

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

J.A. Noble^{1,2}, F. Dulieu², E. Congiu² and H.J. Fraser¹

Abstract. The formation of CO₂ in quiescent molecular cores has long been of interest to astrochemists as CO₂ 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 CO₂ is also observed in the inner, denser regions of clouds, where less UV radiation penetrates. To date, very few studies have been made of CO₂ formation in the absence of energetic particles.

Low-energy routes to the formation of CO₂ 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 CO₂ and other species. Our results indicate that some CO₂ forms concurrently with H₂O 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

CO₂ is one of the most abundant interstellar solid phase molecules and has been observed at abundances of ~10–34 % H₂O 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.*](#)

¹ Department of Physics, Scottish Universities Physics Alliance, University of Strathclyde, Glasgow, G4 ONG, Scotland

² LERMA-LAMAp, Université de Cergy-Pontoise, Observatoire de Paris, ENS, UPMC, UMR 8112 du CNRS, 5 mail Gay Lussac, 95000 Cergy Pontoise Cedex, France;
e-mail: francois.dulieu@obspm.fr

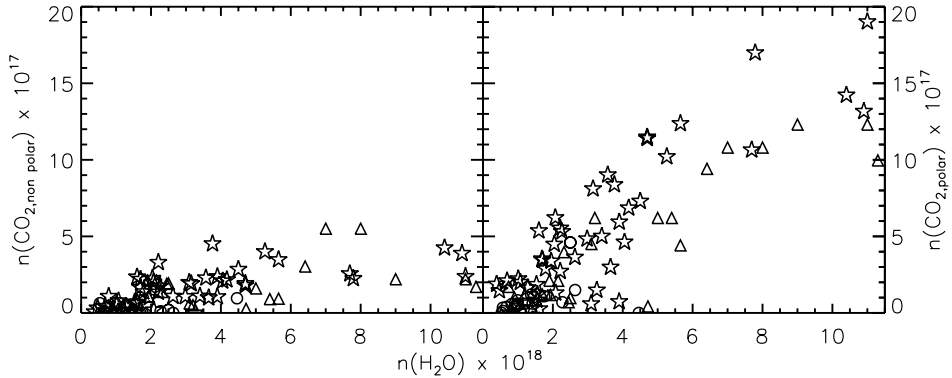


Fig. 1. A correlation plot of solid phase CO₂ vs. H₂O compiled from observations of background stars (circles), low mass YSOs (stars) and high mass YSOs (triangles). The left hand plot is the abundance of CO₂ in non-polar environments, *i.e.* the CO₂ component in CO ices, while the right hand plot is of CO₂ in polar environments, *i.e.* in H₂O 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 CO₂ 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 CO₂, as a function of its ice components, plotted against the abundance of solid H₂O. The clear difference observed between the relative abundances of CO₂ in CO ice compared to CO₂ in H₂O ice suggests that different formation mechanisms are responsible for CO₂ formation in different ice environments.

2 Experimental results

We investigated the formation of CO₂ via the reaction CO + OH at very low surface coverages (Noble *et al.* 2011). Around one monolayer of O₂ or O₃ was deposited on *np*-H₂O or silicate surfaces, followed by less than half a monolayer of ¹³CO; finally, the ice was irradiated with a beam of H atoms. Reaction of the O₂ or O₃ substrates with the H atoms produced OH radicals which, upon reaction with ¹³CO, produced ¹³CO₂. 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 dependency of the reaction, and the generation of OH radicals via H irradiation of both O₂ and O₃ substrates allowed the kinetics of the reaction network to be modelled.

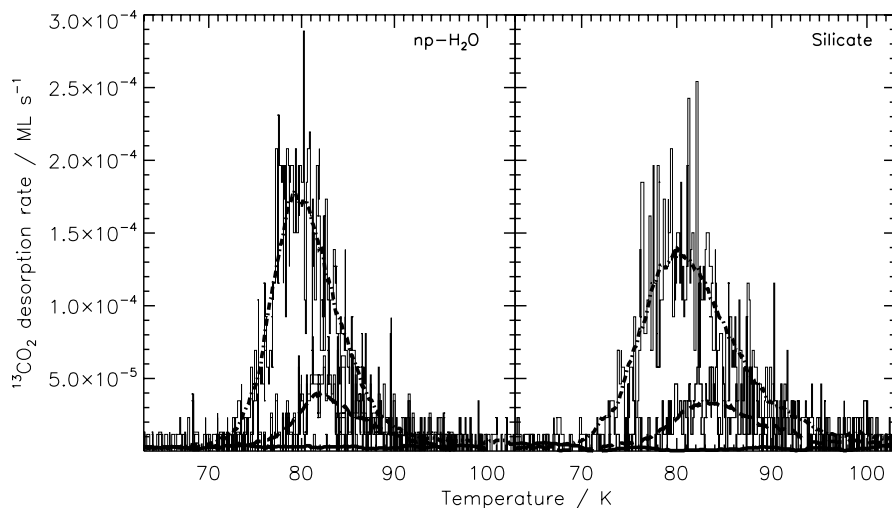


Fig. 2. Temperature programmed desorption spectra of Mass 45 ($^{13}\text{CO}_2$). The *left panel* shows desorption from a water surface while the *right panel* shows desorption from a bare silicate surface. Experimental data are plotted in their raw form, accompanied by a smoothed version to guide 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 CO₂ can form via the reaction $\text{CO} + \text{OH}$, and that the reaction is not surface dependent for the surfaces investigated. Experiments using O_3 as a substrate generated more CO₂ 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 $^{13}\text{CO}_2$ were relatively low, peaking at $\sim 8\%$ 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 CO₂ very well within the limits of experimental uncertainty. The model, fully detailed in Noble *et al.* (2011), suggests that the low yields of CO₂ are largely explained by the competing reaction $\text{OH} + \text{H}$, which produces H₂O. The overall effective reaction rate of $\text{CO} + \text{OH}$ was determined to be 24 times slower than the rate of $\text{H} + \text{OH}$.

2.1 Astrophysical implications

The competition between the formation of CO₂ and H₂O via the OH radical is potentially very important in describing the correlation between these two species,

as seen in Figure 1. CO₂ is observed in two distinct environments: CO₂ in a H₂O-dominated ice, and CO₂ in a CO-dominated ice. The results of this study, combined with previous observational, theoretical and experimental data, suggest a complex CO₂ formation scenario with multiple epochs and mechanisms. At early stages in the molecular cloud, CO₂ could form concurrently with H₂O via the OH radical pathway investigated here. This produces the CO₂ component in H₂O ice seen towards background stars and quiescent regions of molecular clouds, seen at low CO₂ and H₂O abundances in Figure 1. A second stage of CO₂ formation could be responsible for the large abundance of CO₂ 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 CO₂ formation, responsible for the high CO₂ abundances towards YSOs and protostars, is likely to be CO₂ formed in H₂O-dominated ice due to energetic reactions of H₂O with CO which has migrated into the H₂O ice due to temperature or time. In this scenario, the reaction CO + OH is likely to be important to CO₂ formation in quiescent regions, and potentially also plays a role in CO₂ formation at later stages in the cloud's evolution.

We acknowledge the support of the national PCMI programme funded by the CNRS, the Conseil Régional d'Ile de France through SESAME programmes (contract I-07-597R), the Conseil Général du Val d'Oise and the Agence Nationale de Recherche (contract ANR 07-BLAN-0129). J.A.N. thanks The Leverhulme Trust, SIET, the University of Strathclyde and SUPA for funding this work.

References

- Gerakines, P.A., Whittet, D.C.B., Ehrenfreund, P., *et al.*, 1999, *ApJ*, 522, 357
- Gibb, E.L., Whittet, D.C.B., Boogert, A.C.A., & Tielens, A.G.G.M., 2004, *ApJS*, 151, 35
- de Graauw, T., Whittet, D.C.B., Gerakines, P.A., *et al.*, 1996, *A&A*, 315, L345
- d'Hendecourt, L.B., & Jourdain de Muizon, M., 1989, *A&A*, 223, L5
- Ioppolo, S., van Boheemen, Y., Cuppen, H.M., van Dishoeck, E.F., & Linnartz, H., 2011, *MNRAS*, 413, 2281
- Knez, C., Boogert, A.C.A., Pontoppidan, K.M., *et al.*, 2005, *ApJ*, 635, L145
- Noble, J.A., Dulieu, F., Congiu, E., & Fraser, H.J., 2011, *ApJ*, 735, 121
- Nummelin, A., Whittet, D.C.B., Gibb, E.L., Gerakines, P.A., & Chiar, J.E., 2001, *ApJ*, 558, 185
- Oba, Y., Watanabe, N., Kouchi, A., Hama, T., & Pirronello, V., 2010, *ApJ*, 712, L174
- Pontoppidan, K.M., Fraser, H.J., Dartois, E., *et al.*, 2003, *A&A*, 408, 981
- Pontoppidan, K.M., 2006, *A&A*, 453, L47
- Pontoppidan, K.M., Boogert, A.C.A., Fraser, H.J., *et al.*, 2008, *ApJ*, 678, 1005
- Shimonishi, T., Onaka, T., Kato, D., *et al.*, 2010, *A&A*, 514, A12
- Zins, E.-L., Joshi, P.R., & Krim, L., 2011, *ApJ*, 738, 175