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Diode-Laser Spectroscopy of Supersonic Free Jets

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Abstract. A supersonic-free-jet infrared spectrometer has been constructed for investigation of molecular vibrational spectra at low rotational and vibrational temperatures. The sensitivity of measurement in a pulsed jet is increased by employing a phase-sensitive detection method synchronized with the pulse frequency. The performance of the spectrometer is examined for the absorption lines of the NH_3 ν_2 band. A rotational temperature as low as 16 K is attained when seeded in He. Cold-jet spectra are demonstrated for the ν_3 bands of PF_5, $^{34}SF_6$, and $^{182}WF_6$.

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Supersonic free expansion is well known as a method for producing substantial lowering of rotational and vibrational temperatures of molecular gases without condensation [1,2]. This method has been applied to high-resolution spectroscopy of stable and unstable molecular species in the visible and radiofrequency region. There have been a number of reports of the use of a cold jet in laser-induced fluorescence [2,3], molecular-beam electric resonance [4,5] and pulsed Fourier-transform microwave spectroscopy [6,7].

In the infrared region, however, only a small number of works have been reported on high-resolution spectroscopy using a cold jet [8–14]. We have constructed a supersonic-free-jet infrared absorption spectrometer using a frequency-tunable semiconductor-diode laser, which will allow this method to be applied extensively to various fields of molecular spectroscopy. An important improvement in our apparatus is the employment of a phase-sensitive detection method in a pulsed jet measurement, which produces a large increase in sensitivity. A Stark modulation method is also found to be useful for detection of weak absorption lines in polar molecules. Cold-jet spectra are observed in many organic and inorganic compounds. This letter paper reports on experimental details and performance of the spectrometer examined on the ν_2 band absorption lines of NH_3. A part of the ν_3 bands of PF_5, $^{34}SF_6$, and $^{182}WF_6$ is presented for demonstration of the cooling effect and the sensitivity.

1. Experimental

Figure 1 shows a block diagram of the spectrometer which is similar to those reported previously [9, 13]. Pure or seeded gas at a pressure of 0.1–5 atmosphere was injected from a nozzle into a stainless steel chamber which was evacuated by a 15 cm oil diffusion pump (1000 l/s) backed up with a rotary pump (500 l/min). A cold trap at liquid-nitrogen temperature was used to cryopump the injected sample.

The nozzle employed was either a modified automobile fuel injector for a pulsed flow [15, 16], or for a continuous flow a pin-hole in a Pyrex glass or in a thin metal sheet. The pulse nozzle with a 0.1 mm orifice was operated with a repetition rate up to 200 Hz with a 1 ms minimum pulse width. Laser diodes provided by Fujitsu and Laser Analytics were mounted on a SP 5000 Laser Spectrometer. The laser beam was

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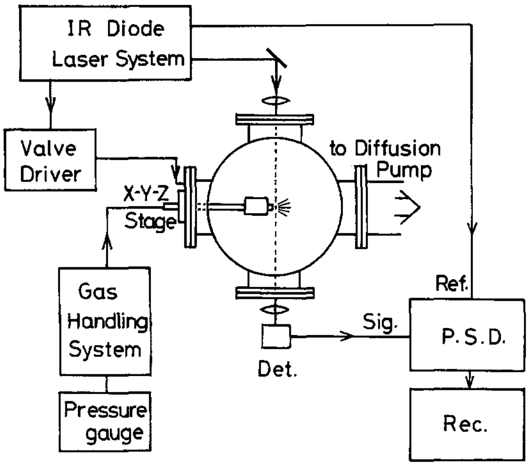

Fig. 1. A block diagram of supersonic-free-jet infrared absorption spectrometer. An arrangement for a pulsed jet measurement is shown

focused to 1 mm diameter near the nozzle head. A single-path absorption in the pulsed flow was detected phase-sensitively synchronized with the pulse frequency. The nozzle was mounted on an *X*-*Y*-*Z* stage to allow adjustment of the position of the nozzle head relative to the laser beam. The Stark effect of infrared absorption lines was observed by applying 0–1 kV 100 kHz square waves on two small parallel-plate electrodes (5 mm gap) attached on a pyrex nozzle.

2. Results and Discussion

The cooling effect by supersonic free expansion was examined on the NH_3 ν_2 $aQ(1,1)$ and $aQ(2,2)$ lines at 930 cm^{-1} under various experimental conditions. A typical trace of the cold-jet spectrum over the Q-branch region is shown in Fig. 2 with a room-temperature gas spectrum in the upper part. Only the $aQ(1,1)$ and $aQ(2,2)$ lines, which had the lowest rotational energies among the observed lines, were strong in the cold-jet spectrum indicating substantial lowering of the rotational temperature by supersonic free expansion. The rotational temperature was calculated from the intensity ratios, I_{jet}/I_{gas}, of the two lines by assuming that the intensity was proportional to the lower-level population density. The variation of the rotational temperature T vs. the distance between the nozzle head and laser beam X is shown in Fig. 3 for different source pressure and mixture ratios of NH_3 and He. A rotational temperature of 16 K was attained in a NH_3 : He = 1 : 9 mixture at 780 Torr total pressure. The rotational temperature attained its lowest value at a distance of a few millimeter from the nozzle head with a slight increase as the distance increased. The latter effect may be due to insufficient pumping speed of our vacuum line when He is used.

Spatial distribution of the $aQ(1,1)$ absorption intensity was measured for various relative positions of the laser beam to the nozzle head. The result is shown in Fig. 4 where Y indicates the distance of the laser beam from the X axis. The distribution shows deviation from the cosine law with higher density in the direction of X axis. Although the intensity is not necessarily proportional to the molecular density in the jet since the rotational temperature depends on X and Y, the figure can be considered as a density distribution of the injected gas. From these measurements, the optimum position for observation of a cold-jet spectrum was determined to be 1–2 mm from the nozzle head where the rotational temperature was low enough to suppress hot-band and high-J rotational lines while the density of molecules was still high enough to observe infrared absorption in a single path.

The line shape observed in the cold jet shows a remarkable deviation from the Gaussian form. As the source pressure increases, the line shape tends to take a

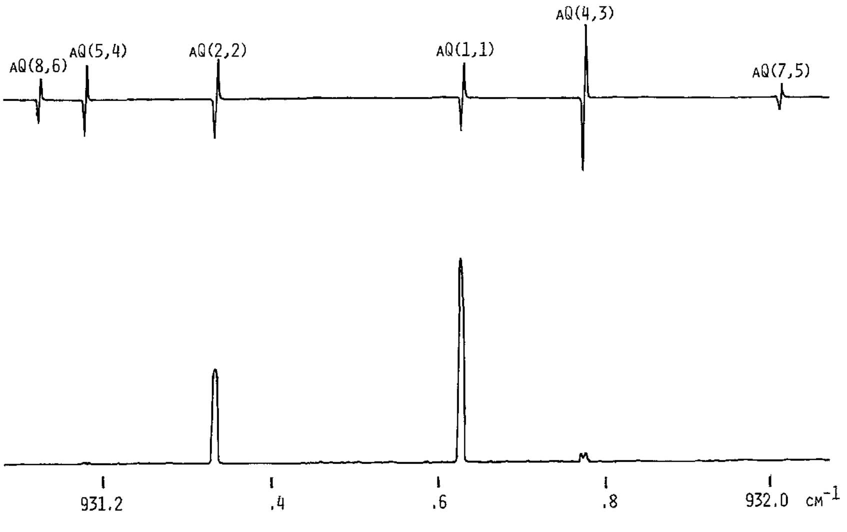

Fig. 2. Infrared absorption spectra of the NH_3 ν_2 Q-branch region in the pulsed jet (lower) and room temperature gas (upper). The cold-jet spectrum was recorded in the mixture of NH_3 : He = 1 : 2 with 870 Torr total pressure. The spectra are not normalized by the laser power. The dispersive line shape in the gas spectrum is due to phase-sensitive detection of the source modulation. Note the increase in line width of the cold-jet spectrum

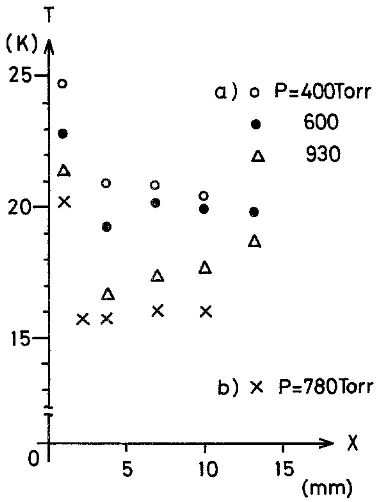

Fig. 3a and b. Variation of rotational temperature vs. the distance between the nozzle and laser beam. Mixture ratios of NH_3 with He are 1:2.5 in (a) and 1:9 in (b). Data were taken in a pulsed jet

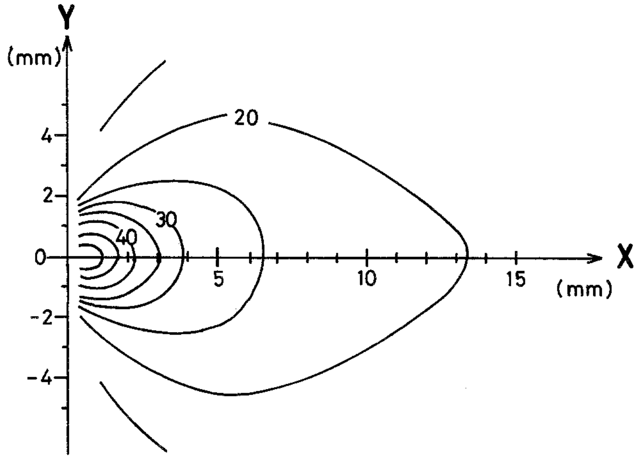

Fig. 4. Spatial distribution of the $aQ(1,1)$ absorption intensity measured in a pulsed jet. Data were taken for pure NH_3 with 950 Torr source pressure. Figures on the contour lines indicate relative intensities

pillar-shaped form, frequently showing a shallow dip on the top. The line width of the cold-jet spectrum in Fig. 2 is about 200 MHz (FWHM), which is 2.4 times the Doppler width at a room temperature. This increase in line width has been observed more or less in all of the pure and seeded cold-jet spectra. The effect will be partly due to the increase in the velocity of molecules by conversion of internal energy to translational energy during the cooling process.

Under the condition of phase-sensitive detection, absorption of the order of 0.01% can be measured with the spectrometer. In addition to the enhancement of sensitivity by two order of magnitudes compared to a direct absorption method, the phase sensitive detection method provides another advantage of a flat base line of the signal. The sensitivity, which is limited at present by fluctuation of the laser power caused by mechanical vibration of the cold head, will be improved by using a pulse nozzle with a higher repetition frequency. As one of the methods to avoid low-frequency noise associated with the laser source, Stark modulation at 100 kHz was attempted for detecting weak absorption lines of polar molecules in a continuous flow. The result on the NH_3 lines indicated that an absorption of 10^{-6} could be measured if the infrared absorption line had a large Stark shift. This method may be useful for detection of weakly-bound complexes.

Infrared absorption spectra were observed in NH_3, SF_6, SiF_4, PF_5, CF_3H, CF_2Cl_2, CF_3Br, C_2H_2, BCl_3, MoF_6, and WF_6. Extensive spectra have been taken for PF_5 (ν_3, 946 cm^{-1}; ν_5, 1023 cm^{-1}), CF_3H (ν_1, 3035 cm^{-1}), and WF_6 (ν_3, 713 cm^{-1}). The results will be published elsewhere. Figure 5 shows a cold-jet spectrum of the PF_5 ν_3 band with a room-temperature gas spectrum in the upper part. In spite of relatively simple rotational structure characteristic to a parallel

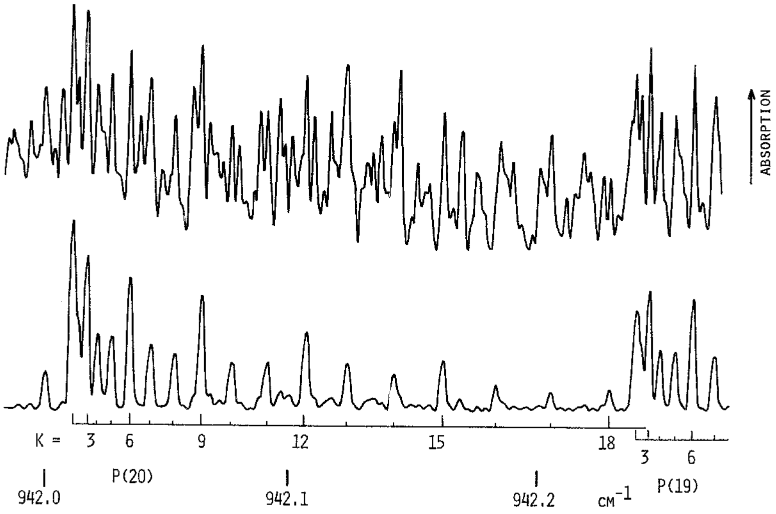

Fig. 5. A part of the PF_5 ν_3 P-branch spectrum in the pulsed jet (lower) and room temperature gas (upper). Pure sample at a pressure of 900 Torr is used. When seeded in Ar, the absorption lines are too weak to be recorded with a good S/N ratio

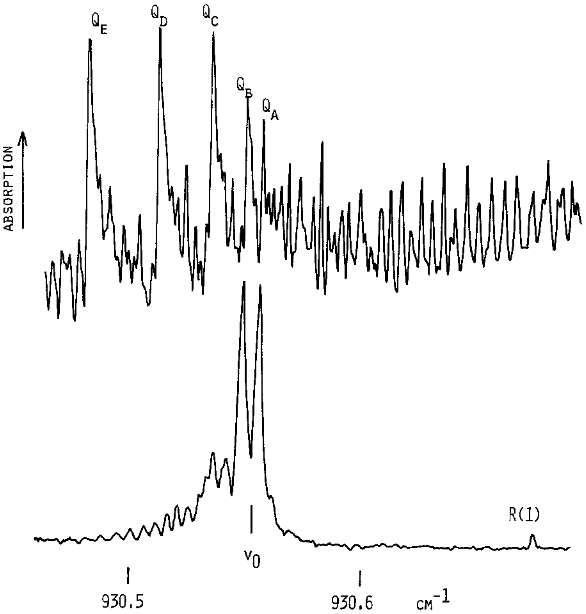

Fig. 6. Cold-jet (lower) and room-temperature gas (upper) spectra of the $^{34}SF_6$ ν_3 Q-branch. Naturally abundant species (4.2%) in the mixture of 150 Torr SF_6 and 600 Torr Ar was used. Peaks denoted by Q_A, Q_B, etc. correspond to sub-band heads formed by the sixfold degenerate clusters. The cold spectrum has much simpler structure by depletion of high J lines. The estimated rotational temperature is 25 K

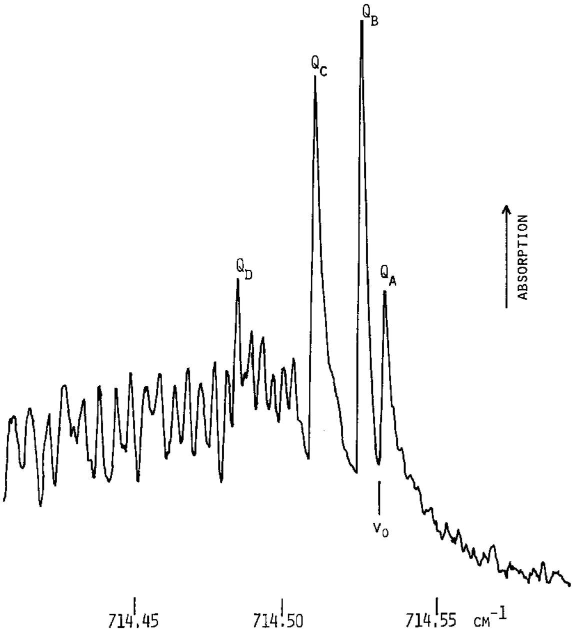

Fig. 7. Cold-jet spectrum of the $^{182}WF_6$ ν_3 Q-branch. The spectrum was taken with a naturally abundant isotopic species (26.4%) in a pure sample. The source pressure was a saturated vapor pressure at a room temperature (slightly over 1 atm). The pulse frequency was 141 Hz. Fine structure similar to SF_6 is clearly resolved

band of symmetric top molecules, measurement at low rotational and vibrational temperatures is definitely necessary because only 20% of PF_5 is in the ground vibrational state at a room temperature. The advantage of measurement in a cold jet is obvious: the dense hot-band lines which cover the ν_3 fundamental in the room-temperature spectrum are almost entirely depleted in the cold-jet spectrum. The spectrum was taken with a pure sample because, when seeded in Ar, the rotational temperature was too low to record the absorption lines of this region with a good signal-to-noise ratio.

Figure 6 shows a cold-jet spectrum of the $^{34}SF_6$ ν_3 Q-branch region taken with naturally abundant isotopic species (4.2%) in the mixture of 150 Torr SF_6 and 600 Torr Ar. Peaks denoted by Q_A, Q_B, Q_C etc. are sub-band heads formed by sixfold degenerate clusters of lines [17]. Since the sub-band head Q_C (turning point at $J=23$) is completely depleted while Q_B (turning point at $J=13$) still remains strong, the rotational temperature is estimated to be approximately 25 K. This measurement indicates that an infrared absorption spectrum of isotopic species with 1% natural abundance can be measured easily without using an isotopically enriched sample if the relevant absorption band is strong.

Spectroscopic measurement in a cold jet becomes more important for heavy molecules because, as the mass of molecules increases, less molecules are populated in the ground vibrational state at a room temperature. As an example of the cold-jet spectrum of heavy molecules, the ν_3 Q-branch of $^{182}WF_6$ is shown in Fig. 7. The spectrum taken with a pure sample shows a structure similar to SF_6 with longer tails to the low frequency side. Although the cooling effect is less efficient in a pure sample, the result indicates that cold jet spectroscopy of heavy molecules is practical even with a pure sample unless measurement under a very low rotational temperature is necessary. Further works are in progress.

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