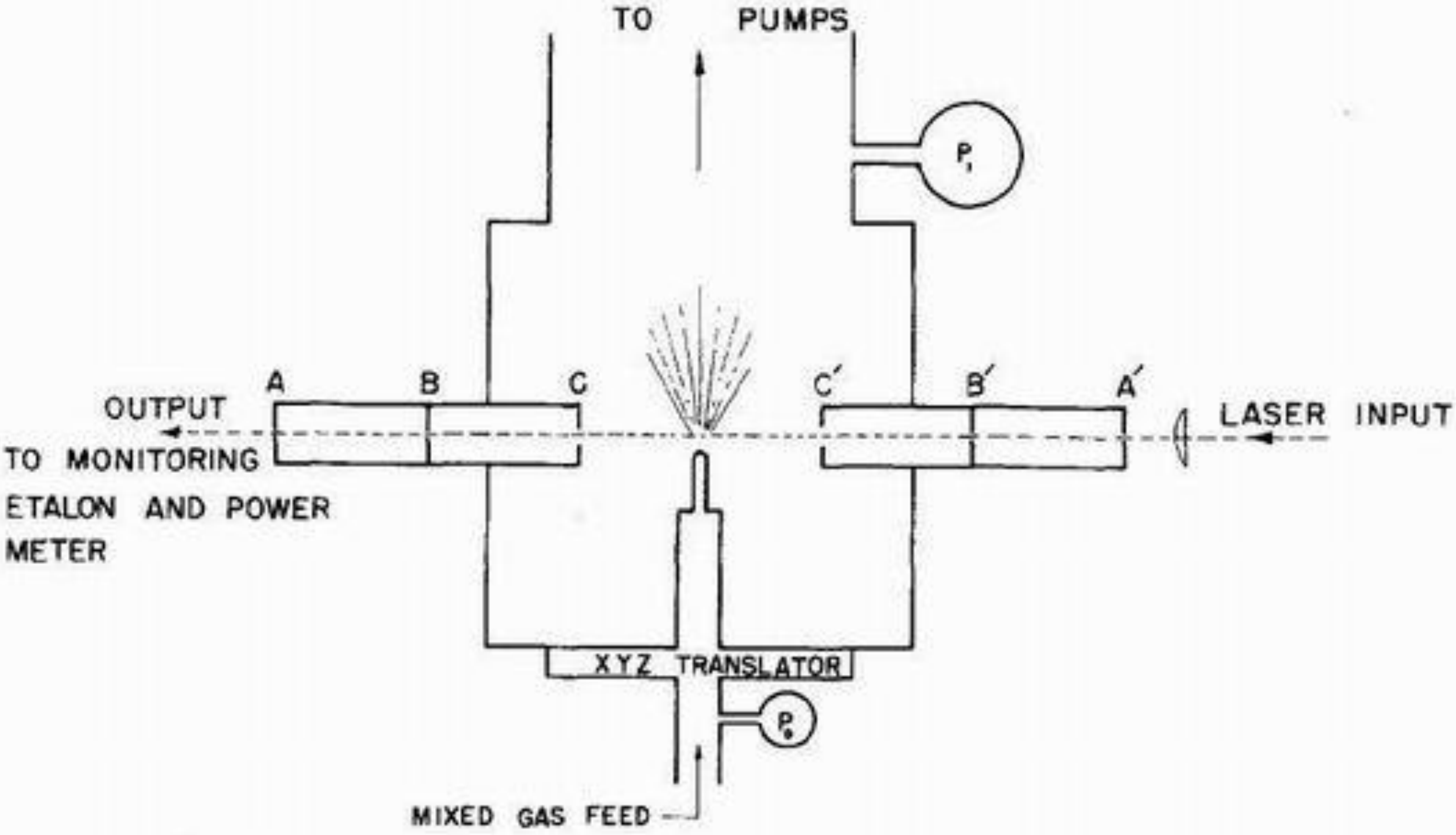
Molecular beam technique

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 (~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.

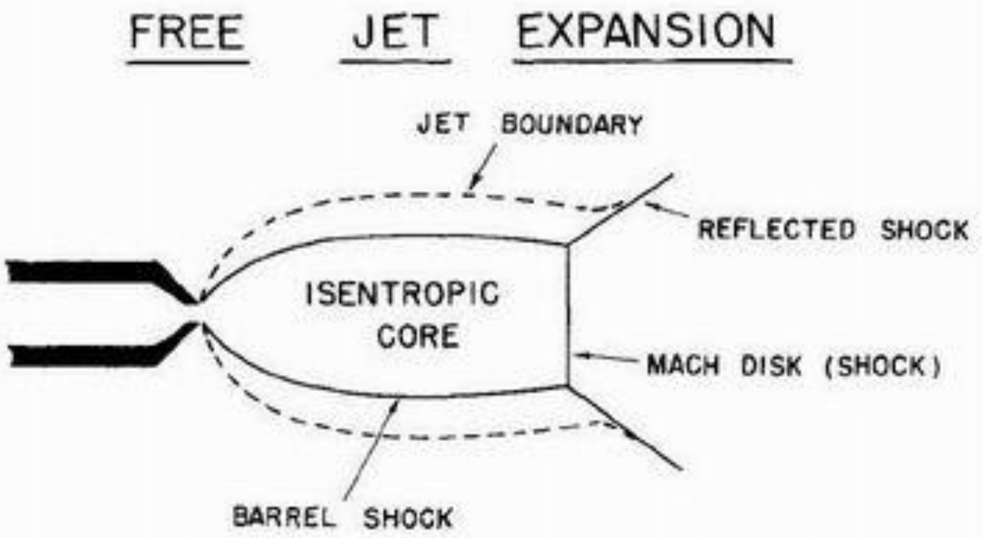
Schematic of supersonic jet apparatus



MBFIG. 2. Schematic of supersonic jet apparatus.

Ref.: Smalley, et al. J. Chem. Phys. 64, 3266 (1976).
The fluorescence excitation spectrum of the HeI_2 van der Waals complex

Shock structure surrounding the expanding of a free jet



$$\frac{X_m}{D} = .67\left[\frac{P_0}{P}\right]^{\frac{1}{2}}$$

MBFIG. 1. Shock structure surrounding the expanding gas of a free jet. Nozzle pressure is P_0, ambient pressure in expansion chamber is P_1; D is the diameter of the nozzle opening. X_m is the distance to the mach disk from the nozzle.

For an isentropic expansion of an ideal gas, e.g. He or Ar,

$T_2 / T_1 = (P_2/P_1)^{[(\gamma-1)/\gamma]}$

$\gamma = Cp/Cv = 5/3$,

If $T_1 = 273$ K, $P_2 = 10^{-4}$ torr, $P_1 = 84$ atm,

then

$T_2 = T_1\ (P_2/P_1)^{[(\gamma-1)/\gamma]}$

$= 273\ [10^{-4} /(84 \mathrm{x} 760)]^{[2/3]}$

$T_2 = 3.7\mathrm{x}\ 10^{-4}$ K (translational temperature)

Ref.: Smalley, et al. J. Chem. Phys. 64, 3266 (1976).

The fluorescence excitation spectrum of the HeI_2 van der Waals complex

Velocity distributions of effusive and supersonic molecular beams

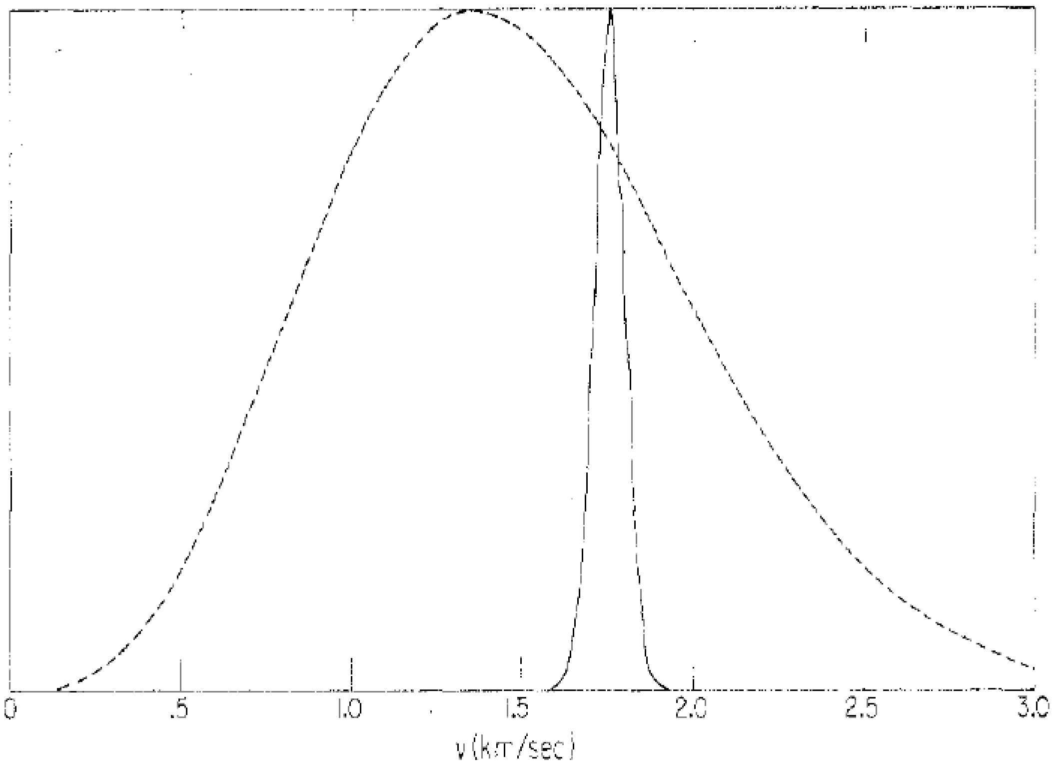


Figure 1. Velocity distribution in effusive molecular beam (dashed curve) and supersonic molecular beam (solid curve). Both curves are normalized to unity at the most probable velocity and are for helium at a reservoir temperature of 300 K. The curve for the supersonic molecular beam assumes the gas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

Smalley, et al. Acct. Chem. Res. 10 (1977) 139-145. Spectroscopy with supersonic jets

Vibronic spectrum of NO_2

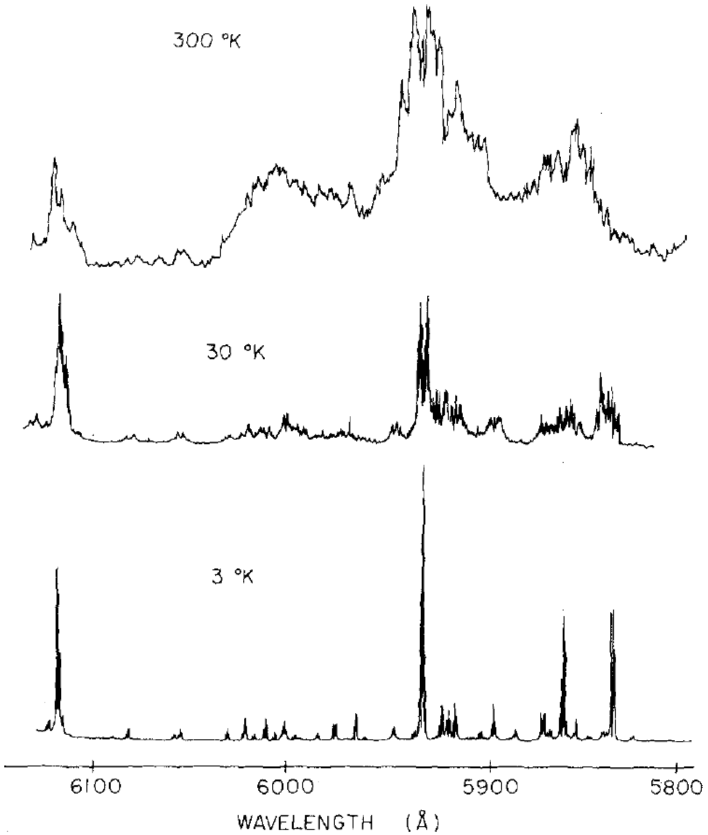


FIG. 1. A portion of the fluorescence excitation spectrum of NO_2 for (top) a conventional room temperature sample of pure NO_2 at 0.04 torr pressure, (middle) a supersonic beam of pure NO_2, and (bottom) a supersonic beam of 5% NO_2 in Ar. All spectra were taken using a cw dye laser. Laser bandwidth 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

Smalley, et al. J. Chem. Phys. 61 (1976) 4363-4364. Laser spectroscopy of supersonic molecular beams: Application to the NO_2 spectrum

(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 NO_2 molecules per cm^3 ?

(b) The excitation fluorescence spectrum of supersonically cooled pure NO_2.
At very low translational temperature (e.g 30 K), NO_2 molecules still rotate and vibrate.
Important features of a molecular beam include (1) molecular density is very high (e.g. 10^{15} molecules per cm^3), (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 NO_2 at STP?

(c) The excitation fluorescence spectrum of supersonically cooled 5% NO_2 in Ar. At very low translational temperature (e.g 3 K), NO_2 molecules still rotate and vibrate. This is called seeded molecular beam technique. The probability of inter-molecular NO_2-NO_2 collisions is substantially reduced.

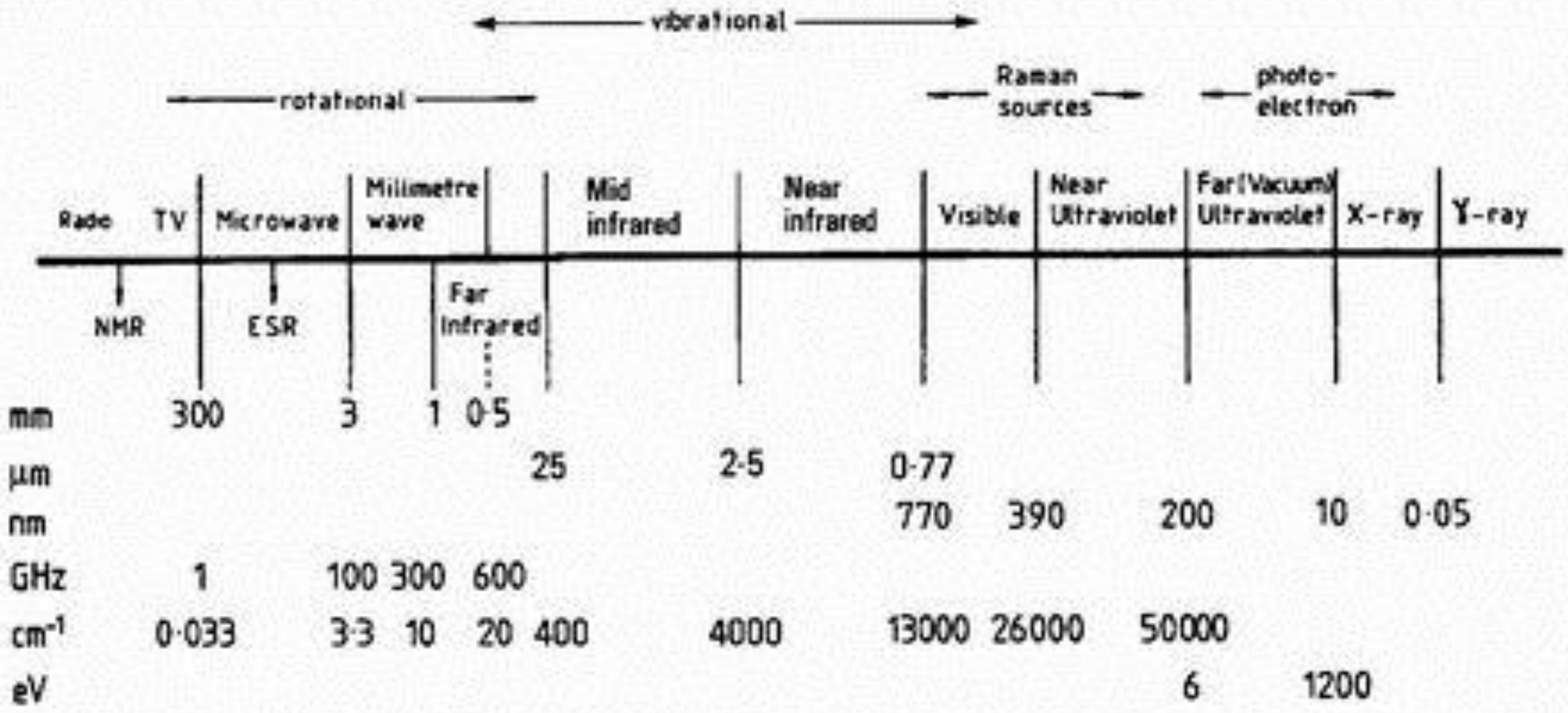


Figure 3.1 Regions of the electromagnetic spectrum

Vibronic (excitation LIF) spectrum of HeI_2

$D = 0.025$ mm, $P_0 = 110$ atm, $P = 10^{-4}$ torr

$X_m / D = 0.67\ [P_0/P]^{(1/2)}$, $X_m = 484$ mm $= 48.4$ cm

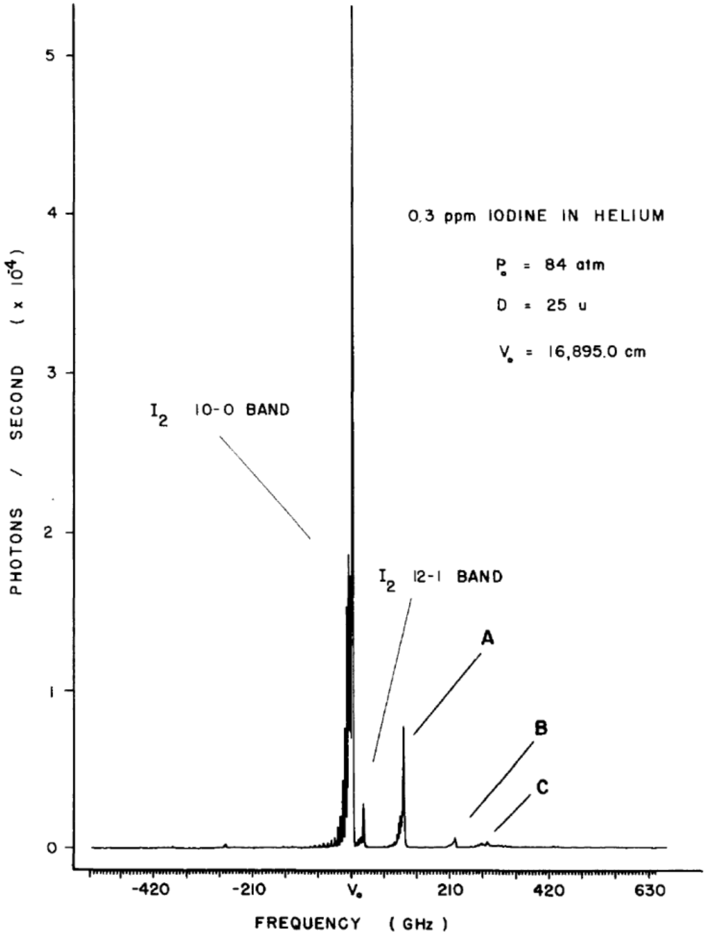


FIG. 4. Fluorescence excitation spectrum of a supersonic jet of I_2 in He in the spectral region near the 10–0 vibronic band of the $\tilde{B} \leftarrow \tilde{X}$ transition of I_2. Laser bandwidth was 1 GHz FWHM.

The molecular beam travels along flow streamline at 2×10^5 cm/s. The focused laser intersect the molecular beam at 2 mm downstream from the nozzle. The translational temperature is estimated to be 3.1×10^{-4} K. The rotational temperature of I_2 is less than 1 K and the vibrational temperature is 50 K.

Smalley, et al. J. Chem. Phys. 64 (1976) 3266 (1976).

Rotational temperature of a supersonically cooled I_2 molecular jet

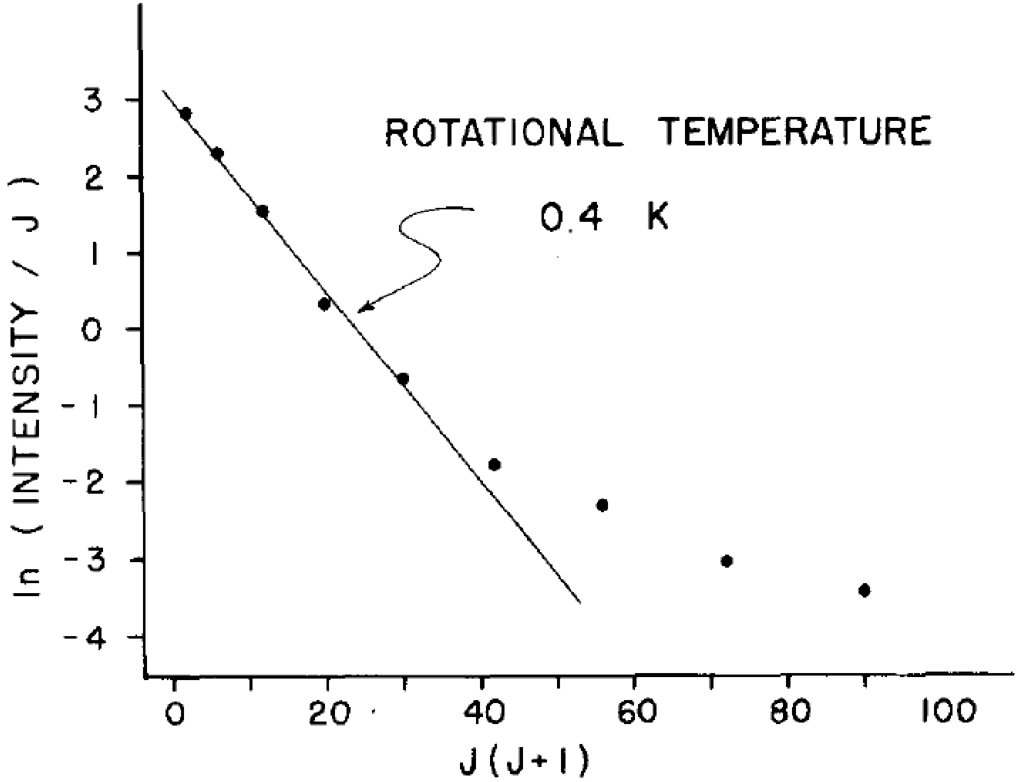
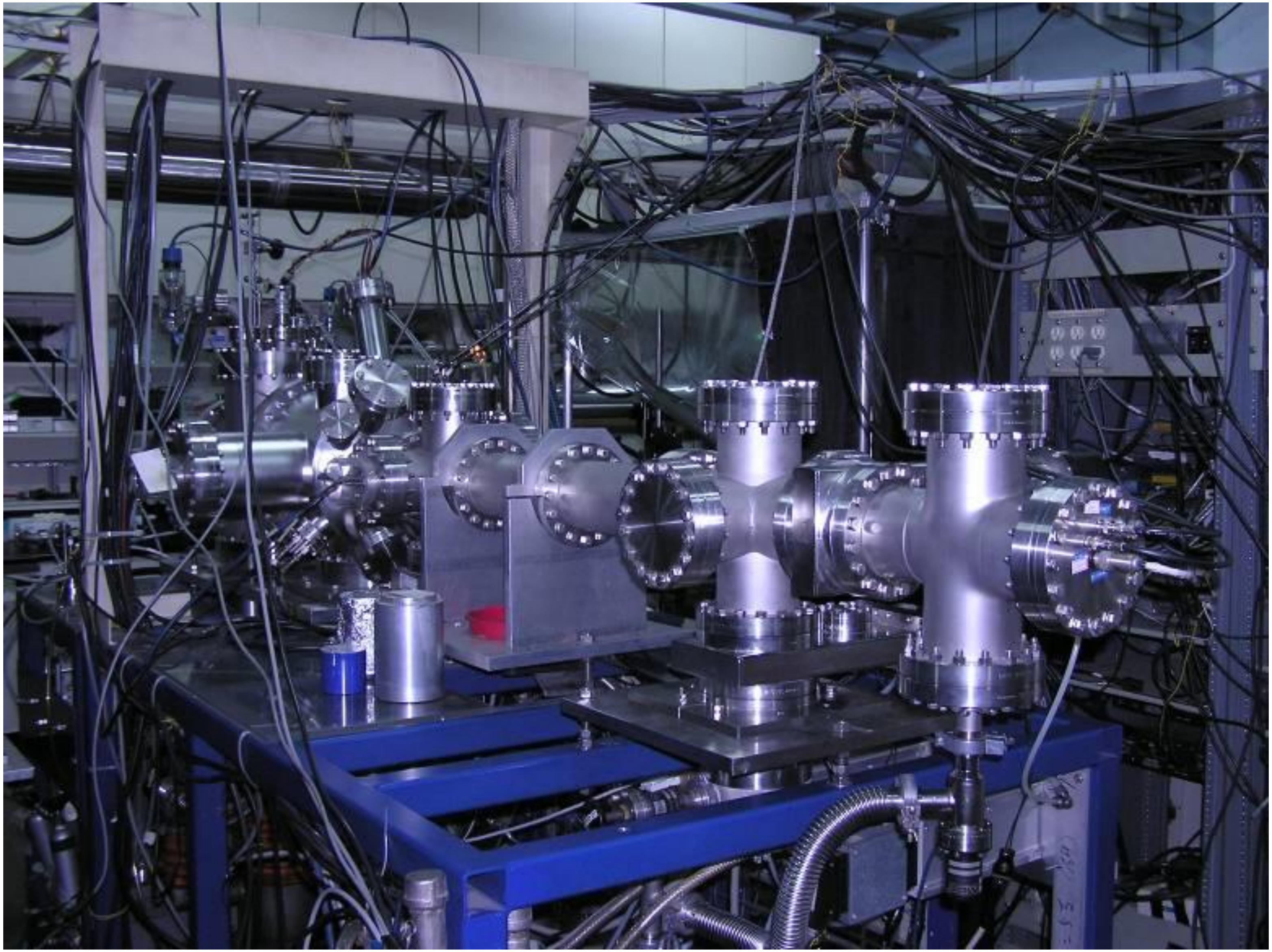


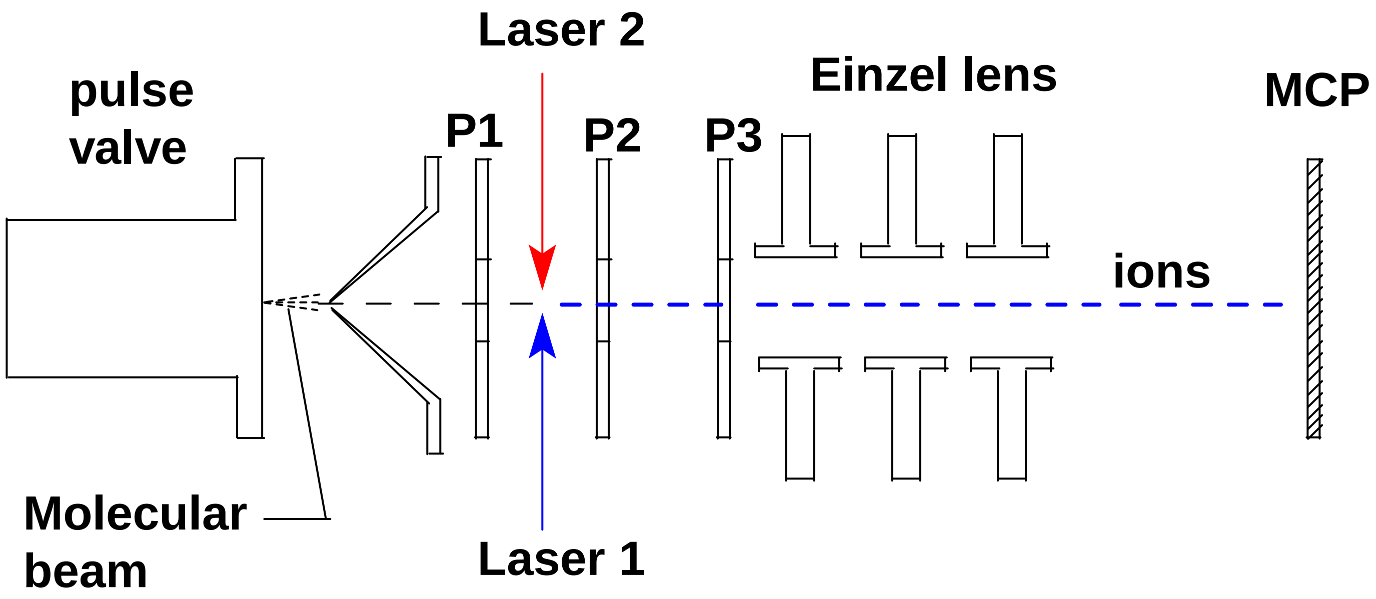
FIG. 7. Plot of the observed intensity of members of the *P* branch of the 10–0 vibronic transition of I_2 in the supersonic jet ($P_0 = 91$ atm, $D = 25$ μm, $X = 0.5$ cm. The axes have been chosen so as to produce a linear plot for a Boltzmann distribution of intensities.

Smalley, et al. J. Chem. Phys. 64 (1976) 3266 (1976).

TOF mass spectrometer for REMPI and MATI experiments



A linear co-axial type time-of-flight (TOF) mass spectrometer for laser spectroscopic experiments



For an isentropic expansion of an ideal gas, e.g. He or Ar,
$T_2 /T_1 = (P_2/P_1)^{[(\gamma-1)/\gamma]}$
$\gamma = Cp/Cv = 5/3$,
If $T_1 = 300$ K, $P_2 = 10^{-6}$ torr, $P_1 = 1000$ torr,
then $T_2 = 0.07$ K (translational temperature)

Under this experimental condition, the gas phase molecule is prepared at electronically ground S_0 state for laser spectroscopy (LIF, REMPI, etc.) experiments.

Velocity distributions of *p*-fluoroaniline/He, Ne, Ar seeded beams

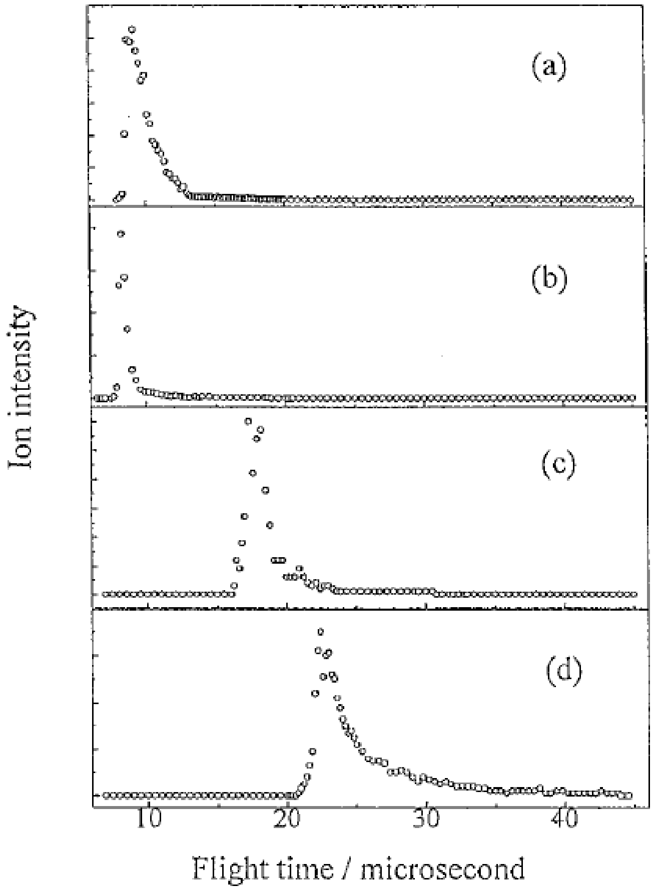


Figure 3. TOF spectra of *p*-fluoroaniline beams with the carrier gas of (a) He at 1.1 bar, (b) He at 2.3 bar, (c) N_2 at 2.3 bar, and (d) Ar at 2.3 bar.

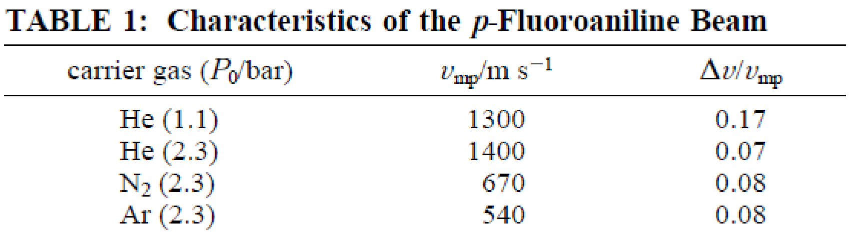


TABLE 1: Characteristics of the *p*-Fluoroaniline Beam

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

Tzeng, et al. J. Phys. Chem. A 103 (1999) 8612-8619. Ionization energy of *p*-fluoroaniline and vibrational levels of *p*-fluoroaniline cation determined by mass-analyzed threshold ionization spectroscopy