# ${ m H}_2$ photochemistry in interstellar ices: The formation of HCO in UV irradiated CO:H<sub>2</sub> ice mixtures

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Abstract. The role of  $H_2$  in forming interstellar complex organics is still not clear due to the high activation energies required for "non-energetic" association reactions. In this work, we investigated the potential contribution of  $H_2$  to the hydrogenated species ( $H_nCO$ ) formation on dust grains when the "energetic" processing is involved. The goal is to test whether an additional hydrogenation pathway is possible upon UV irradiation of a CO:H<sub>2</sub> ice mixture. It is proposed that the electronically excited carbon monoxide (CO<sup>\*</sup>) induced by UV-photons can react with a ground-state  $H_2$  to form HCO, ultimately enhancing the production of COMs in ice mantle.

Keywords. astrochemistry, methods: laboratory: solid state, ultraviolet: ISM, ISM: molecules

### 1. Introduction

The formation of complex organic molecules (COMs) has extensively been studied and proposed to have an icy origin on grain surfaces through the recombination of radicals induced by "energetic" and "non-energetic" processes (Chuang et al. 2017). The formyl radical (HCO) is one of the key precursors of COMs, e.g., glycolaldehyde, and is predominantly formed via CO hydrogenation (i.e., H-atom addition reactions) on grain surfaces in dense molecular clouds. Although the abundance of  $H_2$  can be four orders of magnitude higher than those of free H-atoms, the solid-state H<sub>2</sub> chemistry is largely ignored due to a high activation energy required for molecule-molecule reactions. However, CO, the second most abundant molecule after  $H_2$ , can be radiatively pumped into its vibronically excited state ( $CO^*$ ) upon the secondary UV-photon ( $\sim$ 8-9 eV) impact. Consequently, the excess energy can be transferred to the first few top-layers resulting in a photo-desorption event or used to overcome the energy barrier for reactions with other molecules in ice mantle. In this contribution, we aim to kinetically investigate the surface reactions between an electronically excited CO and  $H_2$  and propose a new hydrogenation channel to form  $CH_nO$  involving abundant  $H_2$  under dense cloud conditions (e.g., temperatures as low as ~10 K and density  $n_H = 10^{4-6}$  cm<sup>-3</sup>).

Experiments are performed under ultra-high vacuum conditions, using SURFRESIDE<sup>2</sup> in the Laboratory for Astrophysics (Leiden, the Netherlands). The details of the set-up

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**Figure 1.** IR difference spectra obtained after UV irradiation of pre-deposited (a) CO:H<sub>2</sub>, (b) CO:D<sub>2</sub> and (c) CO ice with a photon-flux of  $6 \times 10^{12}$  photons cm<sup>-2</sup>s<sup>-1</sup> over 60 min at 8 K. The inset figure shows the induced H<sub>2</sub> IR features before UV-photon irradiation.

and procedure have been described in previous paper (Ioppolo *et al.* 2013). The photolysis experiments of the pre-deposited  $\text{CO:H}_2(\text{or } D_2)$  ice mixture were performed at 8-20 K under dense cloud conditions and *in situ* monitored by Reflection Absorption Infrared Spectroscopy.

#### 2. Results and Conclusion

Figure 1 presents the IR difference spectra obtained after UV-photon irradiation of pre-deposited  $\text{CO:H}_2(\text{CO:D}_2)$  ice mixture at 8 K with a photon-flux of  $6 \times 10^{12}$  photons cm<sup>-2</sup>s<sup>-1</sup> for 60 min. The product HCO(DCO) can be identified by the spectral features at 1859(1798), 1090(852) and 2488(1938) cm<sup>-1</sup> due to the CO stretching, bending and CH stretching vibrational modes, respectively. The HCO peak at 1859 cm<sup>-1</sup> in spectrum (b) and (c) is much weaker than in (a) and possibly results from the presence of icy H<sub>2</sub> and H<sub>2</sub>O as contamination reacting with CO. IR features of H<sub>2</sub> ice are barely visible in the inset figure due to extremely weak band strength originating from induced dipole. For more details on this work see (Chuang *et al.* (2018)). Systematic investigations on temperature dependence and kinetic as a function of UV-fluence are studied:

• The UV-excited CO in ice mantle may react with  $H_2$  absorbed or trapped in interstellar ices forming HCO through two consecutive reaction steps:  $CO^*+H_2 \rightarrow HCO+H_{dis}$ and  $CO+H_{dis} \rightarrow HCO$ .

• The derived effective formation cross-section shows temperature dependence in the studied temperature range of 8-20 K, which is determined by the cumulative effect of H-atom diffusion rate and initial  $H_2$  concentration.

• Clearly, UV-photon induced hydrogenation enriches interstellar ices with HCO radicals that can further react with other radicals or molecules in ice mantle ultimately also increasing the formation efficiency of COMs. The interstellar ice chemistry will be further investigated with special focus on the contacting regions with dust grains.

#### References

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