National Aeronautics and Space Administration

Laboratory and Modeling Constraints on the Origin of Anomalously Depleted ^{13}C on Mars

Principal Investigator: Stanley P. Sander (320)
Yuk Yung (Caltech), Xu Zhang (329)
Program: Topics (Solar System Science)

Objectives:

The goal was to combine laboratory studies, modeling and the latest observational data to constrain the sources, transport, and sinks of organics on Mars, with emphasis on interpreting the isotopic fractionations reported by House et al. Two possible primary pathways for the origin of the depleted ^{13}C isotopologues of organics on Mars are proposed (Fig.1). This year we studied pathway (1).

Objectives *I)* to study the photolysis of CO_2 and the photolysis of $CO_2 + H_2$, and to detect the photochemical production of CO, H_2CO and organics; ***II)*** to study the isotopic fractionations of these products, so we can determine whether ^{13}C is depleted; ***III)*** to model oxyhydrocarbons and isotopic fractionations on paleo-Mars using the Caltech/JPL photochemical model.

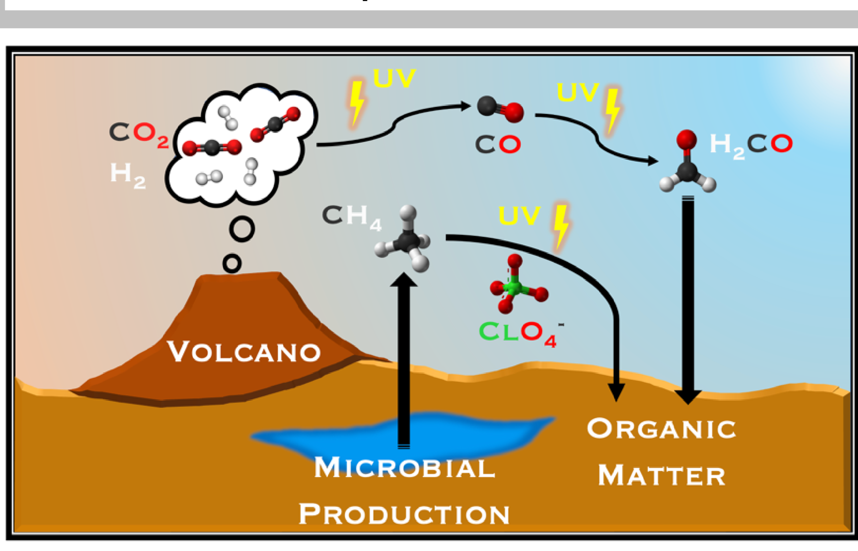


Fig. 1. Two possible scenarios for the origin of depleted ^{13}C in the carbon isotopic composition observed by SAM TLS. (1) Deep Brown: volcanic sources of CO_2 and H_2, followed by photochemical production of H_2CO and organics. (2) Blue: biotic sources of CH_4, followed by photochemistry and organic synthesis. Adapted from House et al.

Background:

- One of the key goals of Mars exploration is to detect organic species which could implicate possible habitable environment on Mars.
- Recent measurements (House et al. 2022) from Curiosity showed that methane (CH_4) evolved from pyrolysis of powder samples at Gale crater are isotopically light in ^{13}C by as much as -137 per mil.
- The authors of the aforementioned paper proposed three possible explanations: (1) and (2) are shown in Fig. 1. (3) deposition of cosmic dust during passage through a gigantic molecular cloud. They pointed out that "no single explanation can be accepted without further research"
- Our studies of the origin of the organics and their isotopic signature is at the heart of Mars science, as well as NASA programs such as Exobiology and Habitable Worlds.

Benefits to NASA and JPL (or significance of results):

- This is a combined laboratory and modeling study investigating proposed mechanisms for the large depletion of ^{13}C in Martian organics observed by SAM/TLS on the Curiosity rover.
- The objectives are to conduct lab studies and modeling to constrain the sources, transport and sinks of organics on Mars, by elucidating ^{13}C fractionation processes.
- Our findings of the origin of the organics and their isotopic signature is at the heart of Mars science, as well as NASA programs such as Exobiology and Habitable Worlds.
- In addition, our results could have a major influence on the choice of instrumentation and site selection in the future.

Approach and Results:

(1) $CO_2 + h\nu$ (185 nm) $\rightarrow$ CO + $O(^3P)$, probed by IR laser absorption spectroscopy

Experimental procedures: *1)* Fill the gas cell with 300-350 torr CO_2; *2)* Photolysis using two Hg Lamps for about 90 mins; *3)* Photolysis products pass through a LN_2 trap (to trap the CO_2). This yields about 70 mTorr of CO_2 (~50 mTorr) + CO (~20 mTorr) in ~1L volume. A small amount of the CO_2 + CO product mixture was added to a multi-pass Herriott cell (30 m path length). An IR laser beam passed through the Herriott cell and detected with a cooled HgCdTe detector. The laser frequency was swept through lines originating from ^{12}CO and ^{13}CO.

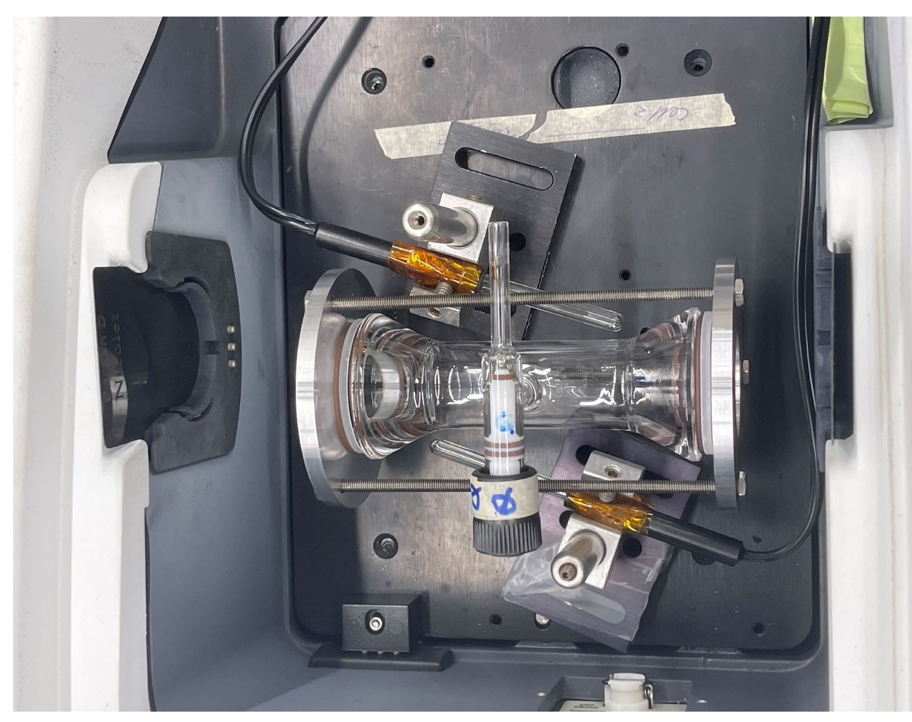


Fig. 2. Photolysis of CO_2 in a gas cell using two Hg lamps

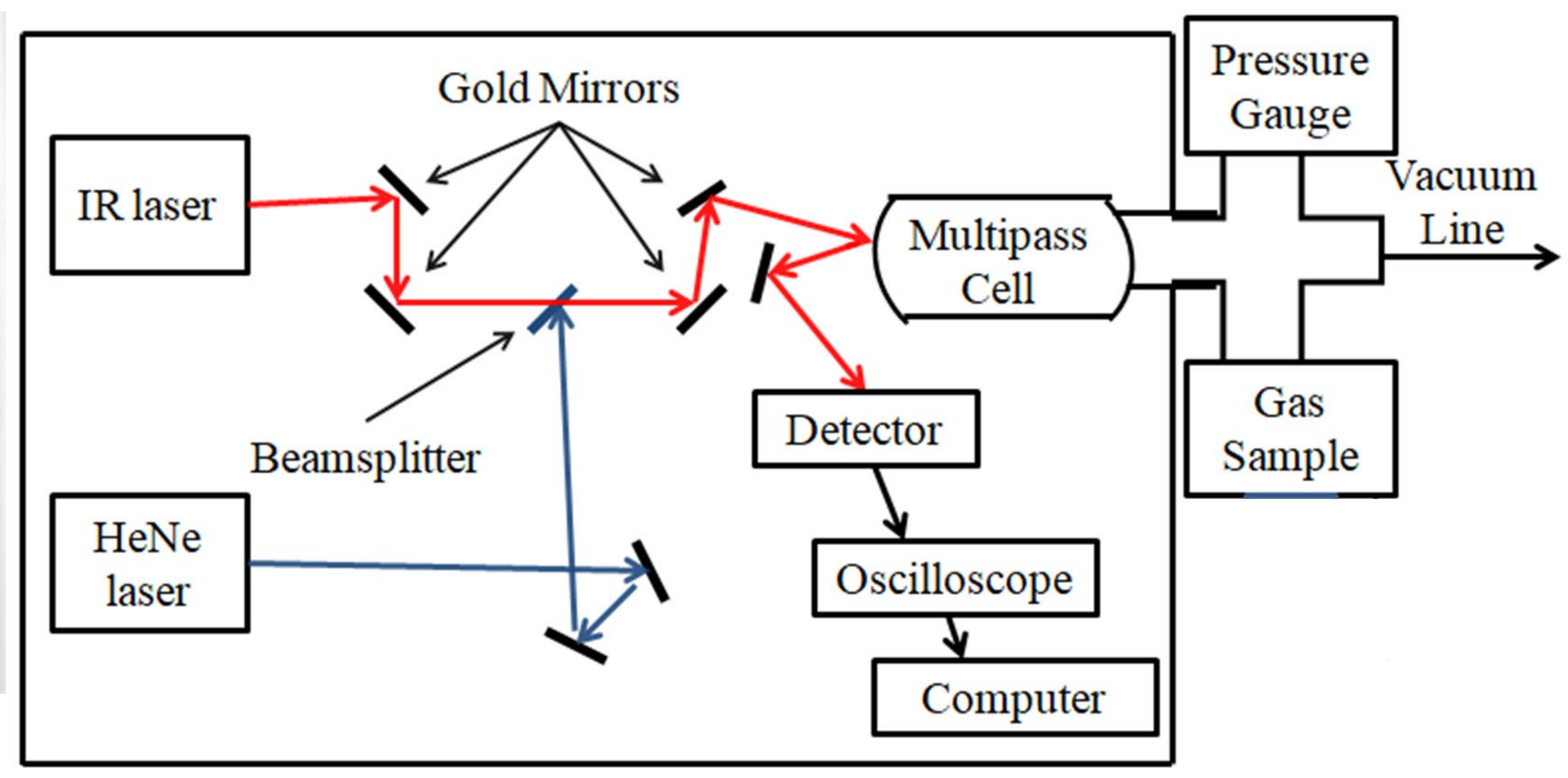


Fig. 3. Schematic of IR laser absorption spectral collection setup.

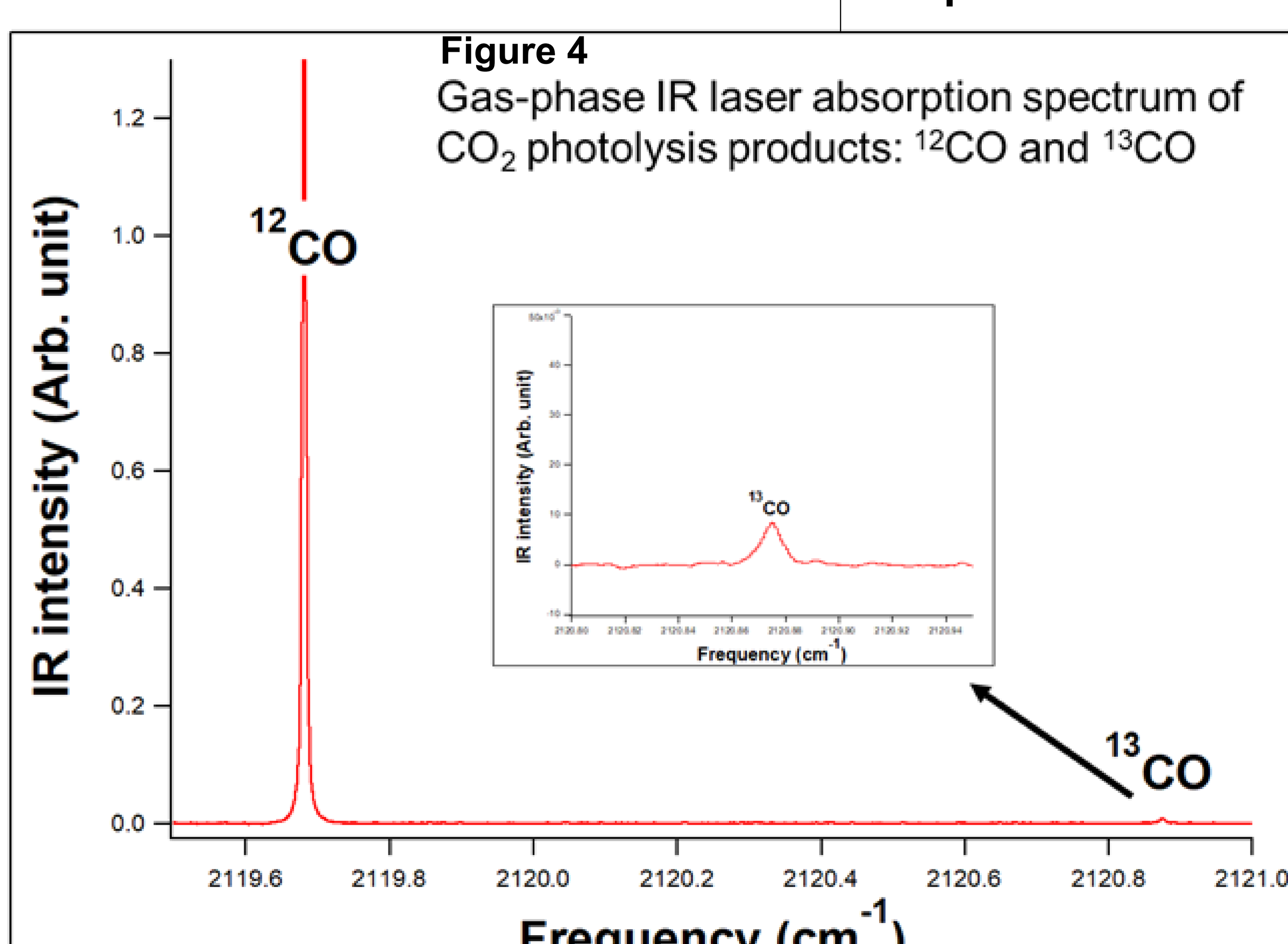
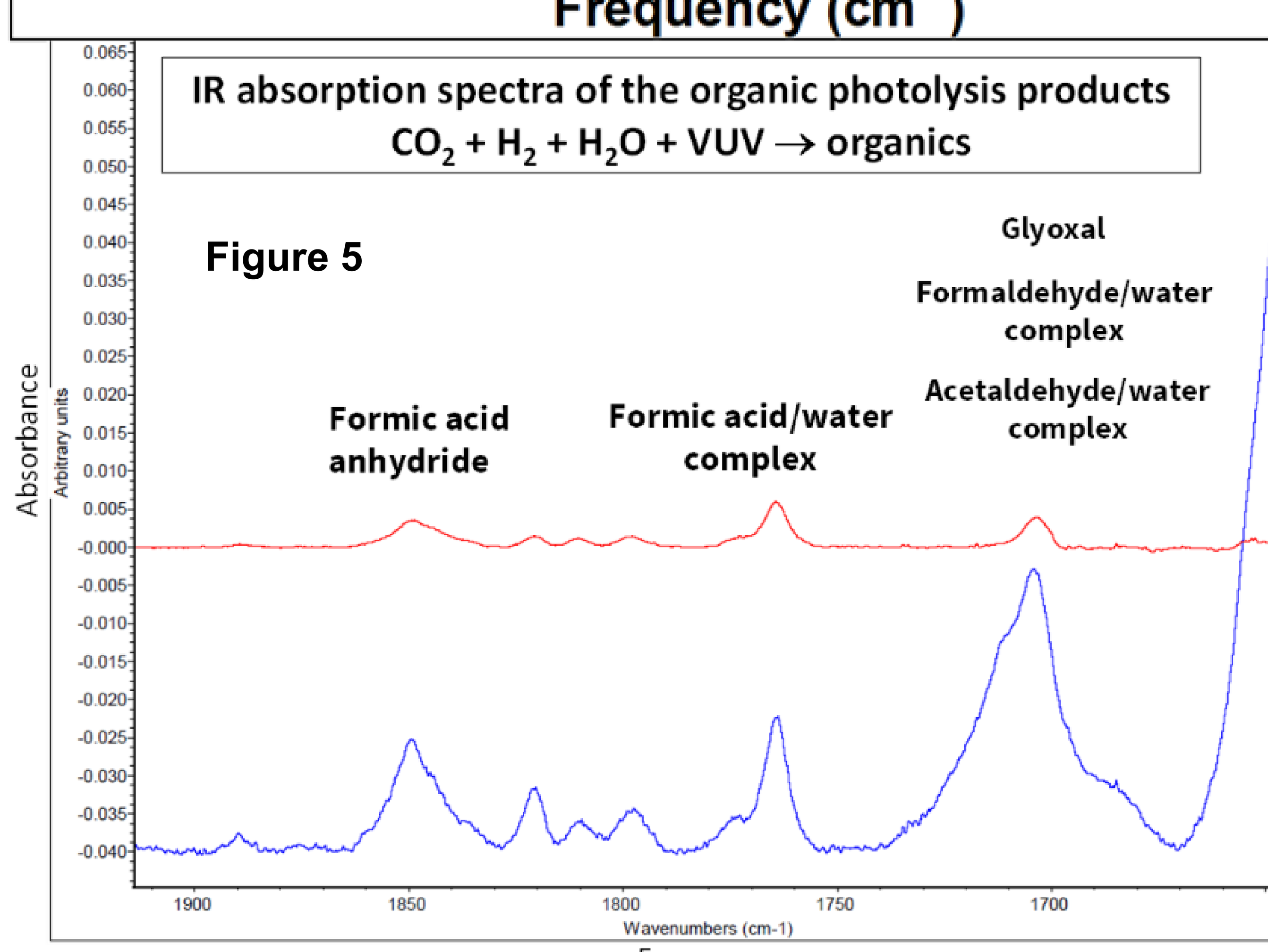


Fig. 4 illustrates the IR absorption spectra of photolysis products, ^{12}CO and ^{13}CO. The spectra are still being analyzed, the results will be available soon. These results will be compared to the previous result from matrix IR spectra: **-125 ± 15‰.**

(2) $CO_2 + H_2$ (+ H_2O as catalyst) photolysis to form CO and H_2CO and organics

Experiment procedures *1)* Fill the gas cell with roughly 250 torr CO_2, 20 torr H_2 and 16 torr H_2O; *2)* Photolysis using two Hg Lamps for about 54 hours; *3)* Photolysis products were collected in a cold trap (about - 60°C). Most CO and CO_2 are in gas phase and pumped out. The products in the trap were warmed up and mixed with Ne gas, then deposited in a cold matrix (at 4K). Matrix IR absorption spectra were collected.



Matrix IR absorption spectra were shown in Fig. 5. Organic molecules such as H_2CO, HCOOH are likely contributors to the signals observed in the matrix IR spectra. We have also conducted experiment with the mixture of ($^{12}CO_2$ + $^{13}CO_2$) + H_2 + H_2O + 185 nm UV, the preliminary results show the possibility of ^{13}C depletion in the organic products. More studies need to be done to confirm the result.

Results (Summary):

- Detected CO as the main product of CO_2 + VUV; Collected gas-phase IR laser absorption spectra of the products. The results will be compared to the matrix IR results: isotope value ($\delta^{13}C$) of CO is -125 ± 15‰.
- Observed organics from the photolysis of $CO_2 + H_2$ (+ H_2O as catalyst), and possible ^{13}C depletion.
- For modeling studies, we have modeled oxyhydrocarbons and isotopic fractionations on paleo-Mars using the Caltech/JPL photochemical model, accounting for about 50% of the extreme ^{13}C depletion observed by the MSL Curiosity Rover.

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National Aeronautics and Space Administration
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
www.nasa.gov

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PI/Task Mgr. Contact Information: Stanley P. Sander: ssander@jpl.nasa.gov; (818) 354-2625;
Co-PI: Yuk Yung: yly@caltech.edu; Xu Zhang: xu.zhang@jpl.nasa.gov

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