METHANE OVERTONE ABSORPTION BY INTRACAVITY LASER SPECTROSCOPY

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ABSTRACT

Interpretation of planetary methane (CH_4) visible-near IR spectra, used to develop models of planetary atmospheres, has been hampered by a lack of suitable laboratory spectroscopic data. The particular CH_4 spectral bands are due to intrinsically weak, high overtone-combination transitions too complex for classical spectroscopic analysis. The traditional multipass cell approach to measuring spectra of weakly absorbing species is insufficiently sensitive to yield reliable results for some of the weakest CH_4 absorption features and is difficult to apply at the temperatures of the planetary environments.[1] A time modulated form of intracavity laser spectroscopy (ILS), has been shown to provide effective absorption pathlengths of 100 - 200 km with sample cells less than 1 m long. The optical physics governing this technique and the experimental parameters important for obtaining reliable, quantitative results are now well understood.[2] Quantitative data for CH_4 absorption obtained by ILS have been reported recently.[3] Illustrative ILS data for CH_4 absorption in the 619.7 nm and 681.9 nm bands are presented. New ILS facilities at UM-St. Louis will be used to measure CH_4 absorption in the 700 - 1000 nm region under conditions appropriate to the planetary atmospheres.

INTRODUCTION

CH_4 absorption features in the visible-near IR spectra of the outer planets and their major planets provide some of the most important diagnostic data for the atmospheres of those bodies. With the possible exception of the 614-624 nm region, however, laboratory data appropriate for properly interpreting the planetary observational data are unavailable.[4] Data from measurements made with long, multipass White cells are usually used. These have provided only room temperature absorption coefficients at pressures largely dictated by detection sensitivities since it is experimentally difficult to employ this approach under conditions applicable to the outer planets.[1] Smith and coworkers[5] have used photoacoustic absorption spectroscopy (PAS) to obtain temperature dependent (77-300 K) pressure broadening coefficients for prominent vibration-rotation lines in the CH_4 619 nm and 682.5 nm absorption bands and relative absorption coefficients for

the 604-627 nm region. Absolute line intensity measurements can be obtained by PAS only indirectly, however, and with the assumption that nonradiative quantum yields are constant over a given wavelength region.[6] Computation of the temperature dependence of the CH_4 visible-near-IR absorption spectrum has not been possible to date and does not seem likely in the foreseeable future.[7] Consequently, in models of the albedo spectra of the planetary bodies, it has been necessary to adopt mostly room-temperature laboratory data for the CH_4 absorption coefficients. This has impaired the precision to which the structure and dynamics of the planetary atmospheres can be constrained.

A time-modulated form of intracavity laser spectroscopy (ILS) has been adopted recently to measure CH_4 absorption coefficients at the range of cryogenic temperatures of the planetary environments. When properly implemented, ILS has been shown to provide true, quantitatively accurate absorption line strengths and profiles. For example, ILS data for weak, visible H_2O and O_2 absorption bands[8] are in excellent agreement with data obtained by other methods such as with the FT spectrometer associated with the McMath Solar Telescope at Kitt Peak, Arizona.

EXPERIMENTAL

Sensitivity enhancement factors $> 10^6$ corresponding to absorption pathlengths of 100's km have been achieved with ILS lasers.[2] In ILS, enhanced sensitivity for measuring absorption spectra is obtained by placing the absorbing species inside the cavity of a longitudinally multimode laser. The ILS laser is operated just above threshold in a time resolved, quasi-CW fashion. Absorptions by intracavity species constitute losses within the laser resonator and alter the competition that occurs as the modes of the laser resonator cavity compete for gain. The absorption spectrum of the intracavity absorber becomes superimposed on the output of the ILS laser and can be measured by dispersing the output of the laser and observing its spectral profile at a well-defined time, the generation time t_g ($\sim 10^{-4}$ seconds), after the onset of ILS laser operation. The enhanced detection sensitivity obtained by ILS has been accounted for by the effect of intracavity mode competition.[8-10] It has been shown that when the ILS laser is operating close to threshold[2,11] and within certain boundary conditions of absorption strength and t_g values, the absorbance data obtained by ILS obey a Beer-Lambert relationship.[8,9,12] The averaged, time-resolved spectrum observed by ILS is given by

$$\ln[I_0(v)/I(v)] = k(v) \ \phi(v) \ N(l/L) \ c \ t_g \qquad (1)$$

where $I_0(v)$ is the intensity of the laser at spectral frequency v in the absence of intracavity absorption, $I(v)$ is the intensity of the laser at v when there is intracavity absorption at v, $k(v)$ is the intensity of the absorption line, $\phi(v)$ is the normalized absorption line profile, N is the number density of the intracavity absorber, l/L is the fraction of the laser resonator cavity occupied by the absorber, c is the velocity of light, and $(l/L)ct_g$ is the effective absorption pathlength. The sensitivity and dynamic range of ILS measurements can be controlled, therefore, by adjustment of t_g. In practice, it is found for ILS systems based on dye lasers that equation (1) applies for t_g values up to 300 - 500 μs.[2,10-13] Mechanical instabilities in the resonator cavity impose an upper limit on the value of t_g that can be used.[10] There also exist limits to absorptivity beyond which equation (1) is not a good representation of the absorption. Detailed descriptions of the instrumentation have been provided elsewhere.[14]

RESULTS AND FUTURE WORK

Illustrative temperature dependent ILS data for the weakest CH_4 band distinguishable in the long pathlength absorption spectra obtained by Giver,[1] are presented in Fig. 1 where they are compared with pressure dependent ILS data for the CH_4 619 nm band recorded at room temperature. The data are presented in the form of spectral profiles of the ILS laser's broadband output, which consists of a Gaussian spectral distribution on which is superimposed the spectral features due to an intracavity absorber. Control and precise specification of sample conditions were not possible in some of the measurements because the gas cell was improvised and sample pressures varied dramatically when temperatures were near the CH_4 phase transition temperatures. The series of profiles shown in Fig. 1 reveal pronounced variations in the intensity distribution within the 681.89 nm feature with changes in temperature and pressure. These data are in complete accord with corresponding PAS results recently submitted for publication.[5b] In contrast to this, the most prominent line in the 619 nm CH_4 band (i.e., 619.68 nm) shows nothing like this degree of variation as pressure and temperature conditions are altered. Line strength and self-broadening coefficients obtained by ILS for the 619.68 nm line of CH_4 at room temperature have been reported recently.[3] Since the instrumental resolution employed in these studies (0.18 cm^{-1}) is significantly broader than the absorption line-width (Doppler half-width = 0.025 cm^{-1}), line intensity and line-width information were obtained using the curve of growth method.[15] An illustrative curve of growth, obtained for the 619.68 nm line of CH_4, is presented in Fig. 4 of Ref. 3. The validity and accuracy of the approach were first verified by establishing that line strength
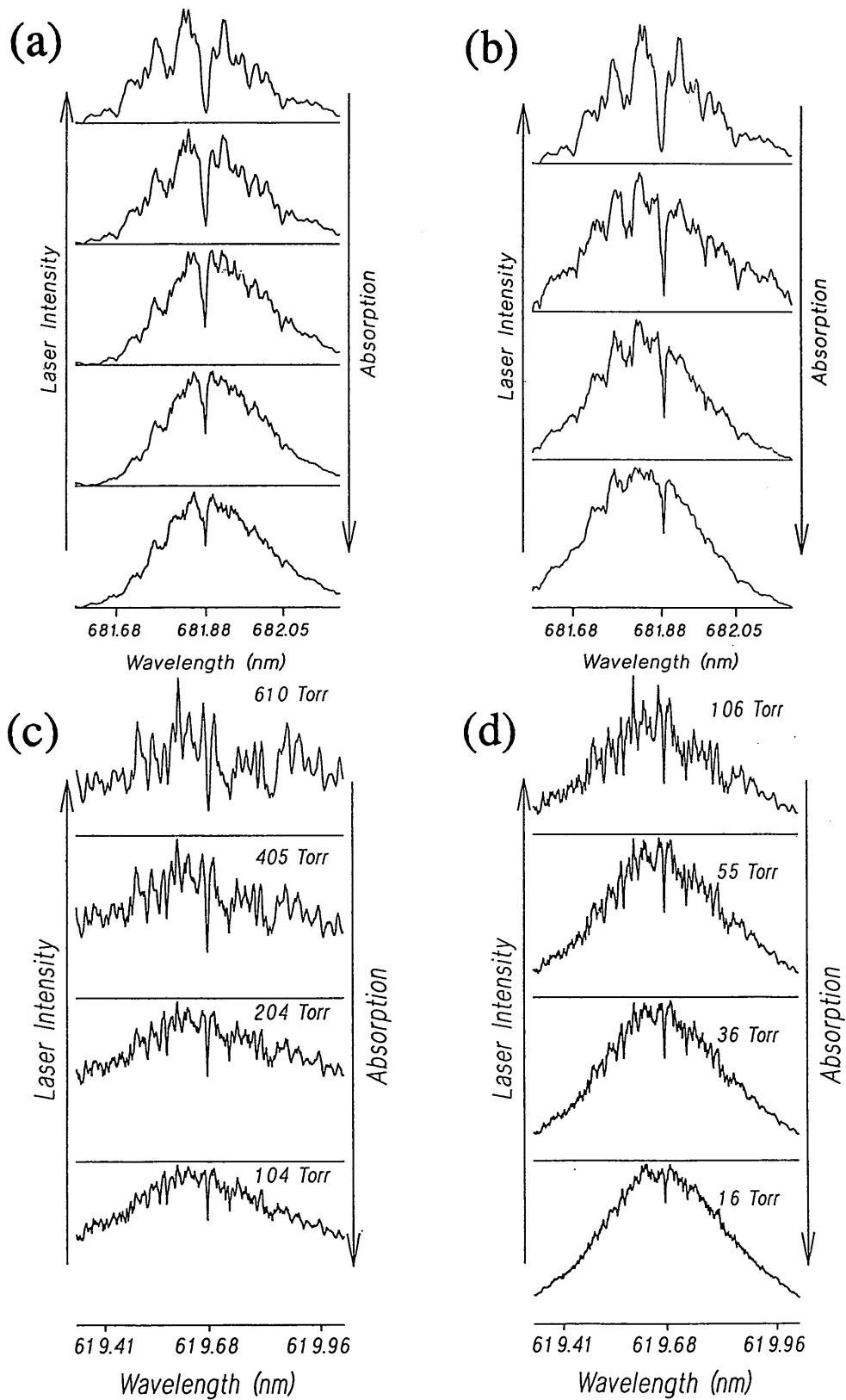
Figure 1. ILS spectral profiles for CH$_4$ absorption in the 681.86 nm (top panels) and 619.68 nm (bottom panels) bands under various conditions: (a) ~180 K, CH$_4$ pressures from top to bottom profile: 364, 184, 95, 45, 22 Torr, t$_g$=170 μs, effective absorption pathlength (L$_{eff}$)=36 km; (b) L$_{eff}$=36 km, conditions from top to bottom profile: 364 Torr & 175K, 70 Torr & 110-160 K, 20 Torr & ~110 K, 10 Torr & <110 K; (c) 295 K, t$_g$=10 μs; (d) 295 K, t$_g$=100 μs.

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and line shape parameters for well studied lines of the O_2 γ band replicated results obtained by other workers using ILS and other methods. Stoeckel and coworkers,[8] using much higher spectral resolution (0.18 cm^{-1}), have determined absorption line strength and width parameters by fitting ILS data directly to Voigt profiles.

Plans are that new, recently installed ILS equipment at UM-St. Louis be used in obtaining quantitative absorption data for methane absorption bands in the 700-1000 nm region for the range of of conditions applicable to the atmospheres of outer planetary bodies. Special attention will be given to determining the absorption parameters for the relatively weaker bands and for the inter-band regions of pseudo-continuum absorption. Models of planetary atmospheres based on conventional laboratory measurement show the most severe discrepancies in these regions. It is hoped that the current dye-laser based ILS system can be enhanced by the addition of a Ti:sapphire laser which in addition to providing superior performance and convenience of operation over dye lasers in the near-IR, have intrinsic advantages over dye lasers when utilized in ILS applications.

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