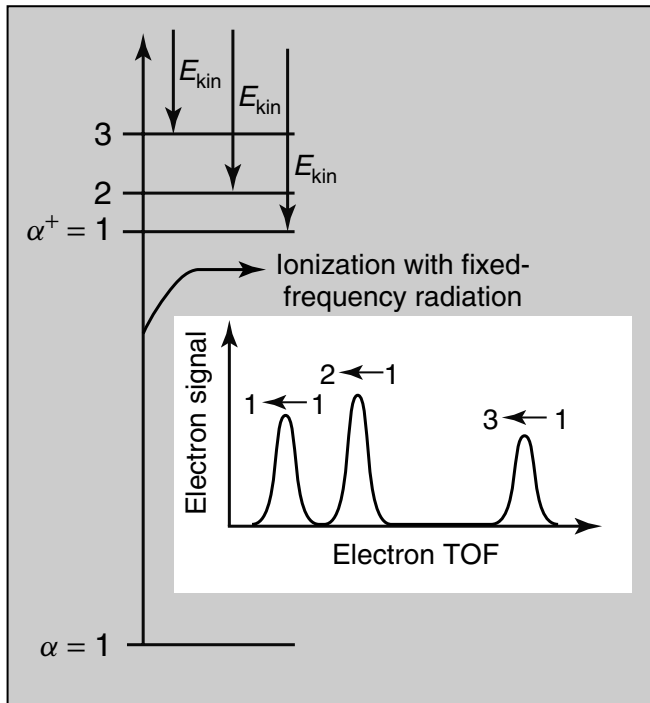
Photoelectron spectroscopy

Two different approaches

The frequency of the light source is:

①

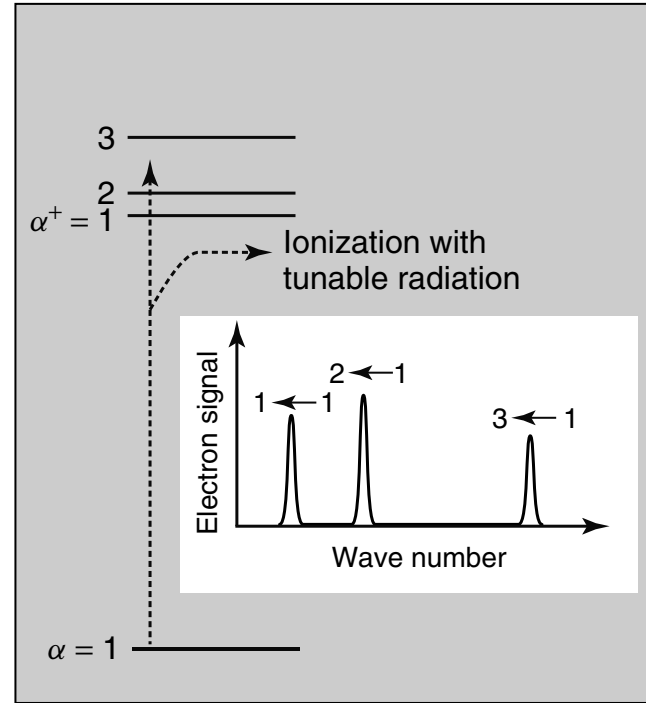
Fixed



Ultraviolet photoelectron spectroscopy (UPS)

②

Tunable



Threshold photoelectron spectroscopy (TPES)

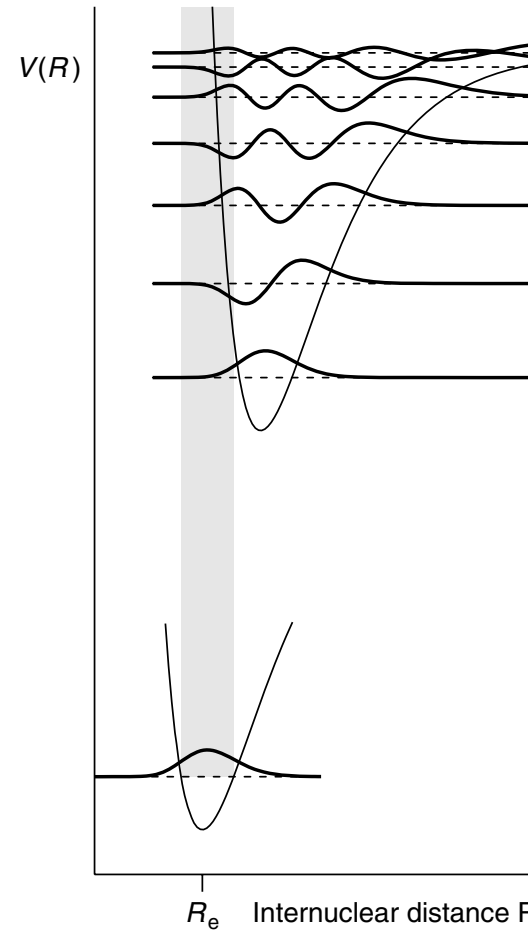
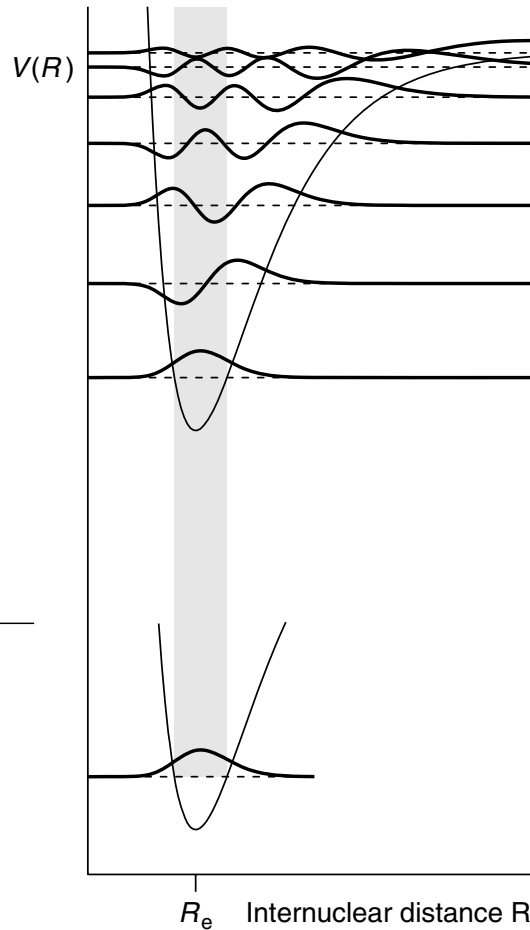
Photoelectron spectroscopy: Effect of a change of geometry

Structure of the cation compared to the structure of the neutral

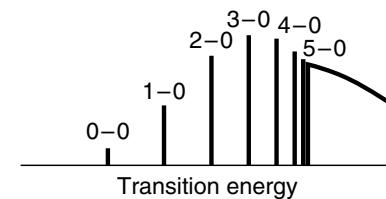
Similar

Different

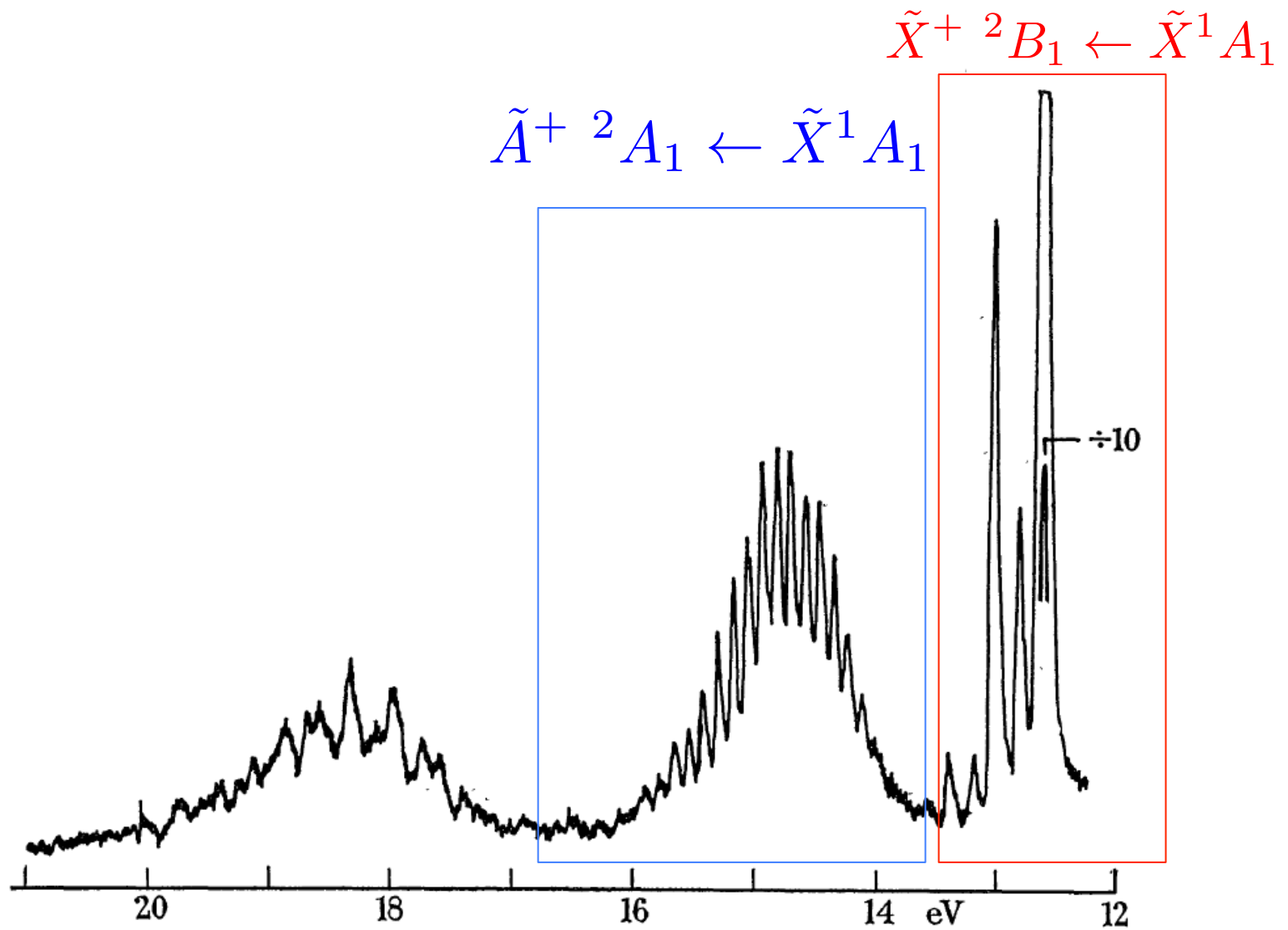
Vibrational bands visible on the spectrum



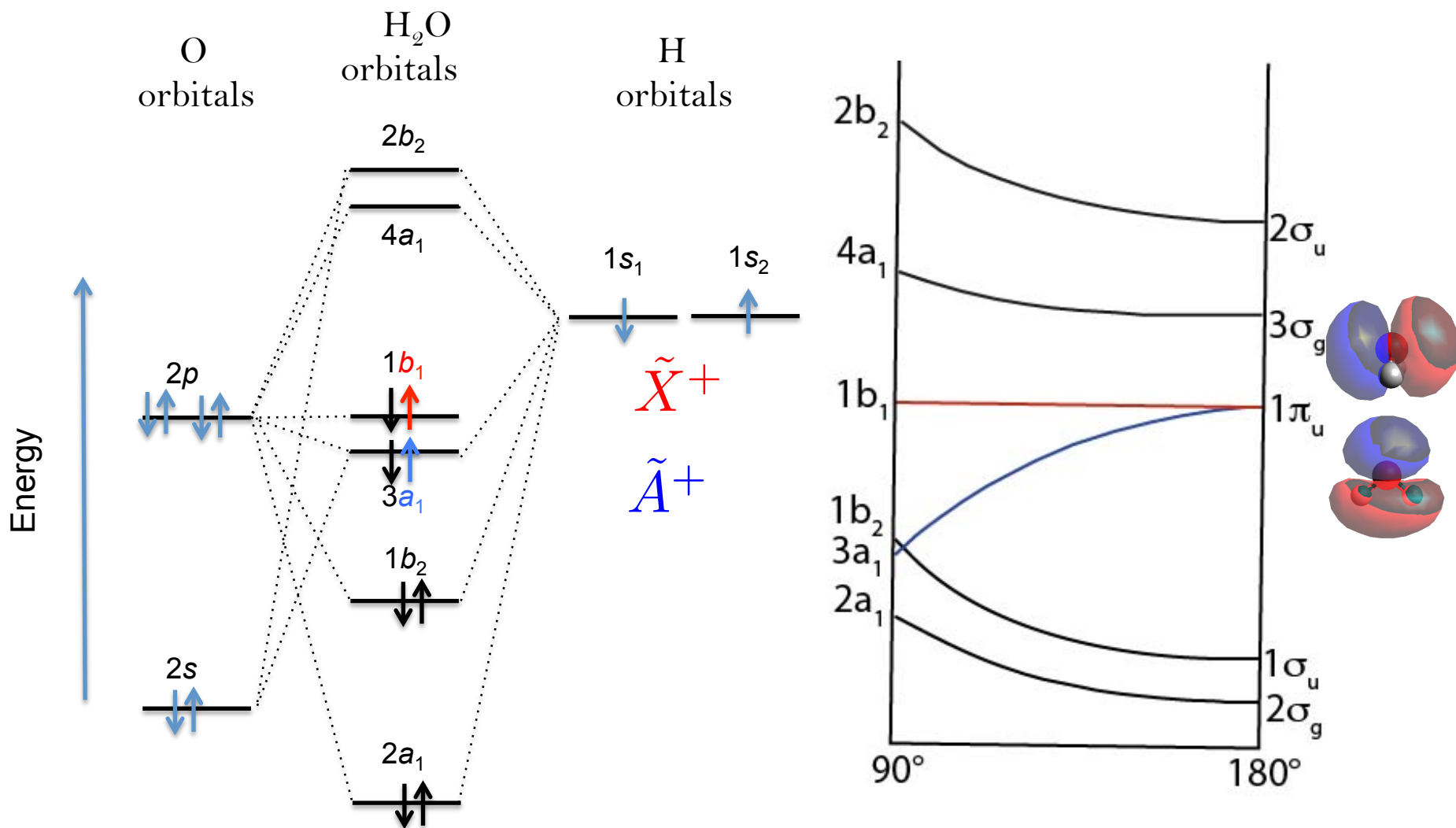
Vibrational bands visible on the spectrum



Photoelectron spectroscopy: What about H₂O?



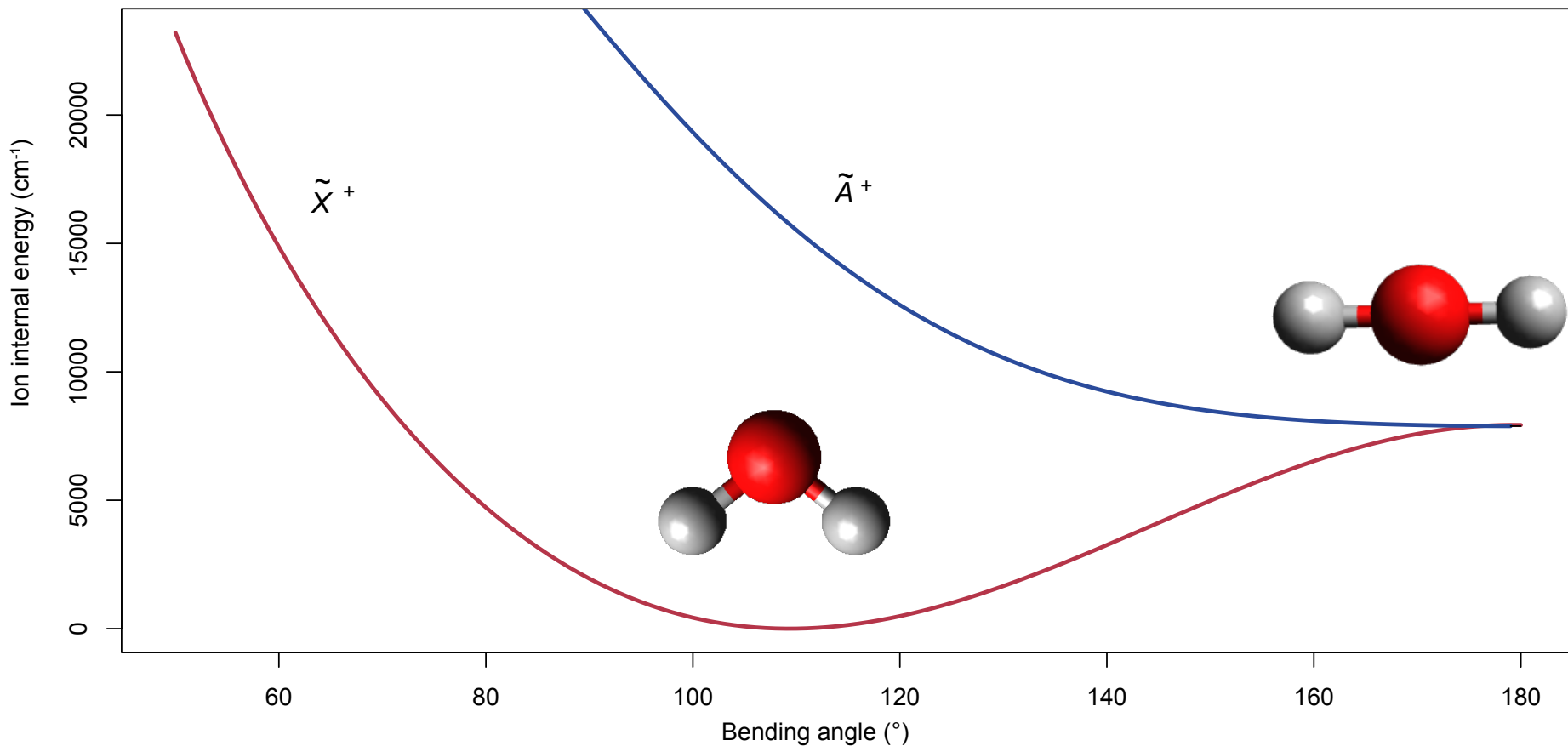
Water: Electronic configuration



Water: Electronic configuration

ab initio calculations

Potential energy along the bending angle

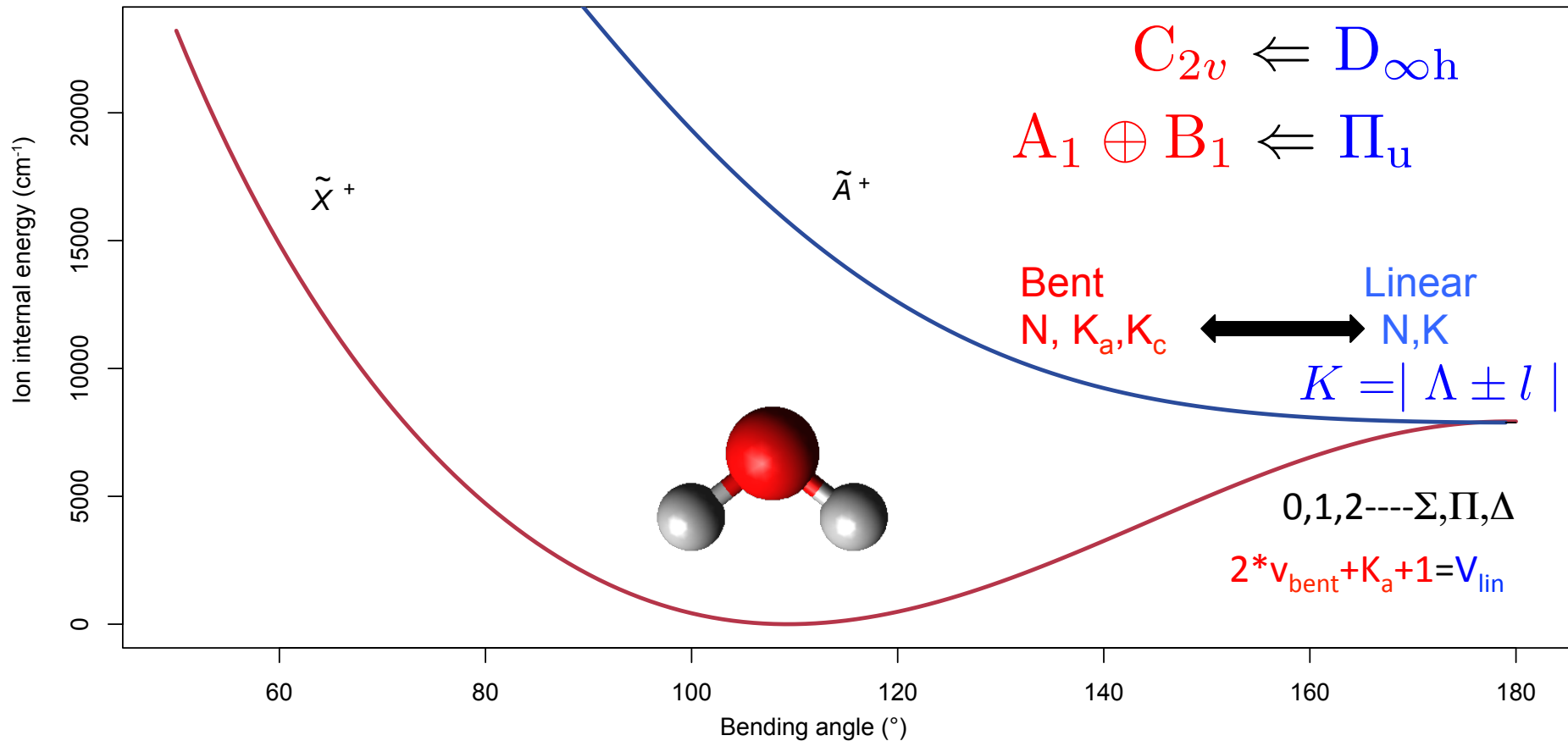


M. Brommer, B. Weis, B. Follmeg, P. Rosmus, S. Carter, N. C. Handy, H. J. Werner, and P. J. Knowles, *J. Chem. Phys.* **98**, 5222 (1993)

Water: Electronic configuration

ab initio calculations

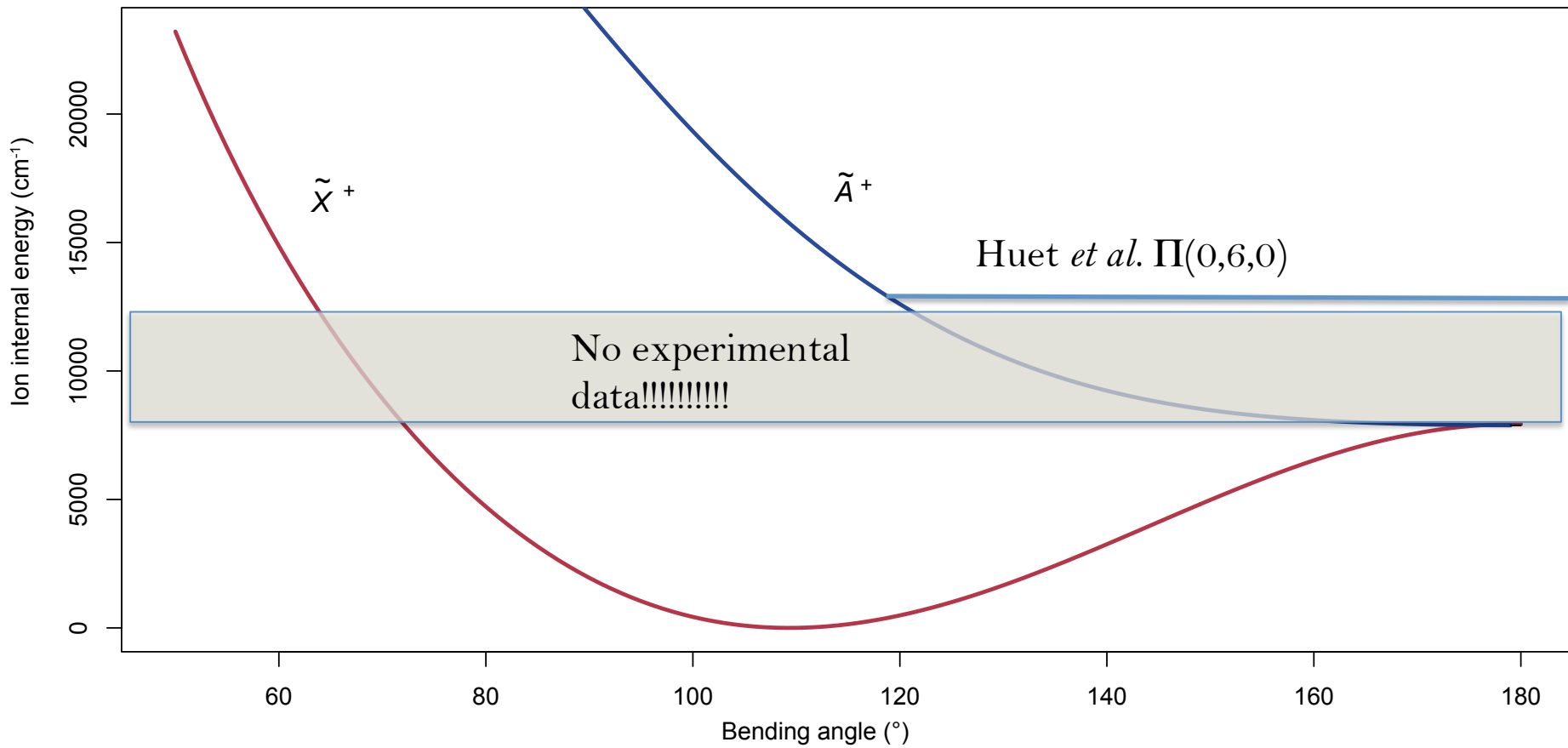
Potential energy along the bending angle



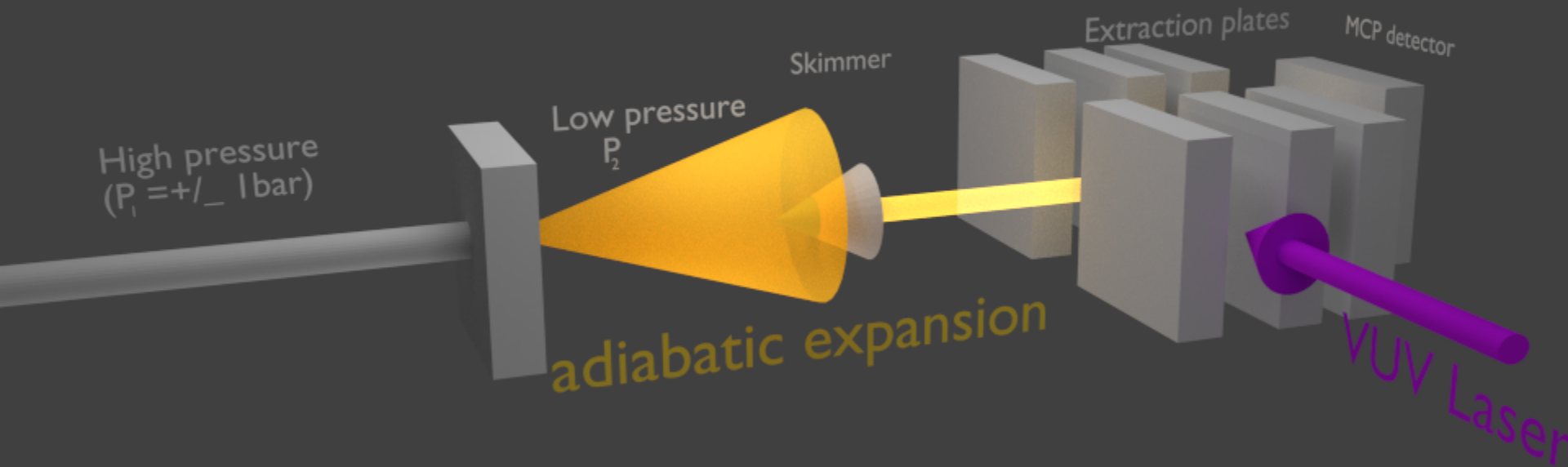
Water: Electronic configuration

ab initio calculations

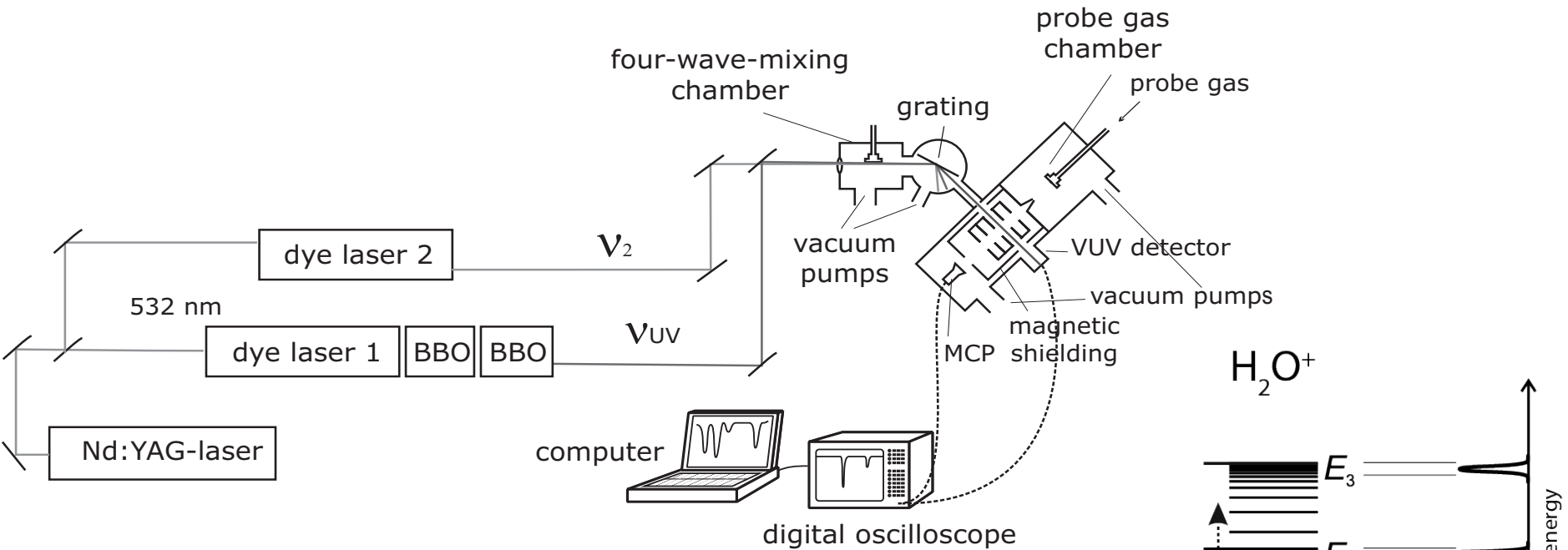
Potential energy along the bending angle



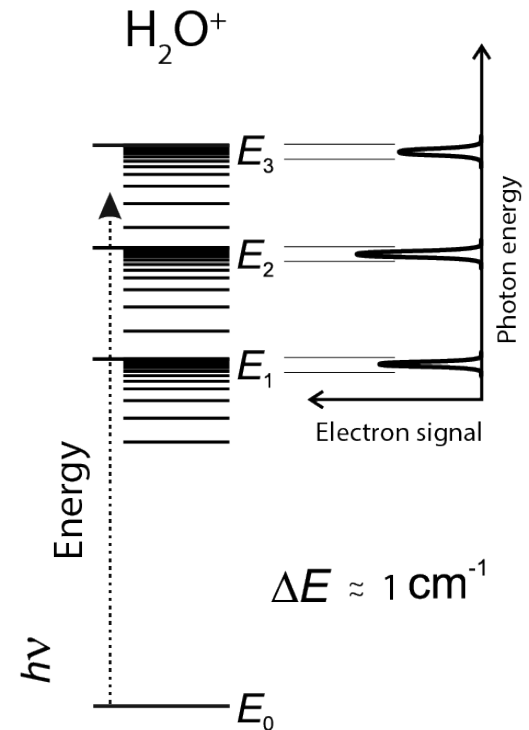
Experimental set-up



Experimental set-up (II)



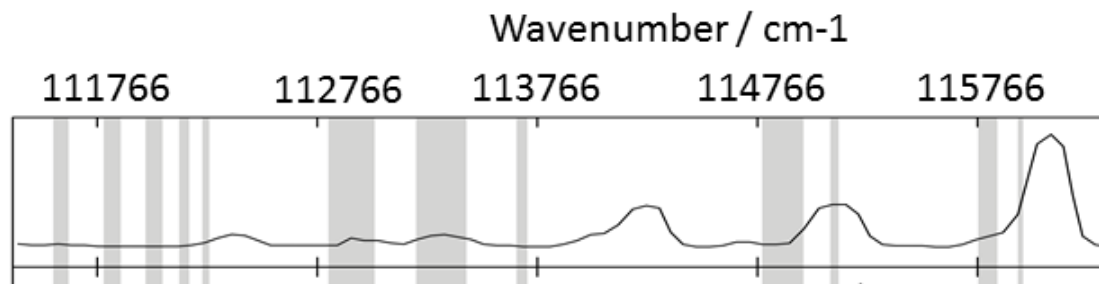
PFI-ZEKE photoelectron spectroscopy
PFI= Pulsed field ionization
ZEKE= Zero kinetic energy



Vibrational assignment

Resolution
/ cm^{-1}

J. E. Reutt, *et. al.*, J. Chem. Phys., **85**,
6928-6939, (1986).



89

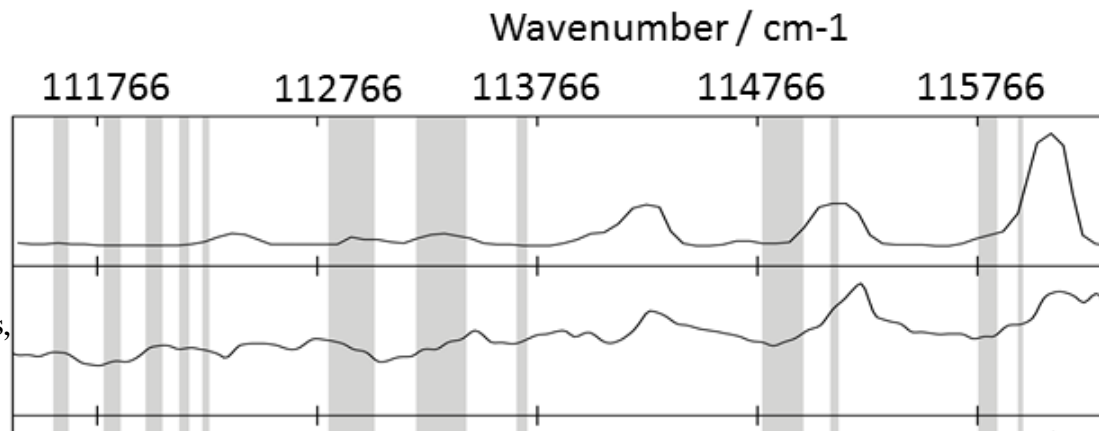
Molecular beam and a resolution of 11 meV (89 cm^{-1})



unscanned from low quality pictures of pdf
files and do not account for the high quality
of the original data

Vibrational assignment

Resolution
/ cm^{-1}



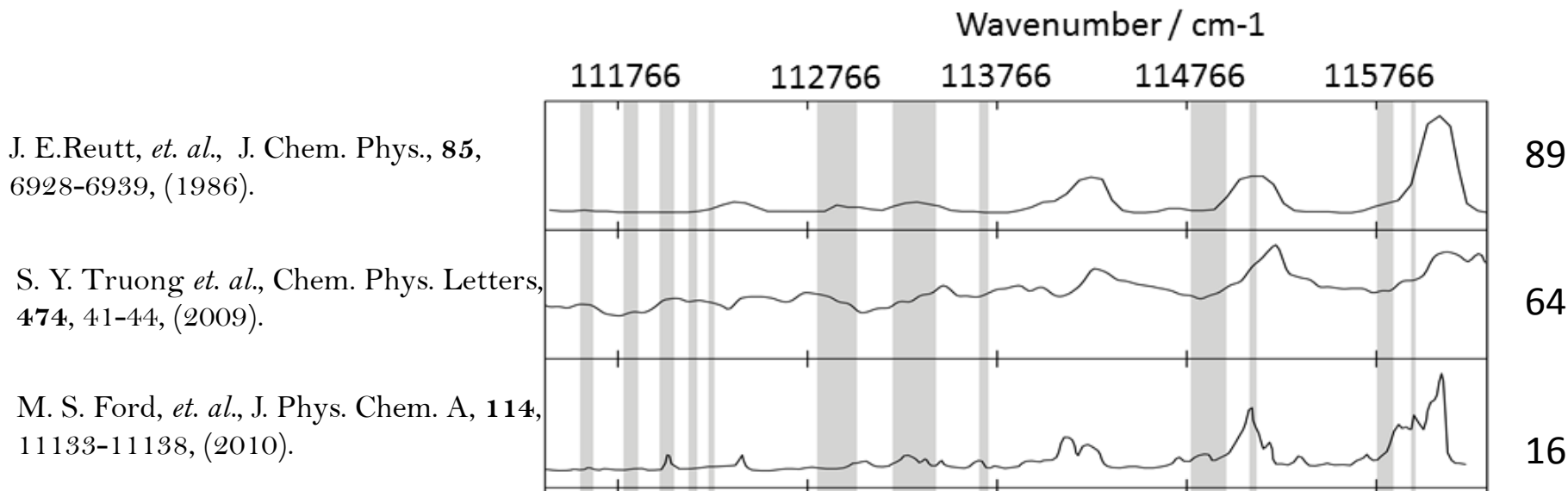
J. E. Reutt, *et al.*, *J. Chem. Phys.*, **85**,
6928-6939, (1986).

S. Y. Truong *et al.*, *Chem. Phys. Letters*,
474, 41-44, (2009).

Room temperature threshold photoelectron spectrum
Resolution of 8 meV (64 cm^{-1})

Vibrational assignment

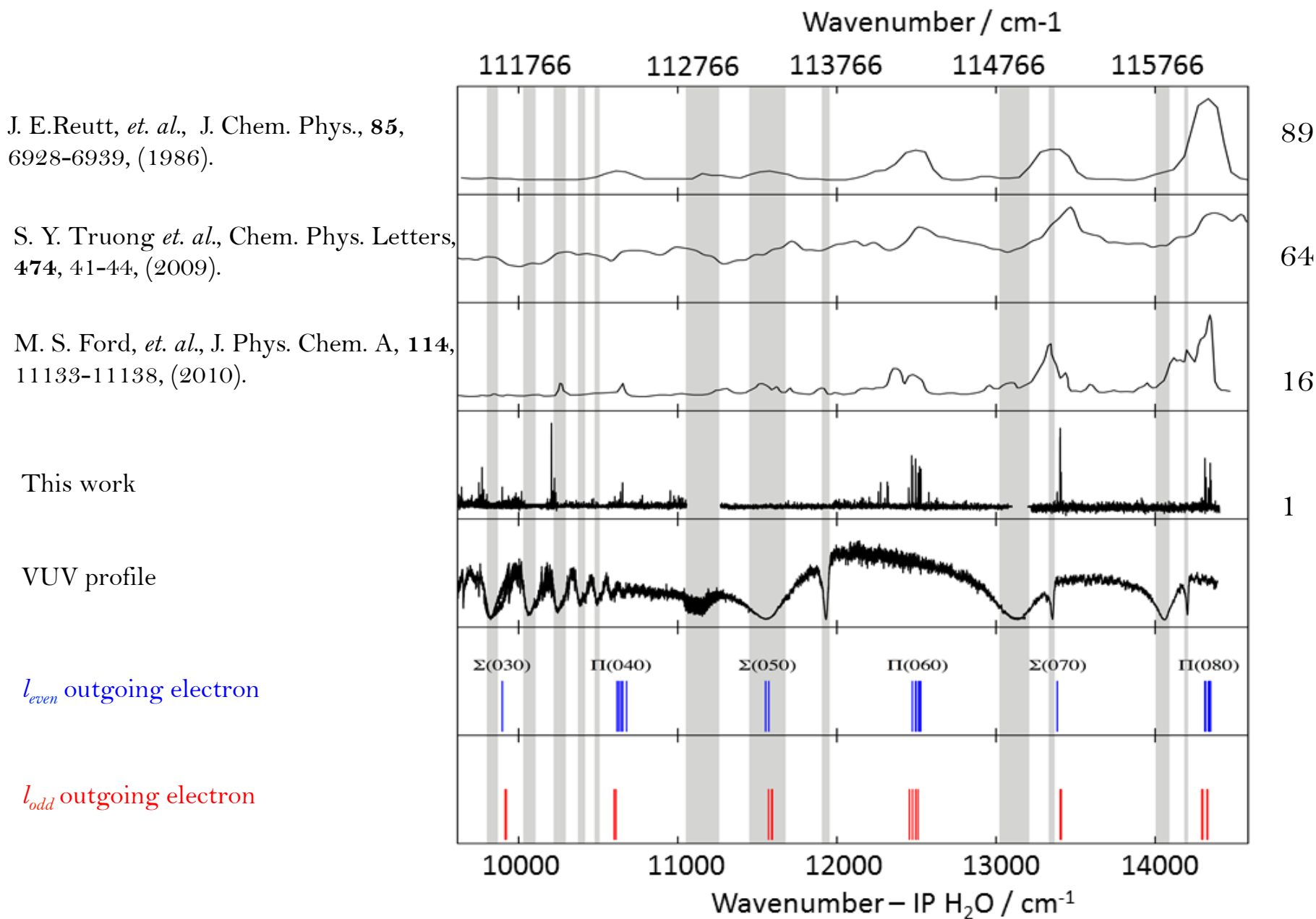
Resolution
/ cm^{-1}



He I radiation source coupled with a Doppler free beam device
Resolution of 2 meV (16 cm^{-1})

Vibrational assignment

Resolution
/ cm^{-1}



(D) (B) (C) (A)

Wavenumber / cm⁻¹

111766 112766 113766 114766 115766

J. E. Reutt, *et al.*, J. Chem. Phys., **85**,
6928-6939, (1986).

S. Y. Truong *et al.*, Chem. Phys. Letters,
474, 41-44, (2009).

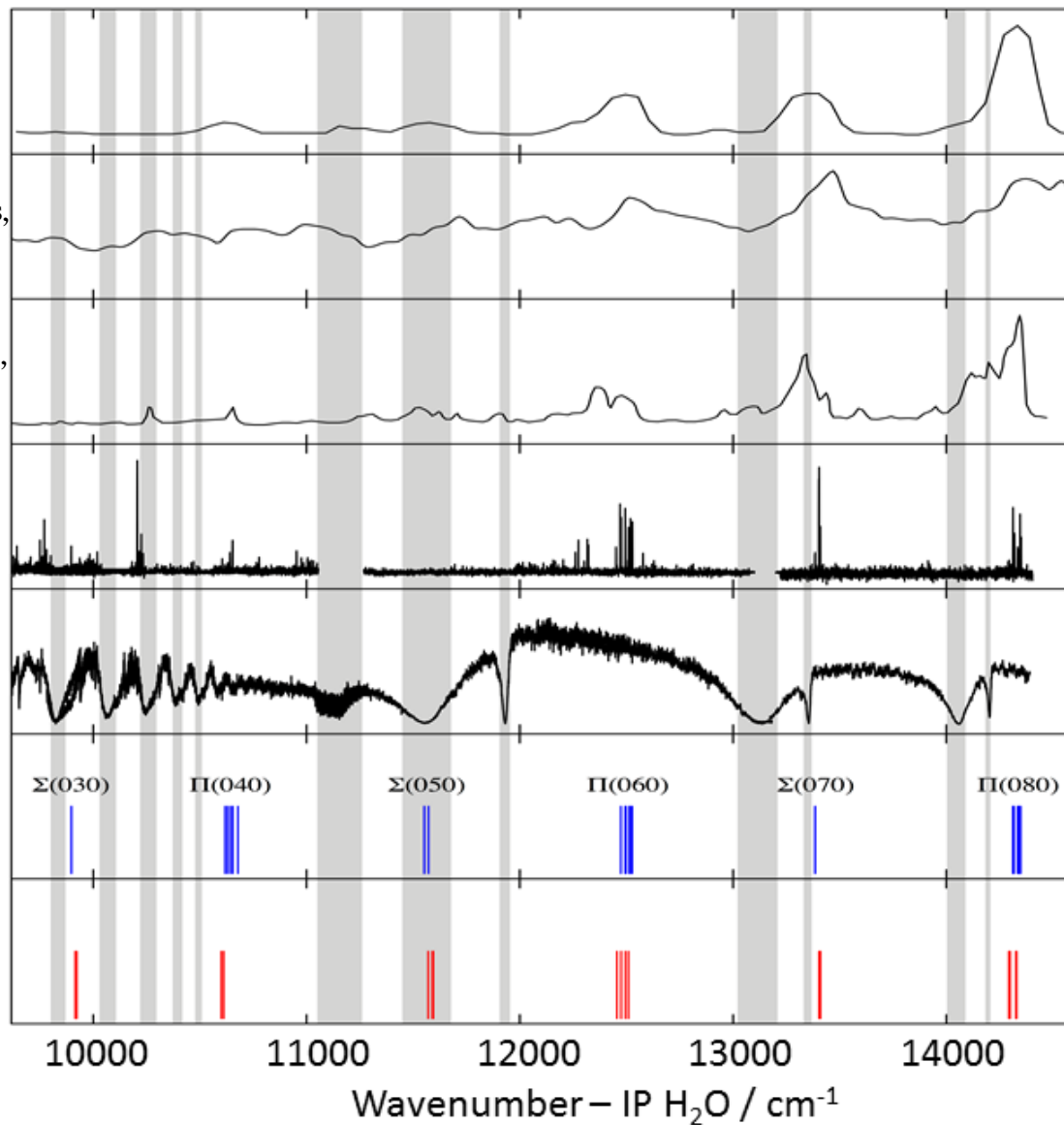
M. S. Ford, *et al.*, J. Phys. Chem. A, **114**,
11133-11138, (2010).

This work

VUV profile

l_{even} outgoing electron

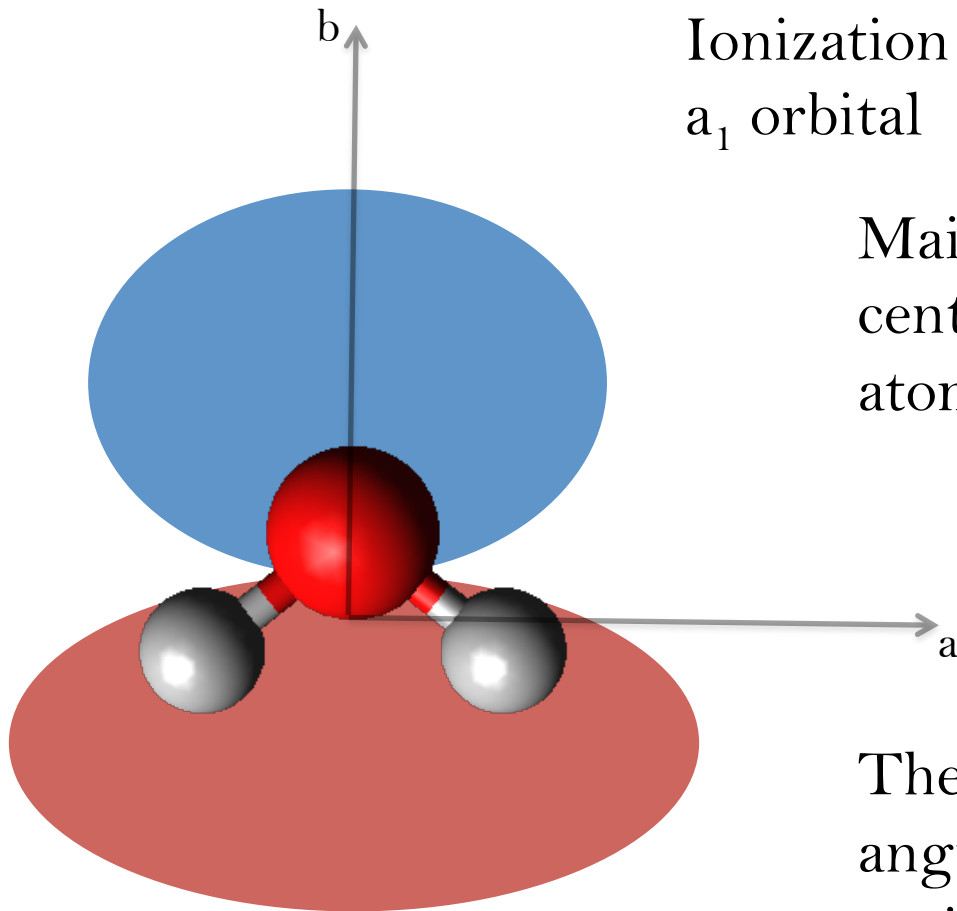
l_{odd} outgoing electron



Selection rules

Ionization from the HOMO-1,
 a_1 orbital

Mainly a p orbital
centered on the oxygen
atom



The outgoing electron
angular momentum
parity is expected to be
more even (l_{even}) than
odd (l_{odd}) !

Selection rules

$$\langle \Psi(\text{ion}) \Psi(\text{electron}) | \mu | \Psi(\text{neutral}) \rangle$$

$$\Gamma_{e^-, l} \otimes \Gamma_{rve}^+ \otimes \Gamma_{rve}'' \supset \Gamma^*$$

A_1, A_2
 $l_{\text{even}}, l_{\text{odd}}$

$$\left. \begin{aligned} \Delta K_a = K_a^+ - K_a'' = \text{odd} \\ \Delta K_c = K_c^+ - K_c'' = \text{odd} \end{aligned} \right\} \text{for } l \text{ even}$$

$$\left. \begin{aligned} \Delta K_a = K_a^+ - K_a'' = \text{even} \\ \Delta K_c = K_c^+ - K_c'' = \text{even} \end{aligned} \right\} \text{for } l \text{ odd}$$

$C_{2v}(M):$	E	(12)	E^*	$(12)^*$
$C_{2v}:$	E	C_{2b}	σ_{ab}	σ_{bc}
Equiv.rot.:	R^0	R_b^π	R_c^π	R_a^π
$A_1:$	1	1	1	1
$A_2:$	1	1	-1	-1
$B_1:$	1	-1	-1	1
$B_2:$	1	-1	1	-1

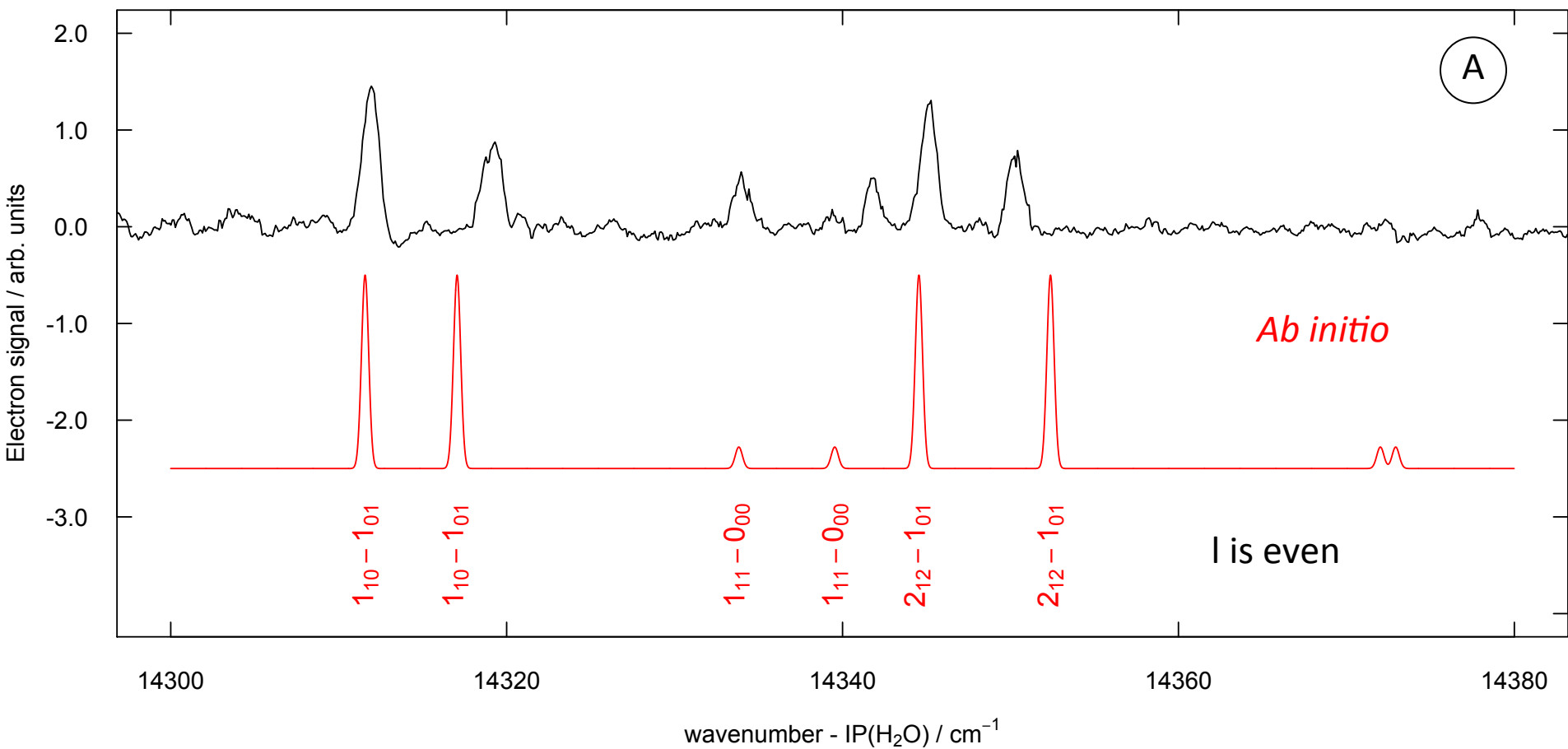
$A_1 \longleftrightarrow A_2, B_1 \longleftrightarrow B_2$ for l even

$A_1 \longleftrightarrow A_1, A_2 \longleftrightarrow A_2, B_1 \longleftrightarrow B_1, B_2 \longleftrightarrow B_2$ for l odd

$K_a K_c$ parity	$\Gamma_{elec} \otimes \Gamma_{rot}$	
	H_2O (GS)	$H_2O^+(\tilde{A}_1^+ \ ^2\tilde{A}_1)$
ee	A_1	A_1
eo	B_1	B_1
oe	B_2	B_2
oo	A_2	A_2

Comparison with ab initio predictions

$$\Pi(0,8,0), v_{2,\text{bent}}=3$$

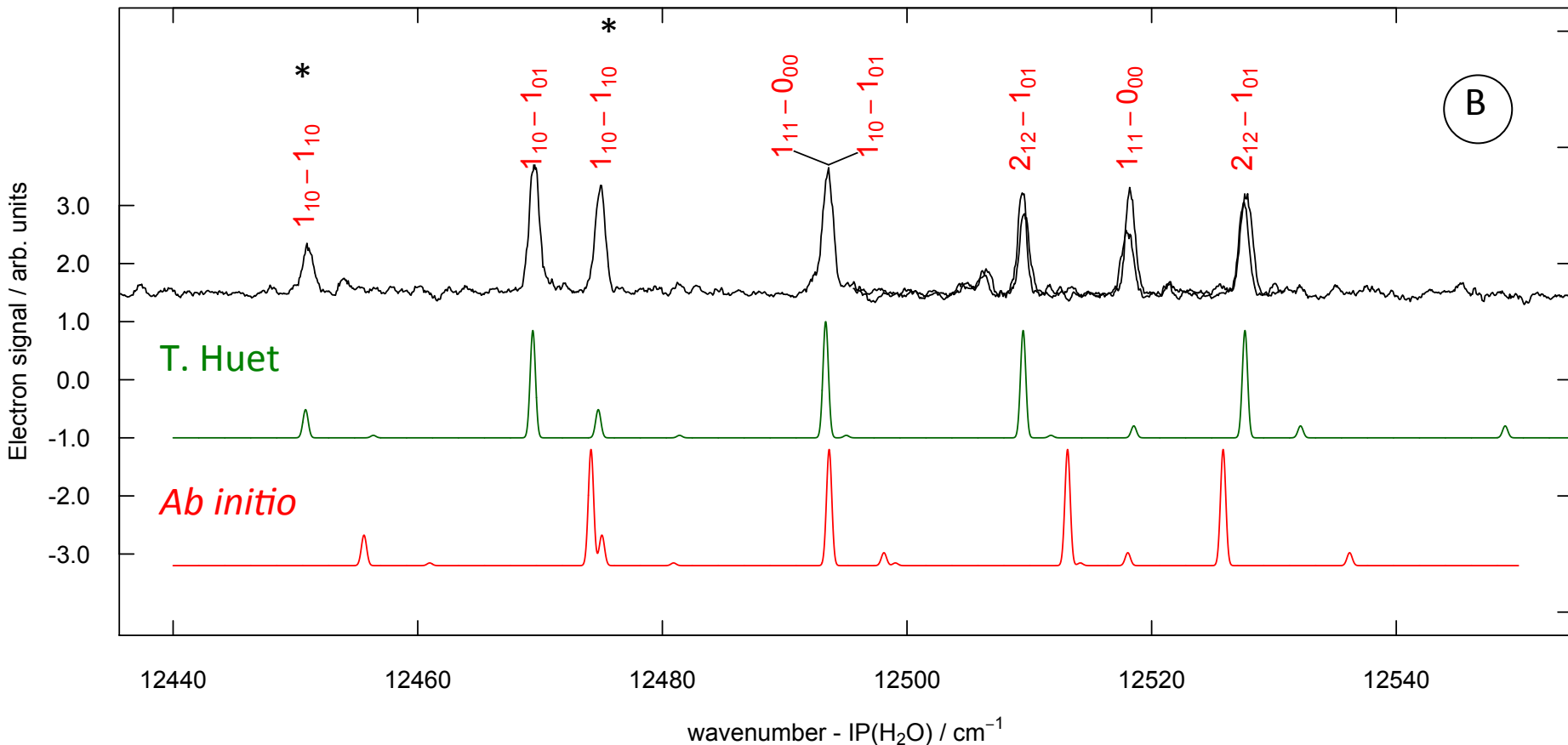


In agreement with the rotational assignment of H. Lew, Can. J. Phys. 54, 2028 (1976).

M. Brommer, B. Weis, B. Follmeg, P. Rosmus, S. Carter, N. C. Handy, H. J. Werner, and P. J. Knowles, J. Chem. Phys. 98, 5222 (1993)

Comparison with previous results

$$\Pi(0,6,0), V_{2,\text{bent}}=2$$



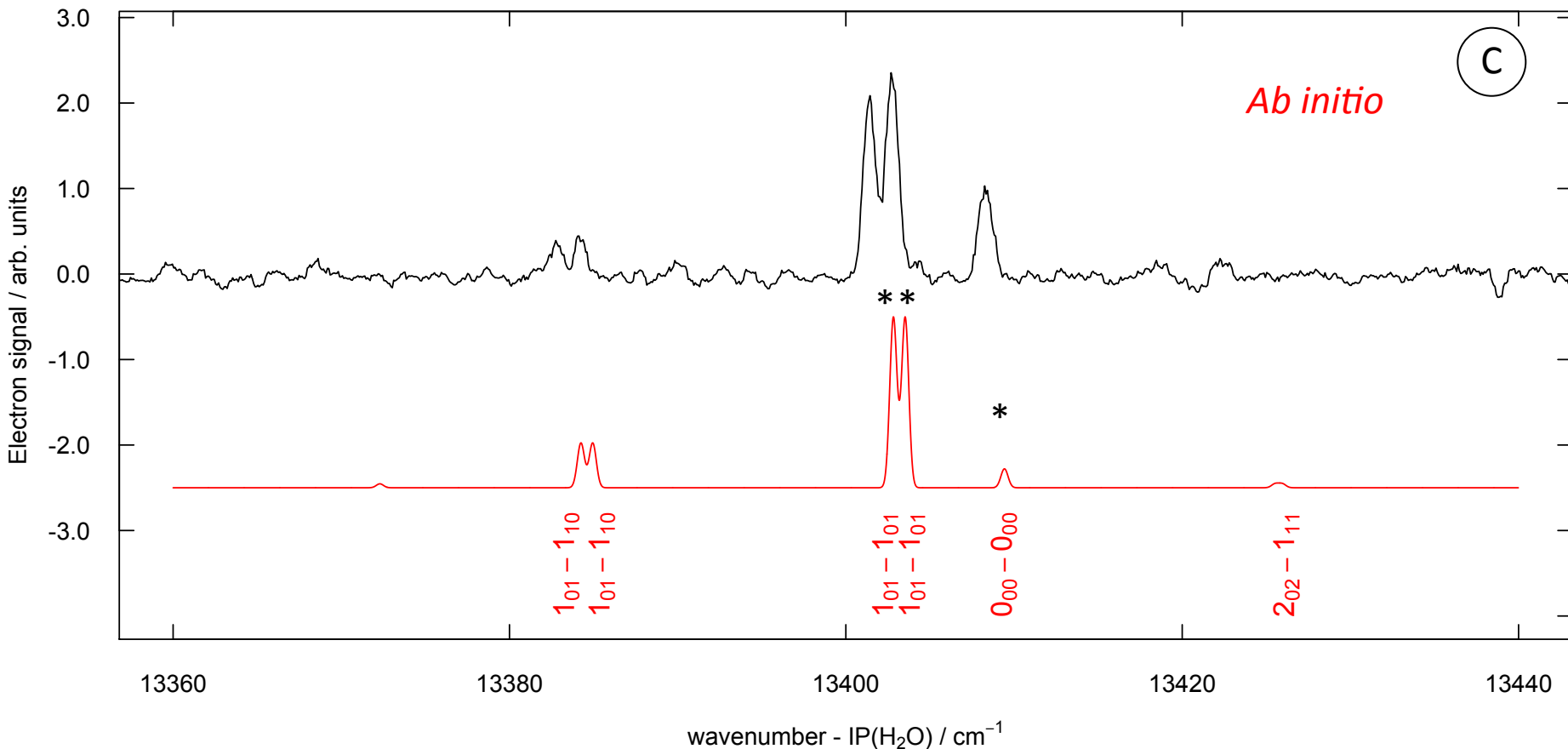
* = l odd

T. R. Huet, I. H. Bachir, J. L. Destombes, and M. Vervloet, *J. Chem. Phys.* **107**, 5645 (1997)

M. Brommer, B. Weis, B. Follmeg, P. Rosmus, S. Carter, N. C. Handy, H. J. Werner, and P. J. Knowles, *J. Chem. Phys.* **98**, 5222 (1993)

Comparison with ab initio predictions

$$\Sigma(0,7,0), V_{2,\text{bent}}=3$$

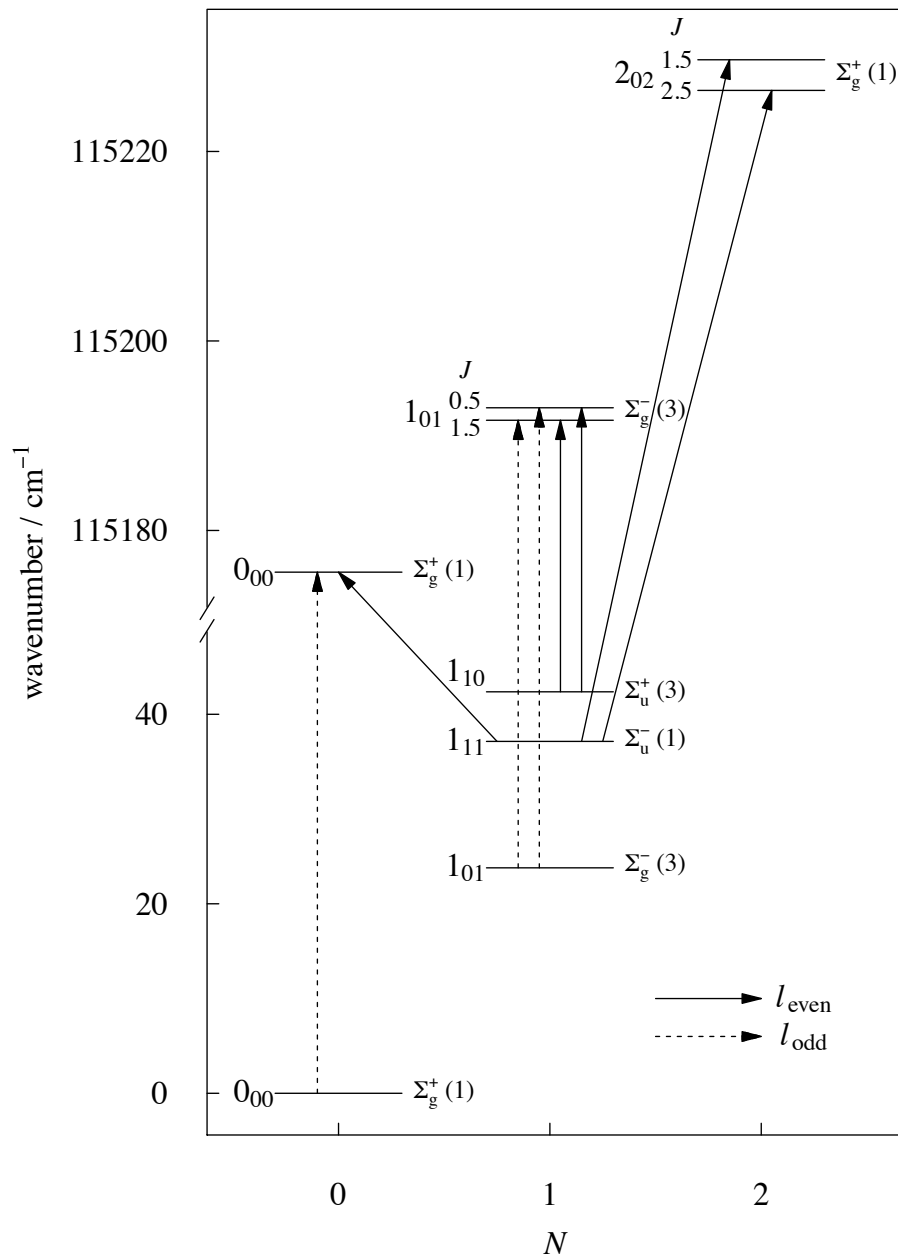


* = l odd

M. Brommer, B. Weis, B. Follmeg, P. Rosmus, S. Carter, N. C. Handy, H. J. Werner, and P. J. Knowles, *J. Chem. Phys.* **98**, 5222 (1993)

Rotational assignment-Interesting case of Σ bands

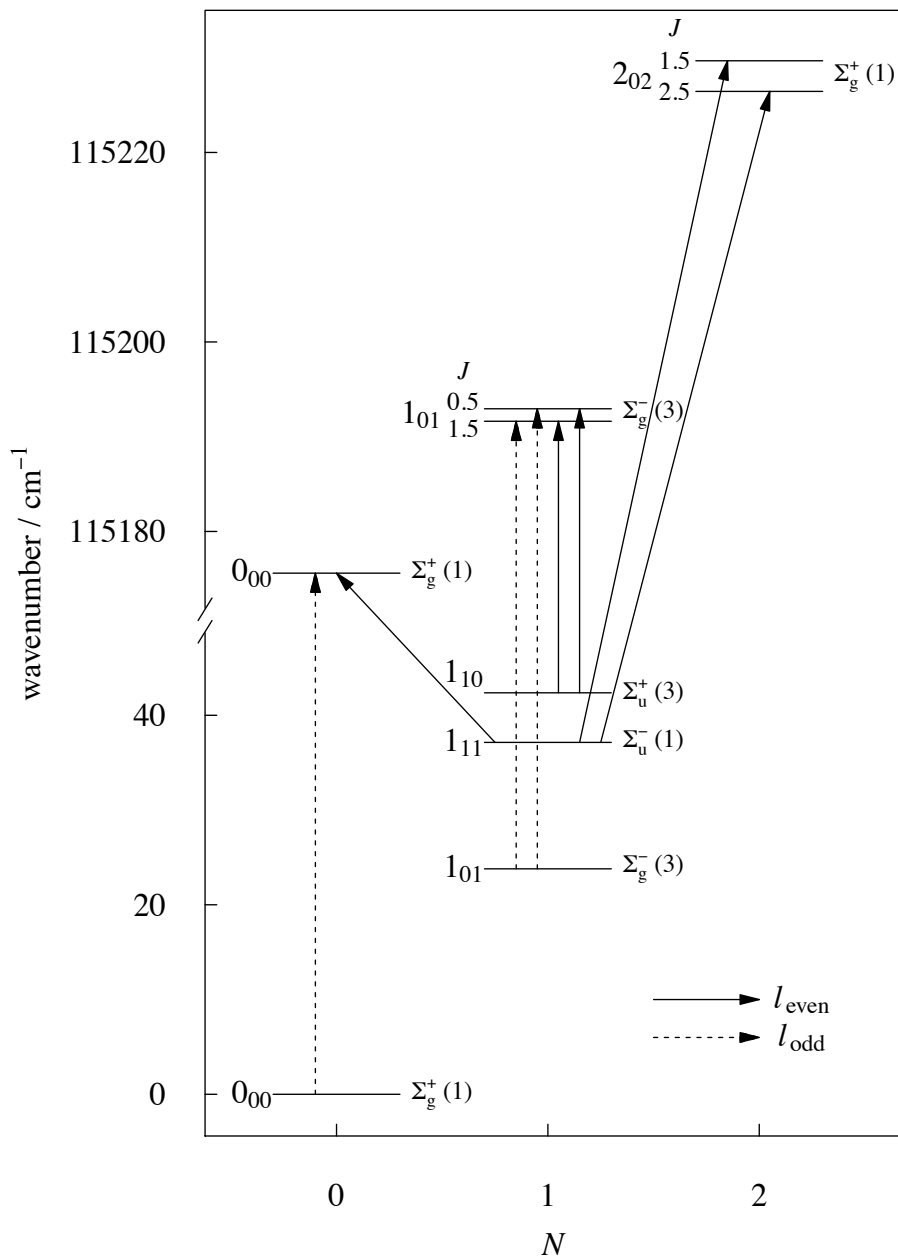
(1)



Why do we observe stronger l_{odd} component for this Σ band?

Rotational assignment-Interesting case of Σ bands

(1)

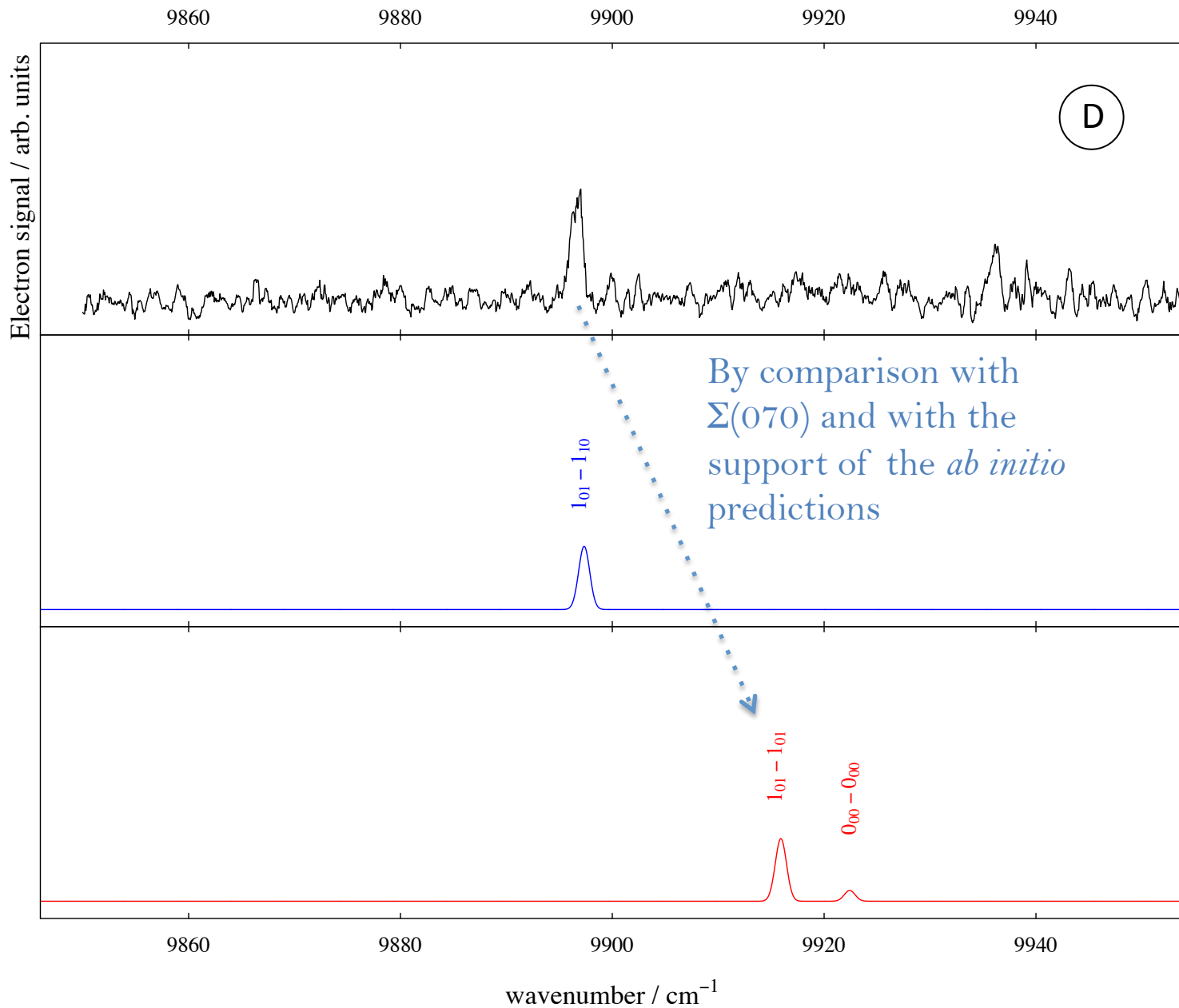


Why do we observe stronger l_{odd} component for this Σ band?

(2)

In our supersonic expansion (10K) and without nuclear spin relaxation: One needs to consider only the $0_{00}, 1_{01}, 1_{10}$ ground state rotational levels.

Tentative assignment of $\Sigma(030), V_{2,\text{bent}}=1$



Conclusions:

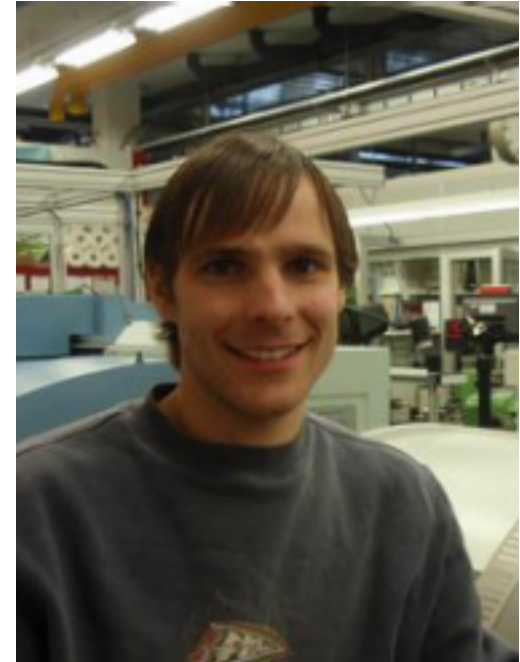
- First jet-cooled rotationally resolved photoelectron spectrum of the $\tilde{A}^+ 2A_1 \leftarrow \tilde{X}^1A_1$ transition.
- Confirmation of the rotational assignment of the $\Pi(080)$ band.
- Tentative assignment of the $\Sigma(030)$.
- These measurements could support a future potential energy surface refinement.

Acknowledgements

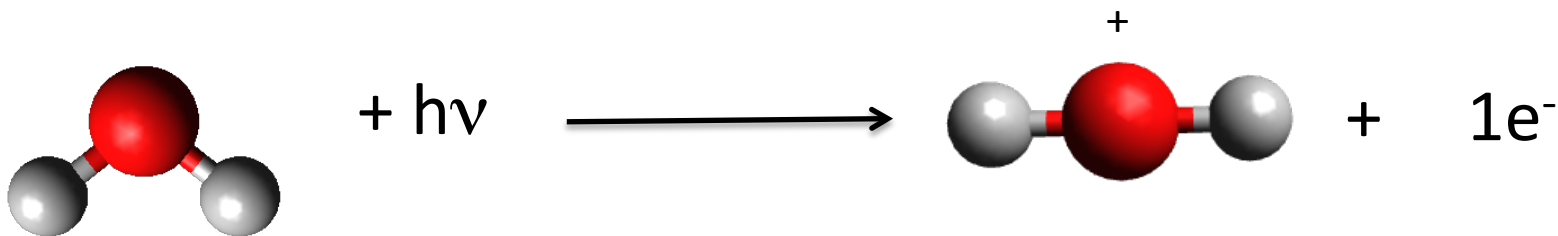
H. SCHMUTZ



Joseph-Anton Agner



And you for your attention!!!!



chemical reaction¹:

A process that results in the interconversion of chemical species.

Chemical reactions may be elementary reactions or stepwise reactions

chemical species¹:

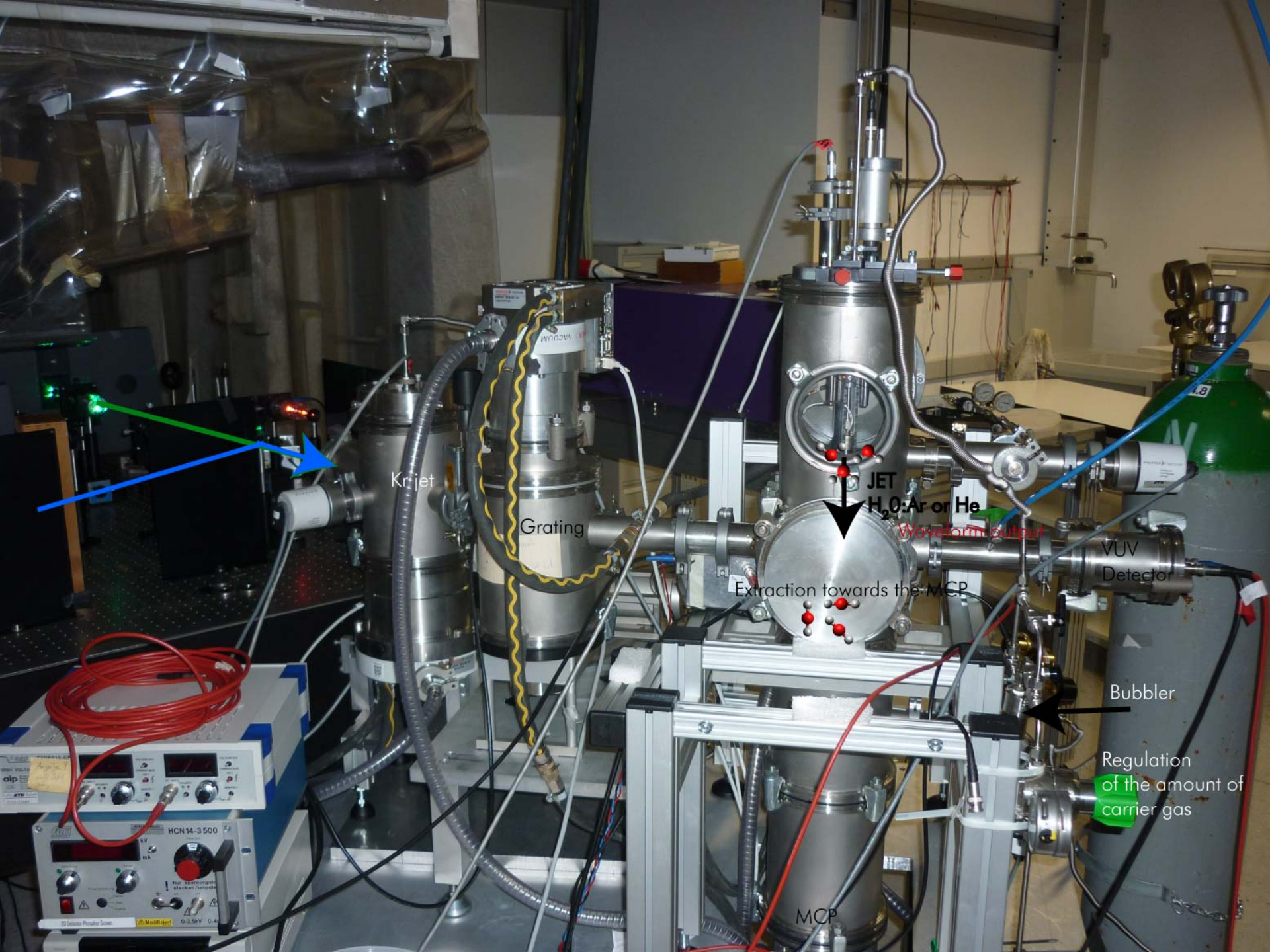
An ensemble of chemically identical molecular entities that can explore the same set of molecular energy levels on the time scale of the experiment.

Chemical reaction following selection rules

$$\langle \Psi(\textit{ion}) \Psi(\textit{electron}) | \mu | \Psi(\textit{neutral}) \rangle$$

$$\Gamma_{e^-,l} \otimes \Gamma_{rve}^+ \otimes \Gamma_{rve}'' \supset \Gamma^*$$

¹IUPAC Gold book 2014, <http://goldbook.iupac.org/C01033.html>



Krijet

Grating

JET
 $H_2O:Ar$ or He

Waveform output

Extraction towards the MCP

VUV
Detector

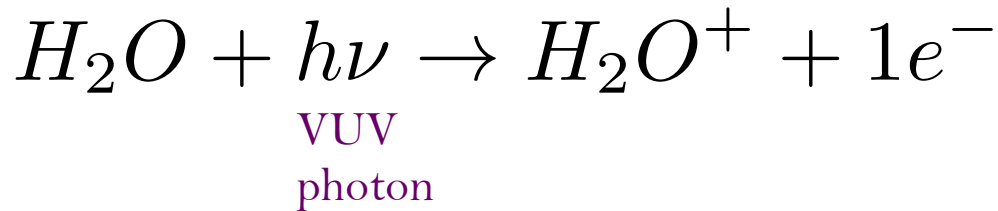
Bubbler

Regulation
of the amount of
carrier gas

MCP

Photoelectron spectroscopy

Photoionization process



$$h\nu = E_I(\alpha^+, \alpha) + E_{kin}^{(\alpha^+, \alpha)}$$

$E_I(\alpha^+, \alpha)$ represents the energy difference between the ionized species in quantum state α^+ and the neutral parent in quantum state α .

$E_{kin}^{(\alpha^+, \alpha)}$ Kinetic energy released during the photoionization process.