Detection of Polar Structures Assembled by Long-Range Intermolecular Forces via Electrostatic Deflection of Doped Helium Nanodroplets

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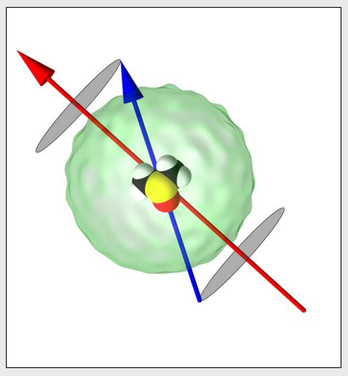
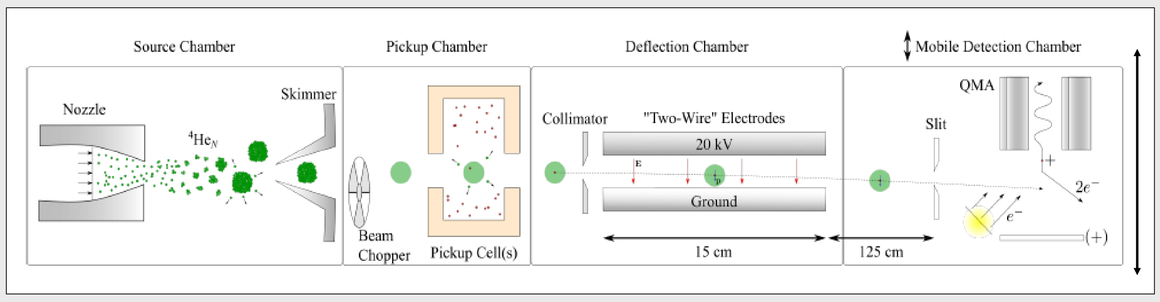
1. Cooling and Orienting Polyatomic Molecules



By using polar molecules as dopants in He_N it is possible to cool individual polyatomic molecules and their assemblies, and to orient and control them using external electric fields [1].

Dimethyl sulfoxide (DMSO) and imidazole (IM) are highly polar and promising candidates to probe the formation of dipole-aligned structures [2] by means of our deflection technique.

2. Experimental Apparatus

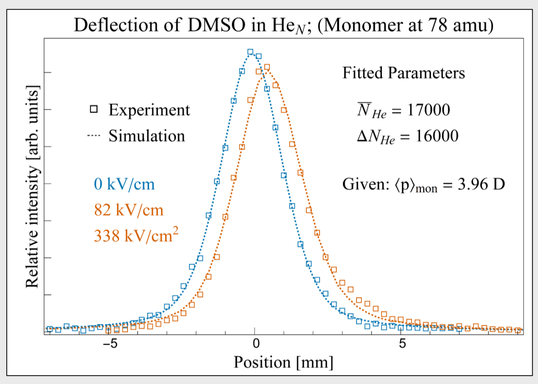


Droplets pick up impurities in the pick-up cell following Poisson statistics, allowing for multiple doping by adjusting cell pressure.
A strong inhomogeneous electric field (82 kV/cm) nearly fully orients the dopants in the droplets and deflects them by several millimeters.

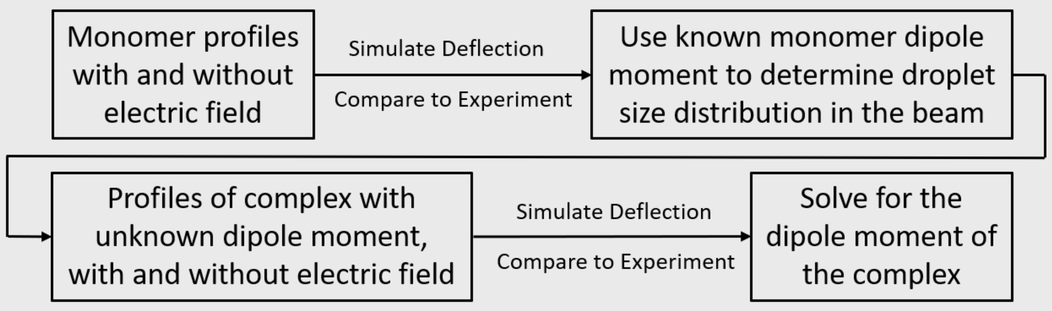
3. Deflection Technique for Measuring Dipoles

By using beam deflection we directly obtain a measurement of an important physical observable: the absolute values of the electric dipole moment of the embedded molecular complex. This is a key supplement to spectroscopy.

Beam parameters are determined from monomer deflection for each molecule (each with known dipole moment).



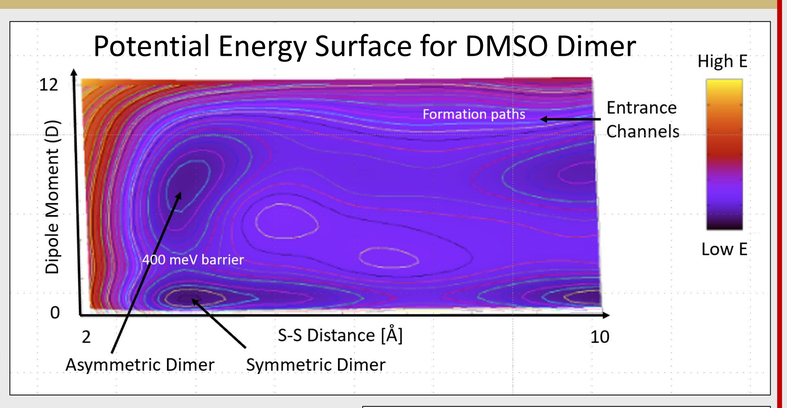
Sample calibration profile for DMSO

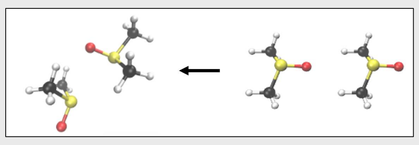


4. Theoretical Predictions and IM Geometries

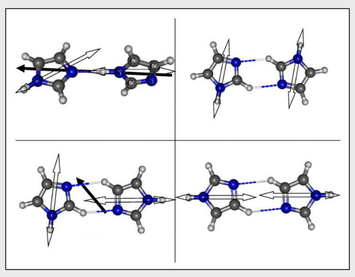
Calculations show that **DMSO**$_{n=even}$ have a symmetrical ground state with zero dipole moment [3].

Therefore the observation of a non-zero dimer dipole moment in helium nanodroplets would reveal a metastable polar arrangement steered by long-range interactions.



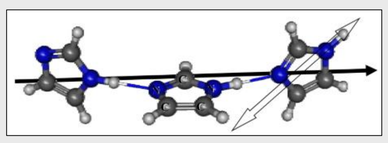


For **IM**, the four lowest energy structures of the IM dimer and highly polar IM trimer structure were predicted in Refs. [4,5].



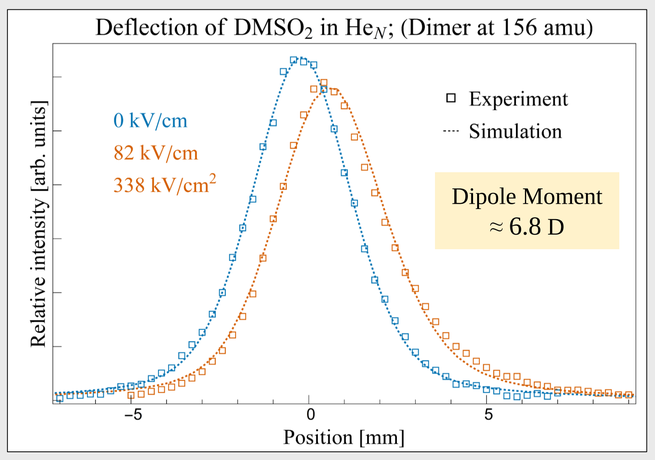
Imidazole	Dipole Moment (Debye)
IM	3.8
IMD	9.3
IMT	14.8

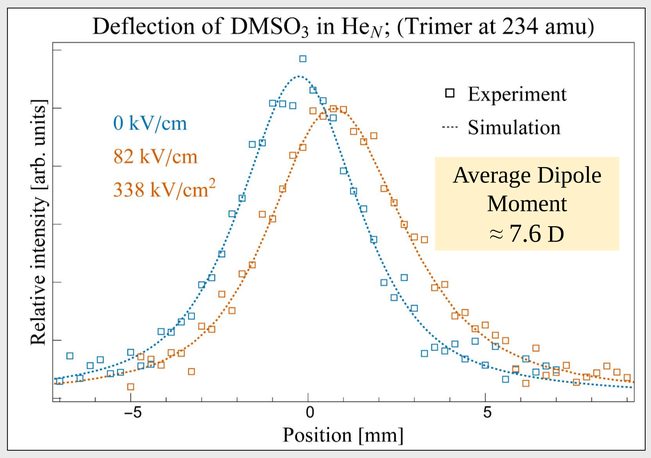
Table of dipole moments for most polar IM structures



Computed IM dimer and trimer structures from [4,5]. The black arrow is the dipole moment and the white arrow is the vibrational transition moment angle

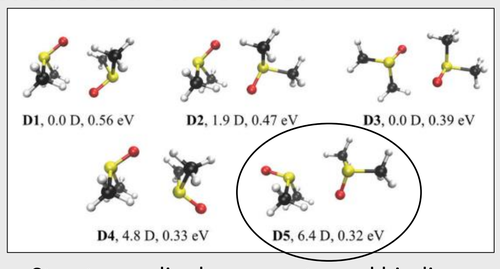
5. This Work: Measured Dipole Moments for $(DMSO)_{n=2,3}$



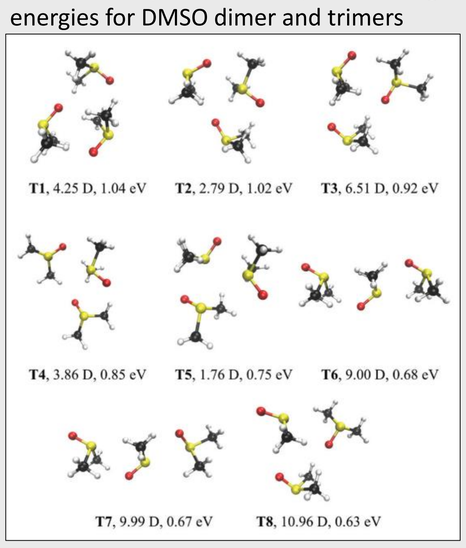


The large measured dipole of the trimer structure directly confirms that the DMSO molecules also constructively align their dipoles in an unusual metastable state.

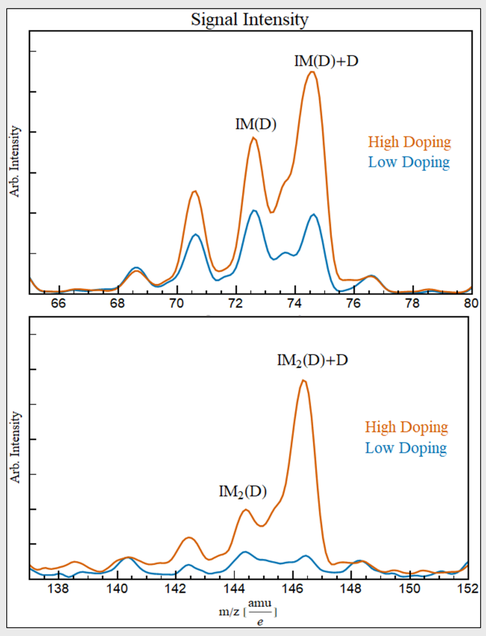
Strong dimer deflection directly reveals the formation of a polar, metastable asymmetric structure. The experimentally determined dipole moment (6.8 D) is in good agreement with the most polar predicted structure.



Structures, dipole moments, and binding energies for DMSO dimer and trimers

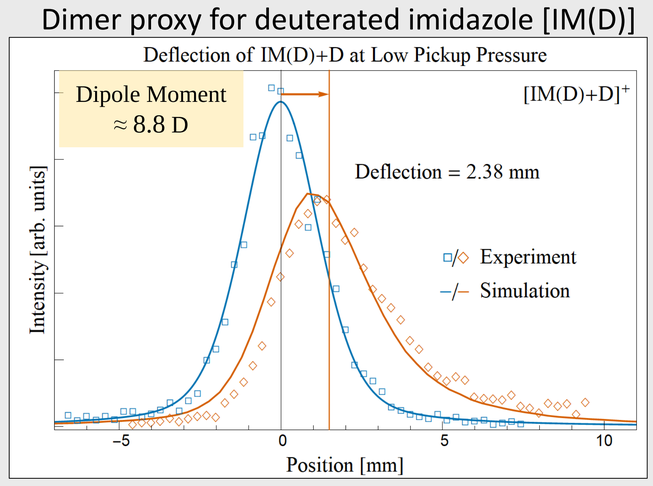


6. This Work: Measured Dipole Moments for $(IM)_{n=2,3}$

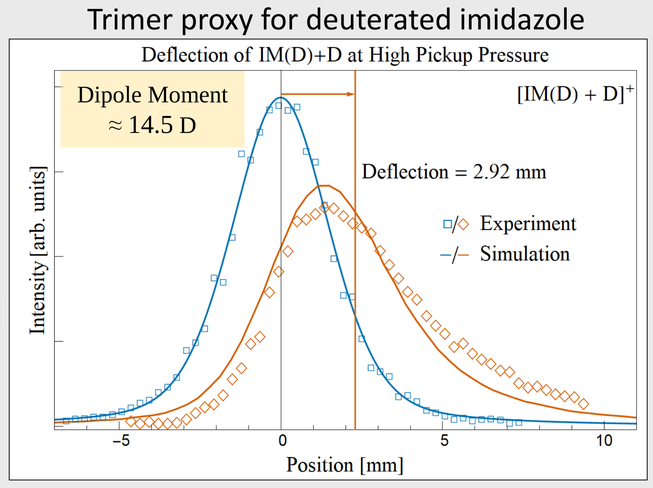


For IM(D), two different doping conditions are used: in the low doping case the measured peak comes primarily from dimers, and in the high doping case, higher order oligomers are evident.

Dimer proxy for deuterated imidazole [IM(D)]



Trimer proxy for deuterated imidazole



The measured dipole moments in the two doping cases are in excellent agreement with the calculated values for the aligned polar dimer and trimer configurations [4,5].

7. Conclusions

Doped nanodroplet deflection allows direct measurement of the dipole moments of cold molecules and structures which are almost completely oriented by the external electric field.

The dimers and trimers for both DMSO and IM form highly polar aligned states whose assembly is driven by long-range interactions within nanodroplets, in good agreement with theory.

This work is presently being extended to alkali halide and fullerene-metal atom complexes.

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[1] D. J. Merthe and V. V. Kresin, *J. Phys. Chem. Lett.* **7**, 4879 (2016); [2] K. Nauta and R. E. Miller, *Science* **283**, 1895 (1999); [3] N. S. Venkataramanan, A. Suvitha, and Y. Kawazoe, *J. Mol. Liq.* **249**, 454 (2018); [4] M. Y. Choi and R. E. Miller, *Chem. Phys. Lett.* **477**, 276 (2009); [5] S. Lee et al., *Bull Korean Chem. Soc.* **32**, 885 (2011).

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