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TITLE: USE OF A FREE-EXPANSION JET IN ULTRA-HIGH-RESOLUTION RAMAN SPECTROSCOPY

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B302

Use of a free-expansion jet in ultra-high-resolution Raman spectroscopy

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Abstract

Rotationally-resolved, ultra-high-resolution stimulated Raman spectra of CH_4, CD_4, and SF_6 have been obtained in cw and pulsed free-expansion jets, using a simple and inexpensive nozzle-and-vacuum-chamber apparatus. Through variation of the nozzle orifice diameter, nozzle backing pressure, and axial location of the spectroscopic probe region it is possible to nearly independently control the spectral Doppler width, rotational temperature, and molecular density in the jet. Using relatively mild expansion conditions we have been able to cool a pure methane jet to a rotational temperature of 13K. We show here how this control of temperature, independent of density, allows separation of otherwise unresolvable spectral features and unambiguous identification of band-heads, hot-bands, and other spectral features.

Introduction

Free-expansion jets have been shown to be extremely useful as spectroscopic media.[1] Most of the work done to date has involved electronic spectroscopy of molecules far downstream in the jet, where the temperature is very low, typically a few kelvin. However, the earlier part of the jet, where the temperatures are 300K to 10K, provides a unique environment for high-resolution rotational and vibrational spectroscopy. In this paper we report the use of cw and pulsed free-expansion jets in a high-resolution coherent Raman study. We have chosen stimulated Raman spectroscopy as the spectroscopic probe because of its high sensitivity and spatial resolution and also because, in contrast to other nonlinear techniques, it yields direct Raman spectra.

Experimental

The stimulated Raman technique uses a high power pulsed laser to produce a "pump" beam which induces an absorption (inverse Raman spectroscopy) or emission (stimulated Raman gain spectroscopy) in the sample at the anti-Stokes or Stokes shifted frequency. A gated cw laser, the "probe," is used to monitor this transient absorption or emission, which is detected by a photodiode and averaged by a boxcar integrator. Spectral scanning of the pump laser results in a display of the Raman spectrum.

Our stimulated Raman system uses a 10 pps, 6 nsec pulse length frequency-doubled Nd:YAG laser system to pump three successive dye amplifiers, which are used to amplify (to 2 MW peak power with 75 MHz linewidth) the input from a single-mode electronically-scannable cw dye laser oscillator. This provides the pump beam. A single frequency cw ion laser is used as the probe beam.

We have used both cw and pulsed free-expansion sources for these experiments. The jet emanated from a pinhole nozzle into a vacuum chamber pumped by two 10-inch oil diffusion pumps. The optical pump and probe beams were focused by a 40 cm F.L. lens into the molecular jet perpendicular to the jet axis, with a relative crossing angle of 5 degrees, yielding a sampling volume of approximately 100 μm diameter and 1.4 mm length.

Since the expansion produces a jet of finite divergence (~90°), an optical interaction length which was short compared to the jet diameter was necessary to reduce the effective Doppler width. This was achieved by using a fairly "steep" (~5°) laser crossing angle. Despite the small interaction volume, the high density and reduced partition function in the jet resulted in observed signal strengths comparable to those observed in gas cells at a few Torr pressure.

Results

We have obtained rotationally resolved spectra of CH_4 in a cw free-expansion jet, and of CD_4 and SF_6 in a pulsed free-expansion jet. These spectra, and for comparison room temperature static gas spectra, are shown in Figures 1-4. In the CH_4 spectra of Figure 1 one can

B302

see how the Doppler width reduction effected by the cooling in the jet permits improved resolution, the fine structure in Q(3) and Q(4) lines being clearly resolved in the mild expansion jet spectrum. The CD_4 spectra of Figure 2 indicate how this cooling can aid considerably in identifying band-heads and hot-bands. The nozzle spectrum allows unambiguous identification of the Q(0), Q(1), Q(2), and Q(3) lines, due to the disappearance of the hot bands at low temperature. In free-expansion jets the rotational cooling is generally greater than the vibrational cooling, i.e., $T_{rotation} < T_{vibration}$. This feature of the jet can be exploited to reveal vibrational hot-bands which are concealed by rotational structure of the fundamental at room temperature. An example of this situation is shown in the SF_6 spectra of Figure 3. The ν_6 hot band near 774.18 cm^{-1} is strongly overlapped by the high rotational states of the fundamental in the room temperature spectrum, but is clearly evident in the jet spectrum.

It is important to note that the spectra obtained here of cold molecules in the jet could not be obtained by simply cooling a gas cell to low temperature. At the temperatures produced in the jet the equilibrium vapor pressure of almost all molecular species are 10^{-4} to 10^{-15} Torr or less, much too low to allow stimulated Raman spectroscopic studies. However, since the molecules in the jet are not in thermodynamic equilibrium, pressures much greater than equilibrium values are commonly obtained. For example, in our jet spectrum of SF_6 in Figure 3 the pressure of SF_6 in the jet at the point at which the spectrum was recorded was $\sim$10 Torr, 10^{10} times greater than the equilibrium vapor pressure.

Conclusion

Our results demonstrate the desirability and feasibility of applying coherent Raman techniques to precise spectroscopic studies in molecular jets. As indicated by our preliminary work on CH_4, CD_4, and SF_6, the free jet affords great control over the Doppler width, molecular density, and rotational temperature, and this should prove to be considerably helpful in spectroscopic analysis. This technique should also allow Raman spectroscopic studies of weakly bound, so called van der Waals molecules, such as Ar_2, as well as studies of rotational and vibrational relaxation in free jets.

Acknowledgments

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References

1. Smalley, R. E., Wharton, L., and Levy, D. H., "Molecular Optical Spectroscopy with Supersonic Beams and Jets," Accounts Chem. Res., Vol. 10, p. 139 (1977).
2. Owyoung, A., Laser Spectroscopy IV, H. Walther and K. W. Rothe, Eds., Springer-Verlag, NY 1979.

B302

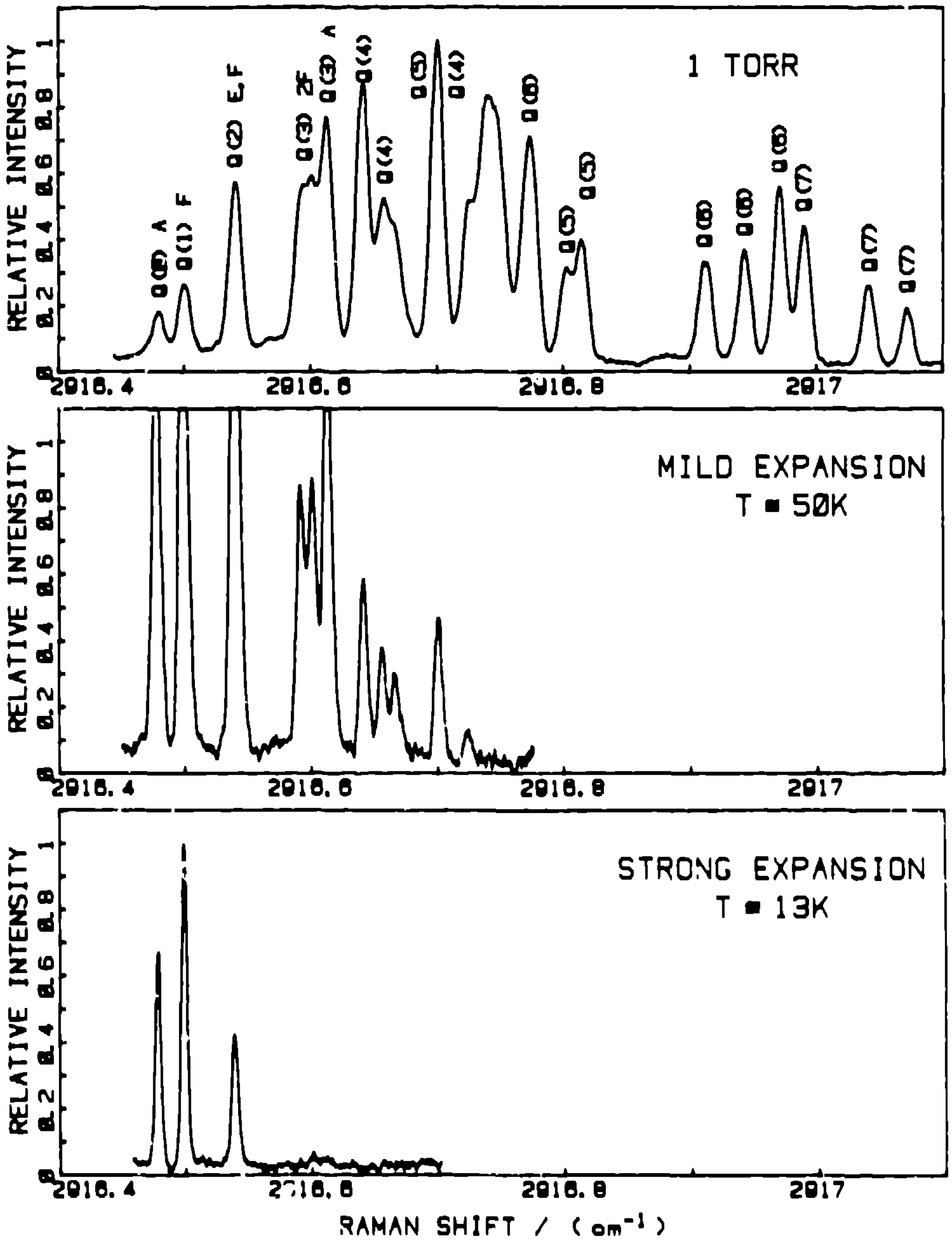

Figure 1. Spectra of the ν_1 Q branch of CH_4. The top spectrum is that obtained in a room temperature, static gas sample of CH_4 at 1 Torr. The two lower spectra were obtained in a cw free expansion jet, the mild expansion with 150 μm diameter orifice, 4.8 psi backing pressure, 1.8 mm downstream; the strong expansion with 100 μm orifice, 55 psi pressure, 4.5 mm downstream. Note the resolution of the Q(3) and Q(4) lines in the mild expansion spectra, and the greatly reduced linewidth in the strong expansion.

B302

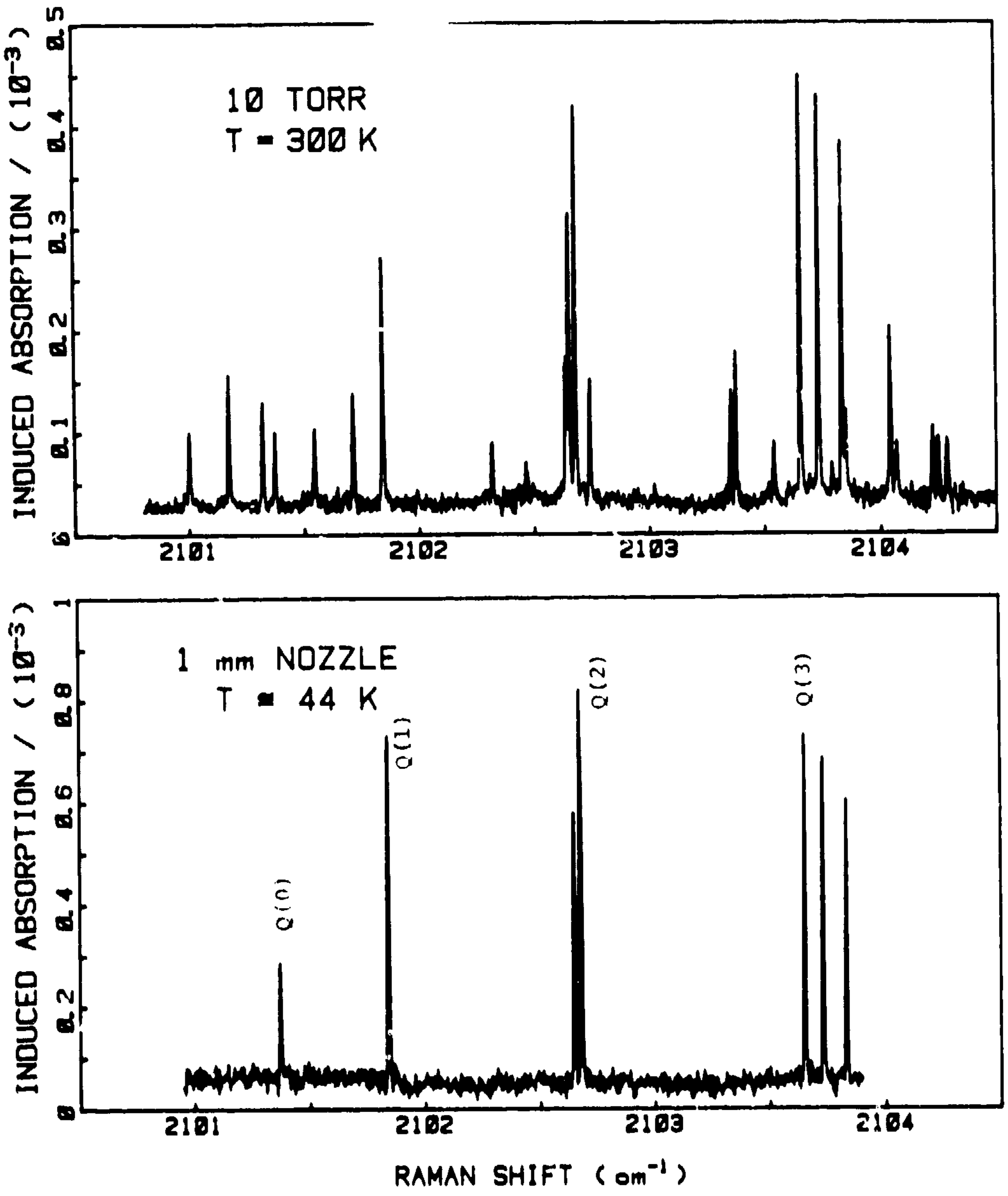

Figure 2. Spectra of the ν_1 Q branch of CD_4. The top spectrum is that obtained in a room temperature, static gas sample of CD_4 at 10 Torr. The bottom spectrum is that obtained in a pulsed jet with 1000 μm diameter orifice, 50 psi backing pressure, 2.7 mm downstream The rotational temperature in the jet is 44K. The jet spectrum shows unambiguously that the Q(0) line is that at ~2101.35 cm^{-1}, and allows easy identification of hot bands in the static gas spectrum.

B302

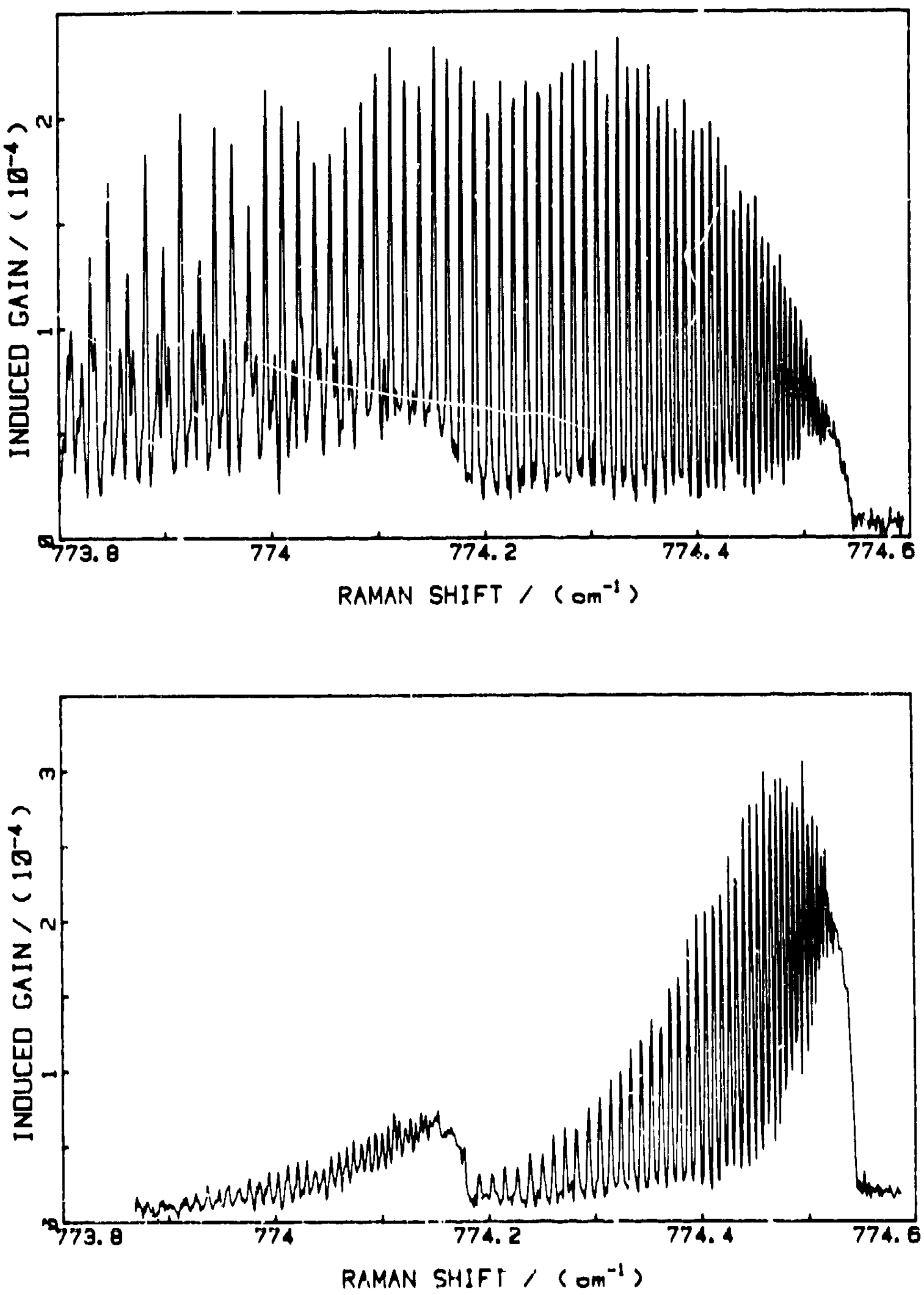

Figure 3. Spectra of the Q-branch of the ν_1 mode of SF$_6$. The top spectrum is that obtained in a room temperature, static gas sample of SF$_6$ at 3.5 Torr. The bottom spectrum is that obtained in a pulsed free-jet expansion in SF$_6$. The jet backing pressure was 92 psi, the nozzle orifice was 1000 μm diameter, and the spectroscopic interaction region was located 5.5 mm downstream of the orifice. The rotational temperature in the jet is ~70K. Note the separation of the ν_6 hot band in the jet spectrum.