COLD MOLECULES

A cryofuge for cold-collision experiments with slow polar molecules

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Ultracold molecules represent a fascinating research frontier in physics and chemistry, but it has proven challenging to prepare dense samples at low velocities. Here, we present a solution to this goal by means of a nonconventional approach dubbed cryofuge. It uses centrifugal force to bring cryogenically cooled molecules to kinetic energies below 1 K ×kB in the laboratory frame, where kB is the Boltzmann constant, with corresponding fluxes exceeding 10^15 per second at velocities below 20 meters per second. By attaining densities higher than 10^13 per cubic centimeter and interaction times longer than 25 milliseconds in samples of fluoromethane as well as deuterated ammonia, we observed cold dipolar collisions between molecules and determined their collision cross sections.

Here, we present a nonconventional solution, dubbed cryofuge, that delivers a guided beam of cold and slow molecules. Cryofuge denotes successive cryogenic buffer-gas cooling (20–22) and centrifuge deceleration (23). Because neither step involves the specific internal structure of the molecules, this renders the method generic. We demonstrate the capabilities of the cryofuge by showing internal-state cooling and deceleration of fluoromethane (CH₃F). We illustrate the generality of the method by extension to several other compounds, including ammonia (ND₃), methanol (CH₃OH), (trifluoromethyl)acetylene (CF₃CCH), and isopropanol (C₃H₇OH). The high intensities achieved at laboratory velocities below 20 m/s allow for molecule interaction times exceeding 25 ms and thus enable the observation of cold dipolar collisions with a measured collision rate of ~10 Hz, which we demonstrate with CH₃F and ND₃.

The operating principle of the cryofuge is illustrated in Fig. 1. Warm molecules first thermalize with a helium or neon buffer gas in the cryogenic buffer-gas cell. Cell operation is possible in two density regimes, a lower-pressure boosted regime and a higher-pressure supersonic regime (22, 26), resulting in either higher total flux or higher state purity, respectively. Molecules are extracted from the cryogenic environment by means of a bent electrostatic quadrupole guide (radius of curvature, 20 cm) and transferred with a straight guide to the centrifuge decelerator. Here, the molecules enter a rotating guide in which the centrifugal potential slows them down almost to a standstill. A final straight guide brings the molecules to a quadrupole mass spectrometer (QMS) for detection.

Inserting an optional parallel-plate capacitor with radio-frequency strip electrodes and a removable QMS into the guide, before the centrifuge, enables probing of rotational states with resonant depletion spectroscopy, as described in (26). Moreover, the straight guide between the centrifuge output and the QMS detector can be toggled on and off to determine longitudinal velocities (v∥) via time-of-flight (TOF) measurements. Varying the guiding voltage, and hence the trap depth, on the straight guide before the centrifuge can control molecular densities for cold collision measurements after deceleration.

We first studied rotational-state cooling of CH₃F, tracking the variation of the internal state distribution as a function of the buffer-gas density for the boosted (Fig. 2A) and the supersonic (Fig. 2B) regimes. In both cases, a higher buffer-gas density results in a higher state purity, with an increasing population in the |J,K⟩ = |1,1⟩ ground level of the para nuclear spin states. We achieved a maximum population of (43.2 ± 0.3)% and (92.9 ± 0.5)% in the |1,1⟩ state of CH₃F in the boosted and supersonic regime, respectively.

An inherent problem of buffer-gas cooling in both of these regimes is that slow molecules are missing in the extracted samples because of collisions with the buffer gas in the vicinity of the nozzle. This is resolved with the centrifuge. The deceleration of CH₃F for cell operation in the boosted regime is illustrated in Fig. 3A. The two-dimensional (2D) map shows the variation of the output v₅-distributions (horizontal axis) as a function of the centrifuge rotation speed (vertical axis). Two effects are apparent. First, the peak of the v₅-distribution shifts toward lower velocities with increasing rotation speed, as expected for deceleration. Second, the molecular density increases for rotation speeds below 30 Hz and then decreases. The increase comes from deceleration, with more molecules surviving the small bend (radius, 5 cm) at the exit of the centrifuge. The decrease of density toward higher rotation speeds is due to over-deceleration, with the molecules no longer having sufficient kinetic energy to climb the centrifugal potential and reach the output of the centrifuge (33).

The deceleration of a beam in the supersonic regime is shown in Fig. 3B, where the measured v₅-distributions at both the input and the output of the centrifuge are compared. The fit to the input distribution indicates a peak velocity of 165 m/s and a velocity spread corresponding to 3.3 ± 0.1 K in the comoving frame. By rotating the centrifuge at 62 Hz, the v₅-interval near the peak of the input distribution (Fig. 3B, red stripe) is shifted to below 1 K × kB kinetic energy in the laboratory, where kB is the Boltzmann constant (Fig. 3B, blue area). Because the vertical scale Δv₅/Δv₅ is proportional to the phase space density, the ratio of the two heights gives the output efficiency of the centrifuge deceleration, which is ~8% for the supersonic input. For a boosted input, the efficiency improves to typically 20% because of the lower input velocities and
hence better electrostatic guiding in the centrifuge. The decrease of signal toward zero velocities is due to the divergence of the very slow molecules in the gap between the centrifuge output and the TOF guide, as confirmed with Monte-Carlo trajectory simulations.

A key figure of merit is the flux of slow ($<1 \times k_B$) molecules obtained. Such molecules are required for trap loading as well as for cold-collision studies and cold-chemistry experiments with long interaction times. The flux of slow molecules obtained in the boosted [with molecule input at 0.1 and 0.2 standard cubic centimeters per minute (sccm)] and the supersonic regime are shown in Fig. 3C. At 0.2 sccm in the boosted regime, we have obtained a slow-molecule flux of $(1.2\pm0.2) \times 10^{10} \text{s}^{-1}$, with a peak density of $(1.0\pm0.1) \times 10^{9} \text{cm}^{-3}$ at 30 Hz rotation. The factor-of-two error results from systematics in the QMS sensitivity calibration. Compared with the first demonstration of centrifuge deceleration (29), the current results represent an enhancement by at least one order of magnitude in the obtained slow-molecule flux and density alone, and about three orders of magnitude if population in a single quantum state is taken into account. The phase-space density is estimated to be $-5 \times 10^{-16}$, which is comparable with the value achieved for a molecular magneto-optical trap (30), but now already for temperatures around 1 K instead of $<1 \text{mK}$. In comparison, the flux of slow molecules obtained in the supersonic regime is about 40 times smaller, mainly because of the limited buffer-gas cell extraction and the lower guiding efficiency.

The generic principle underlying the cryofuge enables its application to a wide range of compounds. For ND$_3$ and CF$_3$CH$_2$, which are symmetric-top molecules and CH$_3$F, fluxes of $-1 \times 10^{10} \text{s}^{-1}$ and densities of $-1 \times 10^9 \text{cm}^{-3}$ have been obtained below 1 K $< k_B$ kinetic energy. We have also applied the cryofuge to methanol and isopropanol. For methanol, a flux of $-3 \times 10^9 \text{s}^{-1}$ at a peak velocity of 40 m s$^{-1}$ and $-1 \times 10^7 \text{s}^{-1}$ below 1 K $k_B$ was produced (Fig. S2). The comparably lower flux results from both the weaker Stark shifts (27) and the much lower vapor pressure of methanol. We have achieved a similar flux of $-1 \times 10^9 \text{s}^{-1}$ for isopropanol, but maintaining stable operation requires additional effort because isopropanol is prone to freezing owing to its even lower vapor pressure. The high density of the decelerated molecules brings us into the cold-collision regime, which we investigated for CH$_3$F and ND$_3$. We observed increasing losses for decreasing velocities in the molecular beams (Fig. 4) and attribute this to dipolar collisions mainly in the TOF guide.

To quantify the collisional loss, we examined its dependence on the molecular density $n$ and the longitudinal velocity $v_z$ of the guided beam, as well as on the averaged dipole moment $\mu$ of the molecule. The $v_z$ dependence occurs because the collision probability is proportional to the passage time through the guide, hence $\approx 1/v_z$. Shown in Fig. 4 are the normalized ratios of $v_z$ distributions taken at high and low molecule densities corresponding to a density difference $\Delta n$, set by varying the voltage on the straight guide before the centrifuge. In addition, for a fixed voltage difference, $\Delta n$ can be tuned by regulating the molecule inflow to the cryosource. For guided beams, the collisional loss modifies the original $v_z$ distribution $P(v_z)$ into $P = \frac{1}{v_z} \frac{1}{V_{ceff}} \frac{1}{L_{ceff}} \frac{1}{D}$, where $k_{loss} = \sigma_{loss} V_{tot}$ is the loss rate coefficient—with $\sigma_{loss}$ being the total collision cross section for all loss channels and $v_{tot}$ being the relative velocity between colliding partners—and $L = L_{TOF} + L_{ceff}$ is the guide length. $L$ includes the contribution from the TOF-guide $L_{TOF} = 46 \text{cm}$ and additionally an effective guide length inside the centrifuge $L_{ceff}$. The latter takes into account the variation of

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**Fig. 1. Schematic illustration of the cryofuge (not to scale).** A cryogenic buffer-gas cell and a centrifuge decelerator are connected by a quadrupole electrostatic guide. The buffer-gas cell operates with either He at 6.5 K or Ne at 17 K. The centrifuge decelerator consists of a pair of circular static electrodes (radius, 20 cm) around the periphery (silver) and a spiral-shaped rotating quadrupole guide (red). The inner pair of rotating electrodes is extended to form a storage ring with the static electrodes around the periphery, enabling the deceleration of continuous beams. The optional components, a parallel-plate capacitor and a detector, can replace the straight guiding segments (blue), when characterizing the internal-state distribution of the buffer gas–cooled molecules by means of resonant radiofrequency depletion spectroscopy. The asterisk indicates methanol was introduced at 400 K.

**Fig. 2. Measured rotational-state mapping of CH$_3$F in an electrostatic guide, as a function of the buffer-gas flux.** (A) Buffer-gas cooling in the boosted regime (with a moderate He inflow at 6.5 K). Unit of gas flow, 1 sccm = $4.1 \times 10^{17} \text{s}^{-1}$. The left axis labels the rotational states $|J,K\rangle$ in ascending order in energy. The seven lowest states with substantial guided population are shown. The vertical scale shows the relative population of each probed state in the guide. (B) Buffer-gas cooling in the supersonic regime (with a much higher Ne inflow at 17 K). The error bars of the measured populations in (A) and (B) are all below 0.6%, and are not visible in the plots.
from both elastic and inelastic contributions, static filtering in the bent guide (fig. S3). A collision-independent background, which is the only fit parameter that accounts for the deviation between theory and the experimental data reveals the theoretical values and the model accounts for all inelastic losses and uses a factor of 0.2. A comparison of these elastic rate coefficients is presented in the supplementary materials.

Not all elastic collisions contribute to losses, but only those that increase the transverse energy to a value exceeding the maximum guiding potential. With this in mind, we compute the probability for a molecule to be lost for a given collision event with scattering angle θ, relative longitudinal velocity vz, and relative transverse velocity and radial position where the collision occurs. We then integrate this loss probability over the transverse velocity and spatial distribution to obtain \( P_{\text{loss}}(v_z^\perp, \theta) \) (fig. S5A). We also calculate the differential cross section \( \frac{d\sigma}{d\Omega} \) for the dipole interaction (fig. S5C).

The elastic loss cross section is then \( \sigma^\text{el}_{\text{loss}}(v_z^\perp) = 2\pi \int d\theta \sin \theta P_{\text{loss}} \frac{d\sigma}{d\Omega} \). For the inelastic loss, it has been suggested that the presence of an external electric field could induce pronounced orientation-changing collisions between polar molecules (30, 31). As an estimate, we assume the Langevin model accounts for all inelastic losses and use it to compute \( k^\text{th} \). A comparison of these \( k^\text{el}_\perp \) and k^th dependent rate coefficients is presented in the supplementary materials.

With the averaged dipole \( d_{CH_3F} = 0.56 \text{D} \) and \( d_{ND_3} = 0.77 \text{D} \) in our decelerated beams, we obtain the theoretical values \( k^\text{th}_{\text{CH}_3\text{F}} = 7.7 \times 10^{-10} \text{cm}^3\text{s}^{-1} \) and \( k^\text{th}_{\text{ND}_3} = 1.3 \times 10^{-9} \text{cm}^3\text{s}^{-1} \) at 0.8 K × \( k_\text{B} \) and 1.1 K × \( k_\text{B} \) collision energy, respectively. The fit to the data reveals \( \sigma^\text{CH}_3\text{F} = 1.4 \pm 0.1 \) and \( \sigma^\text{ND}_3 = 1.6 \pm 0.3 \), meaning that the measured loss rate coefficients are between 40 and 60% larger than theory, respectively. This deviation can be attributed to our underestimation of molecular...
density in the centrifuge and the imprecision of the Langevin model. Although the total elastic cross sections are large, calculated to be $\sigma_{\text{cal}} = 2.0 \times 10^{-12} \text{cm}^2$ and $\sigma_{\text{el}} = 2.5 \times 10^{-12} \text{cm}^2$, the loss ratio is small, with $\sigma_{\text{loss}}/\sigma_{\text{total}} = 6\%$ for both cases. Only 1 out of 17 elastic collisions leads to loss.

For dipolar collisions, the semiclassical calculation predict a rate coefficient $k \approx d^2$. Hence, we expect $k_{\text{ND}_3}/k_{\text{CH}_3F} = d_{\text{ND}_3}^2/d_{\text{CH}_3F}^2$ to be $=1.9$. This agrees nicely with the experimental value $k_{\text{ND}_3}/k_{\text{CH}_3F} = 1.9 \pm 0.4$. The systematic error from the density calibration cancels out in this ratio for reasons explained in the supplementary materials.

Last, to show that we indeed explored the onset of the huge and long-range dipolar interaction between cold polar molecules, we compare its strength $V_{\text{dip}}(r) = -d^2/4\pi a_0 r^3$ to that of the van der Waals interaction $V_{\text{vdW}}(r) = -C_6/r^6$, where $C_6$ is the dispersion coefficient and $r$ is the intermolecular distance. The $C_6$ values for CH$_3$F-CH$_2$F and ND$_3$-ND$_3$ collisions estimated from the London formula (34) are 100 and 55 atomic units (a.u.) (1 a.u. = $1E_0a_0^6$, where $E_0 = 4.36 \times 10^{-18}$ J and $a_0 = 0.529$ Å), respectively. At the distance $r_0 = \sqrt{\sigma_{\text{loss}}/\pi} \approx 4$ nm for $\sigma_{\text{loss}} \approx 0.5 \times 10^{-32}$ cm$^2$ (table S4), $V_{\text{dip}}(r_0)/V_{\text{vdW}}(r_0) \approx 200$, and thus the dipole-dipole interaction dominates by far.

The measured molecular density and the elastic collision rate give a collision frequency of ~10 Hz, which would imply a thermalization rate of ~1 Hz (35). Thus, once combined with the previously developed and readily compatible electrostatic trap featuring minute-long trapping times (17, 25), it becomes possible to measure thermalization rates for different internal states and collision energies as well as various molecular species. Furthermore, implementing optoelectrical Sisyphus cooling (36) to reach a lower temperature in such a trap might allow us to explore the scattering resonance at the threshold limit (32) and the giant dipolar collision cross sections in or close to the quantum regime and possibly even implement evaporative cooling of polyatomic molecules.

In addition to enabling the observation of cold dipolar collisions, the broad versatility of the cryofuge could drastically extend the scope of current cold-molecule research. For instance, the cold and slow beam of methanol we produced could be ideal for measuring variations in the proton-to-electron mass ratio (37). Moreover, the cryofuge could serve as a perfect source for ongoing experiments with laser-cooled diatomic molecules (36, 38) because many of the species considered there possess rotational states with Stark shifts sufficiently large to apply our cryofuge technique.

REFERENCES AND NOTES

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SUPPLEMENTAL MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S7

Table S1 to S4

References (38–48)
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Cooling molecules in the spin cycle
A block of ice might look solid, but the molecules inside it are shaking vigorously. Slowing molecules all the way down in the laboratory offers enticing prospects to study and apply their quantum behavior. However, methods to cool dense samples to the necessary temperatures below 1 K have tended to be restricted to rather specialized diatomics. Wu et al., present a general cooling technique that applies to a wide range of conventional polar molecules such as methanol, fluoromethane, and ammonia. Their apparatus combines a preliminary cooling step in a buffer gas with a centrifuge that spins the molecules down using electric fields.

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