Electronic supplementary information (ESI)

for

UNTANGLING THE METHANE CHEMISTRY IN INTERSTELLAR AND SOLAR SYSTEM ICES TOWARD IONIZING RADIATION: A COMBINED INFRARED AND REFLECTRON TIME-OF-FLIGHT ANALYSIS

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**Deuterium lamp details and broadband dose determination.** The continuous wave vacuum ultraviolet photolysis source consisted of a deuterium lamp coupled to a monochromator and light collimation chamber to supply either broadband or selective photon energies to the methane ice (c.f. Sect. 2 Experimental Details). The flux output of the photolysis source for these two experimental setups of broadband and narrowband output are shown in Figure A1. In order to calculate the dose of the broadband photolysis experiment the VUV absorption cross section of methane ice from 120 to 160 nm (10.33-7.75 eV) was first used to calculate the penetration depth for each region of the VUV output from the deuterium lamp in increments of 0.3 eV from 7.75 to 10.33 eV. The absorption cross sections for methane ice at photon energies less than 9 eV are relatively negligible and 95 % of the impinging photon energy was absorbed from photons with energies greater than 9 eV. By determining the contribution of each section of the deuterium lamp output, in the same VUV region as above, to the overall flux a weighted average can then be determined for the penetration depth as well as for the overall dose absorbed by the methane ice.
Figure S1. The photon flux profile of the continuous wave VUV photolysis source coupled to a monochromator and light collimation chamber at high (black) and low (red) resolution from 7.3-11.0 eV using a NIST calibrated photodiode.
Figure S2. Sublimation profiles recorded during temperature programed desorption via the RGA for ethane (C$_2$H$_6$/C$_2$D$_6$), propane (C$_3$H$_8$/C$_3$D$_8$), the C$_3$H$_7^+$ fragment, and butane (C$_4$H$_{10}$/C$_4$D$_{10}$) from the electron irradiation (first and second columns), Lyman α photolysis (third column), and broadband photolysis (fourth column).
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Figure S9. Overlay of TPD profiles after electron irradiation of products from methane (CH\textsubscript{4}; black) and D4-methane (CD\textsubscript{4}; green) ices with prospective $^{13}$C isotopologues (red and yellow, respectively).
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