Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for

Radiation-induced transformations of acetaldehyde molecules at cryogenic temperatures: a matrix isolation study

Pavel V. Zasimov, Elizaveta V. Sanochkina, and Vladimir I. Feldman*

Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia

*Corresponding author, e-mail: feldman@rad.chem.msu.ru (V.F.)

Table S1 Main absorption maxima (cm^{-1}) of the CH_3CHO and CD_3CDO isolated molecules absorption bands in solid noble gas matrices. The gas-phase values may be found elsewhere.[S1] Tentative assignments are in italic.

Assignment	Ne	Ar	Kr	Xe	Gas phase
			CH_3CHO		
$2\nu_4$	*3481.5*	3463.3	*3462.4*	*3452.0*	3480
$\nu_1(CH_3\ _{d\text{-}str})$	3028.6	3022.8	3018.6	3006.6	3014
	3016.9		3013.2		
$\nu_{11}(CH_3\ _{d\text{-}str})$	2982.8	2961.8	2967.9	2959.4	2968
	2964.8		2952.9	2956.3	2964
$\nu_2(CH_3\ _{s\text{-}str})$	*2938.6*	2921.8	*2923.5*	*2912.1*	2923
	2935.9		*2913.5*		
	2926.4				
	2922.0				
$2\nu_6$	2832.6	2840.6	2833.9	2823.7	2830
				2821.3	
$\nu_5+\nu_6$	2816.7	2817.0	2814.1	2804.5	2809
			2811.2		
$\nu_5+\nu_7/\nu_7+\nu_{12}$	2753.5	2751.1	2751.0	*2743.1*	–
			2745.7	*2731.2*	
$\nu_3(C–H\ _{str})$	2728.3	2736.2	2730.2	2716.6	2716
	2719.8		2724.8	2713.7	
	2716.3				
$2\nu_9$	1758.8	1748.5	*1774.1*	1762.0	–
$\nu_4(CO\ _{str})$	1738.1	1727.2	1740.8	1735.6	1743
			1732.6		
			1724.1		
$\nu_5(CH_3\ _{d\text{-}deform})$	1437.3	1431.6	1428.7	1423.6	1441
	1433.9	1427.0	1424.1		
	1431.2sh				
$\nu_6(C–H\ _{bend})$	1399.4	1398.9	*1404.0*	*1398.0*	1395
			1394.8	*1384.2*	
$\nu_7(CH_3\ _{s\text{-}deform})$	1356.7sh	1354.1	1349.6	1345.5	1352
	1353.7	1348.8	1346.4		
	1349.0	1345.9			
$\nu_8(C–C\ _{str})$	1118.7	1111.3	1118.8	1116.1	1114
	1114.9		1112.7		
			1109.9		
$\nu_9(CH_3\ _{rock})$	876.4	871.3	887.9	882.2	867
	873.6sh				
$\nu_{14}(C–H\ _{bend})$	767.4	772.4	771.3	765.7	764
			769.4		
$\nu_{10}(CCO\ _{deform})$	513.0sh	509.9sh	516.9	515.5	509
	509.5	505.9	515.0	512.6	
			510.5	508.6sh	
			505.4		

			CD_3CDO		
$2\nu_4$	3453.8	3436.1	3446.2	3436.8	3457
$\nu_1(CD_{3\ d\text{-}str})$	2273.1	2267.3	*2265.4sh*	2257.1	2262
	2270.8		2263.1		
	2265.3		2260.5		
$\nu_{11}(CD_{3\ d\text{-}str})$	2234.3	2219.4	2223.9	2215.3	2223
	2206.7		2213.4		
			2207.9		
$\nu_6+\nu_{12}$	–	–	*2195.0*	*2200.8*	–
$\nu_2(CD_{3\ s\text{-}str})$	2131.7	2127.6	2129.9sh	2118.6	2125
	2129.0		2125.5		
	2124.4sh		2122.3		
$2\nu_{12}$	2099.4	*2104.9*	*2100.4*	*2086.6*	–
		2099.0	*2094.9*		
		2093.6			
$\nu_6+\nu_8/\nu_6+\nu_{13}$	2085.3	2085.4	*2086.1*	*2073.9*	–
	2081.4	2070.9	*2081.5*	*2069.4*	
			2079.6		
			2076.2		
$\nu_3(C–D_{\ str})$	*2061.8*	2063.3	*2065.2*	2049.3	2054
	2054.7	2053.7	2057.0		
	2047.8				
$\nu_8+\nu_{13}$	1897.1	1895.1	*1907.5*	*1899.2*	–
	1895.3		1895.6	1892.2	
			1892.4		
$\nu_4(CO_{\ str})$	1736.1	1730.0sh	1732.0	1726.9	1735
	1731.5sh	1726.9	1727.9sh	1723.3sh	
	1728.3	1723.3	1725.1	*1715.5*	
	1722.0	1721.3	*1721.1*		
		1719.2	*1716.9*		
$\nu_6(C–D_{\ bend})$	1154.0	1152.3	1157.0	1152.5	1151
	1147.7	1147.9	1150.5	1142.9	
		1143.5	1145.8		
			1140.6		
$\nu_{12}(CD_{3\ d\text{-}deform})$	1049.6	1044.7	1044.8sh	1040.3	1047
	1047.9		1042.6		
	1046.0sh		1037.1		
$\nu_7(CD_{3\ s\text{-}deform})$	1028.7	1024.0	1022.5	1019.3	1029
	1026.8sh				
	1024.7sh				
$\nu_{13}(CD_{3\ rock})$	*950.6*	*947.2*	*948.2*	*947.9*	–
	947.7		*947.9*		
$\nu_8(C–C_{\ str})$	940.6	941.1	941.2	939.2	938
		938.6	937.4	936.8sh	
$\nu_{10}(CCO_{\ deform})$	443.4	440.6	443.5	442.2	436
	436.6	*436.1*	441.4	439.7	
		433.4	436.8	436.2	
			432.8		

sh – shoulder

Table S2 Maxima (cm^{-1}) of the unassigned absorption bands detected in the irradiated CH_3CHO/Ng and CD_3CDO/Ng (Ng = Ne, Ar, Kr, or Xe) samples.

Ne	Ar	Kr	Xe
		CH_3CHO	
2226.0	2223.7	1873.2	849.7
1474.0	2221.9	718.8	
1288.3	2207.9		
1223.2	2201.3		
	1884.7		
		CD_3CDO	
1967.6	1735.1	–	–
1587.3	1166.4		
1417.2			

Table S3 Absorption intensities of the CH_3CHO radiolysis products used in the present work.

Species	Mode	Value, km mol^{-1}	Method	Ref.
CO	CO_{str}	66	Ar matrix isolation	S2
$C_2H_2\cdots H_2O$	$C–H_{str}$	257	MP2/aug-cc-mpVTZ	S3
CH_4	$CH_{3\ d\text{-}deform}$	29	CCSD/aug-cc-pVTZ	S4
H_2CCO and $H_2CCO{-}H_2$	CO_{str}	695	CCSD/aug-cc-pVTZ	S4
$HCCO^{\bullet}$	$CCO_{a\text{-}str}$	760	CCD/cc-pV(T+d)Z	S4
$CH_3^{\bullet}$	OPLA	73	CCSD/aug-cc-pVTZ	S4
CH_2CHOH	Mixed mode	175	CCD/6-31G(2df, p)	S4
$CH_3CO^{\bullet}$	CO_{str}	150	CCD/6-311G*	S4
CCO	$CCO_{a\text{-}str}$	230	CCD=FULL/aug-cc-pVQZ	S4

OPLA – out of plane

Supplementary References

S1. H. Hollenstein and H. H. Günthard, *Spectrochim. Acta A*, 1971, **27**, 10, 2027–2060.

S2. G. J. Jiang, W. B. Person and K. G. Brown, J. Chem. Phys., 1975, **62**, 1201–1211.

S3. D. Tzeli, A. Mavridis, and S. S. Xantheas, J. Chem. Phys., 2000, **112**, 14, 6178–6189.

S4. NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 21, August 2020, Editor: Russell D. Johnson III, http://cccbdb.nist.gov/. DOI:10.18434/T47C7Z.

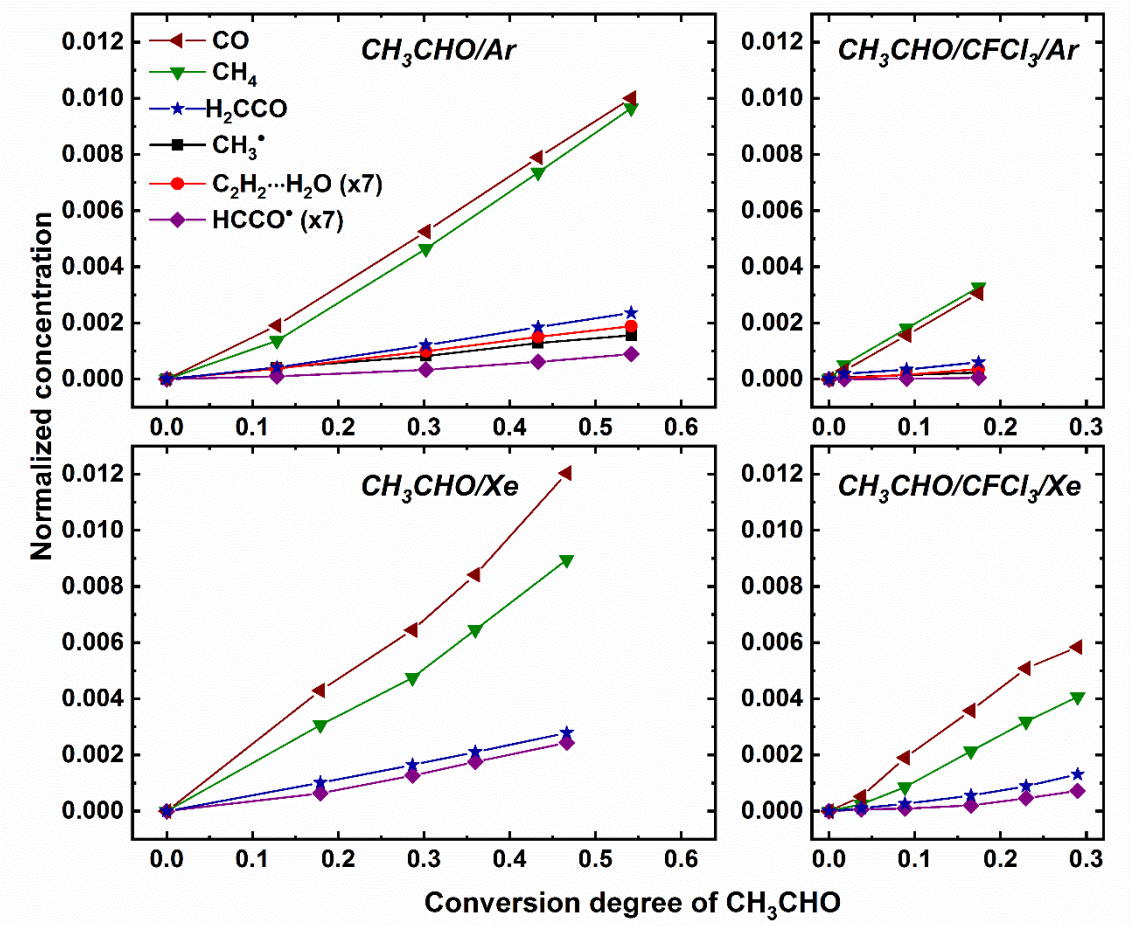

Fig. S1 Build-up profiles of the major CH_3CHO radiolysis products in the $CH_3CHO/CFCl_3/Ng$ (Ng = Ar, Xe) 1:0−2:1000 matrices. Note that the H_2CCO curves represent the total integrated intensity of perturbed and unperturbed ketene signals. All of the absorption band integrals were normalized to an appropriate absorption coefficient (see Table S3 of ESI) and the integrated absorption intensity of the CH_3CHO C–C $_{str}$ absorption band in the corresponding non-irradiated sample.

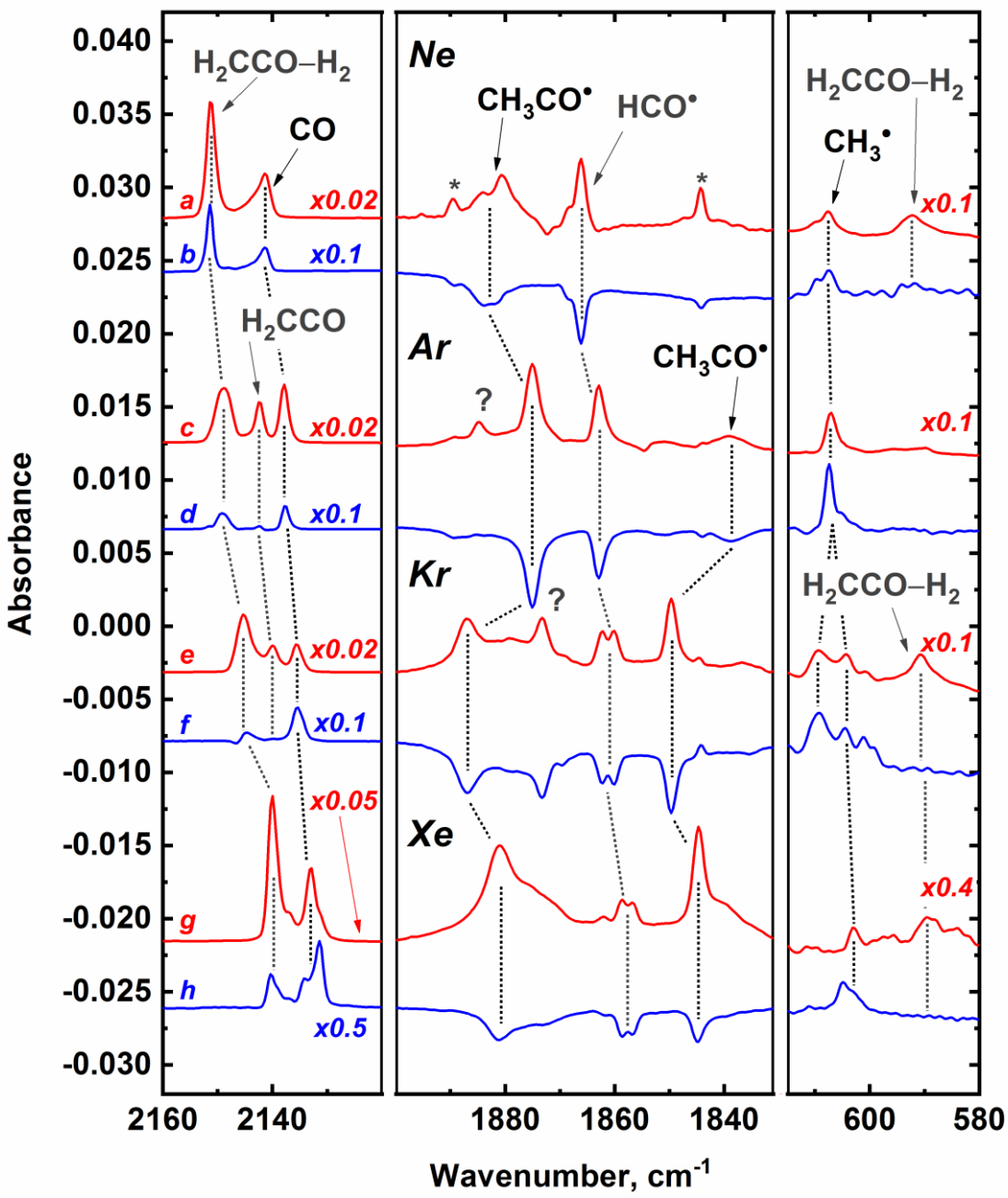

Fig. S2 Difference FTIR spectra of the CH_3CHO/Ng 1:1000 matrices (Ng = Ne, Ar, Kr, and Xe) showing the effect of irradiation with X-rays (a, c, e, and f) and subsequent photolysis with λ_D = 620 nm and λ_D = 520 nm light (b, d, f, and h). The absorbed dose was 110.9, 115.8, 43.7, and 132.0 kGy for Ne, Ar, Kr, and Xe samples, respectively. The λ_D = 620 nm photolysis time was 15, 10, 10, and 10 min for Ne, Ar, Kr, and Xe, respectively. The λ_D = 520 nm photolysis time was 30, 10, 30, and 40 min for Ne, Ar, Kr, and Xe, respectively. Spectra in the left and right panels are scaled for a better representation. Absorptions due to atmospheric water are marked with asterisks. The unassigned absorption bands with maxima at 1884.7 and 1873.2 cm^{-1} are marked with question signs.