Observation of a *π*-Type Dipole-Bound State in Molecular Anions

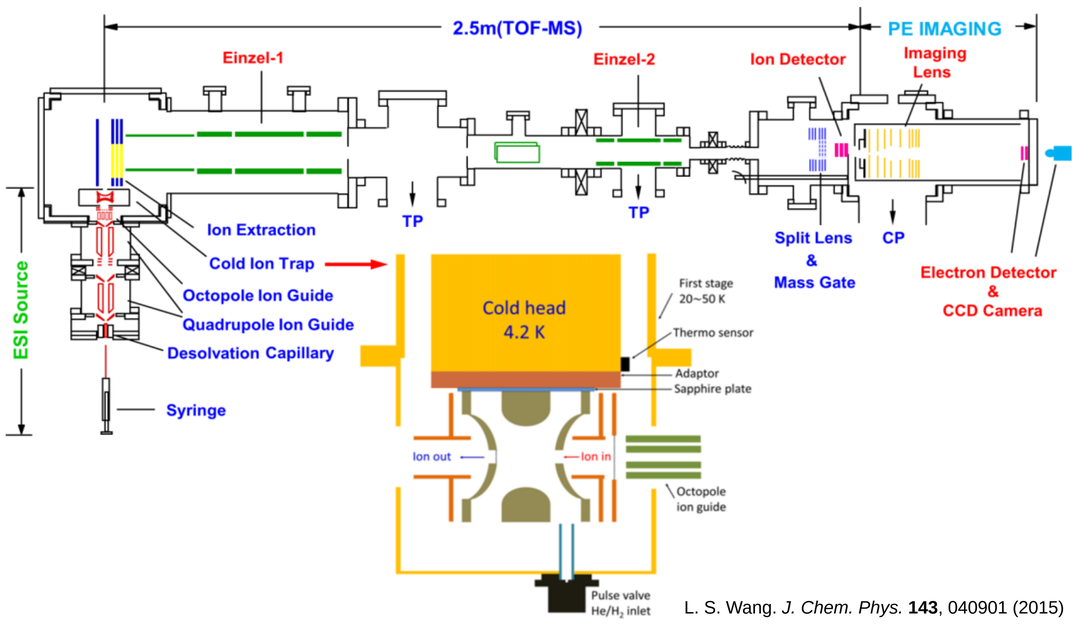
Dao-Fu Yuan, Yuan Liu, Chen-Hui Qian, Yue-Rou Zhang, Brenda M. Rubenstein, Lai-Sheng Wang*

Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

Introduction

Polar molecules with sufficiently large dipole moments can form highly diffuse dipole-bound anions, and possess noncovalent dipole-bound states (DBSs) just below the electron detachment threshold. DBSs have been proposed as the "doorway" to the formation of valence-bound anions, and exploited as a means to develop high resolution resonant photoelectron spectroscopy. The π-type DBS (π-DBS) with one additional angular node in the wave function was predicted to exist as an excited electronic state in addition to the σ-type ground state. However, π-type noncovalent states have never been observed in isolated molecular systems. Here we report the observation of a π-DBS in cryogenically cooled 9-anthrolate anions ($9AT^-$, $C14H9O^-$) by resonant two-photon photoelectron imaging. A DBS is observed 191 cm^{-1} (0.0237 eV) below the detachment threshold, and the existence of the π-DBS is revealed by a distinct (s + d)-wave photoelectron angular distribution. The π-DBS is stabilized by the large anisotropic in-plane polarizability of 9AT. The population of the dipole-forbidden π-DBS is proposed to be via a nonadiabatic coupling with the dipole-allowed σ-type DBS mediated by molecular rotations

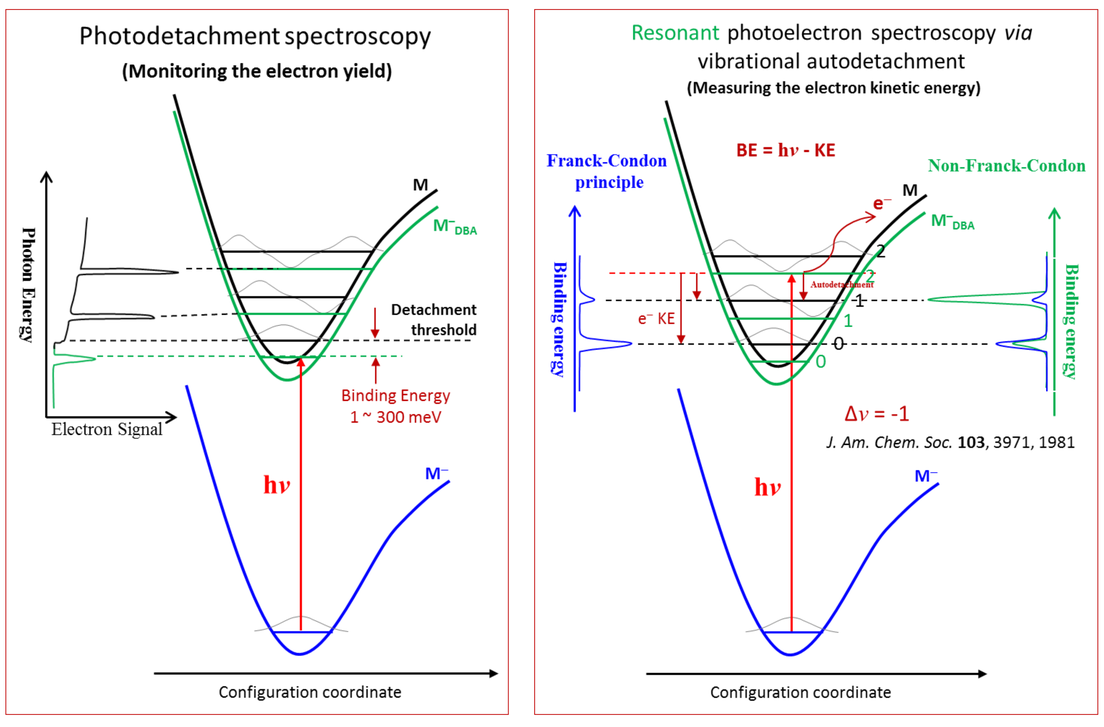
Experimental Apparatus



L. S. Wang. *J. Chem. Phys.* **143**, 040901 (2015)

Electrospray photoelectron spectroscopy apparatus equipped with a cryogenically-cooled Paul trap and a high-resolution photoelectron imaging system

Principles



Acknowledgement

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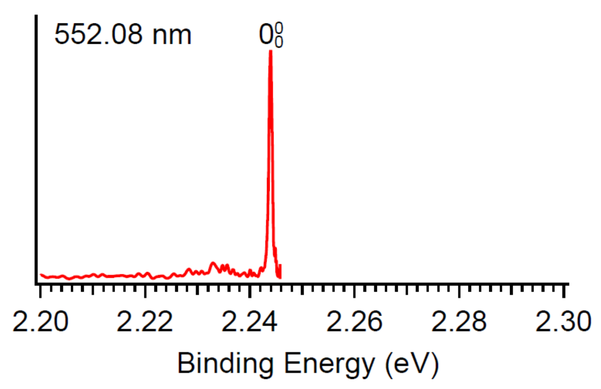
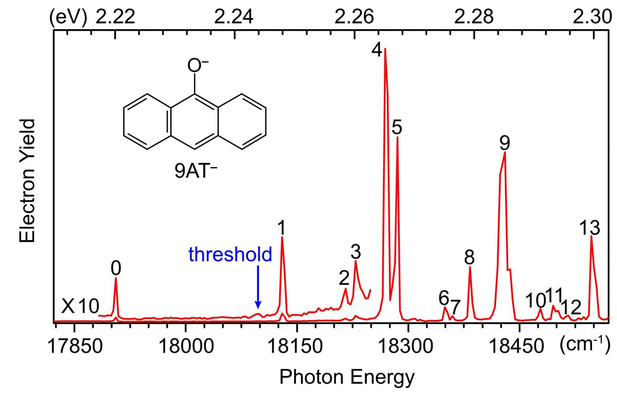
Results

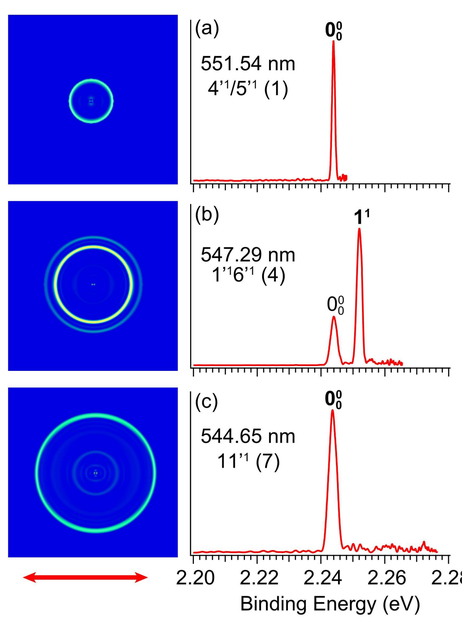
Phys. Rev. Lett. **125**, 073003 (2020).

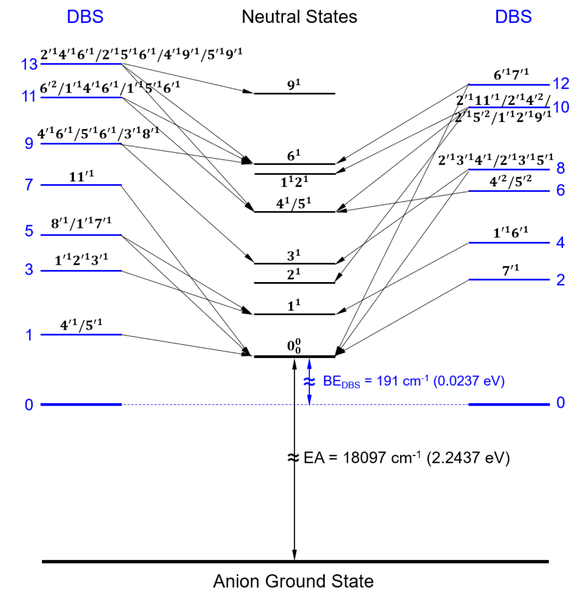


Non-resonant photoelectron spectrum of $9AT^-$ at 552.08 nm. The detachment threshold is 2.2437 eV.

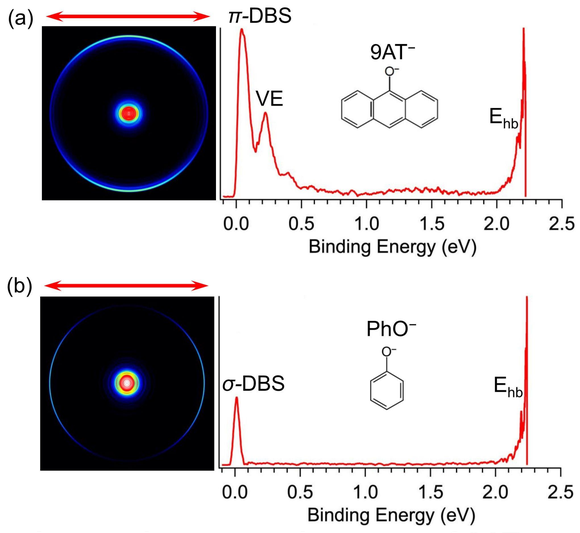


The photodetachment spectrum of $9AT^-$.





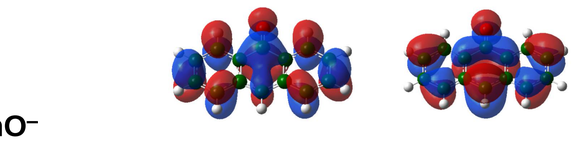
(left) Three Resonant PE images and spectra of $9AT^-$. (right) Schematic energy level diagram for autodetachment from the DBS vibrational levels of $9AT^-$ to the related neutral final states。



Polarizability	9AT	PhO
α_{xx}	78.5	39.2
α_{xy}	0.0	0.0
α_{yy}	284.0	77.1
α_{xz}	0.0	0.0
α_{yz}	0.0	0.0
α_{zz}	173.7	96.9
α_{iso}	178.8	71.1

The theoretical polarizability tensor *α* of the neutral 9AT

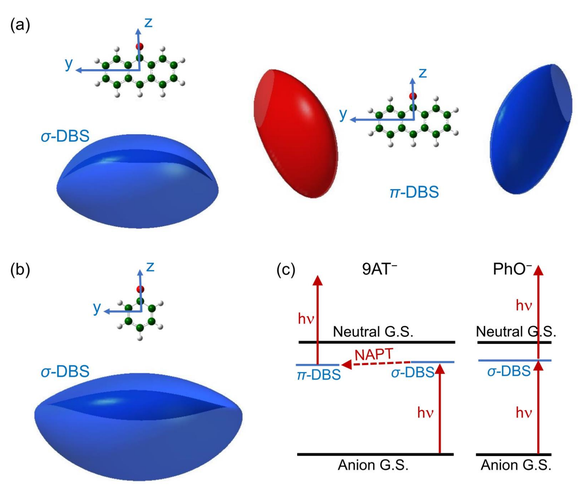
Photoelectron images and spectra of $9AT^-$ and PhO^- from resonant two-photon detachment (R2PD) via the vibrational ground states of their respective DBS



LUMO **HOMO**

	9AT⁻	
	Cal	Exp
σ-DBS (cm^{-1})	336	191
(meV)	41.7	23.7
π-DBS (cm^{-1})	261	116
(meV)	32.4	14.4
EA (cm^{-1})	16884	18097
(eV)	2.0934	2.2437

Binding energies of the DBSs at the CAM-B3LYP/Def2-TZVPP+4s3p2d1f level of theory; The electron affinity (EA) of the neutral 9AT at the B3LYP/Def2-TZVPP level of theory.



The DBS orbitals and a schematic diagram of the R2PD processes

Outlook

The observation of different weakly-bound states in the same molecule and their sensitivity to molecular structures make it possible to control molecular quantum states via molecular design. The distinct nodal structure of the π-DBS as compared to the σ-DBS also make them candidates as molecular qubits for quantum information science applications. The unique non-adiabatic dynamics mediated by molecular rotation from the σ-DBS to π-DBS further opens up new directions for understanding the electron capture mechanisms by neutral molecules to form molecular anions.