

A NEW SOURCE OF CO₂ IN THE UNIVERSE: A PHOTOACTIVATED ELEY–RIDEAL SURFACE REACTION ON WATER ICES

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The Astrophysical Journal Letters,
791:L21, 2014 August 20

Rabin Rajan J M
06–09–14

Introduction

- Interstellar medium (ISM), in astronomy is the matter that exist between the star system in a galaxy.
- This matter includes gas in ionic, atomic, and molecular form, dust, and cosmic rays.
- Temperature: 4-150 K, pressure: $\sim 10^{-12}$ mbar.
- The molecules are being detected by spectral observations with the telescopes fitted in various parts of the earth as well as in the outer space.
- Hardly 200 different molecules are being detected so far in ISM.
(http://en.wikipedia.org/wiki/List_of_interstellar_and_circumstellar_molecules)
- Most abundant H_2 (89%), He(10%), CO, H_2O (0.1%), CO_2 , methane and lot more (lesser abundant).



This image, taken with the Hubble Space Telescope in 1995, shows evaporating gaseous globules (EGGs) emerging from pillars of molecular hydrogen gas and dust.

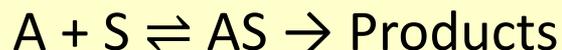
Introduction continued....

- CO₂ is one of the most abundant components of ices in the interstellar medium; however, its formation mechanism has not been clearly identified.
- CO₂ is more abundant in solid phase than in gas phase which suggests a solid phase CO₂ synthesis process is probably involved.
- Carbon monoxide is the second most abundant gas species after hydrogen in the ISM. It may well be the parent molecule for the synthesis of CO₂, as well as for many organic molecules in space.
- ***In this paper*** they report an efficient surface reaction pathway for gas phase CO conversion to solid CO₂ on amorphous solid water (ASW) films or crystalline water ice films in the temperature range 71–82 K, activated by ice absorption of Ly α (10.2 eV) radiation and follows **Eley–Rideal (E-R) surface reaction kinetics**.

Reactions on surfaces

- **Reactions on surfaces** are reactions in which at least one of the steps of the reaction mechanism is the adsorption of one or more reactants. The mechanisms for these reactions, and the rate equations are of extreme importance for heterogeneous catalysis.
- They are classified as...

1. Simple decomposition

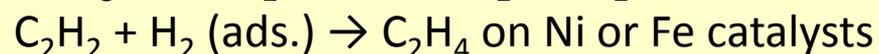
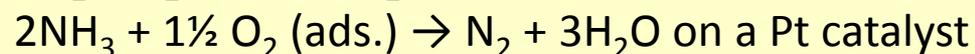
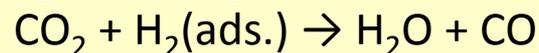
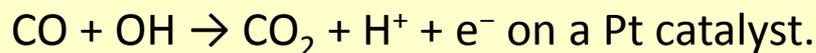
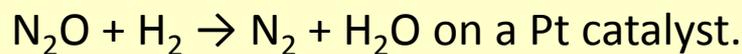
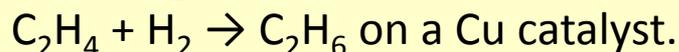
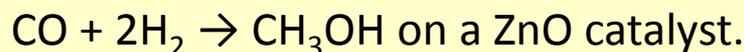
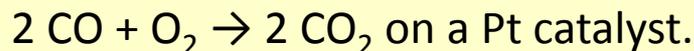
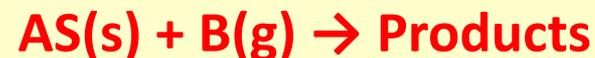


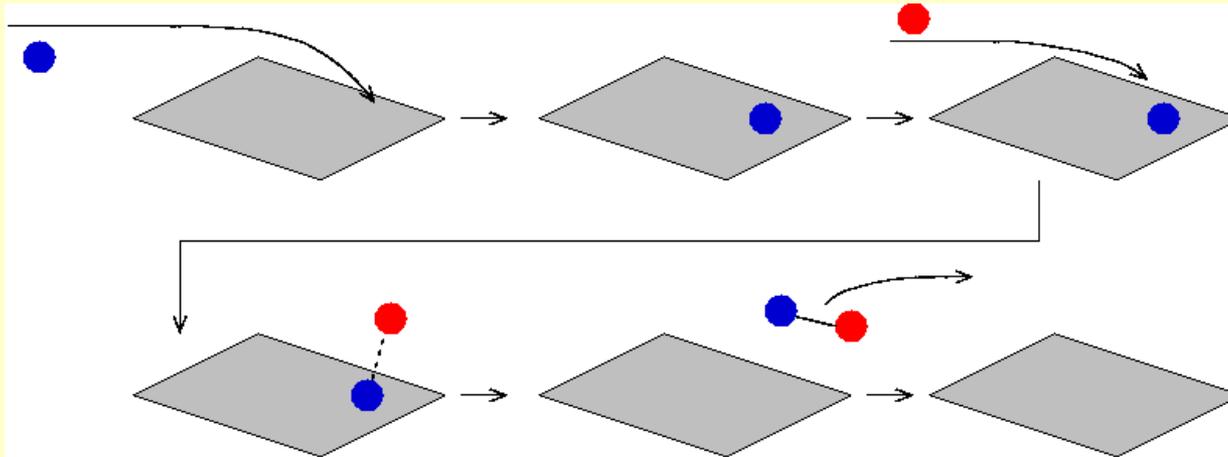
2. Bimolecular reaction

Langmuir–Hinshelwood mechanism



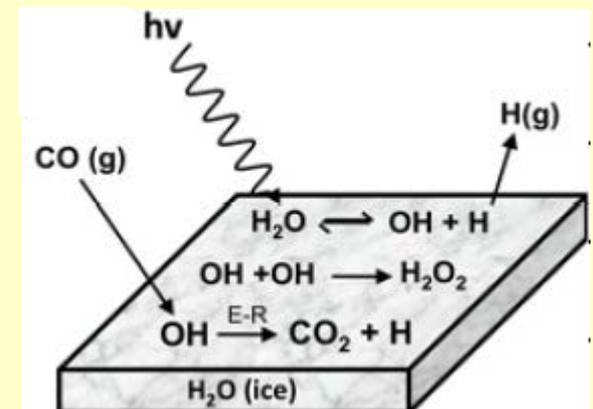
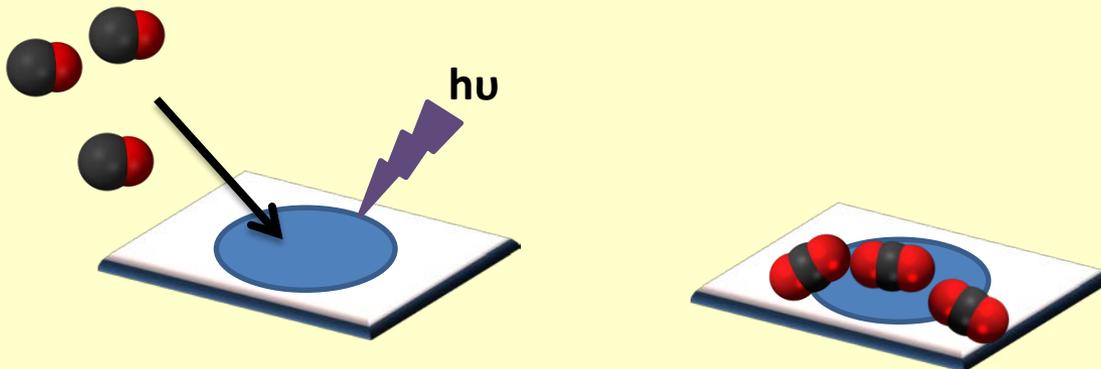
Eley–Rideal mechanism



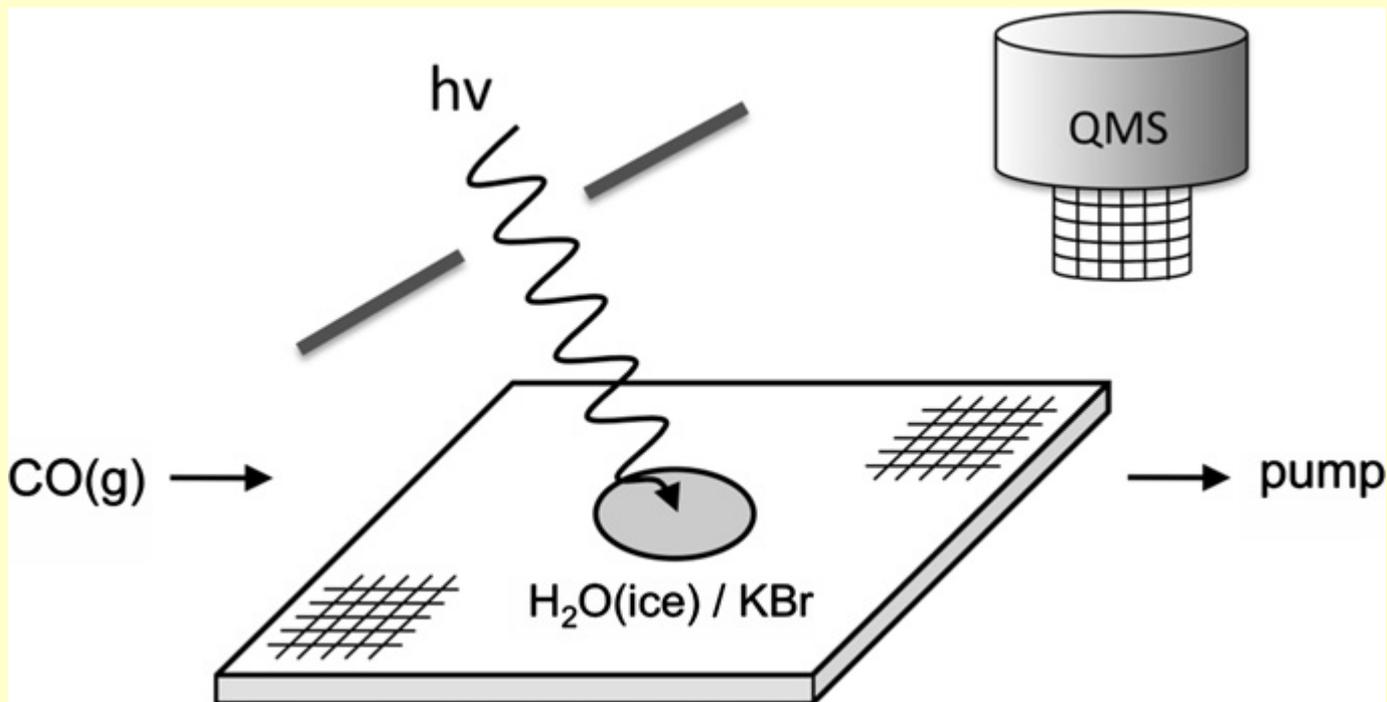


<http://meijer.group.shef.ac.uk/research/gas-surface.html>

- In this reaction a direct Eley–Rideal (E-R) process that does not involve prior energetic accommodation of CO by the ice surface is observed, when the incident CO molecules interact with surface-bound OH radicals that are produced by water photo dissociation.



Experimental



- High vacuum system (10^{-8} torr).
- H_2O (20 nm thick) deposited on a KBr disk (0.3 cm^2) at 76 K.
- $\text{Ly}\alpha$ radiation ($2.7 \times 10^{18} \text{ photons m}^{-2} \text{ s}^{-1}$) passing through LiF window, incident at 45° to the ice film.
- Transmission IR spectroscopy is performed during irradiation.
- A quadrupole MS senses the pressure of $\text{CO}(\text{g})$ flow.
- A mixture of C^{16}O and C^{18}O is employed with a mole fraction, $X_{\text{C}^{18}\text{O}}$.

Results and discussion

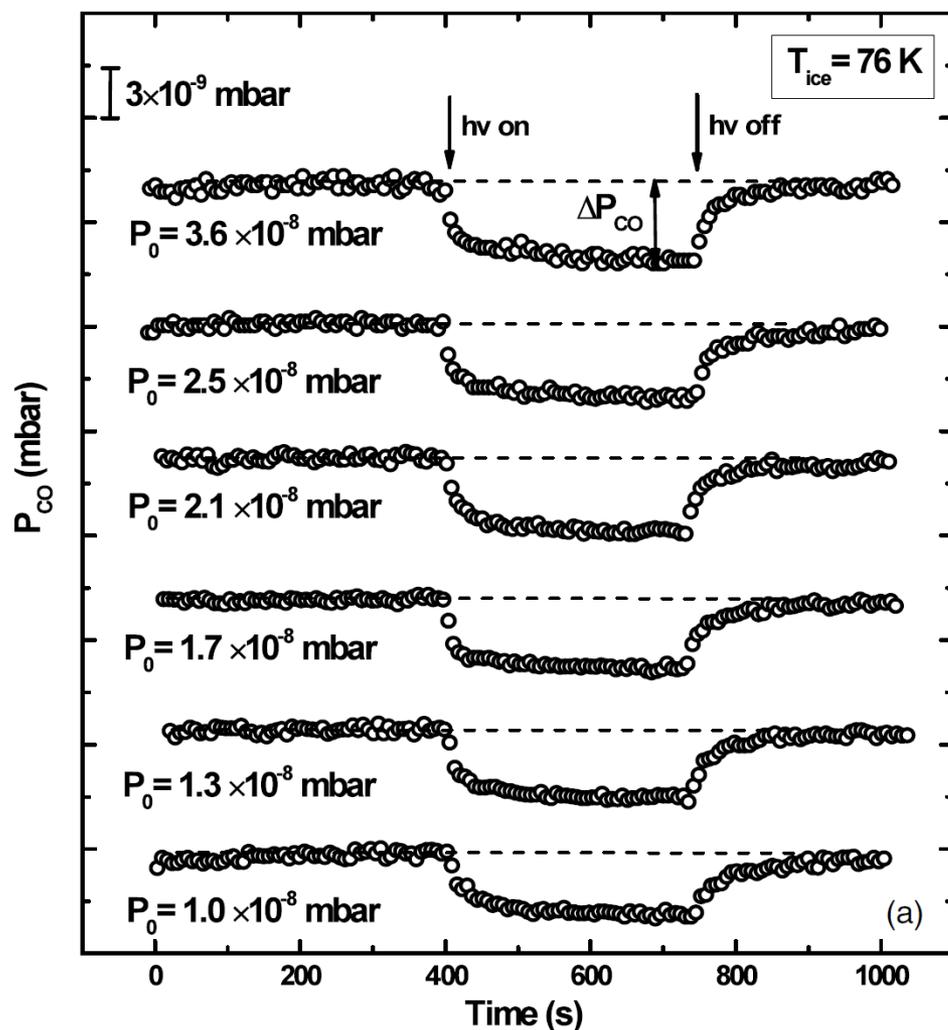


Figure 1. (a) CO(g) consumption during experiments at various CO pressures at 76 K. The curve is determined by measurements of $C^{18}O$ behaviour and then converted to total CO pressure using the fraction of $C^{18}O$. Typically $X_{C^{18}O}$ is in the range 10%–80%.

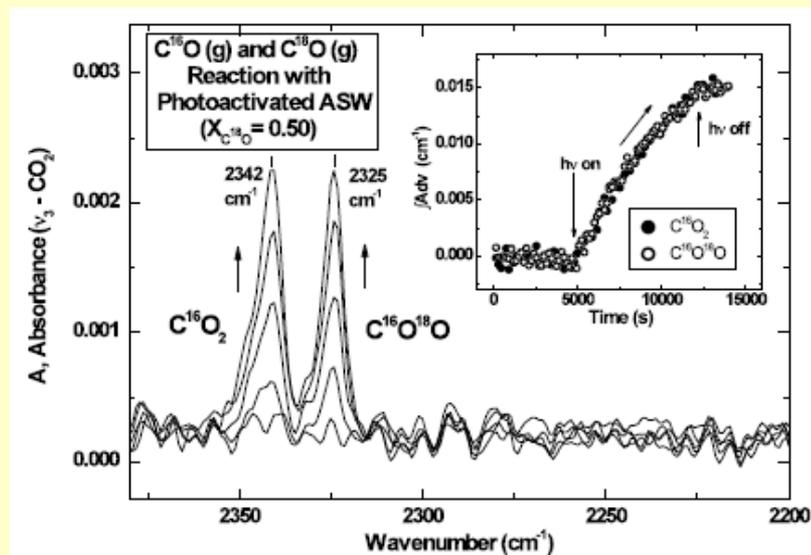
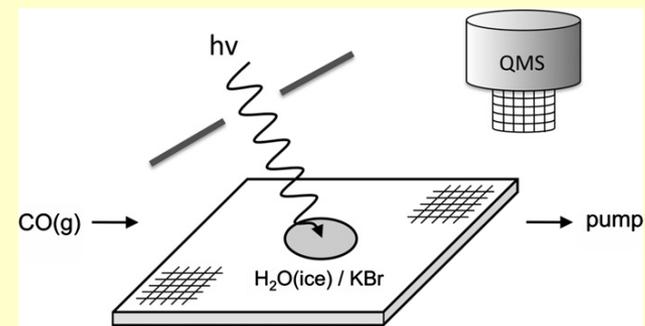


Figure 2. IR spectra of $C^{16}O_2$ and $C^{16}O^{18}O$ isotopomer ices produced during $C^{16}O(g)$ and $C^{18}O(g)$ reaction on irradiated ASW. The inset shows the growth of integrated absorbance of $C^{16}O_2$ and $C^{16}O^{18}O$ isotopomers vs. time.

Evidence for the Eley–Rideal-type Reaction

$$R_{\text{CO}} = \frac{\Delta P_{\text{CO}} \cdot S_{\text{CO}}}{A \cdot k_B T_g}, \quad (1)$$

R_{CO} – Rate of CO(g) consumption (molecules $\text{m}^{-2} \text{s}^{-1}$)

P_{CO} – Change in CO pressure

S_{CO} – Measured pumping speed

A – irradiated sample area

k_B – Boltzmann constant

T_g – CO gas temperature

- **At any CO pressure, the CO consumption rate during irradiation is proportional to the accumulated surface OH coverage, N_{OH} .**
- When the reaction reaches steady state, the surface-bound OH production rate is equal to its consumption rate, including the OH reaction rate with CO(g), and the OH recombination rate with H or OH.
- Molecular dynamics studies show a large fraction of photo produced H desorbs from the ice surface because of its weak binding energy, leaving an OH-enriched surface.
- So they postulate that the $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}$ reaction is the major process that consumes the excess OH.
- After the interruption of the irradiation, the OH species remaining on the surface continue to be consumed by CO(g) and by the recombination reactions, resulting in a decrease of R_{CO} .
- $N_{\text{OH}}^{\text{SS}} = (4 \pm 1) \times 10^{17} \text{ m}^{-2}$ from, corresponding to a fractional surface OH coverage of $\Theta_{\text{OH}}^{\text{SS}} = 0.05 \text{ ML}$ (monolayer) at steady state.

- The incident flux F_{CO} of CO(g) on the ice surface is calculated from the kinetic theory of gases using Equation (2):

$$F_{\text{CO}} = \frac{P_{\text{CO}}^0}{(2\pi mk_B T_g)^{1/2}}, \quad (2)$$

where P_{CO}^0 is the total pressure of CO(g) before irradiation, and m is the mass of the CO molecule.

- $R_{\text{CO}} = d[\text{CO}]/dt = F_{\text{CO}} \cdot \sigma_{\text{CO}} \cdot N_{\text{OH}}$

The reaction cross section, σ_{CO} , is found to be $6 \times 10^{-20} \text{ m}^2$, which is of the order of a geometrical molecular cross section, consistent with a direct E-R-type process.

- When CO molecules strike the ice surface, their average residence time can be calculated from Equation (3):

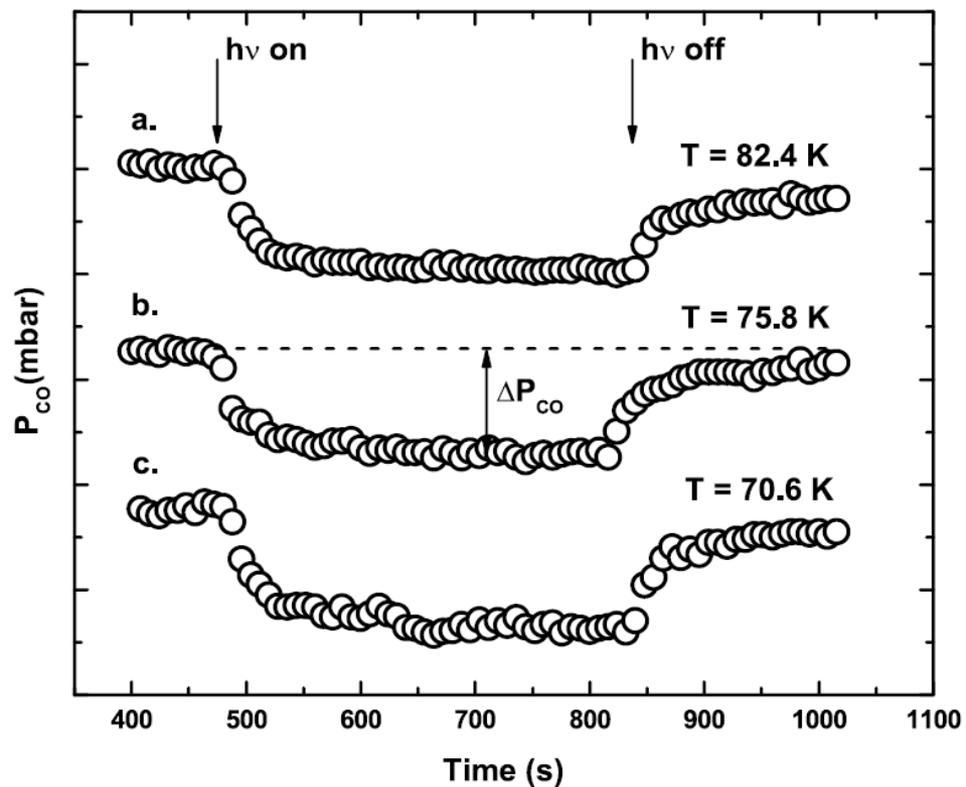
$$t_s = \frac{1}{\nu} e^{E_{\text{des}}/k_B T},$$

(3) where ν is the desorption frequency factor $\approx 10^{12} \text{ s}^{-1}$, E_{des} is the CO desorption energy from the H₂O ice surface, and T is the ice temperature.

The CO desorption energy from H₂O ice has been investigated experimentally and theoretically ($E_{\text{des}} = 0.125 \text{ eV}$). At $T = 76 \text{ K}$, the residence time for CO(g) on the H₂O ice surface is $\sim 2 \times 10^{-4} \text{ s}$.

- The fractional coverage of CO adsorbed on the ASW–H₂O ice surface at a given CO(g) pressure is $\theta_{\text{CO}} = (F_{\text{CO}} \times t_s) / N_{\text{H}_2\text{O}}$, where $N_{\text{H}_2\text{O}} \approx 9 \times 10^{18} \text{ m}^{-2}$ is the surface density of H₂O adsorption sites based on the density (0.94 g cm⁻³) of ASW.
- CO fractional coverage is only $\theta_{\text{CO}} = 1 \times 10^{-6}$ ML, i.e. five orders of magnitude smaller than the steady-state fractional OH coverage.
- This low coverage is consistent with the absence of the adsorbed CO IR absorption band.
- Thus, it is improbable under the conditions of the experiment for the reaction to occur by a mechanism where CO adsorbs on the surface and translates to an OH species.
- As temperature decreases the CO consumption rate remains constant (figure 3). This is an additional evidence to support the E-R reaction mechanism.
- The competitive reactions such as the OH+OH reaction, the H+H reaction, the CO+H and CO+O reactions may interfere with the CO+OH reaction investigated here.

Temperature effect on R_{CO}



Arrhenius plot

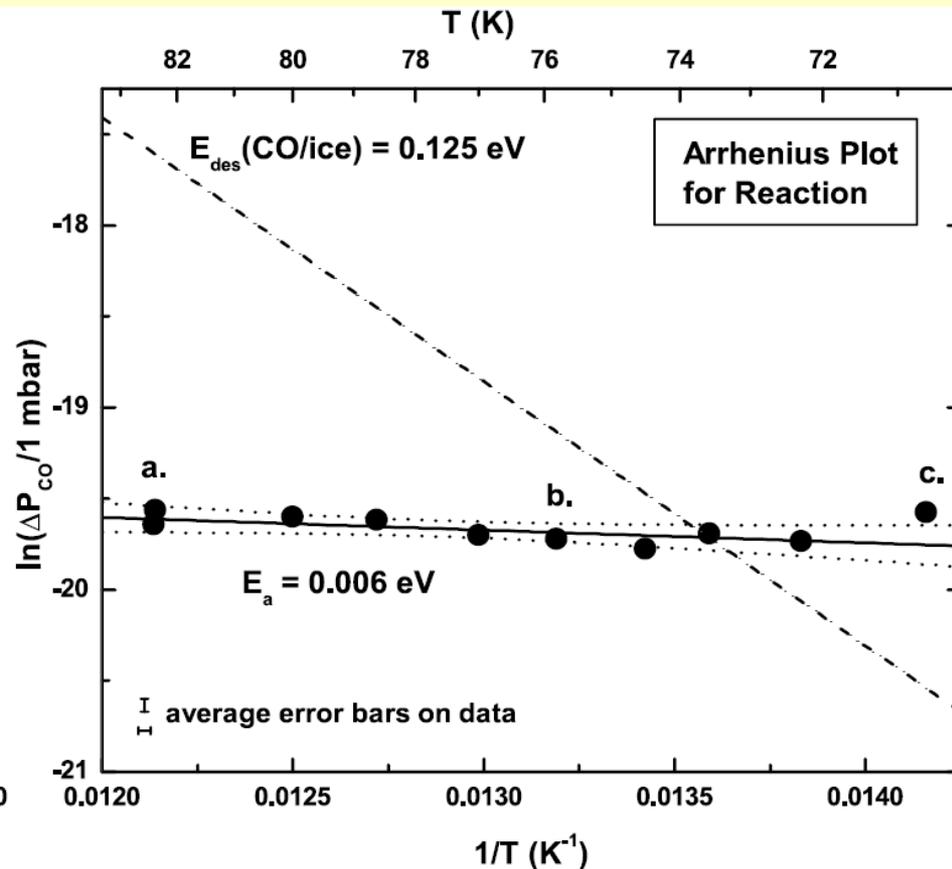
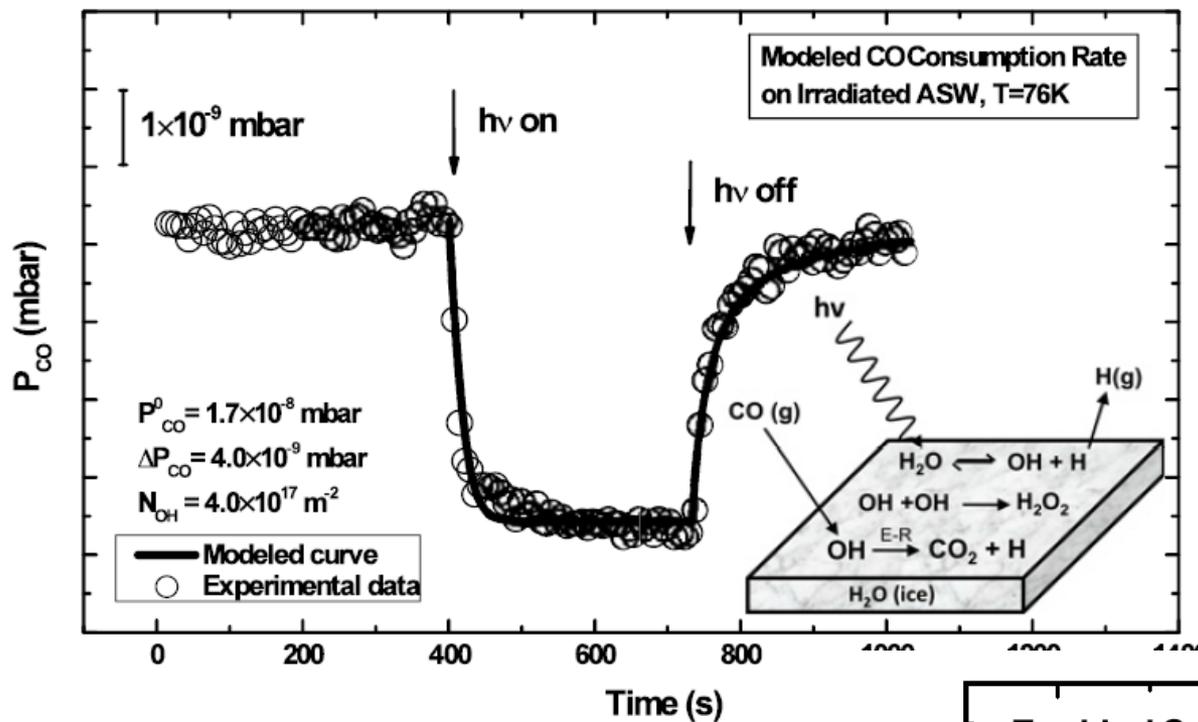


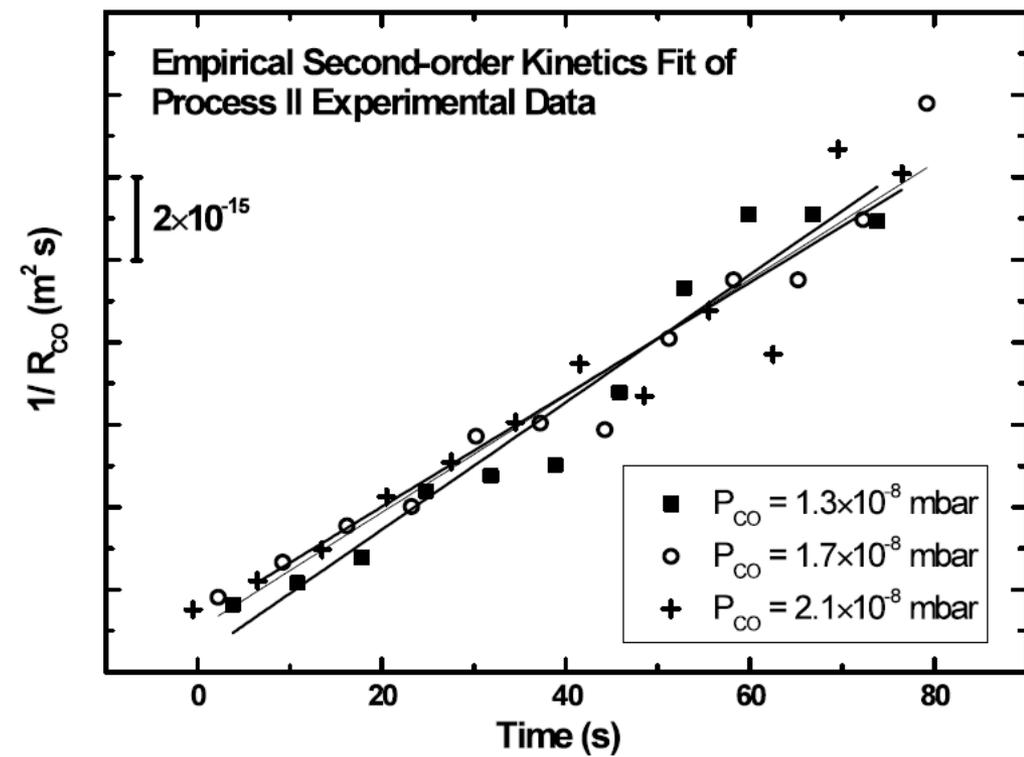
Figure 3. Temperature effect on CO(g) consumption rate between 70.6 K and 82.4 K. CO consumption is displayed for measurements at three temperatures. An Arrhenius plot of the data yields an activation energy of 0.006 eV. Ninety-five percent confidence intervals (dotted lines) on the weighted data show that the activation energy is zero within experimental error. The slope of $E_{des}(\text{CO/ice}) = 0.125 \text{ eV}$ is shown for comparison, and represents the expected temperature effect if the CO surface lifetime is rate controlling in the mobile precursor mechanism.



A kinetic model was used to fit the data of Figure 1 as shown in Figure 4.

Figure 4. Modeled CO(g) consumption rate on irradiated ASW and its comparison to experimental data. The inset shows the schematic of the surface processes on the ice surface.

Figure 5. Empirical second-order kinetic fits of Process II experimental data.



- The model considers the flux of incident light, the cross section for H₂O photodissociation, and the incoming flux of CO(g) in the system of known pumping speed to calculate the solid curve which is superimposed on the data for one measurement.
- To study the kinetics of the CO consumption process, CO(g) + OH → CO₂(ice)+H, they divided the experimental CO pressure curves (as shown in Figures 1, 3, and 4) into two processes.
- Process I describes the CO pressure decay to steady state during irradiation and Process II describes the CO pressure recovery after irradiation ends.

$$R_{\text{CO}} = \frac{\Delta P_{\text{CO}} \cdot S_{\text{CO}}}{A \cdot k_B T_g} = k_1 P_{\text{CO}} N_{\text{OH}}. \quad (4)$$

- In process I CO(g)+OH reaction only consumes a small portion of OH species on the surface. The majority of surface OH species are consumed by the competitive OH+OH second-order recombination process.
- In Process II, they assume that the OH consumption rate is simply determined by the CO(g)+OH reaction rate and by the OH+OH recombination rate, despite other complex processes that could occur in an irradiated water ice.

$$-\frac{dN_{\text{OH}}}{dt} = R_{\text{CO}} + R_{\text{OH+OH}} = k_1 P_{\text{CO}} N_{\text{OH}} + k_2 (N_{\text{OH}})^2 \quad (5)$$

- Because the CO(g)+OH reaction rate is relatively slow, the OH consumption rate is approximately a second-order kinetic process in N_{OH}. The empirical second-order kinetic fits of 1/R_{CO} versus time from the experimental data are consistent for a range of pressures, as seen in Figure 5.

By integrating Equation (5),

$$- \int_{N_{\text{OH}}^{\text{SS}}}^{N_{\text{OH}}} \frac{dN_{\text{OH}}}{k_1 P_{\text{CO}} N_{\text{OH}} + k_2 (N_{\text{OH}})^2} = \int_0^t dt \quad (6)$$

where $N_{\text{OH}}^{\text{SS}}$ is the OH coverage during irradiation at steady state, we get

$$N_{\text{OH}} = \frac{k_1 P_{\text{CO}} N_{\text{OH}}^{\text{SS}}}{k_1 P_{\text{CO}} e^{k_1 P_{\text{CO}} t} + k_2 N_{\text{OH}}^{\text{SS}} (e^{k_1 P_{\text{CO}} t} - 1)}. \quad (7)$$

In Process I, the steady-state OH consumption rate is equilibrated with its production rate by irradiation. The kinetic equation is

$$\frac{dN_{\text{OH}}}{dt} = F_{h\nu} \sigma_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}} - k_1 P_{\text{CO}} N_{\text{OH}} - k_2 (N_{\text{OH}})^2 \quad (8)$$

where $F_{h\nu}$ is the flux of photons, $\sigma_{\text{H}_2\text{O}} = 1 \times 10^{-21} \text{ m}^2$ is the Ly α photodissociation cross section of H₂O ice, and $N_{\text{H}_2\text{O}}$ is the surface density of H₂O molecules. Here they assume that only the first layer of water ice contributes to the surface OH production.

Integrating eqn (8)

$$\int_0^{N_{\text{OH}}} \frac{dN_{\text{OH}}}{F_{h\nu} \sigma_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}} - k_1 P_{\text{CO}} N_{\text{OH}} - k_2 (N_{\text{OH}})^2} = \int_0^t dt \quad (9)$$

$$N_{\text{OH}} = \frac{2c \left(1 - e^{\sqrt{k_1^2 P_{\text{CO}}^2 + 4k_2 c} t} \right)}{k_1 P_{\text{CO}} \left(1 - e^{\sqrt{k_1^2 P_{\text{CO}}^2 + 4k_2 c} t} \right) - \sqrt{k_1^2 P_{\text{CO}}^2 + 4k_2 c} \left(1 + e^{\sqrt{k_1^2 P_{\text{CO}}^2 + 4k_2 c} t} \right)} \quad (10)$$

where $c = F_{h\nu} \sigma_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}} \approx 2 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$

At steady state

$$F_{h\nu} \sigma_{\text{H}_2\text{O}} N_{\text{H}_2\text{O}} = k_1 P_{\text{CO}} N_{\text{OH}}^{\text{SS}} + k_2 (N_{\text{OH}}^{\text{SS}})^2. \quad (11)$$

- Here they assume a steady-state surface OH concentration, $N_{\text{OH}}^{\text{SS}}$, so that the rate constants k_1 and k_2 can be calculated from Equations (4) and (11). These rate constants are used in Equations (7) and (10) to model the curves to best fit the experimental data.
- The value of $N_{\text{OH}}^{\text{SS}}$ can be estimated from the empirical second order kinetics fit in Figure 5, and then be slightly adjusted to best fit the experimental data. An optimum $N_{\text{OH}}^{\text{SS}} = (4 \pm 1) \times 10^{17} \text{ m}^{-2}$ is obtained from the data of six measurements. The fitting result is shown in Figure 4 for one experiment.
- The modeled curve for Process II fits the experimental data well, while the curve for Process I has a small deviation from the data when P_{CO} approaches the steady state. This may be rationalized by postulating a small contribution from slow diffusion of OH from the underlying layers of the water ice. Since the Ly α light penetrates into the ice, the diffusing OH species produced in the bulk may contribute to the surface OH concentration, causing a slightly increasing CO consumption rate as one moves to longer times in the plateau region of Figures 1 and 4.
- With the calculated values of k_1 and k_2 , the OH consumption rate by the $\text{CO}(\text{g}) + \text{OH}$ reaction and by the $\text{OH} + \text{OH}$ recombination are 3% and 97% of the total OH production rate by irradiation at steady state, respectively. Therefore their previous assumptions that the $\text{CO}(\text{g}) + \text{OH}$ reaction rate is relatively small and that the OH consumption rate can be simplified as a second-order kinetic process are reasonable.

Conclusions

- The study observed the reaction between photochemically produced surface-bound OH species and incident CO(g) molecules at water ice surfaces between 71 and 82 K.
- The reaction is found to occur by a direct Eley-Rideal mechanism where a CO(g) molecule collides and reacts directly with a surface OH species to produce CO₂(ice).
- This observation may explain the origin of some of the CO₂(ice) observed in the ISM as well as the CO consumption in the atmospheres of icy moons.
- This experiments demonstrate a new process to convert CO(g) to CO₂ by reaction with surface OH species on astronomical ices which is a new pathway of CO₂ in ISM.

Future perspective

- C⁺ reactivity with solid oxygen (giving CO, CO₂) and also O⁺ collision with solid acetylene (giving acetone) which we are doing now may also need to be looked up with a kinetic modeled like this.
- By the help of isotopically labeled ionic species (or ices) we can proceed the above experiments further and can easily prove the product formation with its kinetics.
- Irradiation of water ice with UV to produce the OH radicals and its reactivity with ultra low energy ions (our instrument capability) seems to be a well fascinating work.

Thank you all...