THE FORMATION OF CARBON DIOXIDE IN MOLECULAR CORES BY A NON-ENERGETIC ROUTE

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Abstract. The formation of CO_2 in quiescent molecular cores has long been of interest to astrochemists as CO_2 is one of the most abundant solid phase molecules present in the interstellar medium. Previous studies have concentrated, for the most part, on formation mechanisms involving high energy particle or UV bombardment of ices, to mimic the influence of cosmic rays on solid phase species in the outer, lower density regions of molecular clouds. However, condensed phase CO_2 is also observed in the inner, denser regions of clouds, where less UV radiation penetrates. To date, very few studies have been made of CO_2 formation in the absence of energetic particles.

Low-energy routes to the formation of CO_2 are crucial to explain the high abundances of this molecule observed in quiescent regions. We discuss recent experimental results of a study of the low-energy reaction CO + OH. A simple model, developed to describe the kinetics of the system, suggests that the various reactions of the OH radical are key in characterising the production of CO_2 and other species. Our results indicate that some CO_2 forms concurrently with H_2O in molecular clouds, in line with both previous observations and theory. The results of this research are published in Noble *et al.* (2011).

1 Introduction

CO_2 is one of the most abundant interstellar solid phase molecules and has been observed at abundances of $\sim$10–34 % H_2O towards numerous environments, including high mass protostars (Gibb *et al.* 2004; d'Hendecourt & Jourdain de Muizon 1989), low mass young stellar objects (YSOs, Nummelin *et al.* 2001; Pontoppidan *et al.*

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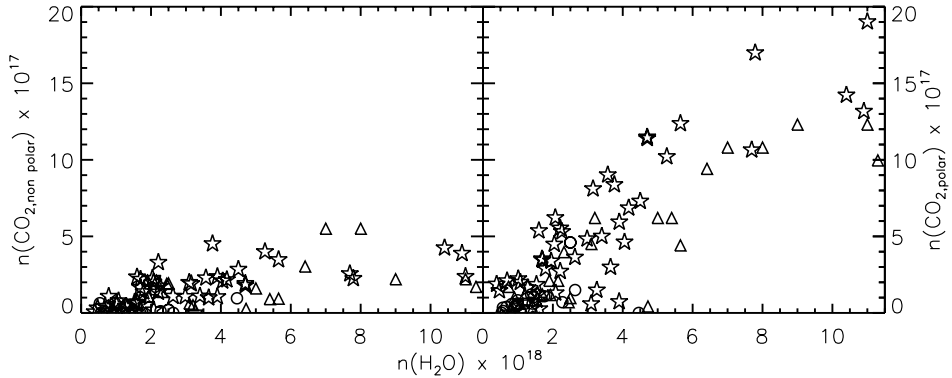e-mail: francois.dulieu@obspm.fr

Fig. 1. A correlation plot of solid phase CO_2 *vs.* H_2O compiled from observations of background stars (circles), low mass YSOs (stars) and high mass YSOs (triangles). The left hand plot is the abundance of CO_2 in non-polar environments, *i.e.* the CO_2 component in CO ices, while the right hand plot is of CO_2 in polar environments, *i.e.* in H_2O ices. All data are obtained from literature (Gerakines *et al.* 1999; Gibb *et al.* 2004; Pontoppidan *et al.* 2008; Noble *et al.* in preparation).

2008), galactic centre sources (de Graauw *et al.* 1996), other galaxies (Shimonishi *et al.* 2010) and stars behind molecular clouds (Knez *et al.* 2005; Noble *et al.* in preparation). Due to its apparent ubiquity in the interstellar medium, the formation of CO_2 has long been of interest to astrochemists, with observational evidence suggesting that much of the formation occurs in quiescent regions (Nummelin *et al.* 2001; Pontoppidan 2006). Figure 1 presents the observed abundances of CO_2, as a function of its ice components, plotted against the abundance of solid H_2O. The clear difference observed between the relative abundances of CO_2 in CO ice compared to CO_2 in H_2O ice suggests that different formation mechanisms are responsible for CO_2 formation in different ice environments.

2   Experimental results

We investigated the formation of CO_2 via the reaction CO + OH at very low surface coverages (Noble *et al.* 2011). Around one monolayer of O_2 or O_3 was deposited on np-H_2O or silicate surfaces, followed by less than half a monolayer of ^{13}CO; finally, the ice was irradiated with a beam of H atoms. Reaction of the O_2 or O_3 substrates with the H atoms produced OH radicals which, upon reaction with ^{13}CO, produced $^{13}CO_2$. Full details of the experimental method are outlined in Noble *et al.* (2011). This reaction has also been studied in a multilayer regime using either an OH beam (Oba *et al.* 2010) or an H beam (Ioppolo *et al.* 2011; Zins *et al.* 2011). The advantages of our investigation are that the approximately monolayer coverages probed the surface dependancy of the reaction, and the generation of OH radicals via H irradiation of both O_2 and O_3 substrates allowed the kinetics of the reaction network to be modelled.
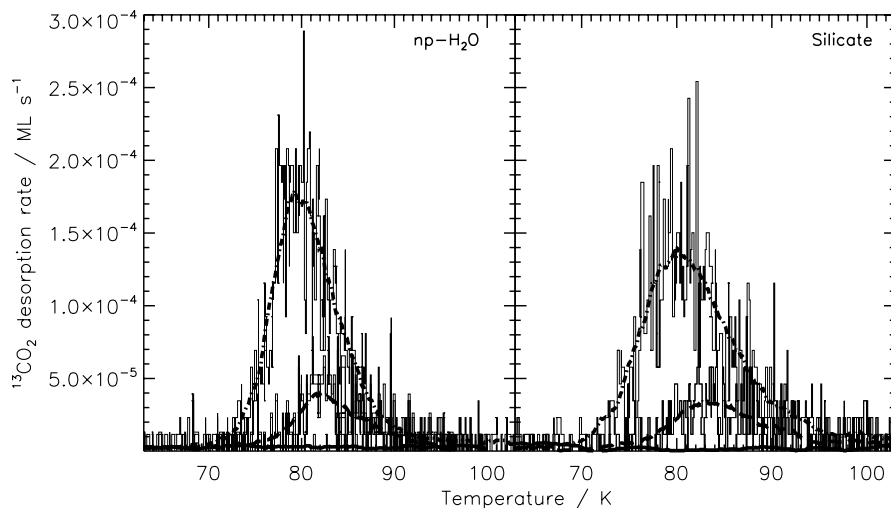
Fig. 2. Temperature programmed desorption spectra of Mass 45 (^{13}CO$_2$). The *left panel* shows desorption from a water surface while the *right panel* shows desorption from a bare silicate surface. Experimental data are plotted in their raw form, accompanied by a smoothed version to guide the eye. Curves are labelled as follows: O$_2$ and ^{13}CO with no H irradiation, solid line (almost flat); O$_2$ and ^{13}CO with 20 minutes H irradiation, dashed line; O$_3$ and ^{13}CO with 20 minutes H irradiation, dot-dashed line. Figure reproduced from Noble *et al.* (2011).

Figure 2 presents temperature-programmed desorption results of the experiments undertaken. From these data, it is possible to conclude that CO$_2$ can form via the reaction CO + OH, and that the reaction is not surface dependent for the surfaces investigated. Experiments using O$_3$ as a substrate generated more CO$_2$ than those using O$_2$, as can be clearly seen by comparing the dot-dashed lines (O$_3$) with the dashed lines (O$_2$) in Figure 2. It is important to note that the yields of ^{13}CO$_2$ were relatively low, peaking at ∼8% with respect to ^{13}CO.

A kinetic model describing the reaction network probed by these experiments was developed, based upon a series of coupled first-order rate equations. It was found that, despite the relatively simplistic approach, this model was able to replicate the observed experimental abundances of CO$_2$ very well within the limits of experimental uncertainty. The model, fully detailed in Noble *et al.* (2011), suggests that the low yields of CO$_2$ are largely explained by the competing reaction OH + H, which produces H$_2$O. The overall effective reaction rate of CO + OH was determined to be 24 times slower than the rate of H + OH.

2.1 Astrophysical implications

The competition between the formation of CO$_2$ and H$_2$O via the OH radical is potentially very important in describing the correlation between these two species,

as seen in Figure 1. CO_2 is observed in two distinct environments: CO_2 in a H_2O-dominated ice, and CO_2 in a CO-dominated ice. The results of this study, combined with previous observational, theoretical and experimental data, suggest a complex CO_2 formation scenario with multiple epochs and mechanisms. At early stages in the molecular cloud, CO_2 could form concurrently with H_2O via the OH radical pathway investigated here. This produces the CO_2 component in H_2O ice seen towards background stars and quiescent regions of molecular clouds, seen at low CO_2 and H_2O abundances in Figure 1. A second stage of CO_2 formation could be responsible for the large abundance of CO_2 in a CO-rich ice, occurring after CO freeze-out onto the grain surface at $A_V \sim 7$ (Pontoppidan *et al.* 2003). A third epoch of CO_2 formation, responsible for the high CO_2 abundances towards YSOs and protostars, is likely to be CO_2 formed in H_2O-dominated ice due to energetic reactions of H_2O with CO which has migrated into the H_2O ice due to temperature or time. In this scenario, the reaction CO + OH is likely to be important to CO_2 formation in quiescent regions, and potentially also plays a role in CO_2 formation at later stages in the cloud's evolution.

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