

Oriented Polar Molecules Trapped in Cold Helium Nanodroplets: Electrostatic Deflection, Size Separation, and Charge Migration

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Helium nanodroplets doped with polar molecules are studied by electrostatic deflection. This broadly applicable method allows even polyatomic molecules to attain subkelvin temperatures and nearly full orientation in the field. The resulting intense force from the field gradient strongly deflects even droplets with tens of thousands of atoms, the most massive neutral systems studied by beam “deflectometry.” We use the deflections to extract droplet size distributions. Moreover, since each host droplet deflects according to its mass, spatial filtering of the deflected beam translates into size filtering of neutral fragile nanodroplets. As an example, we measure the dopant ionization probability as a function of droplet radius and determine the mean free path for charge hopping through the helium matrix. The technique will enable separation of doped and neat nanodroplets and size-dependent spectroscopic studies.

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Introduction.—If the internal and relative motion of molecules is cooled into the subkelvin range, it becomes possible to observe and steer their reactions with precision, to determine their physical parameters and structures with high accuracy, and to use external fields to finely control their motion and orientation [1–4]. For example, buffer-gas cooling [5] can be employed as an entryway to electrostatic guiding and ultracold trapping [6,7], merged beams enable exploration of chemical reactions in the quantum regime [8], and Stark deflection of small molecules in a supersonic beam can be used to spatially separate their low rotational states and conformers [9].

While a high level of control has been demonstrated for individual small molecules, pursuing it for larger polyatomic systems becomes increasingly demanding [10]. Their rotational spectra are more congested, their degrees of freedom are less efficiently and uniformly cooled by nozzle expansion [10,11], and their higher masses reduce the deflection.

A powerful tool to cool and study molecules of a wide range of sizes is “helium nanodroplet isolation” [12–16]. Molecules are entrapped and transported by a beam of $^4\text{He}_N$ nanodroplets generated by the expansion of helium gas through a cryogenic nozzle. Nanodroplets cool by evaporation upon exiting the nozzle, reaching an internal temperature of only $T_0 = 370$ mK and turning superfluid. This temperature is set by the surface binding energy of helium atoms [17,18] and has been verified, as has the onset of superfluidity, by the rotational spectroscopy of entrapped molecules [12]. When the droplet beam passes through one or more vapor-filled cells, atoms and molecules are readily picked up, cooled by heat transfer to the helium matrix (evaporation of surface helium atoms promptly brings the

complex back to T_0), and carried along by the droplet beam.

This method is unique in being applicable to a variety of molecules and atoms: essentially all that is required for embedding is the availability of $\sim 10^{-6}$ – 10^{-4} mbar of vapor. Its other key feature is that it cools all the degrees of freedom of the dopants and ensures that only their lowest vibrational, and in some cases even rotational, levels are occupied. Quantum effects in bimolecular reactions can already become pronounced at T_0 (e.g., [19]) and may remain undisrupted by the viscosity-free superfluid matrix. Furthermore, by using sequential pickup it is possible to coembed multiple (identical or distinct) atoms or molecules in order to explore their interactions and to generate novel or metastable complexes that would be unobtainable by other means.

In the context of control and manipulation by external fields, consider nanodroplet embedding of polar molecules. The salient fact is that by cooling to T_0 in this superfluid environment, they become cold enough to strongly (often almost fully) orient themselves along an applied static electric field [20]. Their rotations transform into “pendular” states, employed in landmark spectroscopic studies [34] (see also the recent review [35]). Molecular alignment effects within helium nanodroplets also were recently demonstrated using short laser pulses [36].

Here, we subject these systems to the method of electrostatic deflection [9,37–39]. A doped nanodroplet beam passes through an inhomogeneous electric field and its resulting deflection is measured with high accuracy. The attractiveness of such a measurement is that it can be performed using a broad array of molecules (diatomic, polyatomic, complex, agglomerates) and directly yields

quantitative observables, without needing to refer to a potentially complex spectroscopic analysis.

However, two potential problems must be considered. First, deflecting neutral droplets by a measurable amount may appear simply unworkable. Indeed, in typical experiments on beams of individual polar molecules or clusters the deflection is at most by a few milliradians, more commonly a fraction of that (translating into millimeters, or fractions thereof, displacement at the detector). Consequently, loading a molecule with a massive coat of barely polarizable helium ought to result in undetectable deflections. Second, the nanodroplets are not identical. Their size distribution is generally log-normal, as is typical of particle growth processes, with a mean \bar{N} that can be shifted by varying the expansion conditions. Can this hinder a deflection experiment?

We report on two principal results. First, we demonstrate that electrostatic deflection of nanodroplets doped with polar molecules is not merely measurable, as we saw in [40], but turns out to be remarkably strong. This is due to the aforementioned orientation effect: when the dipoles' rotational motion is frozen out and they point along the field axis, the resulting great increase in the deflecting force can easily compensate for the additional helium mass. Such a robust effect, in combination with the fact that these may be the most massive (tens of thousands of Daltons) neutral beams subjected to "molecular deflectometry" to date, is noteworthy. The magnitude of the deflections implies that they can be employed for accurate measurements of the dipole moments of complex molecules and to the segregation of doped and undoped nanodroplets.

Second, we demonstrate that instead of hindering deflection analysis, droplet size spread can be turned into an informative resource. We show that deflection measurements can be employed to calibrate the nanodroplet size distribution. Even more valuably, deflection can be used to achieve droplet mass filtering, by spatially dispersing the nanodroplets according to their size. This establishes a novel way to perform spectroscopic experiments on neutral nanodroplets as a function of size. As an application and illustration of this method, we study the droplet size dependence of dopant ionization probabilities and determine the mean free path for the migration of positive charge (He^+ hole) through the liquid helium matrix.

Method.—A supersonic nanodroplet jet is generated by expanding He gas at 80 bar pressure through a cryogenic nozzle, and passes through a pickup cell positioned downstream. This methodology is described in the cited reviews, see also [40]. Dopants chosen for the present work are dimethyl sulfoxide ($\text{CH}_3)_2\text{SO}$ ("DMSO," $p = 4.0$ Debye) and CsI ($p = 11.7$ D). The beam is subsequently collimated by a $0.25 \text{ mm} \times 1.25 \text{ mm}$ slit and travels through the 2.5 mm gap between two 15-cm -long electrodes which create an inhomogeneous electric field of the "two-wire" geometry [41–43]. As formulated above,

the field orients the polar molecule while its gradient exerts a strong deflecting force on this oriented dipole. The field and gradient strengths range up to $\approx 85 \text{ kV/cm}$ and 350 kV/cm^2 , respectively.

Approximately 1.3 m past the electrodes the beam enters an electron-impact ionizer (set to 90 eV) through a 0.25-mm -wide slit, and the resultant ions are detected by a quadrupole mass analyzer. The arrival of a doped nanodroplet is registered by setting the analyzer to one of the characteristic fragment peaks of the dopant [44]. In order to isolate the beam-carried signal, the analyzer's output is read via a lock-in amplifier synchronized with a rotating wheel chopper. Additionally, the phase delay between the chopper and analyzer outputs yields the beam velocity v (which rises from 375 m/s at 15 K nozzle temperature to 415 m/s at 19 K). Importantly for deflection measurements, the velocity spread is very narrow, 1% – 1.5% [45,46]. The deflection angle of a nanodroplet is the ratio of the sideways impulse it receives while traversing the field $F_z \Delta t \propto \langle p_z \rangle (\partial \mathcal{E}_z / \partial z) v^{-1}$ to its original forward momentum mv . Since the field gradient is proportional to the deflection plate voltage V , the droplet's deflection is $d = C \langle p_z \rangle V / (mv^2)$, where C is a constant calculated from the apparatus geometry.

In monitoring the dopant peak in the mass spectrum, one needs to be certain that it is not a fragment of a larger agglomerate deriving from the pickup of multiple molecules. The probability of embedding k dopants is approximately Poissonian [12]: $P_k = \langle k \rangle^k \exp(-\langle k \rangle) / k!$. Here, $\langle k \rangle$ is the average number of pickup collisions, proportional to the vapor density. Therefore, the cell vapor pressure must be low enough for $P_{k>1}$ to remain small. For DMSO we adjust it to produce a usable monomer signal (we use the 78 amu ion peak for deflection measurements) while minimizing the corresponding dimer signal (156 amu). For CsI the procedure is analogous, reinforced by the fact that the Cs^+ peak which we use predominantly derives from dissociative ionization of the CsI monomer but not of larger clusters [47].

Deflections.—Beam profiles in the detector plane are recorded by measuring the intensity of the chosen ion peak as a function of the ionizer entrance slit position.

Our initiatory deflection measurements scanned this entrance slit in front of the quadrupole's ionizer and suggested beam deflections on the order of a few tenths of a mrad (translating into shifts of a few tenths of a mm in our apparatus) [40]. This was already substantial, but further examination revealed that the actual deflections were considerably larger: we discovered that they extended all the way to the edge of the ionizer's entrance aperture and were artificially clipped there. In order to accommodate such large displacements we now fix the slit in the middle of the aperture and place the entire detector chamber onto a precision linear slide. This enables us to obtain accurate beam profiles extending as far as $\pm 20 \text{ mm}$ (16 mrad) from

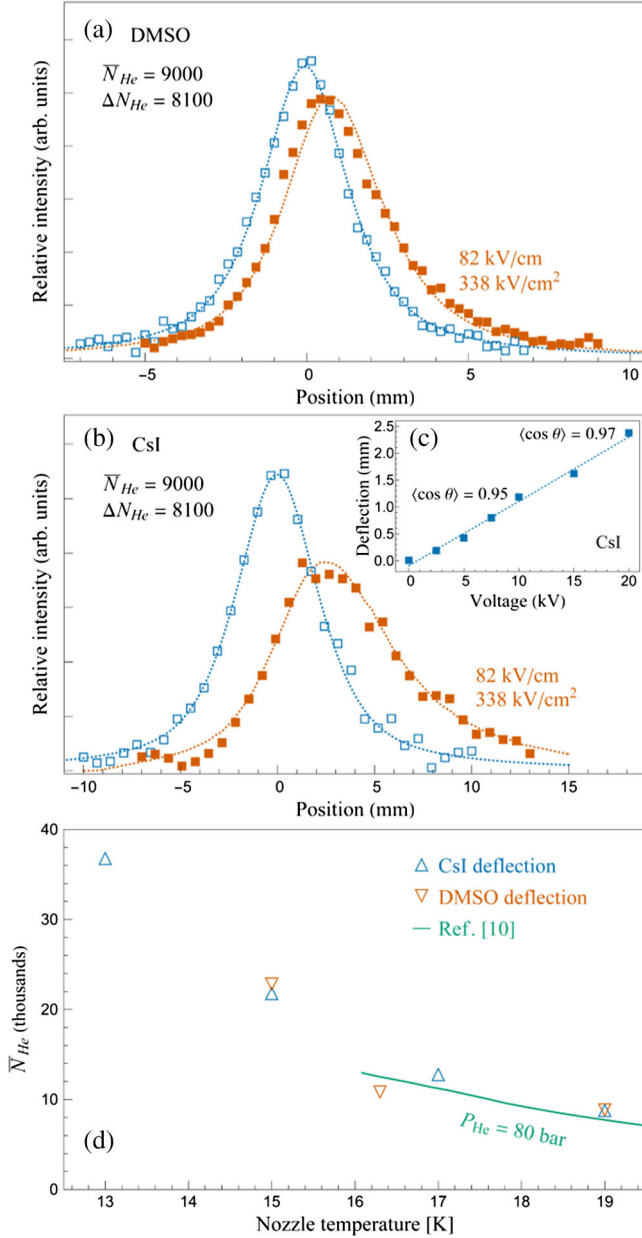


FIG. 1. (a) Deflection of He_N nanodroplets with DMSO dopant. Squares: experimental data; blue line: pseudo-Voigt function fit to the undeflected profile; red line: fit by simulation of the deflection process [20]. (b) Same for CsI dopant. (c) Average deflection of the nanodroplets beam vs electrode voltage. Its linear variation attests to the strong orientation of the cold dopant molecule along the field, cf., calculated orientation cosine labels. (d) Average nanodroplet size as a function of nozzle temperature. Symbols: mean \bar{N} of the log-normal size distribution deduced from our deflection measurements; line: data from Ref. [12]. Fit to the deflection data yielded $\Delta N/\bar{N} = 0.85$ for the FWHM of the distribution, in excellent agreement with Ref. [48].

the central axis, see Figs. 1(a) and 1(b). These figures show the deflections for a diatomic and a polyatomic dopant, both cooled to 0.37 K by immersion in the superfluid droplet, confirming the broad applicability of the technique.

Such profiles contain a wealth of information. For example, Fig. 1(c) shows that the average deflection is proportional to the deflector voltage. This is fundamentally different from the linear susceptibility regime where $\langle p_z \rangle \propto \mathcal{E}_z$ and therefore $d \propto \mathcal{E}_z (\partial \mathcal{E}_z / \partial z) \propto V^2$, as commonly observed in cluster beam experiments [37–39]. The dependence plotted here implies saturated susceptibility and provides unambiguous proof that the dopant dipoles are strongly oriented by the applied field [20].

Nanodroplet sizes and size filtering.—Each measured profile represents the convolution of single nanodroplet deflections with (a) the distribution of droplet masses, (b) the distribution of their pickup and ionization cross sections, and (c) the shape of the original undeflected beam. By fitting these profiles to a simulation of the pickup, deflection, and detection steps [20], we deduce the mean \bar{N} and the width ΔN of the droplet size distribution produced by the nozzle. As shown in Fig. 1(d), these parameters are in excellent agreement with the standard literature values [12,48]. This both validates our analysis and extends the droplet size calibration curve.

An inspection of Figs. 1(a) and 1(b) reveals that the electric field not only shifts the doped droplet beam profile, but also makes it asymmetric. The reason is that smaller, lighter droplets deflect stronger than larger, heavier ones. This immediately suggests that spatial filtering of the deflected beam will translate into size filtering of the neutral nanodroplets.

The ability to scan through nanodroplet sizes within the same beam and within a single experiment is highly appealing, making it possible to explore the influence of droplet size on the spectroscopy and dynamics of embedded molecules. Compared to milestone experiments on droplet sizing by crossed-beam scattering [48,49], here the deflection angles, the size range, and the intensity of the deflected beam are all markedly higher.

Charge migration.—To illustrate this capability, we investigate charge migration as a function of droplet size. Consider the steps involved in electron-impact ionization of doped droplets [50,51]. Since helium atoms surround and greatly outnumber the dopant, an electron strike predominantly results in the creation of a He⁺ ion. The positive hole then resonantly hops from one adjacent helium atom to another, toward the impurity in the middle, until one of two outcomes occurs: it “self-traps” by forming He₂⁺ followed by the nucleation of larger He_n⁺ cluster ions, or it reaches and ionizes the dopant. Both outcomes are accompanied by significant energy release which boils off the helium and ejects the ion from the nanodroplet [16].

It follows that the probability of dopant ion formation can be viewed according to Beer’s law: $P_m = \exp(-\mathfrak{R}/\lambda)$, where \mathfrak{R} is the distance which the positive charge needs to travel before reaching the impurity and λ is its mean free path before self-trapping. Since $\mathfrak{R} \sim$ droplet radius R (see below), a measurement of P_m as a function of droplet size will yield the important physical parameter λ .

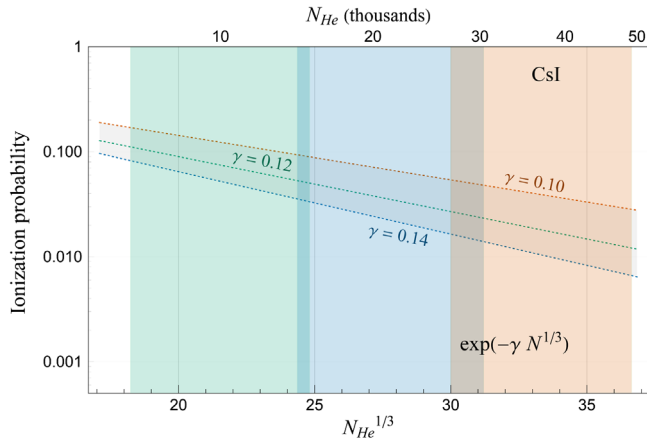


FIG. 2. Probability of ionizing charge transfer to embedded CsI molecules as a function of nanodroplet size. This probability was determined by a fit to the electric deflection profiles which spatially disperse nanodroplets according to their mass, as described in the text. The displayed size range was covered by measurements at three nozzle temperatures (13, 15, and 19 K) corresponding to average droplet sizes \bar{N} of 3.7×10^4 , 2.2×10^4 , and 9×10^3 atoms, respectively [see Fig. 1(d)]. At each of these temperatures the beam contained a log-normal distribution of droplet sizes which then spread out spatially upon deflection. This allowed the data to span a range of sizes, as marked by the three (overlapping) bands of color. For each of those bands the probability of dopant ion formation was fitted to the form $P_m \propto \exp(-\gamma N^{1/3})$. The results are depicted as dashed lines in the figure, color matched to the size band from which the corresponding value of γ was derived. The lines extend into neighboring bands in order to show the range of uncertainty in their slope; the fact that they are close demonstrates the consistency of the analysis.

The concept of the measurement is as follows. If a droplet undergoes electric deflection, this automatically implies that it carries an impurity molecule. However, in the mass spectrum it can register either at the impurity mass or at the helium fragment mass. The ratio between these two outcomes, which is precisely P_m , can be traced as a function of the droplet’s deflection—i.e., of its size.

We developed a procedure to subtract the undoped beam’s contribution to the signal and to fit the dopant ion yield to the exponential form $P_m \propto \exp(-\gamma N^{1/3})$ [20]. Figure 2 assembles the results of measurements using CsI doping performed at three nozzle temperatures, i.e., for strongly distinct \bar{N} . Accordingly, it spans a wide range of droplet sizes N . It is therefore satisfying that over this full range practically the same value of γ ($\pm 17\%$) is found, as anticipated for the ionization pathway described above.

To relate γ to the mean free path, we need to estimate \mathfrak{R} . The He^+ hole is originally created at a random location within the droplet [51]. For its subsequent motion, two models can be considered. One [52] assumes that the positive charge hops radially inwards, the other (similar to [53]) that it hops along the dipole’s electric field lines all the

way from its initial location to the molecule’s negative end. Simulating both scenarios and assuming that the dopant occupies a cavity of ≈ 4 Å radius [54] at the center, we find $\mathfrak{R} \approx 0.7R$ for the former case [56] and $\mathfrak{R} \approx 1.0R$ for the latter. (This neglects the density gradient near the droplet surface which should not appreciably affect the estimation of the mean free path λ [52].) With $R = 2.22N^{1/3}$ Å [12], this translates into $\mathfrak{R} \approx (1.6\text{--}2.2)N^{1/3}$ Å for the two models, respectively, or $\lambda \approx (1.6\text{--}2.2)/\gamma$ Å.

Using the CsI pickup data from Fig. 2 we arrive at $\lambda \approx 16$ Å. (Measurements using DMSO, less accurate and more limited in the spread and assignment of droplet sizes because of its smaller dipole moment and weaker deflections, yielded $\lambda \approx 34$ Å.)

These values are similar to the estimates of 28–35 Å for droplets doped with HCN and HCCCN, found in [52,53] by a very different method: optically selective mass spectrometry. This confirms that our technique is well suited to the task of determining size-dependent parameters of nanodroplet behavior. The referenced estimates are larger than λ determined here for CsI, but they were deduced for beams centered at considerably smaller average droplet sizes and containing broad size distributions. This skews the deduced ionization probability, because when the distribution is broad the smaller droplets within it will yield a higher proportion of the impurity ions. This is avoided in the present approach which scans through much narrower nanodroplet size groupings by spreading out the full distribution along the deflection axis.

Conclusions.—Cold polar molecules entrapped within superfluid helium nanodroplets can be nearly fully oriented by an external electric field. We showed that this can be exploited in beam deflection experiments. Since the electrostatic deflecting force experienced by an oriented molecular dipole becomes extremely large, we observed that an entire beam of massive nanodroplets, containing up to tens of thousands of He atoms, deflects by impressively large angles.

As demonstrated here, if nanodroplets carry a molecule with a known dipole moment the deflection measurement can be used to calibrate the droplet size distribution in the beam. Conversely, by comparing the deflections of a beam doped with a reference molecule and the same beam doped with another species, one can “read out” the dipole moment of the latter in a model-free approach. Since, as emphasized, nanodroplet embedding is applicable to a broad range of molecules (in particular, polyatomic and biological) this introduces a correspondingly broad method of measuring molecular dipole moments. (Note that direct measurements on isolated complex molecules began only recently [37] and many tabulated values still come from liquid phase data with potentially significant uncertainties [57].)

The same approach can be employed with interesting and unusual agglomerates produced via sequential pickup

(this also is a unique capability of helium nanodroplet embedding). For example, it can detect the formation of novel metastable assemblies of cold polar molecules, as we have demonstrated for DMSO dimers and trimers [58]. It should also be usable for the identification of polar vs nonpolar conformers (cf., [37]).

Speaking of molecular characterization, it should also be possible to use strong electrostatic deflections to separate doped and undoped nanodroplets, which is important for emerging applications aiming at structural analysis of embedded molecules by x ray, EUV, and electron pulses [15,59–61].

Finally, we pointed out that since the deflection angle of a doped nanodroplet depends on its mass, the broad size distribution contained within the original beam becomes spatially spread out by the time it reaches the detector plane. In other words, the deflection process disperses the He_N population and establishes a means to probe the behavior of neutral nanodroplets as a function of their size N . To illustrate this, we measured how the dopant ion yield varies with droplet radius, and thus determined the mean free path for the migration of positive charge through the helium matrix. This droplet size-filtering technique will make possible size-resolved spectroscopy of cold dopants and dopant reactions.

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