



Vibrational relaxation of CO₂ (12⁰1) by argon

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ABSTRACT

We present experimental measurements of the vibrational relaxation of CO₂ (12⁰1) by argon, at ambient temperature (295 ± 2 K). The CO₂ molecules were directly excited to the (12⁰1, *J* = 14) ro-vibrational state by a tunable laser radiation at ~2 μm. Time-resolved infrared fluorescence technique was used to study the collisional relaxation process. The bimolecular deactivation rate constant of CO₂ (12⁰1) by argon was found to be (825 ± 43 Torr⁻¹ s⁻¹) while the self-deactivation by CO₂ (00⁰0) was determined to be (3357 ± 135 Torr⁻¹ s⁻¹). The radiative life-time of the vibrational combination band (12⁰1), τ[CO₂ (12⁰1)], was found to be (5.55 ± 0.27) μs. Modern angular momentum theory was used to explain values of the deactivation rate measured. It is concluded that the presence of the (08⁰0) state acts like an angular momentum sink leading to a fast deactivation rate of the CO₂ (12⁰1) by argon.

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1. Introduction

The relaxation of vibrationally excited CO₂ molecules is of interest driven by motivations from fundamental energy transfer study, earth's and planet's atmosphere and combustion science. There are three important vibrational bands that CO₂ molecules may be probed at. These bands are centred at ~4.3, 2.7 and 2 μm, corresponds to 00⁰1, 02⁰1 (or 10⁰1) and 12⁰1 vibrational states, respectively. Although there have been many collisional deactivation studies of CO₂, most of them have been confined to the deactivation of the CO₂ (00⁰1) vibrational state both by small colliders [1–8] and by larger polyatomic colliders [9–15]. In addition to these three bands, which all contain one quanta of *v*₃, CO₂ has strong absorption at ~667 cm⁻¹, corresponding to the 01¹0 bending mode. The collisional deactivation rate constant of the CO₂ (01¹0) in the presence of argon, has been reported by Allen et al. [16].

The (00⁰1)–(00⁰0) transition is one of strongest known vibrational transitions with strength namely 2026 cm⁻¹ atm⁻¹ at 295 K [17]. This may be of great advantage when monitoring IR fluorescence at 4.3 μm for sensitive CO₂ detection, but it is not feasible for remote sensing and laser diagnostics in general due to the absorption of the laser radiation by the CO₂ presence in the atmosphere. The strength of the (12⁰1)–(00⁰0) vibration transition, on the other hand, is only 1 cm⁻¹ atm⁻¹ at 300 K [17] making it very attractive for remote sensing. For this reason a solid-state laser and detector, specifically designed to operate at 2 μm, have been developed by Koch et al. [18] and Refaat et al. [19], respectively.

In addition, the deactivation of variationally excited CO₂ molecules is important in molecular energy transfer. Toselli and Barker [20] observed efficient collision energy transfer from highly vibrationally excited benzene-derivatives to CO₂. Furthermore, the study of the deactivation of CO₂ (12⁰1) is also important in combustion diagnostic. Kirby and Hanson reported planar IR imaging of CO₂ molecules excited with different wavelengths, 10.6, 2.7 and 2 μm [21]. It was concluded that the 2 μm is preferred excitation for linear fluorescence measurements, because of the absence of the strong absorption from CO₂ and H₂O molecules. The deactivation rates and the state life-time are critical parameters needed for quantitative detection. In this paper, we report on the collisional deactivation of CO₂ (12⁰1) in presence of argon gas studied by Time-resolved Infrared Fluorescence technique (TIRLIF).

2. Experimental

The optical arrangement for the experimental set-up is shown in Fig. 1 and a detailed description may be found elsewhere [22,23]. Briefly, an alexandrite flash-lamp pumped ring-cavity laser-system (PAL/PRO™, Light Age Inc.), operated at 10 Hz, with fundamental output in the spectral range from 739 nm to 785 nm was used as the laser source. A tunable, single frequency, external-cavity diode-laser (Newport 2020A) was utilized as a seeding source in order to narrow and continuously scan the output frequency. Based on stimulated Raman scattering, the output laser frequency, in the near IR range, was shifted to the mid IR range by a high pressure cell filled with H₂ gas. The second Stokes component, centred at around 2 μm, has ~5 mJ of power and pulse length and width of 85 ns and 100 MHz, respectively. The 2 μm radiation was selected and directed to a small cell with CaF₂

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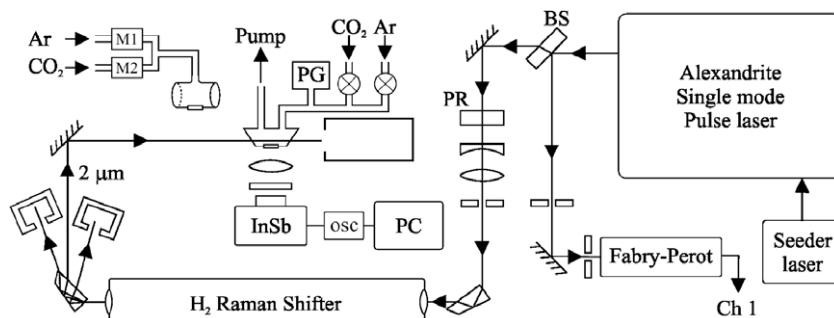


Fig. 1. Schematic diagram of the experimental set-up.

windows at Brewster's angle. The cell was evacuated to ~ 0.1 mTorr by a rotary pump with a leakage/degassing rate of 0.001 mTorr s^{-1} . A small amount of CO_2 was introduced to the cell and then Argon gas was added for total pressure in the range of 100–600 Torr. The pressure in the cell was monitored with a 0–10 Torr and a 0–1000 Torr gauges having an accuracy better than 0.5%. The error on the pressure reading is estimated to be less than 1%, as indicated by the manufactures manuals.

For the atmospheric pressure measurements, the flow rates of the CO_2 and argon were precisely controlled by two separate mass flow controllers (Bronchus HIGH-TECH). The outlets of the two mass flowmeter units were connected to a ~ 10 m long Teflon tube to ensure complete mixing of the gases. The binary mixture was then introduced to the middle of an open-ended 1 cm diameter and 5 cm long tube, as shown in Fig. 1. The mixing system allows the study of any mixing ratio of the two gases under a constant atmospheric pressure. Both CO_2 (AGA, 99.99%) and Ar (AGA, 99.99%) were directly used without any further purification. All measurements were made at room temperature (295 ± 2 K).

The IRLIF was collected through a sapphire side window by two CaF_2 lenses and directed to a 77 K, 2 mm in diameter, InSb infrared photovoltaic detector (Judson, J10D) after passing through an appropriate IR band pass filter. The signal from the InSb detector was connected to a digital oscilloscope (Tektronix TDS 3054). The oscilloscope was used to average decay curves for 512 pulses. The recorded IR decay profiles were transferred to a PC for further analysis.

3. Results

To measure the deactivation of CO_2 (12^0_1) by argon, a low-pressure static cell was used. The initial CO_2 pressure was chosen to be around 10 ± 3 Torr to minimise both self-absorption and heterogeneous deactivation and maintaining good signal to noise ratio [24,25]. Following the laser excitation of the CO_2 (12^0_1 , $J = 14$) ro-vibrational state, IR fluorescence attributed to (12^0_0)–(12^0_1) transitions, near $4.33 \mu m$ was collected. Fig. 2 shows four typical IR decay profiles recorded in presence of different number density of argon atoms. The decay profiles, recorded for different argon pressures, were found to have single exponential form. The single exponential behaviour suggests that there is no rapid population establishment among CO_2 vibrational state having one quanta in the anti-symmetric stretch, namely (02^0_1), (10^0_1), (12^2_1) or (00^0_1).

Using the Marquardt algorithm for non-linear least-squares fitting [26,27], each decay curve was fitted with a single exponential function of the form

$$I_t = B + I_{t=0} \exp(-k^{obs}[Ar]t), \quad (1)$$

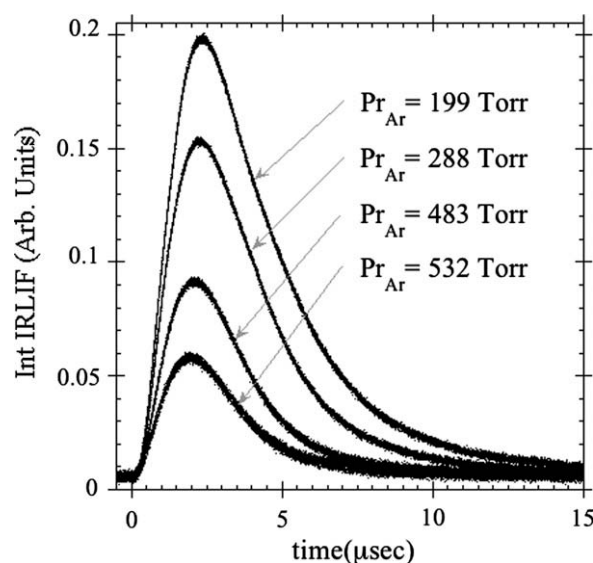


Fig. 2. Typical IR decay profiles of CO_2 in presence argon at four different pressures as indicated by the arrows.

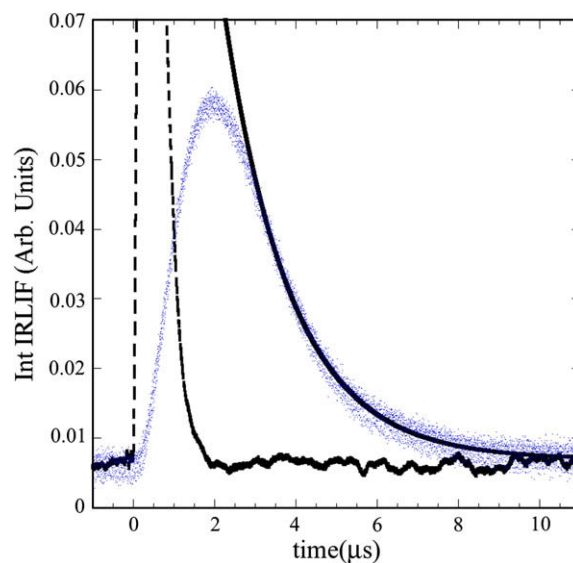


Fig. 3. Plot of IR decay profile of CO_2 in presence 532 Torr of argon, shown by dots, along with a single exponential fitting, shown by solid line. The recorded pulse shape is also shown by dashed line.

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