Radiation-driven Decomposition of Thiophene and Thiophene-derivatives within H_2O-ice

Patrick D. Tribbett[1,2], Christopher K. Materese[2], Yukiko Y. Yarnall[1,2], and Reggie L. Hudson[2]

[1] Center for Space Science and Technology, University of Maryland Baltimore County, Baltimore, MD, 21250, USA
[2] Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, 20771, USA

Background and Motivation

Thiophene and several of its derivatives (2-methylthiophene, 3-methylthiophene) have been detected on the surface of Mars in lacustrine mudstones using the pyrolysis-GC-MS instrument onboard NASA's Curiosity Rover.[1,2] The biosynthesis of thiophenes is considered an important production pathway on Earth, suggesting that thiophenes could serve as a secondary chemical biosignature on Mars.[3] However, Mars lacks a global magnetic field allowing GCRs to readily penetrate the thin CO_2 atmosphere and several meters into the regolith. GCRs can destroy the organic molecules present (i.e., chemical biosignatures). To date, the radiation-driven decomposition of these thiophenes has not been examined and their destruction rates constants have not been measured. Here, we provide radiolytic decomposition rates for thiophene as a neat ice and diluted in water ice to provide additional astrochemical context to the recent detections on Mars.

Experimental Methods

We describe the specifications of the high vacuum (10^{-7} Torr) chamber used in this study in several recent publications (Fig. 1).[4,5] We deposit neat ices and water ice mixtures (100:1) on a ZnSe substrate cooled to 125 K and irradiate the ice with 0.9 MeV p^+ emitted from a beamline coupled to a Van de Graff accelerator. We calculate the absorbed dose (MGy) from the p^+ fluence and total stopping power of each proton. We monitor the ices *in situ* using IR spectroscopy (5500 – 500 cm^{-1}). We quantify the radiolytic decomposition assuming a pseudo first-order reversible reaction[6,7]:

$$Organics \rightleftharpoons Products$$

$$\frac{A}{A_0} = \left(1 - \frac{A_\infty}{A_0}\right) e^{-(k_1+k_2)D} + \frac{A_\infty}{A_0}$$

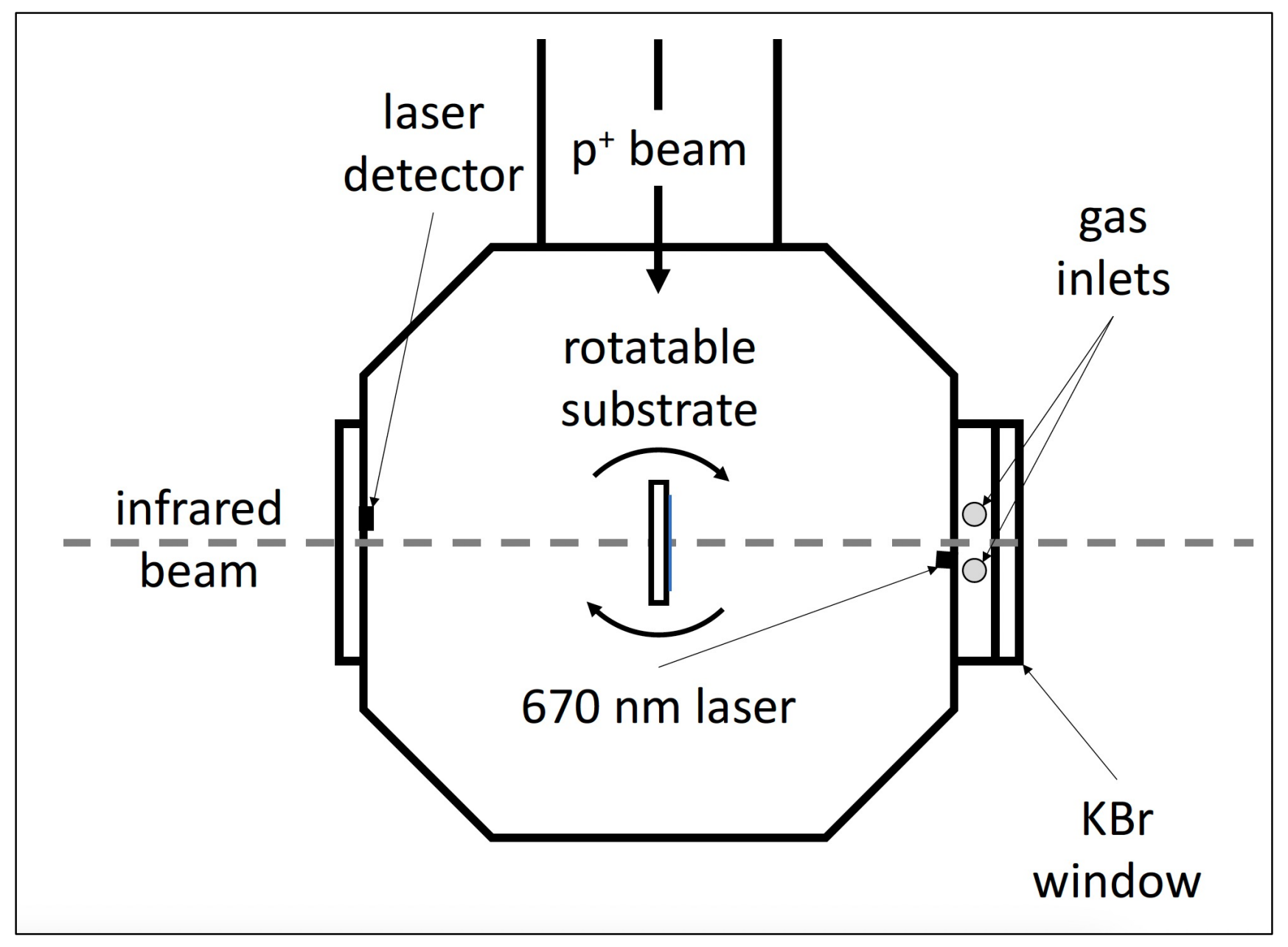


Fig. 1 Schematic of the vacuum chamber used for this study

Questions?
Contact us at patrick.d.tribbett@nasa.gov

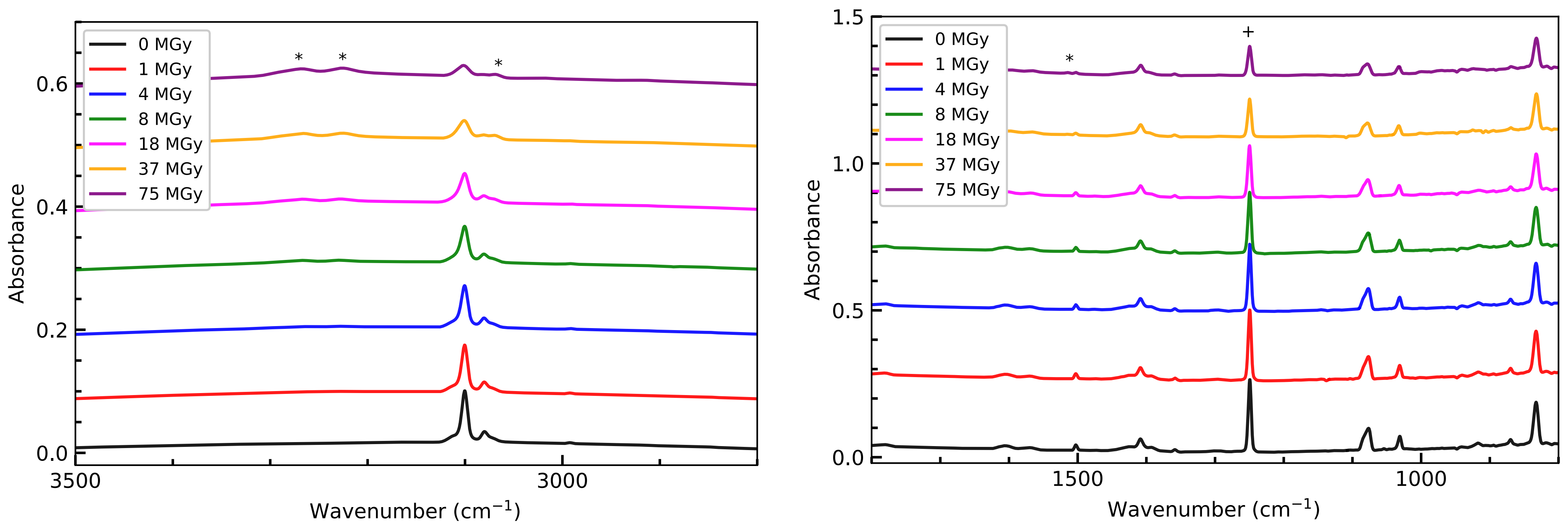


Fig. 2 Left: IR spectra (3400 – 2800 cm^{-1}) of neat thiophene at 125 K and incrementally irradiated to 75 MGy. Right: Same as left, 1800-800 cm^{-1}. Asterisks indicate product bands. Spectra are offset for clarity.

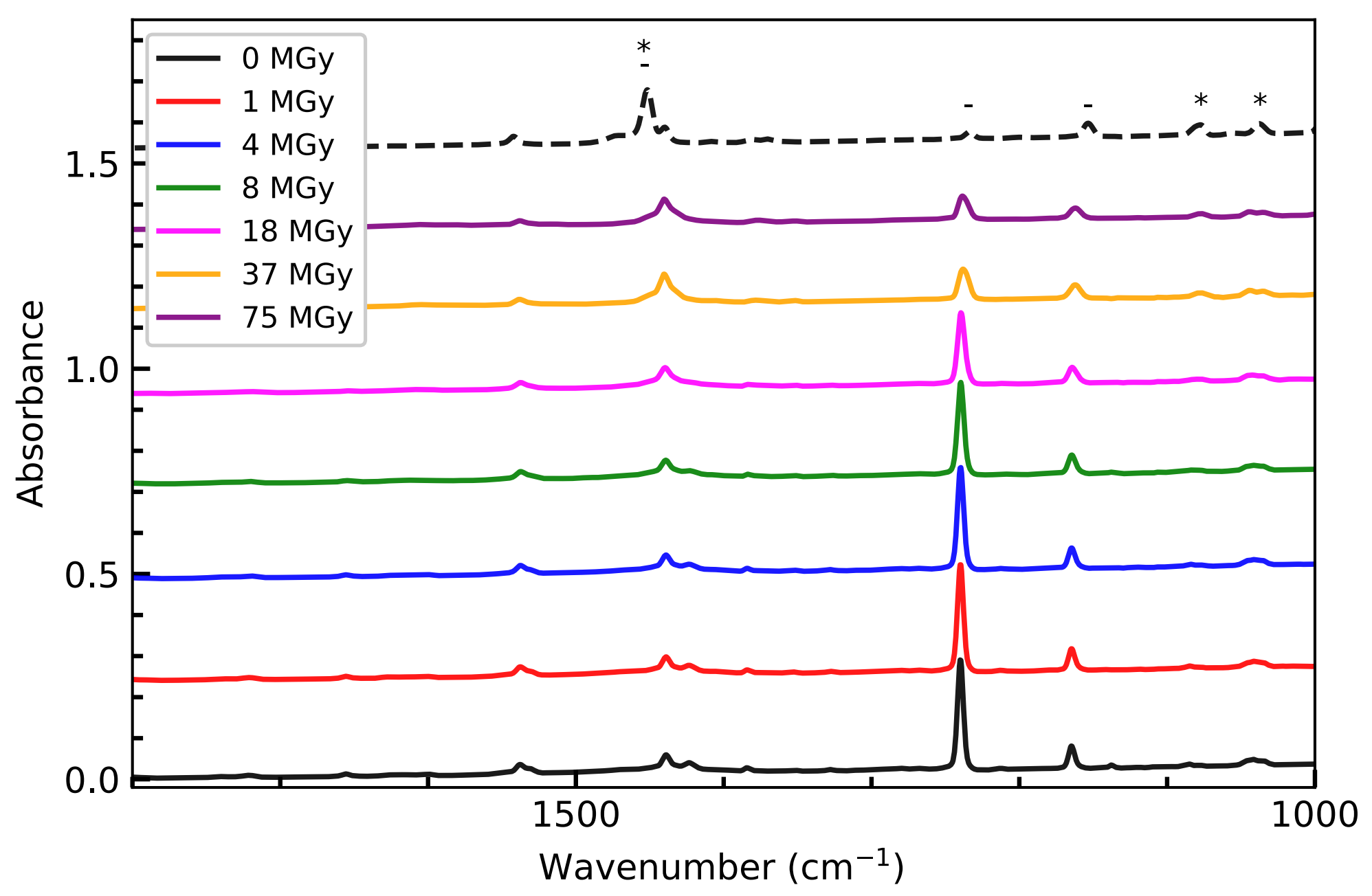


Fig. 3: IR spectra (1800 – 1000 cm^{-1}) of neat 2-methylthiophene at 125 K and incrementally irradiated to 75 MGy (solid). Pristine 3-methylthiophene at 125 K for comparison (dashed). Asterisks indicate band shifts due to methyl-group exchange or removal; dashes indicate broadening due to methyl-group exchange. Spectra are offset for clarity.

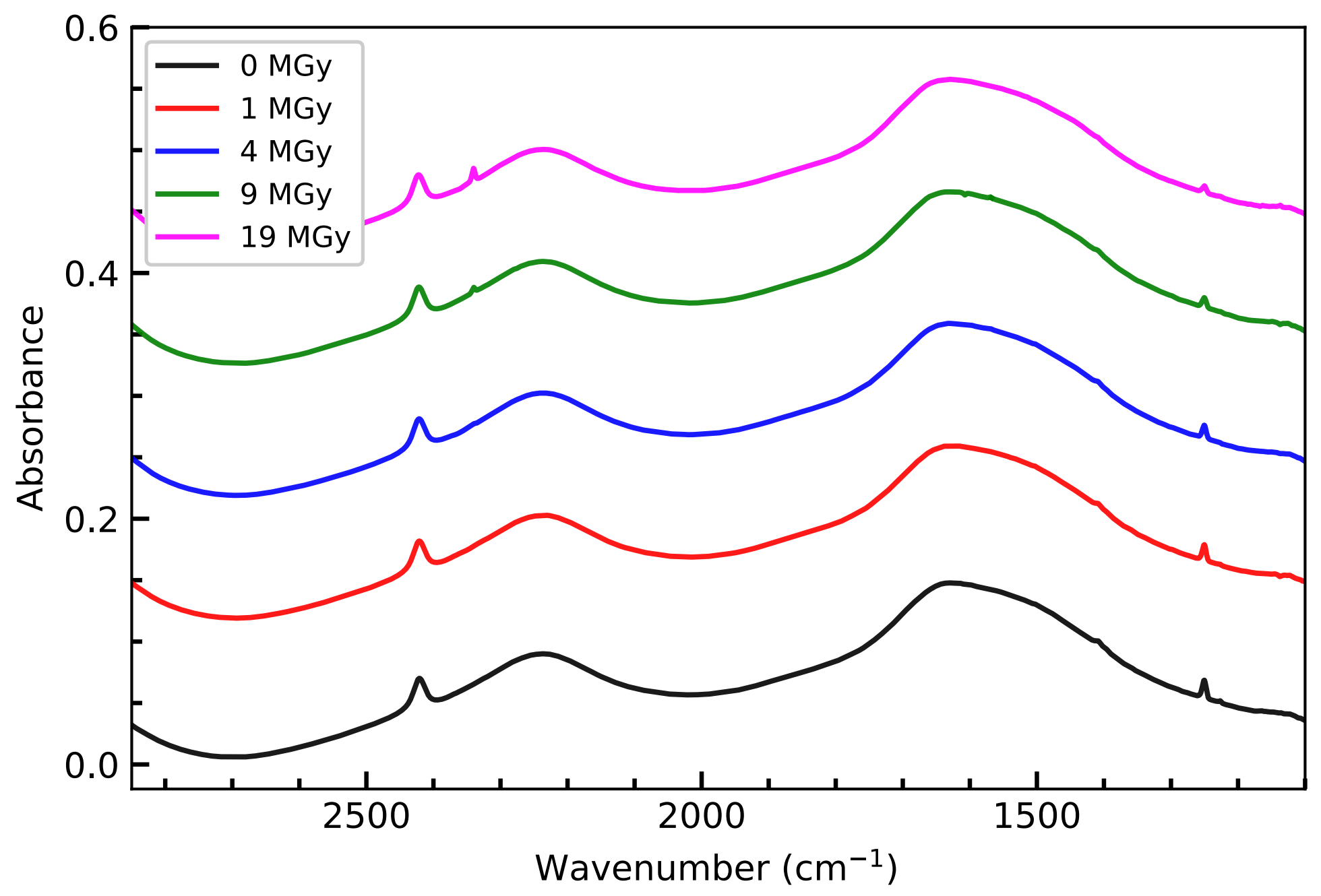


Fig. 4: IR spectra (2400 – 1100 cm^{-1}) of thiophene dilute in water (100:1) at 125 K and incrementally irradiated to 19 MGy. Note that the 2422 cm^{-1} features indicates a minor amount of D_2O contamination. Spectra are offset for clarity.

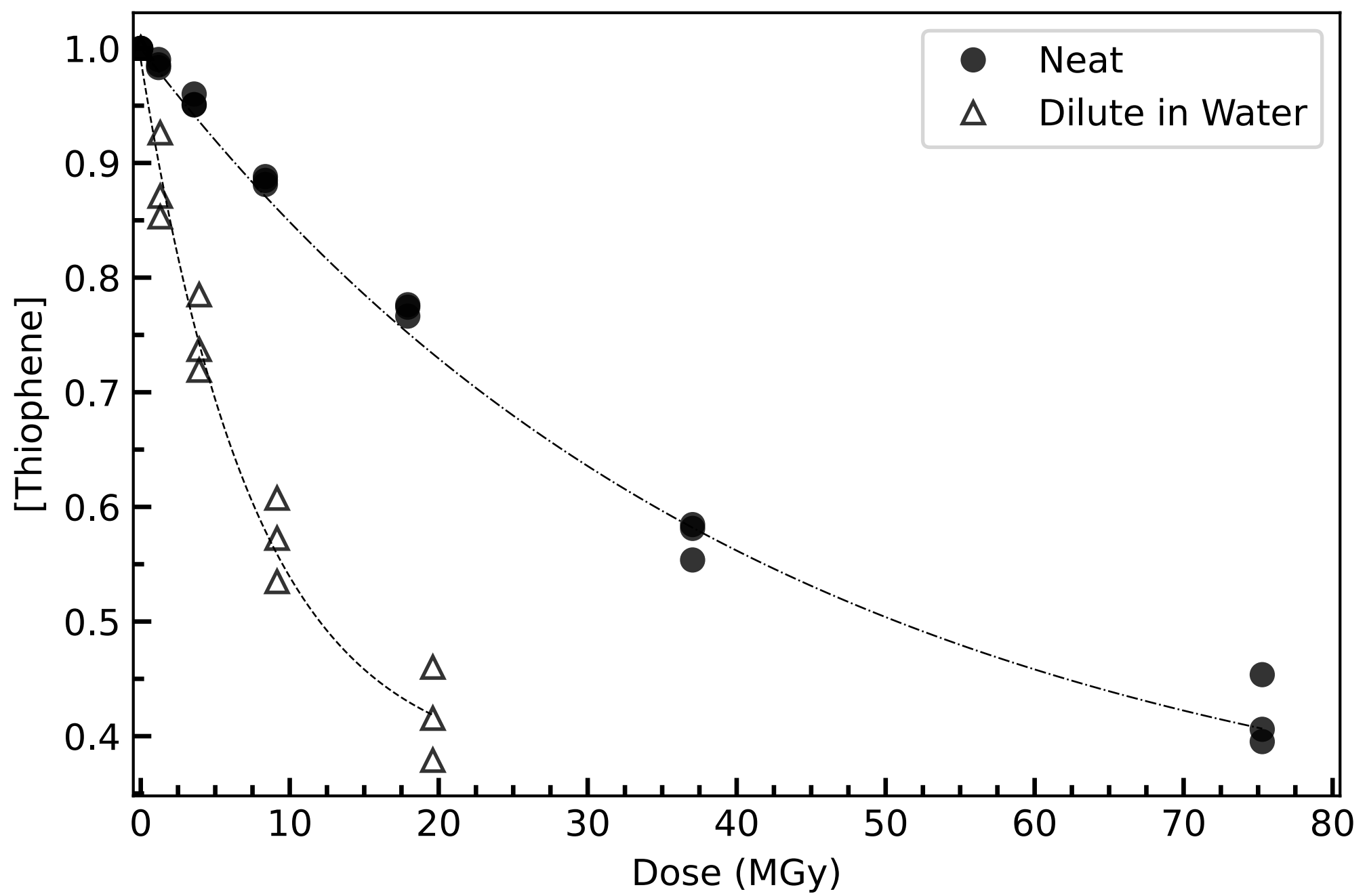
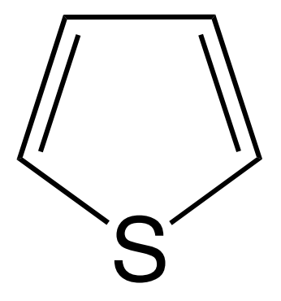
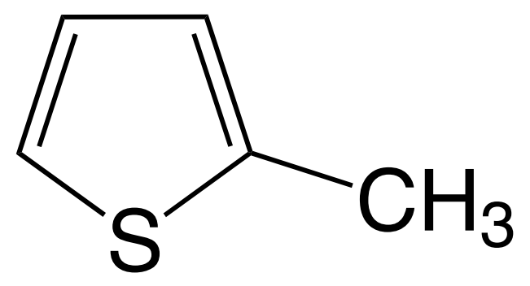
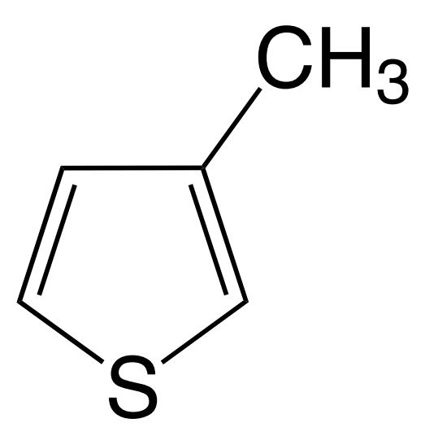


Fig. 5: Normalized thiophene band areas (A/A_0) as a function of dose for neat thiophene (circles) and thiophene dilute in water ice (triangles). Fits correspond to reaction rate constants of 0.017±0.001 and 0.08±0.01 for neat and dilute in water ice, respectively.

Depth	Dose Rate[8]	Thiophene half life (10^9 yr)	
(m)	(mGy yr^{-1})	neat	in H_2O ice
0	76	0.671	0.171
0.1	96	0.531	0.135
1.0	36.4	1.401	0.357
2.0	8.7	5.862	1.494
3.0	1.8	28.33	7.222







References

1. Eigenbrode *et al.*, *Science* **360**, 1096-1101 (2018).
2. Millan *et al.*, *J. Geophys. Res. Planets* **127** (2022).
3. Heinz and Schulze-Makuch, *Astrobio.* **20**, 552-561 (2020).
4. Hudson and Ferrante, *MNRAS*, **492**, 283-293 (2020).
5. Materese, *Astrophys. J.*, **941**, 94 (2022).
6. Materese *et al.*, *Astrobiology*, **20**, 956-963 (2020).
7. Gerakines *et al.*, *Astrobiology, **22***, 233-241 (2022).
8. Hassler *et al.*, *Science*, **343**, 1244797 (2014).
9. Farley *et al.*, *Science*, **343**, 1247166 (2014).

IR Spectra Results

Figure 2, left and right, shows the IR spectra of a neat thiophene ice deposited at 125 K, and incrementally irradiated to a total absorbed dose of 75 MGy (~ 65 eV $molecule^{-1}$). The 1250 cm^{-1} fundamental in-plane C-H bending mode of thiophene decreases with increasing dose, indicating decomposition. Product bands emerge at 1514, 3067, 3225, and 3267 cm^{-1}. These features likely correspond to the production of poly-bithiophenes and open ring products containing an alkyne group.

Figure 3 shows the IR spectra of a neat 2-methlythiophene ice deposited at 125 K, and incrementally irradiated to the same absorbed dose. In addition to the radiolytic products present in irradiated thiophene, several features shift, broaden, and increase until the dose reaches between 18 and 37 MGy, reaching equilibrium and then decreasing at the highest doses studied. The top spectrum (dashed) is pristine 3-methylthiophene ice deposited at 125 K. Comparison of the spectra suggests that the methyl group can undergo radiolytic reversible exchange between the 2 and 3 ring position, and removal resulting in thiophene, in addition to the products observed in neat thiophene.

Figure 4 shows the IR spectra of thiophene dilute in water ice (100:1) deposited at 125 K, and incrementally irradiated to a total dose of 19 MGy (~ 3.3 eV $molecule^{-1}$). Neutral radicals and free electrons produced from the H_2O matrix dominate the chemistry, producing observable amounts of only CO_2.

Analysis and Implications

Figure 5 shows the normalized thiophene band areas as a function of dose with the best fit models, corresponding to reaction rate constants of 0.017 and 0.08 MGy^{-1} for neat and dilute thiophene. Reaction rate constants for all H_2O mixtures are higher than the corresponding neat ices due to the increased number of reaction pathways (H_2O-radiolysis produced neutral radicals, ionized molecules, etc.).[6,7] Thiophene is more stable than either methylthiophene studied, both neat and dilute in water, within measurement uncertainty. Assuming the GCR flux rates at the surface of Mars measured by Curiosity, the radiation half lives of thiophene neat and in water at various depths in the Martian surface are given in Table 1.[8] The half life of neat thiophene (most similar to the solid macromolecular thiophene moieties detected on Mars) is significantly longer than the approximate surface exposure time of the floor of Gale crater (80 Myr).[9] Any thiophene produced (biotic or abiotic) when Mars was most likely wet would not decompose radiolytically, requiring no replenishing source.