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ULTRA HIGH RESOLUTION INVERSE RAMAN SPECTROSCOPY OF METHANE IN A CW FREE EXPANSION JET*

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An ultra-high resolution inverse Raman spectrum of $^{12}CH_4$ has been obtained in a cw free-expansion jet in which the gas has been cooled into a non-Boltzmann distribution of three rotational levels corresponding to the meta, para and ortho nuclear spin states.

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DISCLAIMER

IRS OF METHANE IN A FREE EXPANSION JET

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Supersonic free expansion jets can provide an intense source of molecules in a virtually collision free environment. The resultant low vibrational and rotational temperatures and narrow velocity distributions make these sources particularly effective in spectroscopic applications. Recent developments in coherent Raman spectroscopy offer an excellent opportunity to utilize these special characteristics.

The application of coherent-anti-Stokes Raman spectroscopy (CARS) to a free expansion jet has been previously proposed and considered theoretically.[1] Preliminary low resolution experimental CARS studies of jets have also been conducted recently.[2] In this paper we report the first use of a cw free expansion jet in a high-resolution coherent Raman study. We have chosen quasi-cw inverse Raman spectroscopy[3] as the spectroscopic probe because of its high sensitivity and spatial resolution and also because, in contrast to other non-linear techniques, it yields direct Raman spectra.

The ν_1 fundamental of $^{12}CH_4$ was selected for these preliminary studies because of its large cross section. Furthermore, its complex spectrum would be considerably simplified by both internal state cooling and reduction of its 270 MHz room temperature Doppler width.

The actual apparatus used here has been previously described[3]. In short, a tunable 2 MW pulsed pump source, with a bandwidth of 75 MHz, is used to induce inverse-Raman absorption on a stable, single-mode, cw argon-ion laser anti-Stokes probe source. Backed by 55 psi of pure methane, the free-expansion jet emanates from a 100 μ 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^{o}, yielding an approximate sampling volume of 100 μ diameter and 1.4 mm length.

Since the expansion produces a jet of finite divergence ($\approx 40^{o}$ in this case), an optical interaction length which is short compared to the jet diameter is necessary to reduce the effective Doppler width. We have reduced this length by a factor of five from that used in previous IRS studies. Despite this reduction, the high density and dramatically reduced partition function in the jet result in an observed signal strength, 4.5 mm downstream of the nozzle, comparable to that of 6 Torr of room temperature methane.

The spectra obtained in this jet are striking in their simplicity. The complex ν_1 spectrum, which exhibits over 50 lines at room temperature, is reduced to three well-resolved rotational lines. A comparison of the relative intensities of the observed J = 0, 1 and 2 lines indicates that their populations are distinctly non-Boltzmann. This behavior is traceable to the effects of nuclear spin[4]. In a tetrahedral molecule composed of spin 1/2 nuclei, the J = 0 level is pure spin quintet, the J = 1 level is a pure singlet, and the J = 2 level is mixed singlet and triplet. These total I = 0, 1, 2 states, designated para, ortho and meta respectively, are analogous to the para and ortho modifications of H_2. Because of the very slow relaxation rates of nuclear spins, the rotational state populations of methane are unable to fully equilibrate at low temperatures, and instead they

reflect the same relative abundances (5:2:9) of meta, para and ortho states as occur at room temperature. This effect, which is clearly demonstrated in our spectra, fully accounts for the observed intensities and leads to a rotational temperature in the jet of 13K.

In addition to rotational cooling, a corresponding reduction of the Doppler width to less than 105 MHz has also been observed. Further reduction of the linewidth should be attainable by sampling an even smaller fraction of the diverging molecular jet.

Our preliminary results demonstrate the feasibility of applying coherent Raman techniques to precise spectroscopic studies in molecular beams. Modification of the present apparatus to a pulsed jet should allow peak flow rates two to four orders of magnitude higher than currently possible, thus yielding even lower temperatures and higher sensitivities.

References

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