Supersonic jet and molecular beam

A supersonic jet expansion technique can be used to prepare gas-phase polyatomic molecules, complexes, or clusters in the electronically ground ($S_0$) state. The expansion of a high pressure (e.g. 1-3 atm) of gas (or seeded gas mixture) into a vacuum ($\sim 10^{-6}$ torr) through an aperture (e.g. 150 µm) is termed a supersonic expansion. This isentropic expansion process quenches the internal rotations and vibrations of molecules and can lead to substantial cooling of molecular internal (rotational and vibrational) energy. It results in a narrow spectral line. Since the rotational cooling is more efficient than the vibrational cooling, scientists often referred to as a rationally cooled process. When a supersonic jet is collimated by a skimmer, it is called a molecular beam.
For an isentropic expansion of an ideal gas, e.g. He or Ar,
\[ T_2 / T_1 = (P_2 / P_1)^{((\gamma - 1)/\gamma)} \]
\[ \gamma = C_p / C_v = 5/3, \]
If \( T_1 = 273 \) K, \( P_2 = 10^{-4} \) torr, \( P_1 = 84 \) atm,
\[ T_2 = T_1 \left( P_2 / P_1 \right)^{((\gamma - 1)/\gamma)} \]
\[ = 273 \left[ 10^{-4} / (84 \times 760) \right]^{2/3} \]
\[ T_2 = 3.7 \times 10^{-4} \) K (translational temperature) \]

Under this condition (3.7x 10^{-4} K), HeI_{2} complex can be prepared.

The fluorescence excitation spectrum of the HeI_{2} van der Waals complex
The fluorescence excitation spectrum of the HeI$_2$ van der Waals complex
Velocity Distributions of Effusive and Supersonic Molecular Beams

Mach number, $M = \frac{U}{C}$
$U =$ flow velocity,
$C =$ speed of sound
$M = 1$, e.g. $340 \text{ m/s} = (1225 \text{ km/h})$

**Figure 1.** Velocity distribution in effusive molecular beam (dashed curve) and supersonic molecular beam (solid curve). Both curves are normalized to unity at the most probable velocity and are for helium at a reservoir temperature of 300 K. The curve for the supersonic molecular beam assumes the gas has been expanded to Mach 30.

Molecular Optical Spectroscopy with Supersonic Beams and jets
Fluorescence excitation spectra of NO$_2$

FIG. 1. A portion of the fluorescence excitation spectrum of NO$_2$ for (top) a conventional room temperature sample of pure NO$_2$ at 0.04 torr pressure, (middle) a supersonic beam of pure NO$_2$, and (bottom) a supersonic beam of 5% NO$_2$ in Ar. All spectra were taken using a cw dye laser. Laser bandwidth was 0.5 Å for the lower two spectra.


Gas cell, 0.04 torr, 300 K

NO$_2$ supersonic beam, 30 K

5\%NO$_2$ in Ar seeded supersonic beam, 3 K

Nozzle diameter D = 0.050 mm, skimmer opening = 1 mm, located 0.36 cm from nozzle
Sample Calculations

(a) The broad excitation fluorescence spectrum of pure room temperature NO₂ sample of 0.04 torr may result from molecular rotation and vibrations as well as inter-molecular collisions. In a gas cell with pressure of 0.04 torr at 300 K, can you calculate number of NO₂ molecules per cm³?

(b) The excitation fluorescence spectrum of supersonically cooled pure NO₂. At very low translational temperature (e.g. 30 K), NO₂ molecules still rotate and vibrate. Important features of a molecular beam include (1) molecular density is very high (e.g. 10¹⁵ molecules per cm³), (2) all molecules are moving with the same velocity, (3) probability of inter-molecular collisions is low. Can you calculate the root mean square velocity of NO₂ at STP?

(c) The excitation fluorescence spectrum of supersonically cooled 5% NO₂ in Ar. At very low translational temperature (e.g. 3 K), NO₂ molecules still rotate and vibrate. This is called seeded molecular beam technique. The probability of inter-molecular NO₂-NO₂ collisions is substantially reduced.
Electromagnetic spectrum

Microwave oven
2.45 GHz (12.2 cm)

FM 99.7
99.7 MHz (3 m)

0° of aniline
239.87 nm (UV)
34029 cm⁻¹
Fluorescence excitation spectrum of HeI₂
D₀ = 0.025 mm, P₀ = 110 atm, P = 10⁻⁴ torr
Xₘ / D = 0.67 [P₀/P]^(1/2), Xₘ = 484 mm = 48.4 cm

The molecular beam travels along flow streamline at 2 x 10⁵ cm/s.
The focused laser intersect the molecular beam at 2 mm downstream from the nozzle.
The translational temperature is estimated to be 3.1 x 10⁻⁴ K.
The rotational temperature of I₂ is less than 1 K and the vibrational temperature is 50 K.

The fluorescence excitation spectrum of the HeI₂ van der Waals complex
Rotational temperature of a supersonically cooled I₂ molecular jet

The fluorescence excitation spectrum of the HeI₂ van der Waals complex

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First TOF spectrum of $(\text{NH}_3)_n\text{H}^+$, taken at IAMS, Taiwan

自行設計組裝的多光子游離飛行時間質譜儀所紀錄的第一張質譜，氨團簇分子質譜，訊號最強的是$(\text{NH}_3)\text{H}^+$
TOF spectrum of Gau-Liang wine, taken at IAMS, Taiwan

台灣高粱酒的質譜，主要訊號乙醇分子團簇

$(C_2H_5OH)H^+$
邱紹仁，台灣師範大學化學系
碩士班學生 1993/05/05
TOF and REMPI spectra of phenylacetylene, $\text{C}_6\text{H}_5\text{C}_2\text{H}^+$

First, the TOF (time-of-flight) and REMPI (resonance enhanced multi-photon ionization) spectra were acquired. The strongest peak at 278.78 nm indicated an electron excitation energy of 35871 cm$^{-1}$. 

1995/12/07
TOF and MATI spectra of 4-fluoroaniline, \( \text{FC}_6\text{H}_4\text{NH}_2^+ \)

飛行時間 (TOF) 質譜暨質量分辨雙色共振雙光子游離光譜，譜峰顯示對氟苯胺的離子態分子振動訊號。
TOF mass spectrometer for REMPI and MATI experiments, Lab 108, IAMS
Control area of REMPI-MATI spectrometer, Lab 108, IAMS
Our linear co-axial type time-of-flight (TOF) mass spectrometer for laser spectroscopic experiments

Animation of MATI experiment:  
http://w3.iams.sinica.edu.tw/lab/wbtzeng/indexb.html
For an isentropic expansion of an ideal gas, e.g. He or Ar,
\[ \frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{(\gamma-1)}{\gamma}} \]
\[ \gamma = \frac{C_p}{C_v} = \frac{5}{3}, \]
If \( T_1 = 300 \text{ K} \), \( P_2 = 10^{-6} \text{ torr} \), \( P_1 = 1000 \text{ torr} \),
then \( T_2 = 0.07 \text{ K} \) (translational temperature)

Under this experimental condition, the gas phase molecule can be prepared in the electronically ground \( S_0 \) state for laser spectroscopy (REMPI, PIE, or MATI) experiments.
Velocity distributions of $p$-fluoroaniline/He, Ne, Ar seeded beams

**TABLE 1: Characteristics of the $p$-Fluoroaniline Beam**

<table>
<thead>
<tr>
<th>carrier gas ($P_0$/bar)</th>
<th>$v_{mp}$/m s$^{-1}$</th>
<th>$\Delta v/v_{mp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (1.1)</td>
<td>1300</td>
<td>0.17</td>
</tr>
<tr>
<td>He (2.3)</td>
<td>1400</td>
<td>0.07</td>
</tr>
<tr>
<td>$N_2$ (2.3)</td>
<td>670</td>
<td>0.08</td>
</tr>
<tr>
<td>Ar (2.3)</td>
<td>540</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Ionization energy of $p$-fluoroaniline and vibrational levels of $p$-fluoroaniline cation determined by mass-analyzed threshold ionization spectroscopy


**Figure 3.** TOF spectra of $p$-fluoroaniline beams with the carrier gas of (a) He at 1.1 bar, (b) He at 2.3 bar, (c) $N_2$ at 2.3 bar, and (d) Ar at 2.3 bar.