

**Supplementary data** : Table showing a comparison of daughter ion branching ratios from photon-induced TPEPICO spectroscopy with bimolecular ion-molecule reactions at twenty five defined recombination energies of the reactant ion.

hv / eV	C <sub>2</sub> H <sub>4</sub> BRs (t)pepico <sup>a</sup>	BRs ion-molecule reaction <sup>c</sup>	C <sub>2</sub> H <sub>3</sub> F BRs (t)pepico <sup>b</sup>	BRs ion-molecule reaction <sup>d</sup>	1,1-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> BRs (t)pepico <sup>b</sup>	BRs ion-molecule reaction <sup>d</sup>	C <sub>2</sub> HF <sub>3</sub> BRs (t)pepico <sup>b</sup>	BRs ion-molecule reaction <sup>d</sup>	C <sub>2</sub> F <sub>4</sub> BRs (t)pepico <sup>b</sup>	BRs ion-molecule reaction <sup>e</sup>	
<b>21.56 (Ne<sup>+</sup>)</b>	ca. C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 90	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 82	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 41	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 60	CF <sup>+</sup> 34	CF <sup>+</sup> 34	CF <sup>+</sup> 74	CF <sup>+</sup> 60	CF <sup>+</sup> 80 <sup>f</sup>	CF <sup>+</sup> 80	
	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 10	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 18	C <sub>2</sub> HF <sup>+</sup> 33	C <sub>2</sub> HF <sup>+</sup> 13	C <sub>2</sub> HF <sup>+</sup> 27	C <sub>2</sub> HF <sup>+</sup> 25	CHF <sup>+</sup> 9	CF <sub>2</sub> =CH <sup>+</sup> 13	CF <sub>2</sub> <sup>+</sup> 20 <sup>f</sup>	CF <sub>2</sub> <sup>+</sup> 15	
			CF <sup>+</sup> 15	CH <sub>2</sub> =CH <sup>+</sup> 11	CH <sub>2</sub> <sup>+</sup> 13	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 18	C <sub>2</sub> F <sub>2</sub> <sup>+</sup> 7	CF <sub>2</sub> <sup>+</sup> 11		C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 4	
			CH <sub>2</sub> =CF <sup>+</sup> 12	CF <sup>+</sup> 4	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 11	CH <sub>2</sub> <sup>+</sup> 13	CF <sub>2</sub> <sup>+</sup> 5	C <sub>2</sub> HF <sup>+</sup> 7		CF <sub>3</sub> <sup>+</sup> 1	
			CHF <sup>+</sup> 5	CHF <sup>+</sup> 4	CF <sub>2</sub> =CH <sup>+</sup> 5	CF=CH <sub>2</sub> <sup>+</sup> 8	CF <sub>2</sub> =CH <sup>+</sup> 5	CHF <sup>+</sup> 7			
				CH <sub>2</sub> =CF <sup>+</sup> 3	CF=CH <sub>2</sub> <sup>+</sup> 5	CF <sub>2</sub> <sup>+</sup> 2		CHF <sub>2</sub> <sup>+</sup> 1			
				C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 2	CF <sub>2</sub> <sup>+</sup> 5			C <sub>2</sub> F <sup>+</sup> 1			
				C <sub>2</sub> H <sup>+</sup> 2							
				CH <sub>2</sub> F <sup>+</sup> 1							
<b>17.42 (F<sup>+</sup>)</b>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 85	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 66	CH <sub>2</sub> =CH <sup>+</sup> 47	Reaction not studied	CF=CH <sub>2</sub> <sup>+</sup> 38	CF=CH <sub>2</sub> <sup>+</sup> 45	CF <sub>2</sub> =CH <sup>+</sup> 55	Products not identified	C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 50	CF <sub>3</sub> <sup>+</sup> 40	
	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 15	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 28	CH <sub>2</sub> =CF <sup>+</sup> 24		CF <sup>+</sup> 16	CH <sub>2</sub> F <sup>+</sup> 28	CHF <sup>+</sup> 23		CF <sup>+</sup> 26	CF <sub>2</sub> <sup>+</sup> 38	
		C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 6	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 17		C <sub>2</sub> HF <sup>+</sup> 14	CF <sup>+</sup> 18	CF <sup>+</sup> 15		CF <sub>2</sub> <sup>+</sup> 24	C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 22	
			C <sub>2</sub> HF <sup>+</sup> 7		CH <sub>2</sub> F <sup>+</sup> 12	CF <sub>2</sub> =CH <sup>+</sup> 5	CHF <sub>2</sub> <sup>+</sup> 7				
			CF <sup>+</sup> 5		CH <sub>2</sub> <sup>+</sup> 12	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 4					
					CF <sub>2</sub> =CH <sup>+</sup> 8						
<b>15.76 (Ar<sup>+</sup>)</b>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 80	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 76	CH <sub>2</sub> =CH <sup>+</sup> 52	CH <sub>2</sub> =CH <sup>+</sup> 57	CF=CH <sub>2</sub> <sup>+</sup> 35	CF=CH <sub>2</sub> <sup>+</sup> 44	CF <sub>2</sub> =CH <sup>+</sup> 38	CHF <sub>2</sub> <sup>+</sup> 51	CF <sub>2</sub> <sup>+</sup> 43	CF <sub>2</sub> <sup>+</sup> 28	
	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 20	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 20	CH <sub>2</sub> =CF <sup>+</sup> 22	CH <sub>2</sub> =CF <sup>+</sup> 18	CH <sub>2</sub> F <sup>+</sup> 28	CH <sub>2</sub> F <sup>+</sup> 22	CHF <sub>2</sub> <sup>+</sup> 26	CHF <sup>+</sup> 20	C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 37	CF <sub>3</sub> <sup>+</sup> 27	
		C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 4	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 12	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 12	CF <sup>+</sup> 25	C <sub>2</sub> HF <sup>+</sup> 19	C <sub>2</sub> HF <sup>+</sup> 19	CHF <sup>+</sup> 21	CF <sub>2</sub> =CH <sup>+</sup> 13	CF <sup>+</sup> 15	C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 24
			C <sub>2</sub> HF <sup>+</sup> 8	C <sub>2</sub> HF <sup>+</sup> 7	C <sub>2</sub> HF <sup>+</sup> 11	CF <sup>+</sup> 12	CF <sup>+</sup> 15	CF <sup>+</sup> 15	CF <sup>+</sup> 8	CF <sub>3</sub> <sup>+</sup> 5	CF <sup>+</sup> 17
			CF <sup>+</sup> 5	CF <sup>+</sup> 5	CF <sub>2</sub> =CH <sup>+</sup> 1	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 3			C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 4		C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 4
				C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 1					C <sub>2</sub> F <sub>2</sub> <sup>+</sup> 4		
<b>15.58 (N<sub>2</sub><sup>+</sup>)</b>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 79	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 50	CH <sub>2</sub> =CH <sup>+</sup> 42	CH <sub>2</sub> =CH <sup>+</sup> 40	CH <sub>2</sub> F <sup>+</sup> 35	CF=CH <sub>2</sub> <sup>+</sup> 33	CHF <sub>2</sub> <sup>+</sup> 40	CHF <sub>2</sub> <sup>+</sup> 66	CF <sub>2</sub> <sup>+</sup> 60	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 46	
	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 21	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 20	CH <sub>2</sub> =CF <sup>+</sup> 27	CH <sub>2</sub> =CF <sup>+</sup> 29	CF <sup>+</sup> 29	CH <sub>2</sub> F <sup>+</sup> 28	CHF <sup>+</sup> 24	CF <sup>+</sup> 16	CF <sup>+</sup> 26	CF <sup>+</sup> 25	
		HNC <sup>+</sup> 10	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 13	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 15	CF=CH <sub>2</sub> <sup>+</sup> 23	C <sub>2</sub> HF <sup>+</sup> 20	C <sub>2</sub> HF <sup>+</sup> 20	CHF <sup>+</sup> 12	CF <sub>3</sub> <sup>+</sup> 11	CF <sub>3</sub> <sup>+</sup> 13	
		HNCH <sup>+</sup> 10	C <sub>2</sub> HF <sup>+</sup> 9	C <sub>2</sub> HF <sup>+</sup> 12	C <sub>2</sub> HF <sup>+</sup> 13	CF <sup>+</sup> 11	CF <sup>+</sup> 11	CF <sub>2</sub> =CH <sup>+</sup> 16	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 6	C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 3	CF <sub>2</sub> <sup>+</sup> 11
		N <sub>2</sub> H <sup>+</sup> 10	CF <sup>+</sup> 6	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 4		C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 8					C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 5
<b>14.53 (N<sup>+</sup>)</b>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 66	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 30	CH <sub>2</sub> =CF <sup>+</sup> 41	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 52	C <sub>2</sub> HF <sup>+</sup> 52	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 82	CHF <sub>2</sub> <sup>+</sup> 94	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	CF <sup>+</sup> 55	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 85	
	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 34	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 25	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 22	CH <sub>2</sub> =CF <sup>+</sup> 21	CF=CH <sub>2</sub> <sup>+</sup> 48	CF=CH <sub>2</sub> <sup>+</sup> 16	CF <sup>+</sup> 6		CF <sub>3</sub> <sup>+</sup> 37	CF <sup>+</sup> 9	
		C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 10	CH <sub>2</sub> =CH <sup>+</sup> 20	CH <sub>2</sub> =CH <sup>+</sup> 20		C <sub>2</sub> HF <sup>+</sup> 2			CF <sub>2</sub> <sup>+</sup> 8	C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 4	
		HNC <sup>+</sup> 15	C <sub>2</sub> HF <sup>+</sup> 17	C <sub>2</sub> HF <sup>+</sup> 6							CF <sub>2</sub> <sup>+</sup> 1
		HCNH <sup>+</sup> 10		C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 1							CF <sub>3</sub> <sup>+</sup> 1
		CH <sub>2</sub> CN <sup>+</sup> 10									
<b>14.01 (CO<sup>+</sup>)</b>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 52	No data available	CH <sub>2</sub> =CF <sup>+</sup> 44	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 39	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 84	CHF <sub>2</sub> <sup>+</sup> 100	CHF <sub>2</sub> <sup>+</sup> 50	CF <sub>3</sub> <sup>+</sup> 60	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	
	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 48		C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 37	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 27		CF=CH <sub>2</sub> <sup>+</sup> 16		C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 41	CF <sup>+</sup> 40		
			C <sub>2</sub> HF <sup>+</sup> 13	CH <sub>2</sub> =CF <sup>+</sup> 16					CF <sup>+</sup> 9		
			CH <sub>2</sub> =CH <sup>+</sup> 6	CH <sub>2</sub> =CH <sup>+</sup> 16							

<b>14.00 (Kr<sup>+</sup>)</b>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 52 C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 48	C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 45 C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 45 C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 10	CH <sub>2</sub> =CF <sup>+</sup> 43 C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 37 C <sub>2</sub> HF <sup>+</sup> 13 CH <sub>2</sub> =CH <sup>+</sup> 7	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 39 C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 25 CH <sub>2</sub> =CF <sup>+</sup> 23 C <sub>2</sub> HF <sup>+</sup> 7 CH <sub>2</sub> =CH <sup>+</sup> 6	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Products not identified	CHF <sub>2</sub> <sup>+</sup> 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 86 CHF <sub>2</sub> <sup>+</sup> 14	CF <sub>3</sub> <sup>+</sup> 60 CF <sup>+</sup> 40	Reaction not studied
<b>13.76 (CO<sub>2</sub><sup>+</sup>)</b>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 58 C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 42	No data available	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 57 CH <sub>2</sub> =CF <sup>+</sup> 36 C <sub>2</sub> HF <sup>+</sup> 6	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 90 C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 9 CH <sub>2</sub> =CH <sup>+</sup> 1	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 80 CHF <sub>2</sub> <sup>+</sup> 20	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	CF <sub>3</sub> <sup>+</sup> 80 CF <sup>+</sup> 20	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100
<b>13.62 (O<sup>+</sup>)</b>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 70 C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 30	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 80 C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 15 C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 5	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 45 C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 38 CH <sub>2</sub> =CF <sup>+</sup> 17	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Products not identified	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 98 CHF <sub>2</sub> <sup>+</sup> 2	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 55 CF <sub>3</sub> <sup>+</sup> 38 CF <sup>+</sup> 7	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100 <sup>g</sup>
<b>13.44 ((Xe<sup>+</sup>))</b>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 83 C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 17	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 25-100 C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 75-0	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 96 CH <sub>2</sub> =CF <sup>+</sup> 2 C <sub>2</sub> H <sub>2</sub> <sup>+</sup> 2	Reaction not studied	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied
<b>12.89 (N<sub>2</sub>O<sup>+</sup>)</b>	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	No data available	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100
<b>12.62 (H<sub>2</sub>O<sup>+</sup>)</b>	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	Products not identified	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Data not collected	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Products not identified	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100
<b>12.13 (Xe<sup>+</sup>)</b>	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied
<b>12.07 (O<sub>2</sub><sup>+</sup>)</b>	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100
<b>11.99 (SF<sub>4</sub><sup>+</sup>)</b>	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	No data available	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	Products not identified	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied
<b>11.36 (CF<sub>2</sub><sup>+</sup>)</b>	C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup> 55 C <sub>2</sub> H <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 45	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 88 CH <sub>2</sub> =CH <sup>+</sup> 12	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100
<b>10.31 (SF<sup>+</sup>)</b>	Below IE(C <sub>2</sub> H <sub>4</sub> )	No data available	Below IE(C <sub>2</sub> H <sub>3</sub> F)	Products not identified	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> (P <sup>+</sup> ) 100 ?	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied
<b>10.24 (SF<sub>2</sub><sup>+</sup>)</b>	Below IE(C <sub>2</sub> H <sub>4</sub> )	No data available	Below IE(C <sub>2</sub> H <sub>3</sub> F)	No reaction <sup>l</sup>	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	No reaction	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 100	No reaction	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	Reaction not studied

10.11 (C <sub>2</sub> F <sub>4</sub> <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> 95 C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup> 5	Below IE(C <sub>2</sub> H <sub>3</sub> F)	C <sub>2</sub> H <sub>3</sub> F <sup>+</sup> (P <sup>+</sup> ) 45 C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup> 40 C <sub>3</sub> H <sub>2</sub> F <sub>3</sub> <sup>+</sup> 10 C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> 3 C <sub>4</sub> H <sub>3</sub> F <sub>5</sub> <sup>+</sup> 2	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	C <sub>4</sub> H <sub>2</sub> F <sub>6</sub> <sup>+</sup> 60 C <sub>3</sub> H <sub>2</sub> F <sub>3</sub> <sup>+</sup> 30 C <sub>3</sub> HF <sub>4</sub> <sup>+</sup> 10	Below IE(C <sub>2</sub> HF <sub>3</sub> )	C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> (P <sup>+</sup> ) 72 C <sub>3</sub> HF <sub>4</sub> <sup>+</sup> 28	C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (P <sup>+</sup> ) 100	C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 100 <sup>h</sup>
9.78 (SF <sub>3</sub> <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	No data available	Below IE(C <sub>2</sub> H <sub>3</sub> F)	Products not identified	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	SF <sub>3</sub> <sup>+</sup> 53 C <sub>2</sub> H <sub>2</sub> F <sub>3</sub> <sup>+</sup> 32 C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> <sup>+</sup> 15	Below IE(C <sub>2</sub> HF <sub>3</sub> )	No reaction	Below IE(C <sub>2</sub> F <sub>4</sub> )	Reaction not studied
9.26 (NO <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	No data available	Below IE(C <sub>2</sub> H <sub>3</sub> F)	No reaction	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	No reaction	Below IE(C <sub>2</sub> HF <sub>3</sub> )	No reaction	Below IE(C <sub>2</sub> F <sub>4</sub> )	Reaction not studied
9.11 (CF <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	CH <sub>2</sub> F <sup>+</sup> 80 C <sub>3</sub> H <sub>3</sub> <sup>+</sup> 20	Below IE(C <sub>2</sub> H <sub>3</sub> F)	CH <sub>2</sub> =CH <sup>+</sup> 88 CHF <sub>2</sub> <sup>+</sup> 12	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	CF <sub>3</sub> <sup>+</sup> 88 C <sub>2</sub> H <sub>2</sub> F <sup>+</sup> 7 CHF <sub>2</sub> <sup>+</sup> 5	Below IE(C <sub>2</sub> HF <sub>3</sub> )	CF <sub>3</sub> <sup>+</sup> 100	Below IE(C <sub>2</sub> F <sub>4</sub> )	CF <sub>3</sub> <sup>+</sup> 65 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 32 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> 4 (?)
9.09 (CF <sub>3</sub> <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup> 60 CH <sub>2</sub> =CH <sup>+</sup> 40	Below IE(C <sub>2</sub> H <sub>3</sub> F)	CH <sub>2</sub> =CH <sup>+</sup> 75 CHF <sub>2</sub> <sup>+</sup> 25	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	C <sub>2</sub> H <sub>2</sub> F <sup>+</sup> 50 C <sub>3</sub> H <sub>2</sub> F <sub>5</sub> <sup>+</sup> 44 C <sub>3</sub> HF <sub>4</sub> <sup>+</sup> 6	Below IE(C <sub>2</sub> HF <sub>3</sub> )	C <sub>3</sub> HF <sub>6</sub> <sup>+</sup> 100	Below IE(C <sub>2</sub> F <sub>4</sub> )	C <sub>3</sub> F <sub>7</sub> <sup>+</sup> 94 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 4 (?) C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 2 (?)
8.32 (SF <sub>3</sub> <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	No data available	Below IE(C <sub>2</sub> H <sub>3</sub> F)	No reaction	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	No reaction	Below IE(C <sub>2</sub> HF <sub>3</sub> )	No reaction	Below IE(C <sub>2</sub> F <sub>4</sub> )	Reaction not studied
6.27 (H <sub>3</sub> O <sup>+</sup> )	Below IE(C <sub>2</sub> H <sub>4</sub> )	C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 65 C <sub>2</sub> H <sub>7</sub> O <sup>+</sup> 35	Below IE(C <sub>2</sub> H <sub>3</sub> F)	C <sub>2</sub> H <sub>4</sub> F <sup>+</sup> 100	Below IE(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> )	C <sub>2</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup> 100	Below IE(C <sub>2</sub> HF <sub>3</sub> )	No data collected	Below IE(C <sub>2</sub> F <sub>4</sub> )	Reaction not studied

- a) Data from experiment [46] and statistical modelling [52]
- b) Data from [35]
- c) Data from [4-7,10-21]
- d) This work
- e) Data from [3,8,9]
- f) Data from [54]
- g) Data from [8]
- h) Data from [9]
- j)  $k_{exp} < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Note that the reference numbers used in (a) – (j) are the same as in the main paper.

