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FT-jet spectroscopy: Vibrational energy transfer in N_2O

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Abstract

A set-up combining a high resolution Fourier transform interferometer and a quadrupole mass spectrometer with a supersonic jet expansion produced thanks to a large turbomolecular pumping unit is described. A rotational temperature close to 3 K is demonstrated. Vibration–vibration energy transfer in the expansion affecting the $v_2 = 1$ state in N_2O is monitored in the presence of various collision partners. The transfer from the $v_2 = 1$ state of N_2O towards the quasi resonant, lower energy $v_2 = 1$ state of OCS is demonstrated, in particular.

1. Introduction

Fourier transform-jet spectroscopy (FTJS) was demonstrated in the literature to successfully address a variety of issues including the complete or partial unravelling of dense spectra of larger species over broad energy ranges (see review in [1]). Recent instrumental developments were reported in the FTJS literature, all exploiting powerful pumping units to produce the supersonic expansion, (e.g. [2,3]). We have significantly modified our set-up at ULB, previously relying on Roots blowers and now using a turbomolecular pump. A quadrupole mass spectrometer with a retractable sampling probe was also interfaced to the new jet cell. We are describing this set-up in this Letter and reporting on initial experiments exploiting these facilities.

2. Experimental set-up and performances

The experimental set-up is schematized in Fig. 1. It includes a high resolution Fourier transform spectrometer Bruker IFS120HR with $0.0043\ cm^{-1}$ optimal resolution (defined as $0.9/\delta$, with δ the maximum optical path difference). All experiments reported here were achieved at full instrumental resolution. The light source is a heated resistor, focused onto the entrance iris of the FT instrument. The light exiting the spectrometer through the iris is focused using two plane mirrors and a torroïdal one into the jet chamber. The light is then collected and focused onto a MCT or InSb detector. The waist of the light spot under the jet expansion is the image of the iris, 1.5 mm in diameter. Compared to laser sources, a large section of the expansion is therefore probed as well as some residual, hotter gas, as usual with FTJS. The hot gas contribution is reduced by setting the cell windows as close to the expansion as possible. Nevertheless, a blend of molecules at different rotational temperatures contributes to the absorption, unfortunately limiting the quantitative analysis of the absorption intensity. Another well known limitation, (e.g. [4]) to quantitative treatment is optical thickness which, combined with resolution limitation, deeply reduces the apparent intensity of the stronger lines in the observed spectrum. We were therefore careful to use pressure conditions such that the transmittance of the lines of interest was limited to 50%.

The present set-up relies on a large turbomolecular pump, Leybold MAG W3200 CT which is backed by an Alcatel ADS 860 HII group. Compared to our previous system, based on a large Roots blower [5], the amount of material probed in the jet is significantly reduced, making the study of non standard gases more practical but leading

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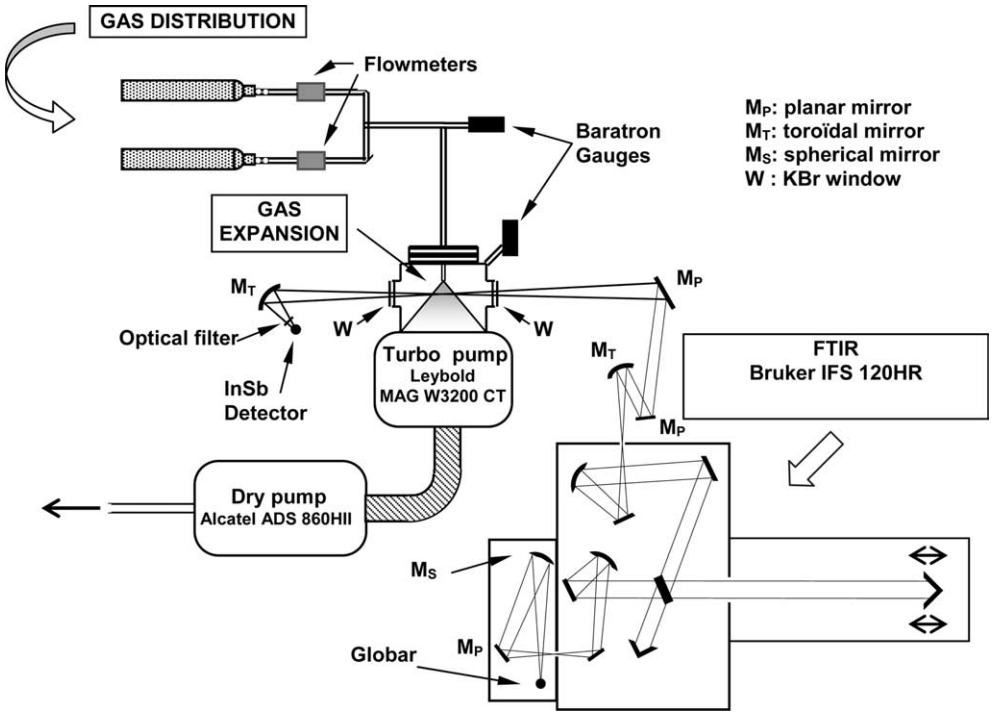

Fig. 1. Schematic view of the experimental FT-jet set-up.

to a decrease in the signal to noise ratio of at least one order of magnitude. On the other hand, the pressure in the absorption cell is dramatically reduced, typically from 0.1 hPa down to 0.01 hPa, for similar injection pressures, of the order of 500 hPa. Stagnation and injection pressures are measured using Baratron gauges (1 and 5000 torr, respectively). The pressure ratio on both sides of the nozzle is of the order of 50 000, i.e., about ten times larger than before. An optimal rotational temperature as low as 3 K could be achieved in N_2O, compared to typically 35 K with our previous set-up. It was determined using conventional analysis of the relative line intensities in the *P* and *R* branches of the v_3 band in N_2O, recorded using a mixture of N_2O (0.3 l/min) and Ar (2 l/min). The gas flow is measured using MKS mass flow controllers and is expressed in US standard conditions. As another test, we recorded the *P*(2) doublet in v_3, $^{12}CH_4$. It is well known (see [6,7]) that, thanks to the independent cooling processes occurring in *para* and *ortho* nuclear spin isomers of methane, the relative intensity of the v_3, *P*(2) *E* and F_2 lines is a sensitive thermometer for the rotational temperature (T_{rot}). As illustrated in Fig. 1 of [8], this ratio E/F_2 evolves from 2/3 at room temperature to, e.g., 55.74 at 5 K. The spectra recorded with the present set-up, presented in Fig. 2, demonstrate that the F_2 component barely emerges from the noise in the observed spectrum. The comparison with the predicted spectrum at $T_{rot} = 8$ K sets this value as an upper limit. These low temperature conditions are achieved with a mixture of CH_4 (0.4 l/min) and Ar (4 l/min).

We have interfaced a quadrupole mass spectrometer (MS) (Hiden RC PIC Analyser-HPR30) to the jet chamber,

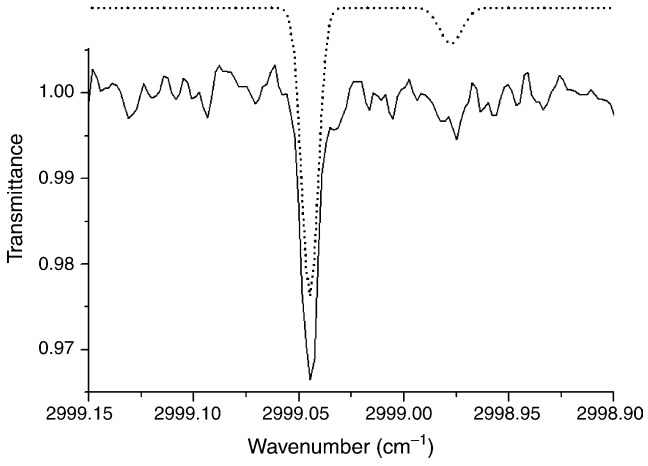

Fig. 2. Observed *P*(2) rotational lines in v_3, $^{12}CH_4$ (bottom). The predicted relative intensity of the *P*(2) lines from *E* and F_2 symmetry nuclear spin isomers at 8 K is shown in dotted line, slightly shifted from the experimental spectrum. Experimental conditions are CH_4 (0.4 l/min) and Ar (4 l/min), coaddition of 400 scans.

which we did not indicate in Fig. 1 for clarity. It has a retractable probe allowing the expansion to be sampled horizontally along half of the jet cone, at the same vertical distance to the nozzle exit (*d*) than the spot of the absorption source. This distance *d* can actually be varied, between 0.5 and 3.5 cm by extending the bellow on the jet chamber, on which the nozzle/slit is attached. Fig. 3 presents the 3-D evolution of the molecular density in the expansion using pure N_2O (1 l/min) through a pinhole nozzle. The signal with mass 30 was detected, corresponding to NO^+ produced