

# The vacuum-ultraviolet photoelectron spectra of $\text{CH}_2\text{F}_2$ and $\text{CH}_2\text{Cl}_2$ revisited

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## Supplementary Material to JMS-15-31

### The vacuum-ultraviolet photoelectron spectra of CH<sub>2</sub>F<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>F<sub>2</sub>, ionisation to  $\tilde{X}^+ {}^2B_1$ , as predicted by harmonic calculations. Only bands with intensity greater than 10 % of the strongest band, the  $2_0^2 3_0^1$  combination, are shown.

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

<sup>a</sup> 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<sub>2</sub>Cl<sub>2</sub>, ionisation to  $\tilde{X}^+{}^2B_2$  and  $\tilde{A}^+{}^2B_1$ , 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  $4^1_0$  ( $3^1_0$ ) component of  $\tilde{X}^+{}^2B_2$  ( $\tilde{A}^+{}^2B_1$ ), are shown.

CH <sub>2</sub> Cl <sub>2</sub> <sup>+</sup> $\tilde{X}^+{}^2B_2$			CH <sub>2</sub> Cl <sub>2</sub> <sup>+</sup> $\tilde{A}^+{}^2B_1$		
Energy / eV	Relative intensity	Assignment	Energy / eV	Rel. Intensity	Assignment
11.228 <sup>a</sup>	0.5	$4^7_1$	11.281	0.4	$4^0_1$
11.230	0.5	$4^8_2$	11.317 <sup>b</sup>	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	$4^{19}_0 3^1_0$			

<sup>a</sup> Set so that the adiabatic ionization energy of this state is 11.0 eV.

<sup>b</sup> 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  $\text{CH}_2\text{F}_2$ , ionisation to  $\tilde{A}^{+2}\text{B}_2$  and  $\tilde{C}^{+2}\text{A}_2$ , 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  $\tilde{A}^{+2}\text{B}_2$  ( $\tilde{C}^{+2}\text{A}_2$ ), are shown.

$\text{CH}_2\text{F}_2^+ \tilde{A}^{+2}\text{B}_2$			$\text{CH}_2\text{F}_2^+ \tilde{C}^{+2}\text{A}_2$		
Energy / eV	Relative intensity	Assignment	Energy / eV	Relative intensity	Assignment
14.702 <sup>a</sup>	1.4	$4^6_0$	15.570 <sup>b</sup>	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	$4^{11}_0 3^3_0$			

<sup>a</sup> Set so that the adiabatic ionization energy of this state is 14.3 eV.

<sup>b</sup> 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<sub>2</sub>F<sub>2</sub>, ionisation to  $\tilde{D}^+{}^2B_2$ , as predicted by harmonic Franck–Condon calculations. Only bands with intensity greater than 10 % of the strongest band, the  $3^6_0$  component of  $\tilde{D}^+{}^2B_2$ , are shown.

Energy / eV	Relative intensity	Assignment
18.211 <sup>a</sup>	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	$3^{10}_0$

<sup>a</sup> 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  $\text{CH}_2\text{Cl}_2$ , ionisation to  $\tilde{B}^{+2}\text{A}_1$  and  $\tilde{C}^{+2}\text{A}_2$ , 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  $\tilde{B}^{+2}\text{A}_1$  ( $\tilde{C}^{+2}\text{A}_2$ ), are shown.

$\text{CH}_2\text{Cl}_2^+ \tilde{B}^{+2}\text{A}_1$			$\text{CH}_2\text{Cl}_2^+ \tilde{C}^{+2}\text{A}_2$		
Energy / eV	Relative intensity	Assignment	Energy / eV	Rel. Intensity	Assignment
12.114 <sup>a</sup>	1.8	$4^0_1$	12.214 <sup>b</sup>	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	$4^4_0 2^1_0$			

<sup>a</sup> Set so that the adiabatic ionization energy of this state is 12.15 eV.

<sup>b</sup> Set so that the adiabatic ionization energy of this state is 12.25 eV.