

## SUPPLEMENTARY INFORMATION

**Table S1: Pressure dependent quantum yields of CH<sub>3</sub> formation and [CH<sub>3</sub>CO]/[CH<sub>3</sub>] ratios from acetone photolysis at 248 nm. The data are plotted in Figure 5.**

Pressure / Torr N <sub>2</sub>	$\Phi_{AC}^{248}(CH_3)$	[CH <sub>3</sub> CO] / [CH <sub>3</sub> ]
5.7	1.44 ± 0.09	0.31 ± 0.10
16	1.41 ± 0.06	0.40 ± 0.07
31	1.42 ± 0.07	0.33 ± 0.07
53	1.37 ± 0.06	0.38 ± 0.08
60	1.37 ± 0.09	0.43 ± 0.10
75	1.30 ± 0.05	0.39 ± 0.06
97	1.35 ± 0.04	0.44 ± 0.04
122	1.33 ± 0.04	0.37 ± 0.05
148	1.31 ± 0.07	0.40 ± 0.09
182	1.32 ± 0.08	0.42 ± 0.13
204	1.32 ± 0.10	0.41 ± 0.10
255	1.20 ± 0.09	0.50 ± 0.12
279	1.25 ± 0.10	0.54 ± 0.14
302	1.29 ± 0.10	0.48 ± 0.12
348	1.20 ± 0.09	0.49 ± 0.12
379	1.28 ± 0.07	0.46 ± 0.09
400	1.20 ± 0.06	0.52 ± 0.07
418	1.25 ± 0.13	0.51 ± 0.15
453	1.07 ± 0.08	0.52 ± 0.12
472	1.16 ± 0.06	0.59 ± 0.09
502	1.12 ± 0.06	0.61 ± 0.09
546	1.14 ± 0.06	0.52 ± 0.09
601	1.11 ± 0.04	0.59 ± 0.06
625	1.10 ± 0.08	0.52 ± 0.12
654	1.12 ± 0.05	0.58 ± 0.07
699	1.10 ± 0.09	0.69 ± 0.17
733	1.14 ± 0.06	0.56 ± 0.07
794	1.11 ± 0.09	0.58 ± 0.17
902	1.08 ± 0.05	0.76 ± 0.10
1004	1.04 ± 0.09	0.66 ± 0.17
1065	1.07 ± 0.08	0.71 ± 0.17
1194	0.99 ± 0.09	0.91 ± 0.22
1296	1.00 ± 0.08	0.80 ± 0.18
1409	1.05 ± 0.09	0.76 ± 0.19
1543	0.99 ± 0.10	0.76 ± 0.13

*Notes:* Errors are 2  $\sigma$  (statistical) as described in the text.

**Table S2: The pressure dependence of the yield of CH<sub>3</sub> and the [CH<sub>3</sub>CO] / [CH<sub>3</sub>] ratio from CH<sub>3</sub>C(O)CH<sub>3</sub> photolysis at 266 nm The data are plotted in Figure 6.**

Pressure / Torr N <sub>2</sub>	$\Phi_{AC}^{266}(\text{CH}_3)$	[CH <sub>3</sub> CO] / [CH <sub>3</sub> ]
64	0.94 ± 0.08	1.29 ± 0.13
64	0.92 ± 0.09	1.21 ± 0.15
65	1.01 ± 0.09	1.18 ± 0.12
96	0.94 ± 0.10	1.04 ± 0.15
200	0.97 ± 0.07	1.14 ± 0.08
306	0.96 ± 0.07	1.22 ± 0.08
403	0.92 ± 0.06	1.28 ± 0.08
499	0.93 ± 0.08	1.03 ± 0.11
601	0.96 ± 0.16	1.20 ± 0.30
601	0.88 ± 0.08	1.17 ± 0.13
700	0.92 ± 0.04	1.11 ± 0.08
760	0.91 ± 0.04	1.24 ± 0.08

*Notes:* Errors are 2  $\sigma$  (statistical) as described in the text.

**Table S3: Pressure dependent quantum yields of CH<sub>3</sub> formation  
CH<sub>3</sub>C(O)Br photolysis at 248 nm. The data are plotted  
in Figure 7.**

Pressure / Torr N <sub>2</sub>	$\Phi_{\text{CH}_3\text{COBr}}^{248}(\text{CH}_3)$
51	0.92
95	0.94
200	0.86
300	0.96
400	0.93 ± 0.1
500	0.95
600	0.90
699	0.90
800	0.93
903	0.90
1007	1.00 ± 0.1
1090	0.81
1229	0.90

*Notes:* Errors are 2  $\sigma$  (statistical) and are reported only for the two pressures at which back-to back experiments with CH<sub>3</sub>I photolysis were conducted.

**Table S4: Pressure dependent quantum yields of CH<sub>3</sub> formation and [CH<sub>3</sub>CO]/[CH<sub>3</sub>] ratios from methyl ethyl ketone photolysis at 248 nm. The data are plotted in Figure 8.**

Pressure / Torr N <sub>2</sub>	$\Phi_{\text{MEK}}^{248}(\text{CH}_3)$	[CH <sub>3</sub> CO] / [CH <sub>3</sub> ]
6.85	0.48 ± 0.10	1.13 ± 0.36
7.10	0.45 ± 0.06	1.06 ± 0.19
7.50	0.50 ± 0.09	1.04 ± 0.27
17.80	0.39 ± 0.06	1.34 ± 0.21
18.60	0.42 ± 0.05	1.42 ± 0.17
51.00	0.41 ± 0.06	1.21 ± 0.19
52.00	0.39 ± 0.05	1.36 ± 0.17
99.90	0.35 ± 0.05	1.52 ± 0.21
150.5	0.36 ± 0.04	1.53 ± 0.17
200.0	0.32 ± 0.04	1.72 ± 0.21
200.4	0.35 ± 0.06	1.54 ± 0.28
250.0	0.29 ± 0.04	1.99 ± 0.25
300.7	0.27 ± 0.04	2.30 ± 0.22
355.4	0.29 ± 0.04	2.07 ± 0.20
400.3	0.24 ± 0.04	2.61 ± 0.27
525.1	0.24 ± 0.05	2.88 ± 0.40
604.5	0.22 ± 0.03	3.09 ± 0.28
704.9	0.20 ± 0.03	3.63 ± 0.29
755.8	0.23 ± 0.04	3.33 ± 0.31
1250	0.19 ± 0.03	4.04 ± 0.28
1402	0.19 ± 0.03	4.54 ± 0.32
1493	0.19 ± 0.03	4.92 ± 0.29

Notes: Errors are 2  $\sigma$  (statistical) as described in the text.

**Table S5: Absorption cross sections of CH<sub>3</sub>C(O)Br at 298 K**

$\lambda$ /nm	$\sigma^*$	$\lambda$ /nm	$\sigma^*$	$\lambda$ /nm	$\sigma^*$
210	42.5	242	23.0	274	12.7
212	47.8	244	23.5	276	11.0
214	51.2	246	23.9	278	9.33
216	51.1	248	24.3	280	7.80
218	47.6	250	24.6	282	6.42
220	42.4	252	24.8	284	5.18
222	37.0	254	24.8	286	4.08
224	32.3	256	24.6	288	3.16
226	28.8	258	24.2	290	2.38
228	26.2	260	23.4	292	1.75
230	24.4	262	22.4	294	1.26
232	23.2	264	21.1	296	0.868
234	22.5	266	19.6	298	0.578
236	22.3	268	18.0	300	0.371
238	22.4	270	16.2	302	0.223
240	22.7	272	14.5	304	0.124

Notes: \*Units of  $10^{-20}$  cm<sup>2</sup> molecule<sup>-1</sup>