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The vacuum-ultraviolet photoelectron spectra of CH₂F₂ and CH₂Cl₂ revisited

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Table S1. Energies, separations from origin band, relative intensities and assignments of vibrational bands in the first photoelectron band of CH_2F_2, ionisation to $\tilde{X}^{+}\,^2B_1$, as predicted by harmonic calculations. Only bands with intensity greater than 10 % of the strongest band, the $2^2_0\,3^1_0$ combination, are shown.

Energy / eV	Relative intensity	Assignment
12.727 [a]	3.1	0^0_0
12.862	7.4	2^1_0
12.887	4.1	3^1_0
12.998	7.6	2^2_0
13.022	9.8	$2^1_0\,3^1_0$
13.043	2.2	1^1_0
13.047	2.9	3^2_0
13.133	4.1	2^3_0
13.158	10.0	$2^2_0\,3^1_0$
13.166	1.0	$2^1_0\,3^1_0\,7^2_0$
13.178	6.0	$1^1_0\,2^1_0$
13.182	7.0	$2^1_0\,3^2_0$
13.203	3.0	$1^1_0\,3^1_0$
13.207	1.5	3^3_0
13.293	5.5	$2^3_0\,3^1_0$
13.314	6.8	$1^1_0\,2^2_0$
13.318	7.2	$2^2_0\,3^2_0$
13.338	8.1	$1^1_0\,2^1_0\,3^1_0$
13.342	3.6	$2^1_0\,3^3_0$
13.363	2.2	$1^1_0\,3^2_0$
13.449	4.3	$1^1_0\,2^3_0$
13.453	3.9	$2^3_0\,3^2_0$
13.474	9.3	$1^1_0\,2^2_0\,3^1_0$
13.478	3.7	$2^2_0\,3^3_0$
13.498	5.9	$1^1_0\,2^1_0\,3^2_0$
13.609	5.8	$1^1_0\,2^3_0\,3^1_0$
13.634	6.8	$1^1_0\,2^2_0\,3^2_0$

[a] Set to our experimentally-determined value.

Table S2. Energies, separations from origin band, relative intensities and assignments of vibrational bands in the first and second (overlapping) photoelectron bands of CH_2Cl_2, ionisation to $\tilde{X}^{+\,2}B_2$ and $\tilde{A}^{+\,2}B_1$, as predicted by harmonic Franck–Condon calculations. Apart from the weak bands at low energy below 11.34 eV (11.40 eV) where there is no overlapping problem, only bands with intensity greater than 10 % of the strongest band, the 4^{17}_0 (3^1_0) component of $\tilde{X}^{+\,2}B_2$ ($\tilde{A}^{+\,2}B_1$), are shown.

$CH_2Cl_2^+$ $\tilde{X}^{+\,2}B_2$			$CH_2Cl_2^+$ $\tilde{A}^{+\,2}B_1$		
Energy / eV	Relative intensity	Assignment	Energy / eV	Rel. Intensity	Assignment
11.228 [a]	0.5	4^7_1	11.281	0.4	4^0_1
11.230	0.5	4^8_2	11.317 [b]	8.7	0^0_0
11.266	0.9	4^8_1	11.320	1.6	4^1_1
11.268	0.5	4^9_2	11.356	1.3	4^1_0
11.302	0.7	4^8_0	11.360	0.5	4^2_1
11.304	1.3	4^9_1	11.399	0.6	7^2_0
11.306	0.5	4^{10}_2	11.404	10.0	3^1_0
11.340	1.2	4^9_0	11.407	1.8	$3^1_0\,4^1_1$
11.342	1.8	4^{10}_1	11.433	1.5	$3^1_0\,4^1_0$
11.377	2.1	4^{10}_0	11.491	5.1	3^2_0
11.379	2.1	4^{11}_1	11.578	1.5	3^3_0
11.415	3.3	4^{11}_0			
11.417	2.2	4^{12}_1			
11.453	4.7	4^{12}_0			
11.455	2.0	4^{13}_1			
11.475	1.3	$4^{10}_0\,3^1_0$			
11.477	1.2	$4^{11}_1\,3^1_0$			
11.491	6.3	4^{13}_0			
11.492	1.5	4^{14}_1			
11.513	2.1	$4^{11}_0\,3^1_0$			
11.515	1.3	$4^{12}_1\,3^1_0$			
11.528	7.8	4^{14}_0			
11.530	1.0	4^{15}_1			
11.551	3.0	$4^{12}_0\,3^1_0$			
11.553	1.2	$4^{13}_1\,3^1_0$			
11.566	9.0	4^{15}_0			
11.588	4.1	$4^{13}_0\,3^1_0$			
11.604	9.7	4^{16}_0			
11.626	5.1	$4^{14}_0\,3^1_0$			
11.641	10.0	4^{17}_0			
11.664	6.0	$4^{15}_0\,3^1_0$			
11.679	9.7	4^{18}_0			
11.702	6.6	$4^{16}_0\,3^1_0$			
11.717	9.0	4^{19}_0			
11.724	1.9	$4^{14}_0\,3^2_0$			
11.739	6.9	$4^{17}_0\,3^1_0$			
11.755	7.9	4^{20}_0			
11.762	2.3	$4^{14}_0\,3^2_0$			
11.777	6.8	$4^{18}_0\,3^1_0$			
11.792	6.6	4^{21}_0			
11.799	2.5	$4^{16}_0\,3^2_0$			
11.815	6.4	$4^{19}_0\,3^1_0$			

a Set so that the adiabatic ionization energy of this state is 11.0 eV.

b Set to our experimentally-determined value.

Table S3. Energies, separations from origin band, relative intensities and assignments of vibrational bands in the second and fourth (overlapping) photoelectron bands of CH_2F_2, ionisation to $\tilde{A}^{+\,2}B_2$ and $\tilde{C}^{+\,2}A_2$, as predicted by harmonic Franck–Condon calculations. Only bands with intensity greater than 10 % of the strongest bands, the $4^{11}_0 3^1_0$ (3^1_0 or $3^1_0 4^1_0$) components of $\tilde{A}^{+\,2}B_2$ ($\tilde{C}^{+\,2}A_2$), are shown.

$CH_2F_2^+$ $\tilde{A}^{+\,2}B_2$			$CH_2F_2^+$ $\tilde{C}^{+\,2}A_2$		
Energy / eV	Relative intensity	Assignment	Energy / eV	Relative intensity	Assignment
14.702 [a]	1.4	4^6_0	15.570 [b]	5.1	0^0_0
14.769	2.4	4^7_0	15.631	5.0	4^1_0
14.773	1.2	$4^5_0 3^1_0$	15.690	2.2	4^2_0
14.836	3.5	4^8_0	15.698	10.0	3^1_0
14.840	2.4	$4^6_0 3^1_0$	15.758	10.0	$3^1_0 4^1_0$
14.903	4.5	4^9_0	15.817	4.3	$3^1_0 4^2_0$
14.907	4.0	$4^7_0 3^1_0$	15.826	9.1	3^2_0
14.912	1.0	$4^5_0 3^2_0$	15.885	9.3	$3^2_0 4^1_0$
14.970	5.3	4^{10}_0	15.945	4.1	$3^2_0 4^2_0$
14.974	6.0	$4^8_0 3^1_0$	15.953	5.2	3^3_0
14.979	2.0	$4^6_0 3^2_0$	16.013	5.4	$3^3_0 4^1_0$
15.037	5.7	4^{11}_0	16.072	2.4	$3^3_0 4^2_0$
15.041	7.8	$4^9_0 3^1_0$	16.080	2.0	3^4_0
15.046	3.3	$4^7_0 3^2_0$	16.140	2.1	$3^4_0 4^1_0$
15.104	5.5	4^{12}_0	16.199	1.0	$3^4_0 4^2_0$
15.108	9.3	$4^{10}_0 3^1_0$			
15.113	5.0	$4^8_0 3^2_0$			
15.117	1.1	$2^1_0 3^3_0$			
15.159	1.1	$4^{10}_0 2^1_0$			
15.164	1.2	$4^8_0 2^1_0 3^1_0$			
15.171	5.0	4^{13}_0			
15.176	10.0	$4^{11}_0 3^1_0$			
15.180	6.6	$4^9_0 3^2_0$			
15.184	1.8	$4^7_0 3^3_0$			
15.238	4.2	4^{14}_0			
15.243	9.8	$4^{12}_0 3^1_0$			
15.247	7.9	$4^{10}_0 3^2_0$			
15.251	2.7	$4^8_0 3^3_0$			
15.298	1.8	$4^{10}_0 2^1_0 3^1_0$			
15.305	3.3	4^{15}_0			
15.310	8.9	$4^{13}_0 3^1_0$			
15.314	8.6	$4^{11}_0 3^2_0$			
15.318	3.7	$4^9_0 3^3_0$			
15.365	1.9	$4^{11}_0 2^1_0 3^1_0$			
15.372	2.4	4^{16}_0			
15.377	7.5	$4^{14}_0 3^1_0$			
15.381	8.5	$4^{12}_0 3^2_0$			
15.385	4.4	$4^{10}_0 3^3_0$			
15.432	1.9	$4^{12}_0 2^1_0 3^1_0$			
15.436	1.5	$4^{10}_0 2^1_0 3^2_0$			
15.439	1.6	4^{17}_0			
15.444	5.9	$4^{15}_0 3^1_0$			
15.448	7.8	$4^{13}_0 3^2_0$			
15.452	4.8	$4^{11}_0 3^3_0$			

[a]   Set so that the adiabatic ionization energy of this state is 14.3 eV.

[b]   Set so that the adiabatic ionization energy of this state is 15.57 eV.

Table S4. Energies, relative intensities and assignments of vibrational bands in the first and second (overlapping) photoelectron bands of CH_2F_2, ionisation to $\tilde{D}^{+\,2}B_2$, as predicted by harmonic Franck–Condon calculations. Only bands with intensity greater than 10 % of the strongest band, the 3^6_0 component of $\tilde{D}^{+\,2}B_2$, are shown.

Energy / eV	Relative intensity	Assignment
18.211 [a]	1.9	3^2_0
18.265	1.3	$3^2_0\,4^1_0$
18.317	4.5	3^3_0
18.370	3.1	$3^3_0\,4^1_0$
18.422	7.6	3^4_0
18.476	5.3	$3^4_0\,4^1_0$
18.528	9.8	3^5_0
18.530	1.3	$3^4_0\,4^2_0$
18.581	7.0	$3^5_0\,4^1_0$
18.602	1.3	$3^4_0\,2^1_0$
18.633	10.0	3^6_0
18.635	1.7	$3^5_0\,4^2_0$
18.687	7.2	$3^6_0\,4^1_0$
18.708	1.7	$3^5_0\,2^1_0$
18.739	8.3	3^7_0
18.741	1.8	$3^6_0\,4^2_0$
18.762	1.2	$3^5_0\,2^1_0\,4^1_0$
18.792	6.1	$3^7_0\,4^1_0$
18.813	1.7	$3^6_0\,2^1_0$
18.844	5.6	3^8_0
18.846	1.6	$3^7_0\,4^2_0$
18.898	4.2	$3^8_0\,4^1_0$
18.949	3.1	3^9_0
19.055	1.5	3^{10}_0

[a] Set so that the adiabatic ionization energy of this state is 18.0 eV.

Table S5. Energies, separations from origin band, relative intensities and assignments of vibrational bands in the third and fourth (overlapping) photoelectron bands of CH_2Cl_2, ionisation to $\tilde{B}^{+2}A_1$ and $\tilde{C}^{+2}A_2$, as predicted by harmonic Franck–Condon calculations. Only bands with intensity greater than 10 % of the strongest band, the 4^2_0 (4^1_0) component of $\tilde{B}^{+2}A_1$ ($\tilde{C}^{+2}A_2$), are shown.

$CH_2Cl_2^+$ $\tilde{B}^{+2}A_1$				$CH_2Cl_2^+$ $\tilde{C}^{+2}A_2$		
Energy / eV	Relative intensity	Assignment		Energy / eV	Rel. Intensity	Assignment
12.114 [a]	1.8	4^0_1		12.214 [b]	2.5	4^0_1
12.150	1.6	4^1_1		12.250	9.7	0^0_0
12.150	3.0	0^0_0		12.282	1.3	4^2_1
12.186	7.7	4^1_0		12.284	10.0	4^1_0
12.221	10.0	4^2_0		12.302	1.0	$4^0_1\,3^1_0$
12.257	1.2	4^4_1		12.315	1.7	4^3_1
12.257	8.6	4^3_0		12.317	4.8	4^2_0
12.262	1.0	$4^1_0\,3^1_0$		12.338	4.3	3^1_0
12.292	1.7	4^5_1		12.351	1.5	4^3_0
12.293	5.5	4^4_0		12.372	4.5	$4^1_0\,3^1_0$
12.298	1.1	$4^2_0\,3^1_0$		12.406	2.3	$4^2_0\,3^1_0$
12.328	1.4	4^6_1		12.426	1.0	3^2_0
12.328	2.8	4^5_0		12.460	1.0	$4^1_0\,3^2_0$
12.360	1.4	$4^1_0\,2^1_0$				
12.364	1.0	4^7_1				
12.364	1.2	4^6_0				
12.395	1.8	$4^2_0\,2^1_0$				
12.431	1.5	$4^3_0\,2^1_0$				
12.466	1.0	$4^4_0\,2^1_0$				

[a] Set so that the adiabatic ionization energy of this state is 12.15 eV.

[b] Set so that the adiabatic ionization energy of this state is 12.25 eV.