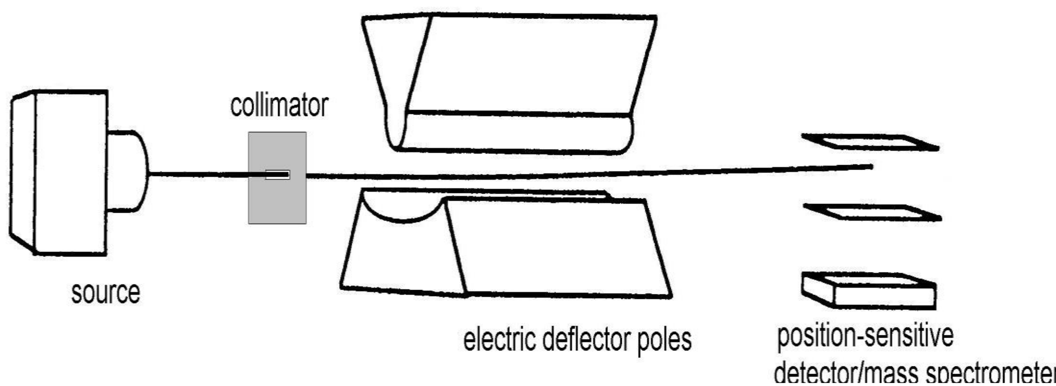
Polar molecules entrapped in helium nanodroplets: Electric deflection, size separation, charge migration

Vitaly Kresin
Department of Physics and Astronomy, USC, Los Angeles

Deflection of atom, molecule, or cluster beams by a strong external inhomogeneous field

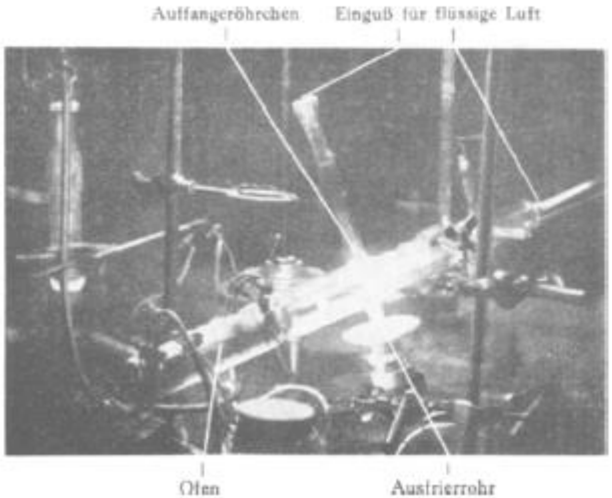


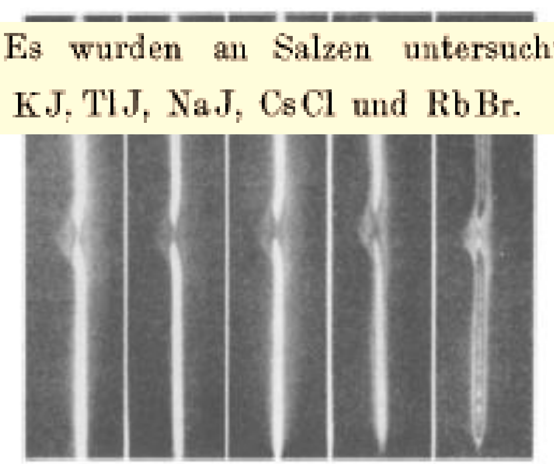
M. Broyer et al., C. R. Physique (2002)
W. A. de Heer & V. V. Kresin, in *Handbook of Nanophysics* (2010)
S. Heiles & R. Schäfer, *Dielectric Properties of Isolated Clusters* (Springer, 2014)
J. Küpper *et al.*, Intern. Rev. Phys. Chem. (2015).

Über die Ablenkung von Molekularstrahlen elektrischer Dipolmoleküle im inhomogenen elektrischen Feld[1].

Von **Erwin Wrede** in Hamburg[2].

Mit 6 Abbildungen. (Eingegangen am 4. Juni 1927.)



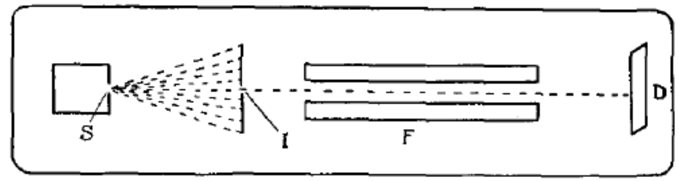


Es wurden an Salzen untersucht:
KJ, TlJ, NaJ, CsCl und RbBr.

JUNE, 1933 JOURNAL OF CHEMICAL PHYSICS VOLUME 1

The Deflection of Molecular Rays in an Electric Field: The Electric Moment of Hydrogen Chloride

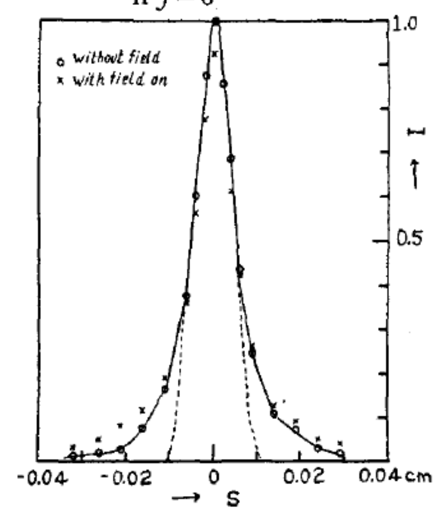
IMMANUEL ESTERMANN AND RONALD G. J. FRASER*



The values of $\bar{\mu}=\beta(j,\ m)\cdot E$ for the rigid dumb-bell molecule were obtained independently by Mensing and Pauli[7] and by Kronig.[8] They are

$$\bar{\mu}=\frac{8\pi^2 I\mu^2 E}{h^2}\,\frac{1}{(2j-1)(2j+3)}\left(\frac{3m^2}{j(j+1)}-1\right)\qquad \text{if } j\neq 0$$

$$=\tfrac{1}{3}8\pi^2 I\mu^2 E/h^2 \qquad \text{if } j=0$$



Experimental distribution of molecules in a deflected and an undeflected beam.

JULY, 1931 REVIEWS OF MODERN PHYSICS VOLUME 3

MOLECULAR RAYS

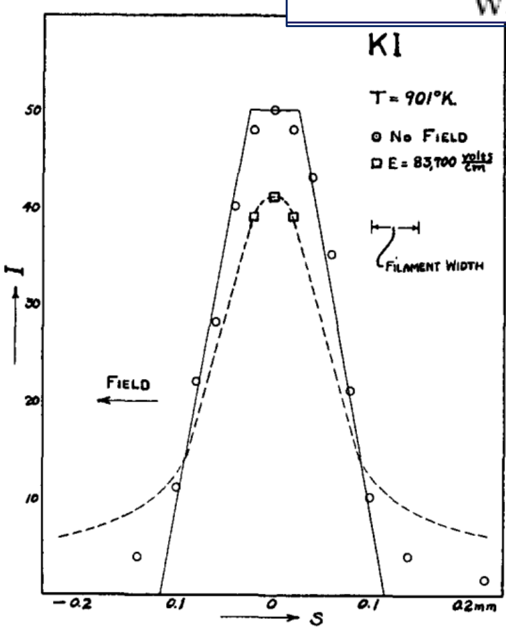
WORTH H. RODEBUSH
CHEMISTRY DEPARTMENT, UNIVERSITY OF ILLINOIS

Molecular-ray experiments do not appear to offer a very satisfactory method for the determination of dipole moments of molecules.

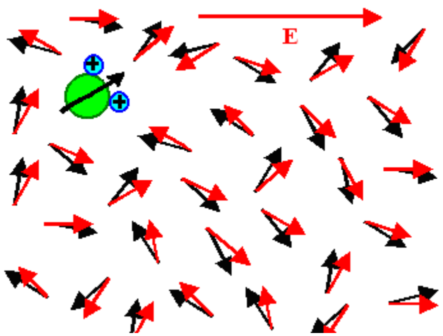
JUNE, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

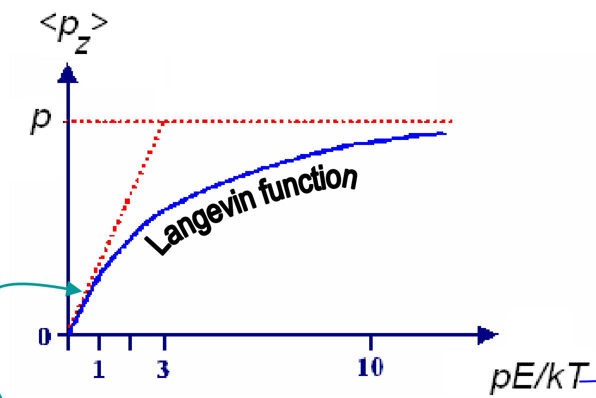
The Dipole Moments of the Alkali Halides

W. H. RODEBUSH, L. A. MURRAY, JR. AND M. E. BIXLER, *University of Illinois*



Field orientation is countered by the molecules' rotational motion





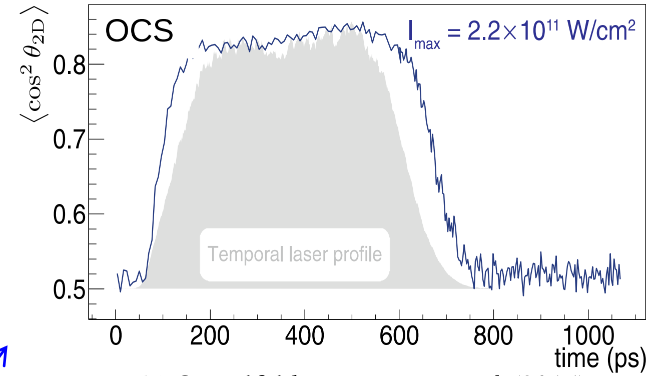
$$\langle p_z \rangle \approx p \cdot \left(\frac{pE_z}{3k_B T} \right)$$

Strong field

Low T

For H_2O molecule (1.9 D) at room T in E= 100 kV/cm, this is only 5×10^{-3}

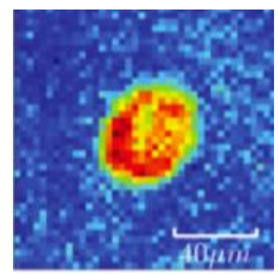
Strong laser fields (*alignment*)

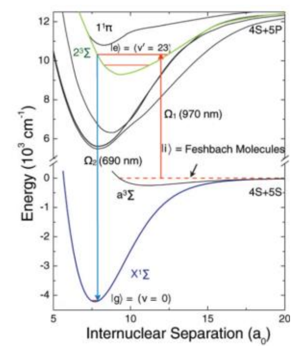


H. Stapelfeldt, J. Küpper *et al.* (2014)

- Limited by pulse duration/spatial extent
- Can ionize/ fragment molecules

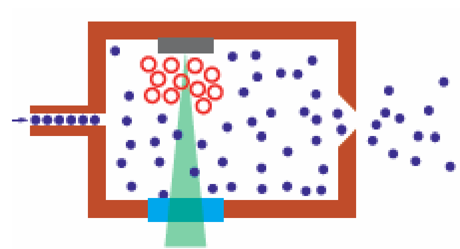
Ultracold optical traps



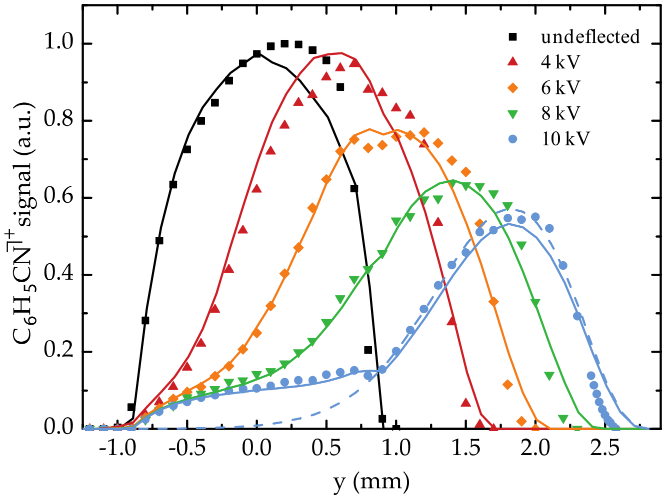


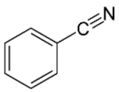
- Limited to certain diatomics

Supersonic beams, buffer gas cooling

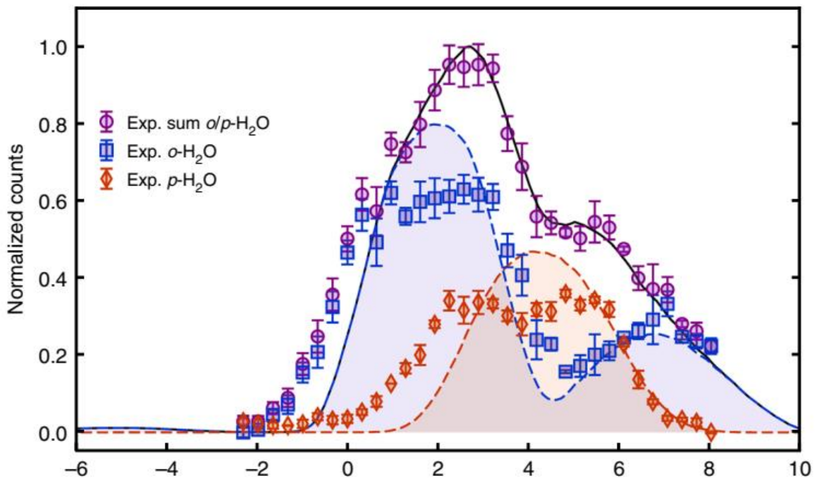


- T > several K; reaching ~1 K requires optimization for each specific molecule



Benzonitrile 

J. Küpper, H. Stapelfeldt *et al.* (2009)



Ortho- and para- water

J. Küpper, S. Willitsch *et al.* (2018)

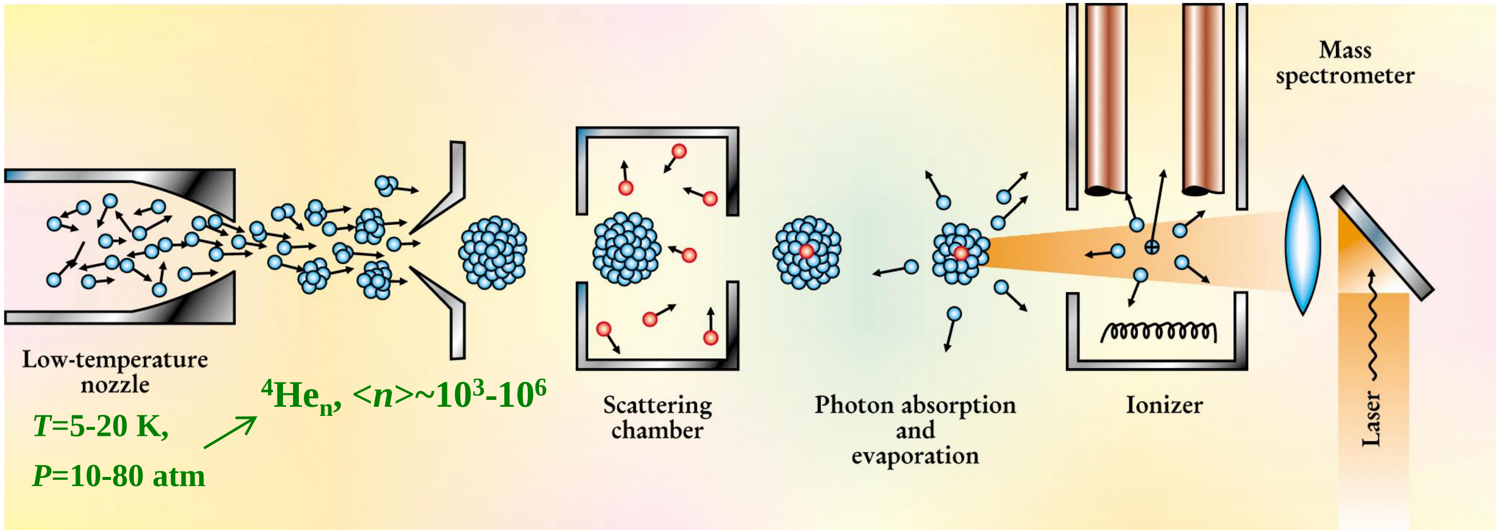
$T \lesssim 1$K

For larger, more complex, molecules supersonic expansion becomes limited in cooling power

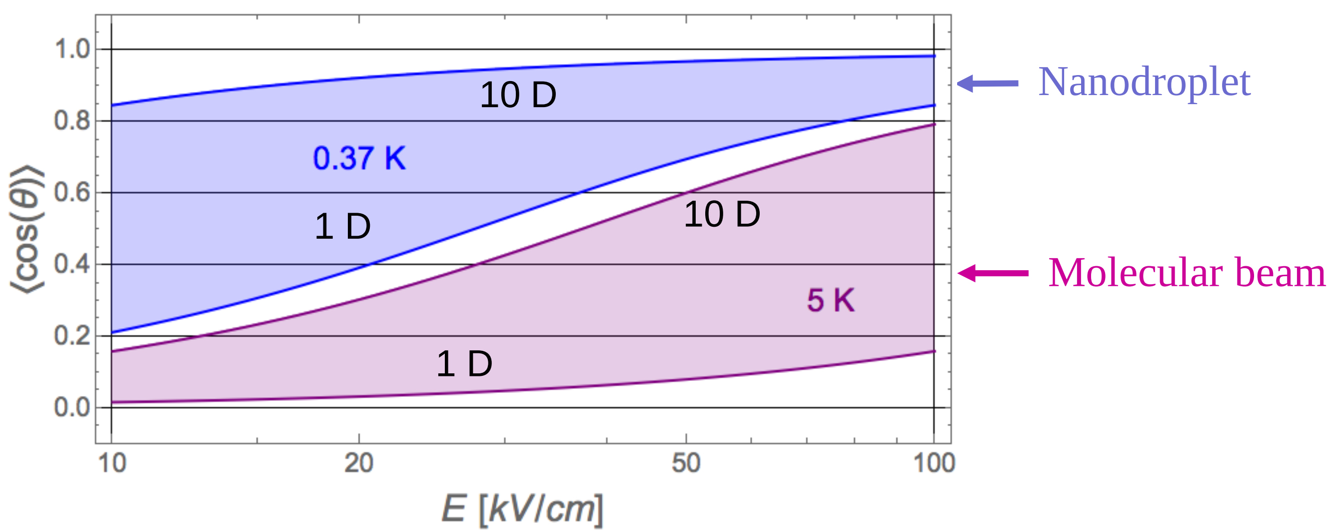
Vibrations not cooled as efficiently

Rotational temperature distribution can broaden and become multimodal

Helium nanodroplet embedding

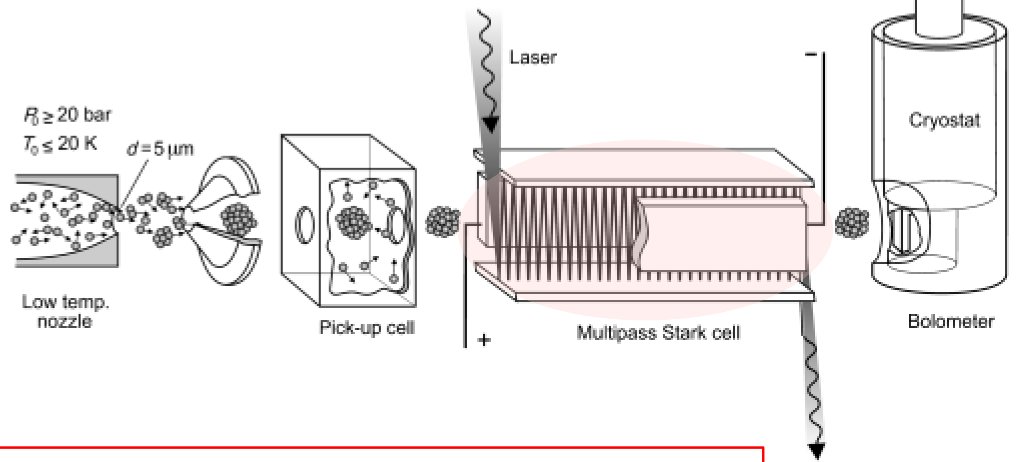


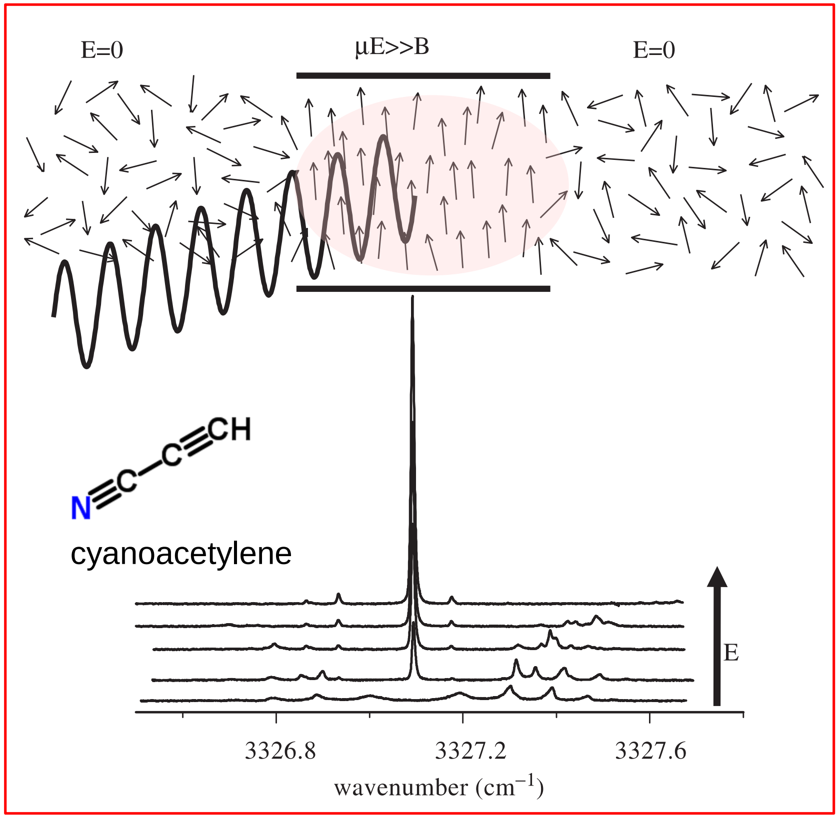
Efficient cooling of all degrees of freedom for molecules of a wide range of sizes and complexity



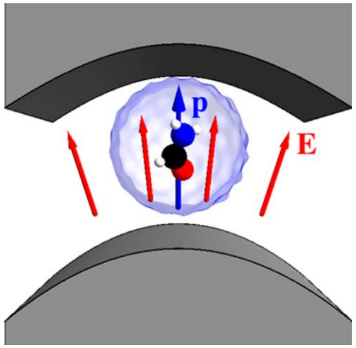
Pendular-state spectroscopy of cold embedded molecules

R. E. Miller; G. Douberly





Interpreting the data entails accurate calculation of structures and simulation of spectra



A benefit of the deflection method is that it can provide direct quantitative observables, such as the magnitude of the dopant's dipole moment.

Using nanodroplets it is possible to orient much larger systems than accessible for beams of free molecules.

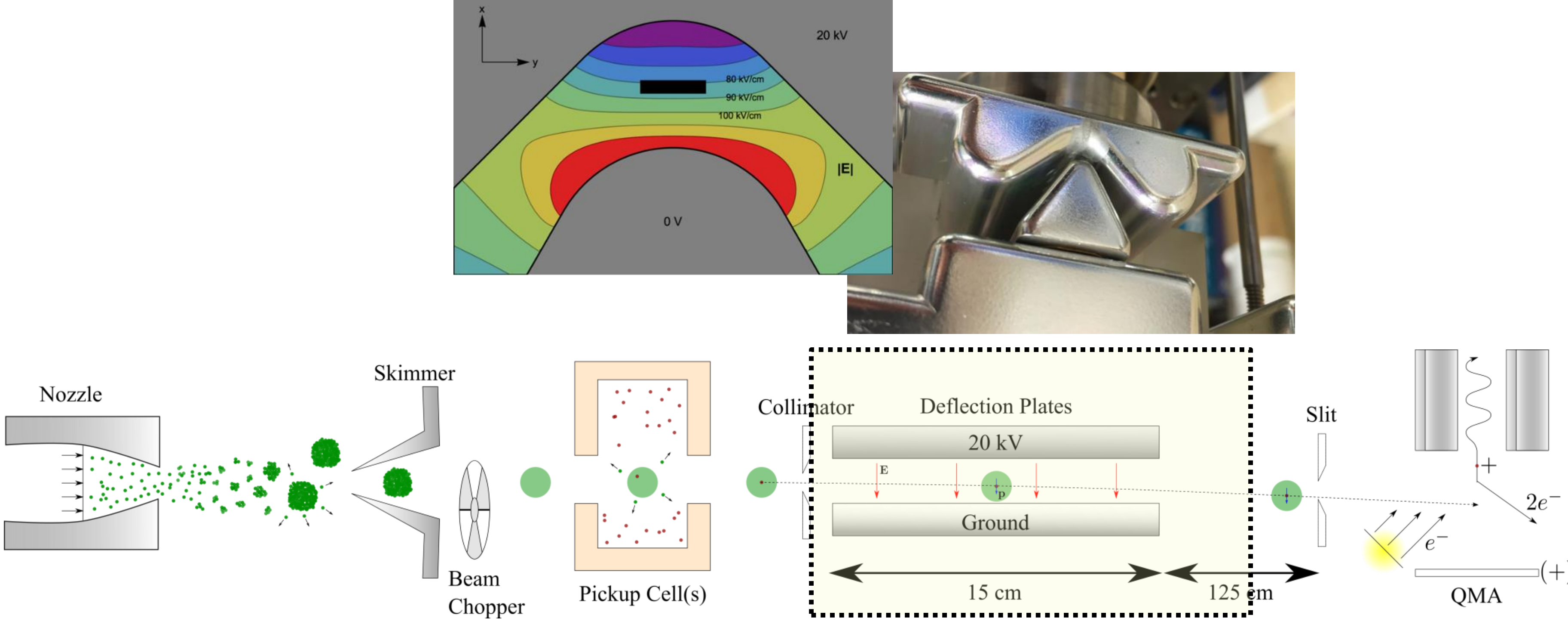
But He_N with N>10^4 are **much** heavier than free molecules.

So can a deflection be detected?

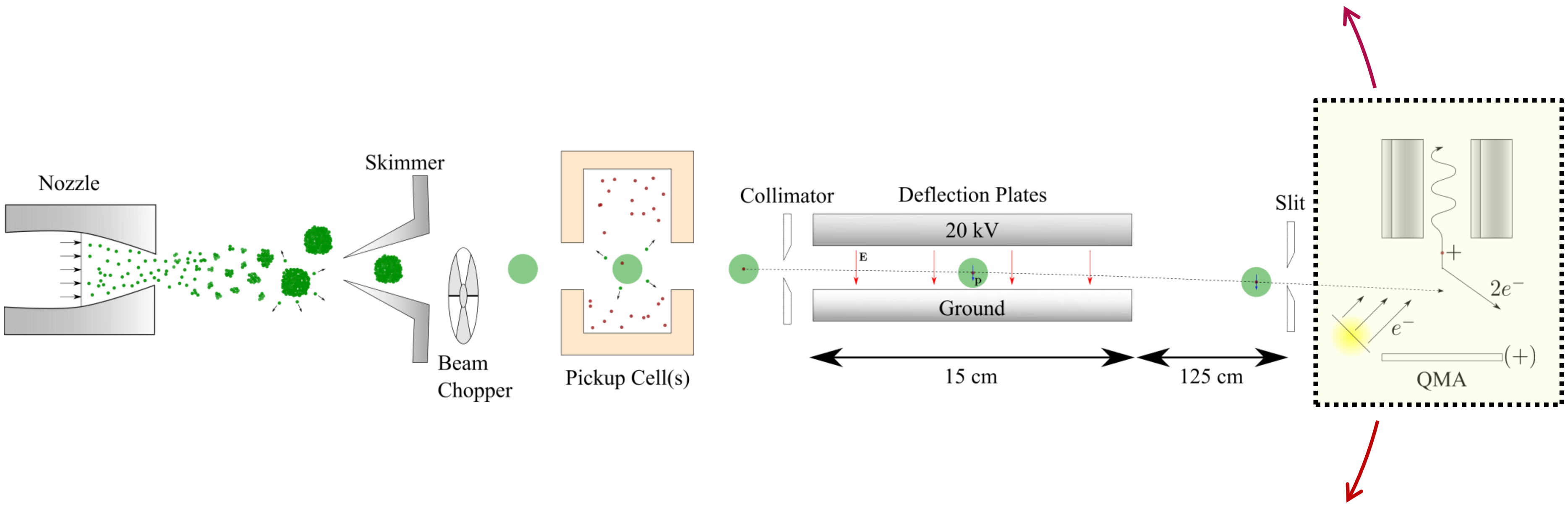
Strong orientation $\Rightarrow$ very strong force,
hence estimates suggested deflections may be measurable

Proof of principle experiments

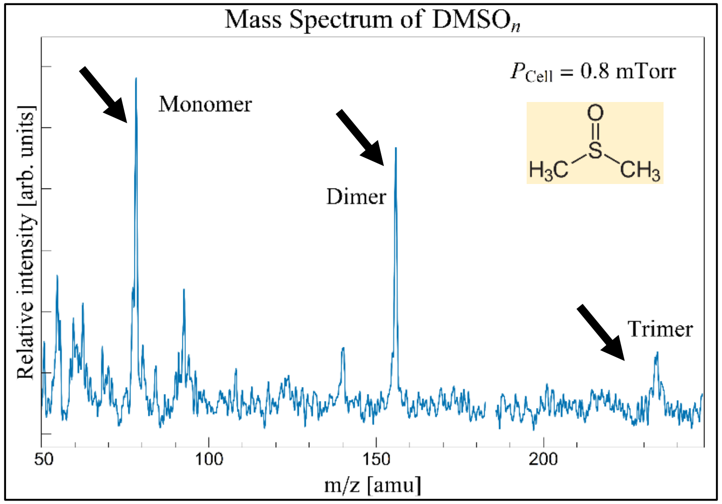
J. Phys. Chem. Lett. 2016, **7**, 4879
Phys. Rev. Lett., 2019 (subm.)



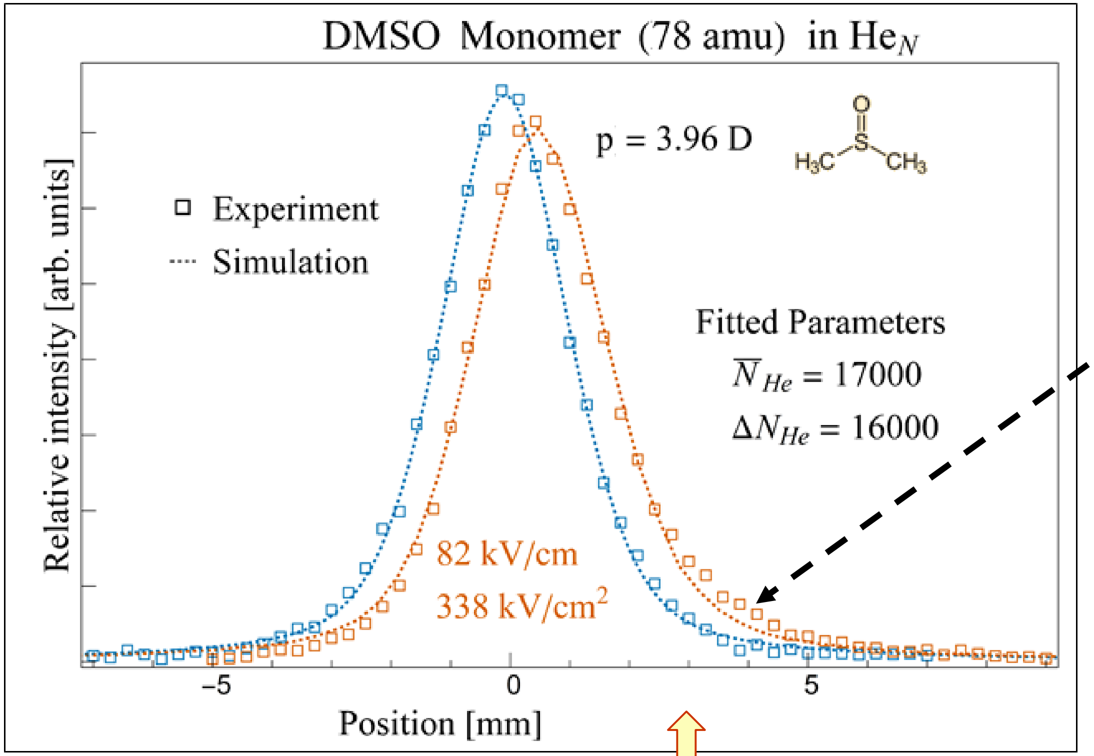
x
y
20 kV
80 kV/cm
90 kV/cm
100 kV/cm
|E|
0 V
Nozzle
Skimmer
Beam
Chopper
Pickup Cell(s)
Collimator
Deflection Plates
20 kV
E
p
Ground
15 cm
125 cm
Slit
+
$2e^-$
e^-
(+)
QMA



The mass spectrometer is set to a strong fragment peak for deflection measurements



Deflection of doped helium nanodroplets



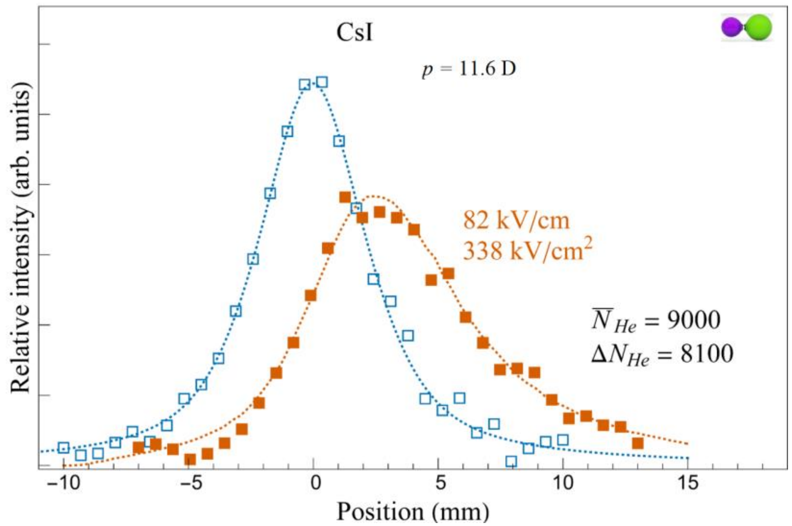
Substantial deflections

Molecular beam "deflectometry" of neutral objects with masses of tens of thousands of Daltons: possibly the heaviest ever

Monte Carlo simulation, incorporating:

- Log-normal droplet size distribution
- Poisson pickup probability
- Size dependence of pickup cross sections
- Evaporation of He due to the dopant's translational and internal energy
- Calculation of the orientation cosine of the cold dopant*
- Nanodroplet polarization correction
- Calculation of the deflection angle
- Size dependence of the droplet ionization cross section
- Probability of dopant ionization*

Highly polar dopants



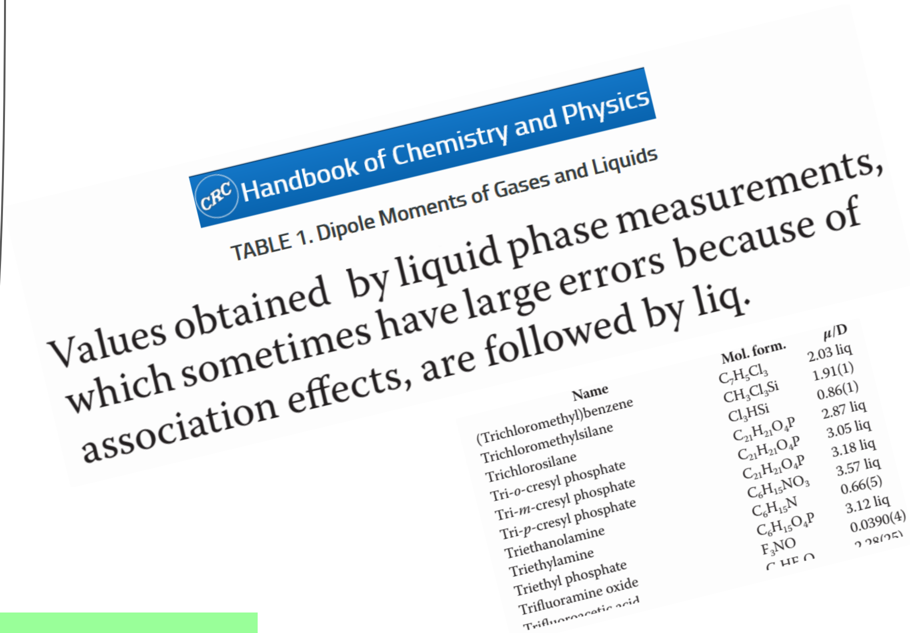
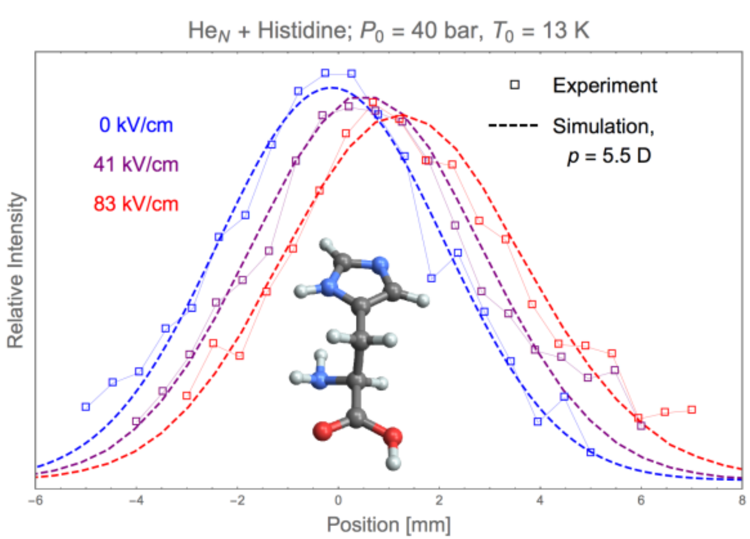


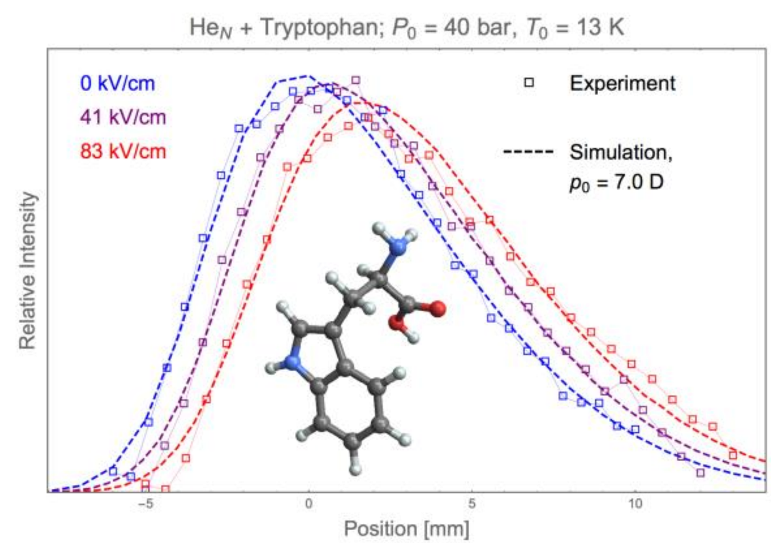
TABLE 1. Dipole Moments of Gases and Liquids

Values obtained by liquid phase measurements, which sometimes have large errors because of association effects, are followed by liq.

Name	Mol. form.	μ/D
(Trichloromethyl)benzene	$C_7H_5Cl_3$	2.03 liq
Trichloromethylsilane	CH_3Cl_3Si	1.91(1)
Trichlorosilane	Cl_3HSi	0.86(1)
Tri-*o*-cresyl phosphate	$C_{21}H_{21}O_4P$	2.87 liq
Tri-*m*-cresyl phosphate	$C_{21}H_{21}O_4P$	3.05 liq
Tri-*p*-cresyl phosphate	$C_{21}H_{21}O_4P$	3.18 liq
Triethanolamine	$C_6H_{15}NO_3$	3.57 liq
Triethylamine	$C_6H_{15}N$	0.66(5)
Triethyl phosphate	$C_6H_{15}O_4P$	3.12 liq
Trifluoramine oxide	F_3NO	0.0390(4)

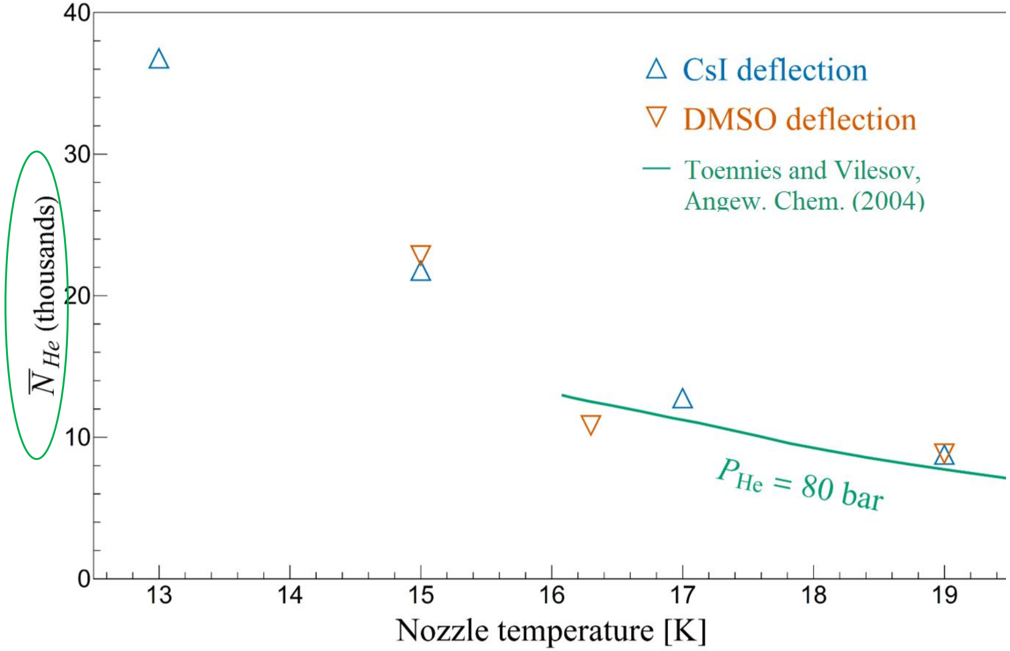
Complex molecules





Application 1: determination of molecular dipole moments

Fitted droplet $\bar{N}$ and ΔN agree with literature parameters, confirming the validity of the procedure



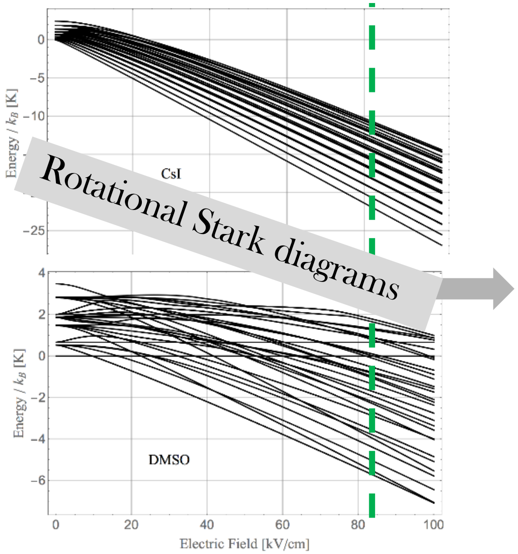
$$\Delta N / \bar{N} = 0.85$$

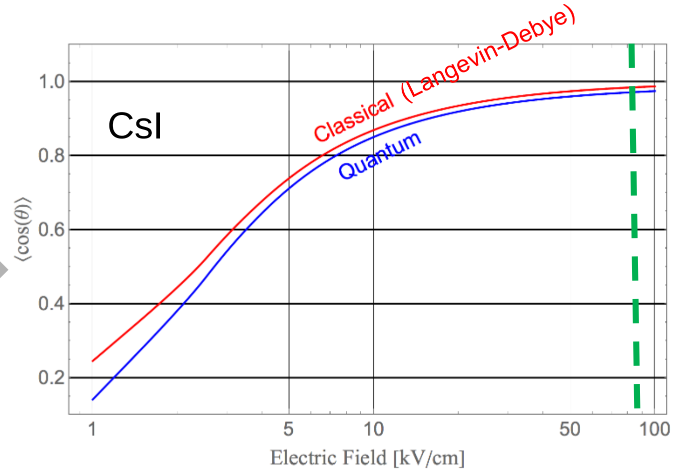
Cf. Harms, Toennies, Dalfovo (1998), beam scattering:

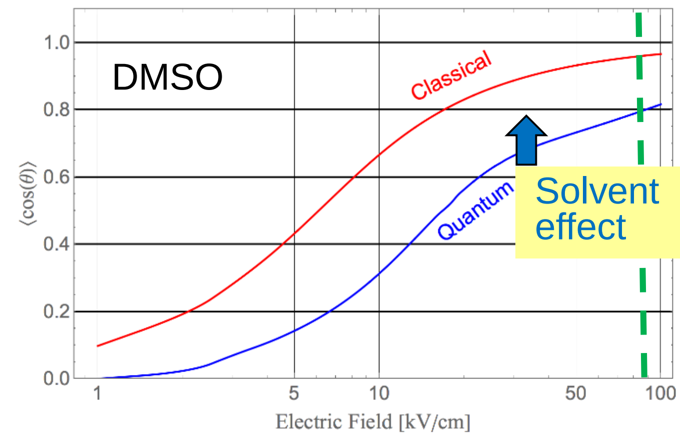
$$\Delta N / \bar{N} = 0.86$$

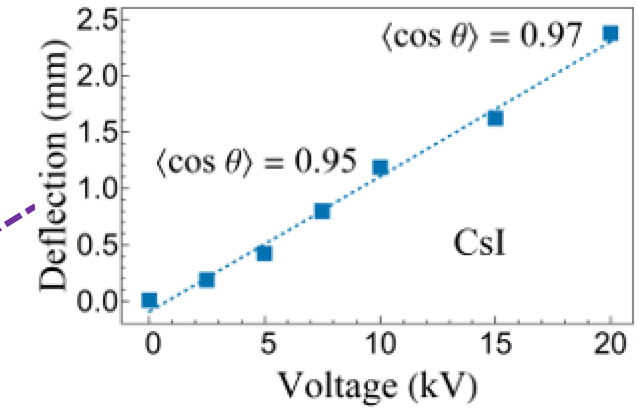
T_0 [K]	P_0 [bar]	sec. gas	$\bar{N}$	$\Delta N_{1/2}$
24.0	40	Kr	703	667
22.0	40	Kr	1700	1632
				73
				58
				31
				84
				19
				[illegible]40
				98
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]24
18.0 [a]	80	Kr	5260	4374
26.0	80	Ar	2114	1967
24.0	80	Ar	3103	2835
20.0	80	Ar	6458	5916
18.0	80	Ar	9487	8530

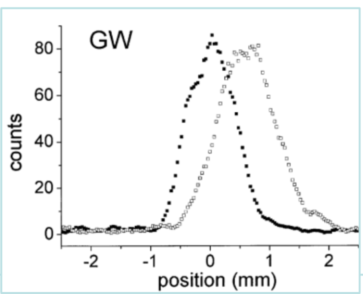
Field dependence of orientation and deflection force

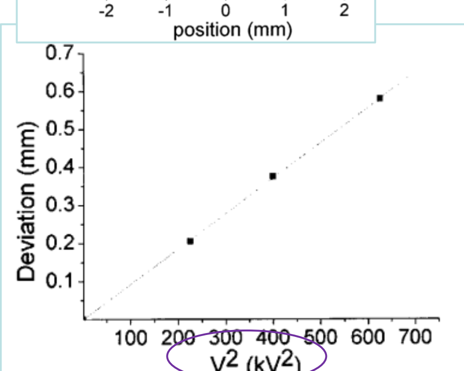




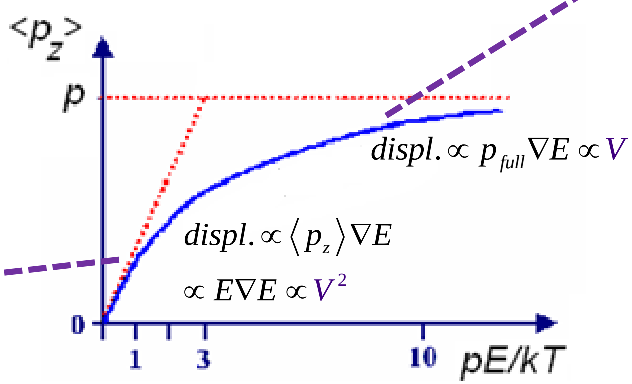








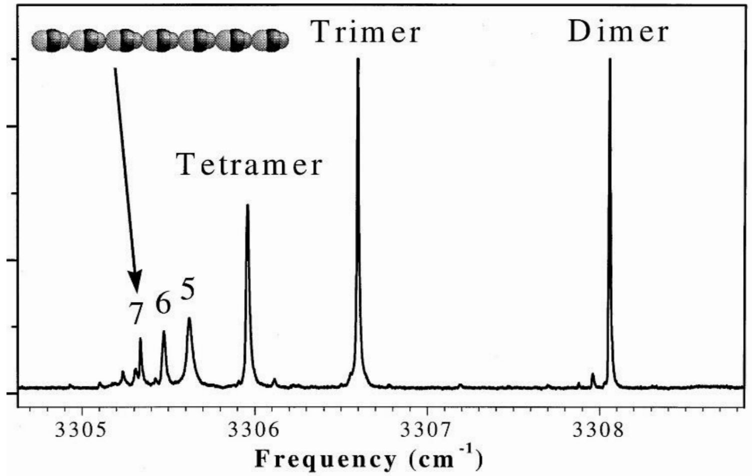
R. Antoine *et al.* (2003)



Signature of near-full orientation

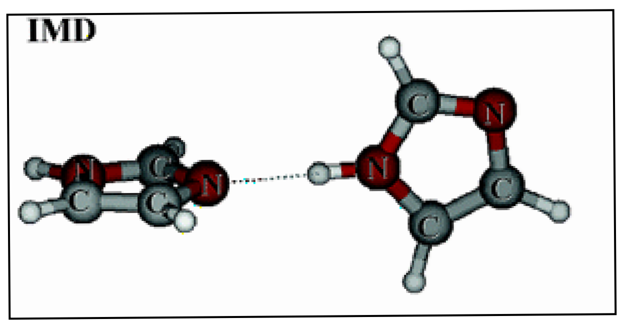
[pendulons?]

Application 2: Identification of polar assemblies

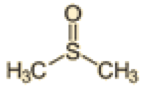


R. E. Miller *et al*.

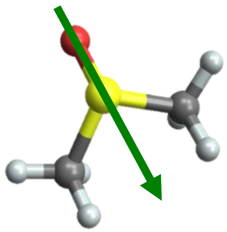
(*identified by pendular spectroscopy*)



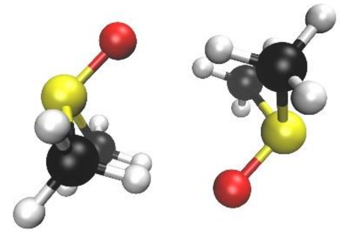
Formation of highly polar metastable structures driven by long-range (dipole-dipole) forces



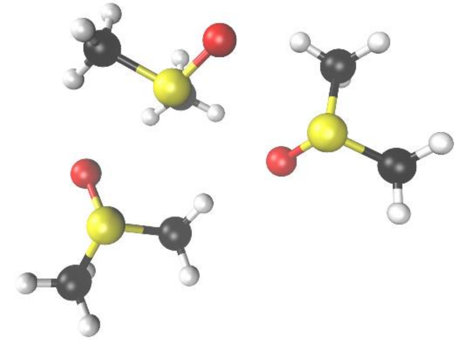
Lowest – energy DMSO structures



p = 3.96 D

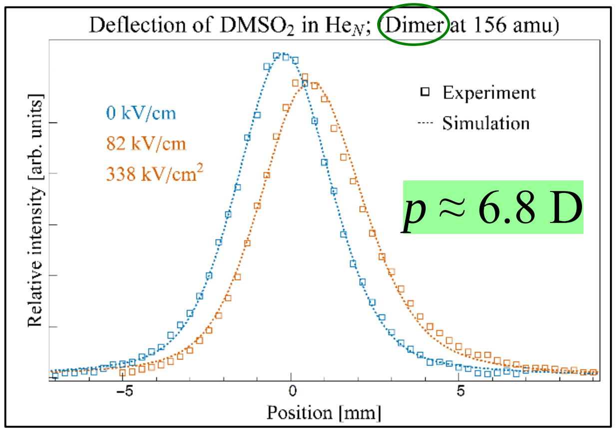


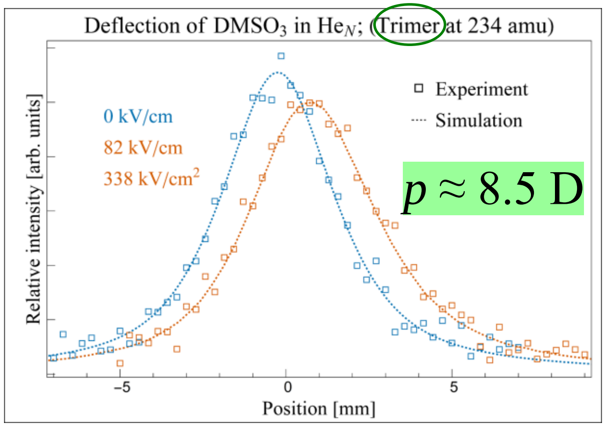
p = 0



p = 3.8 D

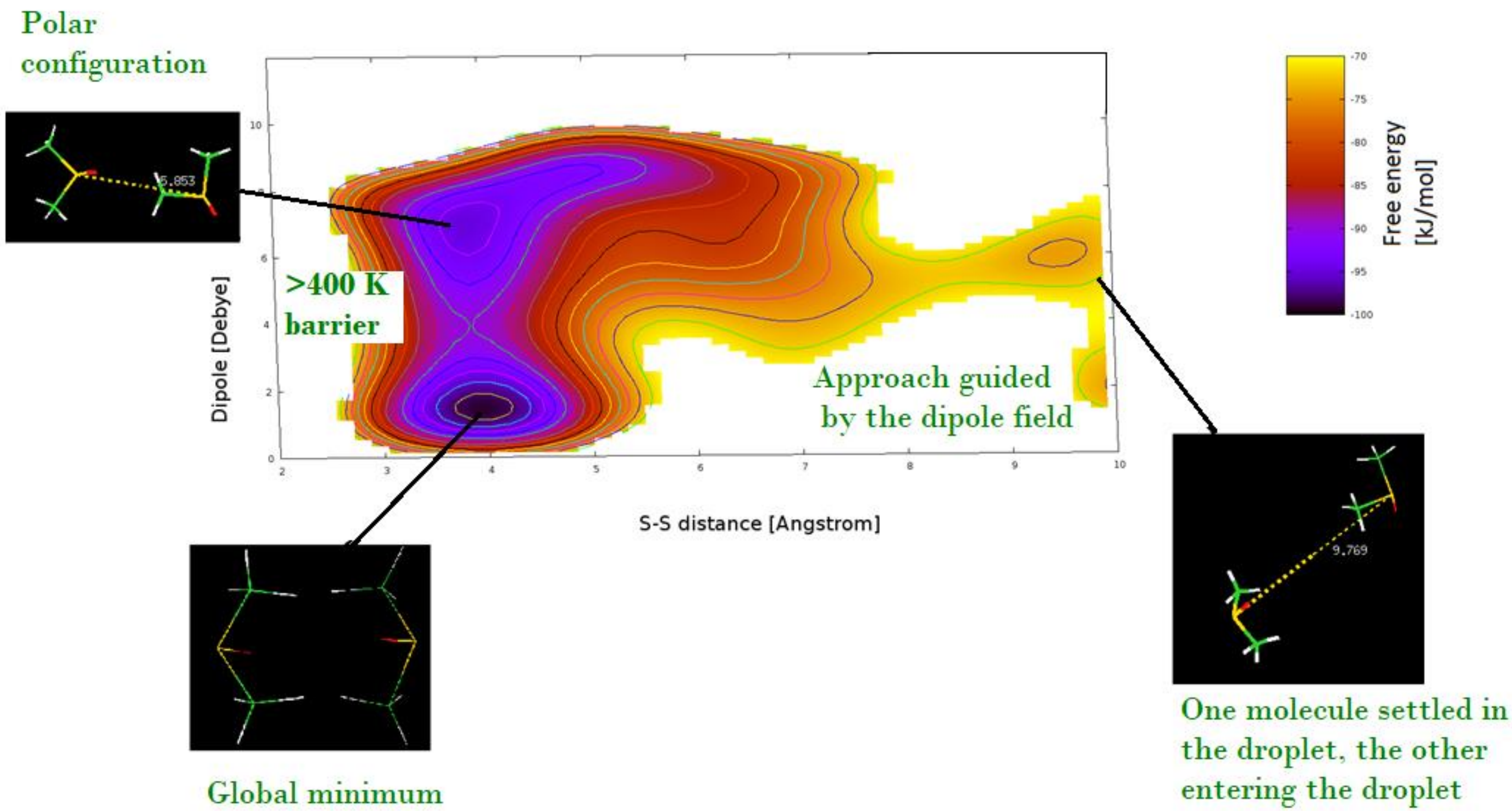
Deflection data:





$\Rightarrow$ Direct detection of polar structure formation

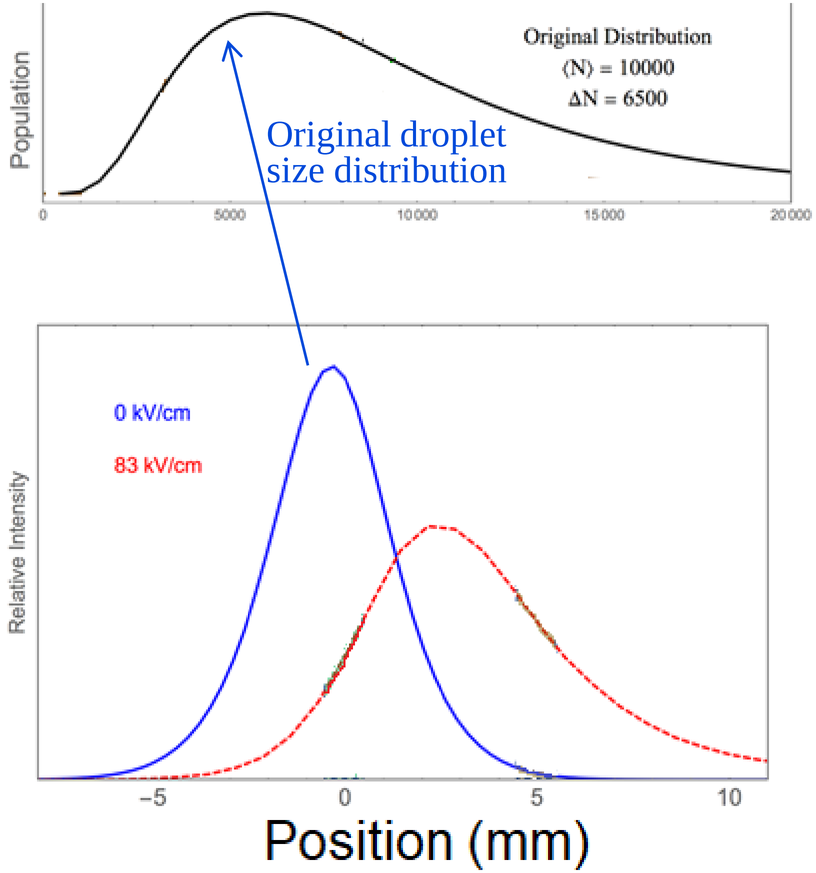
[poster]



B3LYP(D2)/aug-CC-pVDZ

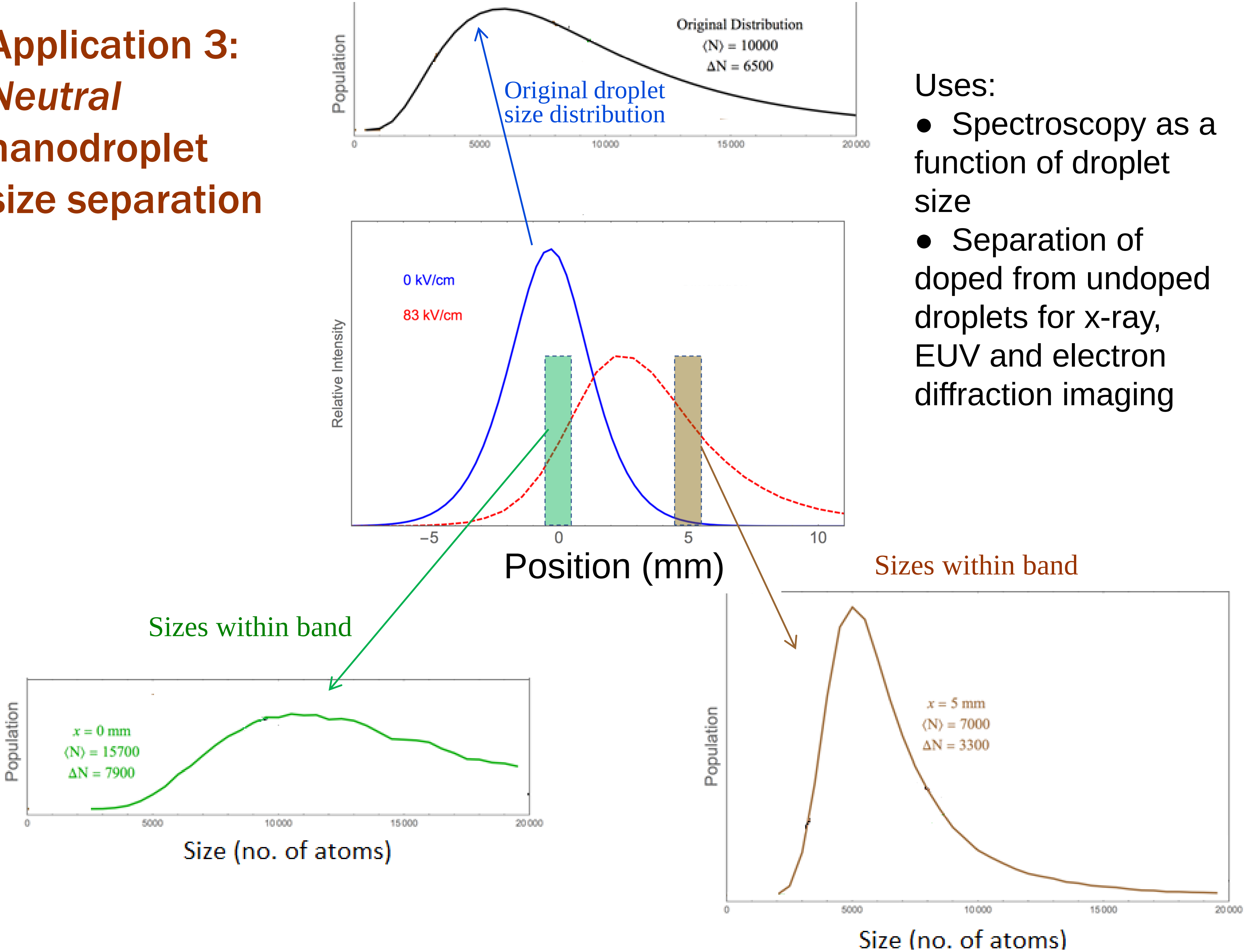
Petr Slavíček

Application 3: Neutral nanodroplet size separation



Calculated
size distributions

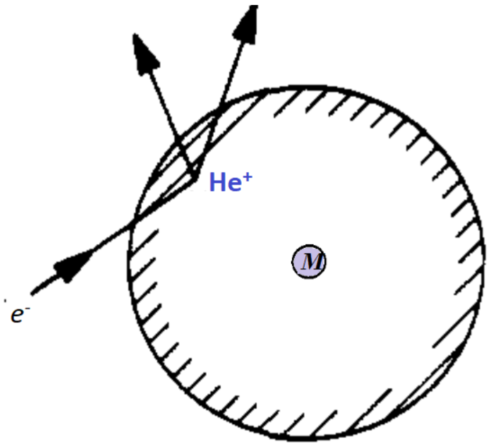
Application 3: *Neutral* nanodroplet size separation

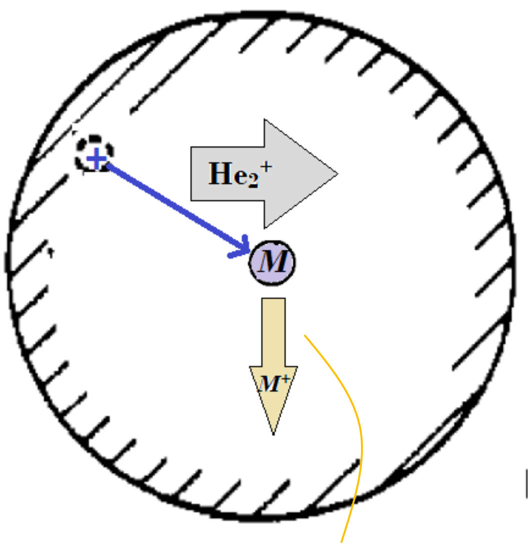


Uses:

- Spectroscopy as a function of droplet size
- Separation of doped from undoped droplets for x-ray, EUV and electron diffraction imaging

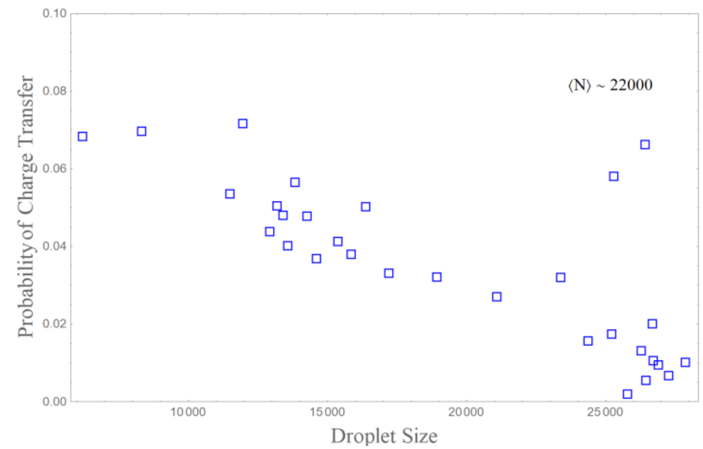
Illustration: Migration of charge to dopant



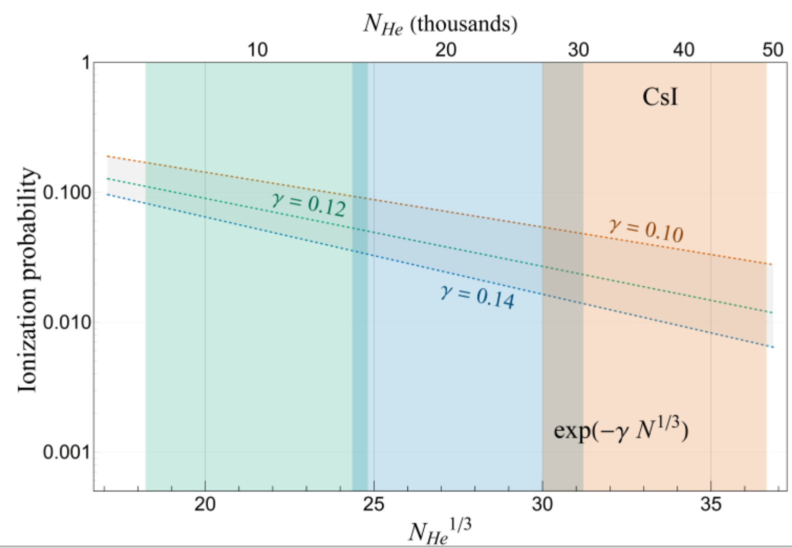


Probability for the ⊕ hole to reach the dopant $\approx e^{-R/l}$

Relative yield of CsI and DMSO dopant ions as a function of droplet deflection (⇔ size)



Fits to Beer's law:

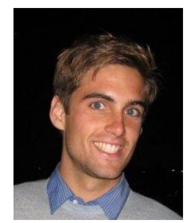


Result: ⊕ recombination mean free path $l \approx 20$ Å ✓

[*cf.* A. Ellis and S. Yang (2007)]

Summary

- Massive nanodroplets doped with a wide variety of polar molecules can be measurably deflected by an electric field
- This can be used to:
  - Determine the dipole moments of complex (including biological) molecules and isomers
  - Identify the appearance of dipole-aligned and ion-pair configurations and reaction products
  - Spatially separate doped and undoped nanodroplets
  - Spatially filter nanodroplets by size, allowing size-dependent spectroscopic, ionization, and reactivity studies

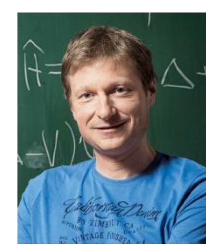


Daniel Merthe

John Niman

Ben Kamerin

Lorenz Kranabetter
(Innsbruck)



Petr Slavíček
(Prague)