Electronic Supplementary Material for PCCP

Supplementary Information for

The photoelectron spectrum of CCl_2^-: The convergence of theory and experiment after a decade of debate

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I. Geometries, frequencies, and normal mode vectors used in simulations.

Table S1 Spectroscopic quantities and molecular constants used in the simulation of the photoelectron spectrum of CCl_2^-. All calculations for CCl_2^- and CCl_2^- used the Gaussian 03 software package and the CCSD(T)/aug-cc-pVTZ method and basis set.

		r /Å	θ /°	ν_1 /cm^{-1}	x_{11}/cm^{-1}	ν_2 /cm^{-1}	x_{22}/cm^{-1}	ν_3 /cm^{-1}
CCl_2^-	Calculated	1.892	103.75	547.612	--	243.338	--	463.312
$X\,^2B_1$	Best Fit	1.90(2) [a]	104(2) [a]	547.612	0.0	243.338	0.0	463.312
CCl_2	Calculated	1.729	109.02	728.652	--	333.692	--	758.091
$X\,^1A_1$	Experimental	1.714(1) [b]	109.3(1) [b]	731.14(22) [c]	-3.34(3) [c]	335.80(1) [c]	-0.305(8) [c]	745 [d]
CCl_2	Calculated	1.684	127.40	681.635	--	296.845	--	992.617
$a\,^3B_1$	Best Fit	1.69(10)	127(10)	681.635	2.8	296.845	0.5	992.617

[a] The "best fit" geometry reflects the geometry change between anion and neutral that yields the best agreement between the simulated and experimental spectra. Changing the anion harmonic frequencies has little effect on the simulated spectra; thus, the DFT computed frequencies were used.

[b] LIF[1]

[c] Dispersed fluorescence[2]

[d] Excitation matrix[3]

Table S2 J-Matrices and K-vectors extracted from the CCSD(T)/aug-cc-pVTZ output from Gaussian 03 used in the simulation of CCl_2^- computed with PESCAL.

	J-Matrix				**CCl_2^- /cm^{-1}**	**CCl_2 /cm^{-1}**	**K-Vector/(g/mol)$^{-1/2}$Å**
CCl_2	0.993	-0.114	0.000	ν_1	547.612	728.651	-0.660613
$X\,^1A_1$	0.141	0.993	0.000	ν_2	243.337	333.692	-0.539615
	0.000	0.000	0.996	ν_3	463.312	758.090	0.000000
CCl_2	0.952	-.305	0.000	ν_1	547.612	681.634	-1.275341
$a\,^3B_1$	0.305	0.952	0.000	ν_2	243.337	296.844	0.476681
	0.000	0.000	0.994	ν_3	463.312	992.616	0.000000

Table S3 Normal Mode Vectors of CCl_2^- extracted from the CCSD(T)/aug-cc-pVTZ output from Gaussian 03.

	ν_1	ν_2	ν_3
CCl_2^- **$X\,^2B_1$**	0.000	0.000	0.000
	0.000	0.000	0.956
	0.963	-0.335	0.000
	0.000	0.000	0.000
	0.098	0.664	-0.164
	-0.165	0.057	0.129
	0.000	0.000	0.000
	-0.098	-0.664	-0.164
	-0.165	0.057	-0.129
CCl_2 **$X\,^1A_1$**	0.000	0.000	0.000
	0.000	0.000	0.958
	0.950	-0.480	0.000
	0.000	0.000	0.000
	0.149	0.615	-0.164
	-0.163	0.082	0.117
	0.000	0.000	0.000
	-0.149	-0.615	-0.164
	-0.163	0.082	-0.117
CCl_2 **$a\,^3B_1$**	0.000	0.000	0.000
	0.000	0.000	0.965
	0.913	-0.672	0.000
	0.000	0.000	0.000
	0.241	0.511	-0.166
	-0.157	0.115	0.082
	0.000	0.000	0.000
	-0.241	-0.511	-0.166
	-0.157	0.115	-0.082

Table S4 Spectroscopic quantities and molecular constants used in the simulation of the photoelectron spectrum of CBr_2^-.

		r /Å	θ /°	ν_1 /cm^{-1}	x_{11}/cm^{-1}	ν_2 /cm^{-1}	x_{22}/cm^{-1}	ν_3 /cm^{-1}
CBr_2^- **$X\,^2B_1$**	Calculated	2.100	106.36	455.786	--	129.655	--	365.775
	Best Fit	2.09(2) [a]	105(4) [a]	455.786	0.0	129.655	0.0	365.775
CBr_2 **$X\,^1A_1$**	Calculated	1.911	110.68	589.1	--	190.082	--	616.314
	Experimental	1.865 [b]	110.7 [b]	606.6(4) [c]	-2.01(4) [c]	199.5 [c]	-1.49(1) [c]	679.8(7) [c]
CBr_2 **$a\,^3B_1$**	Calculated	1.839	129.5	533.6	--	185.4	--	878.7

[a] The “best fit” geometry reflects the geometry change between anion and neutral that yields the best agreement between the simulated and experimental spectra. Absolute geometries are determined using as reference the experimental LIF geometrical parameters[4] of CBr_2 $X\,^1A_1$. Changing the anion harmonic frequencies has little effect on the simulated spectra; thus, the DFT computed frequencies were used.

[b] Combined LIF[4] and Theory[5]

[c] Single Vibronic Level Emission[6]

Table S5 J-Matrices and K-vectors extracted from the B3LYP/6-311++G** output from Gaussian 03 used in the simulation of CBr_2^- computed with PESCAL.

	J-Matrix				**CBr_2^- /cm^{-1}**	**CBr_2 /cm^{-1}**	**K-Vector/(g/mol)$^{-1/2}$Å**
CBr_2	0.999	-0.044	0.000	v_1	455.786	589.135	-0.797633
$X\,^1A_1$	0.044	0.999	0.000	v_2	129.655	190.081	-1.262737
	0.000	0.000	1.000	v_3	365.775	616.313	0.000000
CBr_2	0.982	-0.188	0.000	v_1	455.786	509.051	-1.583948
$a\,^3B_1$	0.188	0.982	0.000	v_2	129.655	183.106	0.195075
	0.000	0.000	0.997	v_3	365.775	830.998	0.000000

Table S6 Normal Mode Vectors of CBr_2^- computed with PESCAL using B3LYP/6-311++G** output.

	v_1	v_2	v_3
CBr_2^-	0.000	0.000	0.000
$X\,^2B_1$	0.000	0.000	0.991
	0.992	-0.388	0.000
	0.000	0.000	0.000
	0.048	0.651	-0.075
	-0.075	0.029	0.056
	0.000	0.000	0.000
	-0.048	-0.651	-0.075
	-0.075	0.029	-0.056
CBr_2	0.000	0.000	0.000
$X\,^1A_1$	0.000	0.000	0.992
	0.991	-0.471	0.000
	0.000	0.000	0.000
	0.061	0.623	-0.075
	-0.075	0.036	0.052
	0.000	0.000	0.000
	-0.061	-0.623	-0.075
	-0.075	0.036	-0.052
CBr_2	0.000	0.000	0.000
$a\,^3B_1$	0.000	0.000	0.993
	0.983	-0.677	0.000
	0.000	0.000	0.000
	0.105	0.518	-0.075
	-0.075	0.051	0.035
	0.000	0.000	0.000
	-0.105	-0.518	-0.075
	-0.075	0.051	-0.035

II. Expanded and enhanced figures.

Expanded view of CCl_2^- contaminated photoelectron spectrum

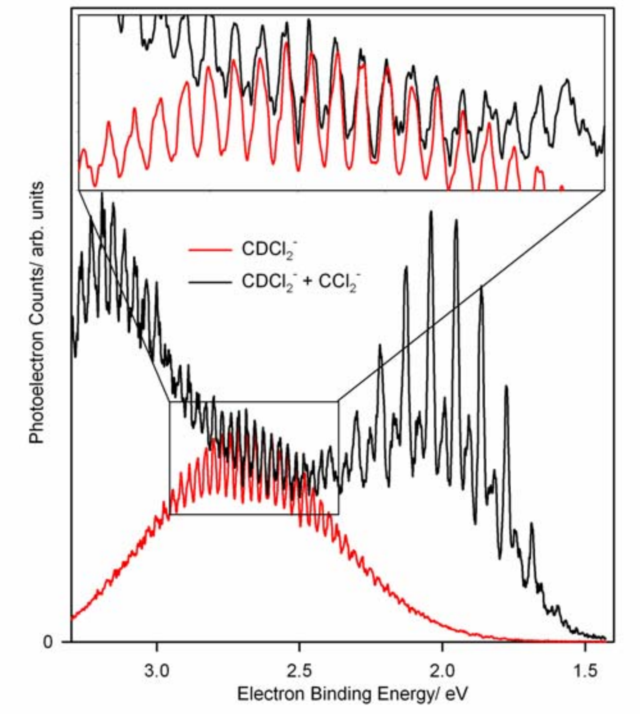

Fig S1 Expanded view of the overlapping spectral features in the contaminated CCl_2^- and the authentic $CDCl_2^-$ photoelectron spectra. The $CDCl_2^-$ spectrum was normalized to match the peak intensities of several common peaks in both spectra, which can be seen in the top portion of Fig. S1.

Expanded view of CCl_2^- $X\ ^1A_1$ photoelectron spectrum

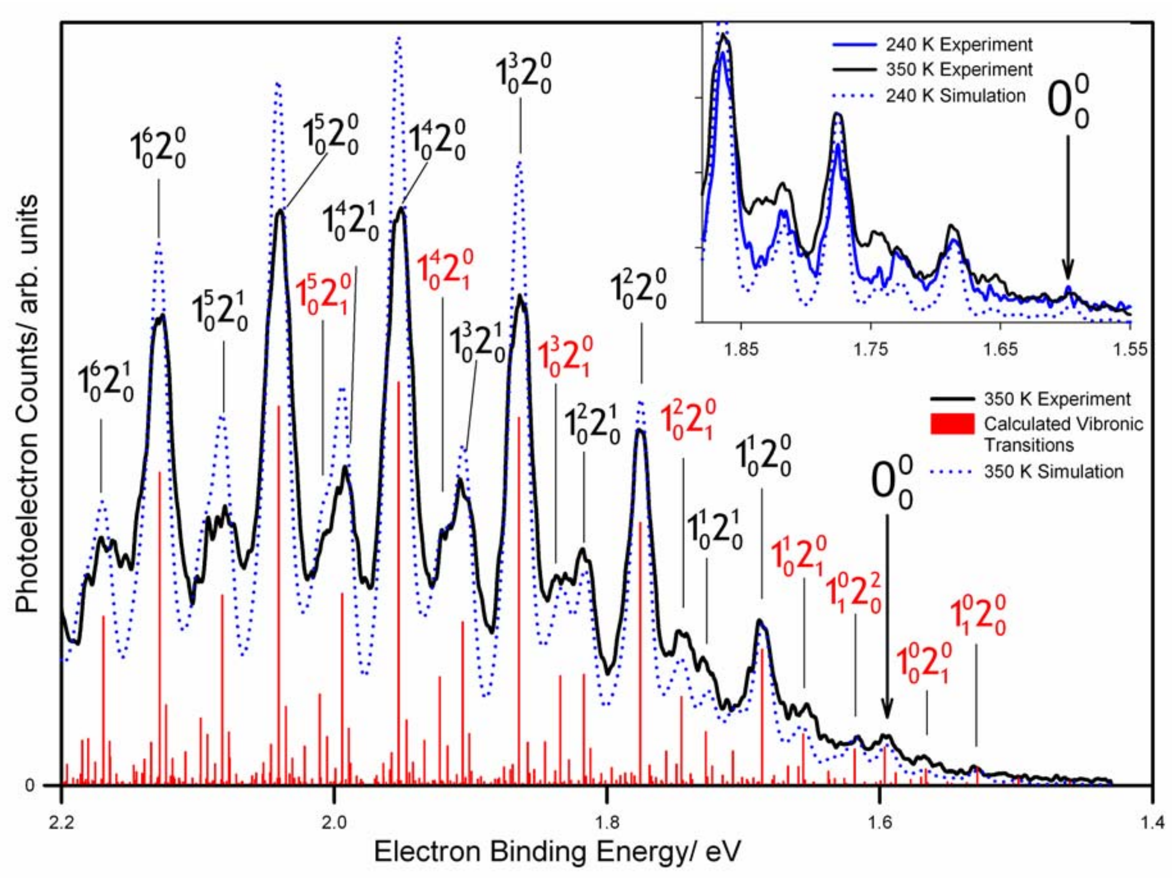

Fig. S2 Expanded view of $X\ ^1A_1$ CCl_2^-. All the resolved features are identified based on peak position, progression spacing, and agreement with the simulated spectrum. The inset is an expanded view of the cooled photoelectron spectrum with the corresponding simulation. The peak labels in red designate hot bands, and the solid arrows indicate the origin for $X\ ^1A_1$ CCl_2.

CBr_2^- photoelectron spectrum

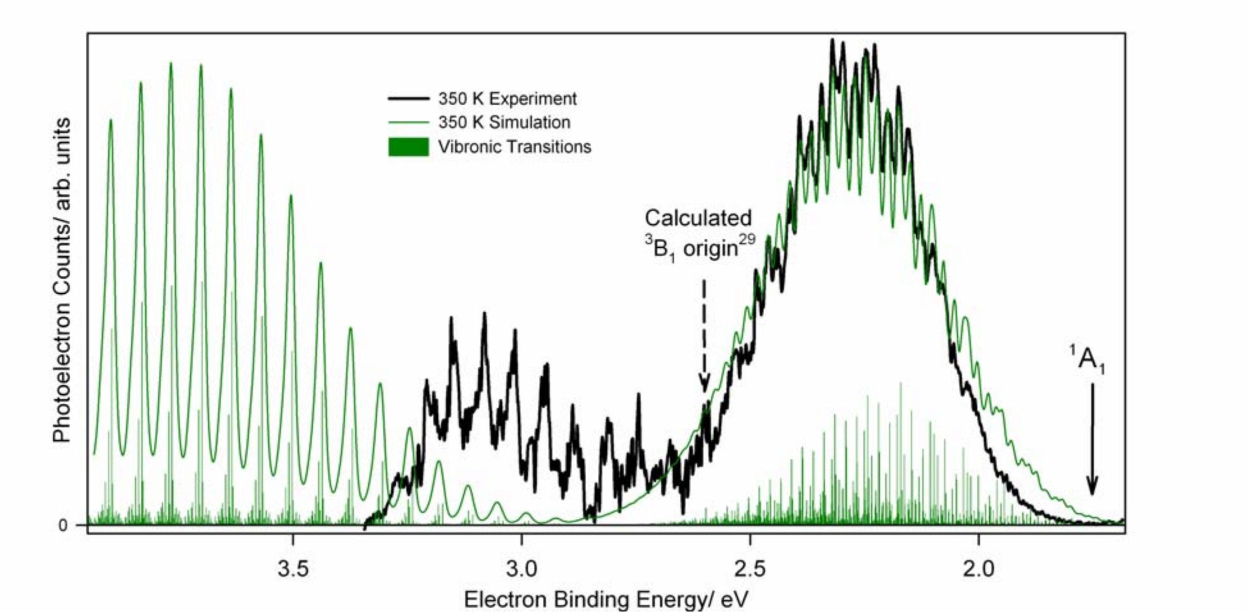

Fig. S3 Comparison of the best fit simulation and the corrected CBr_2^- spectrum, showing both the *a* $^3B_1$ and *X* $^1A_1$ states of CBr_2. The *a* $^3B_1$ state is simulated using the electron affinity and vibrational frequencies calculated by Dyke *et al.*[7] The Franck-Condon factors for both the singlet and triplet states are calculated in the Morse oscillator, parallel mode approximation using numerically integrated Laguerre polynomial wavefunctions.

References

[1] D. J. Clouthier and J. Karolczak, *J. Chem. Phys.*, 1991, **94**, 1.

[2] M. L. Liu, C. L. Lee, A. Bezant, G. Tarczay, R. J. Clark, T. A. Miller, and B. C. Chang, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1352.

[3] V. E. Bondybey, *J. Mol. Spec.*, 1977, **64**, 180.

[4] S. L. Xu and M. D. Harmony, *J. Phys. Chem.*, 1993, **97**, 7465.

[5] C. W. Bauschlicher, *J. Am. Chem. Soc.*, 1980, **102**, 5492.

[6] C. Tao, C. Mukarakate, and S. A. Reid, *J. Mol. Spec.*, 2007, **246**, 113.

[7] E. P. F. Lee, J. M. Dyke, and T. G. Wright, *Chem. Phys. Lett.*, 2000, **326**, 143.