

Supplementary Material

Optical frequency comb-based measurements and revisited assignment of high-resolution spectra of CH₂Br₂ in the 2960 to 3120 cm⁻¹ region

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- S1 PGOPHER input file (*see file "revisited_CH2Br2_linefit.pgo"*).
- S2 Measured absorption-cross section data by the two comb-based setups (*see files "Absorption_cross_section_FTS.txt" and "Absorption_cross_section_VIPA.txt"*).
- S3 Anharmonic vibrational frequencies of the CH₂⁸¹Br₂, and CH₂⁷⁹Br₂ isotopologues calculated at different model chemistries together with the estimated isotopic shifts (*this file*).
- S4 Anharmonic rotational constants of the three isotopologue of CH₂Br₂ in its vibrational ground $v(v = 0)$ and first excited state $v(v = 1)$ of v_4 and v_6 (*this file*).
- S5 Semi empirical rotational constants used as an input for the simulations of the twelve vibrational states of CH₂Br₂ in the C-H stretch region (*this file*).

S3: Anharmonic vibrational frequencies of the CH₂⁸¹Br₂ and CH₂⁷⁹Br₂ isotopologues of CH₂Br₂ calculated at different model chemistries together with the estimated isotopic shifts relative to their two mass unit isotopic shift. The available experimental data are included for comparison. All values are given in cm⁻¹.

		B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)	wB97X/def-2QZVPP	MP2/6-311++G(d,p)	Previous Experiments
v ₄	v(CH ₂ ⁸¹ Br ₂)	163.962	166.258	174.527	173.654	
	v(CH ₂ ⁷⁹ Br ₂)	165.886	168.218	176.549	175.69	
	Isotopic shift	1.924	1.96	2.022	2.036	
v ₈	v(CH ₂ ⁸¹ Br ₂)	1206.259	1202.001	1229.934	1238.769	1196.931 ^a
	v(CH ₂ ⁷⁹ Br ₂)	1206.313	1202.056	1230.004	1238.826	1196.983 ^a
	Isotopic shift	0.054	0.055	0.07	0.057	0.052 ^a
v ₁	v(CH ₂ ⁸¹ Br ₂)	3017.165	3001.021	3116.307	3041.905	
	v(CH ₂ ⁷⁹ Br ₂)	3017.167	3001.016	3116.302	3041.907	
	Isotopic shift	0.002	-0.005	-0.005	0.002	
v ₆	v(CH ₂ ⁸¹ Br ₂)	3083.714	3074.873	3178.094	3106.585	3076.731 ^b
	v(CH ₂ ⁷⁹ Br ₂)	3083.719	3074.868	3178.091	3106.585	3077.406 ^b
	Isotopic shift	0.005	-0.005	-0.003	0	0.675 ^b

^a: Experimental data of Brumfield et al.; ^b: Sadiek and Friedrichs

S4: Anharmonic rotational constants of the three isotopologue of CH₂Br₂ in its vibrational ground v(v = 0) and first excited state v(v = 1) of v₄ and v₆. All values are given in units of cm⁻¹ as calculated at the wB97X/Def2QZVPP

	v ₁ (v = 0)	v ₆ (v = 1)	Δ ₆ /10 ⁻⁶ ^a	v ₄ (v = 1)	Δ ₄ /10 ⁻⁶	v ₄₊₆ (v = 1)	Δ ₍₄₊₆₎ /10 ⁻⁶ ^a
CH ₂ ⁷⁹ Br ⁷⁹ Br							
A	0.883522	0.882879	643	0.887190	-3668	0.886546	-3024
B	0.041172	0.041193	-21	0.041155	17	0.041176	-4
C	0.039641	0.039660	-19	0.039621	20	0.039640	1
CH ₂ ⁷⁹ Br ⁸¹ Br							
A	0.882735	0.882093	642	0.886373	-3638	0.885731	-2996
B	0.040666	0.040686	-20	0.040649	17	0.040669	-3
C	0.039170	0.039189	-19	0.039150	20	0.039169	1
CH ₂ ⁸¹ Br ⁸¹ Br							
A	0.881945	0.881305	640	0.885554	-3609	0.884914	-2969
B	0.040160	0.040181	-21	0.040143	17	0.040164	-4
C	0.038699	0.038718	-19	0.038680	19	0.038699	0

^a Δ_i = X(v_i(v = 1)) - X(v_i(v = 0)) (with X = A, B, C).

S5: Semi empirical rotational constants used as an input for the simulations of the twelve vibrational states of CH₂Br₂ in the C-H stretch region. The v₆ fundamental band involve v₆(v = 1) ← v₆Exp(v = 0) transition and nv₄+n₆-nv₄ hot bands involve v₄₊₆(v = n) ← v₄(v = n), with n = 1-3.

	v _{Exp} (v = 0) ^a	v ₆ (v = 1) ^b	v ₄ (v = 1) ^b	v ₄ (v = 2) ^b	v ₄ (v = 3) ^b	v ₄₊₆ (v = 1) ^b	v ₄₊₆ (v = 2) ^b	v ₄₊₆ (v = 3) ^b
CH ₂ ⁷⁹ Br ⁷⁹ Br								
A	0.8683441	0.8677011	0.8720121	0.8756801	0.8793481	0.8713681	0.8750371	0.8787051
B	0.0413131	0.0413341	0.0412961	0.0412791	0.0412621	0.0413171	0.0413001	0.0412831
C	0.0397255	0.0397445	0.0397055	0.0396855	0.0396655	0.0397245	0.0397045	0.0396845
CH ₂ ⁷⁹ Br ⁸¹ Br								
A	0.8675192	0.8668772	0.8711572	0.8747952	0.8784332	0.8705152	0.8741532	0.8777912
B	0.0408047	0.0408247	0.0407877	0.0407707	0.0407537	0.0408077	0.0407907	0.0407737
C	0.0392537	0.0392727	0.0392337	0.0392137	0.0391937	0.0392527	0.0392327	0.0392127
CH ₂ ⁸¹ Br ⁸¹ Br								
A	0.8667564	0.8661164	0.8703654	0.8739744	0.8775834	0.8697254	0.8733344	0.8769434
B	0.0402973	0.0403183	0.0402803	0.0402633	0.0402463	0.0403013	0.0402843	0.0402673
C	0.0387823	0.0388013	0.0387633	0.0387443	0.0387253	0.0387823	0.0387633	0.0387443

^a Vibrational ground state data of Niide et al.

^b X(v_i(v = n)) = X_{Exp}((v = 0)) + nΔ_i(v = n) (with X = A, B, C, and n = 1-3).