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Investigation of four carbon monoxide isotopomers in natural abundance by laser-induced fluorescence in a supersonic jet

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Abstract

The four carbon monoxide (CO) isotopomers $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ have been detected simultaneously in a CO gas sample of natural isotopic abundance by measuring rovibronic excitation spectra of six vibronic bands in the Fourth Positive System. The CO sample was flow cooled by adiabatic expansion in a pulsed supersonic jet. The rovibronic excitation spectra were obtained using a novel pulsed laser source (pulse duration ~25 ns, spectral bandwidth ~5 GHz) continuously tunable in the 139–155 nm vacuum ultraviolet wavelength region for excitation and recording the total fluorescence. In the present paper we report on the spectroscopic results obtained, including transition wavelengths of three forbidden rovibronic bands ($e^3\Sigma^- - X^1\Sigma^+(1, 0)$, $d^3\Delta - X^1\Sigma^+(5, 0)$, $a'^3\Sigma^+ - X^1\Sigma^+(14, 0)$) of $^{12}C^{16}O$ and band origins of six rovibronic bands ($A^1\Pi(v' = 0–5) - X^1\Sigma^+(v'' = 0)$) of the rare isotopomer $^{12}C^{17}O$, and on the experimental conditions facilitating the high sensitivity of the measurements. The exceptional sensitivity demonstrated by the results has been achieved by fine tuning experimental conditions including the conditions in the supersonic expansion, the jet pulse duration and the laser pulse timing.

Keywords: Carbon monoxide; Isotopomer; Fourth Positive System; Experimental conditions; Forbidden transitions; Supersonic jet; Laser-induced fluorescence; Vacuum ultraviolet

1. Introduction

Carbon monoxide (CO) is important as a prototype diatomic molecule and as a tracer in the study of chemical and physical processes. The spectroscopic study of the rare isotopomers and weak forbidden transitions of CO is strongly motivated by the particular significance of these molecules as tracers in astrophysical research. Not only is CO the second most abundant molecular species in the interstellar space [1], but the distribution and isotopic fractionation of CO in the interstellar gas clouds and stellar envelopes yield important parameters in models of stellar evolution and chemistry [2]. The vacuum ultraviolet (VUV) spectrum of CO in the interstellar space has been made accessible by satellite based spectrographs, such as on the Hubble Space Telescope [3].

The $A^1\Pi - X^1\Sigma^+(v', v'')$ electronic band system (Fourth Positive System) of CO is a dominant feature in the astrophysically observed VUV spectra and accurate laboratory wavelength data for these spectral lines are required. The relevant data for the $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ isotopomers are available [4,5], having been obtained from laboratory measurements—in the case of $^{12}C^{18}O$ using isotope enriched samples.

We have developed a laser-induced fluorescence excitation spectroscopy experiment to investigate the VUV spectrum of CO, with the aim of obtaining the $^{12}C^{17}O$ spectrum (0.04% natural abundance) and the forbidden singlet–triplet transitions of $^{12}C^{16}O$ in this wavelength range. The transition wavelengths obtained in this study for $^{12}C^{17}O$ and

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the application of this data to astrophysical calculations has been published recently [6].

The present paper describes the experimental conditions and methods that facilitated the investigation of the $A^1\Pi - X^1\Sigma^+(v', v'')$ system of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{17}O$ and $^{12}C^{18}O$ simultaneously in natural abundance. The challenge in this work is to detect weak lines and improve their signal-to-noise ratio among strong neighbouring $^{12}C^{16}O$ lines. The specific conditions that facilitated this sensitivity are presented here for the first time and may be used in similar experiments to obtain high sensitivity for low-abundance isotopomers. New results presented in this paper include the wavelength data of forbidden singlet–triplet transitions of $^{12}C^{16}O$ observed during the course of this study, of which 10 have not been measured before, as well as $^{12}C^{17}O$ band origins of six vibronic bands obtained from our measurements.

2. Experimental setup

The experimental setup is shown in Fig. 1. The details of the instrumentation used in the setup has been described elsewhere [7–9] and will not be repeated here. Two pulsed dye laser beams are combined in a magnesium vapour krypton gas medium to generate vacuum ultraviolet (VUV) laser radiation by a two-photon resonant four-wave sum frequency mixing process. The medium is prepared in a heat pipe oven. This narrow bandwidth tunable VUV radiation (pulse duration ~25 ns, spectral bandwidth ~5 GHz) is used to excite individual rovibronic transitions of CO. A pulsed supersonic expansion regulated by a solenoid valve (General Valves, Series 9) driven by a pulse driver (Iota One, General Valve Corporation) is used to introduce the sample gas in natural isotopic abundance and at low temperature. The laser and gas pulses are synchronized by using an electronic delay generator (Stanford Research Systems, DG535).

A solar-blind photomultiplier tube (PMT1: EMR 542G-08-18-03900) measures the fluorescence from the intersection of the gas and laser pulses, while a second solar-blind photomultiplier tube (PMT2: Hamamatsu R973) measures the transmitted VUV laser signal. The transmitted laser is sent through a monochromator (McPherson, model 218) for selection of the VUV wavelength of interest, thereby improving the signal-to-noise ratio of this measurement. The signal from each photomultiplier is integrated over the laser pulse duration using a boxcar gated integrator (Stanford Research Systems, SR250) and digitized. The data acquisition and the scanning of the VUV wavelength and the delay between the laser and gas pulses are controlled by custom software on a computer.

By measuring the laser-induced fluorescence (LIF) and transmitted VUV intensity as a function of excitation wavelength, simultaneous LIF and absorption spectra are recorded (termed wavelength scans). A delay scan is obtained by keeping the wavelength tuned to a spectral line and observing the LIF and absorption signals as a function of the temporal delay between gas and laser pulses.

3. Results and discussion

3.1. Typical spectra

Rovibronic excitation spectra of the $A^1\Pi - X^1\Sigma^+(v' = 0–5,\ v'' = 0)$ bands of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{17}O$ and $^{12}C^{18}O$ were obtained simultaneously using both LIF and absorption. The details of the LIF spectra have been reported elsewhere [6], but a description of the band structure is warranted here. The cooling in the supersonic expansion has the effect of simplifying the spectra, since the lowest-J lines have the highest intensities. This effect, in combination with the relatively high sample density in the interaction region, increases the sensitivity of this measurement for the low-J lines, as compared to room-temperature measurements.

As an example of a typical vibronic band, the $A^1\Pi - X^1\Sigma^+(v' = 1,\ v'' = 0)$ band is shown in Fig. 2 in both LIF (lower trace) and absorption (upper trace). The

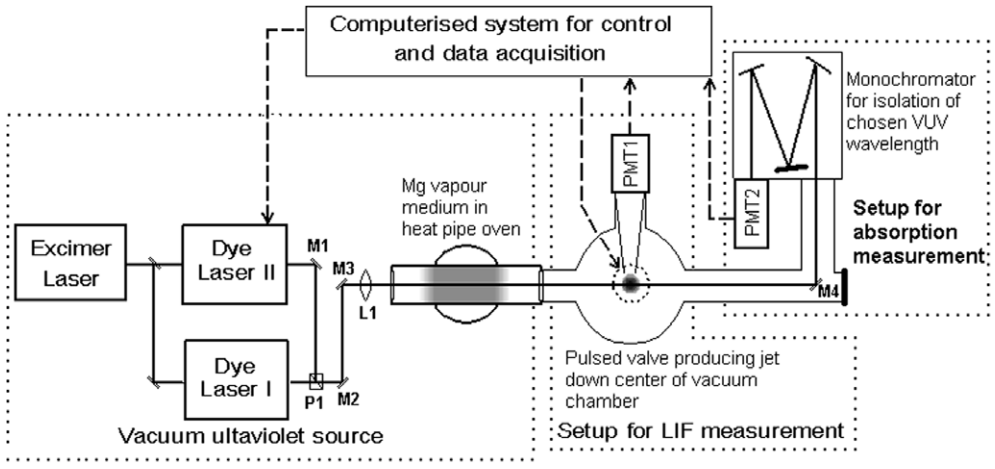

Fig. 1. Schematic of the experimental setup in three sections: the vacuum ultraviolet laser source; the setup for LIF measurement in a pulsed supersonic expansion; and the setup for absorption measurement.