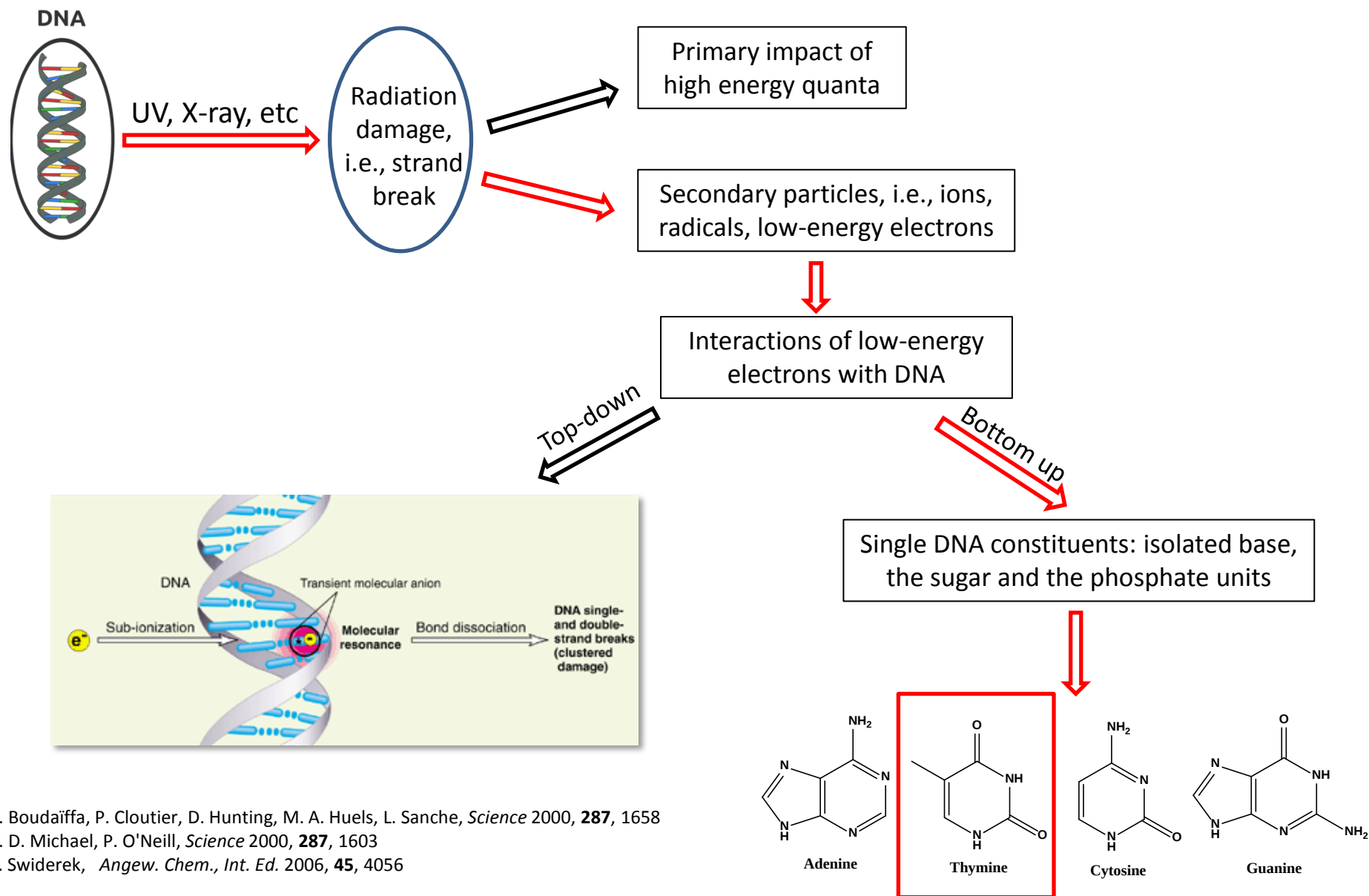


Probing the vibrational spectroscopy of the deprotonated thymine radical by photodetachment and state-selective autodetachment photoelectron spectroscopy via dipole bound states

Dao-Ling Huang, Guo-Zhu Zhu, Lai-Sheng Wang,
Department of Chemistry, Brown University, Providence, RI

71th International Symposium on Molecular Spectroscopy
University of Illinois at Champaign-Urbana
Jun 20-24, 2016

Radiation damage of DNA



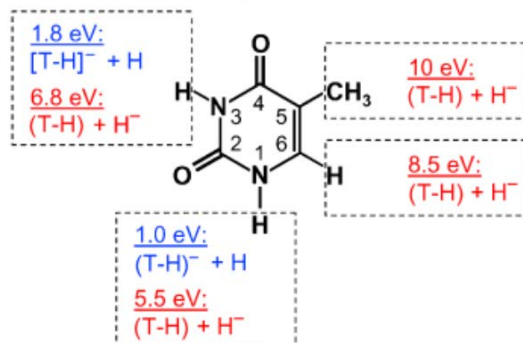
B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, L. Sanche, *Science* 2000, **287**, 1658

B. D. Michael, P. O'Neill, *Science* 2000, **287**, 1603

P. Swiderek, *Angew. Chem., Int. Ed.* 2006, **45**, 4056

Previous studies on thymine

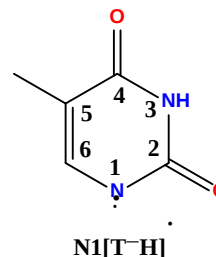
Dissociative electron attachment



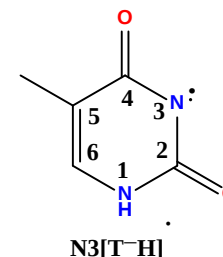
Low-energy (<2 eV) electrons – loss H

- H. Abdoul-Carime, S. Gohlke, E. Illenberger, *Phys. Rev. Lett.* 2004, **92**, 168103
 S. Ptasińska, et al, *Phys. Rev. Lett.* 2005, **95**, 093201
 P. Swiderek, *Angew. Chem., Int. Ed.* 2006, **45**, 4056

Electron affinities calculations



3.2-3.4 eV



3.7-4.5 eV

L. T. M. Profeta, et al, *Mol. Phys.*, 2003, **101**, 3277–3284

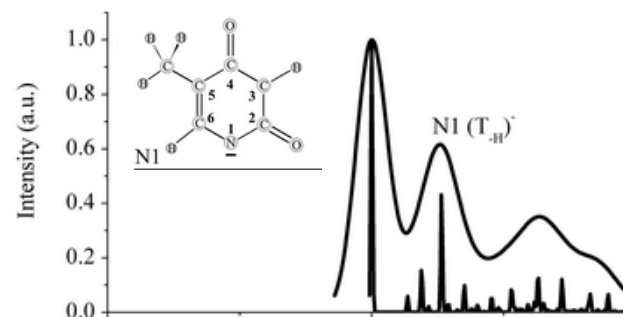
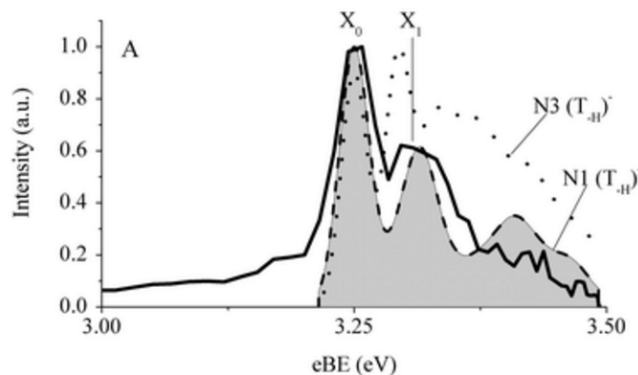
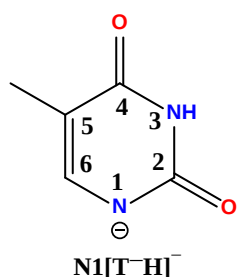
S. Denifl, et al, *J. Phys. Chem. A*, 2004, **108**, 6562–6569

S. Ptasińska, et al, *J. Chem. Phys.*, 2005, **123**, 124302

D. S. Jiao and H. Y. Wang, *Mol. Phys.*, 2008, **106**, 2653–2665

E. C. M. Chen, et al, *Nucleosides, Nucleotides Nucleic Acids*, 2008, **27**, 506–524

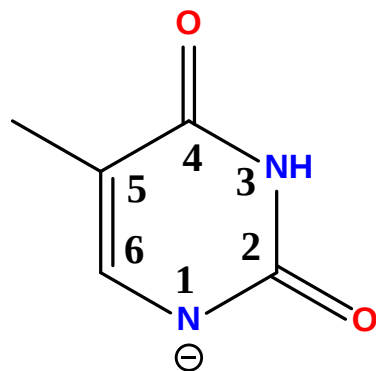
Anion photoelectron spectroscopy



EA = 3.250 ± 0.015 eV

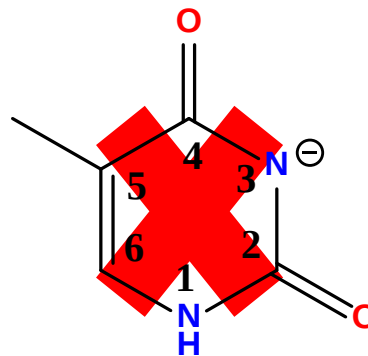
B. F. Parsons, S. M. Sheehan, T. A. Yen, D. M. Neumark, N. Wehres and R. Weinkauf, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3291–3297

Photodetachment and autodetachment photoelectron spectroscopy



N1[T-H]⁻

3.2-3.4 eV

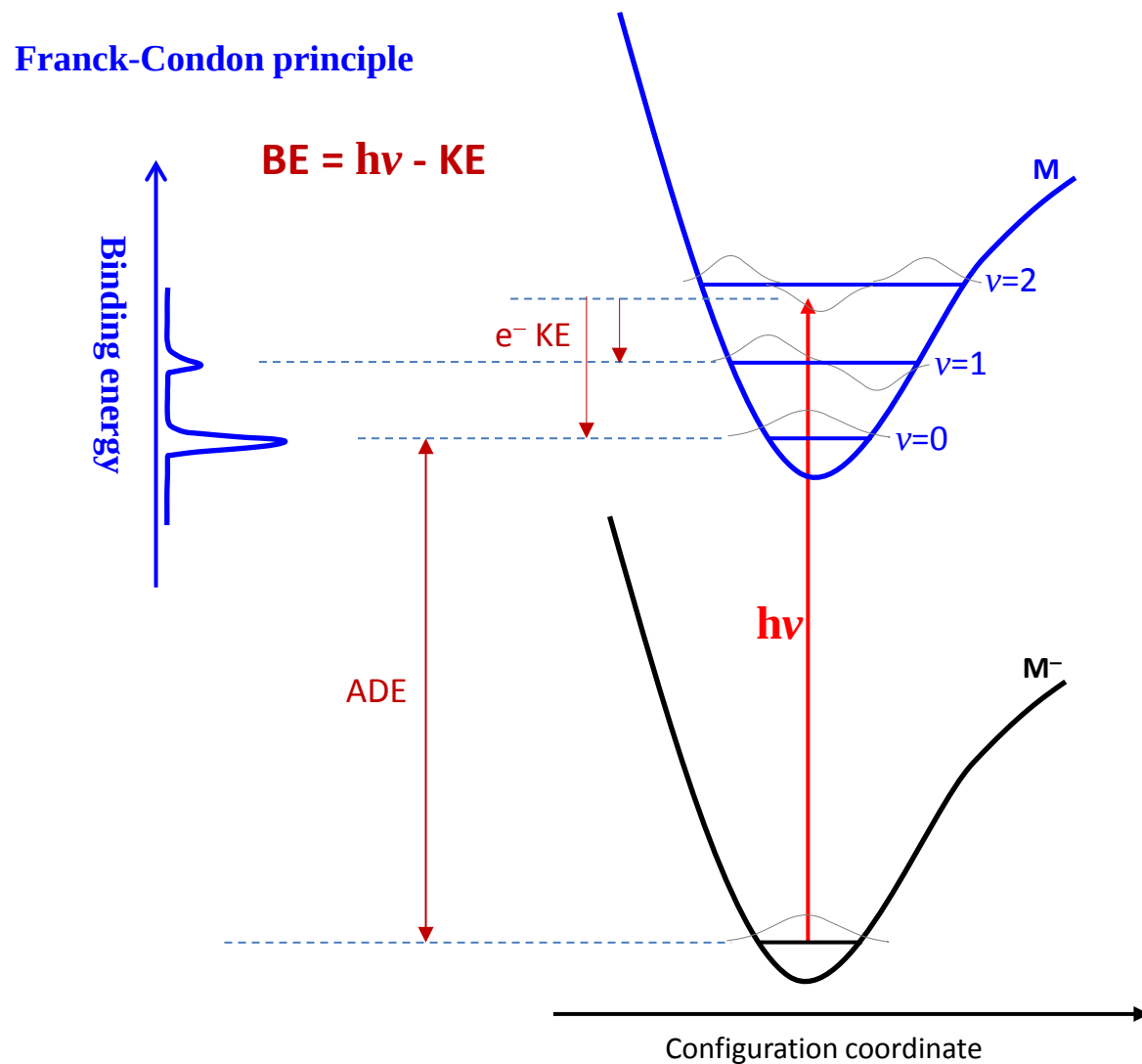


N3[T-H]⁻

3.7-4.5 eV

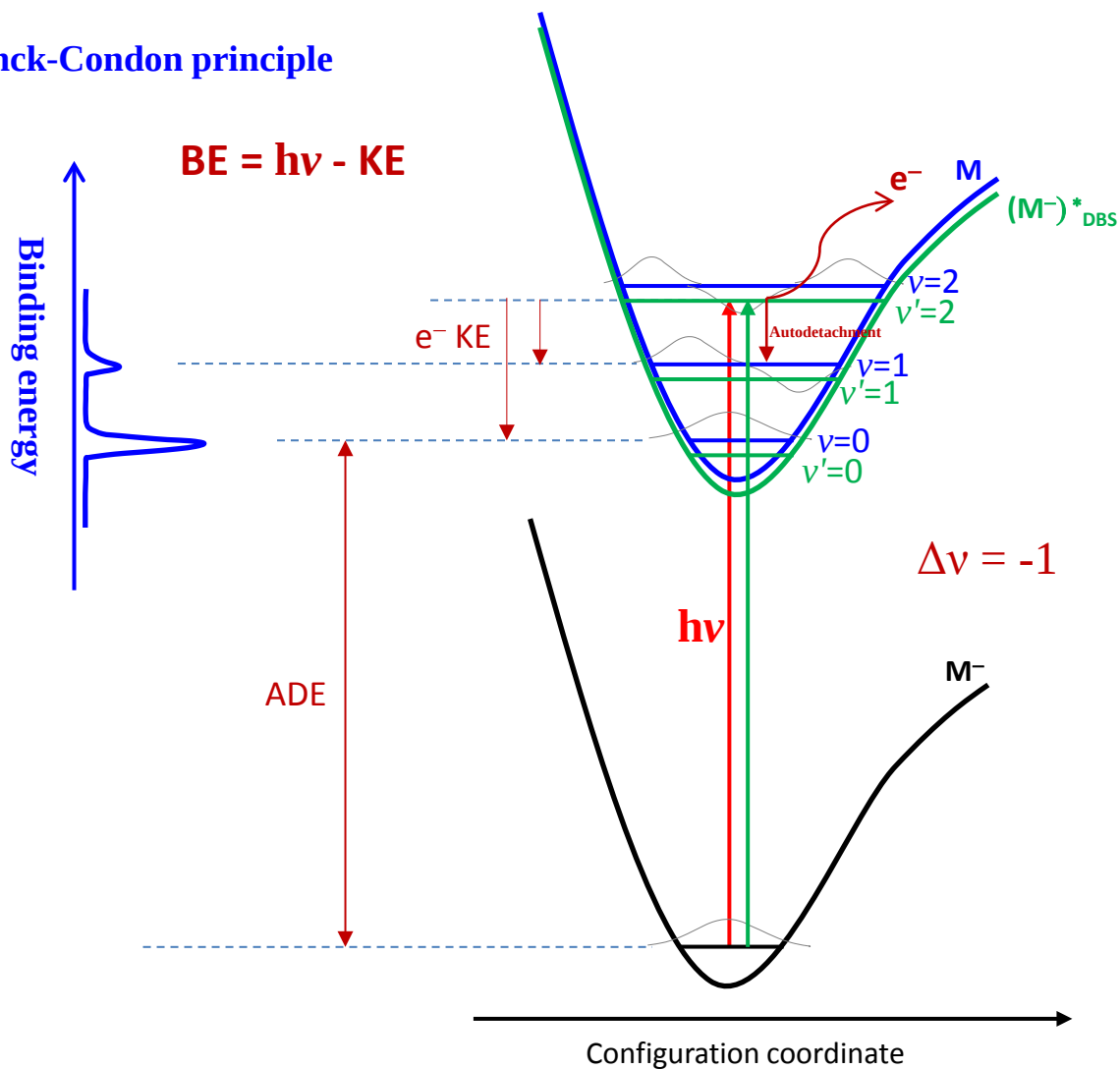
355 nm (3.496 eV)

Principle of photoelectron spectroscopy and autodetachment

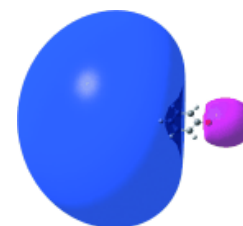


Principle of photoelectron spectroscopy and autodetachment

Franck-Condon principle

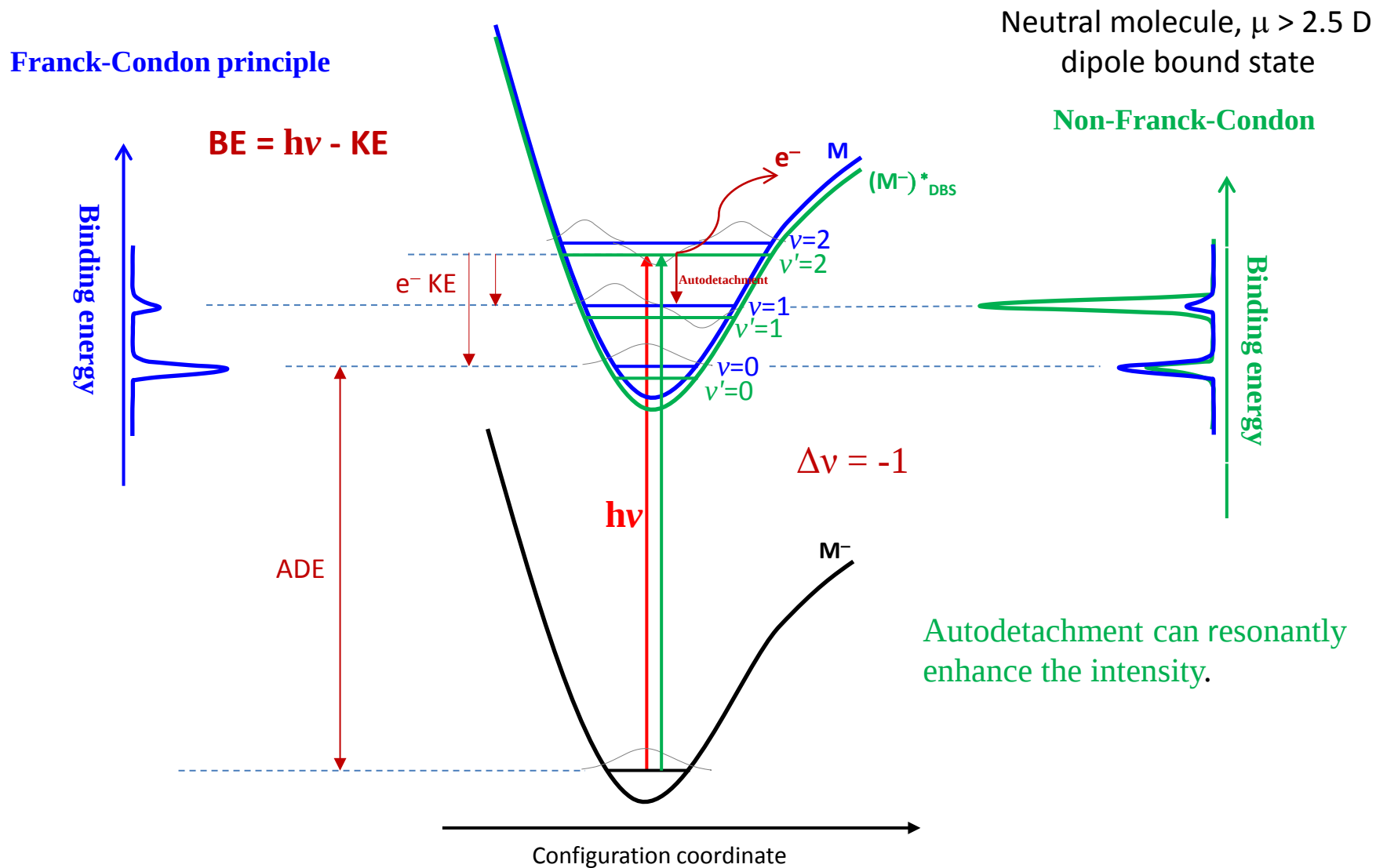


Neutral molecule, $\mu > 2.5$ D
dipole bound state

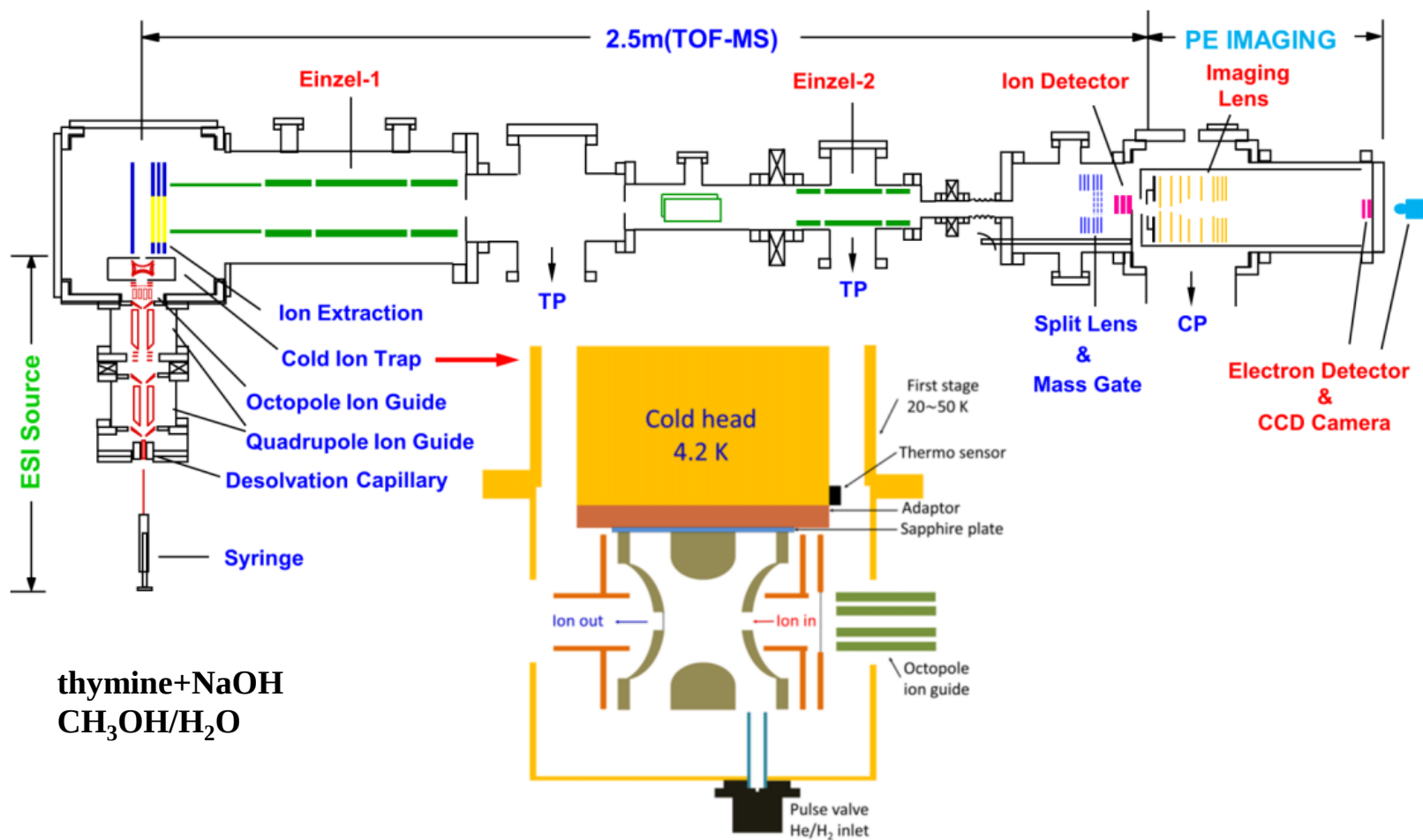


phenoxide anion,
radical $\mu = 4.0$ D

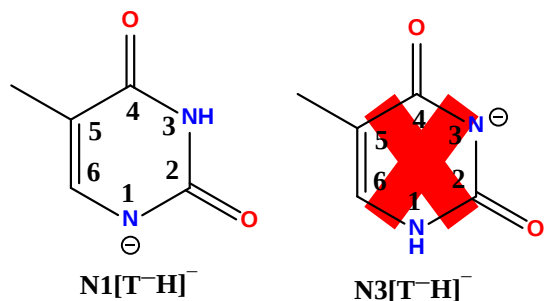
Principle of photoelectron spectroscopy and autodetachment



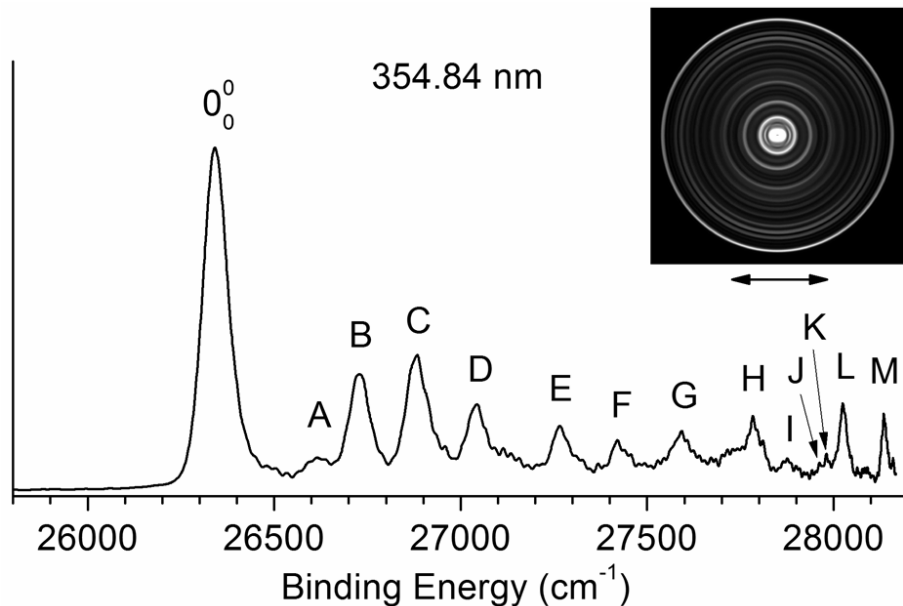
Experimental set-up



Non-resonant photoelectron image and spectrum



[N1-H] •
B3LYP/6-311++G(d,p)
Cs symmetry

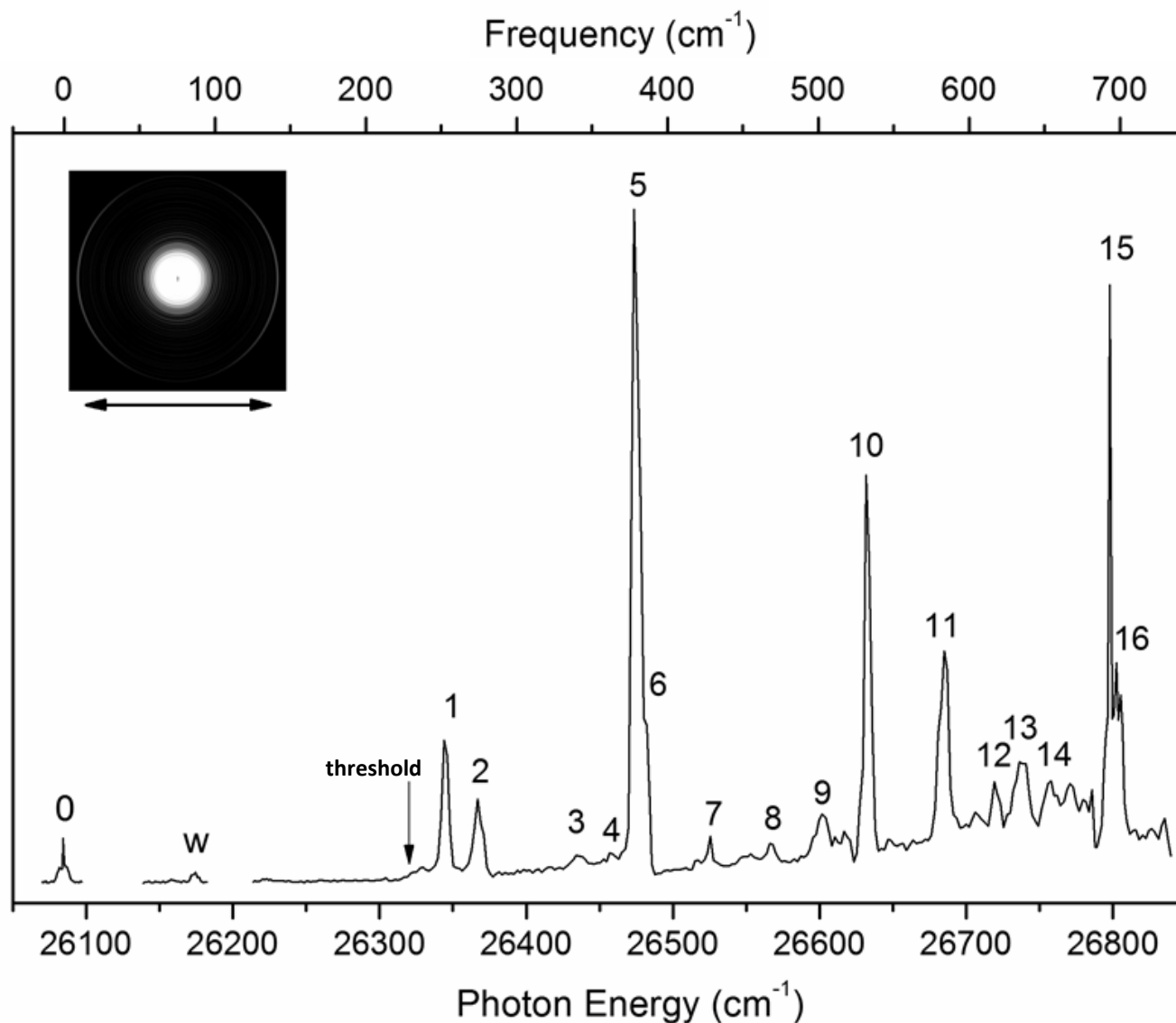


EA = 3.2635 ± 0.0006 eV (by resonant PES)

Mode	Symmetry	Theo. (cm ⁻¹)
v ₁	A''	70
v ₂	A''	93
v ₃	A''	135
v ₄	A''	262
v ₅	A'	285
v ₆	A''	388
v ₇	A'	397
v ₈	A'	450
v ₉	A'	555
v ₁₀	A'	608
v ₁₁	A''	670
v ₁₂	A'	720
v ₁₃	A''	727

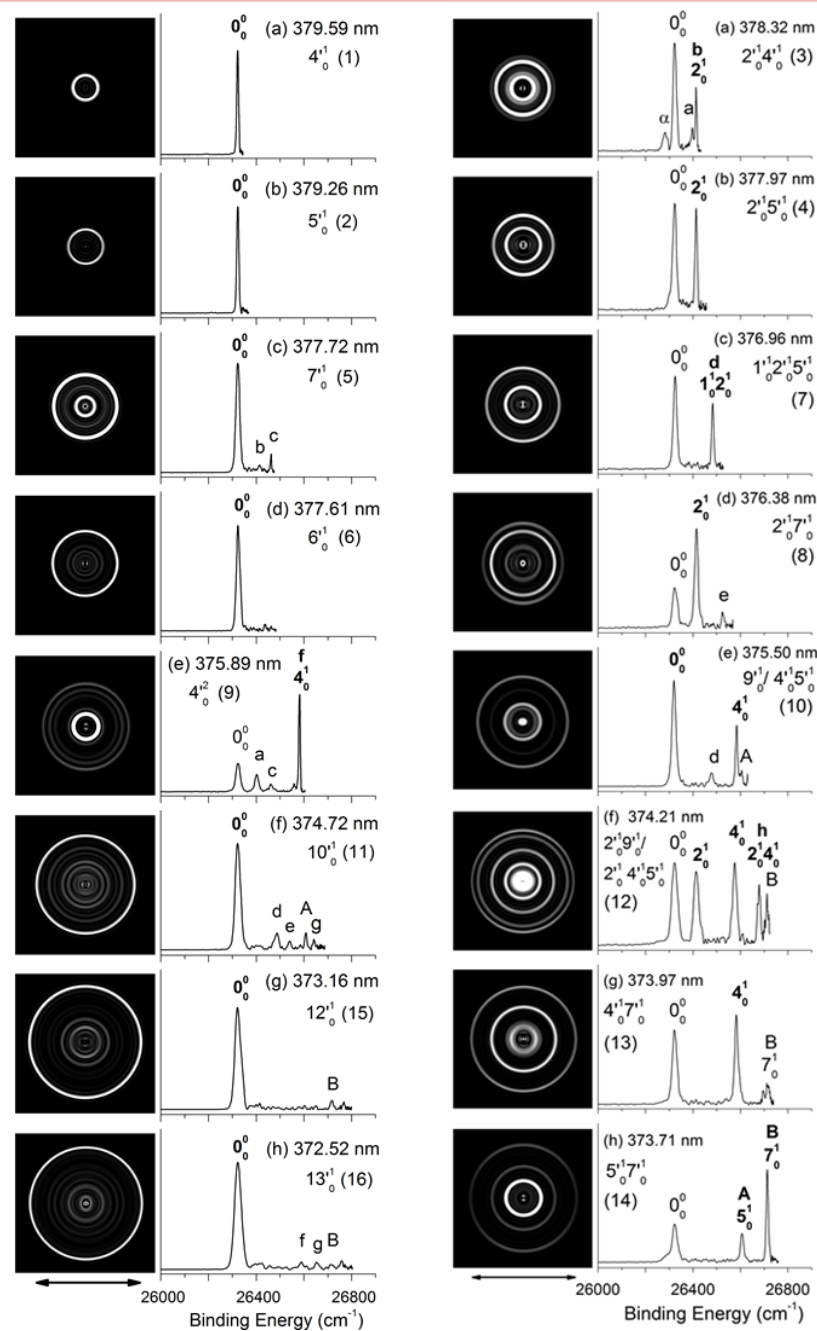
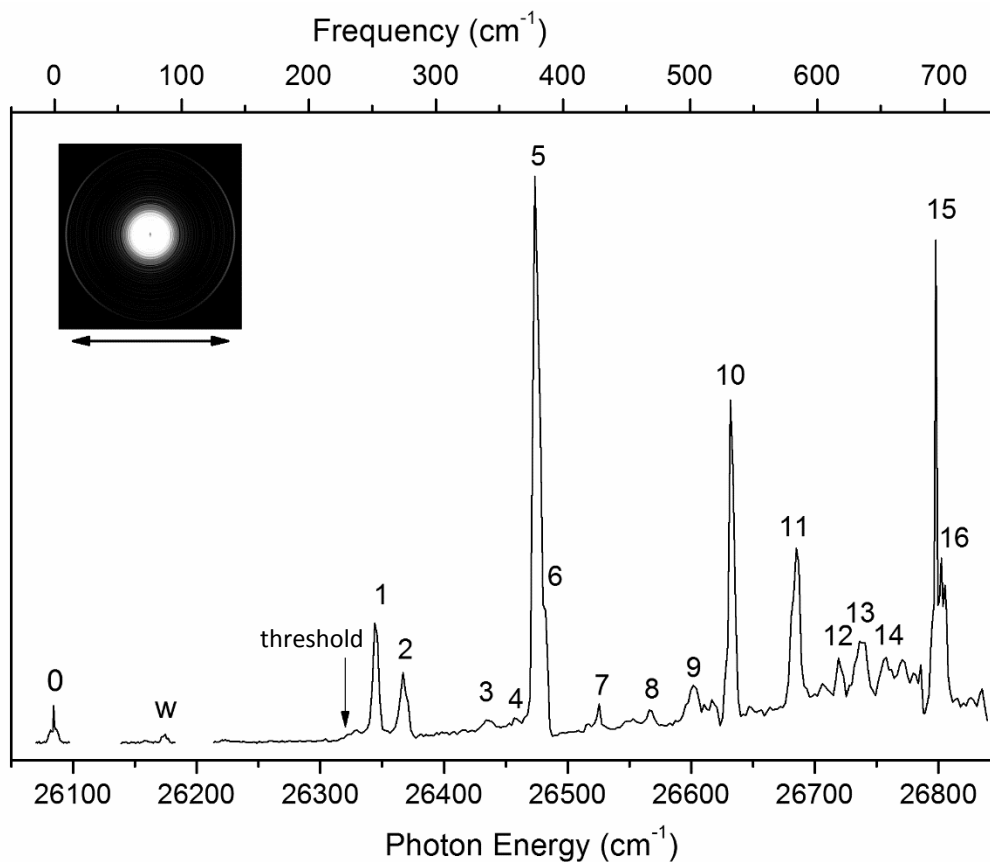
Peak	BE (cm ⁻¹)	Shift (cm ⁻¹)	Assignment
0 ₀	26322(5)	0	
A	26604(5)	282	5 ₀ ¹
B	26715(5)	393	7 ₀ ¹
C	26884(25)	562	9 ₀ ¹
D	27044(22)	722	12 ₀ ¹
E	27267(18)	945	7 ₀ ¹ 9 ₀ ¹
F	27422(16)	1100	9 ₀ ²
G	27593(14)	1271	9 ₀ ¹ 12 ₀ ¹
H	27784(12)	1462	7 ₀ ¹ 9 ₀ ²
I	27873(12)	1551	5 ₀ ¹ 9 ₀ ¹ 12 ₀ ¹
J	27963(10)	1641	9 ₀ ³
K	27983(10)	1661	7 ₀ ¹ 9 ₀ ¹ 12 ₀ ¹
L	28024(8)	1702	5 ₀ ¹ 12 ₀ ²
M	28135(5)	1813	9 ₀ ² 12 ₀ ¹

Photodetachment spectrum

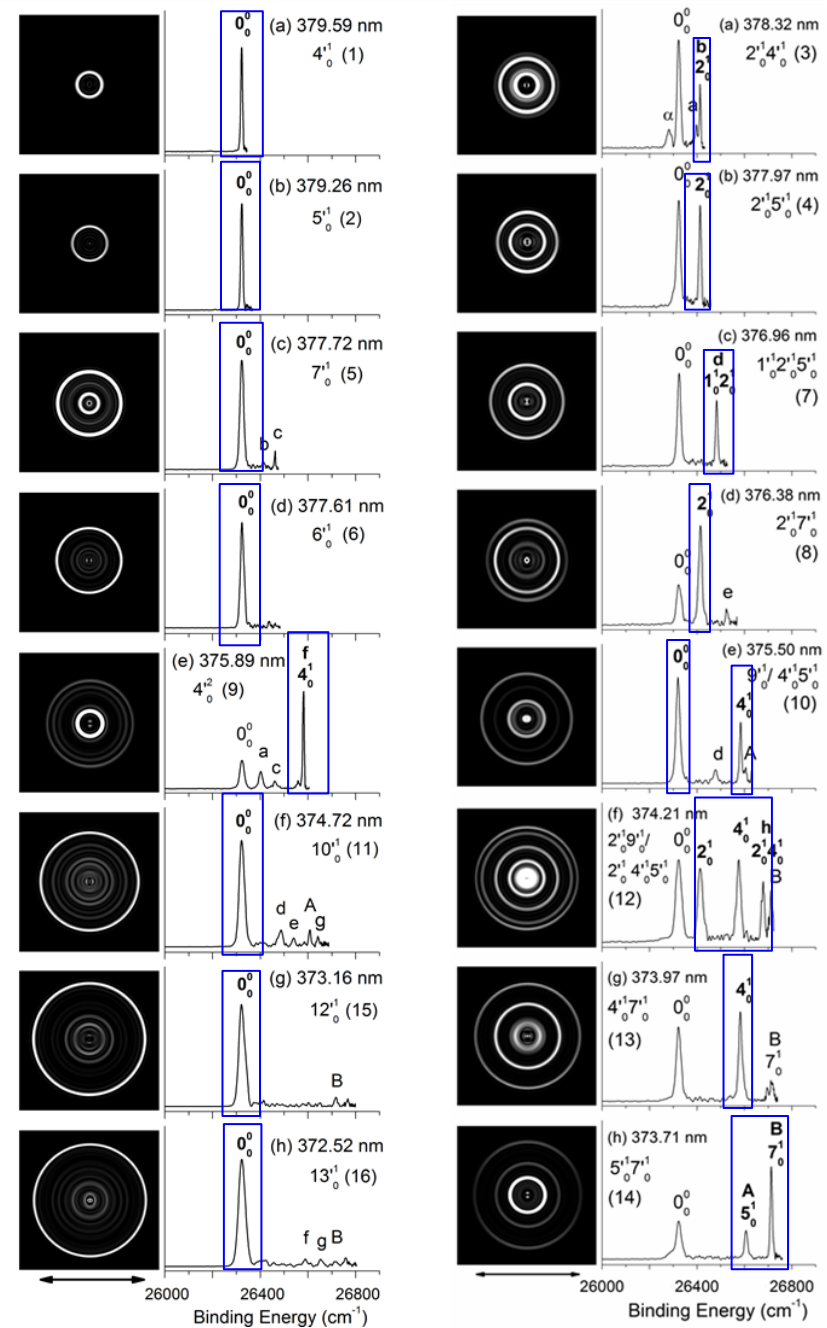
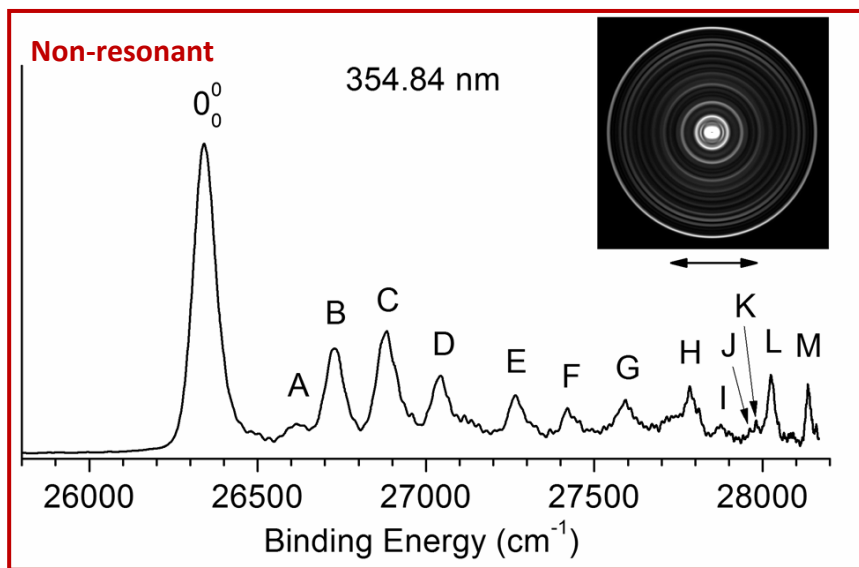


$$\text{BE}_{\text{DBS}} = 238 \pm 5 \text{ cm}^{-1}$$

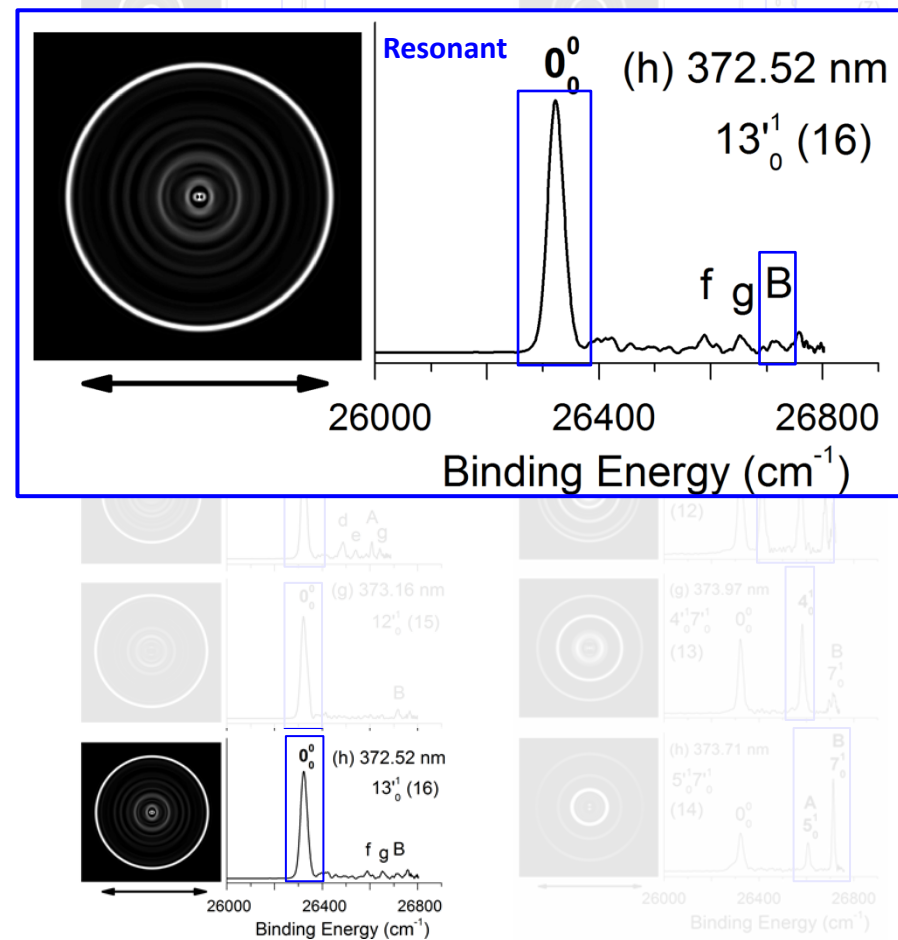
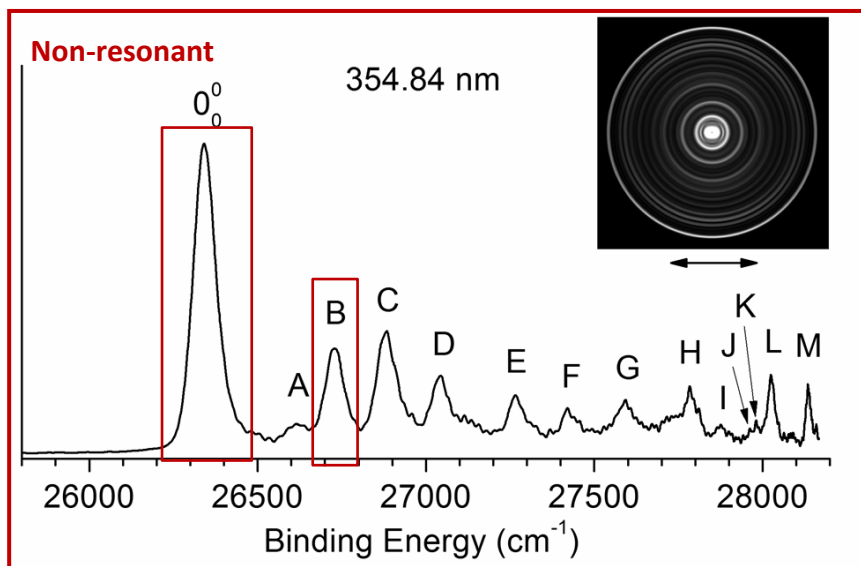
Resonant photoelectron spectra and images



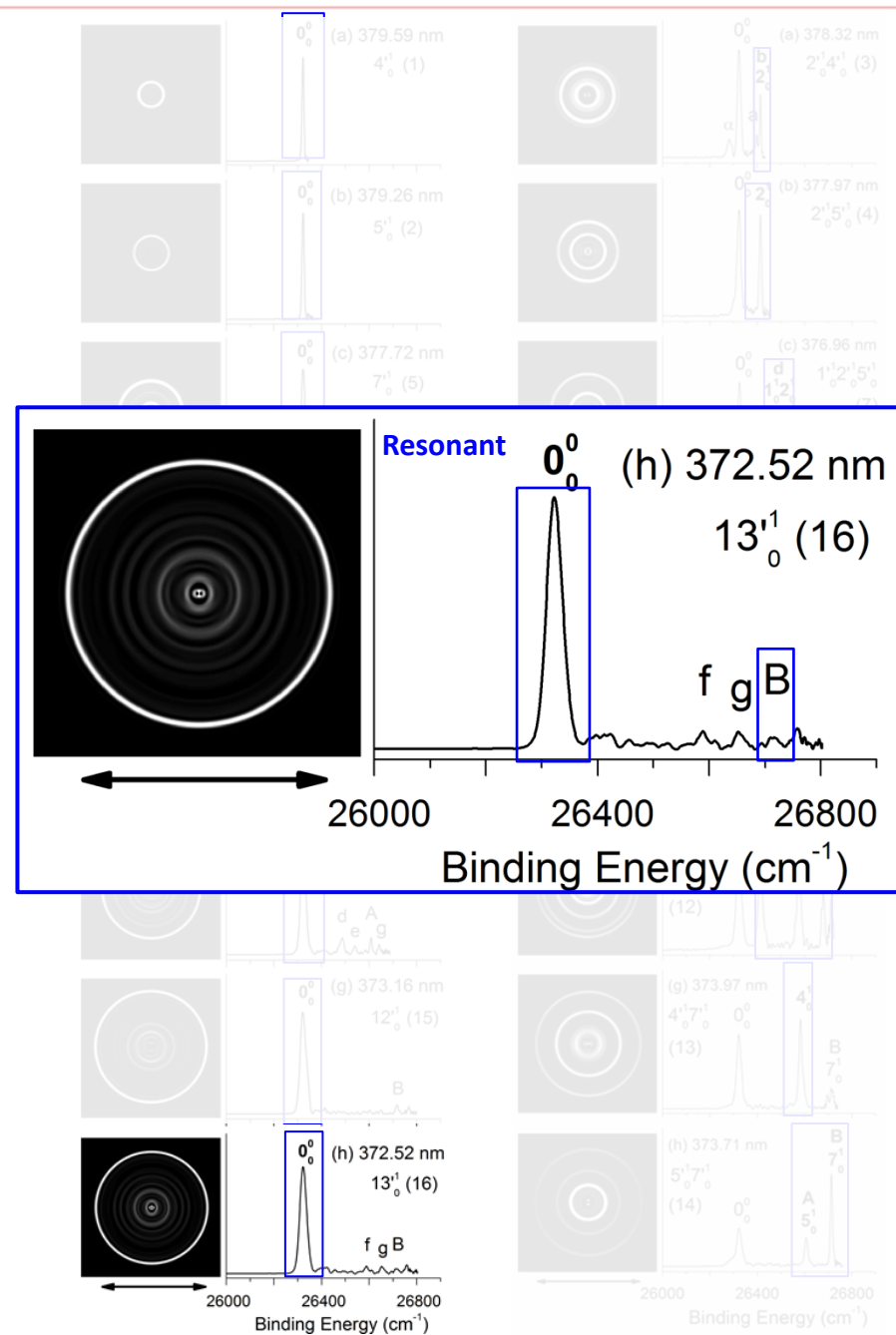
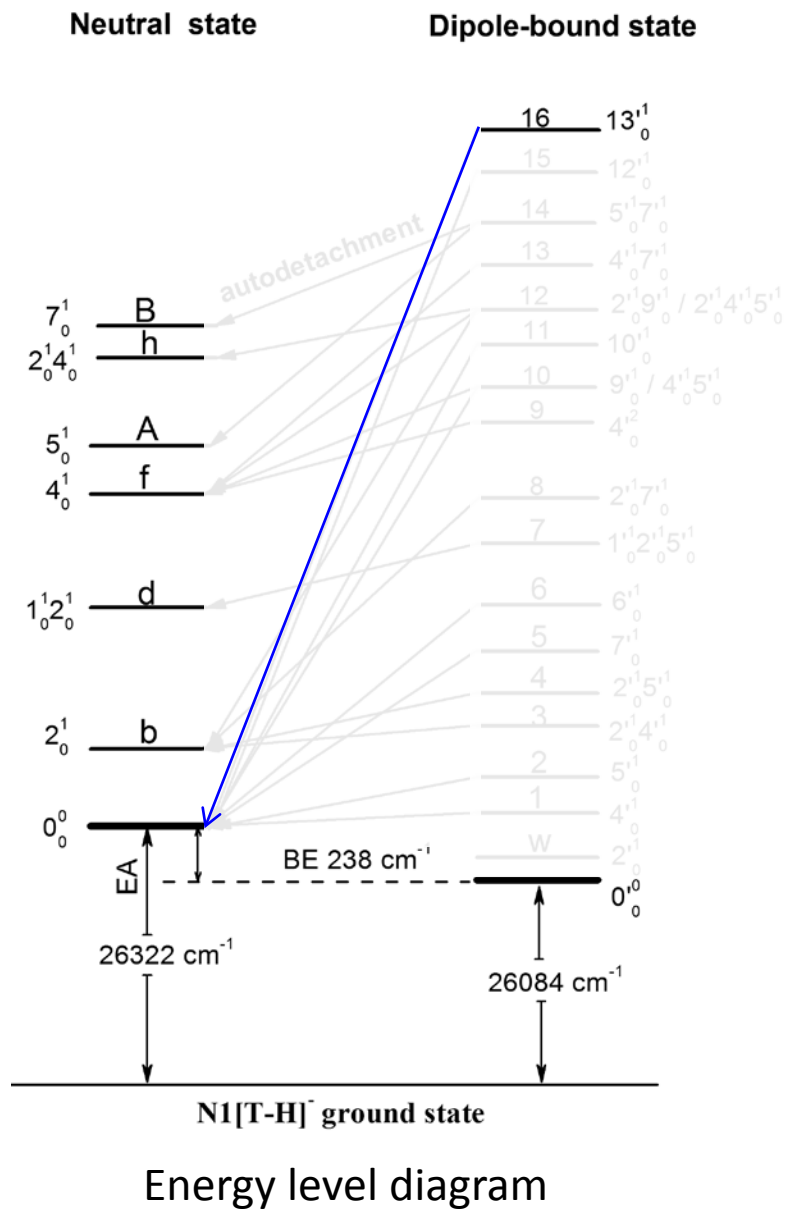
Comparison between non-resonant and resonant spectra



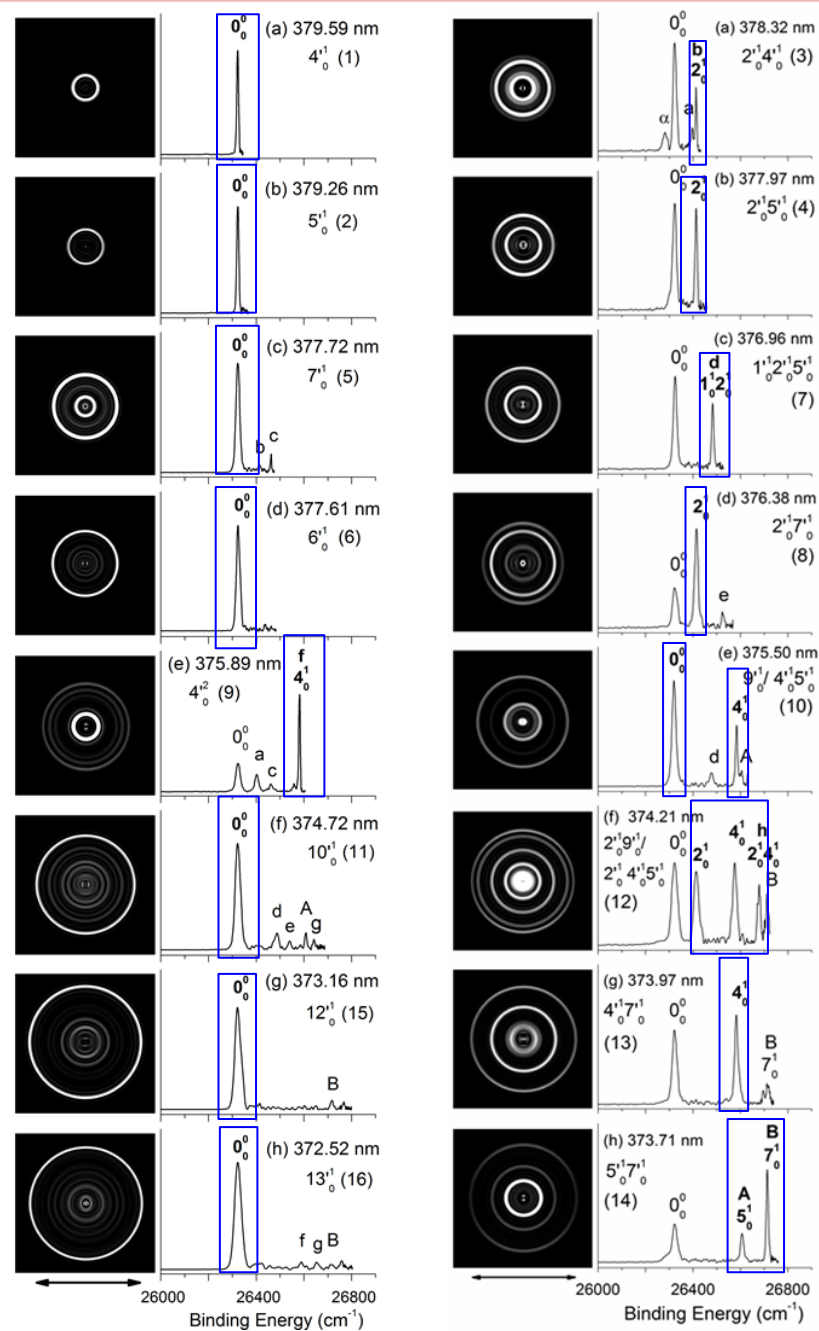
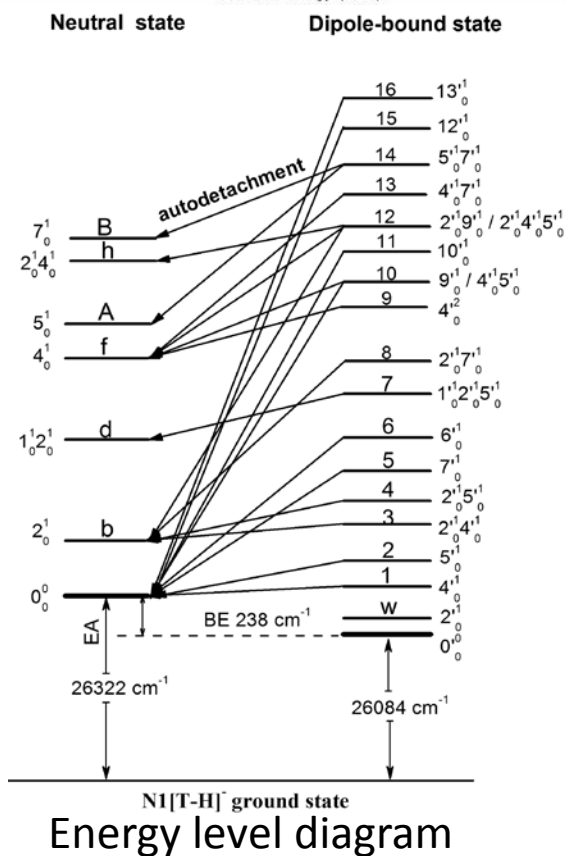
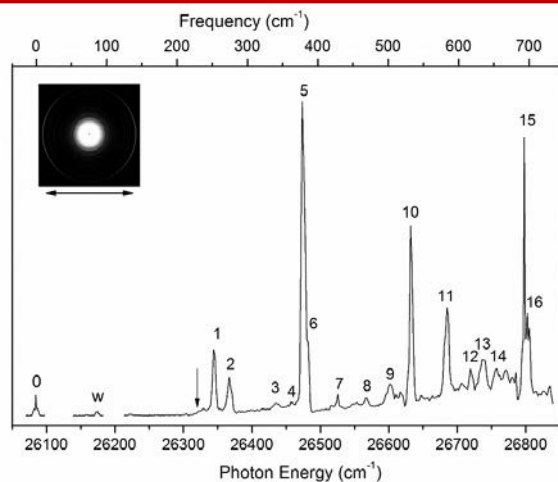
Comparison between non-resonant and resonant spectra



Assignments of dipole-bound states



Assignments of dipole-bound states

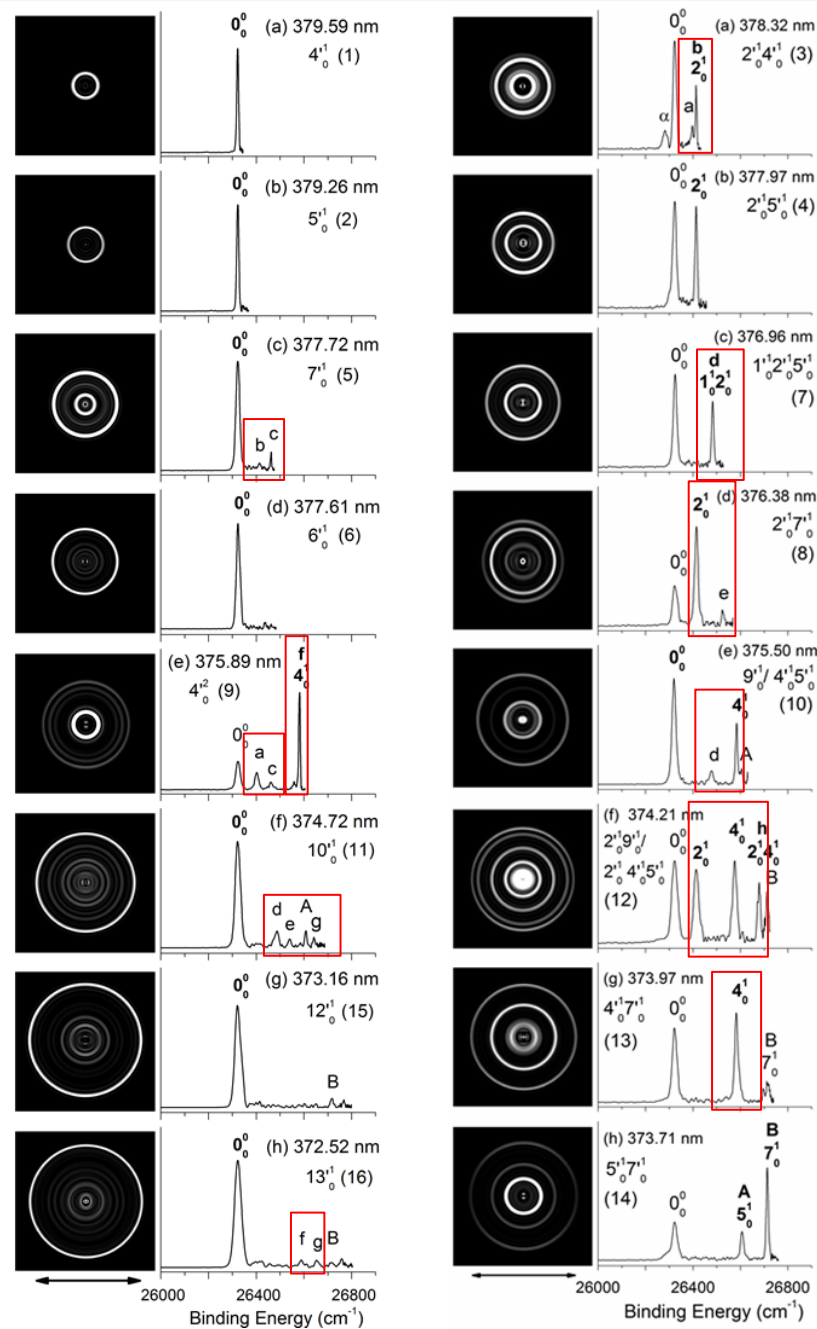


Assignments of Franck-Condon inactive peaks

[N1-H] radical
B3LYP/6-311++G(d,p)
Cs symmetry

Mode	Symmetry	Theo. (cm ⁻¹)
v ₁	A''	70
v ₂	A''	93
v ₃	A''	135
v ₄	A''	262
v ₅	A'	285
v ₆	A''	388
v ₇	A'	397
v ₈	A'	450
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v ₁₀	A'	608
v ₁₁	A''	670
v ₁₂	A'	720
v ₁₃	A''	727

Peak	BE (cm ⁻¹)	Shift (cm ⁻¹)	Assignment
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A	26604(5)	282	5 ₀ ¹
B	26715(5)	393	7 ₀ ¹
C	26884(25)	562	9 ₀ ¹
D	27044(22)	722	12 ₀ ¹
E	27267(18)	945	7 ₀ ¹ 9 ₀ ¹
...	...	...	...
a	26396(8)	74	1 ₀ ¹
b	26413(5)	91	2 ₀ ¹
c	26462(5)	140	3 ₀ ¹
d	26482(5)	160	1 ₀ ¹ 12 ₀ ¹
e	26526(5)	204	1 ₀ ¹ 13 ₀ ¹
f	26582(5)	260	4 ₀ ¹
g	26644(8)	321	1 ₀ ¹ 14 ₀ ¹
h	26678(5)	356	2 ₀ ¹ 14 ₀ ¹



Summary

- Accurately determined the electron affinity of $\text{N1}[\text{T-H}]^\bullet$ to be 3.2635 ± 0.0006 eV and the binding energy of dipole-bound ground state to be 238 ± 5 cm^{-1} ;
- Highly non-Franck-Condon resonant-enhanced photoelectron spectra were obtained due to state-selective vibrational autodetachment via dipole-bound states;
- Obtained 11 fundamental vibrational frequencies in the low-frequencies regime.

Acknowledgement

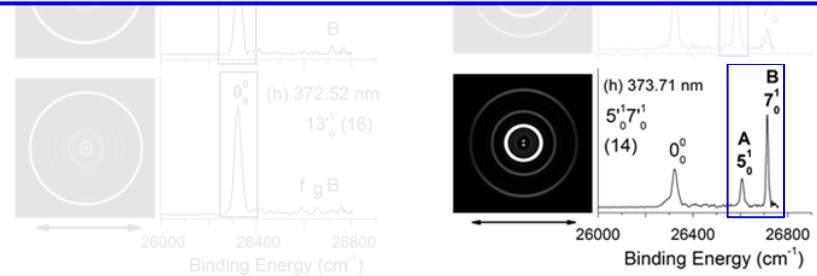
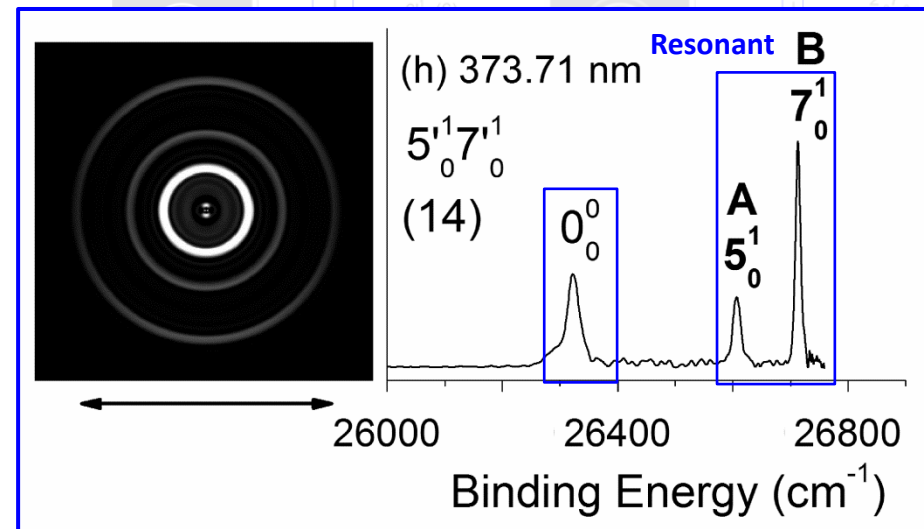
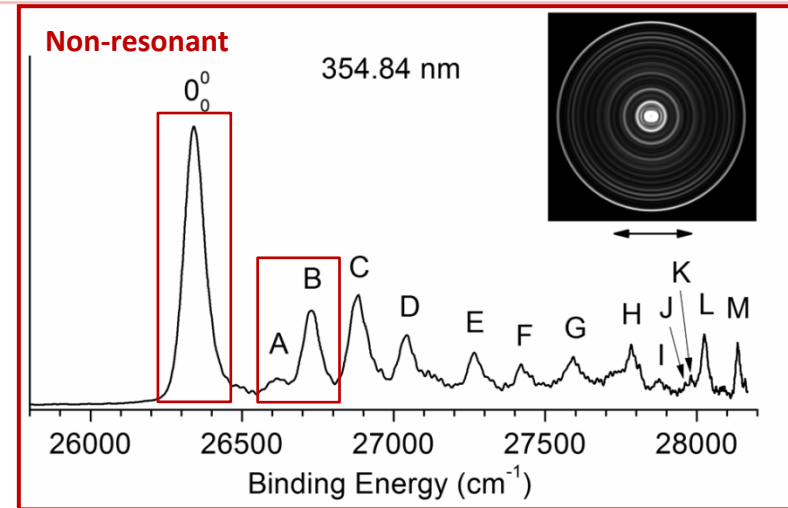
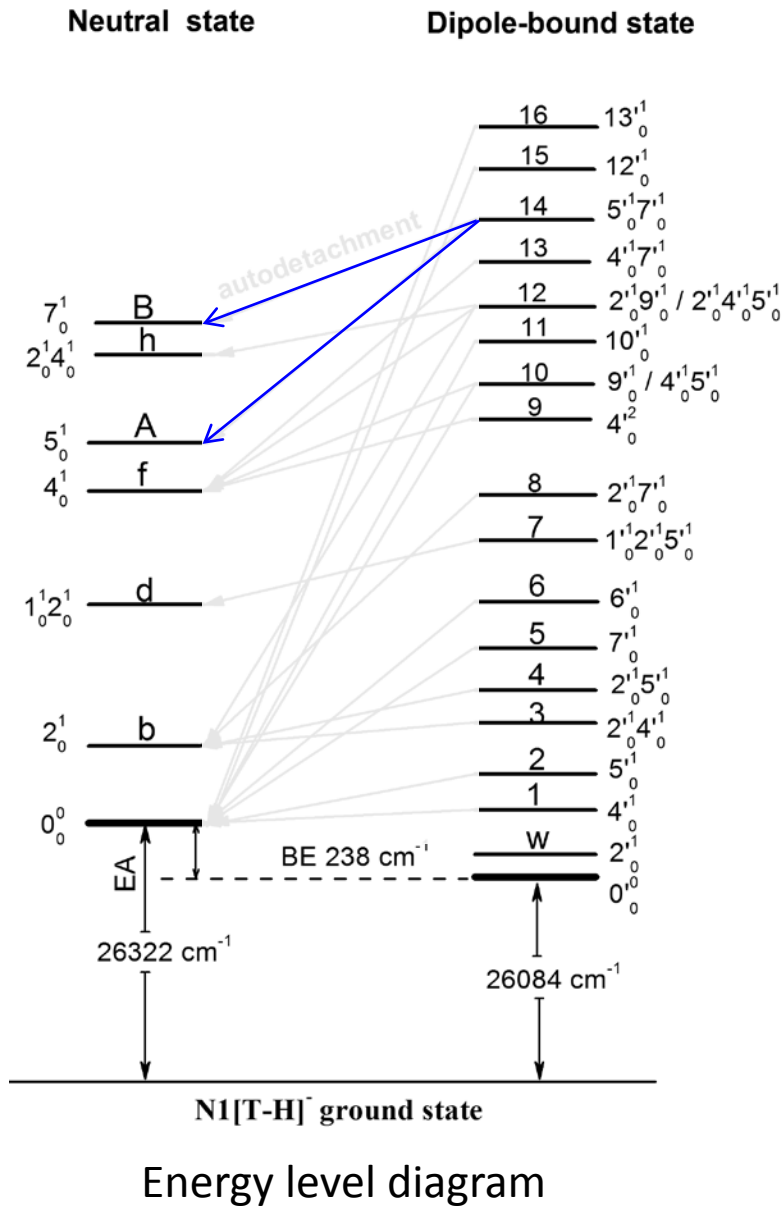
Prof. Lai-Sheng Wang
Dr. Dao-Ling Huang
other group members



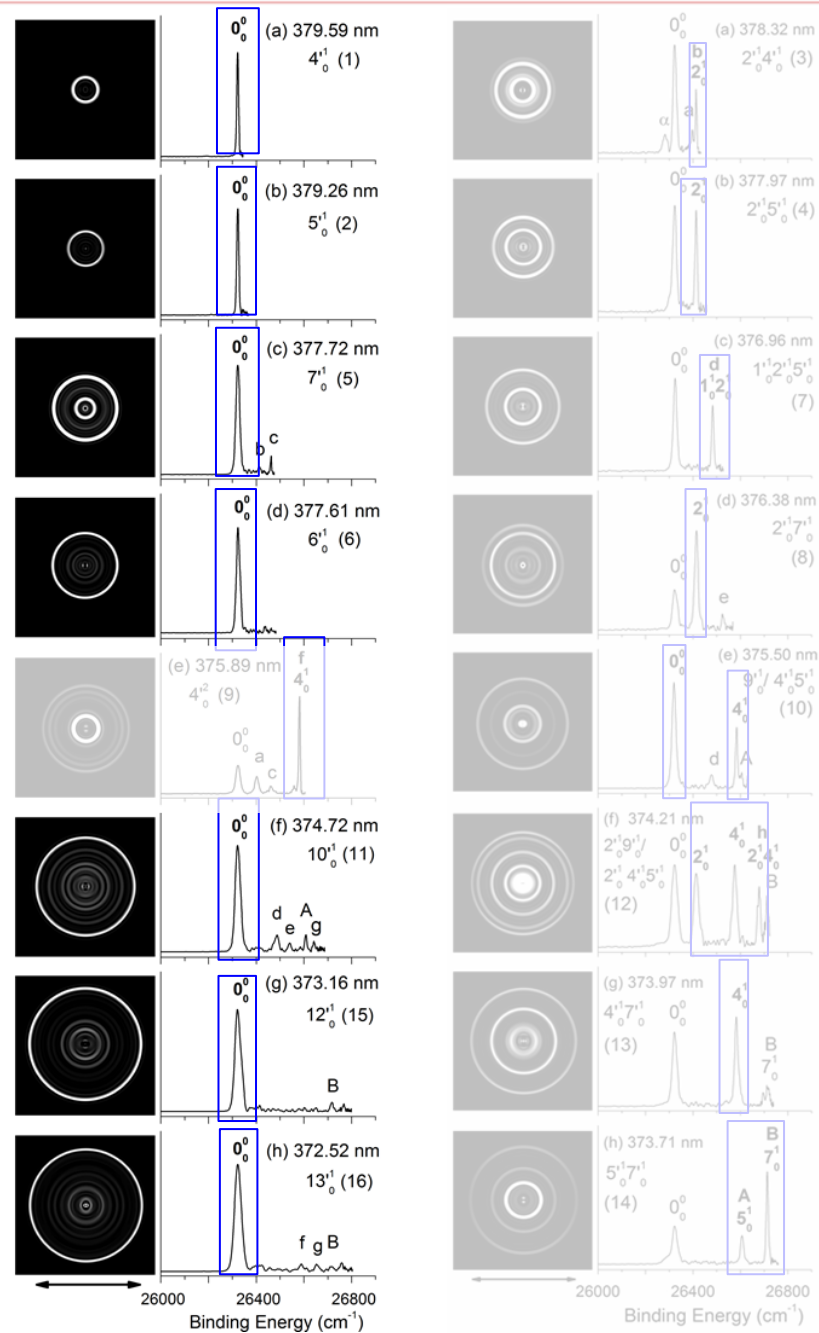
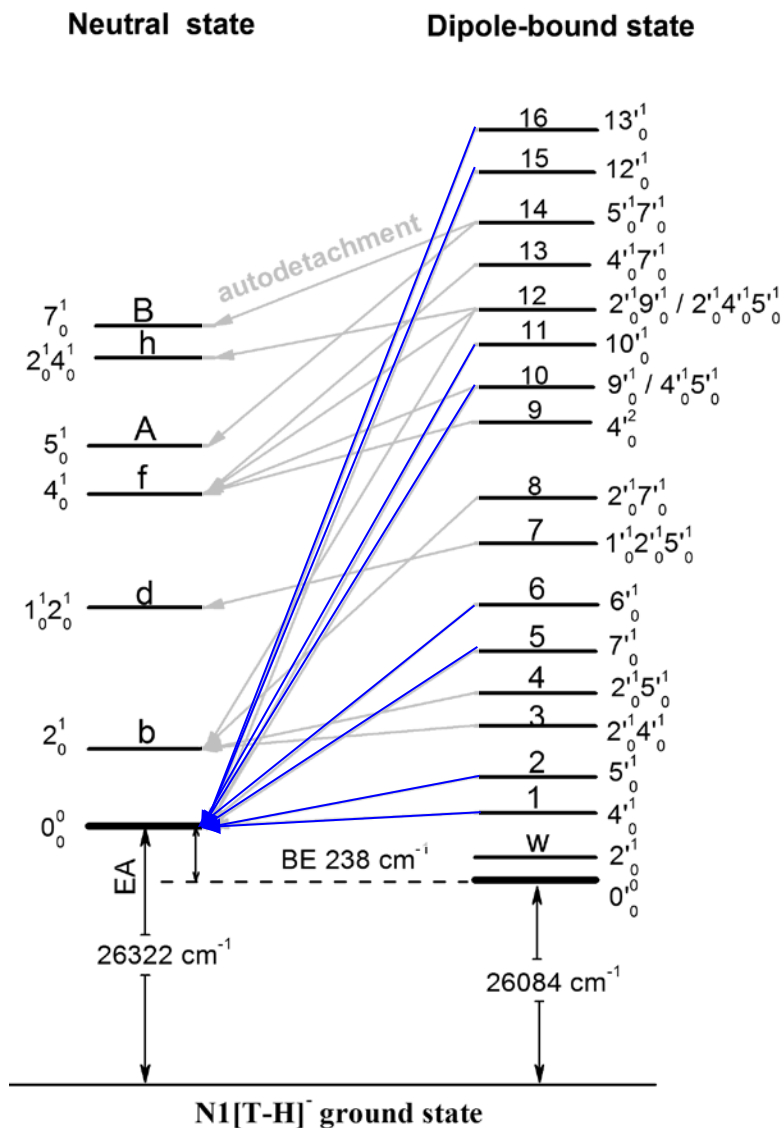
National Science Foundation
WHERE DISCOVERIES BEGIN



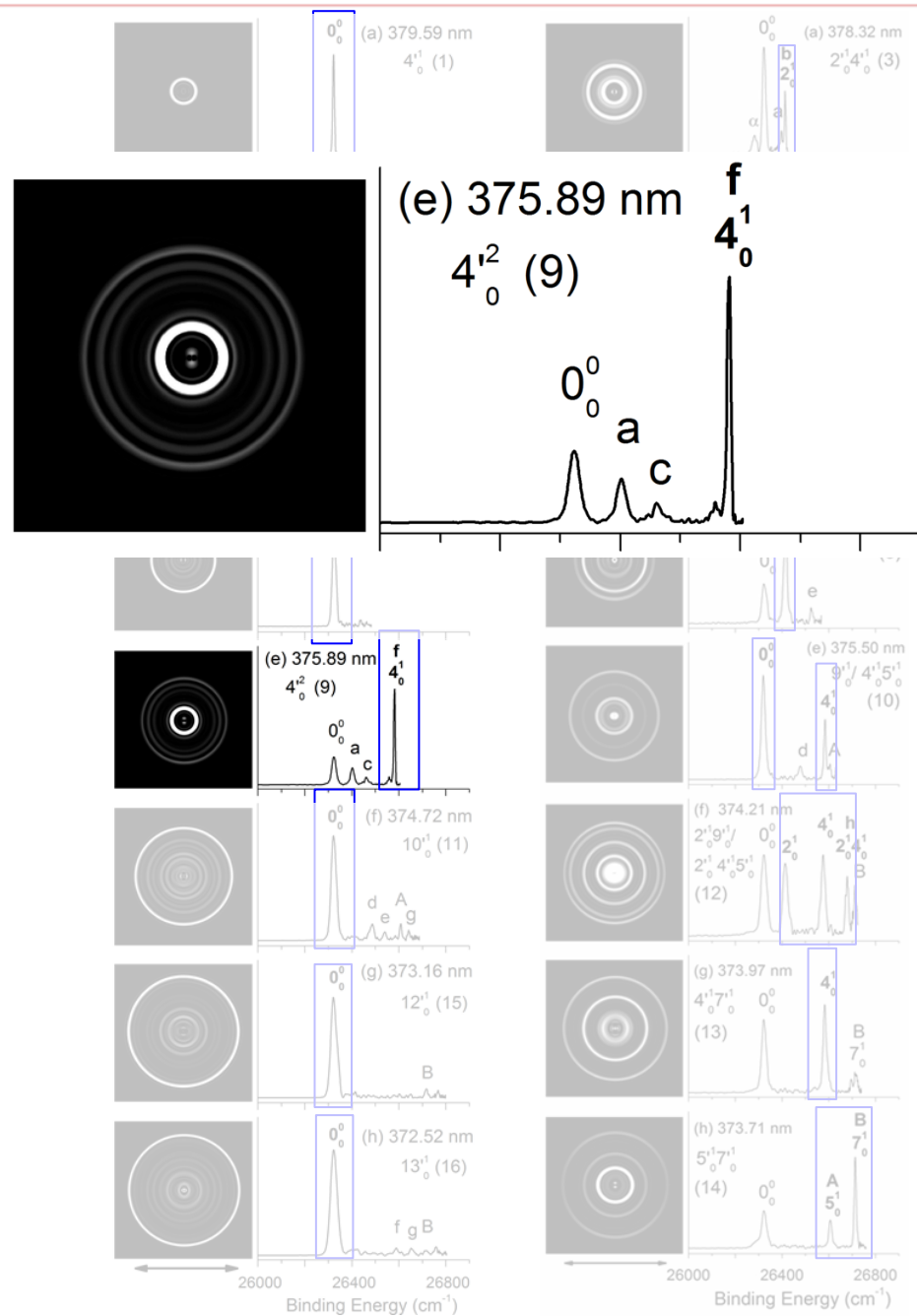
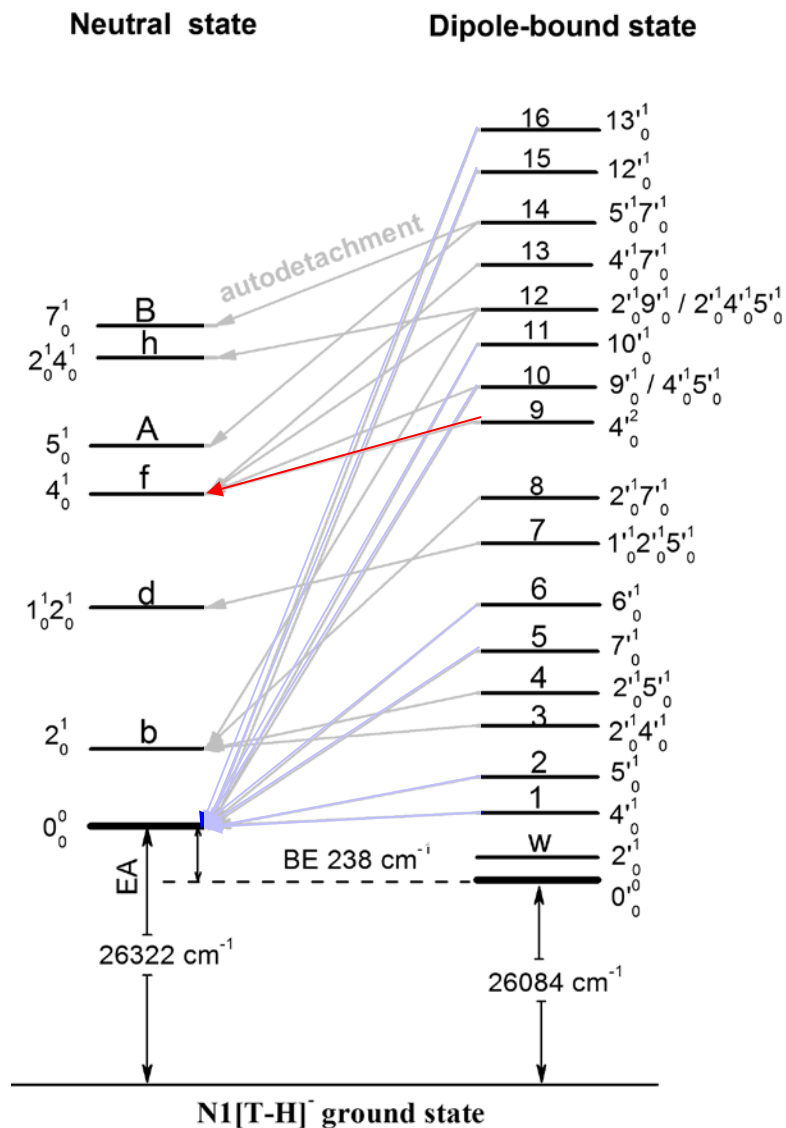
Assignments of dipole-bound states



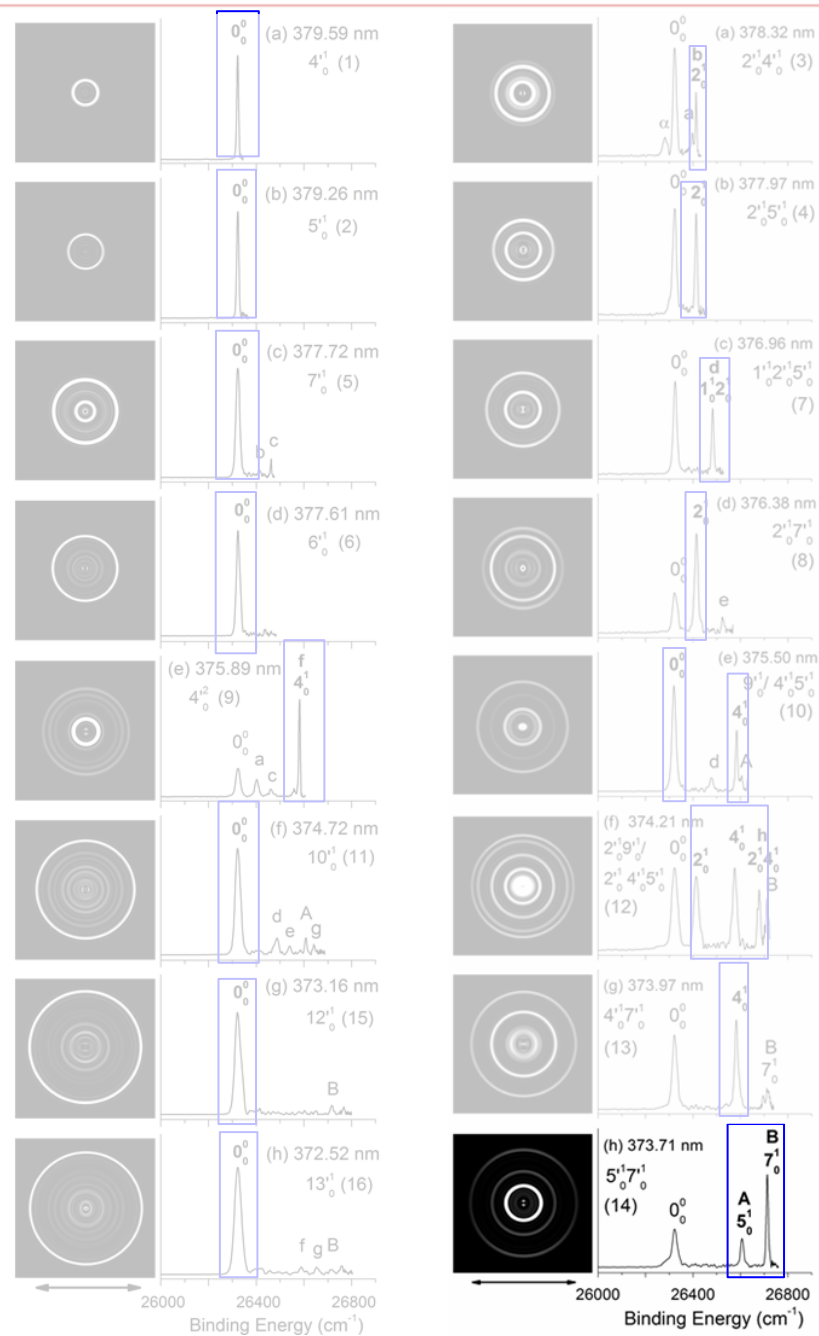
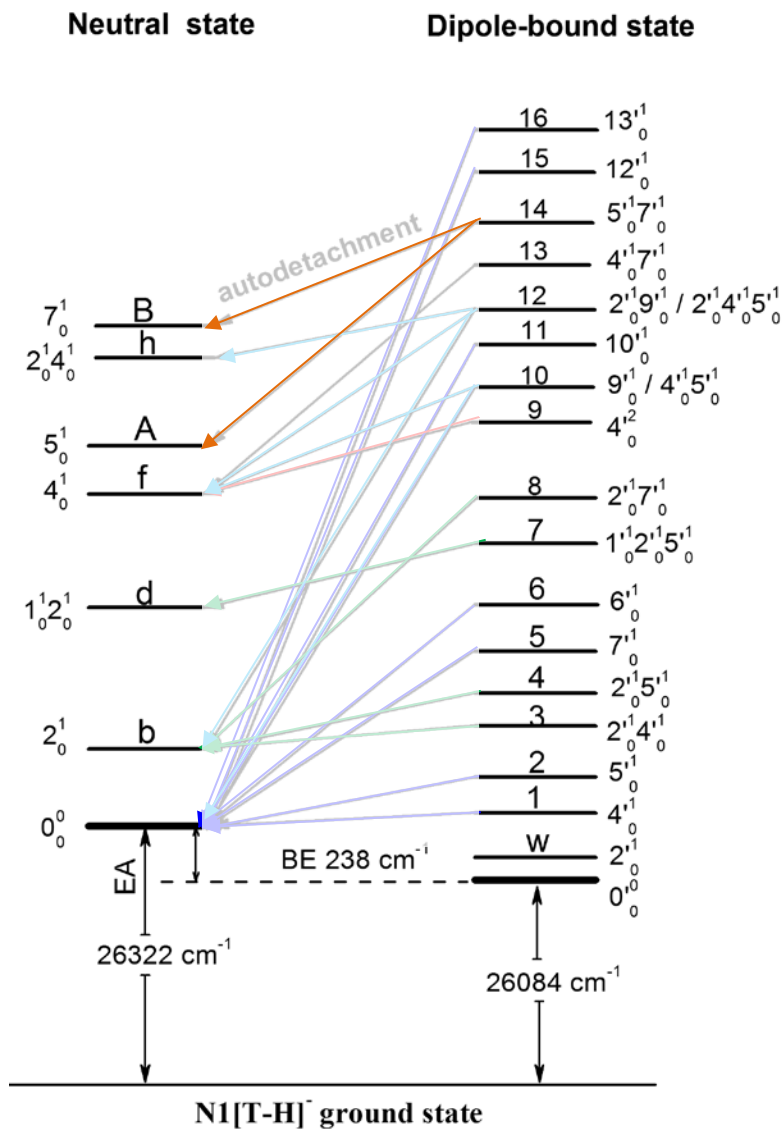
Assignments of dipole-bound states



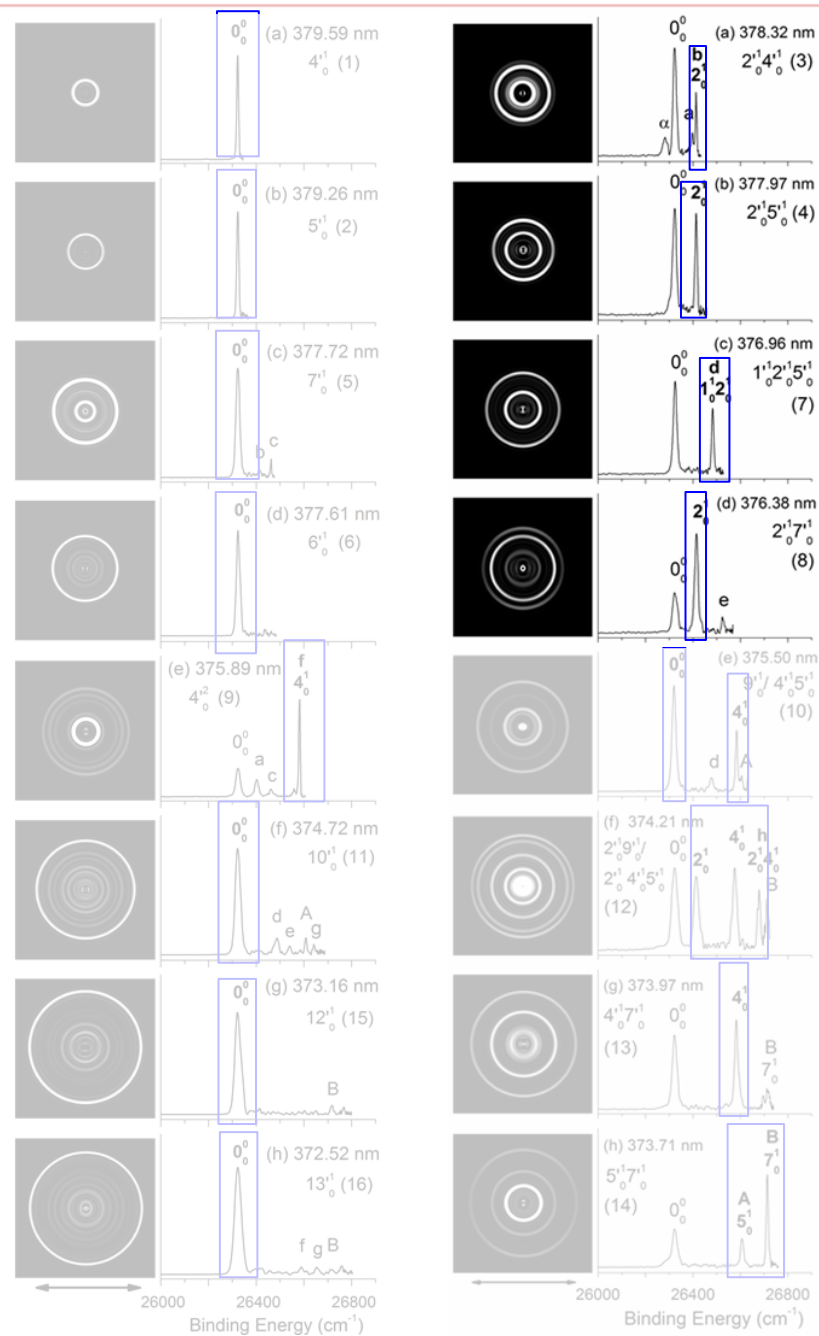
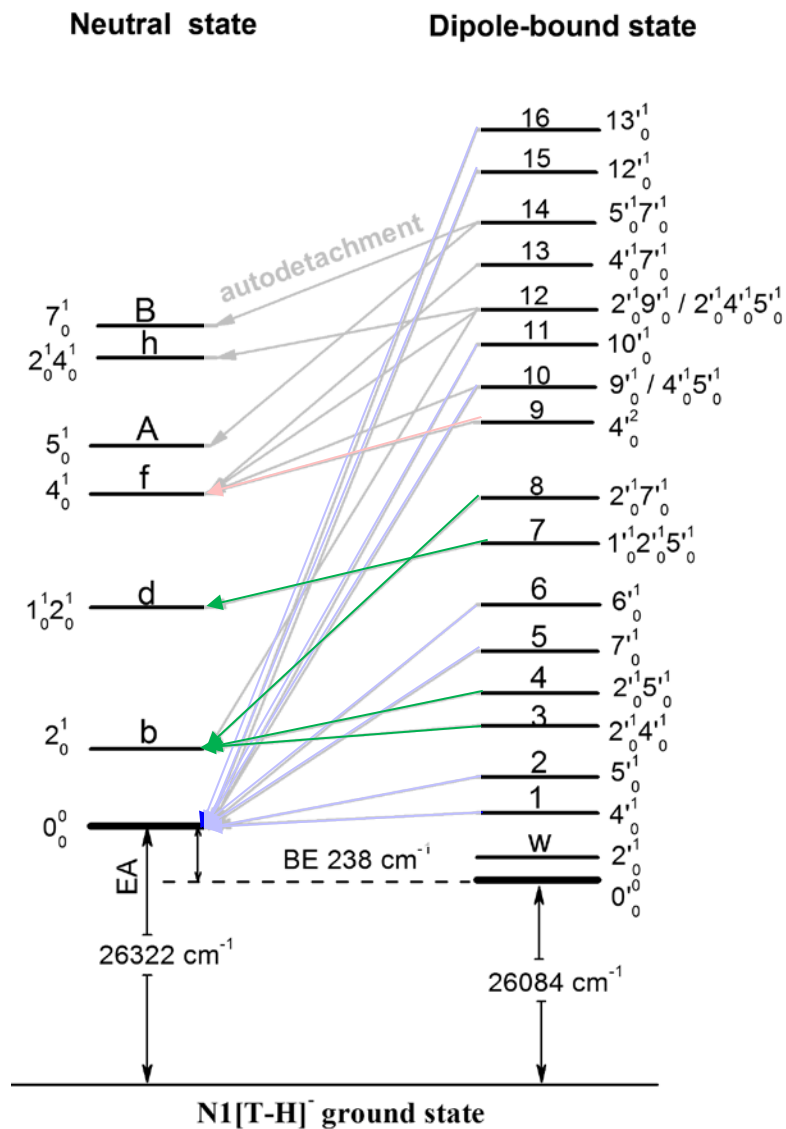
Assignments of dipole-bound states



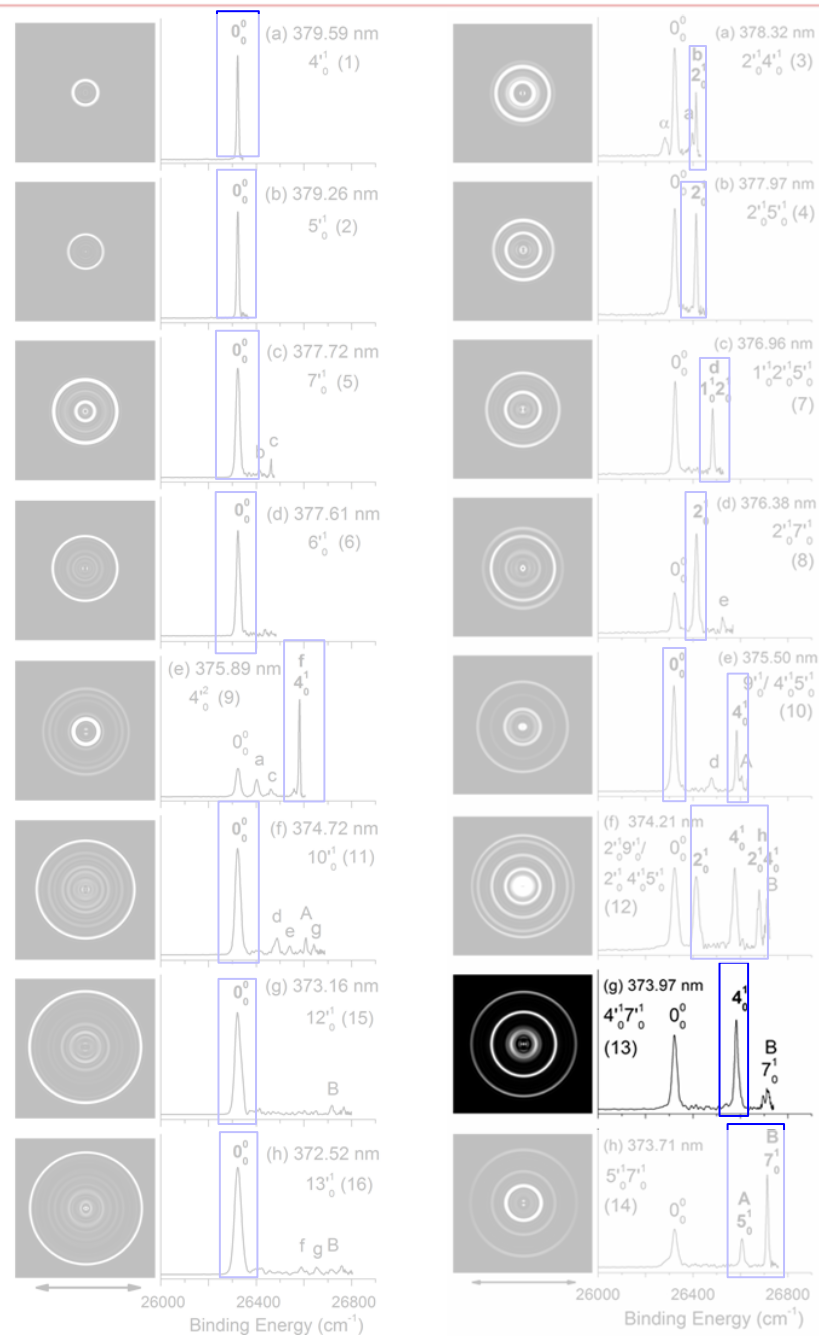
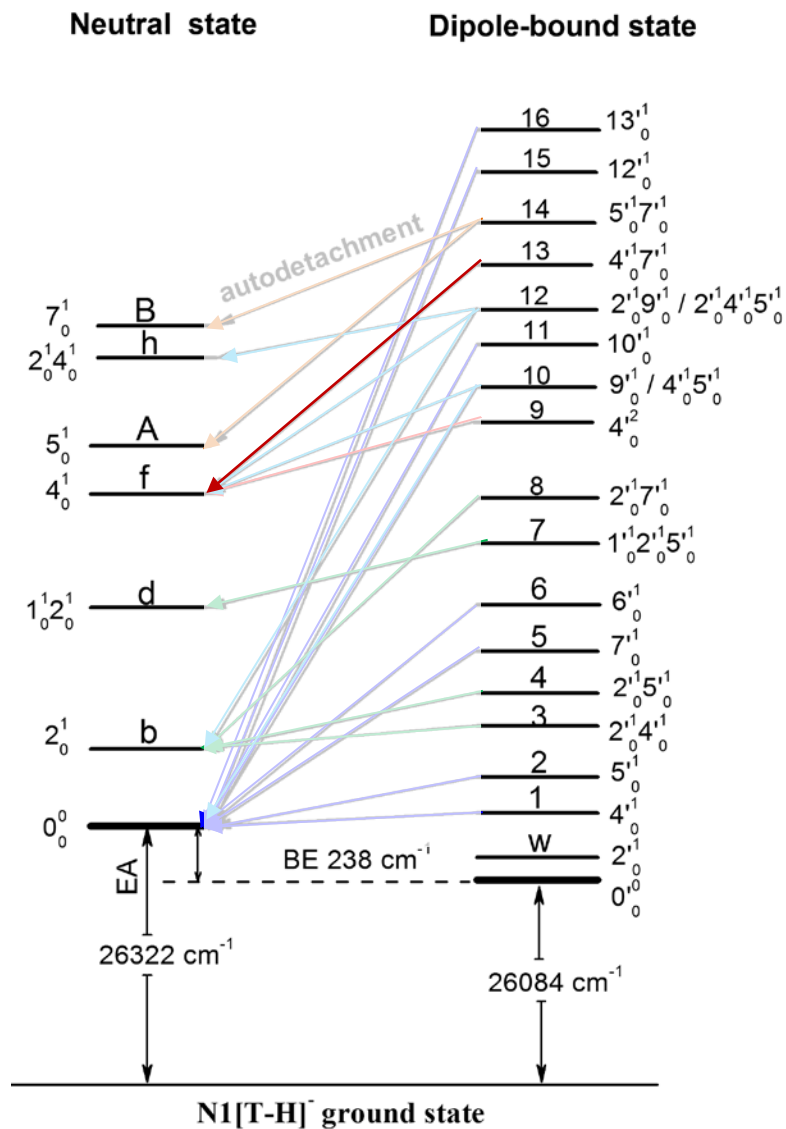
Assignments of dipole-bound states



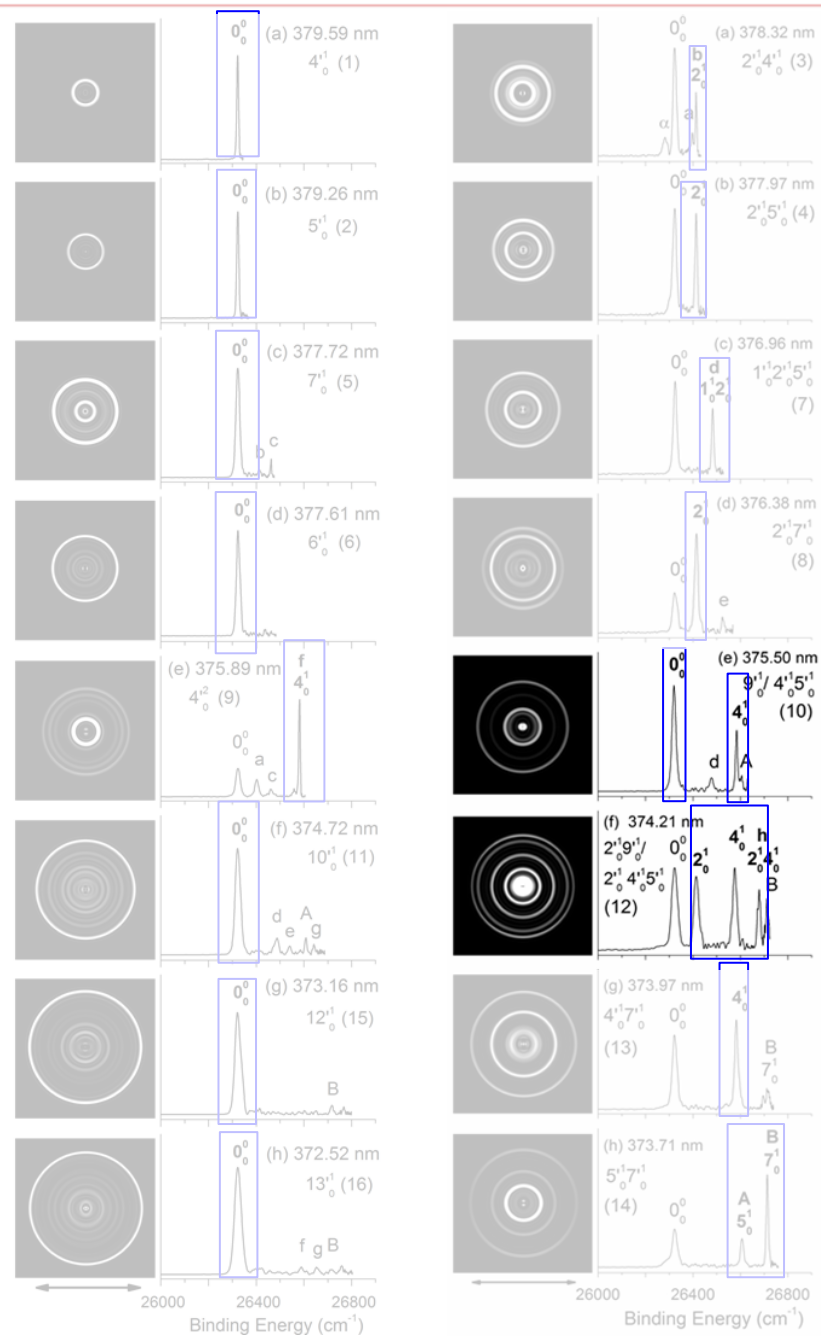
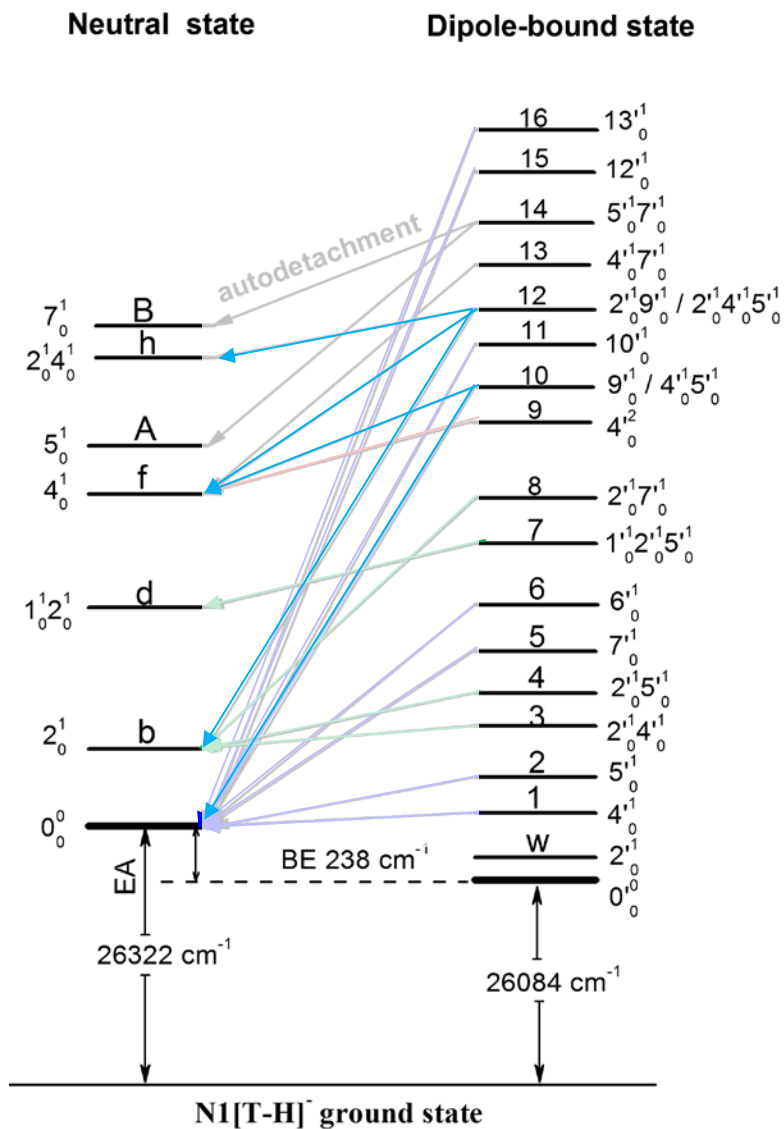
Assignments of dipole-bound states



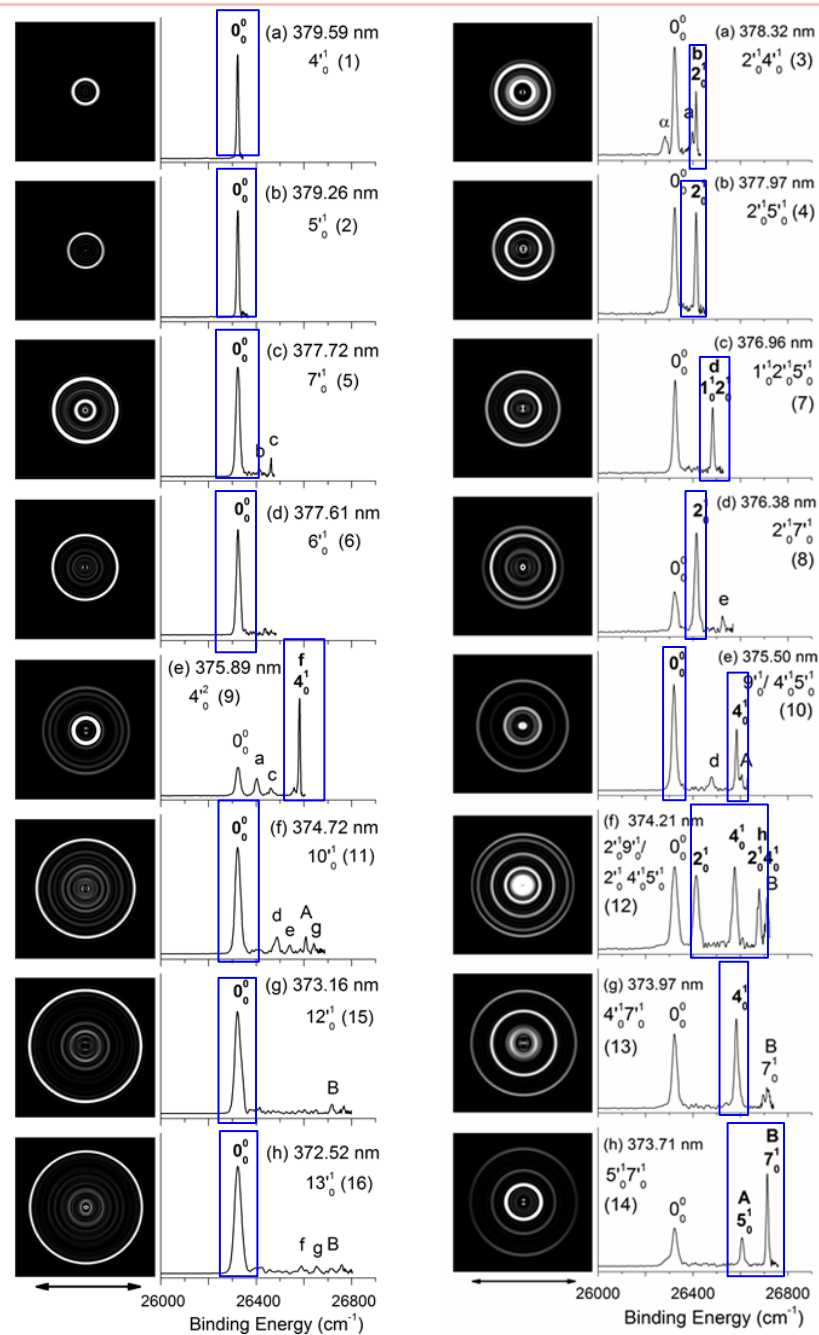
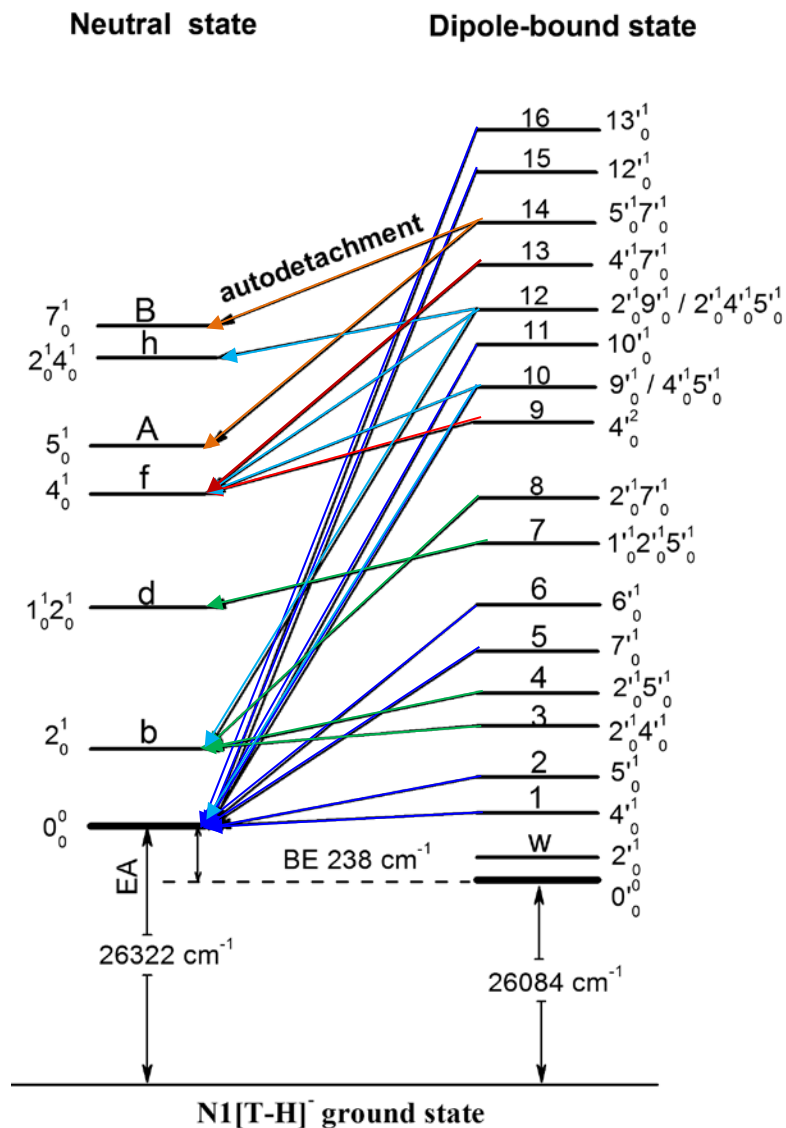
Assignments of dipole-bound states



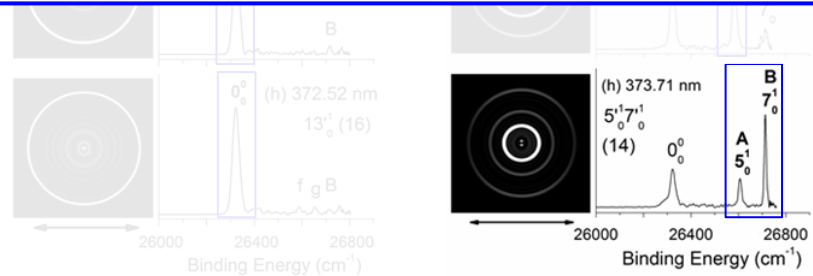
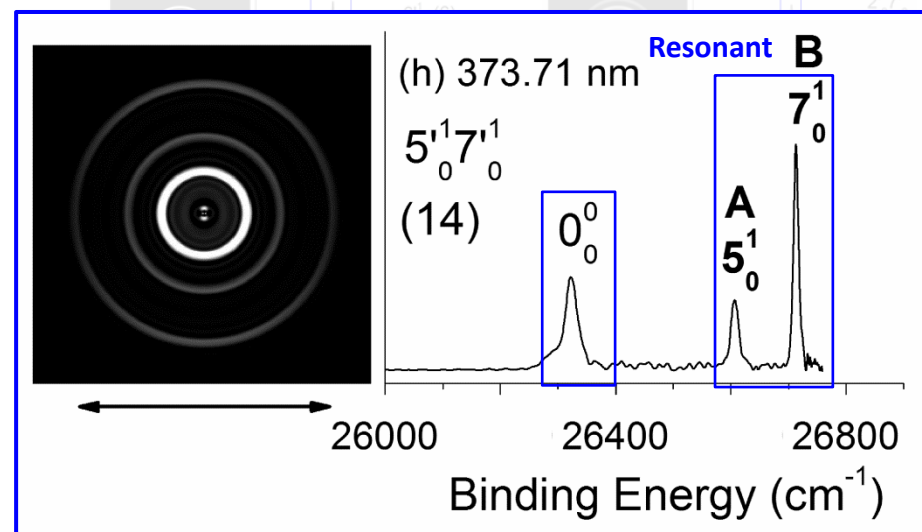
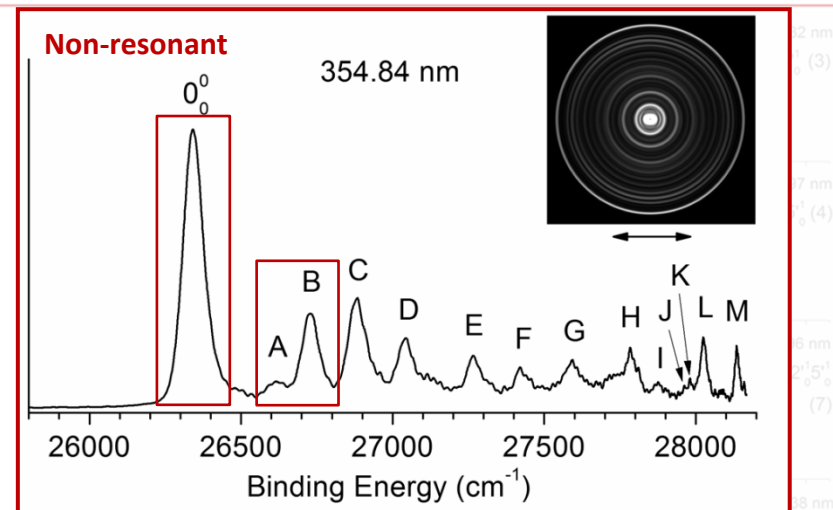
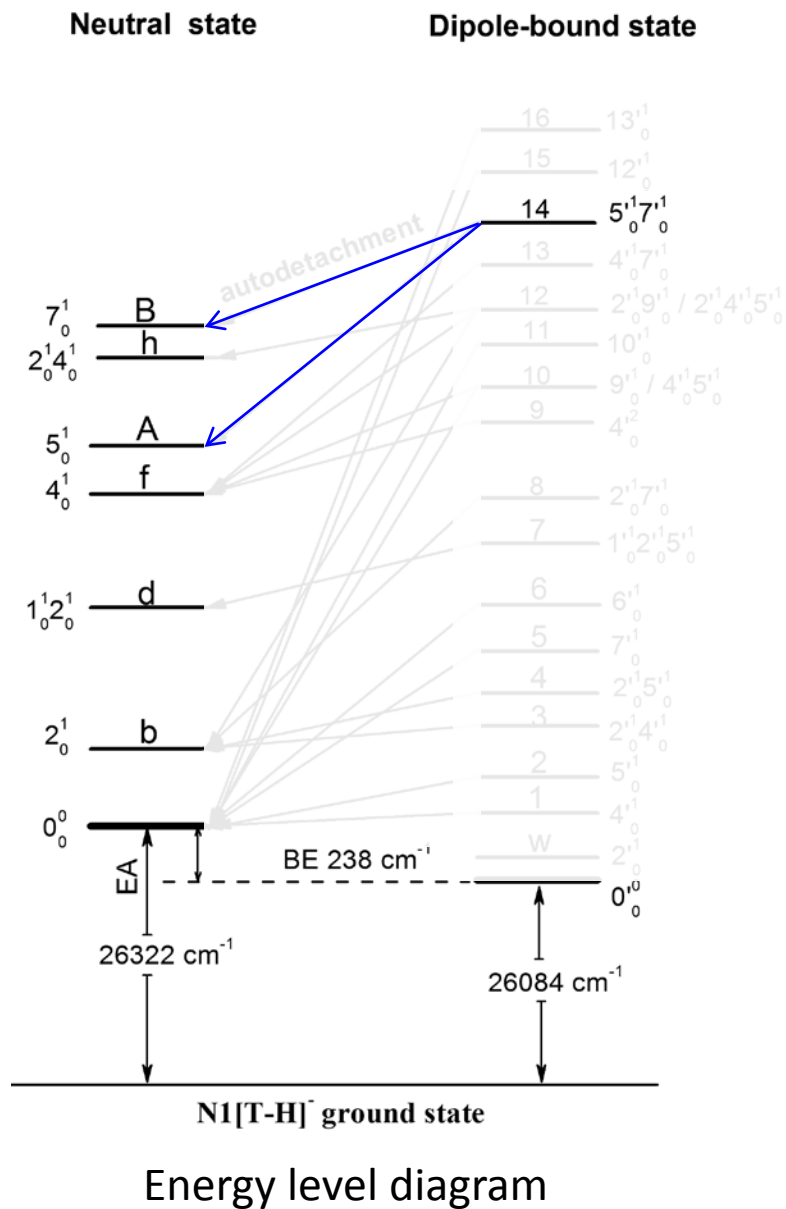
Assignments of dipole-bound states



Assignments of dipole-bound states



Assignments of dipole-bound states



Non-resonant photoelectron image and spectrum

