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MEASUREMENTS OF THE METHANE RELAXATION TIMES FOR APPLICATION TO THE INFRARED EMISSION MODELS OF THE UPPER ATMOSPHERES OF OUTER PLANETS AND TITAN

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ABSTRACT

The 7.8 μm emission from the ν_4 band of methane (CH_4) is a regularly observed feature in the stratosphere of all the giant planets and Titan. On Jupiter, enhancements in this emission are associated with the infrared hot spots in the auroral zone. Attempts to model this phenomenon in particular, and to understand the role of methane in general, have been hampered in part by a lack of adequate laboratory measurerments of the collisional relaxation times for the ν_3 and ν_4 levels over the appropriate temperature range. To provide this needed data, we have initiated a series of laboratory experiments.

In our experimental arrangement the ν_3 band of methane is pumped at 3.3 μm using a pulsed infrared source (Nd:YAG/dye laser system equipped with a wavelength extender). The radiative lifetime of the ν_3 level (~ 37 ms) is much shorter than the ν_4 lifetime (~390 ms); however, a rapid V-V energy transfer rate ensures that the ν_4 level is substantially populated. The photoacoustic technique is used to acquire relaxation rate information. The experiments are performed using a low-temperature, low-pressure cell.

In this paper we describe our experimental apparatus and technique. In addition we discuss some of the experimental difficulties associated with making these measurements and present some preliminary results.

INTRODUCTION

After hydrogen and helium, methane is the third most abundant molecule in the atmospheres of the giant planets - Jupiter, Saturn, Uranus and Neptune - and is an important constituent in the atmosphere of Titan. Of the four fundamental vibrations the molecule possesses, two - ν_3 at 3.3 μm and ν_4 at 7.8 μm - are strongly infrared active. Furthermore, the molecule possesses several combination and overtone bands spread throughout the visible and near IR spectrum. In the atmospheres of outer planets, methane primarily absorbs solar radiation at 3.3 μm and emits in the 7.8 μm. Jupiter, for example, exhibits limb brightening in the 7.8 μm band due to methane emission from the stratosphere[1,2]. In the same band, Jupiter also exhibits an extremely varied and complicated disc, ranging from hot spots in the polar regions to wave like disturbances in the equatorial regions. Since methane does not condense on Jupiter and since alteration in its abundance due to photochemical destruction is negligible, the brightness variations in the 7.8 μm emission is inferred as due changes in the stratospheric temperature. Other hydrocarbons such as ethane and acetylene, which are formed by the solar UV dissociation of methane, also have emissions in the mid-IR range of 8 to 13 μm and along with methane form an important group of molecules taking part in the energy transfer of the uppter atmospheres.

Based on the scant laboratory data available up to the present, it has been customary to assume that the emission in the ν_4 band is Planckian in deriving the temperatures and the minor hydrocarbon species abundances[3]. This assumption of local thermodynamic equilibrium (LTE) may or may not be valid depending on the parameters η_c and η_r, which are the collisional relaxation time and the spontaneous emission time respectively for the transition in question. The collisional relaxation time (η_c) is strongly dependent on temperature and is inversely proportional to pressure. It is also dependent on the type of collision partners. If η_c is smaller than η_r at a given height in the atmosphere, the emission from that height is likely to be Planckian, since a sufficient number of collisions would have occured to maintain the Boltzman distribution among the energy levels before a photon is spontaneously emitted. The emission in this case is thermal, since brightness can be related to the kinetic temperature. However if η_c is greater than η_r, such as at high altitudes where the collisions are infrequent, spontaneous emission occurs before energy is equilibrated, and the brightness of this emission will have less to do with the kinetic temperature and is more indicative of the vibrational temperature of the molecule. In the limiting case, as η_c approaches a large value (as in the interstellar medium), the population of the molecules in the stationary states is radiatively controlled and therefore represents a case of scattering.

Since η_c is a strong function of temperature, pressure and composition, it is important that measurements be made under simulated planetary environment. In the past, methods using shocks, ultra-sound and light (both ordinary and laser light) have been used to measure the relaxation time in methane and mixtures containing methane at different pressures but room temperature[4-10]. For pure methane, it was found using the opto-acoustic method that the relaxation times for both ν_3 and ν_4 excitation were the same[4] - 1.6 μs at 1atm. Further studies[5] with ν_3 excitation indicated that the measured ν_3 relaxation time in the earlier study was actually for ν_4 as well since in methane the V-V transfer between ν_3 and ν_4 occurs at a rapid rate in preference to direct ν_3 relaxation. The lifetime of the ν_3 state (0.03 s) is an order of magnitude faster than that for the ν_4 state (0.39 s) and will, for example, end up as a competing mechanism for ν_3 de-excitation above the 40 μbar pressure level on Jupiter. In this study we have adopted two methods to determine the vibrational relaxation: opto-acoustic method and laser induced fluorescence. We use compositions and pressures which are of interest to the planetary science studies and temperatures as low as liquid nitrogen temperature (77 K).

EXPERIMENTAL

Figure 1 shows a schematic of the experimental arrangement. A portion of the pulsed Nd:YAG laser output at 1.064 μm (750 mJ @ 10 per second) is doubled in frequency using a second harmonic generator (SHG). The 532 nm beam is converted to approximately 813 nm beam (30 mJ) by a pulsed dye laser (PDL). Residual 1.06 μm beam and the PDL output beam are combined in a $LiNbO_3$ crystal in the wavelength extender (WEX) to produce a beam with a difference wavelength of approximately 3.3 μm. The wavelength of this beam is continuously tunable, since the output of the dye is tunable. About 1 mJ per pulse was obtained at 3.3 μm using this commercial (Spectra Physics) setup. Pulse to pulse power fluctuations are monitored by an InSb detector D, which measures the diffuse reflection off of one of the beam steering mirrors. A helium neon laser is used for alignment purposes.

The opto-acoustic cell is about 2.5 cm diameter and 2.4 m long with ZnSe windows positioned at Brewsters angle at the ends to admit the 3.3 μm beam with minimum loss at the interfaces. The microphone (B&K 4134) is mounted flush with the inner wall at the center of the cell. The cell is cooled using liquid nitrogen in the annular space surrounding the long arms. The long arms were thought to be necessary to minimize interference from the acoustic noise arising due to energy absorption by the window material as observed in [11]. Tests have shown that the window interference is minimal in our setup and efforts are underway to use the cell without the long arms, since aligning the 3.3 μm beam will be appreciably simplified. The cell is enclosed in an evacuated QVF glass envelop to prevent condensation on the cell

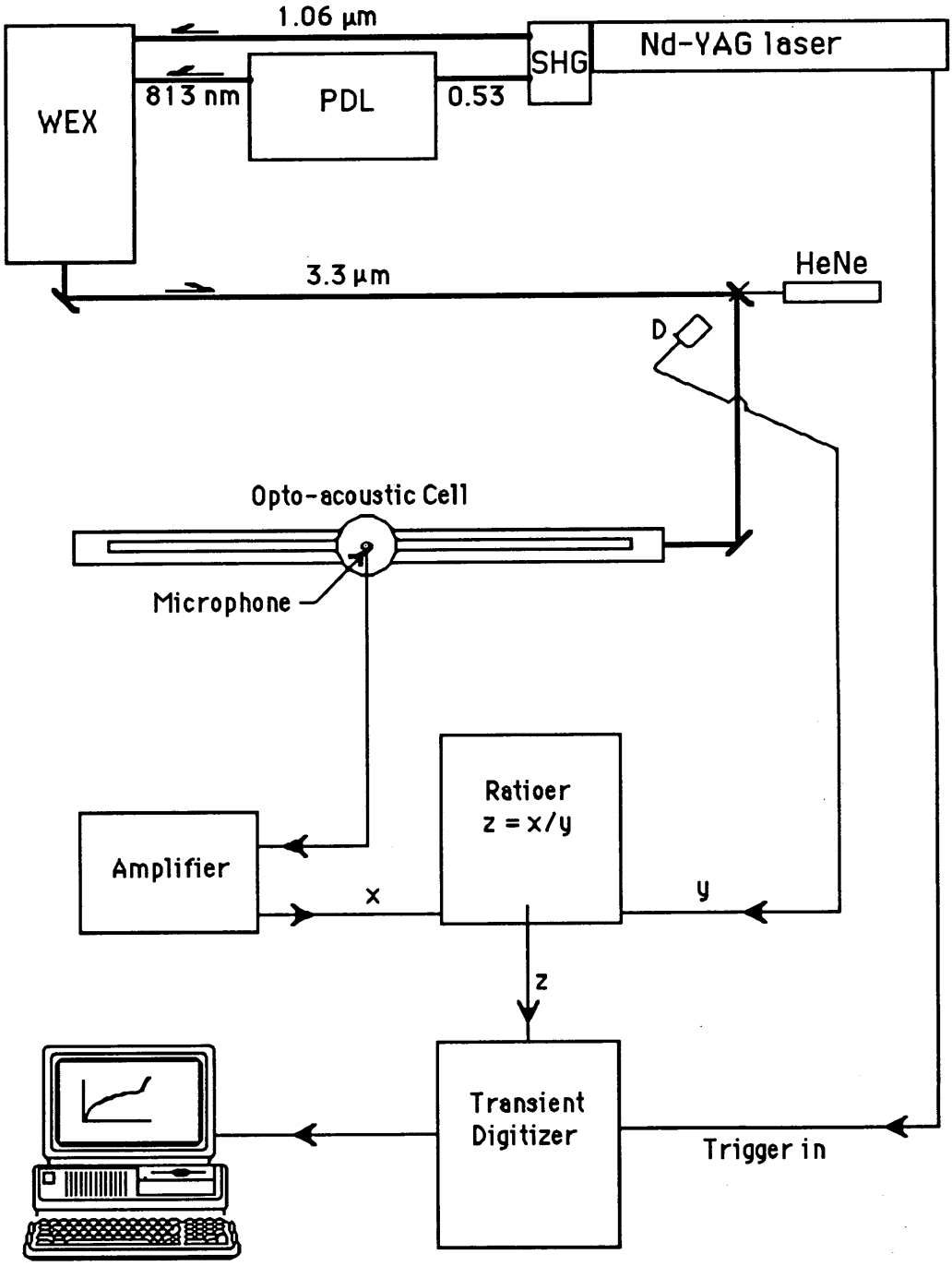

Fig. 1: SCHEMATIC OF THE EXPERIMENTAL ARRANGEMENT

SHG Second Harmonic Generator (Converts 1060 nm output to 532 nm).
PDL Pulsed Dye Laser.
D A detector to sense the laser energy per shot.
WEX Wavelength Extender. Produces the difference of 1060 nm and 813 nm.

windows. A 4" diffusion pump is used to evacuate the QVF and the inner manifold. Pressures down to 1 mtorr have been achieved using this setup.

After amplification, the microphone signal is normalized for laser power fluctuations by dividing the output of the detector D in the ratioer. The output is then fed to a transient digitizer which is triggered by the synchronous Q-switched output of the Nd:YAG laser. The data is stored on floppy disks using a personal computer.

PRELIMINARY RESULTS

When the laser is tuned to the Q-branch, methane absorbs along the beam path. Rapid V-V transfer ensures that all the vibrational modes are excited quickly. Subsequent collisional deactivation of ν_4 level results in the V-T transfer or an increase in kinetic temperature along the beam path. The pressure therefore increases as well. The resultant pressure wave travels radially outwards at sonic speed and is picked up by the microphone. The trace of microphone output versus time will then give the relaxation rate. If the thermal diffusion coefficient α is very high as at low pressures, the energy due to absorption will be conducted to the wall complicating the process thus requiring modelling to unravel the pressure trace.

Three traces are shown in figure 2 - on-line, off-line and the difference. The on-line trace is obtained when the laser beam is tuned in wavelength to the Q-branch and thus represents signal plus noise. The off-line trace is obtained with the laser tuned off-line to get an estimate of the noise. The difference gives the relaxation rate. The figure here pertains to a mixture containing 10% methane in argon at room temperature and 1.2 torr pressure, and the relaxation time is seen to be approximately 0.6 ms. Analysis is not yet complete, for instance, the origin of the peak at about 3 ms is unknown.

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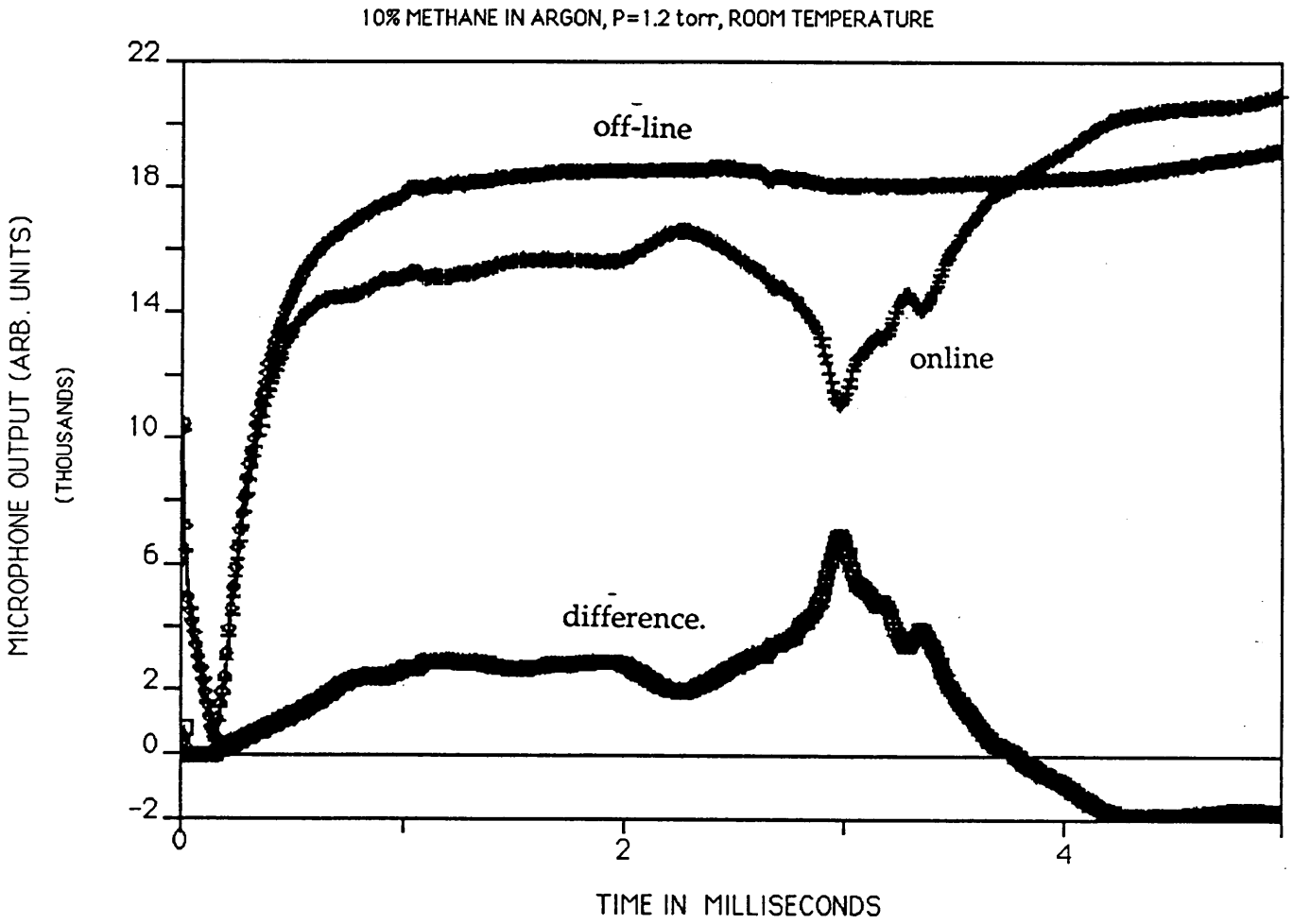

Figure 2. Opto-Acoustic Signal.

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