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Studying Molecular Reactions and Interactions at the Surface of Sea Spray Aerosols using Ab Initio Molecular Dynamics

Laura M. McCaslin

April 26, 2022

Sandia – UC Davis Research Symposium

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Personal Background

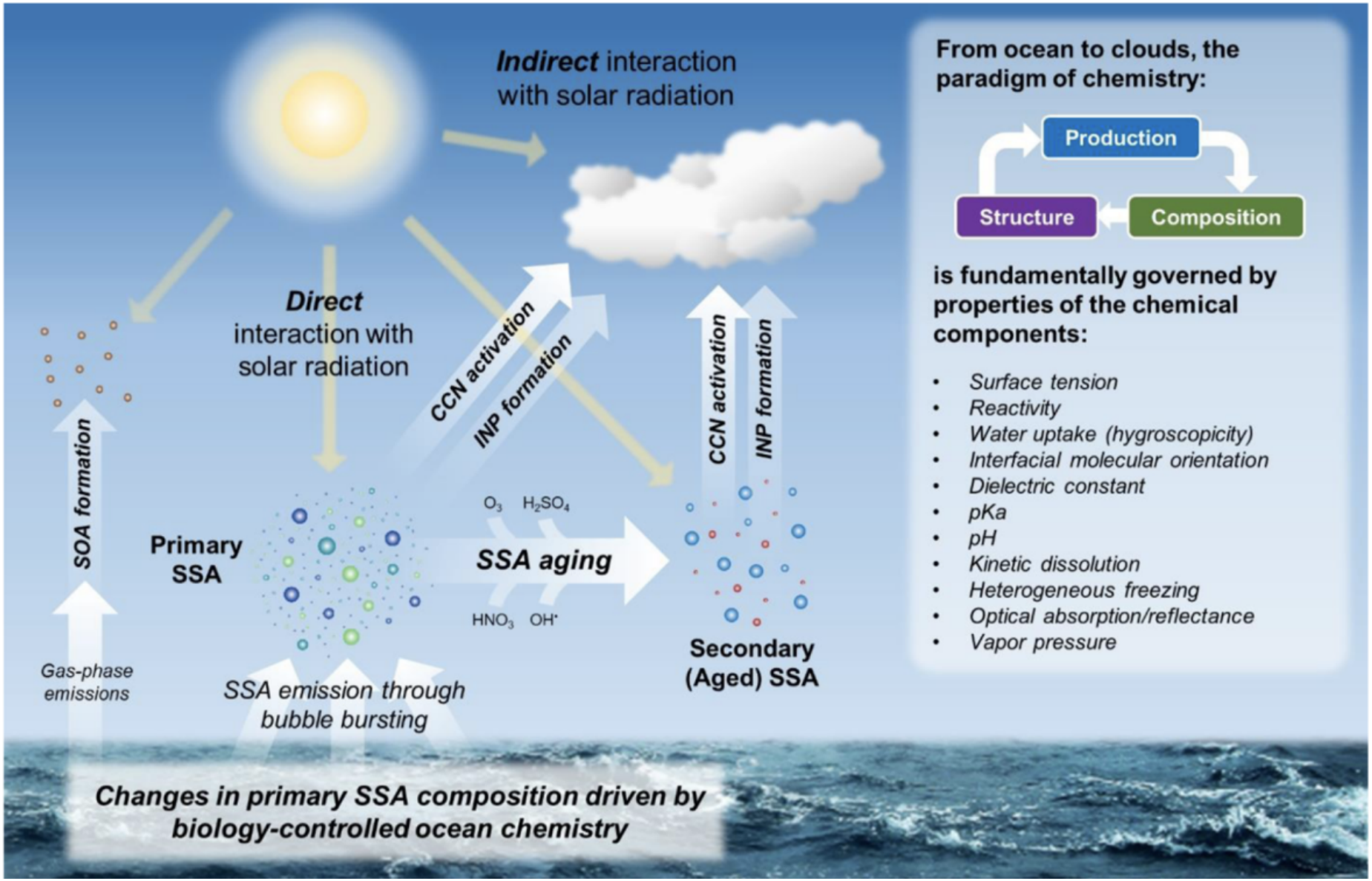
- PhD, UT Austin, Theoretical Physical Chemistry
  Advisor: John Stanton
  Research: electronic and vibrational structure of small molecules

- Postdoc, Hebrew University, Theoretical Physical Chemistry
  Advisor: Benny Gerber
  Research: studying dynamics of small molecules and clusters

- Research interests:
  - Atmospheric chemistry
  - Photochemical dynamics
  - Organic semiconducting materials design

- Email: lmmccas@sandia.gov

Part 1: Studying reaction dynamics at sea spray aerosol interfaces



CAICE

NSF

R.E. Cochran, O.S. Ryder, V.H. Grassian, K.A. Prather, *Acc. Chem. Res.*, 50, 599 (2017).

Studying reactions and interactions with on-the-fly *ab initio* molecular dynamics

Pros:

- Powerful tool for determining reaction mechanisms, timescales, and spectra
- Gives electronic structure at each point along dynamical trajectory

Cons:

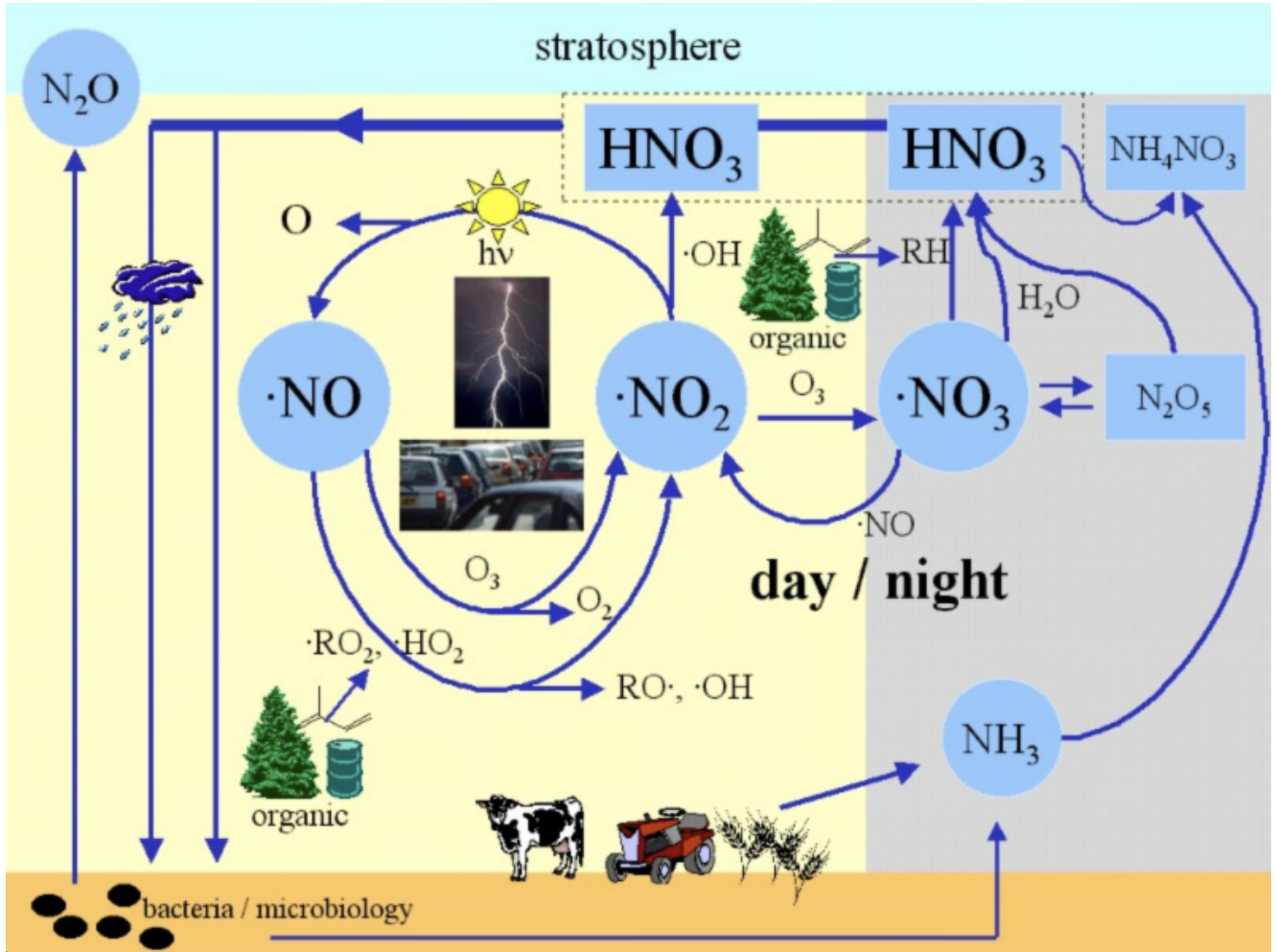
- Many trajectories needed for statistics
- Computationally expensive (relies on electronic structure, many trajectories needed to get statistics)

$$m_j \frac{d^2 x_j}{dt^2} = -\frac{\partial V}{\partial x_j}$$

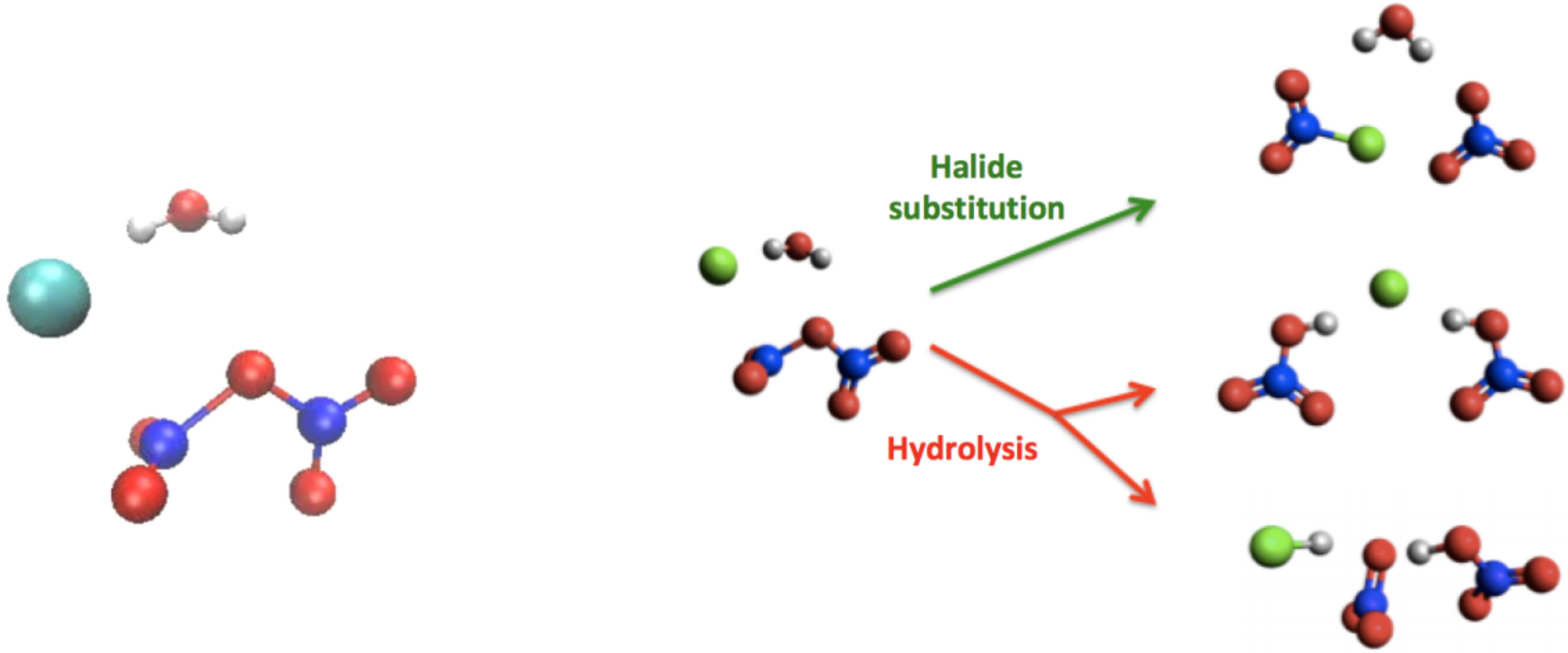
← Potentials obtained on-the-fly from *ab initio* electronic structure calculations

"The dominant heterogeneous reaction in the troposphere is the reactive uptake of N_2O_5...producing nitric acid (HNO_3), thus removing oxides of nitrogen from the atmosphere." –Macintyre and Evans, 2010

Model studies indicate that changes in the probability of reactive uptake of N_2O_5 has huge effects on global levels of key atmospheric components:
NO_x – 25% change, O_3 – 12% change, OH radical – 15% change

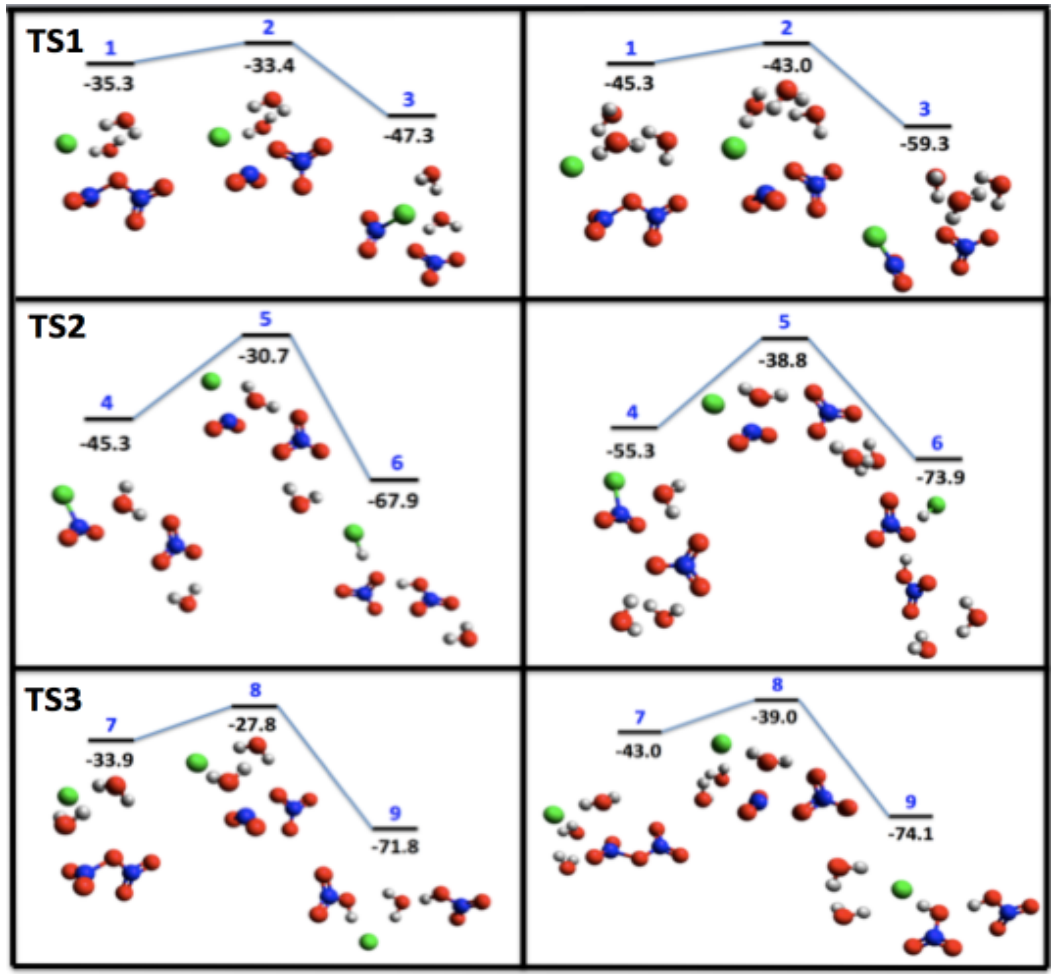


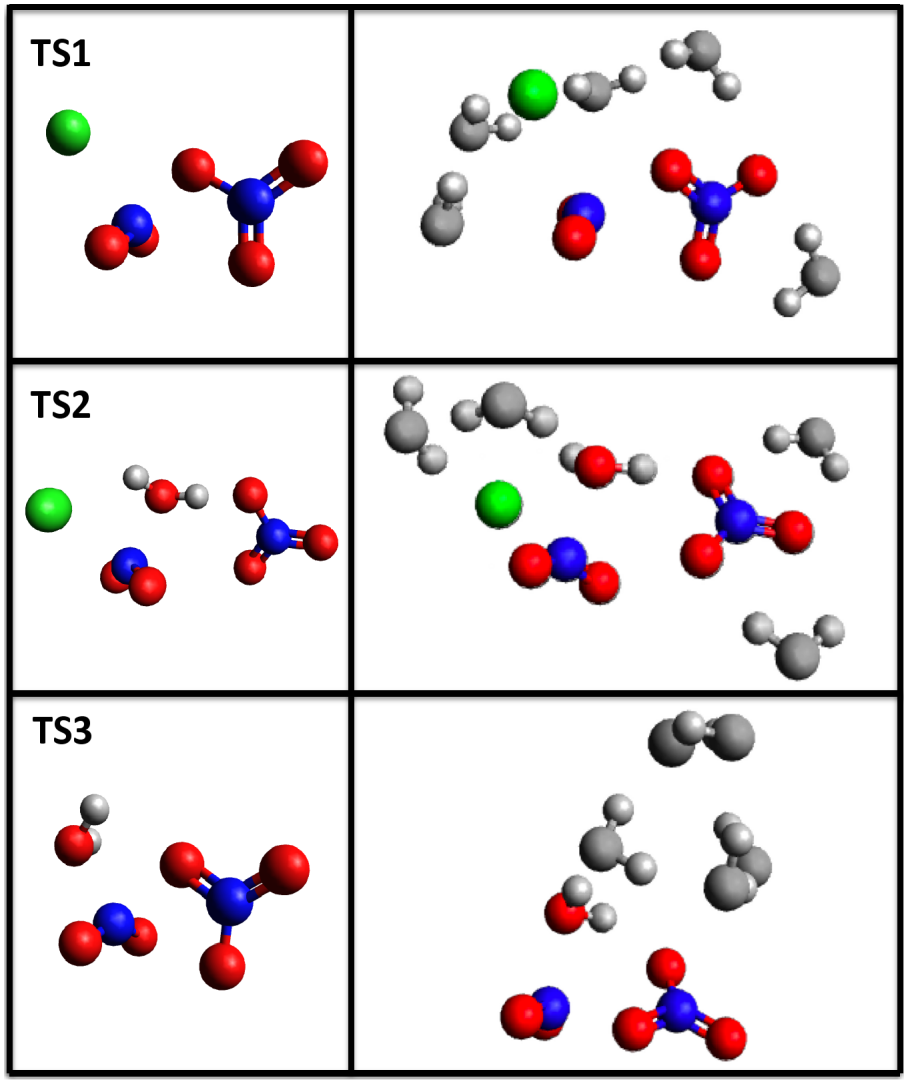
Effects of Microhydration on the Mechanisms of Hydrolysis and Cl^- Substitution in Reactions of N_2O_5 and Seawater



1. L.M.M, MA Johnson, RB Gerber, *Sci. Adv.* 5 (6), eaav6503
2. L.M.M. A.W. Götz, M.A. Johnson, R.B. Gerber (in prep.)

Transition state substructures are preserved upon addition of water molecules!





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Studying the effects of cations (such as Na^+) on the interactions, dynamics, and spectral signatures of molecules at aerosol interfaces

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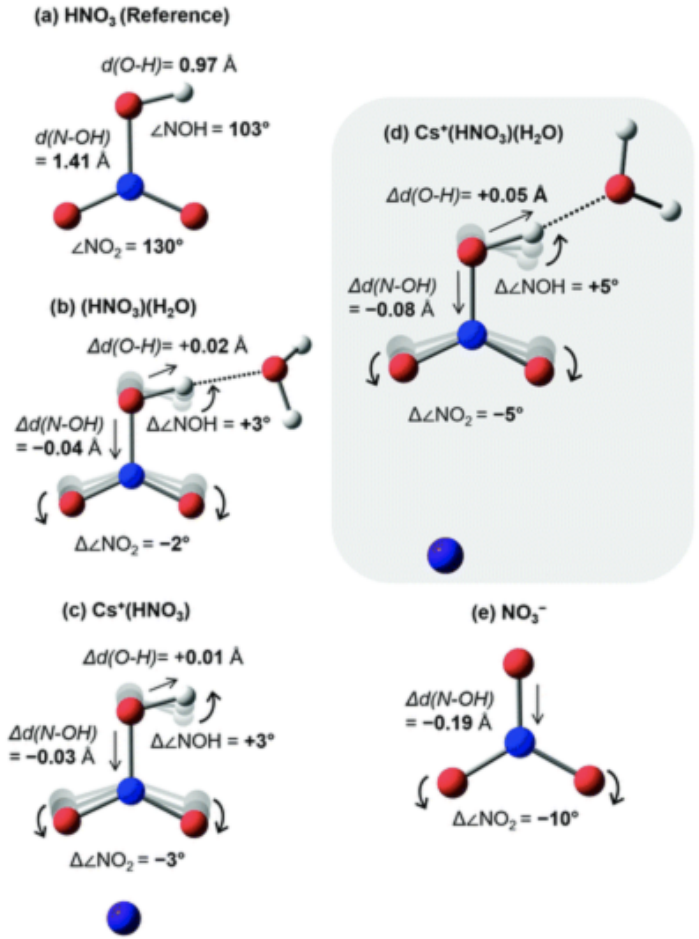
Cite this: Phys. Chem. Chem. Phys., 2020, 22, 4501

Isomer-specific cryogenic ion vibrational spectroscopy of the D_2 tagged $Cs^+(HNO_3)(H_2O)_{n=0-2}$ complexes: ion-driven enhancement of the acidic H-bond to water†

Sayoni Mitra, [a] Chinh H. Duong, [a] Laura M. McCaslin, [bc] R. Benny Gerber [*bc] and Mark A. Johnson [*a]



THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
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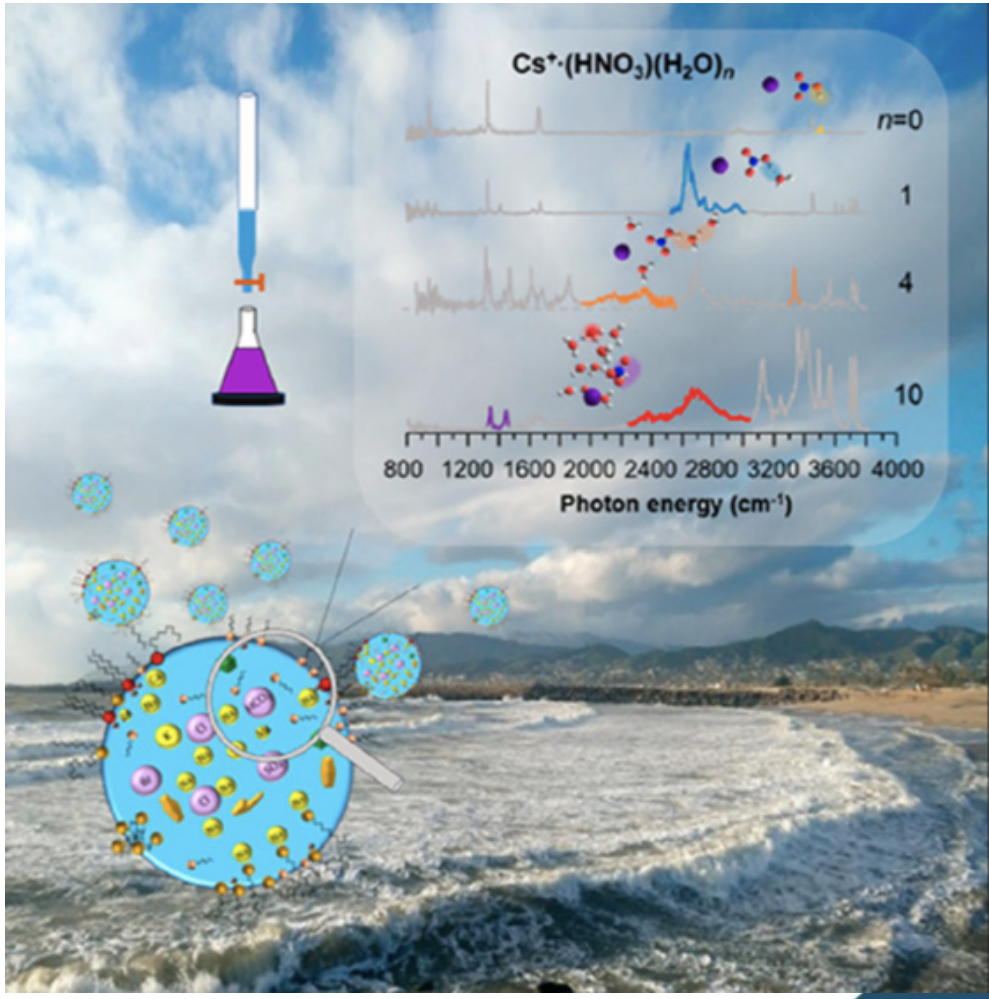
pubs.acs.org/JPCL Letter

Size-Dependent Onset of Nitric Acid Dissociation in $Cs^+\cdot(HNO_3)(H_2O)_{n=0-11}$ Clusters at 20 K

Sayoni Mitra, Nan Yang, Laura M. McCaslin, R. Benny Gerber, and Mark A. Johnson*



THE JOURNAL OF PHYSICAL CHEMISTRY A
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

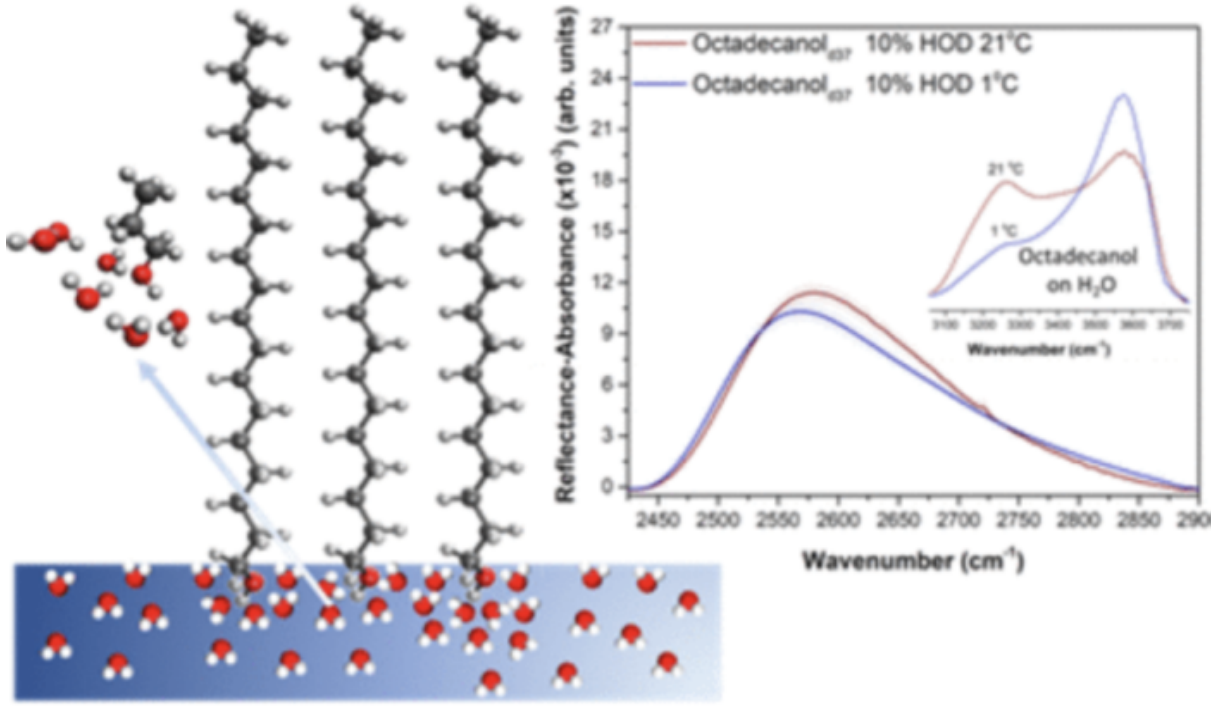
pubs.acs.org/JPCA Article

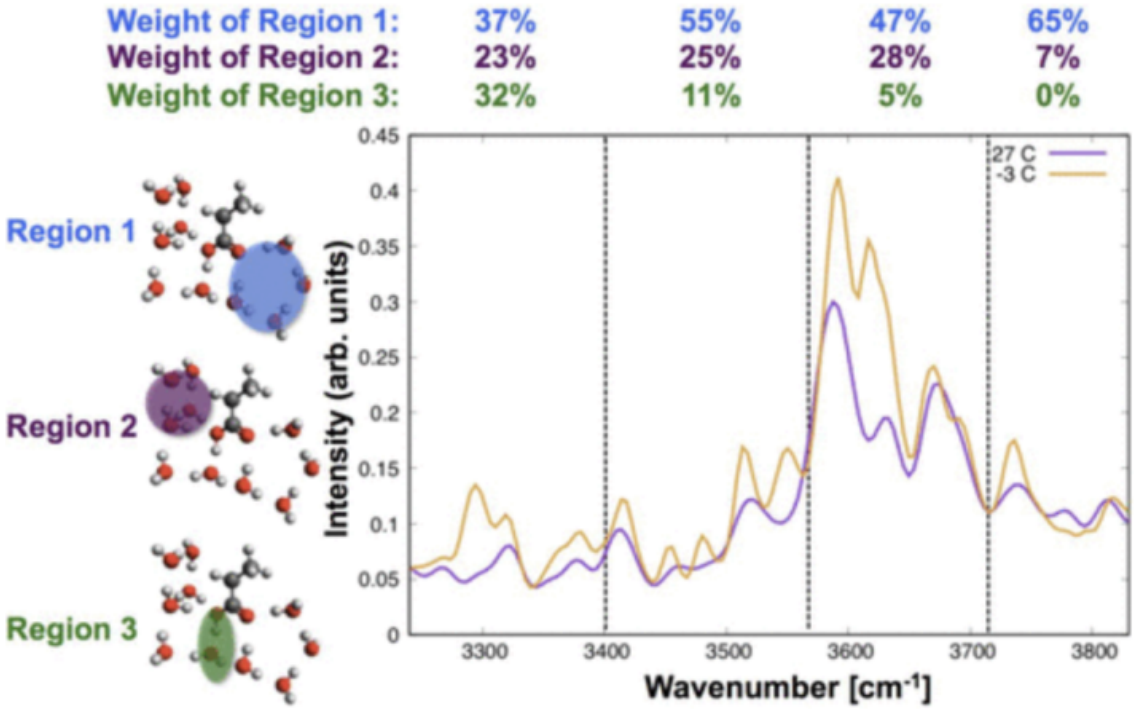
Hydration and Hydrogen Bond Order of Octadecanoic Acid and Octadecanol Films on Water at 21 and 1 °C

Published as part of The Journal of Physical Chemistry virtual special issue "125 Years of The Journal of Physical Chemistry".

Maria G. Vazquez de Vasquez,[§] Kimberly A. Carter-Fenk,[§] Laura M. McCaslin, Emma E. Beasley, Jessica B. Clark, and Heather C. Allen*

Cite This: *J. Phys. Chem. A* 2021, 125, 10065−10078 Read Online



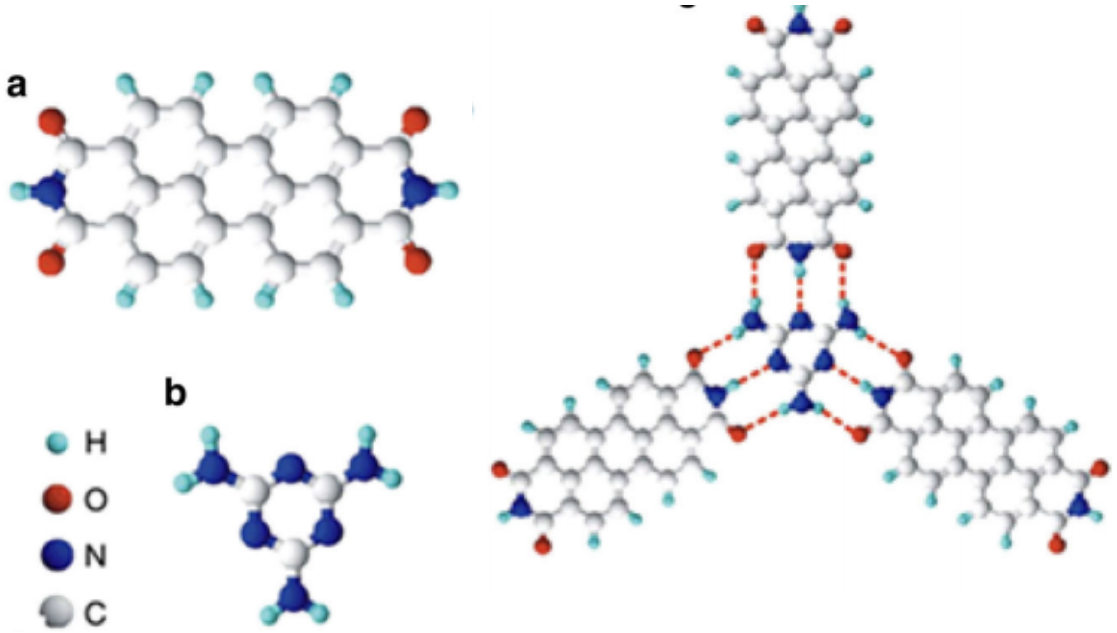


Part 2: Studying photophysical dynamics in model photovoltaics

A new generation of optoelectronic devices using organic co-crystals

Can exhibit new properties

- Balanced ambipolar charge transport at low temperatures due to both donor and acceptor character
- Ferroelectronic properties near room temperature
- Non-linear optical properties

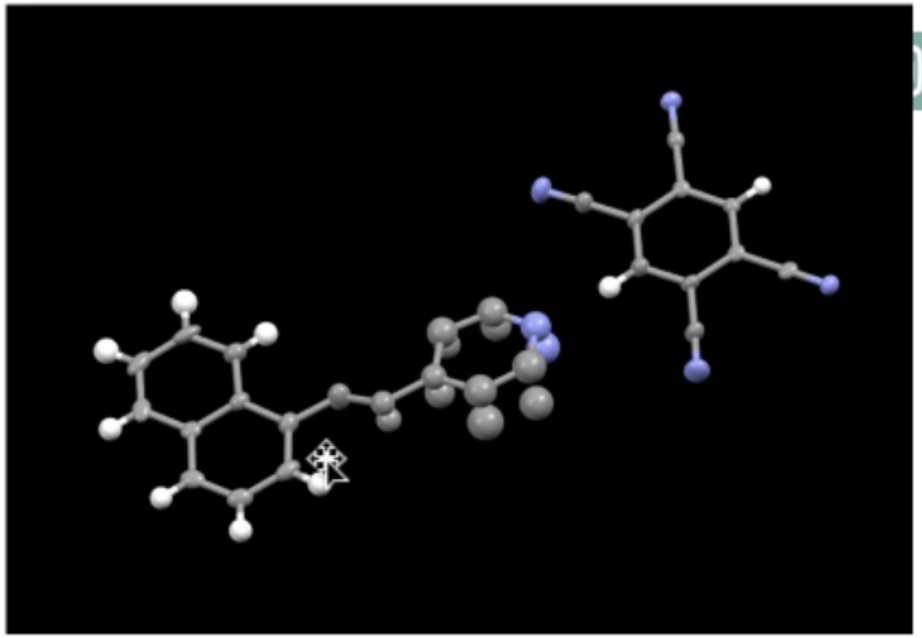


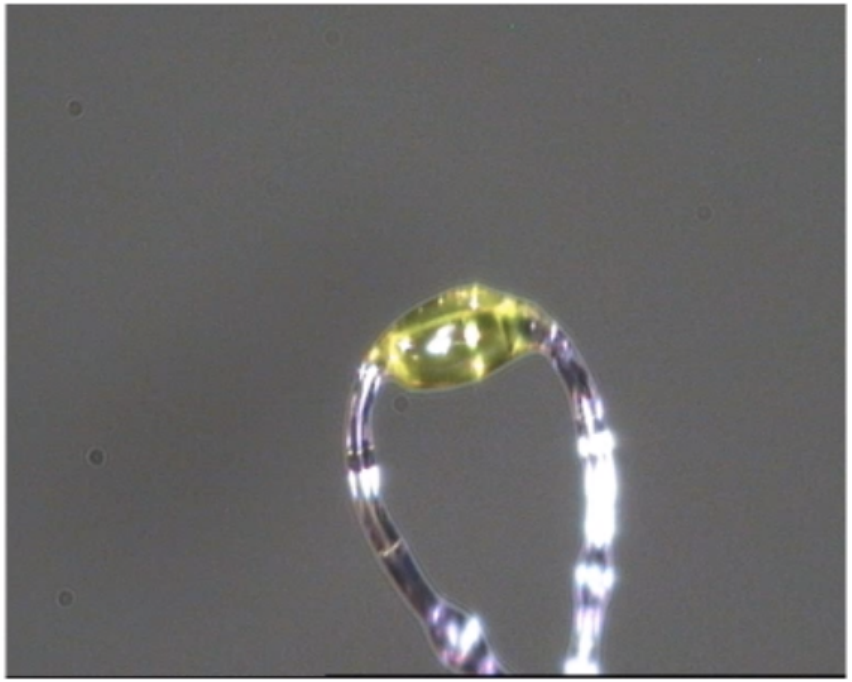
- Definition: a crystalline solid material consisting of two or more molecules in the same crystal lattice
- Donor/acceptor pair co-crystallizing through non-covalent interactions
- Relatively easy to fabricate

Theobald JA, Oxtoby NS, Phillips MA, Champness NR, Beton PH (2003) *Nature* 424(6952):1029–1031

NPE:TCNB (new crystal)

- CY_D1
- Grown from DMF:MeCN and reduced formed in 1:1 ratio
- Crystals are fragile yellow plates
- No structure was previously reported



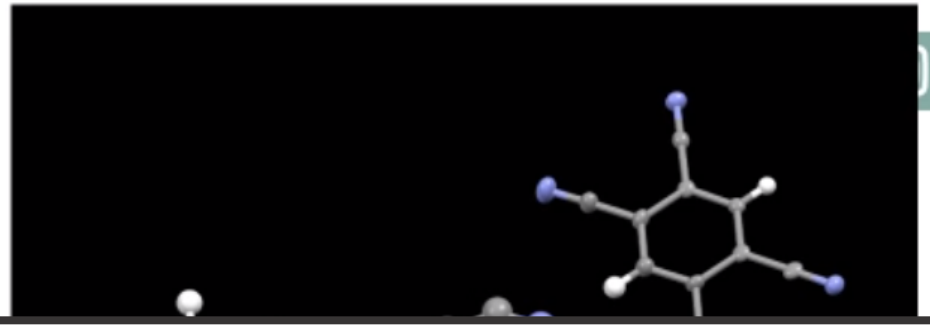


Identifier	cy_d1
Literature Reference	*Unknown* (0)
Formula	C_{10} H_2 N_4,C_{17} H_7 N
Compound Name	
Synonym	
Space Group	P $2_1/c$ (14)
Cell Lengths	**a** 6.7439(2) **b** 36.7099(13) **c** 9.5302(4)
Cell Angles	**α** 90 **β** 106.315(4) **γ** 90
Cell Volume	2264.36
Z, Z'	**Z**: 4 **Z'**: 1
R-Factor (%)	16.78

a = 6.58 Å, b = 9.48 Å, c = 25.49 Å,
α = 84.13°, β = 84.98°, γ = 73.69°

DOI: (10.1002/adma.201600280)

NPE:TCNB (new crystal)



- CY_D1

NPE:TCNB was reported to have triclinic structure

We have found a more complex picture:

- the crystal can form with 2 molecular configurations
- Monoclinic (higher symmetry)

Formula	$C_{10}H_2N_4C_{17}H_7N$
Compound Name	
Synonym	
Space Group	P $2_1/c$ (14)
Cell Lengths	**a** 6.7439(2) **b** 36.7099(13) **c** 9.5302(4)
Cell Angles	**α** 90 **β** 106.315(4) **γ** 90
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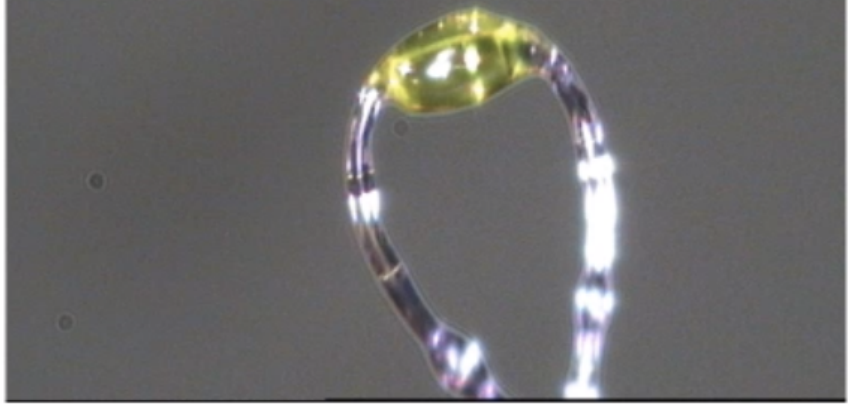
R-Factor (%)	16.78

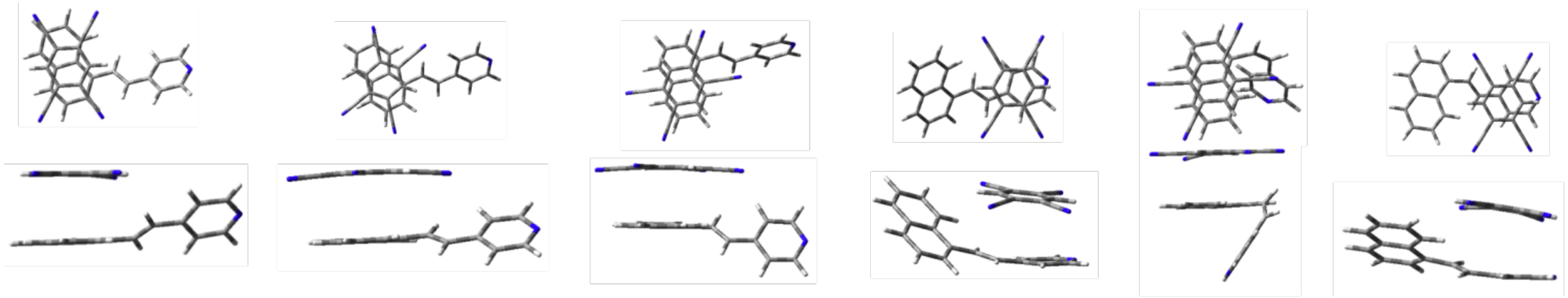
$\alpha = 84.13°, \beta = 84.98°, \gamma = 73.69°$

DOI: (10.1002/adma.201600280)



Cluster models: exploring the potential energy landscape

Rel Energy (eV) (Kcal/mol)
B3LYP-D/6-31G(d,p)



Npe-TCNB-a	Npe-TCNB-b	Npe-TCNB-c	Npe-TCNB-d	Npe-TCNB-e	Npe-TCNB-f
0.000 eV	0.015 (0.341)	0.057 (1.305)	0.117 (2.706)	0.128 (2.952)	0.178 (4.106)

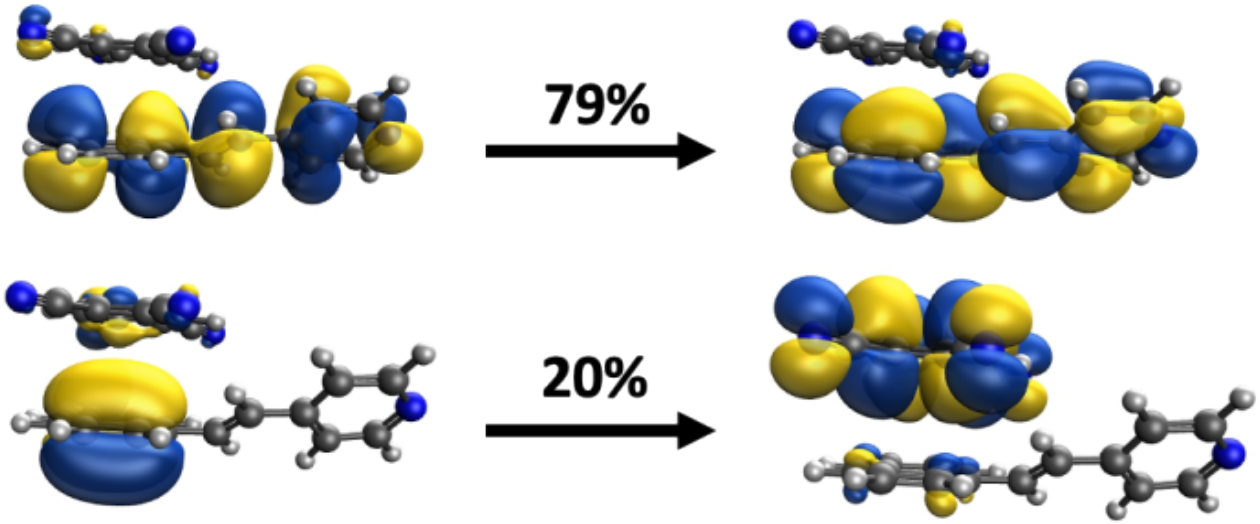
Reported = 2.9 Kcal/mol

Previous study identified 2 conformers

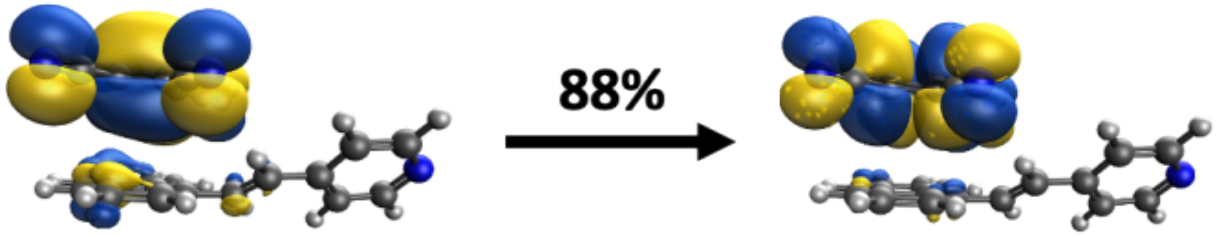
Natural Transition Orbital (NTO) Analysis

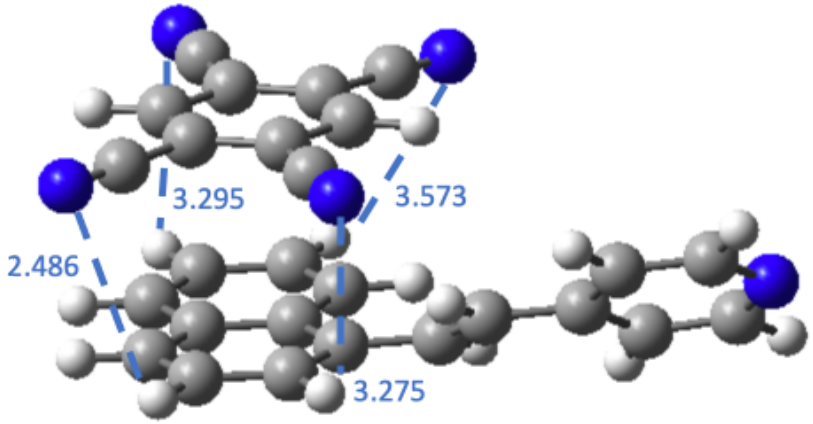
S_1

S_4

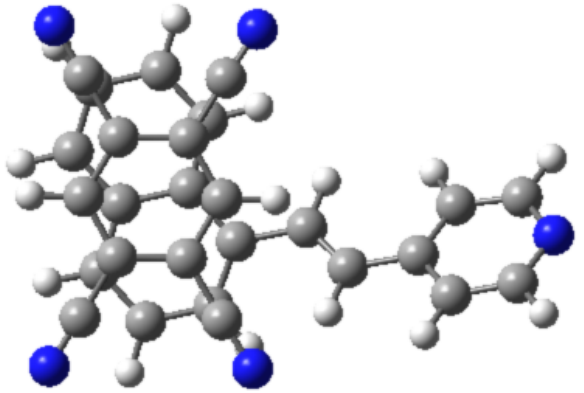


S_9



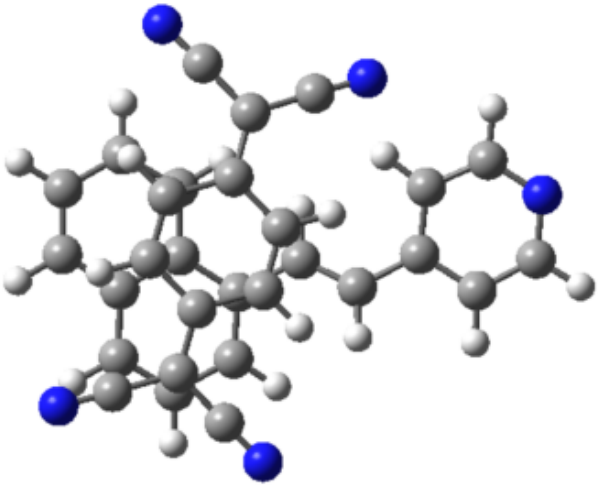


Next Steps: Studying photophysical dynamics in model photovoltaics



Summary:

- Corrected crystal structure of Npe/TCNB
- Newly predicted crystal structure of Npe/TCNQ
- High-level electronic structure calculations
- Comparisons between UV Spectra, excited state structure, and charge transfer of 2 crystals

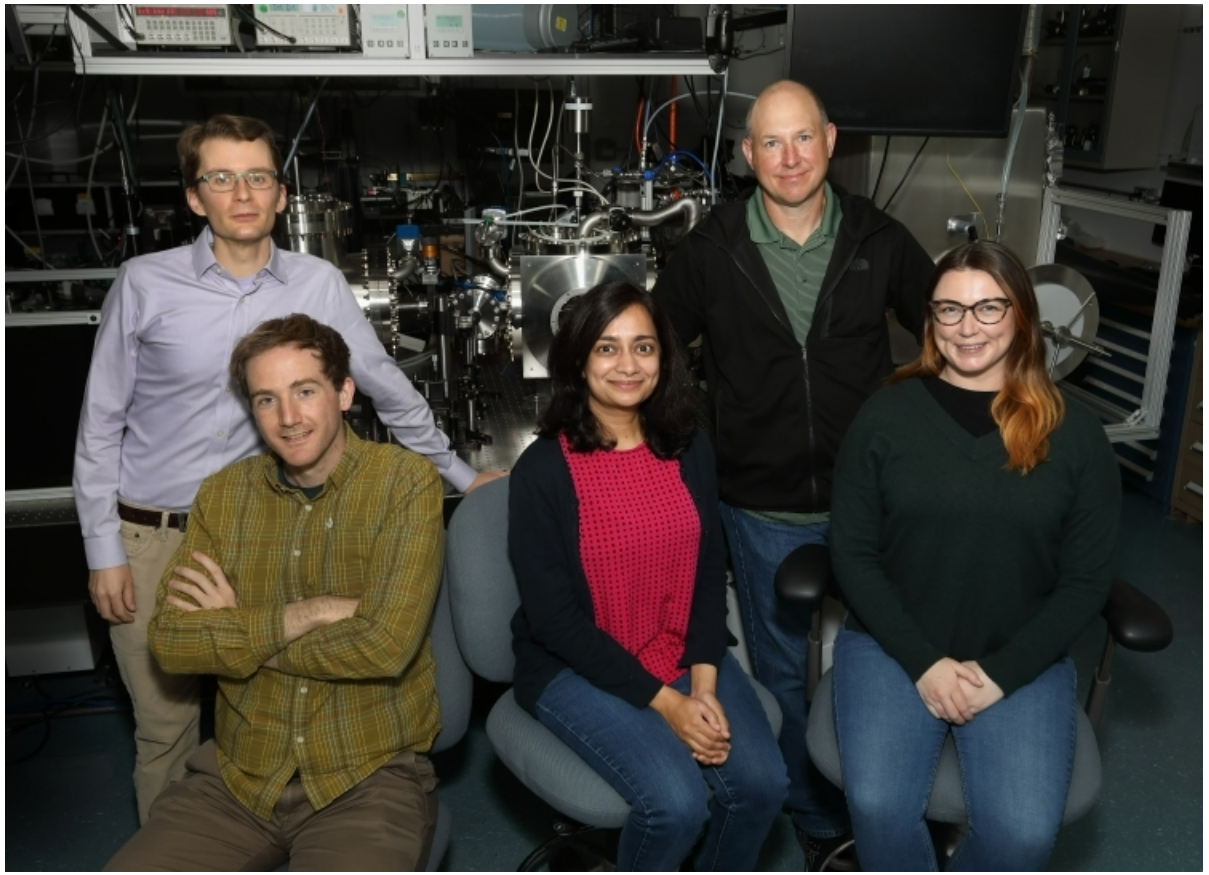


UV pump/UV probe ultrafast transient absorption spectroscopy experiment being built in Krupa's lab → probe correlations between electronic excited states in time

Excited state dynamics calculations are in preparation → predicting experimental observables

Acknowledgments

Email: lmmccas@sandia.gov



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