SUPPLEMENTAL MATERIAL FOR

Electrostatic Deflection of a Molecular Beam of Massive Neutral Particles: Fully Field-Oriented Polar Molecules within Superfluid Nanodroplets

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I. Experiment

The helium nanodroplet apparatus produced a supersonic ^4He_n beam by expansion of high purity helium gas through a 5 μm nozzle at 40 bar stagnation pressure and 13 K temperature. After passing through a skimmer and a mechanical wheel chopper, the droplets picked up the dopant molecules within a copper cell. The data described below were acquired with formamide or DMSO liquids whose vapor was fed from an outside glass container through a capillary (with its flow kept constant using a regulated combination of thermally insulating tape, fine needle valves, and differential pumping with a mechanical vane pump) and with histidine which was loaded into the cell as a powder and heated with the use of a temperature controller. In all cases, the dopant's partial pressure in the pickup cell was adjusted to maximize the signal of characteristic single-molecule ionization products, as identified by the mass spectrometry tables[S1]. For Poissonian pickup statistics this point corresponds to an average of one dopant molecule per droplet. A small fraction of larger dopant clusters may also produce single-molecule ions and their fragments in the mass spectrum, however, based on the good fits of mass spectral line intensities to Poisson distributions of dopant populations in many studies (e.g., refs. S2 and S3) this contribution can be neglected at the present level of precision. The stability of the doped beam was verified by monitoring the intensities of the peaks in the mass spectrum.

In the following chamber, the beam was collimated by a 0.25 mm × 1.25 mm slit and entered the 2.5 mm wide gap between two 15 cm long metal plates shaped to create a "two-wire" inhomogeneous electric field[S4,S5]. The field oriented the polar dopant molecule and its gradient exerted a deflecting force on the oriented dipole. By applying voltage of up to 20 kV between the plates, electric fields up to 80 kV/cm and field gradients up to 250 kV/cm^2 were created.

The droplet beam was detected by a Balzers QMG-511 crossed-beam quadrupole mass analyzer with an electron impact ionization source set to an energy of 70 eV. For each beam deflection measurement the analyzer was tuned to the most intense characteristic fragment peak of the molecular impurity[S1]. Selecting the monomer peak in the mass spectrum mitigates influences from larger dopants agglomerates on the measured deflections. The output of the

analyzer was fed into a lock-in amplifier together with the chopper synchronization pulses, filtering out the background and extracting the signal carried by the helium beam.

In addition, the lock-in's phase delay between the chopper pulse and the analyzer output was used to determine the velocity of the supersonic droplet beam. It was found to be v_0=400 m/s. The distribution of forward velocities is narrow; according to ref. S6 its width can be taken as $\Delta v \approx 0.03\ v_0$. To account for beam divergence one also can assign it a transverse Gaussian velocity distribution with a mean of zero and a standard deviation of $4\times10^{-4}\cdot v_0$, as parametrized from the zero-field beam profiles. This is consistent with what would be expected from a conical projection of the molecular beam from the skimmer through the collimator.

The lock-in was read by a LabVIEW computer program, which also moved a 0.25 mm wide slit in front of the ionizer entrance, a distance L=140 cm past the middle of the deflection field plates. This slit, scanned across the beam by a stepper motor in steps of 0.15 mm, sampled the beam intensity at 20-25 slit positions in a sequence that was randomized for each pass across the beam. Each voltage-on and voltage-off profile typically combined approximately 100 passes for a total acquisition time of 2-3 hours per profile.

II. Helium droplet polarization

To estimate the polarization induced in the helium nanodroplet by the external field and by the embedded polar molecule, we approximated it as a spherical dielectric shell with dielectric constant ε = 1.057[S7], an outer radius of $b = 0.2\times N^{1/3}$ nm[S8] and an inner radius of a = 1 nm, with the inner surface enclosing the dopant molecule.

The total dipole moment of the spherical shell will depend only on the dipole field of the embedded molecule and not on any other multipoles of its charge distribution. Consequently, the problem can modeled as that of an electrostatic shell with a point dipole p at the center and a uniform electric field $E\hat{z}$ applied externally. We assume that the embedded dipole is oriented in the direction of the external field.

By the standard method of polynomial expansion and boundary condition matching, one can calculate the electrostatic potential, the shell polarization $P\hat{z}$ and, by integrating the latter, the total induced dipole moment of the nanodroplet (in Gaussian units):

$$p_z^{He} = \left(1-\frac{a^3}{b^3}\right)\frac{b^3(2\varepsilon+1)(\varepsilon-1)E-2(\varepsilon-1)^2 p}{(2\varepsilon+1)(\varepsilon+2)-2(a/b)^3(\varepsilon-1)^2} \qquad \text{(S.1)}$$

For an electric field E of 80 kV/cm applied to a nanodroplet containing 25,000 helium atoms and a p=4 D impurity, the calculated induced dipole moment is 1 D. Since this effect is an added shift to all doped droplet deflections, its influence on the comparison of embedded molecular dipoles is relatively minor.

III. Nanodroplet size filtering

The fact that the doped droplets are composed of an ensemble of sizes is both a complication and an opportunity. The complication, as described in the Letter, arises from the need to perform a convolution of the deflection over the droplet size distribution $P(N)$. On the other hand, if the droplets are doped with a molecule possessing a sufficiently high dipole moment, a deconvolution of the neutral droplet size distribution can be performed by the deflection process itself. Since light droplets deflect more than heavy ones, spatial filtering of the deflected beam imparts a size bias onto the transmitted doped droplet population.

This is useful, because so far size selection has been practical only for charged nanodroplets, achieved via electron or ion doping (e.g., see refs. S9 and S10). (Neutral droplet diffraction (e.g., see ref. S11) can be used only for the smallest droplets, while droplet deflection through the impact of atoms from a secondary beam (e.g., see ref. S12) is a very low-yield process.) Therefore the proposed ability to experimentally emphasize specific size segments of the deflected beam ensemble is an attractive possibility. For example, it can facilitate studies of dopants' laser or ionization spectroscopy as a function of their host droplet sizes.

To illustrate the discussion, Fig. S.1 shows the result of a deflection simulation, as described in the main text, of a beam of nanodroplets doped with CsI molecules (p = 12 D). The top panel shows the composition of the deflected beam, and the bottom panel shows its relative size enrichment R, that is, the ratio of the proportion of droplets of a certain size N found at various positions in the detector plane to the original proportion of that size in the nozzle beam:

$$R(x;N,\Delta N)=\frac{\int_{N}^{N+\Delta N} I(x;N)dN \Big/ \int_{0}^{\infty} I(x;N)dN}{\int_{N}^{N+\Delta N} P(N)dN}. \qquad \text{(S.2)}$$

Here $I(x;N)$ is the intensity of doped nanodroplets of size N at the position x in the detector plane. The figure shows that it is realistic to locate positions in the deflected beam where specific constituent sizes become more prominent or even dominant.

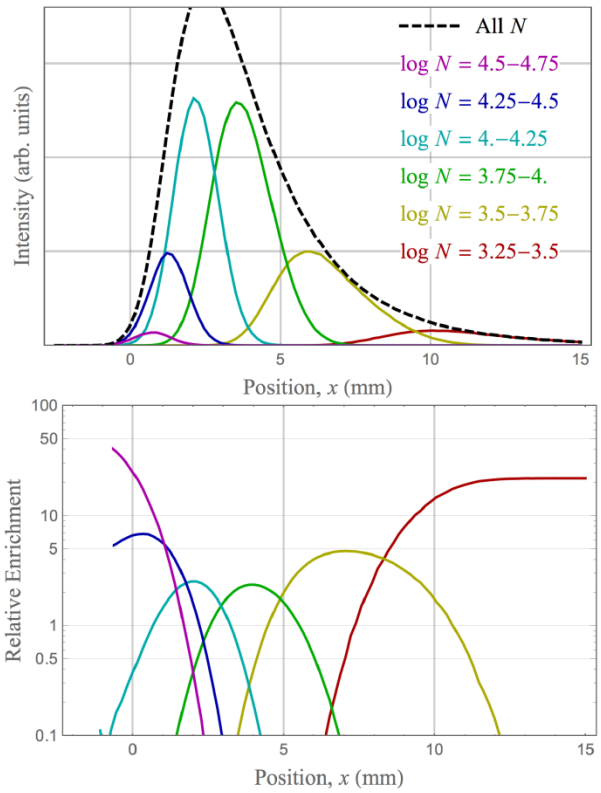

FIG. S.1. Simulated deflection of a beam of He nanodroplets with a log-normal size distribution with the average size $\langle N \rangle = 10^4$ and width $\Delta N = 6500$, doped with CsI. The undeflected beam profile has a width of approximately 1 mm. A 100 kV/cm field is applied to the deflecting plates. Lines of different colors correspond to different segments of the droplet size distribution arriving at the detector. Panel (a) shows the total beam profile and its underlying size composition, and panel (b) shows the relative enrichment of different sizes as a function of deflection position in the detector plane, Eq. (S.2).

References

[S1] Stein, S.E. Mass Spectra. In *NIST Chemistry WebBook, NIST Standard Reference Database No. 69* [Online]; Linstrom, P.J., Mallard. W.G., Eds.; National Institute of Standards and Technology: Gaithersburg. MD, 2016; http://webbook.nist.gov (accessed August 2016).

[S2] Lewerenz, M.; Schilling, B.; Toennies, J. P. Successive Capture and Coagulation of Atoms and Molecules to Small Clusters in Large Liquid Helium Clusters. *J. Chem. Phys.* **1995**, 102, 8191-8207.

[S3] Hartmann, M.; Miller, R.; Toennies, J. P. ; Vilesov, A. F. High-Resolution Molecular Spectroscopy of van der Waals Clusters in Liquid Helium Droplets. *Science* **1996**, 272, 1631-1634.

[S4] Ramsey, N. F. *Molecular Beams*; Oxford University Press: Oxford; 1956.

[S5] Tikhonov, G.; Wong, K.; Kasperovich, V.; Kresin, V. V. Velocity Distribution Measurement and Two-Wire Field Effects for Electric Deflection of a Neutral Supersonic Cluster Beam. *Rev. Sci. Instrum.* **2002**, 73, 1204-1211.

[S6] Buchenau, H.; Knuth, E. L.; Northby, J.; Toennies, J. P.; Winkler, C. Mass Spectra and Time-of-Flight Distributions of Helium Cluster Beams. *J. Chem. Phys.* **1990**, 92, 6875-6888.

[S7] *CRC Handbook of Chemistry and Physics*, 97th Ed., Haynes, W. M.; Lide, D.R.; Bruno, T. J., Eds.; CRC: Boca Raton; 2016.

[S8] Toennies, J. P.; Vilesov, A. F. Superfluid Helium Droplets: A Uniquely Cold Nanomatrix for Molecules and Molecular Complexes. *Angew. Chem. Int. Ed.* **2004**, 43, 2622-2648.

[S9] Knuth, E. L.; Henne, U. Average Size and Size Distribution of Large Droplets Produced in a Free-Jet Expansion of a Liquid. *J. Chem. Phys.* **1999**, 110, 2664-2668.

[S10] Mudrich, M.; Forkl, B.; Müller, S.; Dvorak, M.; Bünermann, O.; Stienkemeier, F. Kilohertz Laser Ablation for Doping Helium Nanodroplets. *Rev. Sci. Instrum.* **2007**, 78, 103106.

[S11] Kornilov, O.; Toennies, J. P. Matter-wave Diffraction of Quantum Magical Helium Clusters. *Europhysics News* **2007**, 38**,** 1, 22-27.

[S12] Harms, J.; Toennies, J. P.; Barranco, M.; Pi, M. Experimental and Theoretical Study of the Radial Density Distributions of Large ^{3}He Droplets. *Phys. Rev. B* **2001**, 63, 184513.