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

Immanuel Estermann and Ronald G. I. Fraser

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

$$\hat{\mu} = \frac{8\pi^2 I \mu^2 E}{h^2} \frac{1}{(2j-1)(2j+3)} \left( \frac{3m^2}{j(j+1)} - 1 \right)$$

if $j \neq 0$.

$$= \frac{1}{3} 8\pi^2 I \mu^2 E / h^2$$

if $j = 0$.

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

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

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

For H$_2$O molecule (1.9 D) at room $T$ in $E= 100$ kV/cm, this is only $5 \times 10^{-3}$

Strong laser fields (alignment)

- 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 $\sim 1$ K requires optimization for each specific molecule
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

Low-temperature nozzle

\( T = 5-20 \text{ K}, \ P = 10-80 \text{ atm} \)

\( ^4 \text{He}_n, <n> \sim 10^3-10^6 \)

Scattering chamber

Photon absorption and evaporation

Ionizer

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

\[ \langle \cos(\theta) \rangle \]

\( E [\text{kV/cm}] \)

Nanodroplet

Molecular beam
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 $\text{He}_N$ 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

The mass spectrometer is set to a strong fragment peak for deflection measurements.
Deflection of doped helium nanodroplets

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*

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

Substantial deflections
Highly polar dopants

\[ p = 11.6 \text{ D} \]

82 kV/cm
338 kV/cm²

Relative intensity (arb. units)
Position (mm)

\[ \bar{N}_{He} = 9000 \]
\[ \Delta N_{He} = 8100 \]

Complex molecules

**Application 1:** determination of molecular dipole moments

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu ) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COCH₃</td>
<td>1.601</td>
</tr>
<tr>
<td>C₃H₇NO</td>
<td>0.89(1)</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>1.87(1)</td>
</tr>
<tr>
<td>C₆H₅NO₂</td>
<td>3.46(1)</td>
</tr>
<tr>
<td>C₃H₅NO₃</td>
<td>3.10(1)</td>
</tr>
<tr>
<td>C₆H₅NO₂</td>
<td>3.57(2)</td>
</tr>
<tr>
<td>C₆H₅NO₂</td>
<td>5.46(5)</td>
</tr>
<tr>
<td>C₆H₅NO₂</td>
<td>5.12(5)</td>
</tr>
<tr>
<td>C₆H₅NO₂</td>
<td>5.03(5)</td>
</tr>
</tbody>
</table>

**Notes:**
- Trichloroacetic acid
- Acetylacetone
- Trioxane
- Triethyl phosphate
- Tri-\( p \)-chlorophenol
- Triphenylamine
- Trichloroacetic acid
- Trifluoroacetic acid
- Trichloroacetaldehyde
- Trichloroacetamide
Fitted droplet $\bar{N}$ and $\Delta N$ agree with literature parameters, confirming the validity of the procedure.

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

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

$$\Delta N / \bar{N} = 0.86$$
Field dependence of orientation and deflection force

Rotational Stark diagrams

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

Deflection data:

$\rho = 3.96 \text{ D}$  \hspace{1cm}  $\rho = 0$  \hspace{1cm}  $\rho = 3.8 \text{ D}$

$\Rightarrow$ Direct detection of polar structure formation
Polar configuration

Dipole [Debye]

>400 K barrier

Approach guided by the dipole field

S-S distance [Angstrom]

Global minimum

One molecule settled in the droplet, the other entering the droplet

B3LYP(D2)/aug-CC-pVDZ

Petr Slavíček
Application 3: Neutral nanodroplet size separation

Original droplet size distribution

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

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

Fits to Beer’s law:

Result: $\oplus$ recombination mean free path $l \approx 20 \, \text{Å}$

[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