IMPROVED SPECTROSCOPIC ANALYSIS FOR THE $A\,^3\Pi_{1u} - X\,^1\Sigma_g^+$ SYSTEM OF Br_2

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Our Research

- $A - X$ system of ICl$^{(1)}$, IBr$^{(2),(4)}$, $I_2^{(3)}$ and $Br_2^{(5)}$ have been studied.
- In order to establish a frequency standard, the line positions of these spectra were determined.
- Spectroscopic constants of A and X-state were calculated.

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(2) Nishimiya et al., "Laser Spectroscopy of the $A^3\Pi_1 - X^1\Sigma^+$ System of IBr", JMS, 173,8(1995).

(3) T. Yukiya et al., "High-Resolution Laser Spectroscopy of the $A^3\Pi_{1u} - X^1\Sigma_g^+$ System of I2 with Ti: Sapphire Ring Laser", JMS, 182, 271(1997).

(4) T. Yukiya et al., "High-Resolution Laser Spectroscopy of the $A^3\Pi_1 - X^1\Sigma^+$ System of IBr with a Titanium:Sapphire Ring Laser", JMS, 214, 132(2002)

(5) Nishimiya et al., "High-Resolution Laser Spectroscopy of $A^3\Pi_{1u} - X^1\Sigma_g^+$ of Br_2", OHIO Columnbus Meeting (2004).

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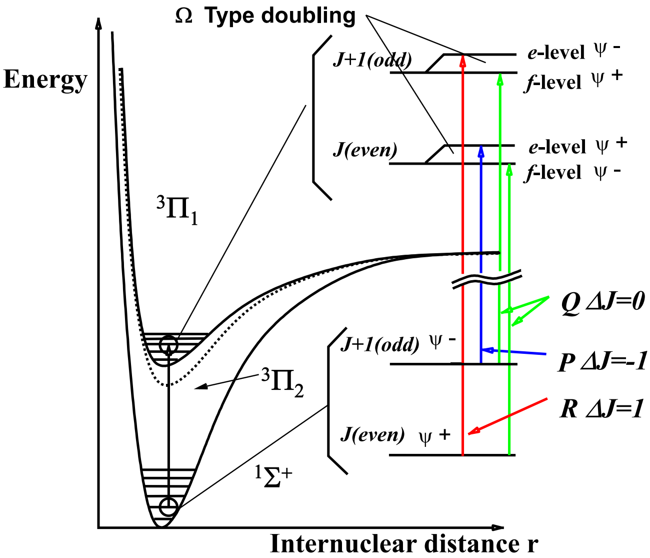
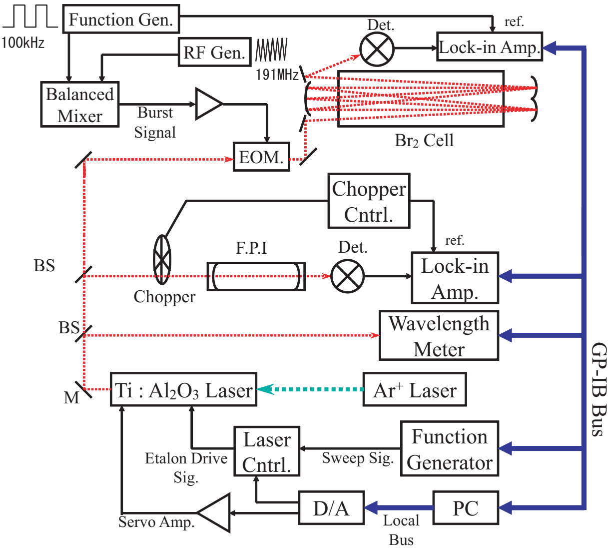
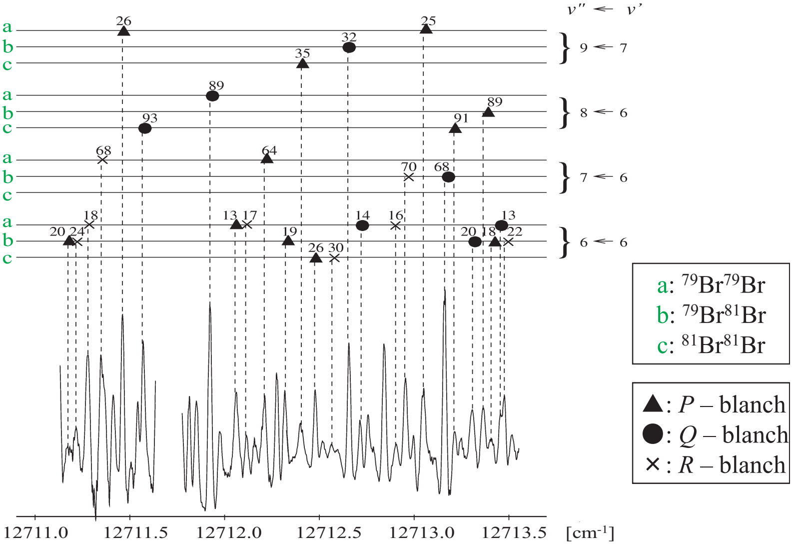
Energy of $A-X$ System



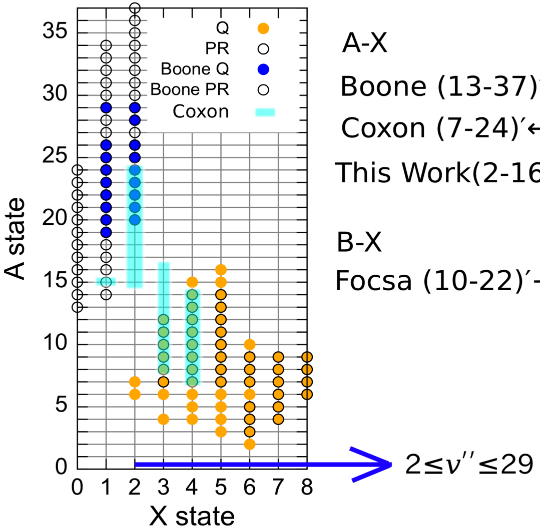
System Block Diagram



Example of Br_2 Spectrum



Assigned Bands



A-X

Boone $(13\text{-}37)' \leftarrow (0\text{-}2)''$

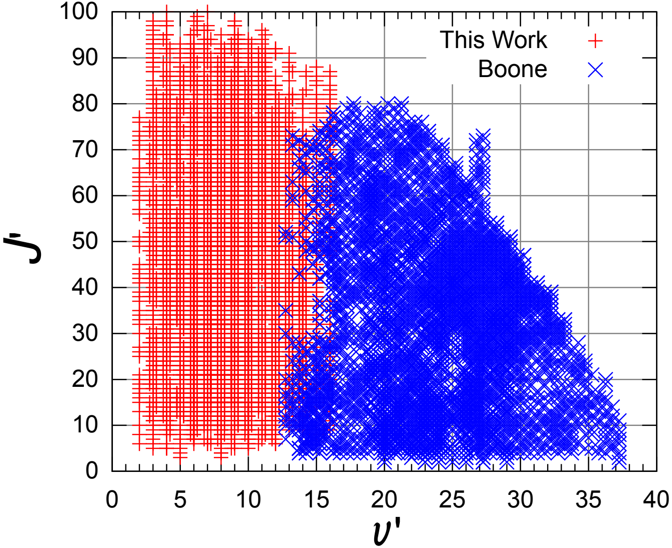
Coxon $(7\text{-}24)' \leftarrow (1\text{-}4)''$

This Work$(2\text{-}16)' \leftarrow (2\text{-}8)''$

B-X

Focsa $(10\text{-}22)' - (2\text{-}29)''$

Assigned Line Quantum Number of A-state



Ro-vibrational Energy

The rotational and vibrational energies of lines are obtained by the equation:

$$\begin{aligned} \nu(v', J'; v'', J'') &= T_{v'} + B_{v'}^{e/f}\{J'(J'+1) - \Lambda^2\} \\ &- D_{v'}\{J'(J'+1) - \Lambda^2\}^2 \\ &+ H_{v'}\{J'(J'+1) - \Lambda^2\}^3 \\ &- \sum_{l=1} \sum_{m=0} Y''_{l,m} \left(v'' + \frac{1}{2}\right)^l \{J''(J''+1)\}^m \end{aligned} \quad (1)$$

Spectroscopic Constants of $^{79,79}Br_2$ in the A-state

v'	T'_v	B'_v	$q'_v \times 10^5$	$D'_v \times 10^7$	$H'_v \times 10^{11}$
13	15453.760 (12)	0.045325 (42)		-1.33 (19)	-0.20 (23)
14	15521.1280(31)	0.043765 (12)		-1.560(67)	-0.190(95)
15	15581.5970(28)	0.0421330(86)		-1.731(45)	-0.240(60)
16	15635.6660(30)	0.0404762(55)		-1.837(24)	-0.340(28)
17	15684.0030(33)	0.0388558(59)		-1.966(26)	-0.370(31)
18	15727.3690(36)	0.0372876(63)		-2.063(27)	-0.410(31)
19	15766.4610(30)	0.0357611(55)	5.60(15)	-2.155(23)	-0.460(27)
20	15801.8810(25)	0.0343216(45)	5.60(27)	-2.235(20)	-0.550(24)
21	15834.0910(24)	0.0329272(46)	5.60(44)	-2.309(19)	-0.690(22)
22	15863.4350(25)	0.0315704(50)	5.90(38)	-2.432(22)	-0.830(27)
23	15890.1726(24)	0.0302285(48)	5.90(28)	-2.557(23)	-1.050(30)
24	15914.4858(25)	0.0288958(52)	5.80(23)	-2.734(28)	-1.310(40)

in cm^{-1} and σ in parentheses

Spectroscopic Constants of $^{79,79}Br_2$ in the A-state - continued

v'	T'_v	B'_v	$q'_v \times 10^5$	$D'_v \times 10^7$	$H'_v \times 10^{11}$
25	15936.5210(48)	0.0275507(83)	5.60(34)	-2.938(43)	-1.660(65)
26	15956.3814(25)	0.0261880(63)	5.60(30)	-3.204(41)	-2.120(74)
27	15974.1603(20)	0.0247140(39)		-2.617(21)	-4.510(30)
28	15989.9010(35)	0.023364 (11)	5.50(100)	-3.930(81)	-3.60 (19)
29	16003.7040(37)	0.021876 (12)	5.70(54)	-4.36 (11)	-5.00 (27)
30	16015.6290(41)	0.020349 (16)		-4.78 (17)	-7.30 (51)
31	16025.7480(54)	0.018746 (31)		-5.51 (42)	-10.00 (160)
32	16034.1430(58)	0.017084 (35)		-6.34 (51)	-15.00 (210)
33	16040.9340(66)	0.015357 (56)		-7.50 (110)	-22.00 (630)
34	16046.2420(54)	0.013714 (34)		-13.30 (44)	
35	16050.236 (11)	0.011850 (80)		-16.00 (130)	
36	16053.0900(68)	0.009910 (85)		-19.00 (200)	
37	16054.987 (12)	0.00790 (31)		-20.0 (170)	

in cm^{-1} and σ in parentheses

Spectroscopic Constants of $^{79,81}Br_2$ in the A-state

v'	T'_v	B'_v	$q'_v \times 10^5$	$D'_v \times 10^7$	$H'_v \times 10^{11}$
2	14269.3310(38)	0.0560757(59)		-0.396 (24)	-0.010 (28)
3	14405.2524(23)	0.0553766(20)	1.270(41)	-0.4244(55)	-0.0120(41)
4	14536.1434(21)	0.0546292(15)	1.360(28)	-0.4546(42)	-0.0170(31)
5	14661.7889(21)	0.0538367(18)	1.500(30)	-0.4950(55)	-0.0210(47)
6	14781.9491(19)	0.0529907(13)	1.590(24)	-0.5430(37)	-0.0260(28)
7	14896.3779(19)	0.0520821(12)	1.710(21)	-0.5921(35)	-0.0420(27)
8	15004.8100(19)	0.0511055(13)	1.820(19)	-0.6645(38)	-0.0470(31)
9	15106.9630(19)	0.0500518(12)	2.010(18)	-0.7480(34)	-0.0650(25)
10	15202.5624(20)	0.0489104(15)	2.250(23)	-0.8518(46)	-0.0850(37)
11	15291.3646(21)	0.0476600(16)	2.560(22)	-0.9470(46)	-0.1350(36)
12	15373.1453(21)	0.0463185(18)	2.740(35)	-1.1010(56)	-0.1670(49)
13	15447.7965(24)	0.0448716(23)	3.220(34)	-1.2590(71)	-0.2200(62)
14	15515.3607(27)	0.0433337(29)	3.570(42)	-1.4290(96)	-0.2760(90)
15	15576.0740(40)	0.0417178(44)		-1.606 (14)	-0.320 (12)
16	15630.4050(39)	0.0400988(50)		-1.768 (16)	-0.350 (14)

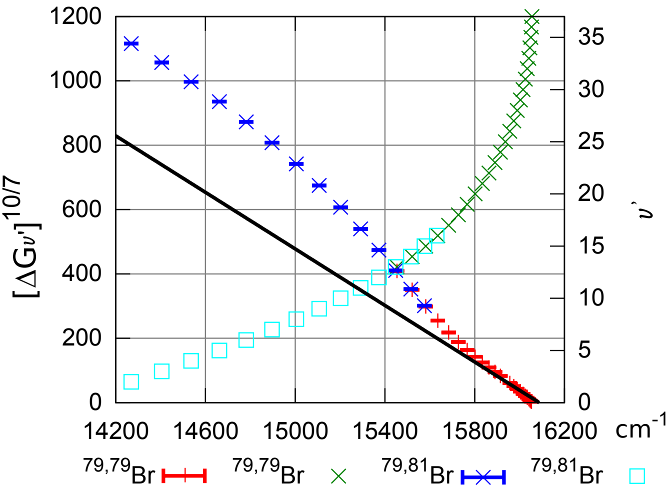
in cm^{-1} and σ in parentheses

Dunham Coefficients for the X-state of $^{79,79}Br_2$

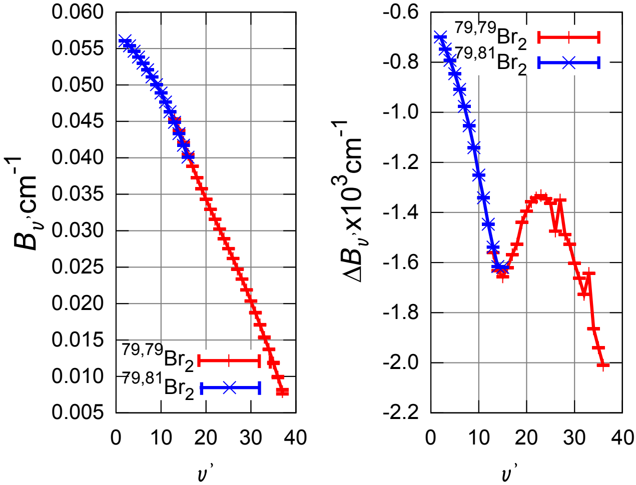
Y-parametesr for the X-state			
$Y''_{1,0}$	3.253167(11)×10^{2}	$Y''_{3,1}$	8.000(12)×10^{-10}
$Y''_{2,0}$	-1.07937(34)	$Y''_{4,1}$	-4.0(26)×10^{-10}
$Y''_{3,0}$	-1.929(49)×10^{-3}	$Y''_{0,2}$	-2.083(45)×10^{-8}
$Y''_{4,0}$	-1.83(36)×10^{-5}	$Y''_{1,2}$	-1.7(28)×10^{-10}
$Y''_{5,0}$	-1.0(12)×10^{-7}	$Y''_{2,2}$	1.3(50)×10^{-11}
$Y''_{6,0}$	-3.0(16)×10^{-9}	$Y''_{3,2}$	-1.0(34)×10^{-12}
$Y''_{0,1}$	8.21077(17)×10^{-2}	$Y''_{4,2}$	2.0(76)×10^{-14}
$Y''_{1,1}$	-3.198(10)×10^{-4}	$Y''_{0,3}$	-4.0(320)×10^{-15}
$Y''_{2,1}$	-9.1(18)×10^{-7}		

LeRoy-Bernstein Plot

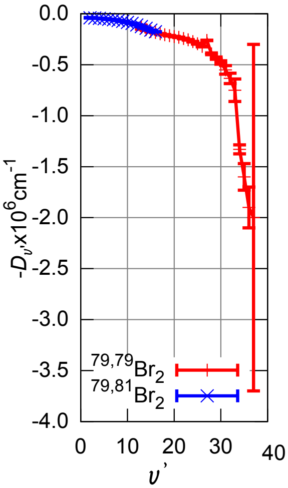
LeRoy-Bernstein

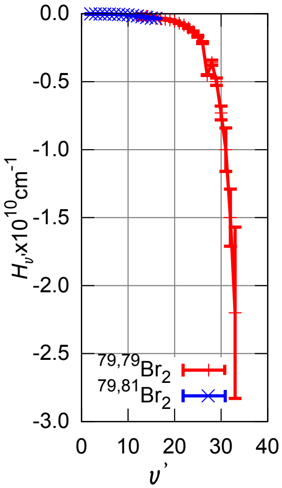


Dependence of $B_{\upsilon'}$ and $\Delta B_{\upsilon'}$ on υ in $^{79,79}Br_2$ and $^{79,81}Br_2$

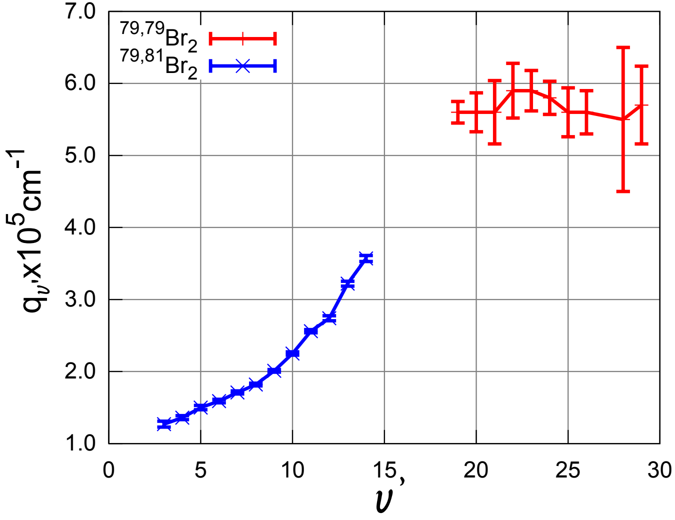


Dependence of $D_{\upsilon'}$ and $H_{\upsilon'}$ on υ in $^{79,79}Br_2$ and $^{79,81}Br_2$





Dependence of $q_{\upsilon'}$ on υ in $^{79,79}Br_2$ and $^{79,81}Br_2$



Potential Equations

$$V_{\mathrm{MLR}}(r) = \mathcal{D}_e \left\{1 - \frac{\mu_{\mathrm{LR}}(r)}{\mu_{\mathrm{LR}}(r_e)} \mathrm{e}^{-\beta(r)\cdot y_p(r,r_e)}\right\}^2$$

$$\mu_{\mathrm{LR}}(r) = C_{m1}/r^{m1} + C_{m2}/r^{m2} + \cdots$$

$$\beta(r) = \beta_{\mathrm{MLR}}(y_p(r,r_{ref})) = y_p(r,r_{ref})\beta_\infty + [1 - y_p(r,r_{ref})] \sum_{i=0}^{N_S,N_L} \beta_i y_p(r,r_{ref})^i$$

$$y_p = y_p(r,r_{ref}) = \frac{r^p - {r_{ref}}^p}{r^p + {r_{ref}}^p}$$

X-state		
C5 cm^{-1}Å^5:	-3.20	$\times 10^2$
C6 cm^{-1}Å^6:	6.37	$\times 10^5$
C8 cm^{-1}Å^8:	1.55	$\times 10^7$
A-state		
C5 cm^{-1}Å^5:	2.70	$\times 10^2$
C6 cm^{-1}Å^6:	6.32	$\times 10^5$
C8 cm^{-1}Å^8:	1.55	$\times 10^7$

All parameters are from M. Saute (Mol. Phys., 51, 1459(1984).

Born–Oppenheimer Breakdown Correction Functions

$$\left\{-\frac{\hbar^2}{2\mu_\alpha}\frac{d^2}{dr^2} + [V_{CN}(r) + \Delta V^{(\alpha)}_{ad,W}(r)] + \frac{\hbar^2[J(J+1)-\Lambda^2]}{2\mu_\alpha r^2}[1 + g^{(\alpha)}_W(r)]\right\}\psi_{v,J}(r) = E_{v,J}\psi_{v,J}(r)$$

$$\Delta V^{(\alpha)}_{ad,W}(r) = \frac{m_e}{M^\alpha_A}\tilde{S}^A_{ad,W}(r) + \frac{m_e}{M^\alpha_B}\tilde{S}^A_{ad,W}(r)$$

$$g^{(\alpha)}_W(r) = \frac{m_e}{M^\alpha_A}\tilde{R}^A_{na,W}(r) + \frac{m_e}{M^\alpha_B}\tilde{R}^A_{na,W}(r)$$

$$\tilde{S}^A_{ad,W}(r) = [1 - y_q(r, r_{ref})]\sum_{i=0}\mu^A_i yq_{ad}(r, r_{ref})^i + \mu^A_\infty yp_{ad}(r, r_{ref})$$

$$\tilde{R}^A_{na,W}(r) = [1 - y_p(r, r_{ref})]\sum_{i=0} t^A_i yq_{na}(r, r_{r_e})^i + t^A_\infty yp_{na}(r, r_e)$$

Λ–Doubling for the *A* state

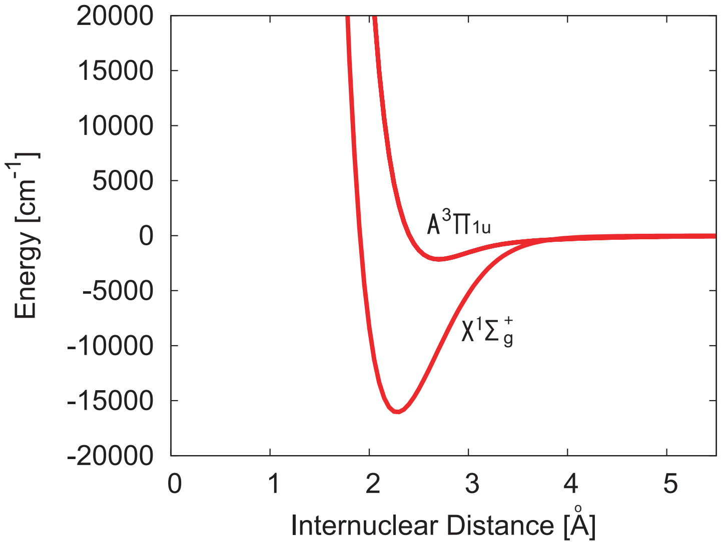
$$\left\{-\frac{\hbar^2}{2\mu_\alpha}\frac{d^2}{dr^2} + [V^1_{ad}(r) + \Delta V^{(\alpha)}_{ad}(r)] + \frac{\hbar^2[J(J+1)-\Lambda^2]}{2\mu_\alpha r^2}[1+g^{(\alpha)}(r)]\right.$$

$$\left. + s\, g_\Lambda(e/f)\Delta V^{(\alpha)}_\Lambda(r)[J(J+1)]^\Lambda\right\}\psi_{v,J}(r) = E_{v,J}\psi_{v,J}(r)$$

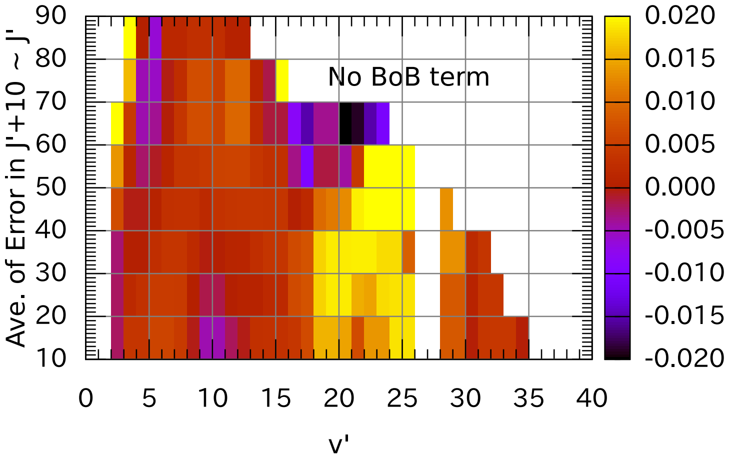
$$\Delta V^{(\alpha)}_\Lambda(r) = \left(\frac{\hbar^2}{2\mu_\alpha r^2}\right)^{2\Lambda} f_\Lambda(r)$$

$$f_\Lambda(r) = [1 - y_p(r, r_e)]\sum_{i=0} w_i^A yp(r, r_{r_e})^i + w_\infty^A yp(r, r_e)$$

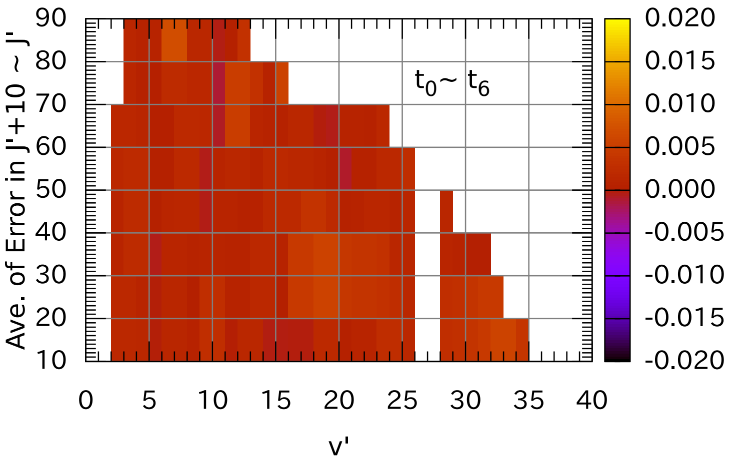
MLR Potentials for Br_2



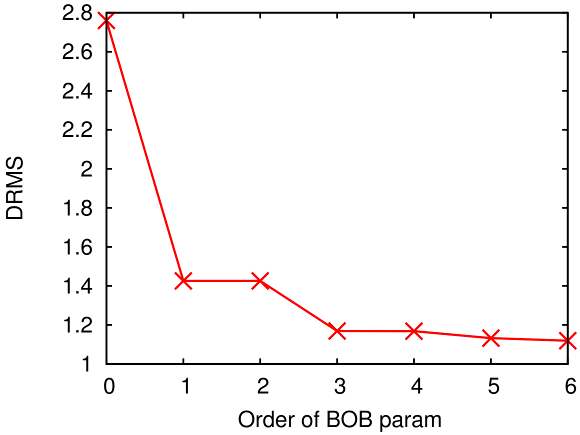
Error Map of Calculated Line Positions without BOB



Error Map of Calculated Line Positions with BOB



DRMS Changing for Order of BOB



Parameters of MLR potential

	Without BOB	
	X-state	A-state
$\mathcal{D}_e$ cm^{-1}	1.6056930(17)$\times 10^4$	2.14814(23)$\times 10^3$
r_e Å	2.2810513(20)	2.703341(46))
C_5 cm^{-1}Å^5	-3.30$\times 10^2$	3.20$\times 10^4$
C_6 cm^{-1}Å^6	6.274$\times 10^5$	6.370$\times 10^5$
C_8 cm^{-1}Å^8	1.550$\times 10^7$	1.550$\times 10^7$
β_0	0.791817	0.69237
β_1	0.8494	-0.6607
β_2	4.5933	0.1209
β_3	9.188	0.3429
β_4	10.84	-0.757
β_5	7.08	1.22
β_6	2.09	-5.20
β_7		2.85
β_9		-16.3
β_{10}		-42.2
β_{11}		22.0
β_{12}		44.6
β_{13}		-10.1
β_{14}		-20.2
β_∞	1.744098	0.3614602
$C_9(eff)$	5.710675$\times 10^5$	5.710675$\times 10^5$
u_0	1.238	
	$N = 6,\ R_{ref} = 2.8$	$N = 14,\ p = q = 5,\ R_{ref} = 4.0$

DMRS = 2.76032

Parameters of MLR potential with BOB

with BOB				
	X-state	A-state		
T_e cm^{-1}		1.39088290×10^4		
$\mathcal{D}_e$ cm^{-1}	1.605683(39)×10^4	2.14801×10^3		
r_e Å	2.28102640(83)	2.702)		
C_5 cm^{-1}Å^5	-3.30×10^2	2.65×10^4		
C_6 cm^{-1}Å^6	6.274×10^5	6.370×10^5		
C_8 cm^{-1}Å^8	1.550×10^7	1.550×10^7		
β_0	0.791925	0.680218	t_0	5.8(57)×10^{-4}
β_1	0.85357	-0.68389	t_1	-1.41(80)×10^{-3}
β_2	4.6088	0.0929	t_2	6.6(23)×10^{-2}
β_3	9.219	0.3091	t_3	-0.29(13)
β_4	10.96	-0.9675	t_4	0.77(28)
β_5	7.25	1.299	t_5	-0.96(29)
β_6	2.000	-3.193	t_6	0.48(11)
β_7		2.268	ω_0	1.964(58) ×10^{-3}
β_8		12.127	ω_1	-0.196(15)
β_9		-16.27	ω_2	-0.1036(18)
β_{10}		-18.456	ω_3	0.280(41)
β_{11}		24.17	ω_∞	0.1171(16)
β_{12}		15.62		
β_{13}		-12.5		
β_{14}		-6.7		
β_∞	1.744052	0.36907150		
$C_9(eff)$	5.753939×10^5			
$C_{10}(eff)$		2.2449986×10^7		
	$N = 6,\ R_{ref} = 2.8$	$N = 14,\ p = q = 5,\ R_{ref} = 4.0$		

DRMS = **1.11910**

Conclusion

- Spectra in the new bands were measured and assigned.
- The spectroscopic constants of each bands were determined with merged data.
- Denpendence of B_v, q_v, D_v, H_v on v number was checked.
- BOB effect of line positions were verified.
- MLR potential was determined in the case with BOB and without BOB.