Spectroscopy and Dynamics of doped helium nanodroplets

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Properties of $^4\text{He}$ Nanodroplets

Helium binding energy of $\sim 5 \text{ cm}^{-1}$ (7 K)
- Evaporative cooling to $T \sim 0.38 \text{ K}$
- $\sim 100\%$ superfluid if bulk Helium

- We generate droplets with $\langle N \rangle \sim 1,000 - 20,000$ atoms
  - $R \sim 2 - 7 \text{ nm}$
  - Broad Log-Normal distribution of size

- There are no thermally populated phonons
  - Lowest excitation energy $534 \text{N}^{-1/3} \text{ GHz} \ > 3 \text{ kT}$

- Surface ‘Ripplons’ form heat bath
  \[ \nu(L) = 78\sqrt{L(L-1)(L+2)}N^{-1/2} \text{GHz} \]
  - Lowest mode ($L=2$) $\sim 2.2 \text{ GHz}$ ($\sim 0.3 \text{ kT}$) for $N = 10^4$
  - Amplitude $\sim 0.4 \text{ Å}$
Why Spectroscopy in He Nanodroplets?

• Rapid Cooling (~nsec) below 1 K
  – Stabilize unstable species and form new compounds
• Vibrations and Rotations are cooled
• Pickup only requires vapor pressure of \( \sim 10^{-4} \) torr
  – Allows study of very nonvolatile species
• Can form controlled clusters
  – Poisson Distribution of sizes
• Gives Rotational Resolution -> structural information
• Higher Resolution and smaller shifts than other Rare gas matrices
  – The Ultimate Spectroscopic Matrix!
Droplet Production and Detection

- 5 µm aperture
- $T=16–35$ K
- flux: $10^{20}$ atoms/s
- dopant inside (except alkali)
- $\sim 6500$ cm$^{-1}$ (2 quanta of $\equiv$CH stretch)
- 9-70 GHz (rotational transitions)
- NEP: 35-45 fW/$\sqrt{\text{Hz}}$

- cold expansion
- cluster formation
- dopant pick-up
- IR photon absorption + He evaporation ($10^3$ He/photon)
- MW multiple photon absorption + He evaporation (0.1 He/photon)

- Detection (bolometer)

- Droplet sizes: 1000-10000 atoms (45-95 Å diameter)
- Droplet temperature: 0.4 K (evaporative cooling)
- Sensitivity (S/N=1 @ 1Hz): $3 \times 10^7$ He atoms
The beginning

SF$_6$ in He droplets

Goyal, Schutt and Scoles, PRL 69, 933 (1992)

- Narrow lines
- Small shifts
- Complexes formed
Rotational resolution in $^4$He droplets
(Hartmann, Miller, Toennies, and Vilesov, PRL 75, 1566 (1995))

$\text{SF}_6$ freely rotates inside the droplet, but the observed $B$ is only 37% of the gas phase value.
OCS in $^3\text{He}$ and $^4\text{He}$ droplets: proof of superfluidity in $^4\text{He}$ droplets

Grebenev, Toennies, and Vilesov, SCIENCE 279, 2083 (1998)

Free rotation is exclusive to $^4\text{He}$ (a boson fluid). In $^3\text{He}$ (a fermion fluid) free rotation does not occur, unless enough $^4\text{He}$ is present to form a shell around the OCS molecule.
Evaporative Cooling of Helium Nanodroplets with Angular Momentum Conservation

KKL & Adriaan Dokter

Thermodynamics of Helium Droplets

Statistical Evaporative cooling calculations of temperature versus cooling time.

• There have been previous classical and quantum statistical evaporative cooling studies
  These predicted droplet temperatures close to those later found experimentally
  They ignored angular momentum constraints
• Droplets pick up considerable angular momentum in pickup process and possibly during formation due to droplet coalescence
  – Can this be completely shed during cooling?
  – Experiments of Portner, Havenith, and Vilesov interpreted as implying that droplets “remember” direction of initial angular momentum
• Droplet Energy and Angular Momentum will be stored in primarily in Ripplons
Distribution of Collisional Angular momentum for $N = 10^4$

Scales as $N^{1/3}$ for other droplet sizes
Monte Carlo Evaporation

- Start with $E$, $L$ from pickup process
  - $E \sim 1700$ K and $L \sim 4000$ for tetracene pickup
- Calculate number of open channels
  - $\text{Droplet}(E, L) \rightarrow \text{Droplet}(E', L') + \text{He}(E_k, J)$
  - $E_k = E - E' - E_{\text{bind}} > 1.23 K J(J+1) N^{-2/3}$ (centrifugal barrier)
- Calculate RRKM rate and increase time by lifetime
- Pick one decay channel at random equal probability
- Repeat until time $> \text{cooling time (10 or 100 } \mu\text{s)}$.
- $J = 10, 1000, 2000, 3000, 4000 \& 5000$ studied, 500 decay trajectories for each
All Points Sampled in Evaporation of $n = 10^4$ Droplet

![Graph showing the relationship between Droplet Energy (K) and Total Angular Momentum Quantum Number. The data points form a linear trend.](image)
Final Droplet Excitation Energy, mean and $\sigma$ interval

Initial droplet size: $N=10000$
Initial droplet energy: $E=1700K$

Final excitation energy (K)

Initial angular momentum

- $E$ No rotor included
- $E$ .6 GHz rotor included
- $E$ 1.2 GHz rotor included
Initial and final Droplet angular momentum

Initial droplet size: N=10000
Initial droplet energy: E=1700K

Final angular momentum

Initial angular momentum

- *: L, No rotor included
- *: L, .6 GHz rotor included
- +: L, 1.2 GHz rotor included
Conclusions

• Droplets have MUCH higher internal energy and angular momentum than for a canonical ensemble at same temperature.
  – Explains why previous attempts to predict lineshapes failed
  – PIMC will not give exact predictions - may be substantial bias

• Molecular Lab frame alignment of embedded molecules should be common.
Density-functional calculations of droplet excitations

KKL & Roman Schmied
Excitation in Helium Droplets are important for....

- Thermodynamic properties.
- Superfluid fraction.
- Provide relaxation channels for excited dopants.
- Are believed to contribute to lineshapes in electronic and perhaps IR spectra.
- Are usually estimated using liquid drop model
  - How accurate is this?
  - How do a dopant change the spectrum of excitation? Are localized phonons created in the solvent shells?
Methods to calculate properties of Helium Nanodroplets

- Assume pairwise additive interactions
  - Helium-molecule interactions weak and difficult to calculate accurately.
- Ground state static properties (energy, density) can be accurately calculated using Diffusion Monte Carlo Methods.
  - Path Integral Monte Carlo calculations give thermal average, BUT for Canonical Distribution.
- Lowest excited states of each symmetry can be estimated from Imaginary Time Dynamics.
  - Real time many body quantum dynamics is not practical due to “sign problem”.
- Can we calculate the entire excitation spectrum of doped droplets?
Density-Functional Theory

- Helium density, NOT electron density
- Bose symmetry included
- continuum theory
- Hydrodynamic description of flow
- Excitations as eigenmodes of oscillation

✔ Large systems
✔ Real-time dynamics
☹ accuracy
Static DFT

- Minimize functional

\[ F_t(\rho) = E^{\text{kin}} + E^{\text{pot}} + E^{\text{cor}} + \int \rho(r)(U_{\text{ext}}(r) - \mu)d^3r \]

\[ E^{\text{kin}}[\rho] = \frac{\hbar^2}{2m} \int |\nabla \sqrt{\rho(r)}|^2 d^3r \]

\[ E^{\text{pot}}[\rho] = \frac{1}{2} \iiint \rho(\vec{r}_1)\rho(\vec{r}_2)V(|\vec{r}_1 - \vec{r}_2|)d^3\vec{r}_1 d^3\vec{r}_2 \]

- \( V \) is effective He-He potential, screened at short range to correct for self-interaction

- \( \mu \) is chemical potential - used to maintain particle normalization
Orsay-Trento DFT

\[ E_{\text{corr},1}[\rho] = \int \left[ \frac{c_2}{2} \rho(\vec{r})\tilde{\rho}^2(\vec{r}) + \frac{c_3}{3} \rho(\vec{r})\tilde{\rho}^3(\vec{r}) \right] d^3\vec{r} \]

\[ E_{\text{corr},2}[\rho] = -\frac{\hbar^2\alpha_s}{4m} \iint F(|\vec{r}_1-\vec{r}_2|) \left[ 1 - \frac{\tilde{\rho}(\vec{r}_1)}{\rho_0} \right] \vec{\nabla}\rho(\vec{r}_1) \cdot \vec{\nabla}\rho(\vec{r}_2) \left[ 1 - \frac{\tilde{\rho}(\vec{r}_2)}{\rho_0} \right] d^3\vec{r}_1 d^3\vec{r}_2 \]

\[ \tilde{\rho}(\vec{r}) = \int \Pi_h(|\vec{r}_1-\vec{r}|)\rho(\vec{r}_1)d^3\vec{r}_1 \]

\[ \Pi_h(r) = \begin{cases} \frac{3}{4\pi\hbar^3} & \text{if } r \leq h \\ 0 & \text{if } r > h \end{cases} \]

\[ F(r) = \frac{e^{-r^2/\xi^2}}{\pi^{3/2}\xi^3} \]
Time Dependent DFT equations

\[
\frac{\partial \rho}{\partial t} - \frac{\partial}{\partial S} E_{\text{dyn}}(\rho, S) = 0
\]

\[
\frac{\partial S}{\partial t} + \frac{\partial}{\partial \rho} \left( F_{\text{tot}} + E_{\text{dyn}}(\rho, S) \right) = 0
\]

\[v = \nabla S / m(He)\]

For Orsay-Paris Functional:

\[E_{\text{dyn},1}^{\text{dyn}}[\rho, \bar{v}] = \frac{m}{2} \int \rho(\vec{r})|\bar{v}(\vec{r})|^2 d^3\vec{r}\]

\[E_{\text{dyn},2}^{\text{dyn}}[\rho, \bar{v}] = -\frac{m}{4} \iint V_J(|\vec{r}_1 - \vec{r}_2|)\rho(\vec{r}_1)\rho(\vec{r}_2)|\bar{v}(\vec{r}_1) - \bar{v}(\vec{r}_2)|^2 d^3\vec{r}_1 d^3\vec{r}_2\]

\[V_J(r) = \sum_{j=1}^{2} (\gamma_{j,1} + \gamma_{j,2} r^2) e^{-\alpha_j r^2}\]
O-P Calibration

- Give number density at $P = 0$.
- Velocity of sound at $P = 0$.
- The chemical potential
- Static susceptibility from neutron scattering data
  - Pressure dependence from DMC calculations also used
  - Based upon harmonic theory but real data has considerable anharmonic contributions
- Dispersion relation of elementary excitations fitted to experimental data.
Figure 4.1: Dispersion relation of single excitations in superfluid helium. Black: experimental data [2]; red: Orsay-Trento density functional [1]. The density-functional dispersion relation is qualitatively wrong beyond 2.3 Å⁻¹ in the single-excitation approximation (Section 4.2).
O-P accurately predicts

- Pressure dependence of density for liquid
- Pressure dependence of speed of sound
  - Including spinodal point where $P = -9.53$ (-9.64 exp) bar where cavitation occurs.
- Total energy and $\mu$ are in good agreement with DMC calculations.
- The surface tension 27.78 vs. 25.67 K/nm$^2$
  - The shape of the liquid-vacuum interface
Dynamic structure factor: Neutron scattering cross section

Static structure factor: FT of 2-particle density

Mismatch: neglected multiphonon excitations
Calculation of phonons

• Solve static DFT problem of pure or doped droplet or in bulk to give density $\rho(r)$
  – chemical potential either treated as fixed at bulk value or treated as Lagrange multiplier to enforce proper particle normalization.
• Consider arbitrary small displacement of density $\delta \rho(r)$ and expand TD-DFT equations to second order.
  – Normal modes found by finding eigenfunctions of “GF” matrix, eigenvalues give squared frequencies.
  – Use dimensionless harmonic oscillator normalization of normal modes.
Harmonic TDFT allows calculation of

- Phonon Spectrum of pure droplets and doped droplets and bulk
  - Phonons localized around impurity likely important in electronic spectra
- Finite temperature corrections to $T = 0$ DFT.
- Coupling of fast rotor to helium
  - Compliments hydrodynamic approach for heavy rotors
- Superfluid fraction at function of $T$ for pure and doped droplets.
Calculations on finite droplets

N=5000:

Compare to liquid-drop model:

Ripplons

- density
- $L=2$
- $L=3$
- $L=4$
- $L=5$
- $L=6$

phonon energy / cm$^{-1}$

radius / nm

angular momentum $L$

bulk waves

surface waves

10x
Figure 5.5: Surface and volume waves in a spherical droplet of 3500 helium atoms. Black dots: numerical calculations, Orsay–Trento density functional theory. Red: liquid-drop model approximation of surface waves (ripplons), Eq. (5-2), for $\ell \geq 2$. Blue: liquid-drop model approximations of volume waves, Eq. (5-5). The increased density of states above the roton energy, $E_{\text{roton}} = 8.83\text{K}$, is clearly visible. Green crosses mark $\ell = 11$ excitations whose wavefunctions are shown in Figs. 5.8 and 5.9. Figure 1 of Ref. [27] qualitatively captures part of the deviations between the liquid-drop model and the numerical calculations.
Figure 5.6: Surface and volume waves in a spherical droplet of 50000 helium atoms. Black dots: numerical calculations, Orsay–Trento density functional theory. Red: liquid-drop model approximation of surface waves (ripplons), Eq. (5-2), for $\ell \geq 2$. Blue: liquid-drop model approximations of volume waves, Eq. (5-5). The increased density of states above the roton energy, $E_{\text{roton}} = 8.83 \text{K}$, is clearly visible. Green crosses mark $\ell = 35$ excitations whose wavefunctions are shown in Fig. 5.10.
Figure 5.10: Lowest-energy $\ell = 35$ ripplons of a $N = 50000$ helium droplet, as examples to illustrate the different ripplon branches in Fig. 5.8. Red: $\hbar \omega = 2.97 \text{ K}$; green: $\hbar \omega = 6.30 \text{ K}$; blue: $\hbar \omega = 8.43 \text{ K}$; black (scaled down 10 times): $\hbar \omega = 8.92 \text{ K}$ (see Fig. 5.6). The vertical black line denotes the liquid-drop surface location at $R = 8.18 \text{ nm}$. Higher-energy excitations penetrate farther into the droplet bulk. The highest excitation (black) is not a surface mode.
Momentum density of excitations

![Momentum density of excitations](image)
DFT test for doped droplet

Ag–He$_{100}$:

- Energy: $-358.8 \text{ cm}^{-1}$
  - DMC: $-357.3(6) \text{ cm}^{-1}$
- Chemical potential: $3.2 \text{ cm}^{-1}$
  - DMC: $3.1(1) \text{ cm}^{-1}$

from Mella, Colombo, Morosi, JCP 117 (21), 2002, 9695
Spherical Simulations

- 1D simulations
- Excitations with any angular momentum
- No phonon-phonon interactions: linear theory

DFT helium density around a $^4$He atom
Excitations around a dopant

$\varepsilon = 40 \text{cm}^{-1} (5.6 \times \text{He-He}), \sigma = 2.556 \text{Å}$

~ density of states

momentum / Å$^{-1}$
Localized phonons

density / nm$^{-3}$

distance / nm

density

phonon (L=6)
"unstable" excitation: symmetry breaking

helium density: energy / yJ:

ε=880 yJ, σ=0.2556 Å:

distance / nm displacement
Figure 5.16: Non-perturbative total free energy $F_{\text{total}}[\rho]$ along several normal mode coordinates $\xi_{\ell,0,k}$, similar to Fig. 5.15 but with a Lennard-Jones interaction point of well depth 86.92 K. The lowest three $\ell = 5$ modes have their origin at 0; the lowest three $\ell = 6$ modes have been offset by +2 K for clarity. The potentials are indicated with green, blue, and red lines with increasing curvature at the origin.
Symmetry breaking

- Quantum phase transition: superfluid $\rightarrow$ nonsuperfluid?
- First helium shell must decouple from the fluid
Conclusions

• Time dependent density theory provides method to calculate real
time dynamics of the helium many-body problem
• Harmonic theory has been developed in general and implemented
  for spherical solutes
  – Allows full excitation spectrum to be calculated
  – Novel Surface localized states found
• We need to improve the functional for high density (→freezing)
  and also treat nonspherical impurities (cost).
• DFT gives much insight and is semi-quantitative!
Conclusions

• With DFT, we can compute:
  – Density
  – Large droplets
  – Doped bulk
  – Doped droplets
  – Phonons: structure factor, low-lying states
  – Superfluid fraction (local and global)
  – Effective rotational constants of light rotors
  – Freezing transition

• DFT gives much insight and is semi-quantitative!
UV-spectroscopy of Aromatic molecules in Helium Nanodroplets

Ozgur Birer, Paolo Moreschini, Roman Schmied, Pierre Çarçabal, Kevin K. Lehmann and Giacinto Scoles.
Multiple Zero phonon lines

Poorly Understood.

In at some cases, due to long lived isomers of helium solvation. like crystal field splitting in solid matrices.

May include low frequency localized phonons

Shapes of phonon wings also not generally understood!

From Alwkin Slenczka
**Table 4:** The zero-phonon line (ZPL) origins of the \(S_1 \rightarrow S_0\) transitions of some molecules in helium droplets.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Frequency in He [cm(^{-1})][^{[a]}]</th>
<th>Frequency shift in He [cm(^{-1})]</th>
<th>Number of the ZPLs</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>glyoxal</td>
<td>21942.8</td>
<td>30.6</td>
<td>1</td>
<td>[171]</td>
</tr>
<tr>
<td>naphthalene</td>
<td>32035</td>
<td>+15</td>
<td>1</td>
<td>[223]</td>
</tr>
<tr>
<td>indole</td>
<td>35282</td>
<td>+43</td>
<td>3</td>
<td>[214]</td>
</tr>
<tr>
<td>3-methylindole</td>
<td>34943</td>
<td>+61</td>
<td>3</td>
<td>[214]</td>
</tr>
<tr>
<td>NATA[^{[b]}]</td>
<td>35014</td>
<td>+59</td>
<td>4</td>
<td>[214]</td>
</tr>
<tr>
<td>tryptophan</td>
<td>34960.8</td>
<td>+55</td>
<td>1</td>
<td>[141]</td>
</tr>
<tr>
<td>tryptamine</td>
<td>34959.6</td>
<td>+44.1</td>
<td>3</td>
<td>[214]</td>
</tr>
<tr>
<td>tyrosine</td>
<td>35538.0</td>
<td>+47.8</td>
<td>1</td>
<td>[141]</td>
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<tr>
<td>tetracene</td>
<td>22293.4</td>
<td>103</td>
<td>2</td>
<td>[154]</td>
</tr>
<tr>
<td>pentacene</td>
<td>18545.0</td>
<td>104</td>
<td>1</td>
<td>[154]</td>
</tr>
<tr>
<td>PTCDA[^{[c]}]</td>
<td>27127.5</td>
<td>[^{[d]}]</td>
<td>1</td>
<td>[13]</td>
</tr>
<tr>
<td>porphin</td>
<td>16310</td>
<td>10</td>
<td>1</td>
<td>[213]</td>
</tr>
<tr>
<td>phthalocyanine</td>
<td>15088.9</td>
<td>43</td>
<td>1</td>
<td>[213]</td>
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<tr>
<td>Mg phthalocyanine</td>
<td>15556.2</td>
<td>56</td>
<td>1</td>
<td>[224]</td>
</tr>
<tr>
<td>C(_{60})</td>
<td>15666</td>
<td>14 ± 4[^{[k]}]</td>
<td>1</td>
<td>[216]</td>
</tr>
<tr>
<td>BaO (A '(\Sigma^+) - X '(\Sigma^+))</td>
<td>16722.3</td>
<td>+40.3</td>
<td>1</td>
<td>[161]</td>
</tr>
</tbody>
</table>

\[^{[a]}\] The typical errors are about 1 cm\(^{-1}\) because of uncertainties in the laser calibration. \[^{[b]}\] NATA, \(N\)-acetyl-L-tryptophanamide \(C_{12}H_{15}N_2O_2\). \[^{[c]}\] PTCDA, 3,4,9,10-perylene-tetracarboxylic-dianhydride. \[^{[d]}\] Gas-phase values in helium. \[^{[k]}\] Uncertainty in identification of \(S_1 \rightarrow S_0\).
Benzene isotopomers

These spectra are qualitatively identical to gas-phase spectra, no phonon wings, but blueshifted by about 30 to 31 cm$^{-1}$.

We also observed spectra of benzene dimers and benzene-Ar.

Conclusions: benzene

- The C$_6$H$_6$ spectrum is too narrow → Helium must be slowing down its rotation: estimated $I_{\text{droplet}}/I_{\text{gas}} \geq 6$
- Blue-shifted ⇐ constrained expansion of electron cloud
- Spectrum is very simple! (no phonon wing)

Comparison with simulated spectra:

\[ T = 0.38 \text{ K} \]
\[ T_S = 300 \text{ K} \]

Gaussian smoothing: FWHM = 0.2 cm$^{-1}$
$C_6H_6$ spectrum fits by scaling gas phase rotational constants

No spin relaxation

With spin relaxation

Moments of inertia must be at least 6 times gas phase values.
Benzene and clusters

\[(\text{C}_6\text{H}_6)_2, \text{C}_6\text{H}_6--\text{Ar}, \text{C}_6\text{H}_6\]
Benzene isotopomer dimers

\((C_6D_6)_2\)

\((1,3,5-C_6H_3D_3)_2\)

\((C_6H_5D)\)

\((C_6H_6)_2\)

Splitting structure is the same as gas phase, but compressed by ~20%
Dimer splittings: librational motion

almost free  \sim 46 \text{ cm}^{-1} \text{ barrier}  \sim 170 \text{ cm}^{-1} \text{ barrier}

\begin{align*}
\text{CCSD(T):} & \quad \sim 3.4 \text{ cm}^{-1} \quad \sim 4.8 \text{ cm}^{-1} \quad \sim 13.6 \text{ cm}^{-1} \\
\end{align*}

from Spirko et al., JCP 111 (1999) 572

but:

- \( (C_6H_6)_2 \rightarrow (C_6D_6)_2 \): qualitative change
- Gas phase \rightarrow droplets: no qualitative change
Fluorescence lifetimes:

**gas phase:**
- monomer 103 ns
- dimer 40 ns

**droplet:**
- monomer 115±5 ns
- dimer 120±10 ns

**Monomer**
closely bound helium layer does not decrease fluorescence lifetime!

**Dimer**
gas phase: short dimer fluorescence lifetime because of rapid excimer formation (~10 ps)

\[ \rightarrow \text{excimer formation is suppressed in helium!} \]

Rayleigh scattering off of cluster beam

[Graph showing fluorescence decay]
Comparison to other Polyacenes

<table>
<thead>
<tr>
<th>Molecule</th>
<th>wavenumber</th>
<th>shift/phonon</th>
<th># of #2260</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>38606</td>
<td>+30.31(3)</td>
<td>1</td>
</tr>
<tr>
<td>naphthalene</td>
<td>32019</td>
<td>+15</td>
<td>1</td>
</tr>
<tr>
<td>anthracene</td>
<td>27695</td>
<td>(-38)</td>
<td></td>
</tr>
<tr>
<td>tetracene</td>
<td>22397</td>
<td>-104.0(5)</td>
<td>2</td>
</tr>
<tr>
<td>pentacene</td>
<td>18649</td>
<td>-104.0(5)</td>
<td>1</td>
</tr>
</tbody>
</table>

(all numbers in cm$^{-1}$)

- Presence/absence of splitting of the zero-phonon line is poorly understood
- Smaller molecules have larger blueshifts
Biphenylene $S_0 \rightarrow S_1$ (electronically forbidden)
Coronene
New Experiment: Driving Ions in Helium

Figure 3: Schematic of proposed ion machine
Figure 1: Classical Simulation of ion motion in He droplet driving by frequency swept microwave field of 20 V/cm. Red is the frequency; blue the ion kinetic energy; and black to energy deposited in droplet. Not the change in scale on the left for the second figure. This demonstrates that the ion will lock onto and follow the frequency until the ion moves at the critical velocity. Above this, the ion no longer can follow and relaxes to zero energy (c).
Thanks for your attention!

If you find this interesting, please stop by to see me:

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Office: Chemistry Rm 126
Coronene

• High symmetry simplifies the spectra.
  – But $S_0 \rightarrow S_1$ is forbidden!
• Sharp peaks with FWHM $< 1 \text{ cm}^{-1}$
  – No phonon wings!
  – Better resolved than previous jet spectra.
• Unlike benzene, non $e_{2g}$ modes are observed.
  – Higher Order Herzberg-Teller coupling?
Benzo[ghi]perylene
Benzo[ghi]perylene $S_1$

- 1st high resolution $S_1$ spectrum.
- Challenge to Quantum chemists
  
  **TD-DFT**:
  
  $S_1 \ 27217 \text{ cm}^{-1} \text{ with } f = 0.00027$
  
  $S_2 \ 27401 \text{ cm}^{-1} \text{ with } f = 0.27$

- Peaks are split by $\sim 1.5 \text{ cm}^{-1}$
  - Multiple phonon lines!
Fluoranthene

![Chemical structure of Fluoranthene](image)

![Spectrum of Fluoranthene](image)
Fluoranthene $S_1$

- Sharp peaks with FWHM < 0.5 cm$^{-1}$
- Prominent phonon wing and roton maxima for each peak, but only one zero phonon line.
Perylene $S_1$

- $S_1$ region of perylene inside helium nanodroplets.
- Spectra scaled for droplet beam intensity and laser power.
- As T (or P) of the pick up cell is increased, broad background becomes stronger. The background is attributed to displaced sandwich dimeric structure. Molecular vs excitonic excitation.
Follow up

- S2 regions...
Some new areas for helium nanodroplet spectroscopy

- Spectroscopy of free radicals and radical complexes.
- Bridge span from dimers and trimers to droplets
  - McKellar (IR) and Jager are making great progress
- Spectra of molecules in bulk helium
  - Ishigura reported NH$_3$ in bulk helium at this meeting!
- Photodissociation of molecules in droplets
  - First work recently reported by M. Drabbels.
- Deposit clusters grown in helium onto cold surfaces
  - Vilesov’s group has built an apparatus for this.
Recently, experiments on clusters of OCS, NNO, and CO$_2$ with small number of helium atoms have been reported using by McKellar (IR) and Jager (MW).

This work is very exciting as it allows the onset of He exchange ("superfluid behavior") to be studied. Nicely complements nanodroplet experiments.

PRL 91, 163401 (2003)
*DT-DFT and CRDS by Tan and Salama JCP 123 014312 (2005)
Benzo[ghi]perylene $S_2$

- Subtle differences between HENDI and CRD.