Supporting Information for

**Interstellar Enolization—Acetaldehyde (CH3CHO) and Vinyl**

**Alcohol (H2CCH(OH)) as a Case Study**

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**Table S1.** IR features associated with acetaldehyde in pure acetaldehyde ices.[[1](#_ENREF_1)]

|  |  |  |
| --- | --- | --- |
| Absorption (cm-1) | Assignment | Approximate type of mode |
| 3416 | 24 | overtone |
| 3123 | 4 + 6 | combination |
| 3001 | 1 | as(CH3) |
| 2964 | 11 | (CH3) |
| 2916 | 2 | s(CH3) |
| 2858 | 6 | overtone |
| 2843 | 6 | overtone |
| 2759 | 3 | (CH) |
| 2736 | 3 | (CH) |
| 2598 | 4 + 9 | combination |
| 2466 | 7 + 8 | combination |
| 2234 | 7 + 9 | combination |
| 2003 | 8 + 9 | combination |
| 1769 | 9 | overtone |
| 1726 | 4 | (CO) |
| 1718 | 4 | (CO) |
| 1680 | 4 (CH313CHO) | (13CO) |
| 1641 | 8 + 10 | combination |
| 1546 | 14 | overtone |
| 1430 | 12 / 5 | (CH3) / as(CH3) |
| 1406 |  + 10 | combination |
| 1392 | 6 | (CH) |
| 1347 | 7 | s(CH3) |
| 1123 | 8 | r(CH3) |
| 1107 | 8 (13CH3CHO) | r(13CH3) |
| 886 |  + 15 | combination |
| 772 |  | (CH) |

**Table S2.** IR features associated with solid acetaldehyde-d4 in the acetaldehyde‑d4 ice.[[1](#_ENREF_1)]

|  |  |  |  |
| --- | --- | --- | --- |
| Absorption (cm-1) | Assignment | Approximate type of mode | |
| 3384 | 24 | overtone |
| 2472 | 4 + 9 | combination |
| 2312 | 5 | overtone |
| 2254 | 1 | as(CD3) |
| 2219 | 11 | (CD3) |
| 2180 | 5 | combination |
| 2134 | 2 | s(CD3) |
| 2104 | 2 | s(CD3) |
| 2088 | 2/Fermi resonance) | (CD)/overtone |
| 2076 |
| 2068 |
| 1908 | 5 + 9 | combination |
| 1884 | 8 + 12 | combination |
| 1870 | 8 | overtone |
| 1709 | 4 | (CO) |
| 1693 | 9 | (CO) |
| 1662 | 4 (CD313CDO) | (13CO) |
| 1597 | 5 + 10 | combination |
| 1157 | 5 | (CC) |
| 1042 | 12 | (CD3) |
| 1021 |  | as(CD3) |
| 952 | 13 |  (CD) |
| 941 | 8 | s(CD3) |

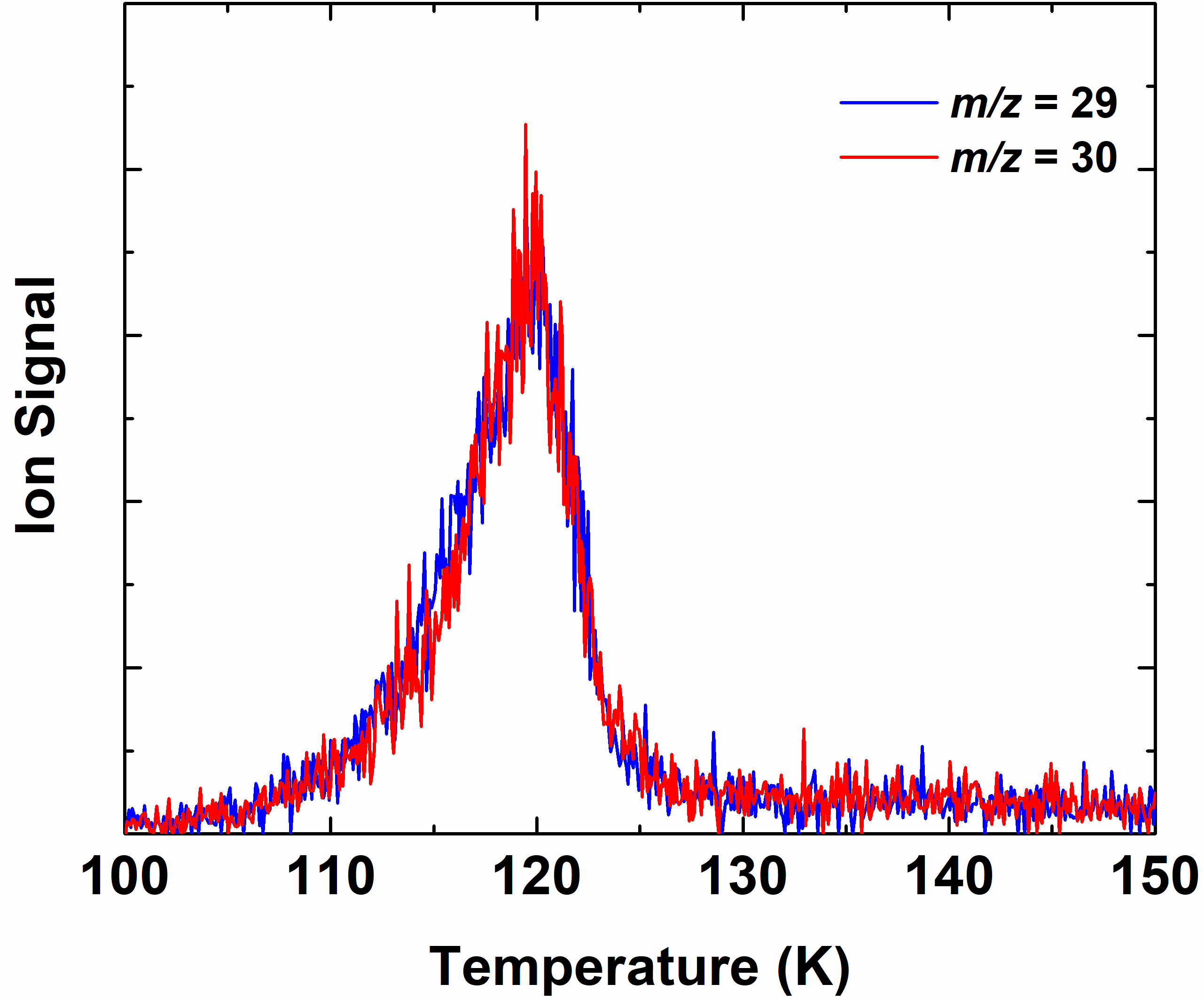
**Table S3.** Detected mass-to-charge ratios in the irradiated ice and tentative assignment of molecules.

|  |  |  |  |
| --- | --- | --- | --- |
| Mass-to-charge ratio | |  |  |
| CH3CHO | CD3CDO | Formula | Assignment |
| 42 | 44 | C2H2O | Ketene |
| 44 | 48 | C2H4O | Vinyl alcohol |
| 45 | 50 | C2H5O+ | Protonated acetaldehyde |
| 58 | 64 | C3H6O | Acetone |
| 70 | 76 | C4H6O | ? |
| 72 | 80 | C4H8O | ? |
| 86 | 92 | C4H6O2 | 2,3-Butanedione |
| 88 | 96 | C4H8O2 | (CH3CHO)2 |
| 89 | 98 | C4H9O2 | (CH3CHO)H(CH3CHO) |
| 101 | 110 | C5H9O2 | (CH3CHCO)H(CH3CHO) |
| 117\* | 126\* | C5H9O3 | (CH3COCHO)H(CH3CHO) |
| 131 | 142 | C6H11O3 | (CH3COCOCH3)H(CH3CHO) |
| 132 | 144 | C6H12O3 | (CH3CHO)3 |
| 133 | 146 | C6H13O3 | (CH3CHO)3H |
| 145 | 158 | C7H13O3 | (CH3CHCO)H(CH3CHO)2 |
| 149 | 162 | C6H13O4 | (CH­3COOH)H(CH3CHO)2 |
| 159 | 174 | C8H15O3 | (CH3COCOCH3)H(C4H8O) |
| 176 | 192 | C8H16O4 | (CH3CHO)4 |
| 177 | 194 | C8H17O4 | (CH3CHO)4H |

Notes: \* also detected in unirradiated acetaldehyde ices

**Table S4.** Relative signals of vinyl alcohol isotopologues expected assuming only ketene hydrogenation as formation pathway compared to relative signals detected.

|  |  |  |  |
| --- | --- | --- | --- |
| m/z | Molecular formula | Relative signal  detected | Relative  signal  expected |
| 44 | C2H4O | 1 | 1 |
| 45 | C2H3DO | 0.83 ± 0.05 | 2.05 |
| 46 | C2H2D2O | 0.34 ± 0.03 | 1.47 |
| 47 | C2HD3O | 0.57 ± 0.04 | 0.77 |
| 48 | C2D4O | 0.45 ± 0.03 | 0.36 |

 **Figure S1.** QMS signal of the HCO+ (*m/z* =29, blue line) and DCO+ (*m/z* = 30, red line) fragments of CH3CHO and CD3CDO, respectively.

**References**

[1] H. Hollenstein, H. H. Günthard, *Spectrochim Acta A* **1971**, *27*, 2027-2060.