Rotational relaxation of fluoromethane molecules in low-temperature collisions with buffer-gas helium

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We propose a method to study the rotational relaxation of polar molecules [here taking fluoromethane (CH₃F) as an example] in collisions with 3.5 K buffer-gas helium (He) atoms by using an electrostatic guiding technique. The dependence of the guiding signal of CH₃F on the injected He flux and the dependence of the guiding efficiency of CH₃F on its rotational temperature are investigated both theoretically and experimentally. By comparing the experimental and simulated results, we find that the translational and rotational temperatures of the buffer-gas cooled CH₃F molecules can reach to about 5.48 and 0.60 K, respectively, and the ratio between the translational and average rotational collisional cross sections of CH₃F-He is γ = σr/σt = 36.49 ± 6.15. In addition, the slowing, cooling, and boosting effects of the molecular beam with different injected He fluxes are also observed and their forming conditions are investigated in some detail. Our study shows that our proposed method can not only be used to measure the translational and rotational temperatures of the buffer-gas cooled molecules, but also to measure the ratio of the translational collisional cross section to the average rotational collisional cross section, and even to measure the average rotational collisional cross section when the translational collisional cross section is measured by fitting the lifetime of molecule signal to get a numerical solution from the diffusion equation of buffer-gas He atoms in the cell.

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I. INTRODUCTION

The buffer-gas cooling technique is based on collisional cooling of thermal molecules (atoms) with cold buffer gas, which works by dissipating the energy of the molecular (atomic) ensemble via elastic collisions with cryogenically cooled helium (or neon) atoms, and directly cools molecules into the kelvin-temperature regime [1]. In 1998 the first cold cooled helium (or neon) atoms, and directly cools molecules (atomic) ensemble via elastic collisions with cryogenically cooled helium atoms, indicating that compared with the translational or rotational degrees of freedom, thermalizing the vibrational degrees of freedom requires more collisions. Recently, Kozyryev and co-workers studied the vibrational relaxation of strontium monohydroxide (SrOH) molecules in collisions with 2 K He atoms [24], they found that the vibrational quenching proceeds relatively quickly, and efficiently thermalize vibrational degrees of freedom with low frequency vibrational modes (ω < 600 cm⁻¹) at the time scales of ~1 ms. The measured vibrational collisional quenching coefficient of γ₁₀₀ = σr/σt = 700 was found in SrOH-He collisions. For the translational cooling of molecules, a typical helium-molecule diffusion elastic cross section is on the order of ~10⁻¹⁴ cm² [1]. At low temperatures a typical rotational quench needs about 10–100 elastic collisions, while it needs more than 10⁸ elastic collisions for a vibrational quench [27,28]. De Lucia and co-workers first measured the rotational cross sections of He-H₂S and He-NO over a 1–40 K temperature range [21,22]. Typical values were on the order of 5 ~10 × 10⁻¹⁶ cm² at ~4 K, which is about 10–20 times smaller than a typical diffusive cross section at the same temperature.

Here we demonstrate a scheme to study a rotational relaxation of CH₃F molecules in low-temperature collisions with 3.5 K He atoms. The buffer gas effectively thermalizes the translational and rotational temperatures of the target molecules. The derived ratio between the translational collisional cross section and average rotational one of CH₃F-He is about 36. The slowing, cooling, and boosting effects of the
guided molecular beam with different injected flux of helium are also observed. In Sec. II, the experimental setup and data acquisition are described. In Sec. III, the stark shift of CH₃F molecules in the external electric field is calculated. In Sec. IV, we characterize the electrostatically guided molecular beams that are cooled directly by the collisions of CH₃F with various fluxes of the cryogenically cooled He atoms and adiabatic cooling of the output CH₃F beam as the boosting effect appears. Some main results and conclusions are summarized in the final section.

II. EXPERIMENTAL APPARATUS AND DATA ACQUISITION

Our experiment is based on a copper buffer-gas cell that is thermally anchored to the cold head of a pulse-tube cooler (Cryomech PT415), which can keep the cell at a temperature of \( \sim 3.5 \) K. Inside the cell, the CH₃F molecular beam is injected by a copper capillary pipe. In order to maintain a sufficiently high vapor pressure and avoid freezing of molecules, the molecular gas line is heated to a temperature of 215 K by a temperature controller.

The buffer-gas He atomic beam is continuously injected into the cell via the other gas fill line, which contains several windings to increase the length and reduces the heat conductance of the gas line to cool down the helium sufficiently. Since the He atoms need to be cooled down to 3.5 K before they enter into the cell, the buffer-gas fill line is tightly wound on the copper cylinder mounted on the first stage of the refrigerator for precooling of the helium gas to 33 K. It then enters into the volume enclosed by the outer radiation shield and mounted to the second stage of the refrigerator with a good thermal contact. The buffer-gas fill line consists of the copper pipe with a length of about 10 m and an outer and inner diameter of 2 mm and 1 mm, respectively; its good thermal contact and long, winding structure ensure that the helium beam is cooled down to 3.5 K before entering into the cell. The copper cell is a cuboid structure with an inner diameter of 25 mm and a length of 38 mm and surrounded by 3.5 K radiation shields, and the diameter of a nozzle at the cell outlet is 3 mm. Activated charcoal on the inner surface of the shields can absorb helium atoms and molecules to maintain high vacuum in the beam outlet area. When the refrigerator has reached 3.5 K, the pumping speed of activated charcoal is about \( 2.1 \times 10^5 \) L/s, which is much more efficient than the turbo molecular pump. The injected gas flows are controlled by mass flow controllers and the flux adjust range is 0.05–5.00 standard cubic centimeters per minute at STP (SCCM). The He flow flux at the outlet of the cell is given by [1]

\[
f_{\text{out}} = \frac{1}{2} n_{\text{cell}} \bar{v}_{\text{cell}} A_{\text{aperture}},
\]

where \( n_{\text{cell}} \) and \( \bar{v}_{\text{cell}} \) are the stagnation number density of the He atoms and the mean thermal velocity inside the cell, and \( A_{\text{aperture}} \) is the exit area of the cell. At the steady state \( f_{\text{out}} = f_{\text{in}} \), where \( f_{\text{in}} \) is the injected He flux; therefore, the number density of the He atoms can be derived as

\[
n_{\text{cell}} = \frac{4f_{\text{in}}}{A_{\text{aperture}} \bar{v}_{\text{cell}}},
\]

Then by controlling the mass flow controller, an adjustable buffer-gas density of \( 1 \times 10^{14} \) to \( 1 \times 10^{16} \) cm\(^{-3}\) inside the cell can be obtained precisely.

Between the main chamber and the detection one there is a differential pumping stage to preserve a low background pressure in the detection chamber during the measurement process. The main chamber and the detection one are pumped by two turbo molecular pumps with a pumping speed of 1000 L/s and 80 L/s, respectively. In buffer-gas cooling experiments, with the increase of inputted He flux, the transverse and longitudinal velocities of the output molecular beam will be increased and its rotational temperature will be reduced due to the increasing collision number, and then both the changes of the transverse velocity and the rotational temperature will determine the guiding efficiency of the electrostatic quadrupole guide when the guiding voltage is unchanged. So in order to greatly reduce the influence of the transverse velocity on the guiding efficiency, two collimators with an aperture diameter of 2 mm are placed in front of the cell, and the gap between the first collimator and the buffer-gas cell is 13 mm. To extract cold polar molecules from the cell, a straight electrostatic quadrupole guide segment is placed in front of the exit aperture of the second collimator, as shown in Fig. 1. The gap between the second collimator and the first guide is about 2 mm to prevent discharge. The guide segment is made of four stainless steel rods with a diameter of 2 mm and a surface-surface separation of 1 mm, and a two-dimensional quadrupole field configuration is formed when positive and negative voltages are applied on the neighboring electrodes (see Fig. 1). The total electrostatic guide consists of two quadrupole segments, separated by a 1 mm gap. The first segment is located in the vacuum vessel with a length of 210 mm and the second segment is located in the high-vacuum detection region with a length of 340 mm. After being thermalized with 3.5 K helium and extracted out of the cell along with continuously flowing helium, the cold polar molecular beam is guided by a hollow electrostatic quadrupole field and then detected by quadrupole mass spectrometry (QMS, QMG 700). This analyzer with a time resolution of 500 \( \mu \)s provides an ion counter, which is used to determine the flux and density of the guided molecular beam. To distinguish the QMS signal from the background, the first segment of the guide is connected with two high-voltage switches (HTS 301, MOSFET Push-Pull Switch, Behlke). Transistor-transistor logic pulses generated by a DIO64 card are applied to set the high-voltage switches on (200 ms) and off (300 ms) repeatedly. After switching on the guiding electric fields, it takes a while until the QMS signal starts rising, i.e., until the fastest molecules arrive. This delay time corresponds to the time of flight (TOF) of the fastest molecules from the cell aperture to the QMS detection volume, and then a TOF signal is generated. The second segment of the guide is permanently switched on to avoid pickup currents on the QMS. Between the second segment of the guide and the ion source of the QMS, there is a grounded grid mesh for further protection. By switching the high voltage on and off repeatedly, TOF signals of guided molecules are generated as shown in Fig. 2(a). Based on the delay time, which is corresponding to the rising slope of the TOF signal after switching on the high voltage, the longitudinal velocity of molecules can be derived by differentiation [29,30]. The velocity distribution of
FIG. 1. Schematic diagram of buffer-gas cooling experimental setup. The helium is injected into the cell through the buffer-gas fill line which is thermally connected to the 33 and the 3.5 K stage, respectively. The heated molecular line is connected to a special inlet assembly, which has a bad thermal connection to the buffer-gas cell through a polyimide tube. This allows for the heating of the molecular fill line up to 215 K without affecting the temperature of the buffer-gas cell much. Outside of the buffer-gas cell, the helium atoms and molecules are pumped away by activated charcoal. After extracted from the buffer-gas cell, the molecular beam is first collimated by two collimators, then guided by two segments of quadrupole electric fields to the detection area and detected by QMS. The inset illustration in the upper right corner shows the electric field distribution of cross sectional area for ±4 kV high voltage applied on the electrodes.

FIG. 2. (a) TOF signals of guided cold CH$_3$F beams; high voltages applied on the quadrupole guide are ±4 kV, respectively. The inset illustration in the upper right corner shows the TOF rising slope after switching on the high voltage, which is applied on the first segment of the quadrupole guide. (b) Velocity distribution of guided cold CH$_3$F beams obtained by differentiation. The forward velocity of the maximum probability density is at 103 m/s and the FWHM of the velocity distribution is 73 m/s, corresponding to a translational temperature of 5.48 K. The error bars in the graph denote statistical errors.

In order to manipulate cold molecules accurately, the response of the molecules to the external electric field, namely, the Stark effect, should be known. As we all know, the external electric field in the laboratory is much weaker than the molecular internal electric field, and its effect on the electron cloud distribution is negligible [31]. In the Born-Oppenheimer approximation, the period of nuclear vibration is shorter than that of nuclear rotation, so the dipole moment of the molecule in a given rotational state is the vibronic expectation value of the first moment of the charge. As follows, we will consider only the influence of the external fields on the molecular rotational levels. In this paper, a symmetrical top vibrational rotator is a very good approximation for CH$_3$F. The Hamiltonian of the CH$_3$F in absence of external fields is denoted by

\[
H_0 = B_v J(J + 1) + (A_v - B_v) K^2 - D_{vJ} J^2 (J + 1)^2 - D_{vJK} J(J + 1) K^2 - D_{iK} K^4,
\]

the molecular beam can be derived from the TOF signal as follows [29]:

\[
f(v) = \frac{S(t + \delta t) - S(t)}{\delta \tau} \frac{L}{v},
\]

where $S$ is the signal of the detected molecular beam, $v$ is the velocity of the guided molecules, and $L$ is the distance between the cell aperture and the detection area of QMS. Figure 2(b) shows the velocity distribution of the guided CH$_3$F molecules obtained from the TOF signal.

III. STARK SHIFT OF CH$_3$F IN AN EXTERNAL ELECTRIC FIELD

In order to manipulate cold molecules accurately, the response of the molecules to the external electric field, namely, the Stark effect, should be known. As we all know, the external electric field in the laboratory is much weaker than the molecular internal electric field, and its effect on the electron cloud distribution is negligible [31]. In the Born-Oppenheimer approximation, the period of nuclear vibration is shorter than that of nuclear rotation, so the dipole moment of the molecule in a given rotational state is the vibronic expectation value of the first moment of the charge. As follows, we will consider only the influence of the external fields on the molecular rotational levels. In this paper, a symmetrical top vibrational rotator is a very good approximation for CH$_3$F. The Hamiltonian of the CH$_3$F in absence of external fields is denoted by

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\]
and the eigenwave function of \( H_0 \) is \( |JKM\rangle \), which is the symmetric top wave function, and can be expressed as

\[
|JKM\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D^{(J)}_{MK}(\phi, \theta, \chi),
\]

(5)

where \( A_v \) and \( B_v \) are the rotational constants along the \( a \) and \( b \) axes of the molecule in a given vibronic state; three centrifugal constants \( D_{vJ}, D_{vJK}, \) and \( D_{vK} \) have been introduced, which are much smaller than the rotational constants \( A_v \) and \( B_v \). The \( K \) and \( M \) are the projections of \( J \) on the molecule-fixed \( z \) axis and the space-fixed internal field \( Z \) axis, respectively, and run from \(-J \) to \( J \). \( D^{(J)}_{MK}(\phi, \theta, \chi) \) is the rotational operator matrices, and the Euler angles \( (\phi, \theta, \chi) \) define the orientation of the space-fixed coordinates \( (X, Y, \text{and} Z) \) with respect to the molecular coordinate frame \((x, y, \text{and} z)\) [32].

The calculation of the Stark effect needs the evaluation of the matrix elements as follows:

\[
\langle J', K', M' | H_{\text{Stark}} | J, K, M \rangle = \langle J', K', M' | T_1^J(\mu)|T_0^J(E) \rangle | J, K, M \rangle
\]

\[
= -E\sqrt{(2J+1)(2J'+1)} \sum_q (-1)^{M'-K} T_q^{J'}(\mu)
\]

\[
\times \left( \begin{array}{ccc}
-1 & 0 & 0 \\
J & 1 & J \\
M' & 0 & K
\end{array} \right) \left( \begin{array}{ccc}
J & 1 & J \\
-1 & 0 & 0 \\
M' & 0 & K
\end{array} \right). \quad (6)
\]

where \( T_q^{J'}(\mu) \) are the components of the dipole moment vector \( \mu \) in the molecular frame, which is the spherical tensor of rank \( 1 \). In Eq. (6), three \( J \) symbols give the selection rules naturally, and these rules indicate which states are coupled with each other. Then we can get the Stark shifts of the rotational levels in the presence of an external electric field, as Fig. 3 shows.

**IV. MEASURED BEAM PROPERTIES**

In buffer-gas cooling experiments, as we know, when the flux of the molecular sample is a constant, with an increase of the buffer-gas flux, the flux of the extracted molecular beam will be first increased and then become steady, and the extraction should saturate [1] when

\[
\gamma_{\text{cell}} \approx \frac{4}{9\pi} \frac{n_{\text{cell}} \sigma_{\text{aperture}}}{L_{\text{cell}}} \approx 1, \quad (7)
\]

where \( n_{\text{cell}} \) is the buffer-gas density inside the cell, \( \sigma_{\text{aperture}} \) is the translational collisional cross section of CH\(_3\)F-He, and \( L_{\text{cell}} \) is the length of the buffer-gas cell. According to Eq. (7), when \( \sigma_{\text{aperture}} = \pi(1.5 \text{ mm})^2 \), \( L_{\text{cell}} = 38 \text{ mm} \), and \( \sigma_{\text{cell}} = 2 \times 10^{14}/\text{cm}^2 \), we find that \( n_{\text{cell}} = 1.4 \times 10^{16}/\text{cm}^2 \) of helium density inside the cell is needed to get the extraction saturation which corresponds to the helium flux of 7 SCCM for our experimental setup.

Figure 4(a) shows the dependence of the guiding signal of CH\(_3\)F on the injected flux of helium. We can find from Fig. 4(a) that when the injected He atomic flux is below 0.25 SCCM, the buffer-gas density is not high enough to extract the molecule species from the cell, the guided CH\(_3\)F signal will be increased with an increase of the injected helium flux \( f_{\text{He}} \), and the number of thermalized and guided molecules extracted from the cell is about proportional to the square of \( f_{\text{He}} \). While further increasing \( f_{\text{He}} \) and experiencing full thermalization, the guided molecules drop slowly, and the maximum signal can be obtained with a helium flux of 0.25 SCCM, corresponding...
to a density of \( n_{\text{He}} = 5 \times 10^{14} \text{ cm}^{-3} \) inside the cell. However, after moving the guide away (i.e., without guiding) the free flight signal of CH\(_3\)F is detected by the QMS, and the results are shown in Fig. 4(b). We can find from Fig. 4(b) that the free flight signal of CH\(_3\)F is quite different; even when the injected helium flux is increased to 5.00 SCCM, the free flight signal of CH\(_3\)F still increases with the increasing of the injected helium flux, which is consistent with other buffer-gas cooling results [1,17–19]. Barry et al. [18] and Hutzler et al. [19] found that the transverse velocity spread was increased with increasing buffer-gas flow; in particular, a typical divergent angle of output molecular beam is about 15°, which is about 1/4 rad from the centerline, that is, a typical transverse velocity is about 1/4 of the forward velocity. According to our measured results, with an increase of the injected helium flux from 0.20 to 5.00 SCCM, the forward velocity of the guided CH\(_3\)F molecular beam is increased from 103 to 170 m/s, and the typical transverse velocity is increased from about 25.8 to 42.5 m/s. However, the total depth of the quadrupole guide is \( \sim 1 \text{ K} \) for low \( J \), which corresponds to \( \sim 20 \text{ m/s} \) for CH\(_3\)F and smaller than the increased transverse velocity (25.8 to 42.5 m/s) of the output CH\(_3\)F molecular beam, so the influence of the increased transverse velocity on the guided signal of CH\(_3\)F cannot be ignored.

In order to greatly reduce this influence, two collimators with an aperture diameter of 2 mm are placed in front of the cell to reduce the influence of the increased transverse velocity of the molecular beam, as shown in Fig. 1. Two collimators are necessary since there are collisions near the beam aperture, which can make the effective source of molecules appear different from the aperture [33]. The first collimator is placed at 13 mm from the cell where collisions have been stopped. Our experimental result shows that the highest forward velocity of CH\(_3\)F is 170 m/s (obtained with an injected helium flux of 5.00 SCCM), so the transverse velocity of the output molecular beam from the buffer-gas cell is about 42.5 m/s [18,19]. According to the results of Monte Carlo simulation, after being collimated by the two collimators, the transverse velocity of CH\(_3\)F is reduced to below 13 m/s (obtained with a forward velocity of 170 m/s) for all buffer-gas flow conditions, so the electrostatic guide can accept almost all weak-field-seeking (WFS) states CH\(_3\)F and the influence of the transverse velocity on guiding efficiency can be ignored after we place the two collimators in front of the buffer-gas cell.

After adding two collimators, we can conclude that the reduction of the guided molecule number in the detection area is caused by rotational cooling of the CH\(_3\)F molecule when the guiding voltage is unchanged and the injected helium flux is more than 0.25 SCCM, so the decreasing of the signal (i.e., the decreasing of the guiding efficiency of the WFS molecules in the electrostatic quadrupole field) after point A in Fig. 4(a) can be mainly caused by the reduction of the rotational temperature, which determines the rotational state population of CH\(_3\)F. That is to say, more molecules in the WFS states are transferred into ones in the strong-field-seeking state during the rotational relaxation process. In support of this claim, Monte Carlo simulations are carried out as follows [34]: for different rotational temperatures the state population \( J = 0–30 \) of CH\(_3\)F can be obtained as seen in Fig. 5. In addition, with an external electric field of \( E = 80 \text{ kV/cm} \), there are totally as many as 10 007 WFS states, as shown in Fig. 6, so it is necessary to simplify our simulations without changing the characters of guiding. In the guide, the changes of molecular velocities and positions mostly depend on Stark shift \( W_{\text{Stark}} \). As the molecules with a larger \( W_{\text{Stark}} \) will suffer a larger gradient force and are apt to stay in the guide, we classify all the WFS states of the molecules into several tens of representative states according to their \( W_{\text{Stark}} \) (e.g., the states whose \( W_{\text{Stark}} \) is between 1.0 and 1.1 cm\(^{-1} \) are represented by the state with \( W_{\text{Stark}} \) as 1.05 cm\(^{-1} \), such as the state \( |16,11,−11\rangle \)). So we can choose 25 representative states to represent all the WFS states with a \( W_{\text{Stark}} \) up to 2.5 cm\(^{-1} \). The variation range of Stark shift represented by each representative state is \( \pm 0.05 \text{ cm}^{-1} \), and the difference of Stark shifts between two adjacent representative states is defined as \( 0.1 \text{ cm}^{-1} \); then our Monte Carlo simulations for the electrostatically guided CH\(_3\)F molecules with the 10 007 WFS states are simplified to the simulations of CH\(_3\)F with 25 representative states. The guiding

FIG. 5. Relative population (royal blue hexagon in the upper right corner) of WFS states of CH\(_3\)F vs Stark shift for the field strength of 80 kV/cm; the black squares, red circles, and blue triangles show the relative population of WFS states of CH\(_3\)F via the rotational energy level for \( J = 0–30 \) at rotational temperatures of 5, 50, and 215 K, respectively.

FIG. 6. The dependence of the Stark shift of the WFS state CH\(_3\)F molecule in 80 kV/cm external electric field on the rotational energy for the rotational quantum number of \( J = 0–30 \).
efficiency for each representative rotational state is obtained by straight quadrupole guide simulations. Then the total guiding efficiency for different rotational temperatures can be obtained. As shown in Fig. 7, when the rotational temperature of CH$_3$F is above 15 K, the guiding efficiency of cold molecules in the electrostatic quadrupole field is nearly not varying and the percentage of the WFS molecules is 47.21%. However, when the rotational temperature is below 15 K, there is a quick decrease of guiding efficiency as the rotational temperature drops from 15 to 1 K, and the percentage of the WFS molecules drops to 2.52% as the rotational temperature decreases to 1 K, which is consistent with our experimental results.

Inside the buffer-gas cooling cell, the density of helium is much larger than the density of molecules since most of the molecules are diffused to the cold cell wall and get lost. Therefore, the process of cold collisions is mainly determined by buffer-gas density. The mean free path of the molecule inside the cell is given by $\lambda = 1/\sqrt{2n\sigma_i}$, where $n$ is the density of helium and $\sigma_i$ is the translational elastic collision cross section of CH$_3$F-He. Based on the cell dimensions, when the injected flux of helium is 0.25 SCCM, the mean free path of the molecule inside the cell is $\sim$0.7 mm; few collisions occurred near the cell aperture and the boosting effect is not obvious. The reduction of the temperature of the colliding molecules can be explained by the elastic scattering model of rigid spheres. According to energy and momentum conservation laws, after statistically averaging for a complete velocity distribution of the thermal molecules, it is easy to obtain a temperature change of the molecular sample after each collision with the buffer gas; colliding $N$ times with cold helium, the translational temperature $T$ of CH$_3$F can be approximately expressed as

$$T_N = T_0 + (T_i - T_0) \times e^{-N/\gamma},$$

where $T_0$ is the translational temperature of the helium and $T_i$ is the initial translational temperature of the CH$_3$F molecule, and $\gamma \equiv (m_{molecule} + m_{helium})^2/(2m_{molecule}m_{helium})$.

However, after being injected from the molecular fill line, CH$_3$F molecules undergo at least 36 times of collisions before being ejected from the cell aperture. After 36 times of collisions with 3.5 K cold helium, the translational temperature of the CH$_3$F molecules is $T_{36} \approx 3.74$ K, which means that 0.25 SCCM helium is sufficient to thermalize the translational temperature of CH$_3$F close to 3.5 K through cold collisions. When the injected flux of helium is increased from 1.00 to 5.00 SCCM, the guiding efficiency under the condition of high buffer-gas fluxes ($f_{he} > 0.25$ SCCM) can be calculated by comparing Figs. 4(a) and 4(b). Then the rotational temperature for different buffer-gas flux conditions can be obtained by its one-to-one correspondence with the guiding efficiency as shown in Fig. 7(a). Figure 7(b) shows the dependence of the rotational temperature of the guided molecules on collision times mainly determined by the buffer-gas density.

As we all know, it needs more collisions to thermalize the rotational temperature of molecules than their translational temperature. Besides, the lowest rotational temperature of the molecules could be much lower than the temperature of the buffer-gas He atoms. Unlike elastic collisions, which govern translational thermalization, it is not easy to find a simple expression for the number of collisions necessary for rotational thermalization, because the rotational relaxation rates depend strongly on molecular structure, and for different relaxation channels and rotational state populations, the molecular rotational cross sections are different. However, for symmetric top molecules at specific rotational temperature, the rotational state population can be definite, therefore, different rotational cross sections can be replaced by an average one. In cryogenics cells, both translational and rotational thermalizations occur with similar efficiency [27]. Based on the model above, the rotational relaxation expression of CH$_3$F can be carried out on the analogy with the translational relaxation process, and the dependence of the rotational temperature of CH$_3$F on the collision times can be obtained by fitting the experimental data in Fig. 7(b) and given by

$$T_{rot}(N) = T_{rot} + (T_{irot} - T_{rot}) \times e^{-N/\gamma},$$

where $N$ is collision times, $T_{rot}$ is the initial rotational temperature of CH$_3$F, $T_{irot}$ is the lowest rotational temperature of CH$_3$F that can be obtained by cold collisions and adiabatic cooling, $\gamma \equiv (m_{molecule} + m_{helium})^2/(2m_{molecule}m_{helium})$, and $\gamma$ is the ratio between the translational collisional cross section and the average rotational collisional cross section. By fitting the data in Fig. 7(b) with Eq. (9) above, the average ratio between the translational collisional cross section and the rotational collisional cross section $\gamma = \sigma_i/\sigma_r = 36.49 \pm 6.15$ can be obtained.

The molecular beam extracted from the cell exit can be operated both in an effusive regime and a hydrodynamically enhanced regime, mainly depending on the buffer-gas density.
The slowing, cooling, and boosting effects of the guided molecular beam with different injected fluxes of helium can be observed in Fig. 8. In order to clearly show these effects, we normalize the velocity distribution of the guided CH$_3$F molecular beam with the injected CH$_3$F flux of 2.00 SCCM. The inset illustration shows the dependence of the absolute guided signal intensity on the molecular velocity for different helium fluxes. When the injected He flux is 0.05 SCCM (corresponding to a helium density of $1 \times 10^{14}$ cm$^{-3}$), CH$_3$F molecules undergo few collisions before being ejected out from the cell aperture, and then the cooling and slowing effects are not clear. When the injected He is increased to 0.20 SCCM, slowing and cooling effects are obvious compared with the injected He flux of 0.05 SCCM. With further increasing the He flux to 2.00 SCCM, the velocity distribution of the buffer-gas cooled CH$_3$F molecular beam moves to a high speed region caused by the boosting effect.

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V. CONCLUSIONS

In this paper, we have proposed an electrostatic guiding scheme to demonstrate the rotational relaxation of polar molecules (such as CH$_3$F) in low-temperature collisions with 3.5 K He atoms, and the dependence of the guiding efficiency of CH$_3$F on its rotational temperature is studied. We found that the translational and rotational temperatures of the buffer-gas cooled CH$_3$F molecules can be reached to about 5.48 and 0.60 K, respectively, and the ratio between the translational and average rotational collisional cross sections of CH$_3$F is about 36. Also, the slowing, cooling, and boosting effects of the guided molecular beam induced by the buffer-gas density has also been observed and studied. Our study shows that our proposed method can not only be used to measure the translational and rotational temperatures of the buffer-gas cooled molecules, but also to measure the ratio between the translational and average rotational collisional cross sections, and even to measure the average rotational collisional cross section when the translational collisional cross section is measured by fitting the lifetime of the molecule signal to get a numerical solution from the diffusion equation of the buffer-gas He atoms in the cell [35,36], and it should work for a large variety of polar molecules.

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