LABORATORY DIRECTED RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

SAND20XX-XXXXR
LDRD PROJECT NUMBER: 218385
LDRD PROJECT TITLE: Molecule Origins of Dipolar Character in Excited Electronic States
PROJECT TEAM MEMBERS: Jacob Harvey (PI), Jordyn Wemhoner (HS Summer Intern)

ABSTRACT:

The molecular level origins for symmetry breaking in the excited state of symmetrical quadrupolar molecules, particularly in polar solvents, was investigated using time-dependent density functional theory approaches. Molecules of the form ADA (A/D electron accepting/donating respectively), have been shown to break their symmetry upon excitation, producing an intramolecular charge transfer event and permanent dipole. Current research indicates that polar solvents stabilize the charge transfer event thereby producing asymmetrical solvent dynamics on opposite ends of the molecules. In this work key structural features of the molecule were identified including (1) incorporation of cyano groups, (2) rotation of grafted phenyl rings, and (3) the length of the conjugated R group chain. More specifically, incorporation of cyano groups appears to decrease the magnitude of the dipole in the excited state, thereby indicating that solvent interactions at these groups do not stabilize the charge transfer. While the rotation of the phenyl groups appears to be necessary to break the symmetry of the excited state in the molecule.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

Molecules of the broad form ADA where A indicates an electron accepting group and D indicates an electron donating group (Figure 2) are of interest due to their large two-photon absorption cross sections which are potentially useful for sensing and additive manufacturing applications. An interesting behavior for (e.g., molecule 1) has been observed in which no permanent dipole is observed in the ground state, however a dipole is formed upon excitation. This indicates that the symmetry of the molecule has been broken and an intramolecular charge transfer event has occurred. This phenomena has been observed using both infrared (IR) spectroscopy and fluorescence spectroscopy.[1-4] In the IR spectrum, due to the symmetry of the molecule, one does not observe the symmetry C≡N stretch, therefore a single C≡N stretch peak is observed in the ground state. However, upon excitation, time resolved IR spectroscopy shows a second peak forming, attributed to the symmetric C≡N stretch while the asymmetric C≡N is red shifted as the polarity of the solvent is increased.

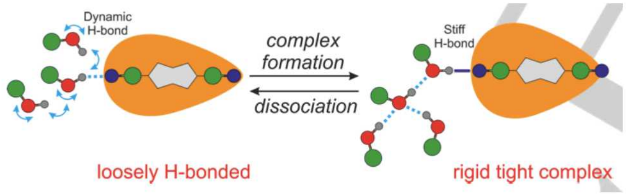
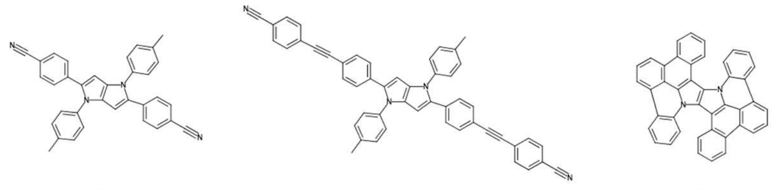


Figure 1. Schematic showing the formation of an asymmetric strong hydrogen bonding network around the molecule upon excitation.

The dynamics of the system has been investigated using two dimensional IR (2D-IR).[3] In this investigation molecule 1 was electronically excited in methanol (low polarization) and the superprotic hexafluoro-iso-propanol (HFP). By monitoring the central line slope of the peaks in the 2D-IR spectrum it was observed that very little spectral diffusion was observed in HFP however only after 40 ps of electronic excitation. While methanol and HFP prior to 40 ps showed normal spectral diffusion behavior. This unexpected result was hypothesized to be due to the formation of strong hydrogen bonding network around the dye molecule; termed a "transient glass (Figure 1). Nearly all experimental evidence has suggested that solvent interactions around the molecule stabilize the charge transfer and lead to the broken symmetry. However, little atomistic modeling work has been performed which is uniquely capable of probing structural features of this kind. The work proposed was intended to answer the key research question what are the molecular level origins for the formation of dipolar character in symmetrical quadrupolar molecules?

Density functional theory (DFT), and its time dependent variant (TD-DFT), was used to probe the electronic properties of the molecule in the gas phase and solvated environments. Solvent was implicitly accounted for using the polarizable continuum model (PCM). Initial efforts were unable to locate a stable minimum in the excited state that contained a permanent dipole, despite numerous attempted initial geometries. In fact, the computed dipole moment was found to be just 0.01 D and was unchanged in the ground and excited state. However, recently published work on a similar molecule (molecule 3) had produced significant TD-DFT results which allowed an opportunity to compare our approaches to. In this molecule a large dipole was found in the excited state (> 13 D) while a very small dipole was observed in the ground state (< 1 D). Interestingly, adding the cyano groups to molecule 3 completely destroyed this effect which indicates that solvent interactions at these hydrogen bond accepting groups plays little role in the stabilization of charge transfer. Using the optimized structure of molecule 3 to initialize optimizations of molecule 1, a permanent dipole in the excited state was finally observed (> 2 D). This appears to be due to a rotation in the attached phenyl groups, another important structural feature discovered. Lastly, molecule 2 was studied and found to have a slightly larger permanent dipole in the excited state suggesting that conjugation length is a third important structural feature discovered here.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:



1 2 3

Figure 2. Schematic of the molecules studied within this work.

The molecules studied here are indicated in Figure 2, which are of the broad form A-D-A where A indicates an electron accepting group while D is an electron donating group. All starting geometries for optimizations were created manually using Materials Studio. As discussed below, the optimizations of molecule 1 and 2 were also performed using the optimized structure of 3 and transforming into the corresponding molecules. Density functional theory (DFT) as implemented within the Gaussian 16 program[5] was used. The CAM-B3LYP[6] or B3LYP[7] functionals with varying basis sets as indicated. Excited states were explored using time dependent DFT (TD-DFT). The "tight" convergence criterion was used for optimizations although "very tight" was also tried with little observed changes in the calculated absorption and fluorescence energies. A pruned 99,590 grid was used for numerical integrations. Symmetry was turned off in all calculations. Atomistic charges were calculated by fitting to the electrostatic potential according to the Merz-Singh-Kollman scheme.[8] Solvent effects were incorporated via the polarizable continuum model (PCM)[9-11] using solvents that are readily available within Gaussian 16.

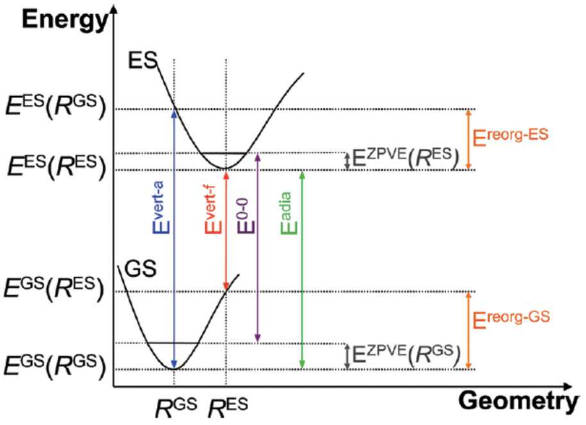


Figure 3. Representation of the ground state (GS) and excited state (ES) potential energy surface with possible absorption and fluorescence energies. Reproduced from Ref 8.

Several possible parameters could be calculated as the absorption and fluorescence energy (Figure 3).[12] The most common approximation is to calculate the vertical adsorption (E^{vert-a}) and fluorescence (E^{vert-f}) energies and compare to experimental λ_{max} values. However, a more physically relevant quantity is E^{0-0}, which is the difference between the energies at the ground state (GS) and excited state (ES) minima (E^{adia}) corrected by the vibrational zero-point energy (ZPVE). Note, that in order to calculate E^{0-0} one must optimize both the GS and ES geometries and subsequently perform a vibrational calculation which can be prohibitively expensive for excited states; particularly in solvated environments. Thus, for the bulk of this work the energies calculated are E^{vert-a} and E^{vert-f}. However, E^{0-0} was calculated in the gas phase. Calculation of E^{vert-a} requires two calculations; an initial optimization of the ground state geometry, followed by a single point TD-DFT calculation using the GS optimized geometry. While E^{vert-f} requires a single calculation; optimization of the structure in the desired excited state using TD-DFT. Importantly, to get the atomistic charges and dipole moment of the excited state one must include the Gaussian keyword *Density=Current* which instructs Gaussian to use the density for the current method. The default density (i.e., without using *Density=Current*) is the DFT density, however, in the excited state the TD density is desired.

RESULTS AND DISCUSSION:

Initial work focused on the investigation of molecule 1. The initial, manually created, geometry was optimized in the ground state and excited state. The various absorption/fluorescence energies are shown in Table 1. The experimental absorption energy shows very little solvent dependence and is ~400 nm, while the fluorescence energy can range from 425-475 nm.[2] The calculated wavelengths show very little agreement with the experimental values, although the fluorescence energy agrees more closely than the absorption wavelength. Moreover, the calculated dipole moment was unchanged in the ground and excited state (0.01 D).

Table 1. Calculated absorption and Fluorescence energies for molecule 1 in the gas phase.

	Wavelength (nm)
E^{vert-a}	340
E^{vert-f}	412
E^{adia}	376
E^{0-0}	385

In order to test the role of solvent the structure was subsequently optimized using the PCM approach with dimethylsulfoxide (DMSO). In this calculation the E^{vert-a} and E^{vert-f} were determined to be 356 nm and 491 nm respectively. In this case the absorption and fluorescence energies are in much better agreement with the experimental values however the calculated dipole moment was found to be 0.01 D in both the ground and excited states; identical to the gas phase results. It should be noted that numerous attempts were made to adjust the starting geometry in an attempt to find an optimized excited state structure that was non-symmetrical and had a

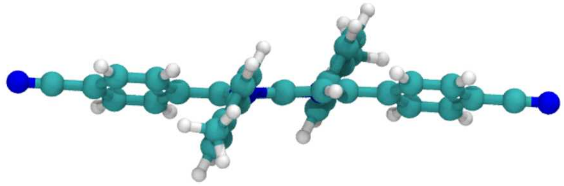


Figure 4. Optimized structure of the excited state of molecule 1 in DMSO (carbon – teal, nitrogen – blue, hydrogens – white.

permanent dipole moment, however the dipole moment consistently remained low (0.01 D). The optimized structure in the excited state is shown in Figure 4 which is clearly symmetrical.

Given the difficulties in observing dipolar character in the excited of molecule 1, attention was then turned to molecule 3, which notably had been synthesized and studied using TD-DFT recently.[13] We attempted to replicated the previous work as a guide to test the Gaussian keywords used. In this work the B3LYP functional was used with a 6-31+G(d,p) basis set. The PCM approach was used for solvation with the DMSO solvent. Key results are shown in Table 2. Identical values were calculated for the S^0-S^3 and the S^0-S^5 vertical transition energies in the gas phase (417/359 nm). Similarly, dipole moments for the GS and ES (vertical) were in good agreement. The vertically excited dipole moment remains small at 1.08 D, however when the excited state structure is optimized the dipole moment increased to 13.4 D. This indicates that solvent stabilizes an intramolecular charge transfer event and dipolar character is observed.

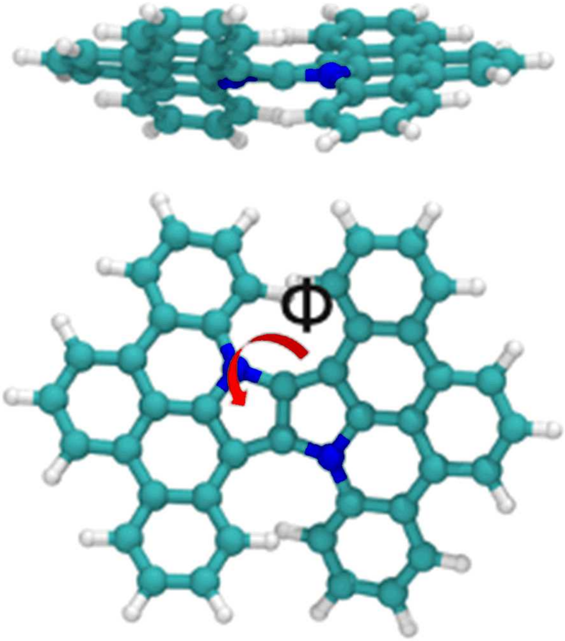


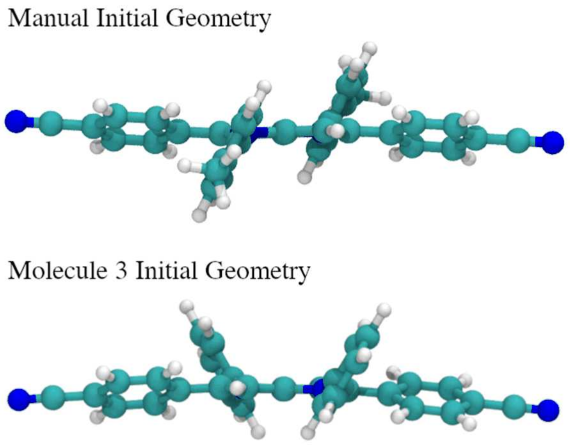
Figure 5. Optimized structure of molecule 3 in the excited state and DMSO.

The structure of the optimized structure is shown in Figure 5. The side view indicates that significant twisting of the core is observed. This is measured by a change in the indicated dihedral angel which is -163° in the ground state vs -156° in the excited state. It is important to mention that the CAM-B3LYP functional generally performs better than B3LYP when charge transfer is observed.[12] However, in this instance the CAM-B3LYP functional was tested and a dipole moment of 0.58 D was observed; including solvation effects. More work is required to understand the effects of functional and basis set on the quantities computed here. Lastly, given that dipolar character was observed in this structure, the role of the cyano groups was tested by placing them in the identical positions on molecule 3 as they appear in molecule 2. The ground and excited state structures were then reoptimized in DMSO. Interestingly, a 1.99 D dipole moment was observed in the ground state, while a 1.77 D dipole moment was observed in the excited. This preliminary evidence indicates that solvent interactions at these groups does not drive dipolar character within the molecule upon electronic excitation.

Table 2. Key calculated properties of molecule 3 from this work and Ref 8.

	REF 8	This Work
S^0-S^3 (nm)	417	417
S^0-S^5 (nm)	359	359
GS Dipole Moment (D)	0.79	0.77
ES Dipole Moment, Vertical (D)	0.61	1.08
ES Dipole Moment, Relaxed (D)	13.5	13.4

Using the optimized structure of molecule 3, which contains a dipole in the excited state, an initial geometry for molecule was created. The structure was then reoptimized using identical conditions. In this geometry, the dipole moment was found to be 1.33 D and 2.31 D in the ground and excited state respectively. A measurable, albeit small, charge transfer and dipolar character was found. The structure was investigated and shown in Figure 6 alongside the optimized structure using the manually created geometry as the initial geometry. Here we observe a twisting in the side phenyl rings which destroys the symmetry. Moreover, a slight bend to the overall core of the molecule is seen. This represents a significant structural feature which drives an intramolecular charge transfer event; the twisting of the phenyl rings attached to the core. The vertical fluorescence energy in this case was found to be 489 nm, a slight change from the previous geometry of 491 nm. A final investigation was performed of molecule 2 in the excited state only. The calculated dipole was found to be 2.77 D which agrees with experimental evidence that molecule 2 has a larger dipole than molecule 1 in the excited state,[2] thereby confirming that longer conjugated chains increase the charge transfer character.


Manual Initial Geometry

Molecule 3 Initial Geometry

Figure 6. Optimized structures of molecule 1 in DMSO and the excited state using the manually created initial geometry (top) and the optimized structure of molecule 3 initial geometry (bottom).

ANTICIPATED OUTCOMES AND IMPACTS:

The work performed here identified three key structural features were found to influence the creation of dipolar character in symmetrical molecules upon electronic excitation, (1) hydrogen bonding groups do *not* necessarily play a role, (2) rotation of phenyl groups grafted to the core break the symmetry, and (3) longer conjugated chains in the electron accepting group increase charge transfer behavior. Previous findings have suggested that asymmetric solvent interactions at one side of the molecule drive the symmetry breaking process. Particularly that anomalously strong hydrogen bonding networks form which massively decreases the dynamics of the surrounding solvent.[3]

Robust structural models, including atomistic charges, for the dye molecules have been developed and will form the basis of parameters needed to perform molecular dynamics (MD) simulations. The MD simulations are necessary to understand the nature of solvent dynamics around the molecule. Furthermore, additional work is needed on the TD-DFT side which is to probe the role of different solvents on the electronic properties in the ground and excited states. This will be used to validate the approach outlined here as significant experimental work exists on molecule 1 and 2 in various solvents.[2] Calculations are currently on-going in this effort. Lastly, the potential energy surface of the rotation of the phenyl groups needs to be explore in the ground and excited states.

In this regard, two publications are currently in process. The first will look at the role of solvent using TD-DFT on the electronic properties of molecule 1 and 2 in the ground and excited states. This manuscript will address the question what structural features of the molecule influence the charge transfer character in symmetrical quadrupolar dye molecules? A second manuscript will be produced which will use the structural model developed in the first manuscript to probe the dynamics of the solvent upon electronic excitation. This manuscript will answer the question, how does the dynamics of the solvent change upon excitation of symmetric quadrupolar dye molecules?

More broadly, this project supported a summer high school intern thereby nurturing the career of a young scientist. Significant expertise was developed in TD-DFT calculations. Significant care and background research was performed to ensure that these calculations were performed at the highest quality level possible; particularly those performed in solvated environments. It should be stressed that these calculations are non-trivial and easily overlooked factors could end up producing erroneous results. Understanding charge transfer and light interactions with matter are of significant interest to the Department of Energy Office of Science, therefore this skillset will likely have broad applicability for future projects.

Lastly, a follow-on funding source was secured in the form of a DOE NA-22 proposal entitled *Chemosensor Computing for In Situ Tree Analysis of Safeguards*. This seeks to meet the DNN R&D FY21 Unconstrained Advancement (3/R/a) which requests “immature concepts”, “loosely formed ideas”, and “out-of-the-box projects” which dramatically improve proliferation detection capabilities. Molecules of this nature undergo stark changes in their behavior in certain environments (i.e., polar vs nonpolar solvents). In this regard, they can be viewed as molecular “switches” that exist either in an on or off state. Several of these molecules placed together could potentially form a “molecular logic gate” and potentially answer yes/no questions in a tree analysis. This proposal will seek to develop a novel solution that both senses and computes for difficult to inspect nuclear waste storage sites. Ambitiously, we hope to traverse TRL level 1 to level 3 and likely capture significant intellectual property gains.

CONCLUSION:

The structural features that drive intramolecular charge transfer events in symmetric quadrupolar dyes was investigated using TD-DFT approaches. Symmetric molecules of the broad form ADA where A is an electron accepting group and D is an electron donating group have been observed to break their symmetry upon electronic excitation leading to the formation of a permanent dipole. The current state-of-the-art indicates that this is due to asymmetric solvent fluctuations around the dye; with some suggesting that an anomalously strong hydrogen bonding network can form which generates glass-like behavior.

Using TD-DFT the dipole of molecule 1 was found to be virtually unchanged in the gas phase and in a highly polar solvent, DMSO. Subsequently molecule 3 was studied and 13.5 D dipole was found in the excited state in DMSO. Interestingly the dipole was much smaller when the cyano groups in molecule 1 were added to molecule 3. This indicates that solvent interactions at these groups (i.e., hydrogen bonding) does not play a large role in stabilizing charge transfer and symmetry breaking events in quadrupolar molecules; in stark contrast to previous findings. Using the broken-symmetry geometry of molecule 3 as a starting point, molecule 1 was re-optimized and a noticeable, but small, dipole was found in the excited state (2.31 D). By examining the differences in the optimized structure of molecule 1 with and without a dipole in the excited state, we identified the rotation of the phenyl groups attached to the core as crucial for breaking the symmetry of the molecule. This, again, is in contrast with the previous hypothesis as it is unlikely that this leads to a change in hydrogen bonding strength around the molecule. Lastly, molecule 2 was explored and found to have a slightly larger dipole in the excited state (2.77) than molecule 1, which suggests that longer conjugated chains in the R groups increase the charge transfer character.

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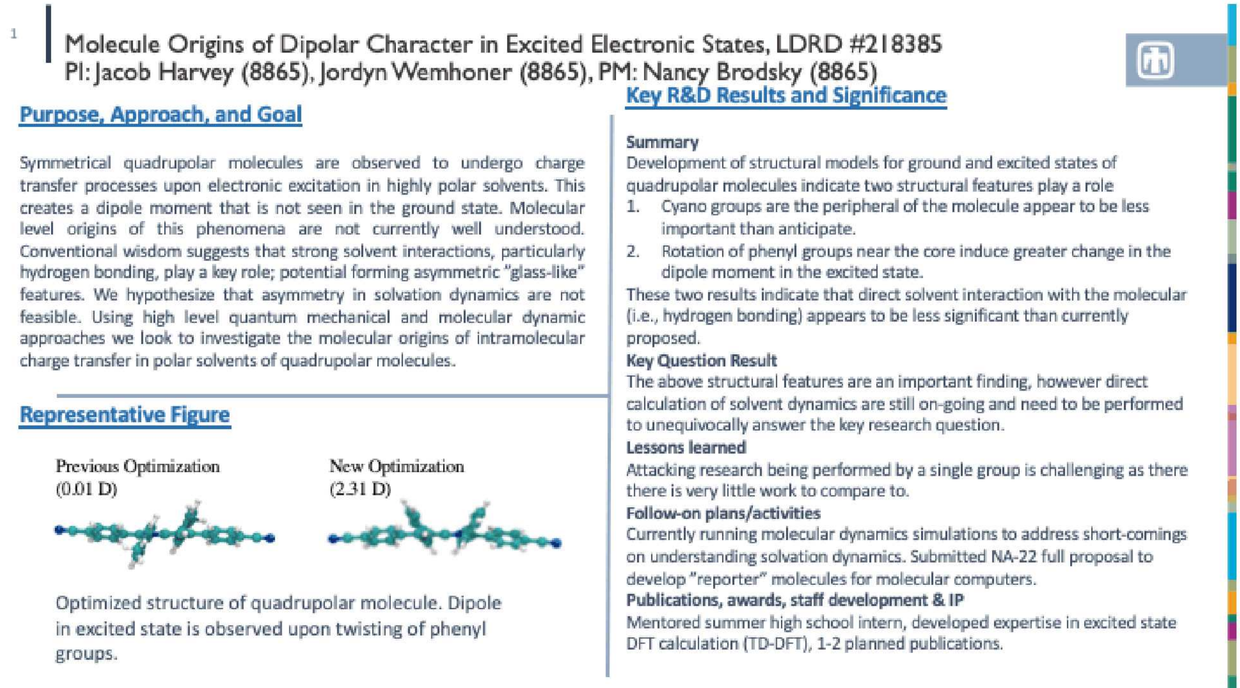
ADDENDUM:



Molecule Origins of Dipolar Character in Excited Electronic States, LDRD #218385

PI: Jacob Harvey (8865), Jordyn Wemhoner (8865), PM: Nancy Brodsky (8865)

Purpose, Approach, and Goal

Symmetrical quadrupolar molecules are observed to undergo charge transfer processes upon electronic excitation in highly polar solvents. This creates a dipole moment that is not seen in the ground state. Molecular level origins of this phenomena are not currently well understood. Conventional wisdom suggests that strong solvent interactions, particularly hydrogen bonding, play a key role; potential forming asymmetric "glass-like" features. We hypothesize that asymmetry in solvation dynamics are not feasible. Using high level quantum mechanical and molecular dynamic approaches we look to investigate the molecular origins of intramolecular charge transfer in polar solvents of quadrupolar molecules.

Representative Figure

Optimized structure of quadrupolar molecule. Dipole in excited state is observed upon twisting of phenyl groups.

Key R&D Results and Significance

Summary

Development of structural models for ground and excited states of quadrupolar molecules indicate two structural features play a role

1. Cyano groups are the peripheral of the molecule appear to be less important than anticipate.
2. Rotation of phenyl groups near the core induce greater change in the dipole moment in the excited state.

These two results indicate that direct solvent interaction with the molecular (i.e., hydrogen bonding) appears to be less significant than currently proposed.

Key Question Result

The above structural features are an important finding, however direct calculation of solvent dynamics are still on-going and need to be performed to unequivocally answer the key research question.

Lessons learned

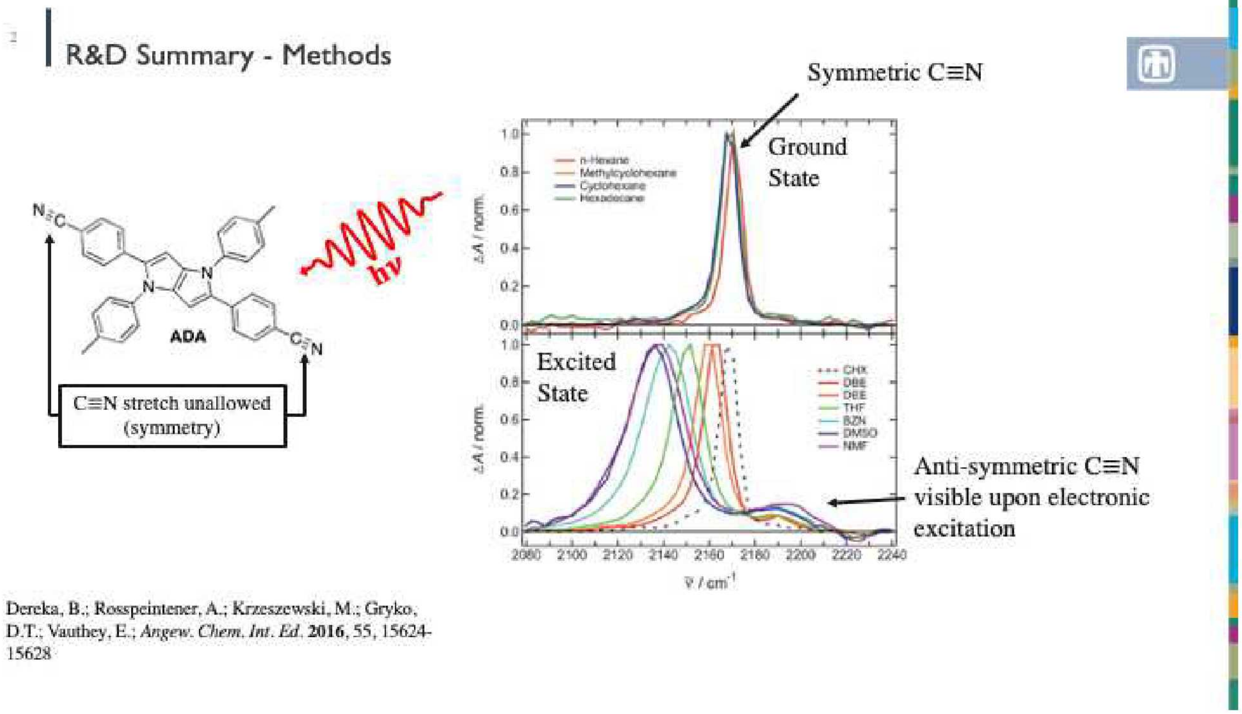
Attacking research being performed by a single group is challenging as there there is very little work to compare to.

Follow-on plans/activities

Currently running molecular dynamics simulations to address short-comings on understanding solvation dynamics. Submitted NA-22 full proposal to develop "reporter" molecules for molecular computers.

Publications, awards, staff development & IP

Mentored summer high school intern, developed expertise in excited state DFT calculation (TD-DFT), 1-2 planned publications.



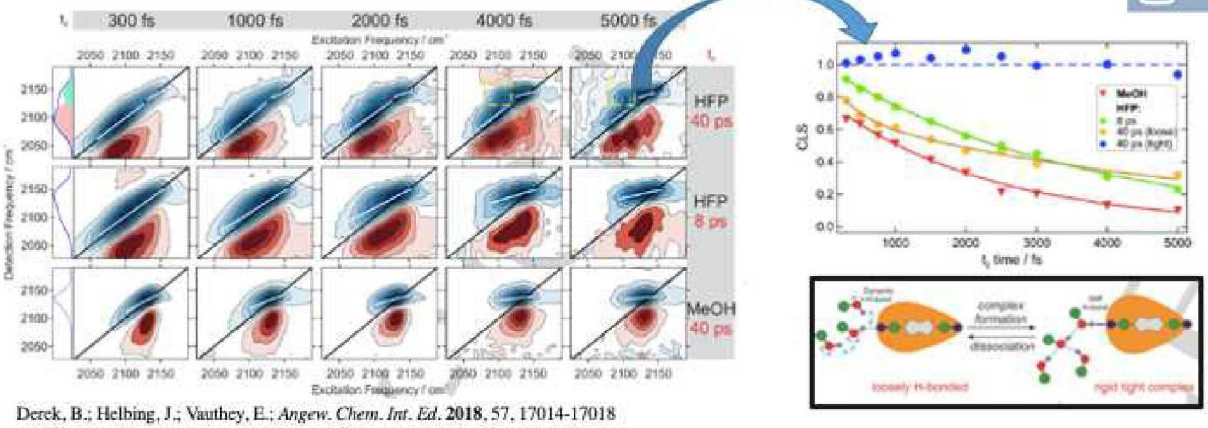
R&D Summary - Methods

C≡N stretch unallowed (symmetry)

Anti-symmetric C≡N visible upon electronic excitation

Dereka, B.; Rosspeintener, A.; Krzeszewski, M.; Gryko, D.T.; Vauthey, E.; *Angew. Chem. Int. Ed.* **2016**, 55, 15624-15628

R&D Summary - Methods



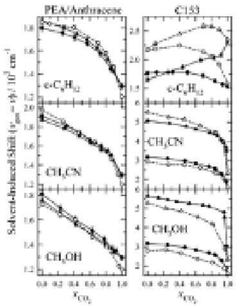
Derek, B.; Helbing, J.; Vauthey, E.; *Angew. Chem. Int. Ed.* **2018**, 57, 17014-17018

Key Research Question

What are the molecular origins for symmetry breaking in photoexcited quadrupolar dye molecules?

R&D Summary – Computational Work Flow

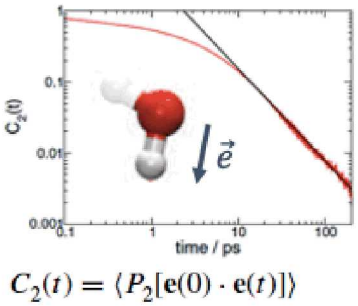
Develop Structural Model for Ground/Excited State (Atomistic Charges) → Run Molecular Dynamics in GS/ES Equilibrium – Solvation Dynamics → Calculate Vibrational Spectra in GS/ES – 2D IR



Closed – Experimental
Open – Simulated

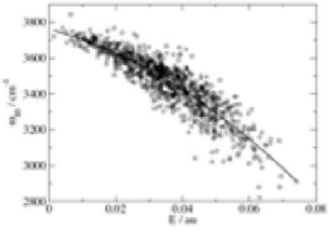
Circles – Absorption
Triangles - Emission

J. Phys. Chem. B **2007**, 111, 3208-3221

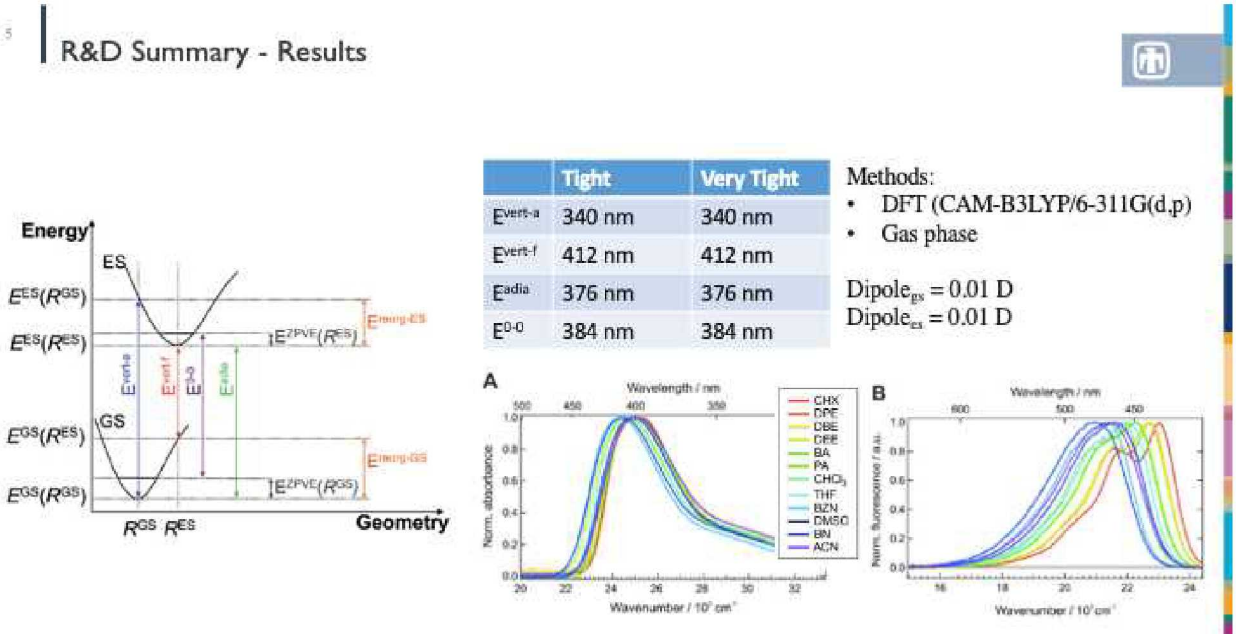


$$C_2(t) = \langle P_2[\mathrm{e}(0) \cdot \mathrm{e}(t)] \rangle$$

J. Chem. Phys. **2014**, 141, 18C523



PNAS **2007**, 104, 14215-14220

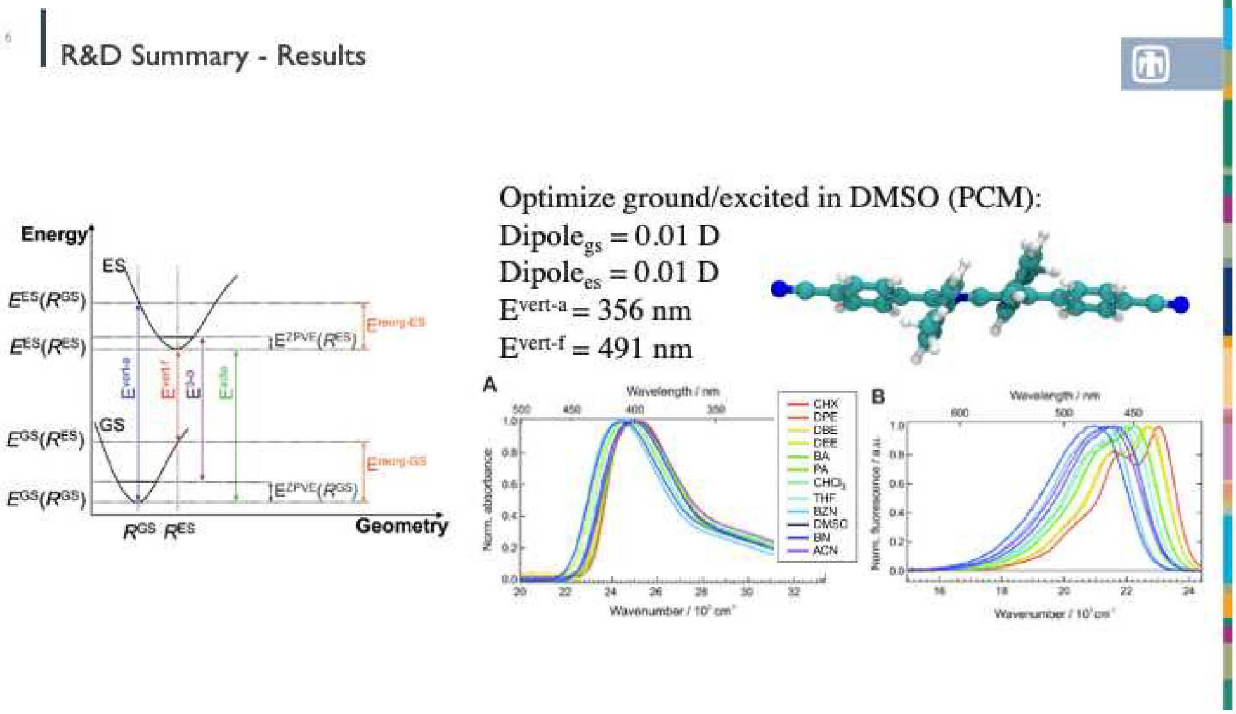


R&D Summary - Results

	Tight	Very Tight
$E^{vert\text{-}a}$	340 nm	340 nm
$E^{vert\text{-}f}$	412 nm	412 nm
E^{adia}	376 nm	376 nm
$E^{0\text{-}0}$	384 nm	384 nm

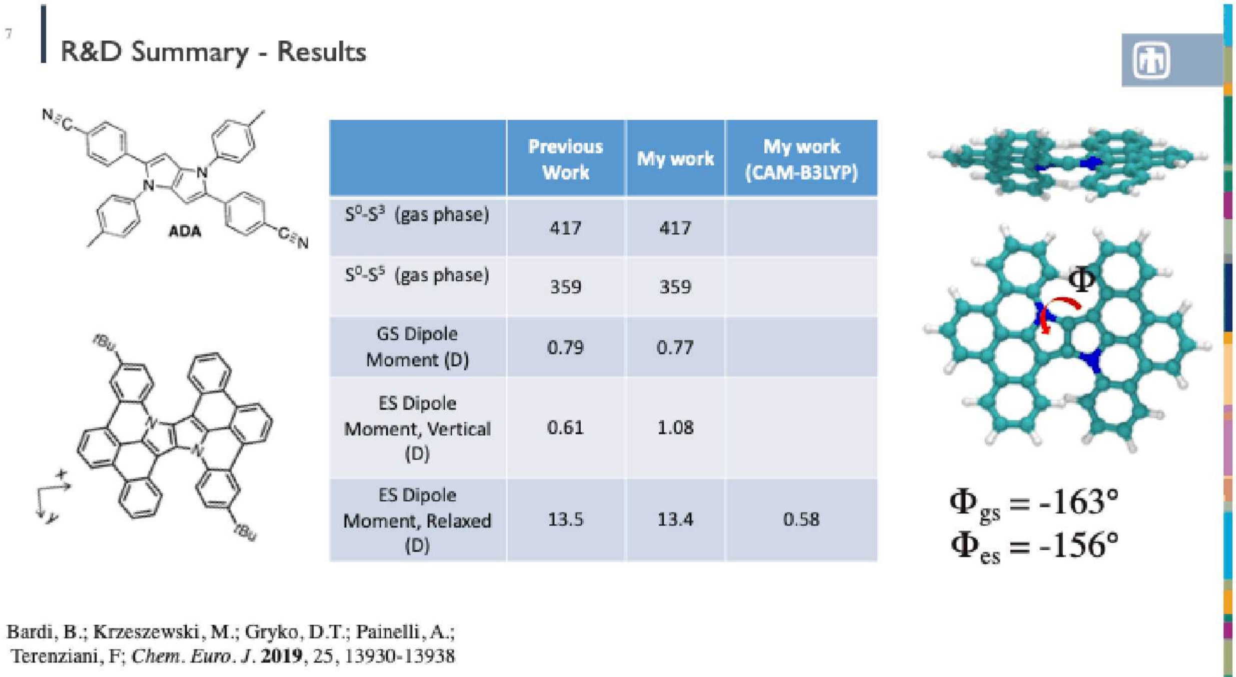
Methods:
- DFT (CAM-B3LYP/6-311G(d.p)
- Gas phase

$\text{Dipole}_{gs} = 0.01$ D
$\text{Dipole}_{es} = 0.01$ D



R&D Summary - Results

Optimize ground/excited in DMSO (PCM):
$\text{Dipole}_{gs} = 0.01$ D
$\text{Dipole}_{es} = 0.01$ D
$E^{vert\text{-}a} = 356$ nm
$E^{vert\text{-}f} = 491$ nm

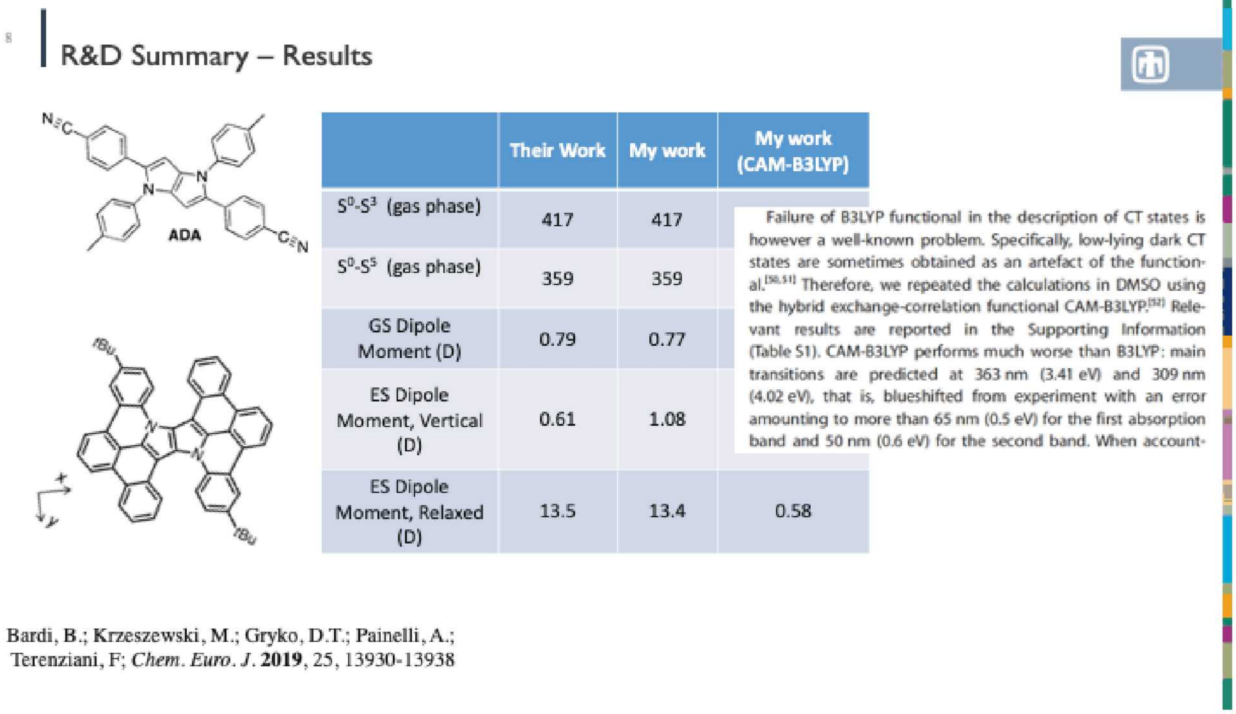


R&D Summary - Results

	Previous Work	My work	My work (CAM-B3LYP)
S^0-S^3 (gas phase)	417	417	
S^0-S^5 (gas phase)	359	359	
GS Dipole Moment (D)	0.79	0.77	
ES Dipole Moment, Vertical (D)	0.61	1.08	
ES Dipole Moment, Relaxed (D)	13.5	13.4	0.58

$\Phi_{gs} = -163°$
$\Phi_{es} = -156°$

Bardi, B.; Krzeszewski, M.; Gryko, D.T.; Painelli, A.;
Terenziani, F; *Chem. Euro. J.* **2019**, 25, 13930-13938



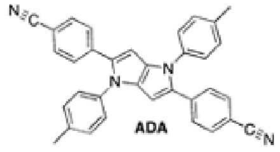
R&D Summary – Results

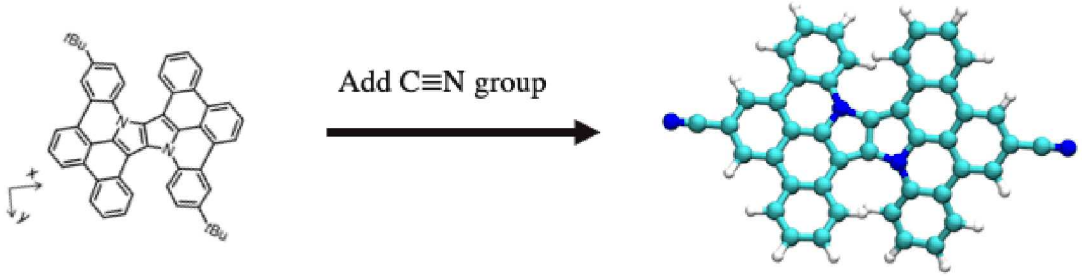
	Their Work	My work	My work (CAM-B3LYP)
S^0-S^3 (gas phase)	417	417	
S^0-S^5 (gas phase)	359	359	
GS Dipole Moment (D)	0.79	0.77	
ES Dipole Moment, Vertical (D)	0.61	1.08	
ES Dipole Moment, Relaxed (D)	13.5	13.4	0.58

Failure of B3LYP functional in the description of CT states is however a well-known problem. Specifically, low-lying dark CT states are sometimes obtained as an artefact of the functional.[50,51] Therefore, we repeated the calculations in DMSO using the hybrid exchange-correlation functional CAM-B3LYP.[52] Relevant results are reported in the Supporting Information (Table S1). CAM-B3LYP performs much worse than B3LYP: main transitions are predicted at 363 nm (3.41 eV) and 309 nm (4.02 eV), that is, blueshifted from experiment with an error amounting to more than 65 nm (0.5 eV) for the first absorption band and 50 nm (0.6 eV) for the second band. When account-

Bardi, B.; Krzeszewski, M.; Gryko, D.T.; Painelli, A.;
Terenziani, F; *Chem. Euro. J.* **2019**, 25, 13930-13938

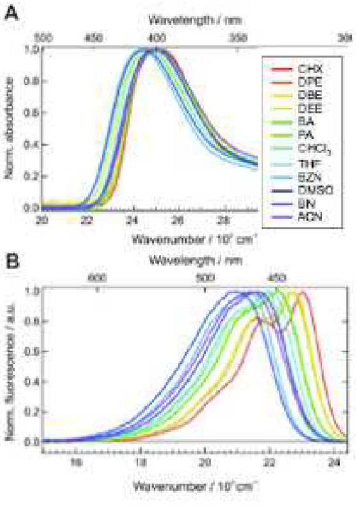
R&D Summary – Results





$\text{Dipole}_{gs} = 1.99$
$\text{Dipole}_{es} = 1.77$

R&D Summary - Results

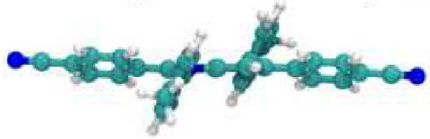


Methods:

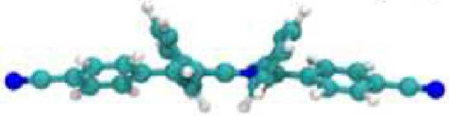
- DFT (CAM-B3LYP/6-311G(d,p)
- Use nanographene structure to initialize geometry

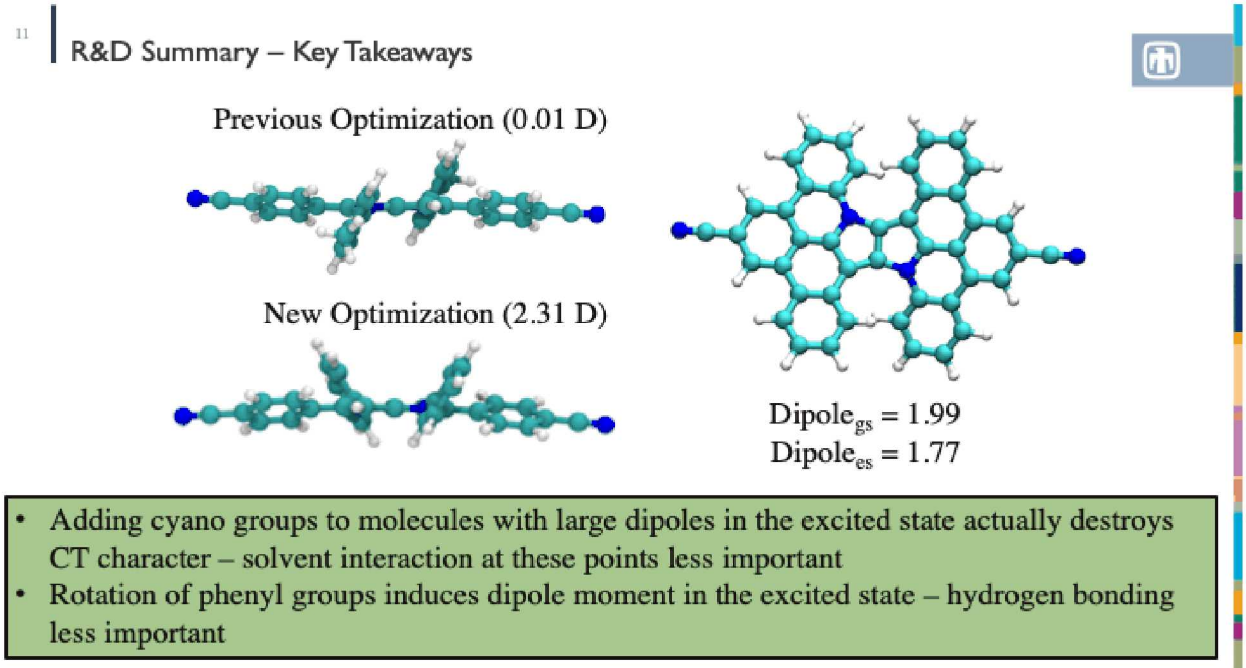
$\text{Dipole}_{gs} = 1.33$ D
$\text{Dipole}_{es} = 2.31$ D
Evert-f = 489 nm

Previous Optimization (No dipole)



New Optimization (No dipole)





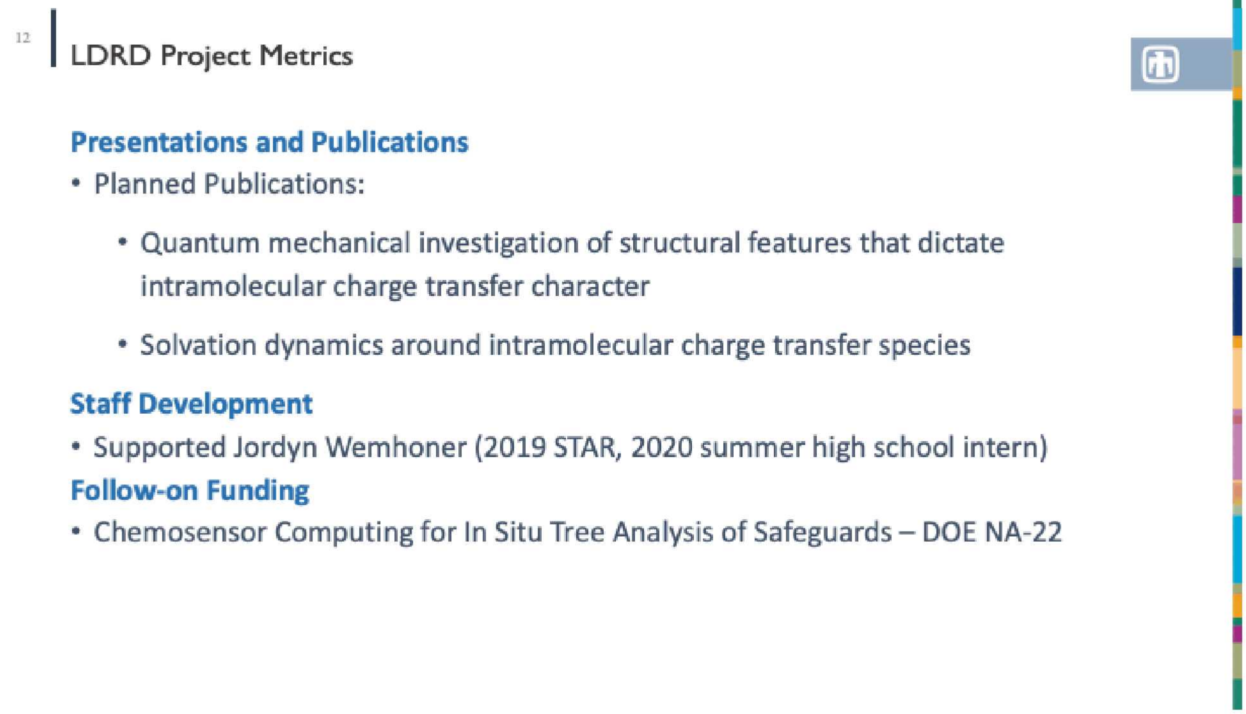
R&D Summary – Key Takeaways

Previous Optimization (0.01 D)

New Optimization (2.31 D)

Dipole$_{gs}$ = 1.99
Dipole$_{es}$ = 1.77

- Adding cyano groups to molecules with large dipoles in the excited state actually destroys CT character – solvent interaction at these points less important
- Rotation of phenyl groups induces dipole moment in the excited state – hydrogen bonding less important



LDRD Project Metrics

Presentations and Publications

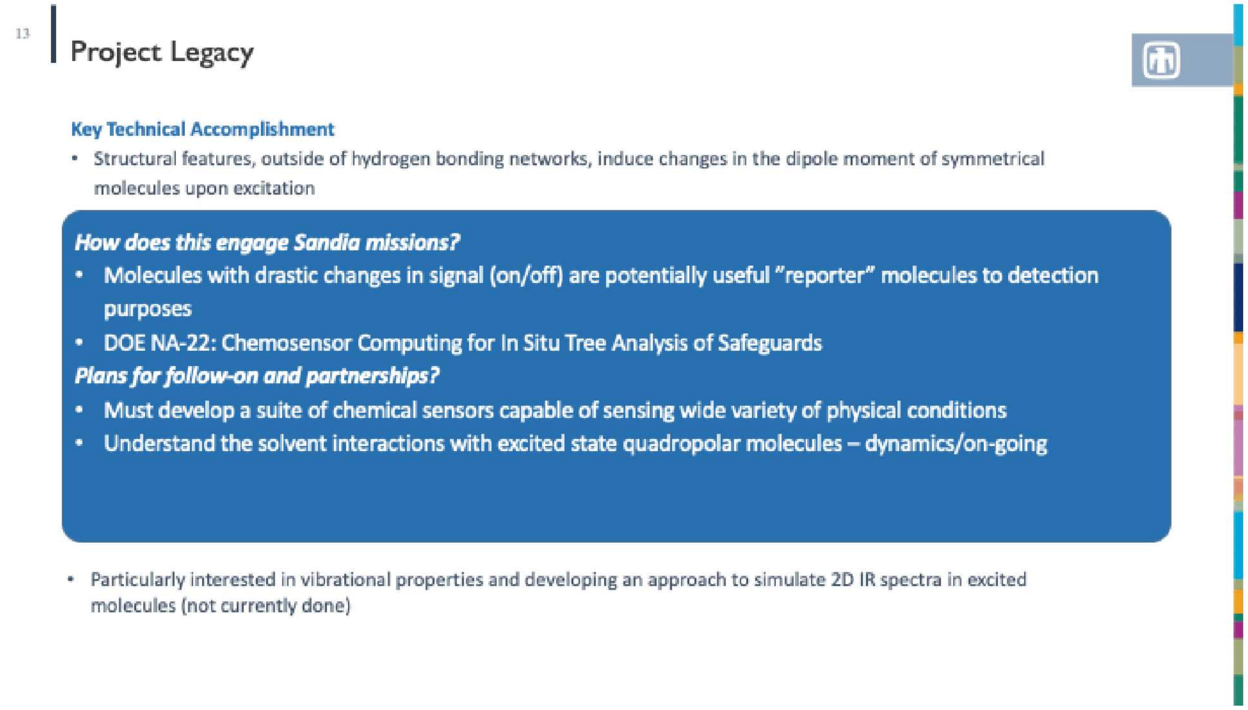
- Planned Publications:
  - Quantum mechanical investigation of structural features that dictate intramolecular charge transfer character
  - Solvation dynamics around intramolecular charge transfer species

Staff Development

- Supported Jordyn Wemhoner (2019 STAR, 2020 summer high school intern)

Follow-on Funding

- Chemosensor Computing for In Situ Tree Analysis of Safeguards – DOE NA-22



Project Legacy

Key Technical Accomplishment

- Structural features, outside of hydrogen bonding networks, induce changes in the dipole moment of symmetrical molecules upon excitation

How does this engage Sandia missions?

- Molecules with drastic changes in signal (on/off) are potentially useful "reporter" molecules to detection purposes
- DOE NA-22: Chemosensor Computing for In Situ Tree Analysis of Safeguards

Plans for follow-on and partnerships?

- Must develop a suite of chemical sensors capable of sensing wide variety of physical conditions
- Understand the solvent interactions with excited state quadropolar molecules – dynamics/on-going

- Particularly interested in vibrational properties and developing an approach to simulate 2D IR spectra in excited molecules (not currently done)