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Supersonic beams of mixed gases: A method for studying cold collisions

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ABSTRACT

We show that collisions in a single supersonic molecular beam reach characteristic temperatures in the range of a few Kelvin. Experiments have been carried out for mixtures of H_2 and HD as well as HD and D_2 in a pulsed supersonic expansion. From the measured time-of-flight spectrum, we find that the high velocity edge of the distribution for both species is nearly coincident, but the average speed of the heavier species is slightly greater than the lighter one. By working in the few Kelvin regime, this relatively simple technique reduces the number of partial waves in the collision process, which allows the observation of collision resonances. Additionally, copropagation of scattering partners in a single molecular beam precisely defines the direction of their relative velocity vector, which is essential for the study of stereodynamics.

Because molecular beam experiments permit the study of single-collision events, they have become the chief way of exploring the detailed dynamics of molecular collisions [1]. Supersonically expanded beams have been particularly important because they produce high densities of internally cooled molecules with well-defined kinetic energies. In an ideal, that is, monoenergetic molecular beam, there are no collisions between molecules in the beam, but real molecular beams never fully satisfy this condition. Although the intrabeam collision rate is quite small [2,3] and is usually ignored, what some might regard as an imperfection in beam scattering experiments can be turned into an advantage as described in what follows.

A large number of molecular resonances appear at collision temperatures ranging from 10 mK to 10 K [4–7]. Therefore, much interest exists in achieving collision temperatures in this range. It is well known that in order to preserve the plane-wave character of an incoming particle with well-defined linear momentum a large number of coherently coupled, orbital angular momentum states (partial waves) must be present in the input channel [8]. However, in this range of temperatures only a few of the partial waves, having sufficiently small impact parameters, present actually contribute to the scattering process [9]. It is a subset of this limited set of incoming partial waves that provide the appropriate centrifugal barrier to support orbiting resonance states of the quasi-bound complex.

Reaching these collision temperatures presents the experimentalist with a significant challenge. Narrow angle crossing of two molecular beams is perhaps the most common way to reduce the collision temperature, and has produced collisions in the range of a few Kelvin [6]. A much newer set of techniques involving merging two molecular beams using electric or magnetic field induced deflection techniques has reached temperatures as low as a few mK [10,11]. These techniques can not only reduce the collision temperature, but also tune the collision energy to observe collision resonances in the range of a few mK to a few K. However, a major drawback of all two-beam techniques is a significant reduction in molecular density caused by the necessity of long molecular beam propagation distances [12]. We have recently employed a single-beam technique in which the two colliding species are co-expanded in the same molecular beam [9,13]. This technique is relatively easily implemented to reach collision temperatures in the range of 0–5 K for H_2 and its isotopologues, without sacrificing beam intensity. Following this technique, we were able to bring down the relative speed of two molecular species to the point of achieving nearly overlapping velocity distributions (see Figs. 1 and 2). Additionally, the co-expansion of the colliding partners in a single collimated beam defines the direction of their relative velocity vector within a few mRad, which is essential for the study of stereodynamics and the measurement of vector correlations. To produce a well-collimated molecular beam a skimmer is placed an appropriate distance from the pulsed valve, severely limiting the transverse velocity spread. As detailed below, we were able to reduce the angular divergence to 12 mRad, corresponding to a transverse velocity spread of only 26 m/s. The well-defined relative velocity between co-expanded gas pairs in a highly collimated single molecular beam makes the analysis of scattering processes studied using this technique extremely simple.

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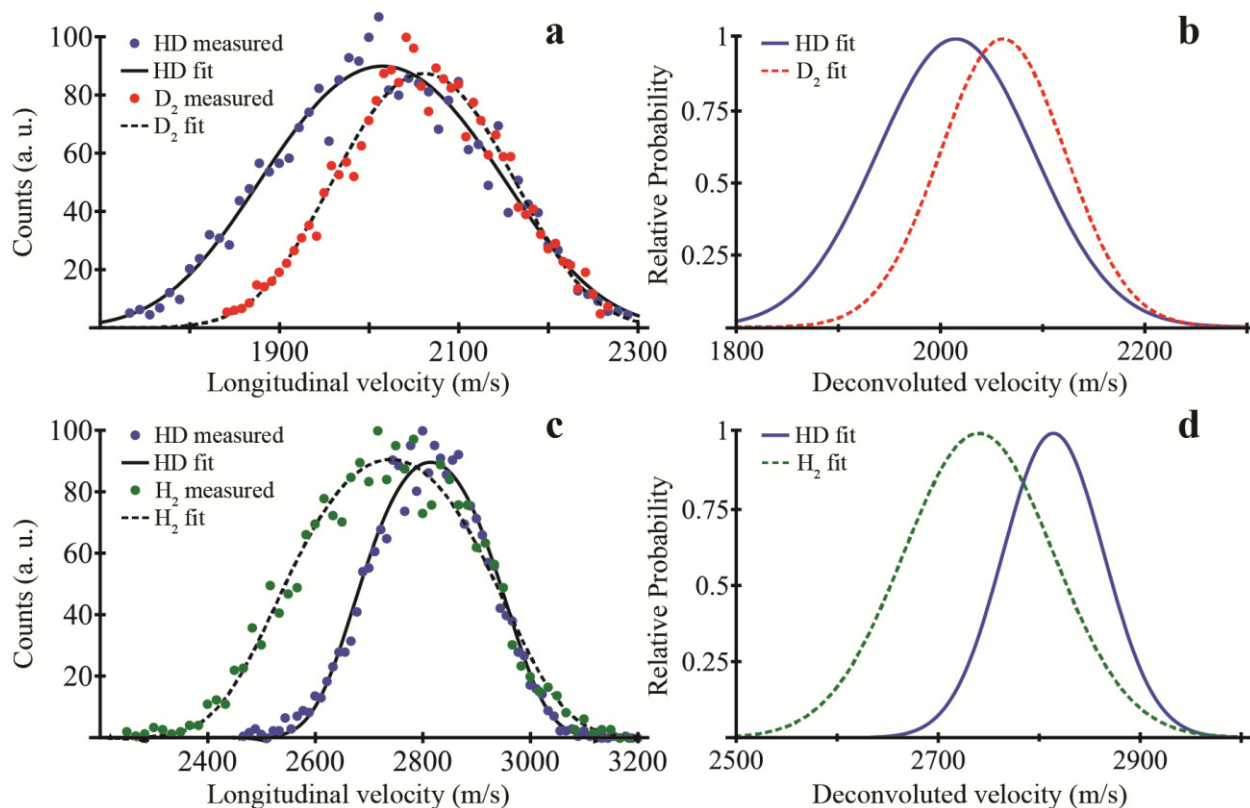 E-mail address: zare@stanford.edu (R.N. Zare).

Fig. 1. (a) Experimentally determined velocity distributions of both HD and D_2 in the HD/D_2 mixed beam, which were fit taking into account the broadening effect of REMPI photoelectron recoil. The HD fit has ($R^2 = 0.987$), and the D_2 fit has ($R^2 = 0.991$). (b) Deconvoluted Gaussian speed distributions of HD ($v = 0$, $j = 0$), given by $P_{HD}(u) = \exp\left\{-[(u - 2015)/109]^2\right\}$, and D_2 ($v = 0$, $j = 0$), given by $P_{D_2}(u) = \exp\left\{-[(u - 2061)/86]^2\right\}$. (c) Experimentally determined velocity distributions of both HD and H_2 in the HD/H_2 mixed beam, which were fit taking into account the broadening effect of REMPI photoelectron recoil. The HD fit has ($R^2 = 0.991$), and the H_2 fit has ($R^2 = 0.99$). (d) Deconvoluted Gaussian speed distributions of HD ($v = 0$, $j = 0$), given by $P_{HD}(u) = \exp\left\{-[(u - 2814)/71]^2\right\}$, and H_2 ($v = 0$, $j = 0$), given by $P_{H_2}(u) = \exp\left\{-[(u - 2740)/105]^2\right\}$.
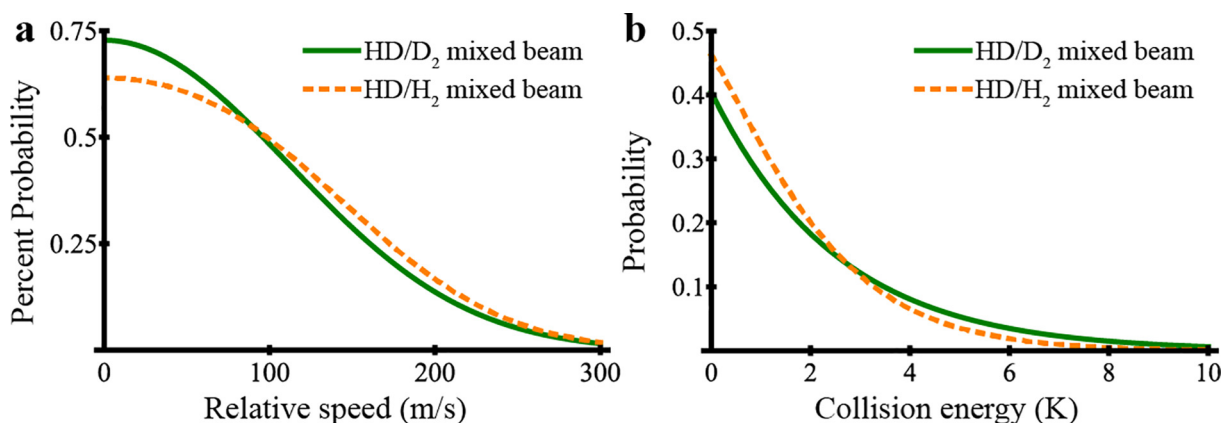

Fig. 2. Relative speed and energy distributions. (a) Relative speed distributions between HD ($v = 1$, $j = 2$) and D_2 ($v = 0$, $j = 0$) (green solid curve) and HD ($v = 1$, $j = 2$) and H_2 ($v = 0$, $j = 0$) (orange dashed curve), derived by convolution of the velocity distribution of the two species present in each mixed molecular beam shown in Fig. 1b and d. ∼85% of collisions take place with a relative velocity of 160 m/s or less for both H_2/HD and D_2/HD mixed beams. (b) Collision energy distributions for D_2/HD (green solid curve) and H_2/HD (orange dashed curve), calculated using the relative speed distributions shown in (a). The two beams have nearly the same range of collision energies present. Greater than 85% of the collisions have collision energy less than 5 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Recently, we demonstrated stereodynamic effects in rotationally inelastic scattering of HD by D_2 and H_2 by selectively preparing the internal quantum states of HD and simultaneously reducing the collision temperature by co-expanding the collision partners [9,13]. The scattering angular distribution convincingly demonstrated involvement of only s ($l = 0$) and p ($l = 1$) partial waves. In addition, the large scattering cross-section determined from these experiments seems to suggest presence of a collisional resonance, which is supported by theoretical predictions [14]. Additionally, Amarasinghe and Suits have recently employed intrabeam scattering to study collisions between Xe Rydberg atoms and ground state Xe at temperatures as low as 2.5 mK [15].

In our collision studies, we co-expanded HD and its collision partner (either D_2 or H_2) in a single molecular beam at a ratio of

1:6 HD to D_2 and 1:8 HD to H_2. The mixtures were co-expanded using an Even-Lavie pulsed valve [16] with a backing pressure of ~11 bar. The gas mixture was expanded adiabatically into a source chamber and then passed through a skimmer with an orifice of 0.6 mm, kept at a distance of ~8 cm from the pulsed valve. The skimmed molecular beam then entered the reaction chamber where it was probed using (2 + 1) resonance enhanced multiphoton ionization (REMPI) from their ground rovibrational level ($v = 0, j = 0$) via the two-photon resonant E,F $^1\sum_g^+$ electronic state with tunable VUV pulses near 200 nm. The source and the reaction chambers were pumped differentially, resulting in a background pressure of 10^{-5} Torr and 10^{-7} Torr, respectively, while the pulsed valve was operating. The REMPI pulses were obtained using third harmonic generation of a tunable pulsed dye laser (ND6000, Continuum Lasers, Inc.) pumped by the second harmonic of a Q-switched Nd^{3+}:YAG (PL9020, Continuum Lasers, Inc.) resulting in pulse durations of ~5 ns and a pulse energies of ~10 μJ. The laser beam was focused using a 40 cm focal length lens to a spot size of ~20 μm. The REMPI generated ions were detected on a multichannel plate situated at the end of a time-of-flight mass spectrometer with its axis parallel to the molecular beam axis. The optical field of the VUV laser pulses was polarized perpendicular to the time-of-flight axis. A detailed description of our apparatus can be found elsewhere [17]. The measured ion time-of-flight distribution was converted into the velocity distribution using a known calibration constant of the mass spectrometer. However, the measured ion velocity distribution is artificially increased compared to the velocity distribution of the neutral molecule due the recoil of the REMPI photoelectron. The neutral velocity distribution can be deconvoluted from the recoil due to the REMPI [17], as we describe in the Appendix. Further, REMPI allowed the characterization of the divergence of the molecular beam by measuring the diameter of the molecular beam in the probe region (1.5 mm). Using the known distance of the skimmer (35 mm) from the probe region, the angular divergence was determined to be 12 mRad. We have also used REMPI to characterize the rotational temperatures of each molecule in each beam. Measurement of the rotational distributions shows that in the HD/H_2 mixed beam, 25% of the H_2 molecules were found in ($v = 0, j = 0$), 75% in ($v = 0, j = 1$), and less than 1% in ($v = 0, j = 2$). In the HD/D_2 mixed beam, 59% of the D_2 molecules were found in ($v = 0, j = 0$), 33% in ($v = 0, j = 1$), and 8% in ($v = 0, j = 2$). In both beams, greater than 98% of the HD population was found in ($v = 0, j = 0$) with the remainder in ($v = 0, j = 1$).

Fig. 1a and c show the velocity distributions of the HD/D_2 and HD/H_2 beams, respectively, as determined from time-of-flight measurements. The velocity distributions in Fig. 1a and c are fitted using the convolution of a Gaussian representing the speed distribution of the neutral molecules with a function giving the angular distribution of the recoil velocity from REMPI photoelectrons [17], as detailed in the Appendix. Fig. 1b and d show the Gaussian velocity distributions of the neutral molecules deconvoluted from the effects of photoelectron ejection.

The significant overlap between the distributions in Fig. 1b and d demonstrates that in each molecular beam the velocities of the co-propagated molecules have come relatively close, corresponding to a low collision temperature. This effect is well-known [18,19] when one gas only accounts for a few percent of the total pressure (i.e., a seeded beam). Noteworthy is the work of Kolodney and Amirav [19], who showed that seeding of I_2 in He and H_2 at partial pressure of a few percent or less results in significant acceleration of I_2 such that its velocity is only a few hundred m/s below the lighter carrier gas. We show here that this equilibration of the velocities also occurs for mixtures where the "carrier" gas accounts for only ~85% of the total pressure. More notably, Fig. 1b and d show that the peaks of the two distributions in each beam are

slightly different, with the lighter molecules moving more slowly than the heavier ones. This reverse velocity slip observed in our experiment differs from the observation of Kolodney and Amirav [19]. The reverse slip is highly surprising, even though our experimental conditions differ from that of Kolodney et al. Neither our higher stagnation pressure nor the fact that masses of the gas molecules are similar explains the higher average speed of the heavier gas. Additionally, it can be seen that the two gases in each mixed beam have slightly different longitudinal temperatures. As expected, Fig. 1 shows that lighter gases have wider velocity distributions.

Fig. 2a shows the relative velocity distributions between HD and its partner molecule in the two mixed beams, which are calculated using the deconvoluted Gaussian velocity distributions of HD, D_2, and H_2 shown in Fig. 1b and d. Fig. 2b shows the corresponding collision energy distribution in Kelvin. Fig. 2b shows that for both pairs, HD/D_2 and HD/H_2, more than 85% collisions have collision energy in the range of 0–5K. In this temperature range the ($l = 1$) partial wave corresponds to an impact parameter greater than 3.5 Å for D_2/HD and 4.7 Å for H_2/HD, whereas the ($l = 2$) partial wave corresponds to an impact parameter greater than 6 Å and 8.1 Å, respectively. By severely restricting partial waves present in the input channel, the coexpanded beam allows the determination of the interaction potential by correlating the input waves with the outgoing waves. Additionally, because ($l \neq 0$) partial waves are still present in the input channel, this technique allows the experimental observation of orbiting resonances.

The cooling of the relative speed distribution by co-expansion provides a simple way to reach collision temperatures of a few Kelvin while maintaining high molecular densities necessary for the measurement of scattering events with small cross-sections. Further, this technique produces beams with transverse temperatures as low as a few μK. This is because the transverse velocity becomes highly defined by the skimmer, which defines the direction of the relative velocity within a few mRad, a necessity for precise stereodynamic studies. We believe that the reverse slip measured here is highly notable and bears further investigation. Whatever the explanation for this behavior, intrabeam collisions in a supersonically expanded gas mixture offer an appealing way to study cold chemistry.

Acknowledgements

Appendix A. Determination of the velocity distribution for neutral molecules

The velocity distribution of the neutral molecule is modified by the recoil of the photoelectron [17] in REMPI. The velocity distribution of the molecular ion along the axis of detection, designated as the z axis, can be expressed by

$$g(u) \propto \int f(u - v_e \cos\theta)h(\theta, \phi)d\Omega, \tag{A.1}$$

where the function $f(u)$ represents the longitudinal velocity distribution of the neutral molecule along the molecular beam axis, which is coincident with the detection axis z, v_e represents the speed imparted on the neutral molecule due to recoil from photoionization, and $h(\theta, \phi)$ is the probability of finding a recoil velocity v_e along (θ, ϕ) per unit solid angle about the detection axis z. The longitudinal velocity distribution is given by:

$$f(u) = \exp\left[-\left(\frac{u - u_0}{\Delta u}\right)^2\right], \tag{A.2}$$

where Δu is the longitudinal velocity spread, which defines the longitudinal temperature of the molecular beam, and u_o is the mean speed along the z axis.

For the UV optical field oriented at an angle Θ with respect to z, the photoelectron angular distribution $h(\theta,\phi)$ can be found in the following way. Designating the direction of the UV optical field as z′, the photoelectron angular distribution $S(\theta',\phi')$ about z′ is given by:

$$S(\theta', \phi') \propto 1 + \beta P_2(\cos\theta'), \tag{A.3}$$

where $P_2(\cos\theta')$ is the second order Legendre polynomial. The angular distribution $h(\theta,\phi)$ can be found using the transformation property of the Legendre polynomial P_2 under a rotation of the coordinate system bringing z′ onto z. Thus, under rotation of the coordinate system, S (θ',ϕ') transforms into:

$$\begin{aligned}
h(\theta,\phi) &= 1 + \sqrt{4\pi/5}\,\beta \sum_{m=-2}^{2} D_{0m}^2(0, \Theta, 0) Y_{2m}(\theta, \phi) \\
&= 1 + \sqrt{4\pi/5}\,\beta \{ P_2(\cos\Theta) Y_{20}(\theta, \phi) \\
&\quad + \sqrt{6}\,\cos(\Theta/2)\cos\Theta\sin(\Theta/2)[Y_{2-1}(\theta, \phi) - Y_{21}(\theta, \phi)] \\
&\quad + \sqrt{6}\,\cos(\Theta/2)^2 \sin(\Theta/2)^2 [Y_{22}(\theta, \phi) + Y_{2-2}(\theta, \phi)] \}
\end{aligned} \tag{A.4}$$

where $D_{0m}^2(0, \Theta, 0)$ is the Wigner rotation matrix element for the second-rank spherical harmonic $Y_{2m}(\theta, \phi)$. The velocity distribution for the recoiling ions is found by inserting Eqs. (A2) and (A4) into Eq. (A1) and integrating over the azimuthal angle ϕ about the detection axis z:

$$g(u) \propto \int_0^\pi f(u - v_e\cos\theta) \times [1 + \beta P_2(\cos\Theta)P_2(\cos\theta)]\sin\theta d\theta \tag{A.5}$$

When the REMPI optical field is polarized perpendicularly to the time-of-flight (z) axis, $\Theta = 90°$, and we have:

$$g(u) \propto \int_0^\pi f(u - v_e\cos\theta) \times \left[1 - \frac{\beta}{2}P_2(\cos\theta)\right]\sin\theta d\theta \tag{A.6}$$

Eq. (A6) is used to fit the experimentally determined longitudinal velocity distributions shown in Fig. 1a and c, using the value of the anisotropy parameter experimentally determined previously [17], namely, $\beta = 1.72$. In our previous work on H_2, we have shown that in the (2 + 1) REMPI process more than 99% of the H_2^+ is born in its vibrational ground state. Using this information, we have calculated the values of the recoil speed v_e as: 280 m/s for H_2^+, 187 m/s for HD^+, and 140 m/s for D_2^+. The width (Δu) and the center (u_0)

of the velocity distribution $f(u)$ for each neutral molecule were found from the respective fits. The curves in Fig. 1b and d show the velocity distributions $f(u)$ for neutral H_2, HD, and D_2, for the two different gas mixtures.

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