Electronic Supplementary Information

Dynamics of the Reaction $CH_2I + O_2$ Probed via Infrared Emission of CO, CO_2, OH, and H_2CO

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Table S1 Comparison of yield and internal energies of CH_2I produced from photolysis of CH_2I_2 at various wavelengths

		$CH_2I_2 \rightarrow CH_2I + I$ [a]		$CH_2I_2 \rightarrow CH_2I + I^*$ [b]		
wavelength /nm	energy /kJ mol^{-1}	yield	E_{INT} /kJ mol^{-1}	yield	E_{INT} /kJ mol^{-1}	Ref.
248	482	0.54	267.8	0.46	177.0	[c]
248	482				151.9	[d]
248	482	0.50	233.5	0.50	149.4	[e]
266	450		202.6		116.7	[e]
280	427		176.6		97.5	[e]
304	394		141.8		90.4	[e]
308	388	0.75		0.25		[c]
355	337	1.00	99.6			[e]

[a] Dissociation energy to form $CH_2I + I$ is $D_0 = 2.155 \pm 0.008$ eV (207.9 ± 0.8 kJ mol^{-1}). [b] Dissociation energy to form $CH_2I + I^*$ is $D_0 = 3.098 \pm 0.008$ eV (298.9 ± 0.8 kJ mol^{-1}). [c] Transient infrared emission of CH_2I. S. L. Baughcum and S. R. Leone, J. Chem. Phys. **72**, 6531 (1980). [d] velocity-mapped ion imaging with 2 + 1 REMPI. J. H. Lehman, H. Li, and M. I. Lester, Chem. Phys. Lett. **590**, 16 (2013). [e] VUV ionization with 2 + 1 REMPI. B. W. Toulson, J. P. Alaniz, J. G. Hill, and C. Murray, Phys. Chem. Chem. Phys. **18**, 11091 (2016).

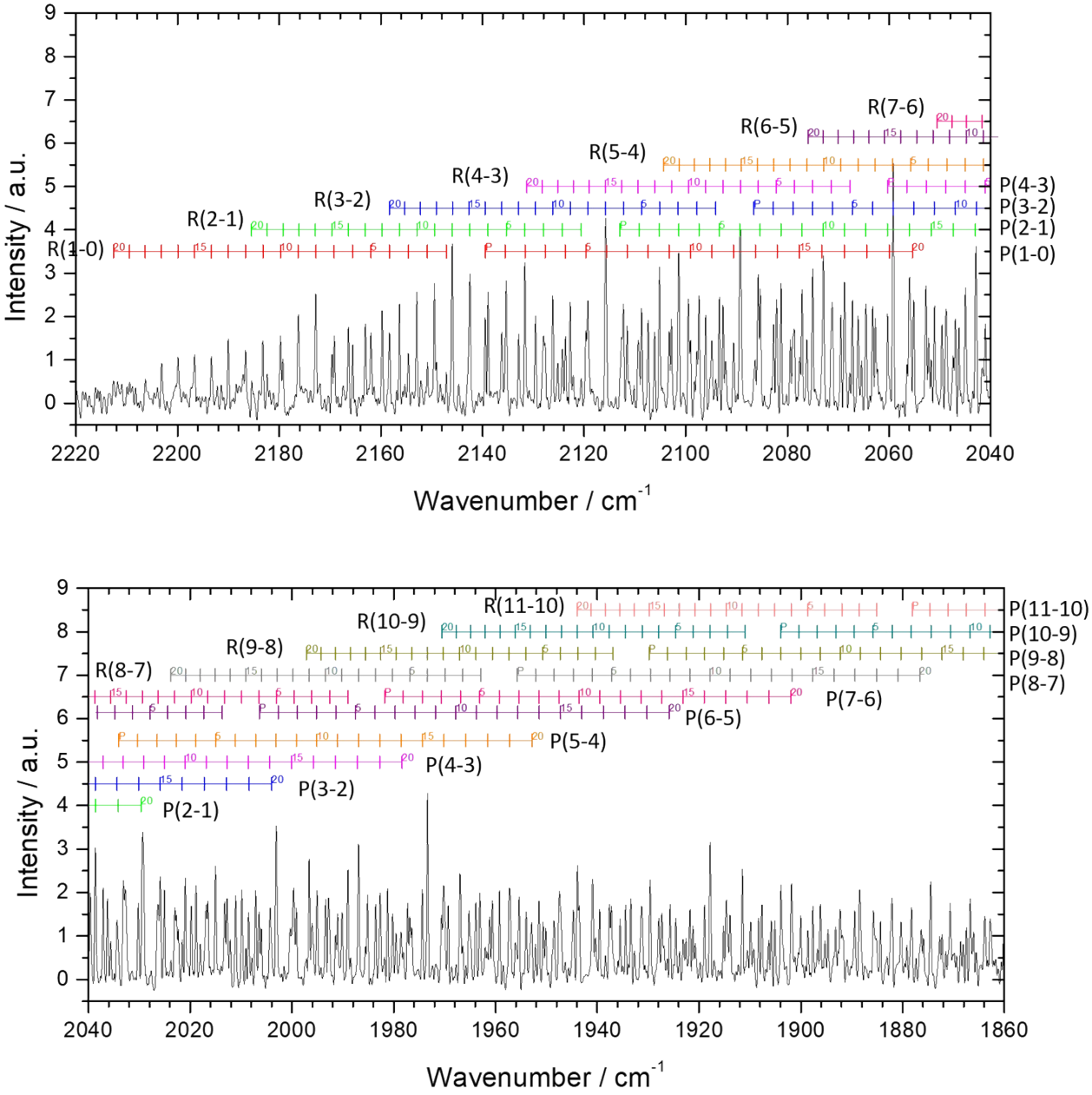

Fig. S1 Assignments of observed IR emission lines of CO recorded 3–4 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 248 nm. The spectral resolution was 0.3 cm^{-1}. The assignments of vibration-rotational transitions are shown as sticks; the numbers correspond to J'; P(v'–v'') and R(v'–v'') represent the vibrational transition v'–v''.

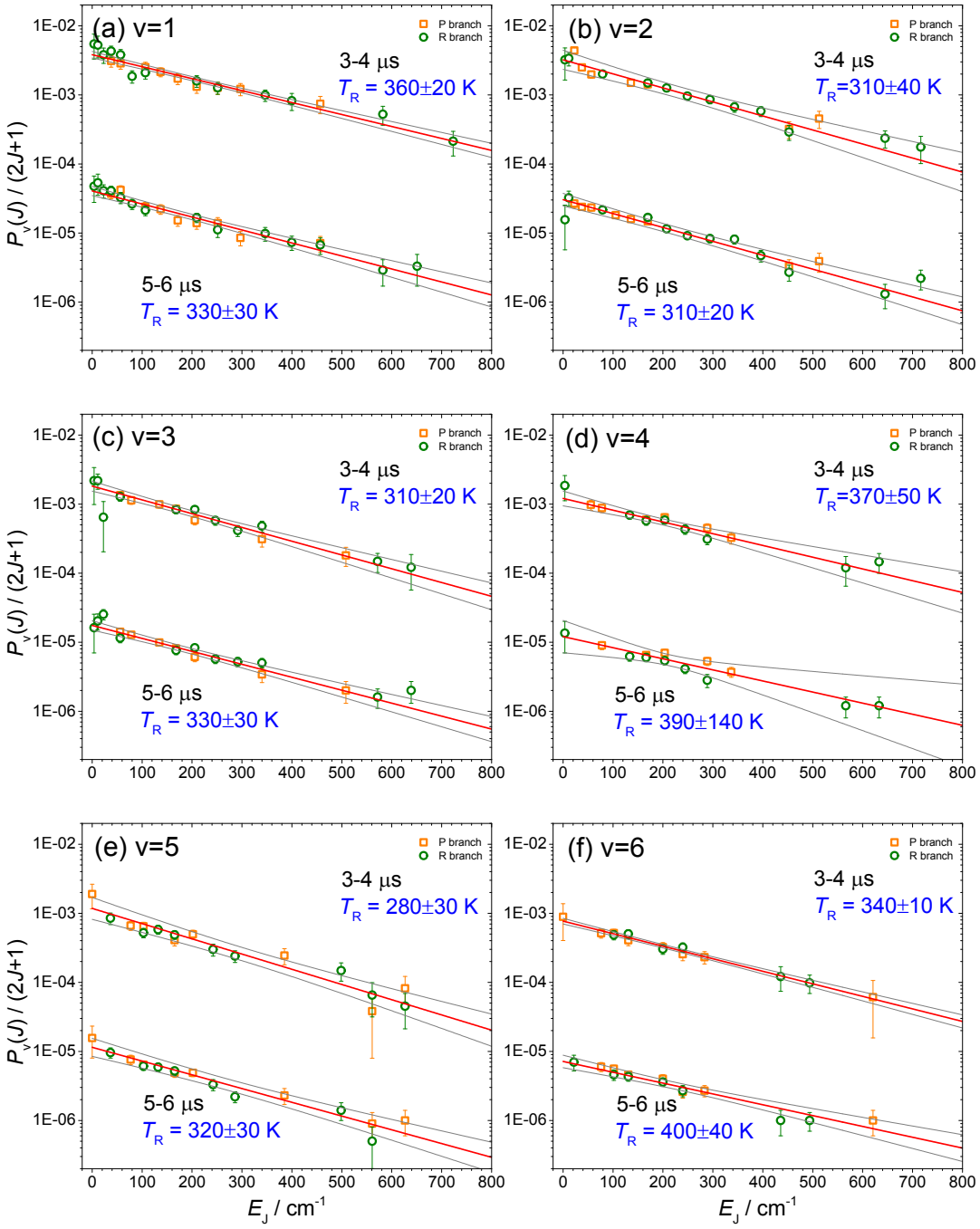

Fig. S2 Semi-logarithmic plots of relative rotational populations of CO (v = 1–6) 3–4 μs and 5–6 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 248 nm (symbols □ for the *P*-branch and ○ for the *R*-branch). Solid lines represent least-square fits; the confidence ranges are also shown.

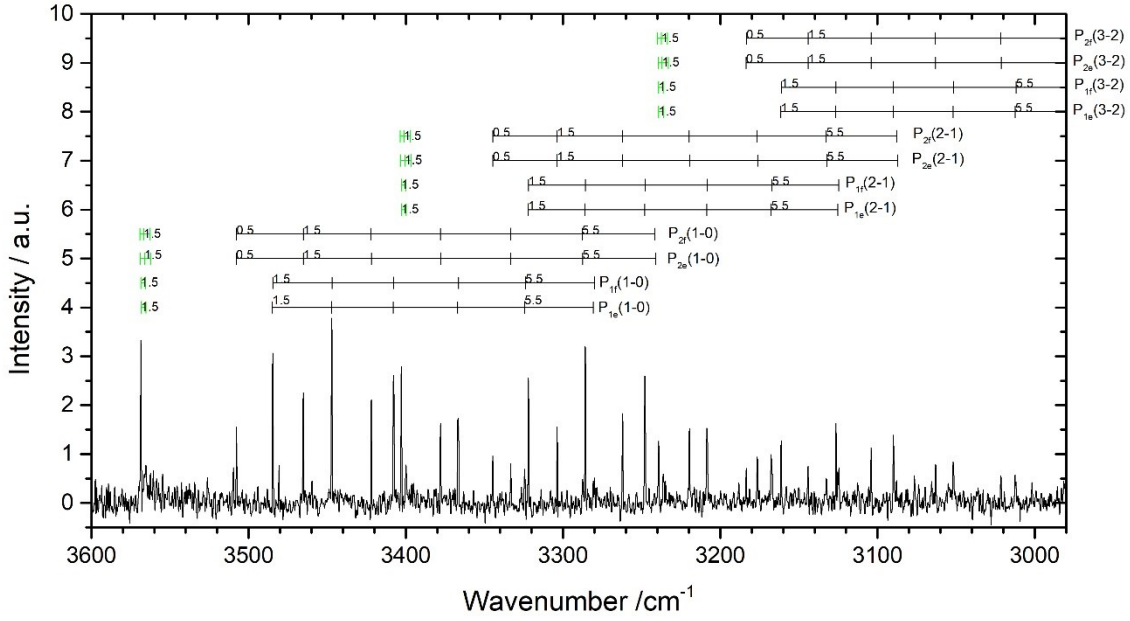

Fig. S3 Assignments of observed IR emission lines of OH produced 3–4 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 248 nm. The spectral resolution was 0.5 cm^{-1}. The assignments of vibration-rotational transitions are shown as sticks; the numbers correspond to J'; P(v'–v'') represents the vibrational transition v'–v''.

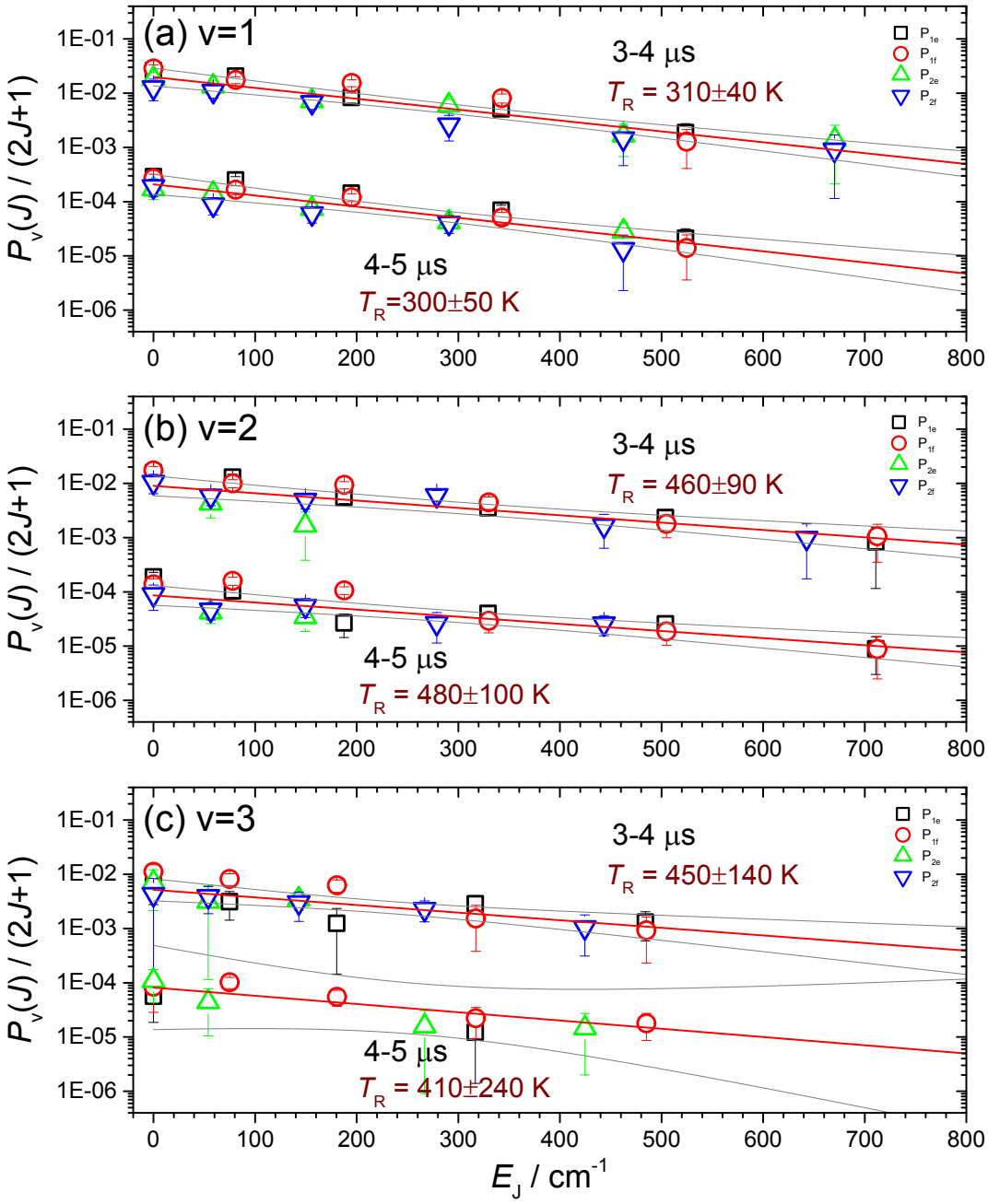

Fig. S4 Semi-logarithmic plots of relative rotational populations of OH (v = 1–3) 3–4 μs and 5–6 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 248 nm (symbols □ for the P_{1e}-branch, ○ for the P_{1f}-branch, △ for the P_{2e}-branch, and ▽ for the P_{2f}-branch). Solid lines represent least-square fits; the confidence ranges are also shown.

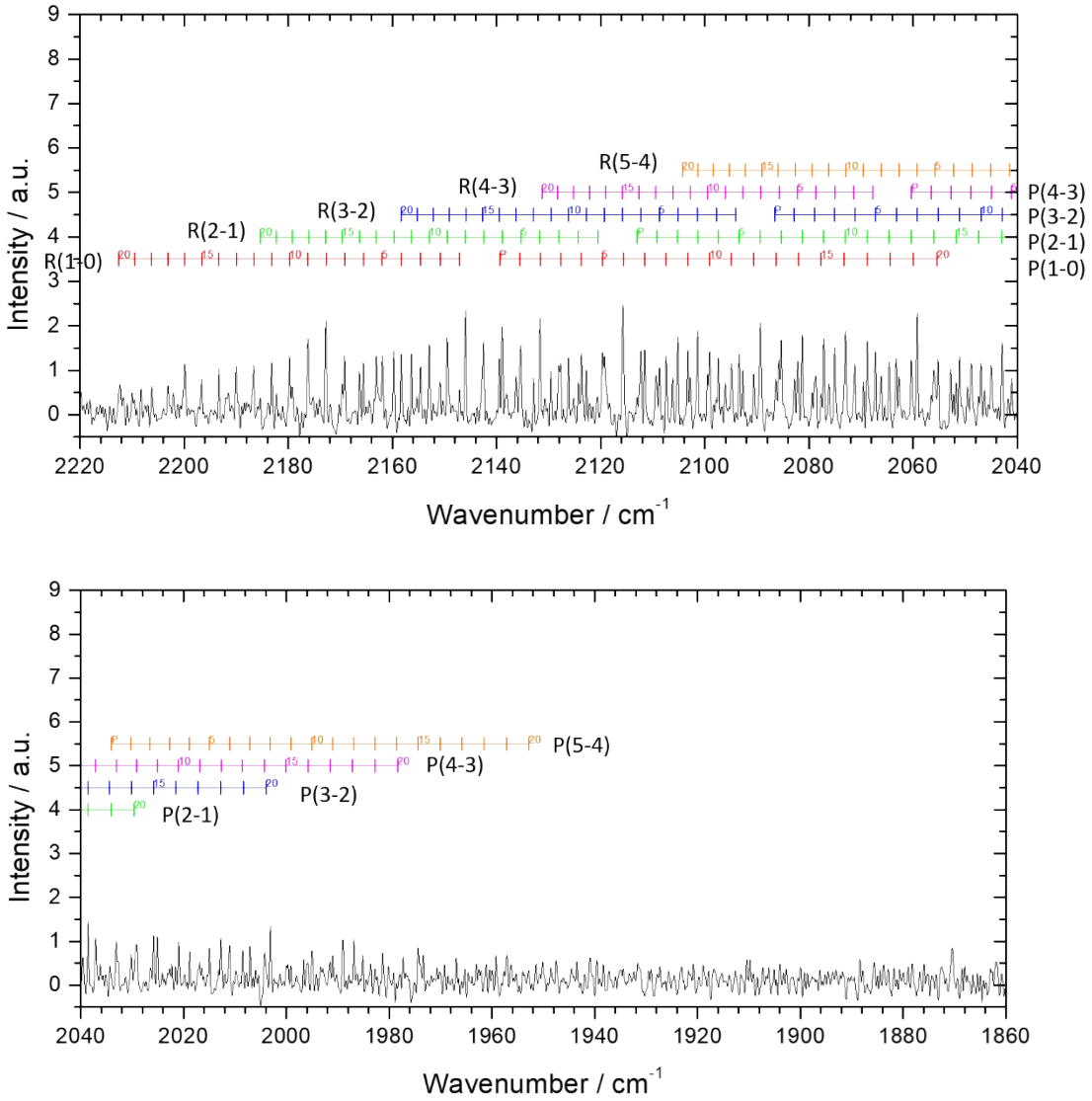

Fig. S5 Assignments of observed IR emission lines of CO recorded 3–4 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 308 nm. The spectral resolution was 0.3 cm^{-1}. The assignments of vibration-rotational transitions are shown as sticks; the numbers correspond to J'; P(v'–v'') and R(v'–v'') represent the vibrational transition v'–v''.

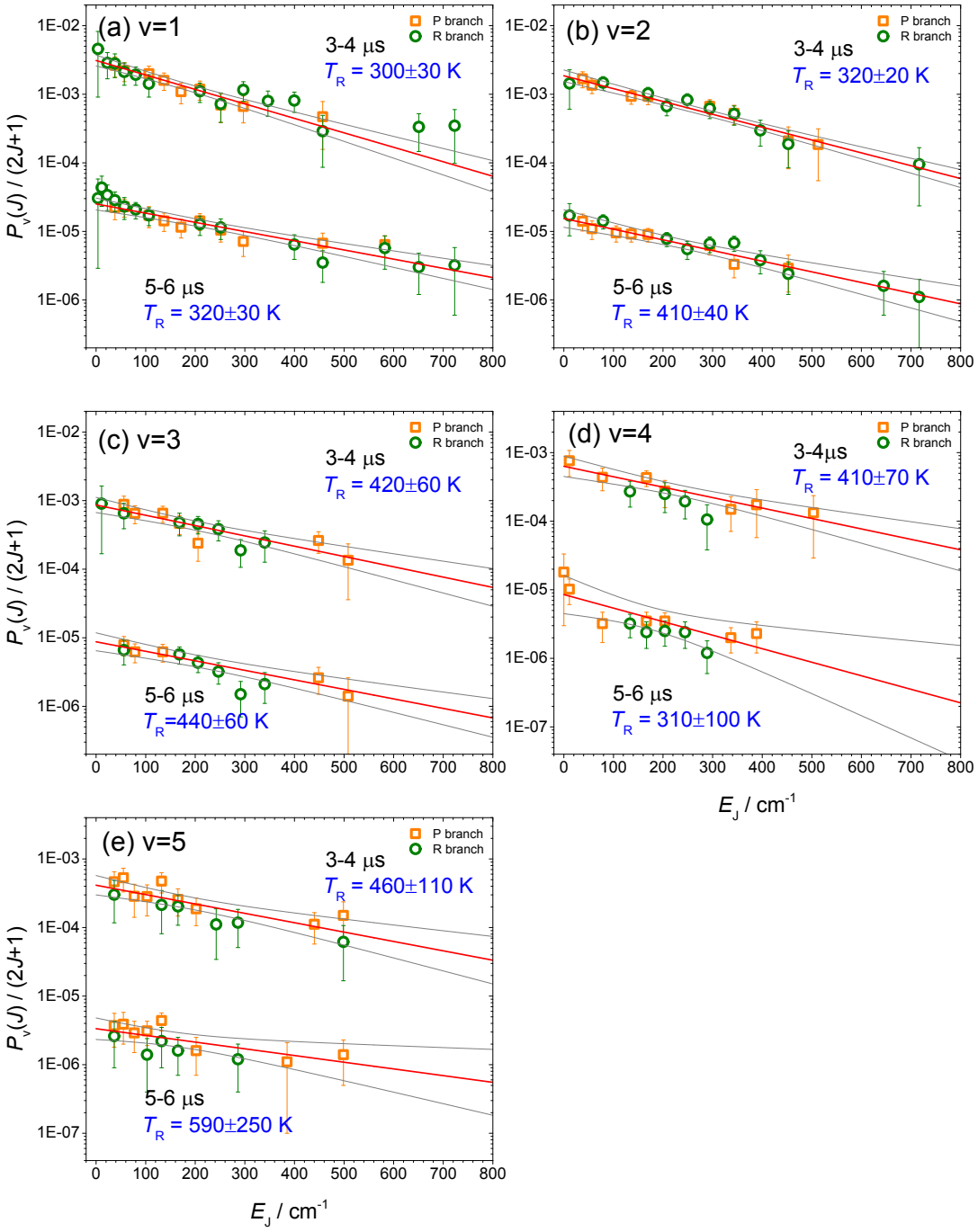

Fig. S6 Semi-logarithmic plots of relative rotational populations of CO (v= 1–5) 3–4 μs and 5–6 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 308 nm (symbols □ for the *P*-branch and ○ for the *R*-branch). Solid lines represent least-square fits; the confidence ranges are also shown.

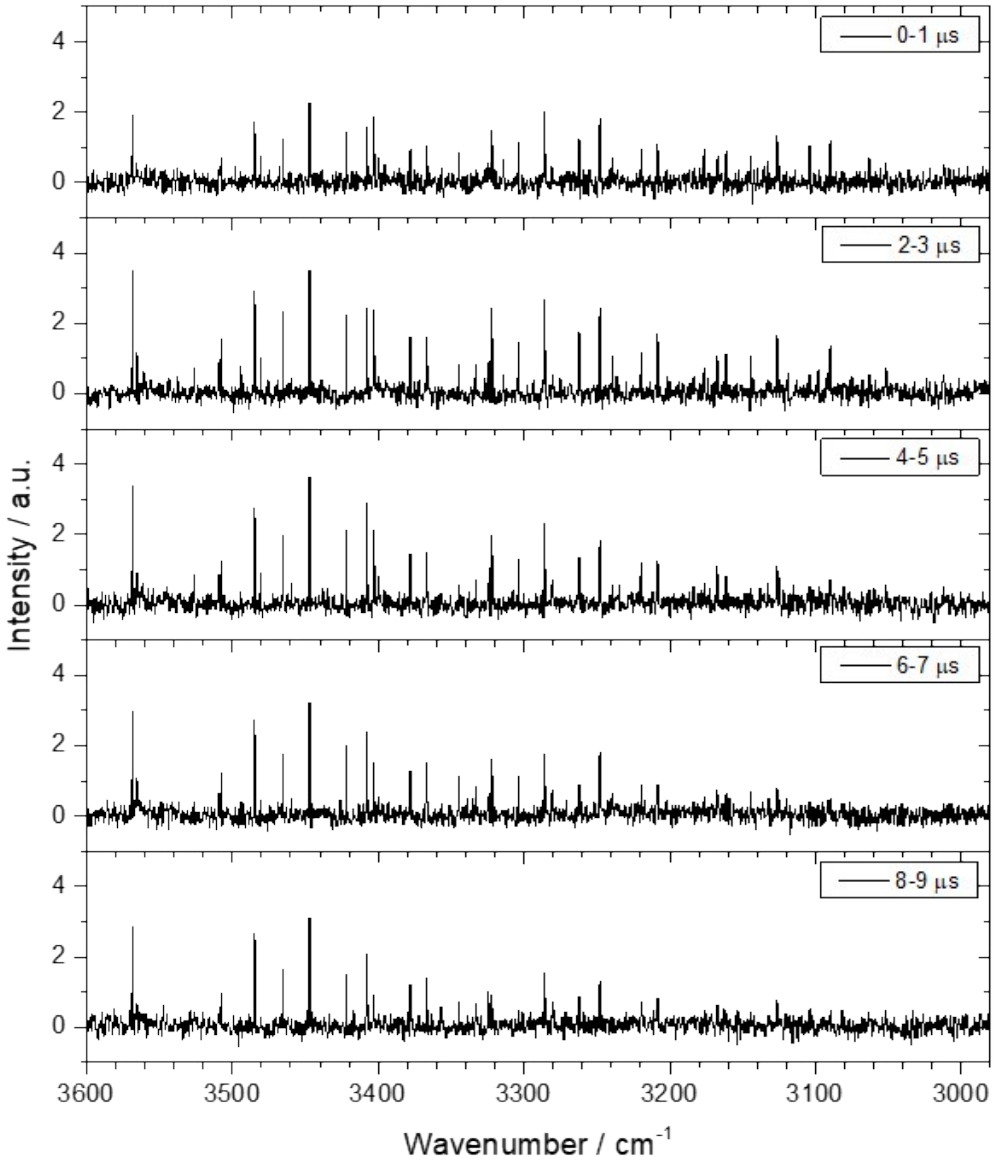

Fig. S7 Representative IR emission spectra of OH recorded 0–9 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 308 nm. The spectral resolution was 0.5 cm^{-1}. Four spectra recorded under identical experimental conditions were averaged to yield these spectra.

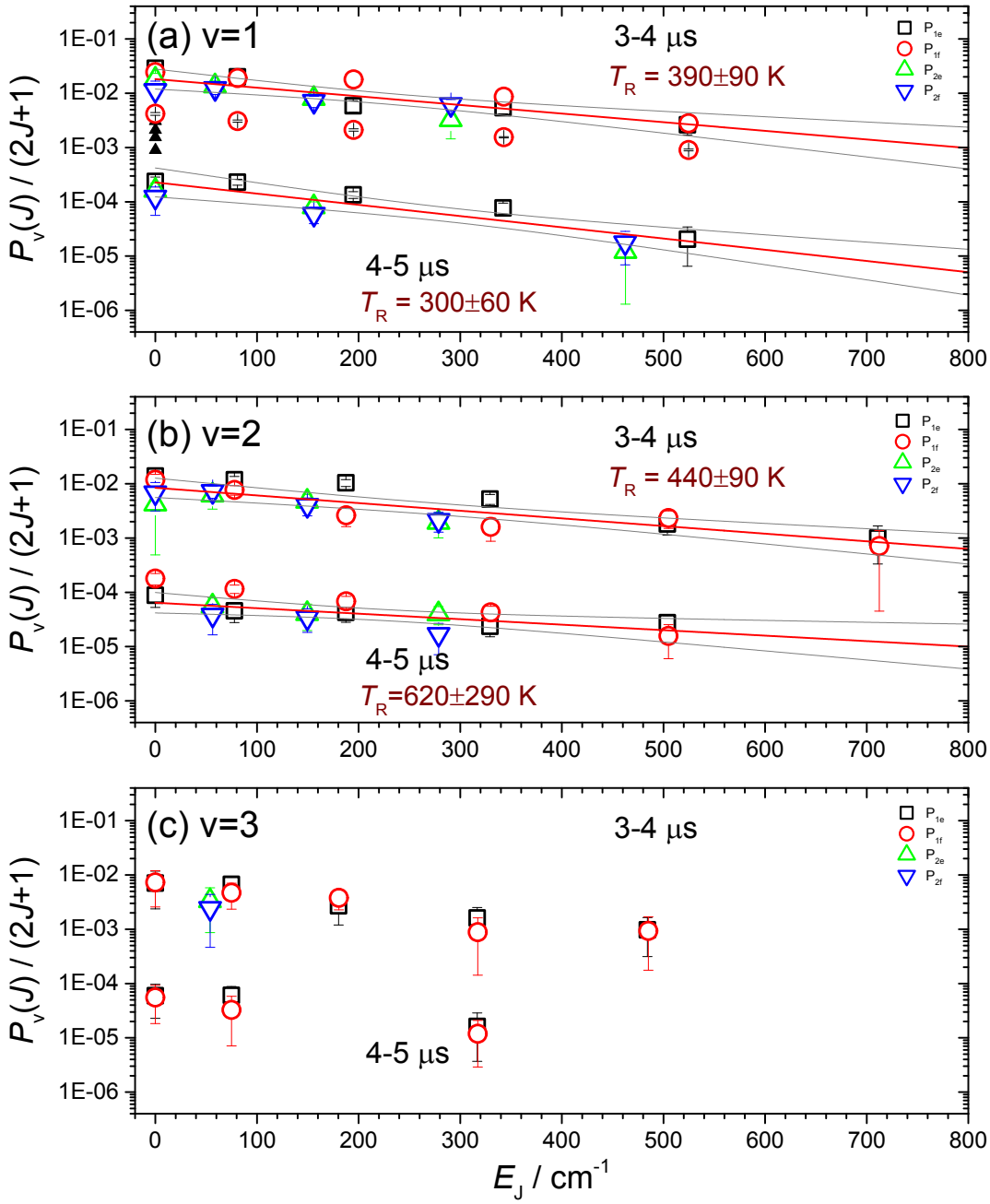

Fig. S8 Semi-logarithmic plots of relative rotational populations of OH (v= 1–3) 3–4 μs and 5–6 μs after photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 308 nm (symbols □ for the P_{1e}-branch, ○ for the P_{1f}-branch, △ for the P_{2e}-branch, and ▽ for the P_{2f}-branch). Solid lines represent least-square fits; the confidence ranges are also shown.

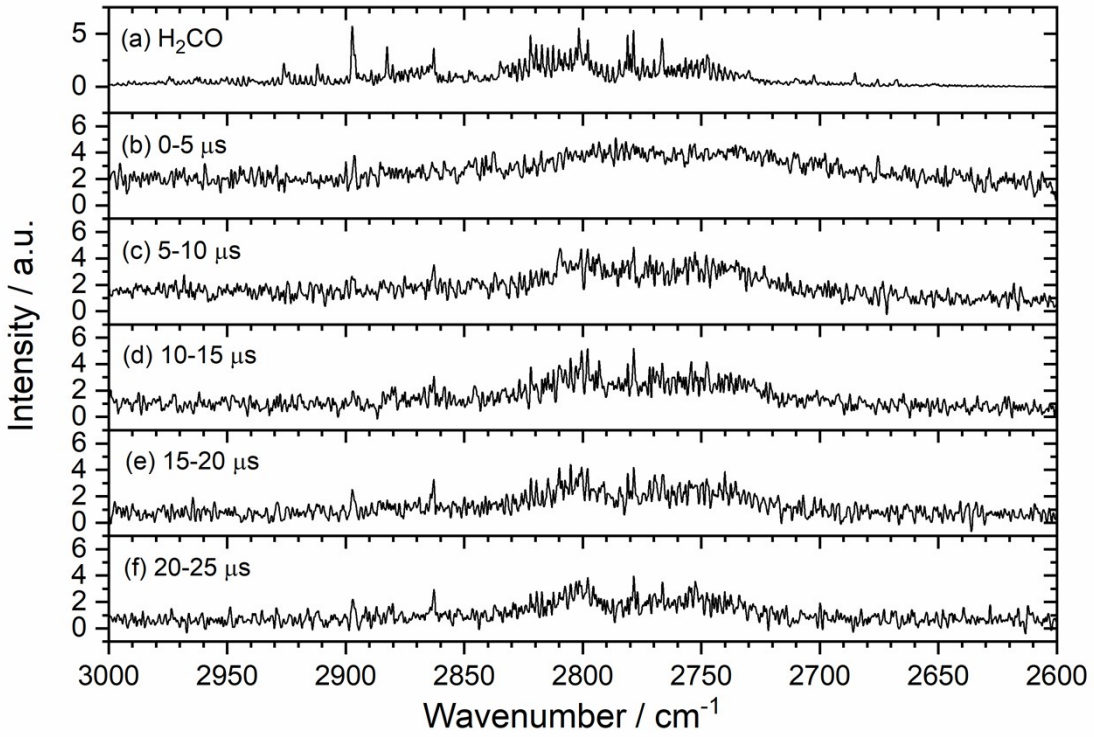

Fig. S9 Emission spectra of H_2CO in spectral region 2600－3000 cm^{-1} recorded 0–5 μs (b), 5–10 μs (c), 10–15 μs (d), 15–20 μs (e), and 20–25 μs (f) upon photolysis of a flowing mixture of $CH_2I_2/O_2/Ar$ (0.07/8.00/0.07 Torr) at 308 nm. IR absorption spectrum of H_2CO is shown in (a) for comparison. Spectral resolution was 0.7 cm^{-1}; six spectra recorded under similar conditions were averaged.