

**Chem, Volume 6**

**Supplemental Information**

**Interstellar Formation of Biorelevant**

**Pyruvic Acid (CH<sub>3</sub>COCOOH)**

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## Supplementary Information

### Methods

#### *Materials and Experimental Setup*

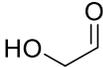
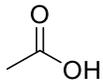
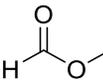
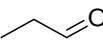
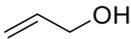
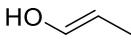
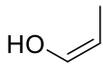
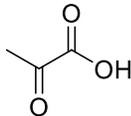
A detailed description of the experimental setup can be found elsewhere.<sup>1</sup> Briefly, the experiments were conducted in a hydrocarbon-contamination-free stainless steel ultrahigh-vacuum chamber pumped down to  $10^{-11}$  Torr. This low pressure ensures that during the typical duration of an experiment of 12 h, less than one monolayer of residual gas condenses on the sample. Two different ice mixtures were prepared on a silver mirror cooled down to 5 K by simultaneously supplying acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and either carbon dioxide ( $\text{CO}_2$ ) or isotopically labeled carbon dioxide- $^{18}\text{O}_2$  ( $\text{C}^{18}\text{O}_2$ ) at partial pressures of  $1.5 \times 10^{-8}$  Torr each to achieve a 1:1 mixture. The thicknesses of the deposited ices were determined to be  $800 \pm 100$  nm by interferometry measurements with a helium-neon laser.<sup>2</sup> This thickness ensures that no electrons are transmitted through the ice to the silver mirror. After deposition, the ices were irradiated with 5 keV electrons for 30 min at an average current of 40 nA. According to Monte Carlo simulations performed with CASINO,<sup>3</sup> this corresponds to a dose of  $4.4 \pm 0.7$  eV molecule<sup>-1</sup>, equivalent to  $(4 \pm 2) \times 10^7$  years of exposure to galactic cosmic rays inside a typical molecular cloud.<sup>4</sup> After deposition and during irradiation, IR spectra were recorded with a Fourier Transform Infrared Spectrometer (Nicolet 6700) for *in situ* detection of new bands corresponding to new molecules formed during the irradiation. After irradiation, temperature programmed desorption (TPD) was performed by heating the sample from 5 K to 320 K at a defined rate of  $0.5 \text{ K min}^{-1}$ . Molecules subliming into the gas phase during the TPD were detected using single photon photoionization reflectron time of flight mass spectrometry (PI-ReToF-MS). In contrast to electron impact ionization, photoionization is essentially fragmentation free, facilitating the assignment of the measured mass-to-charge ratio to a particular molecule. By tuning the photon energy, different isomers at a given mass-to-charge ratio could be distinguished based on their ionization energy. To achieve this, pulsed coherent vacuum ultraviolet (VUV) radiation was generated at a repetition rate of 30 Hz exploiting (non)resonant four-wave-mixing. Three different photon energies were produced for these experiments to identify pyruvic acid and 2-hydroxyacrylic acid based on their computed adiabatic ionization energies (Table S2). To produce 10.49 eV photons, the output of a Nd:YAG Laser was frequency tripled by nonresonant four-wave-mixing using xenon as nonlinear medium. Photon energies of 9.75 eV and 9.20 eV were produced by resonant four-wave-mixing of the outputs of two tunable dye lasers in krypton gas and xenon gas, respectively.<sup>1</sup>

The experiments reported here were performed to simulate the interaction of GCRs with interstellar ices inside molecular clouds. As GCRs are mainly protons and helium nuclei that span a broad range of high energies – from several MeV up to the PeV range – their direct interaction with interstellar ices cannot be studied directly in experiments performed on interstellar analog ices in laboratories. However, it is established that the primary channel for energy deposition of GCRs in interstellar ices is ionization of the molecules. Consequently, the high energy electrons released can generate a cascade of secondary electrons with kinetic energies ranging from a few eV to a few keV depending on the energy of the GCR particle.<sup>5-6</sup> The linear energy transfer of the electron kinetic energies of 5 keV used in the present experiment is similar to that of 10–20 MeV GCRs.

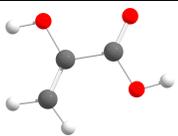
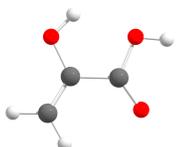
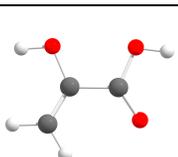
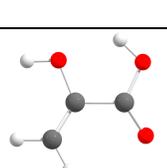
**Table S1.** Infrared absorption peaks before and after irradiation for acetaldehyde (CH<sub>3</sub>CHO) + carbon dioxide (CO<sub>2</sub>)/<sup>18</sup>O-carbon dioxide (C<sup>18</sup>O<sub>2</sub>) ices<sup>a</sup>

Pristine ice, before irradiation (5 K)		
Assignment	Position with <sup>16</sup> O (cm <sup>-1</sup> )	Position with <sup>18</sup> O (cm <sup>-1</sup> )
CH <sub>3</sub> CHO (ν <sub>1</sub> )	3006	3006
CH <sub>3</sub> CHO (ν <sub>2</sub> )	2920, 2860	2920, 2860
CH <sub>3</sub> CHO (ν <sub>3</sub> )	2762	2762
CH <sub>3</sub> CHO (ν <sub>4</sub> )	1718	1718
CH <sub>3</sub> CHO (ν <sub>5</sub> )	1429	1429
CH <sub>3</sub> CHO (ν <sub>6</sub> )	1404	1404
CH <sub>3</sub> CHO (ν <sub>7</sub> )	1348	1348
CH <sub>3</sub> CHO (ν <sub>8</sub> )	1123	1123
CH <sub>3</sub> CHO (ν <sub>9</sub> )	886	886
CH <sub>3</sub> CHO (ν <sub>11</sub> )	2965	2965
CH <sub>3</sub> CHO (ν <sub>12</sub> )	1429	1429
CH <sub>3</sub> CHO (ν <sub>13</sub> )	1123	1123
CH <sub>3</sub> CHO (ν <sub>14</sub> )	774	774
CO <sub>2</sub> (ν <sub>1</sub> )	2336	2300
CO <sub>2</sub> (ν <sub>3</sub> )	665	656
New peaks after irradiation (5 K)		
-CH <sub>2</sub> wagging	954	-
ν <sub>(C-O)</sub>	1052	-
δ <sub>(COH)</sub>	1268	1255
CH <sub>4</sub>	1304	1304
CH <sub>3</sub> CO•	1840	1840
CO	2137	2087
ν <sub>C-H</sub>	2979	2973

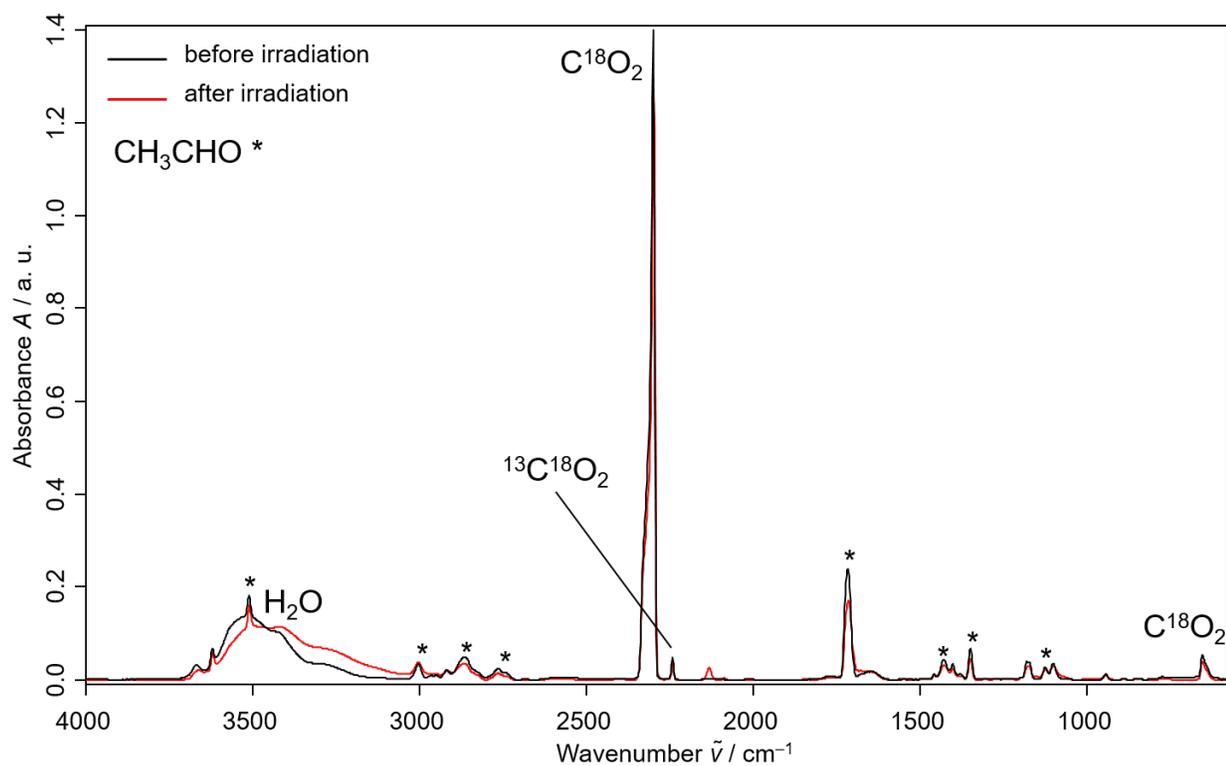
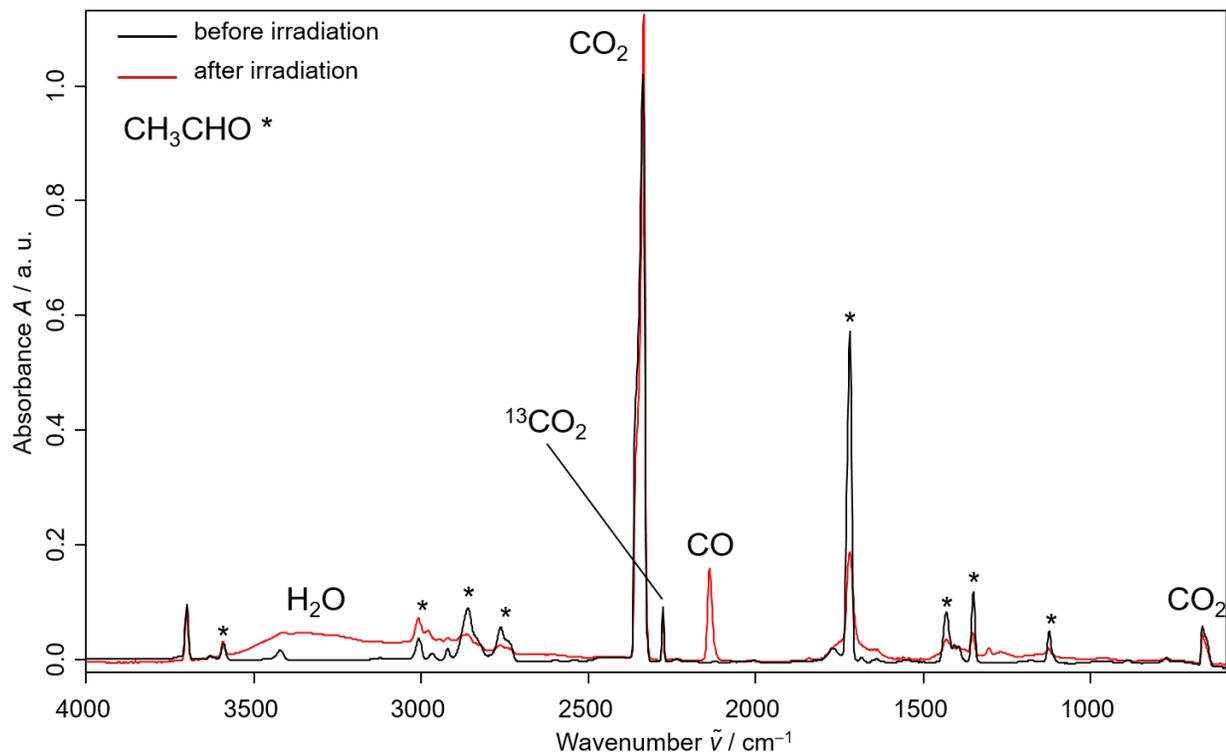
**Table S2.** Computed and measured ionization energies of select organic molecules

Structure	Name	IE <sub>lit</sub> / eV	IE <sub>theor</sub> / eV
	Glycolaldehyde	9.95 ± 0.05 <sup>7</sup>	9.84 – 10.06 (4 conformers)
	Acetic Acid	10.65 ± 0.02 <sup>8</sup>	10.52 – 10.65 (2 conformers)
	Methyl Formate	10.835 <sup>8</sup>	10.68 – 10.83 (2 conformers)
	Acetone	9.703 ± 0.006 <sup>8</sup>	9.71
	Propenal	10.11 ± 0.01 <sup>8</sup>	9.97 – 10.01 (2 conformers)
	Propylene oxide	10.22 ± 0.02 <sup>9</sup>	10.24
	Prop-1-en-2-ol	8.67 ± 0.05 <sup>10</sup>	8.71 – 8.82 (2 conformers)
	2-Propen-1-ol	9.67 ± 0.03 <sup>8</sup>	9.65 – 9.95 (4 conformers)
	(E)-1-Propenol	8.64 ± 0.02 <sup>11</sup>	8.61 – 8.73 (2 conformers)
	(Z)-1-Propenol	8.70 ± 0.03 <sup>11</sup>	8.63 – 8.76 (2 conformers)
	Pyruvic Acid	10.1 ± 0.1 <sup>12</sup>	9.90 – 10.02 (2 conformers)

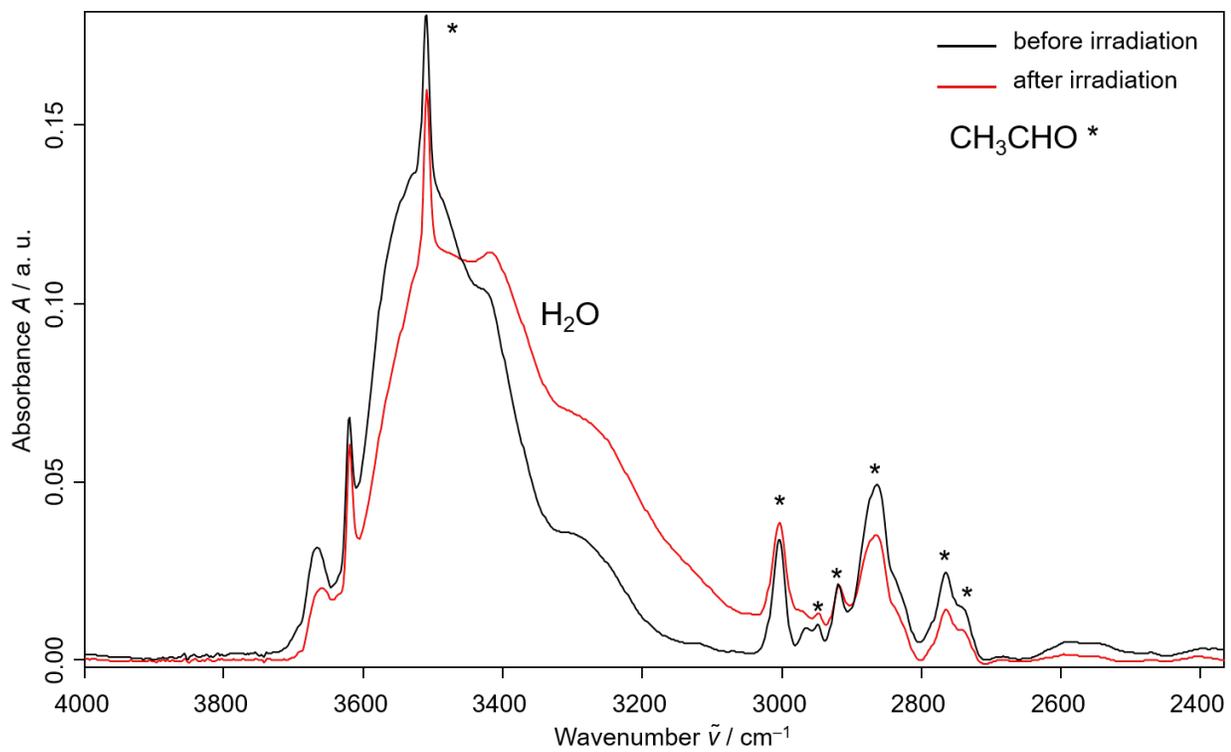
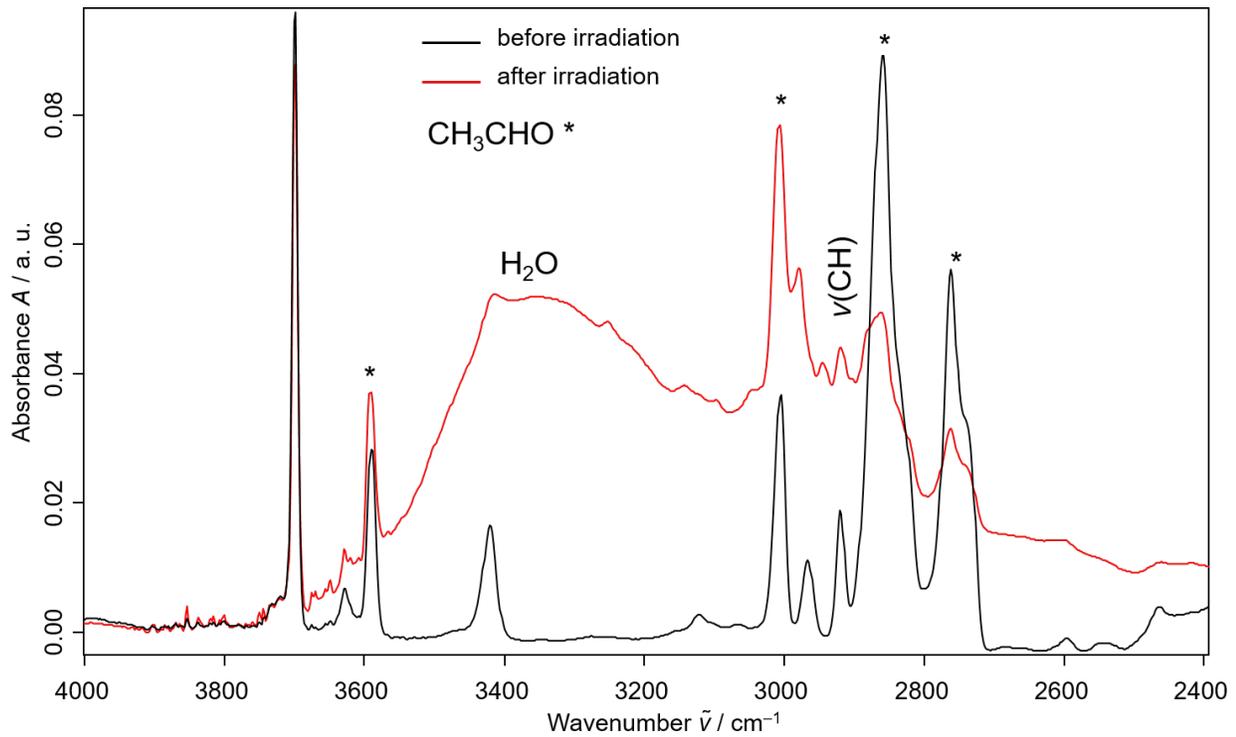
**Table S3.** Computed Adiabatic Ionization Energies (IE) and Relative Energies ( $E_{rel}$ ) of distinct  $C_4H_4O_3$  Isomers at CCSD(T)/CBS//B3LYP/cc-pVTZ + zero point vibrational energy (ZPVE).

Structure	Name	IE (eV) <sup>a</sup>	$E_{rel}$ (kJ mol <sup>-1</sup> ) <sup>b</sup>
	<i>anti</i> -( <i>E</i> )-pyruvic acid	10.02	0.0
	<i>anti</i> -( <i>Z</i> )-pyruvic acid	9.90	10.7
	<i>anti</i> -( <i>Z,E</i> )-2-hydroxyacrylic acid	9.68	45.2
	<i>anti</i> -( <i>Z,Z</i> )-2-hydroxyacrylic acid	9.41	28.4
	<i>anti</i> -( <i>E,Z</i> )-2-hydroxyacrylic acid	9.28	75.9
	<i>anti</i> -( <i>E,E</i> )-2-hydroxyacrylic acid	9.60	71.9
	<i>syn</i> -( <i>Z,Z</i> )-2-hydroxyacrylic acid	9.39	38.5
	<i>syn</i> -( <i>E,Z</i> )-2-hydroxyacrylic acid	9.54	49.1
	<i>syn</i> -( <i>E,E</i> )-2-hydroxyacrylic acid	9.84	48.4

**Notes:** <sup>a</sup>Relative ionization potential by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in eV. Errors are  $\pm 0.05$  eV. <sup>b</sup>Relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in kJ mol<sup>-1</sup>.

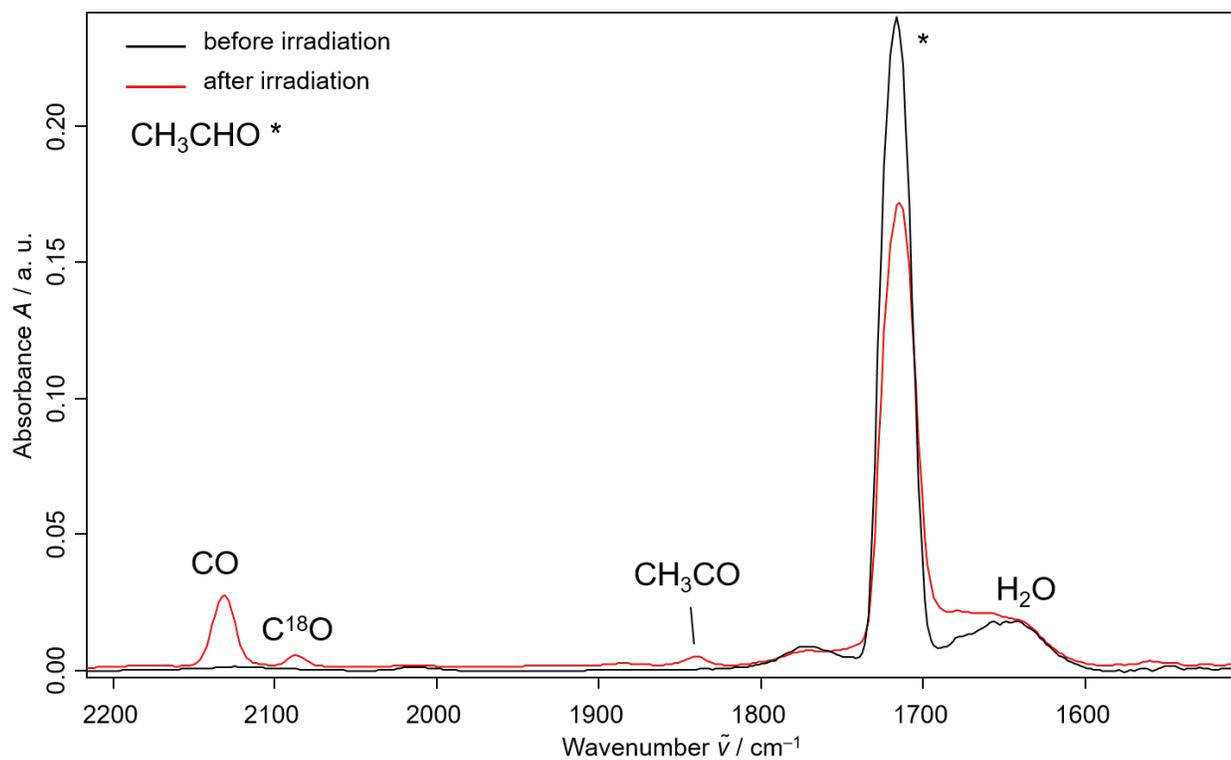
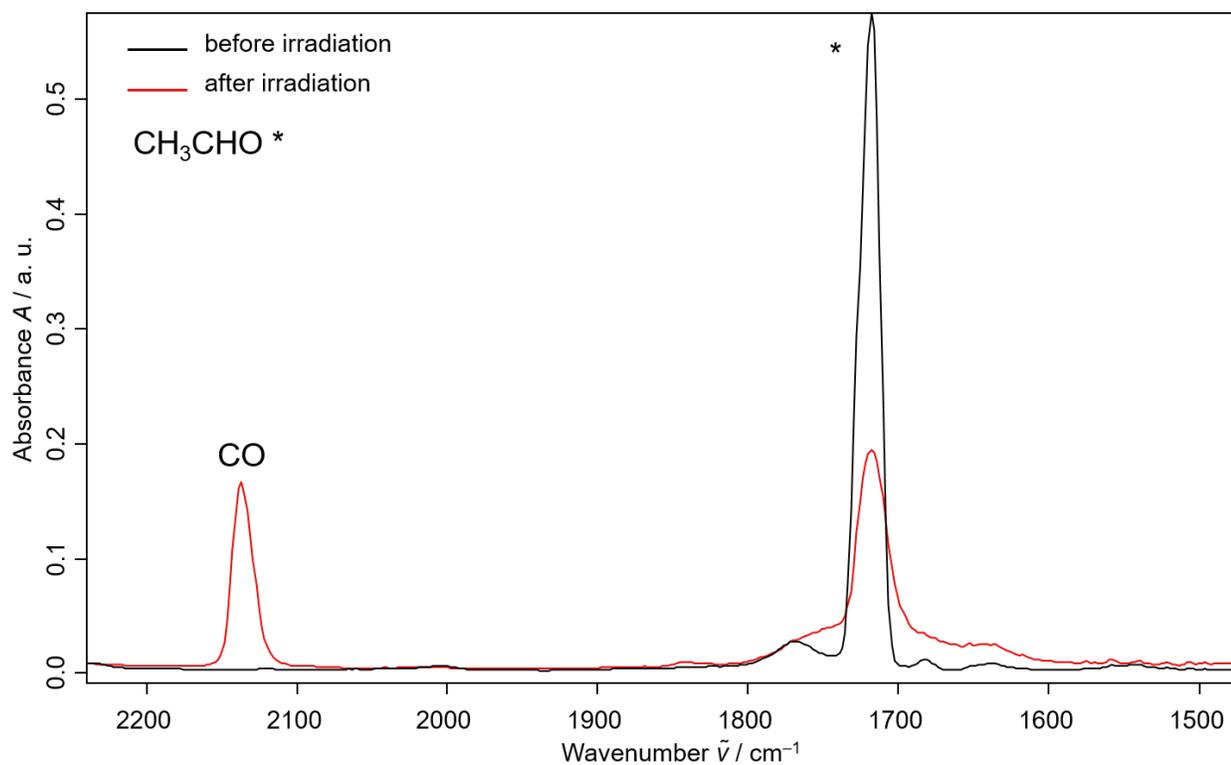


**Figure S1.** FTIR spectra of acetaldehyde + CO<sub>2</sub> ices (top) and acetaldehyde + C<sup>18</sup>O<sub>2</sub> ices (bottom) before and after irradiation.

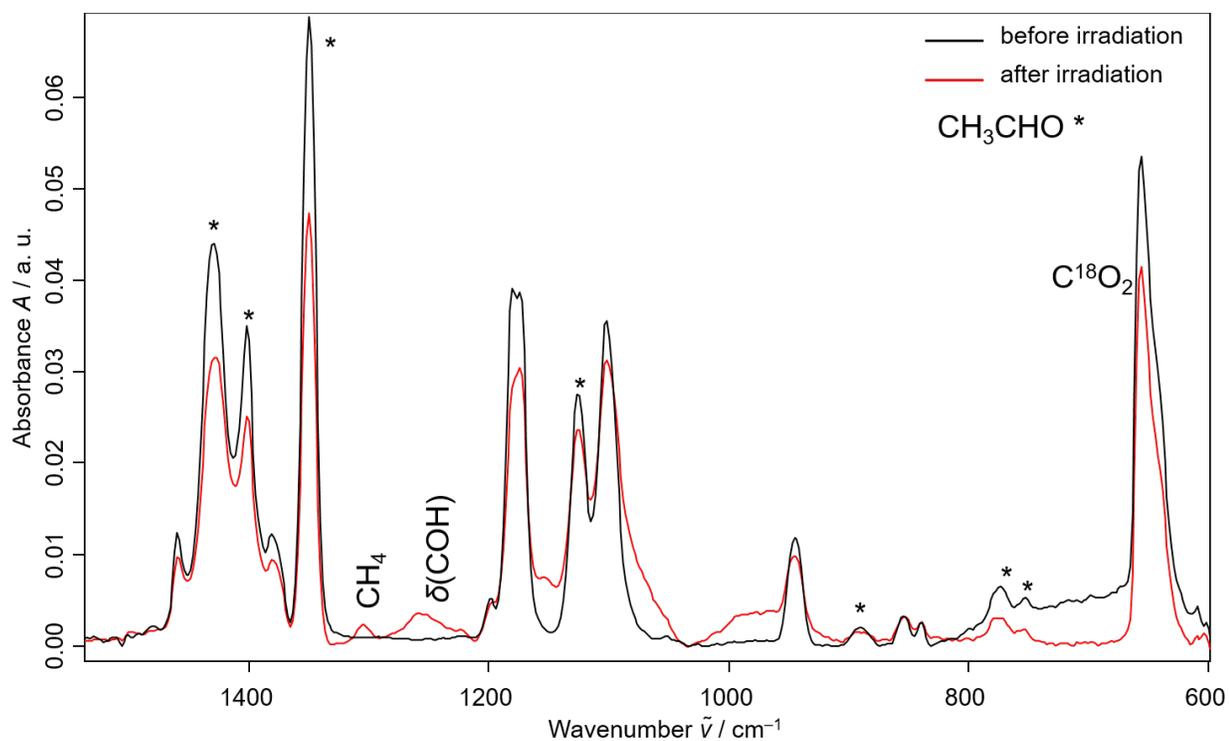
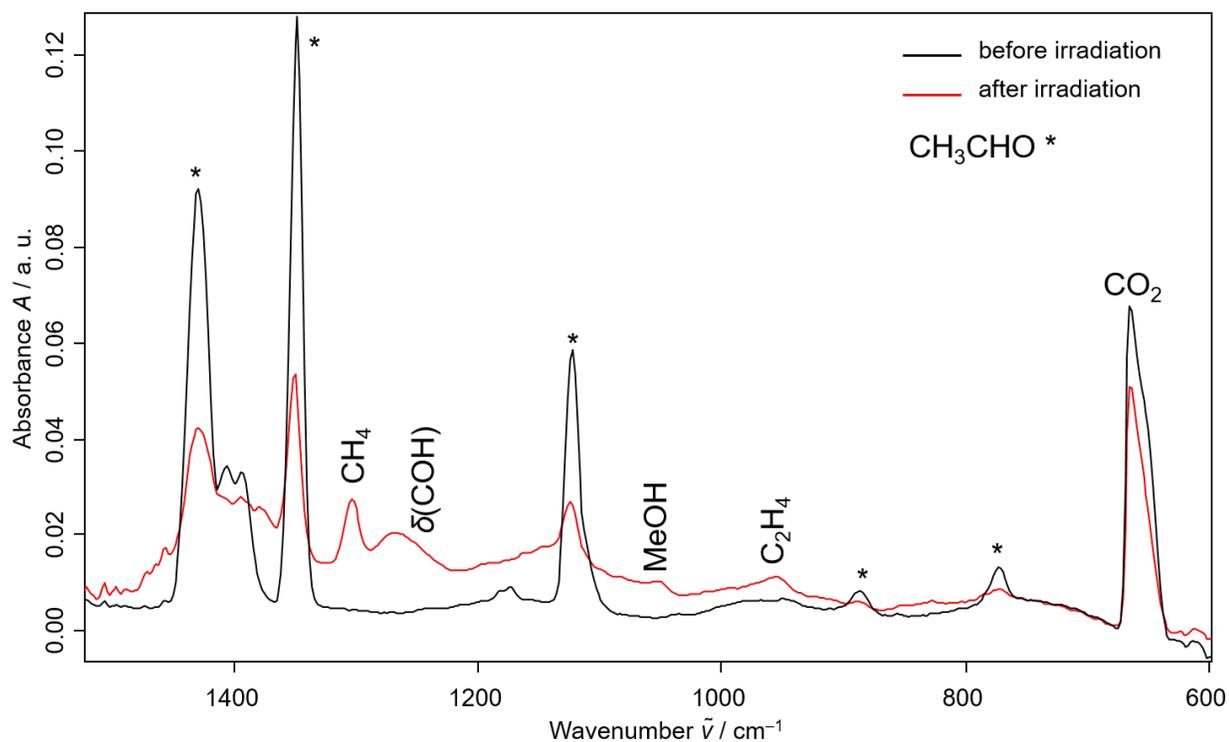


Figure

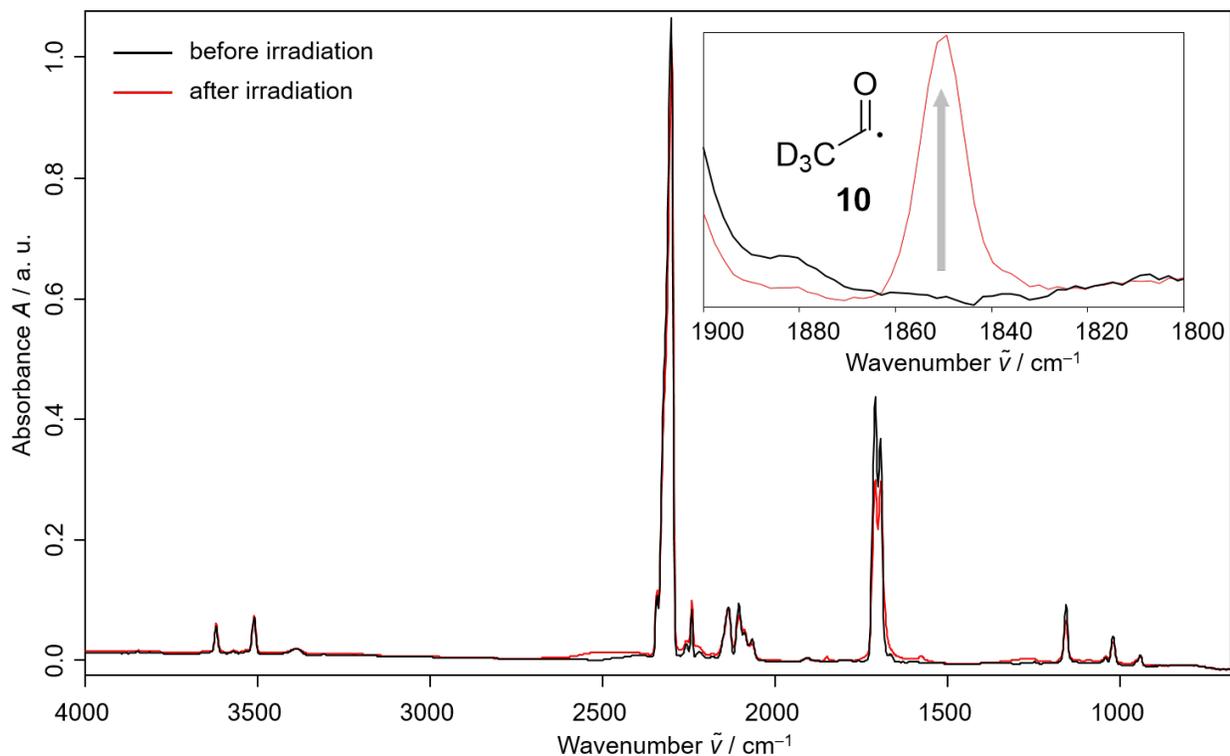
S2. FTIR spectra of the OH-stretching region of acetaldehyde + CO<sub>2</sub> ices (top) and acetaldehyde + C<sup>18</sup>O<sub>2</sub> ices (bottom) before and after irradiation.



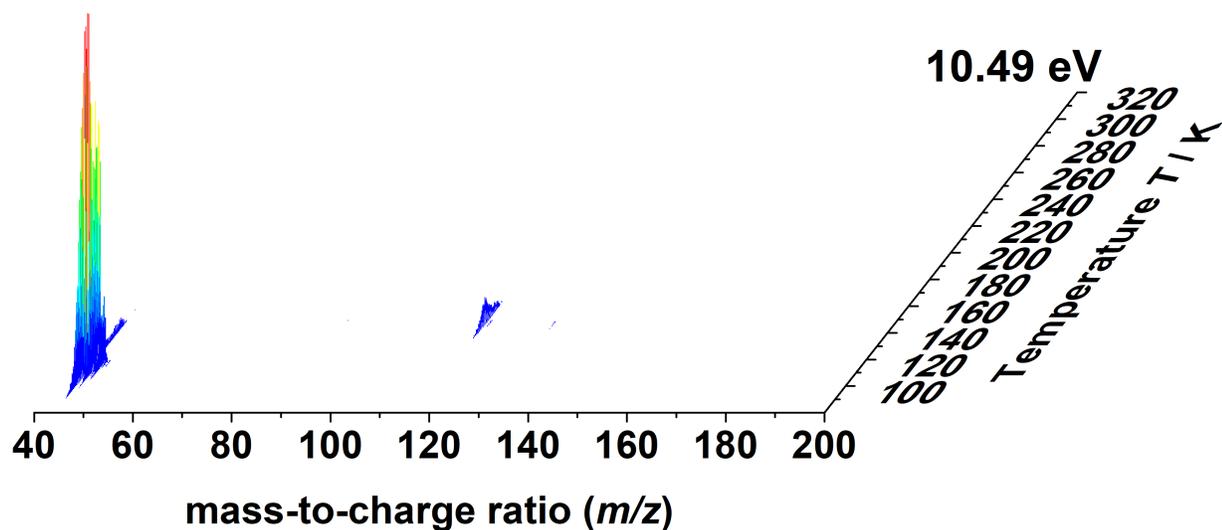
**Figure S3.** FTIR spectra of acetaldehyde + CO<sub>2</sub> ices (top) and acetaldehyde + C<sup>18</sup>O<sub>2</sub> ices (bottom) before and after irradiation showing the formation of carbon monoxide and acetyl.



**Figure S4.** FTIR spectra of acetaldehyde +  $\text{CO}_2$  ices (top) and acetaldehyde +  $\text{C}^{18}\text{O}_2$  ices (bottom) before and after irradiation for energies 600–1500  $\text{cm}^{-1}$ .



**Figure S5.** FTIR spectra of deuterated acetaldehyde ( $\text{CD}_3\text{CDO}$ ) +  $\text{C}^{18}\text{O}_2$  ices before and after irradiation. The signal at  $1850\text{ cm}^{-1}$  can be clearly assigned to deuterated acetyl radical ( $\text{CD}_3\text{CO}\bullet$ ). Formyl radicals ( $\text{DCO}\bullet$ ) cannot be identified and are probably not formed by the irradiation process.



**Figure S6.** Temperature-dependent PI-ReToF-MS spectra of unirradiated acetaldehyde and  $^{18}\text{O}$  isotopically labeled carbon monoxide ( $\text{C}^{18}\text{O}_2$ ) ice recorded at  $10.49\text{ eV}$ .

## References

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