

HIGH RESOLUTION LASER SPECTROSCOPY FOR ABSORPTION TO LEVELS LYING NEAR THE DISSOCIATION LIMIT OF THE $A^3\Pi_1$ STATE OF IBr

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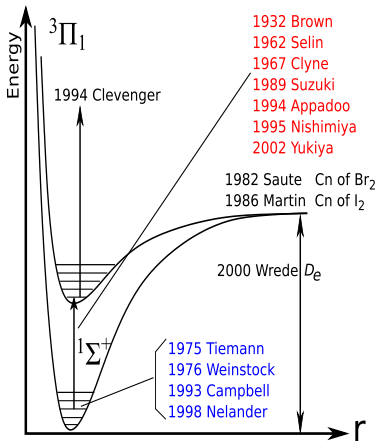
Jun. 22, 2015

Our Objectives

- Define frequency standards based on the $A-X$ transition of IBr
- Determine reliable spectroscopic constants for calculation of line positions
- Provide realistic predictions for the unobserved levels of IBr
- Obtain accurate analytic potential energy functions for the A and X state

References

the A – X system



- 1932 W.G. Brown, "Absorption Spectrum of Iodine Bromide"
- 1962 L.E.Selin, "Analysis of the absorption spectrum of IBr "
- 1967 M.A.A.CLYNE AND J.A.COXON, "The Emission Spectra of Br and IBr Formed in Atomic Recombination Processes"
- 1994 D. R. T. Appadoo, P. F. Bernath, Robert J. Le Roy , "High-resolution visible spectrum for the $A^3\Pi_1 \leftarrow X^1\Sigma^+$ system of IBr"
- 1995 N. Nishimiya , T .Yukiya and M .Suzuki, "Laser Spectroscopy of the $A^3\Pi_1 \leftarrow X^1\Sigma^+$ System of IBr"
- 2002 T. Yukiya, N. Nishimiya and M. Suzuki , "High-Resolution Laser Spectroscopy of the $A^3\Pi_1 \leftarrow X^1\Sigma^+$ System of IBr with a Titanium:Sapphire Ring Laser"

References

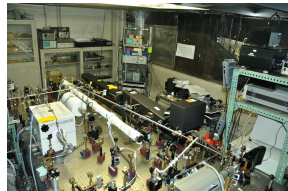
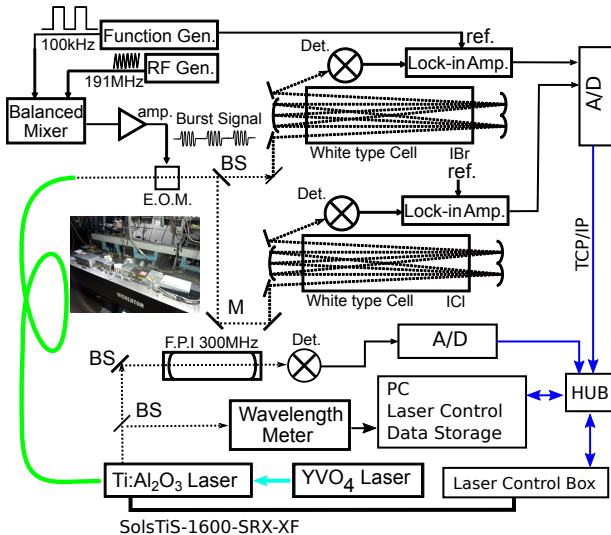
Data and Parameters

- 1976 E. M. Weinstock , "The laser-induced fluorescence of IBr"⁷⁹
- 1982 M. Saute, M. Aubert-Frécon, "Calculated long-range potential-energy curves for the 23 molecular states of I₂"
- 1986 F. Martin, R. Bacis, S. Churassy, J. Vergès, "Laser-induced-fluorescence Fourier transform spectrometry of the $X0_g^+$ state of I₂: Extensive analysis of the $B0_u^+ \rightarrow X0_g^+$ fluorescence spectrum of $^{127}\text{I}_2$ "
- 1993 J. M. Campbell, P. F. Bernath, "Vibration-rotation spectrum of iodine monobromide"
- 1994 J.O.Clevenger, Q.P.Ray, J.Tellinghuisen, X.Zheng and M.C.Heaven , "Spectroscopy of metastable species in a free-jet expansion: the $\beta \leftarrow A$ transition in IBr"
- 1994 D. R. T. Appadoo, P. F. Bernath, Robert J. Le Roy , "High-resolution visible spectrum for the $A^3\Pi_1 \leftarrow X^1\Sigma^+$ system of IBr"
- 1998 B. Nelander, V. Sablinskas, M. Dulick, V.Braun and P. F. Bernath, "High resolution far infrared spectroscopy of IBr using a synchrotron source"
- 2000 E. Wrede, S. Laubach, S. Schulenburg, A. J. Orr-Ewing, M. N. R. Ashfold, Velocity map imaging of the near-threshold photodissociation of IBr: accurate determination of $D_e(\text{I-Br})$

Hyperfine Structure

- 1975 E.Tiemann and Th.Möller, "Rotational Spectrum of IBr"
- 1992 F. Biraben, D. Jasmin, L. Julien, F. Nez and J. Vigué "Hyperfine Structure of the $A^3\Pi_1$ state of IBr"
- 1993 C. M. Western, T. J. Slotterback, J. R. Johnson, D. W. Pratt and K. C. Janda "Variation of the electronic wave function with internuclear separation: High-resolution spectroscopy of the $A^3\Pi_1$ state of ^{35}Cl near the dissociation limit"
- 1994 N. Nishimiya, T. Yukiya, M. Suzuki "Nuclear Quadrupole Coupling Effect in the $A \leftarrow X$ System and Spectroscopic Constants for $v = 2, \leftarrow 4, 3, \leftarrow 5, \text{ and } 4, \leftarrow 5$ Progressions of ICl"

Experimental system



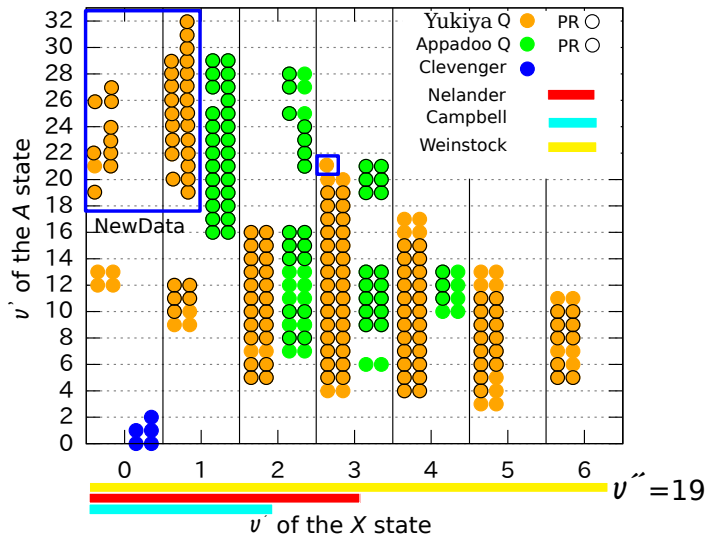
Laser:
SolsTiS-1600-SRX-XF
(M Squared Lasers)

Wavelength meter:
WS6-200
(HighFiness)

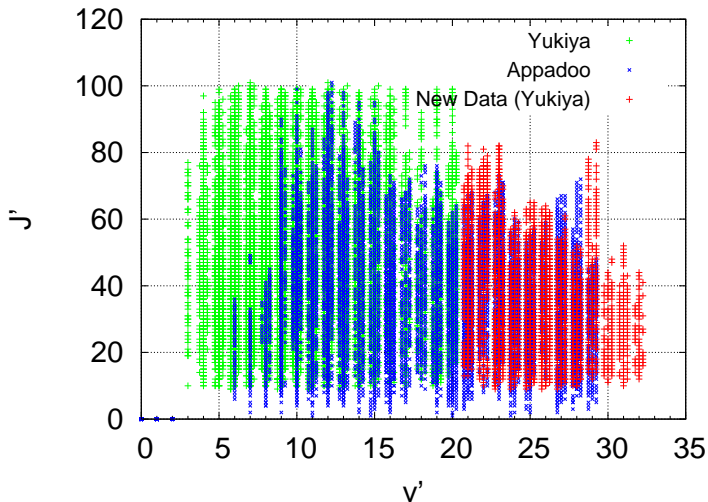
Path length:
12m

Pressure:
Saturated Vapor Pressure at
Room Temperature

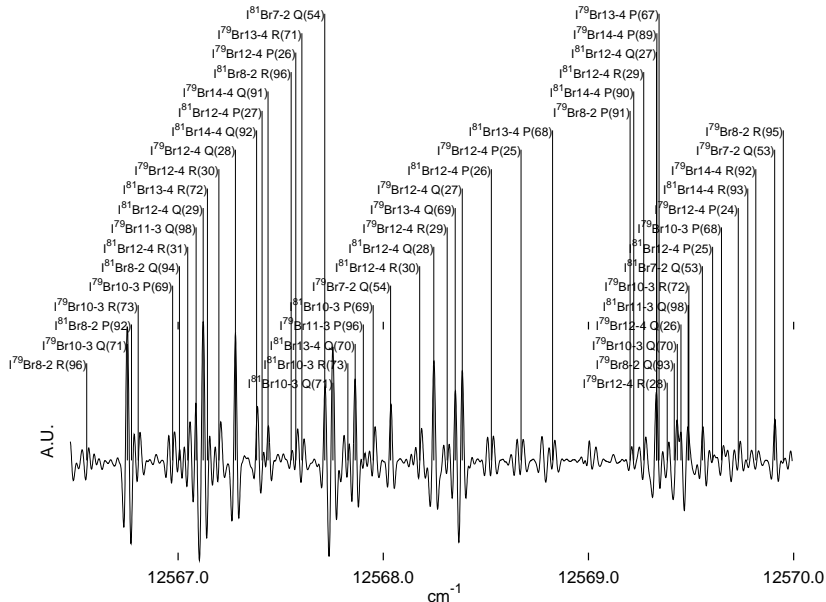
Observed Band System of $I^{79/81}Br$



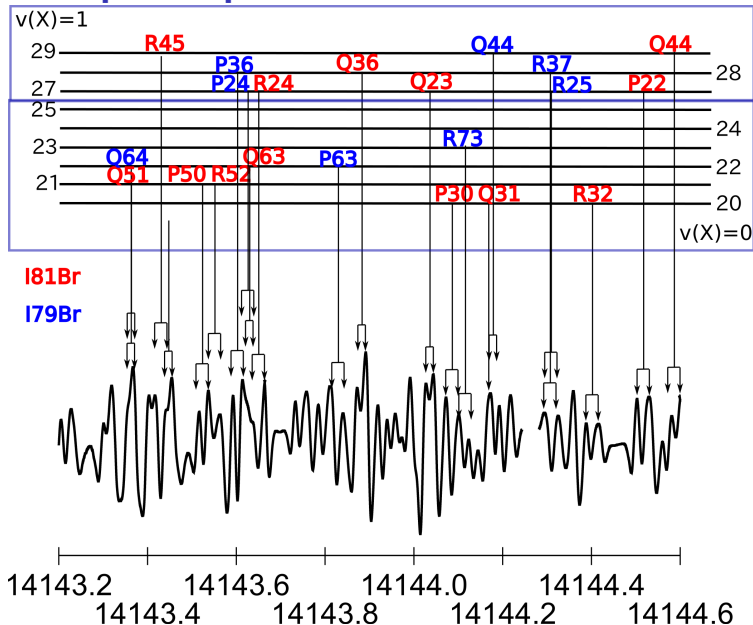
Rotational levels assigned for the A state.



Absorption Spectrum of IBr near 12568 cm^{-1}



Absorption Spectrum of IBr near 14144 cm^{-1}



Hyperfine Structure of the A – X System

$$E_{HF}^{e/f}(A) = \left(\frac{a(I)}{2} \right) \frac{C(J, I_1, F_1)}{J(J+1)} + \left(\frac{a(\text{Br})}{2} \right) \frac{C(J, I_2, F_2)}{J(J+1)} + W^{e/f}(v_a; J, I_1, F_1, F) \quad (1)$$

$$\begin{aligned} W^{e/f}(v_a; J, I_1, F_1, F) &= W_1^{e/f}(v_a; J, I_1, F_1) + W_1^{e/f}(v_a; I_2, F_2) \\ &= Y(J, I_1, F_1) \left[-eQq'_0(\text{I}) \left\{ 1 - \frac{3}{J(J+1)} \right\} \pm \left(\frac{1}{2} \right) eQq'_2(\text{I}) \right] \\ &\quad + Y(J, I_2, F_2) \left[-eQq'_0(\text{Br}) \left\{ 1 - \frac{3}{J(J+1)} \right\} \pm \left(\frac{1}{2} \right) eQq'_2(\text{Br}) \right] \end{aligned} \quad (2)$$

$$E_{HF}(X) = -eQq''_0(\text{I})Y(J, I_1, F_1) - eQq''_0(\text{Br})Y(J, I_2, F_2) \quad (3)$$

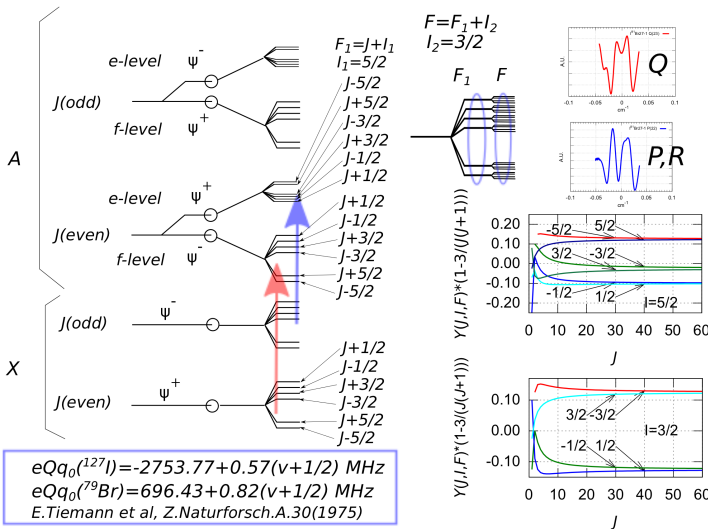
$$F_1 = J + I_1, F_2 = J + I_2, F = F_1 + I_2 \quad (4)$$

Casimir Function:

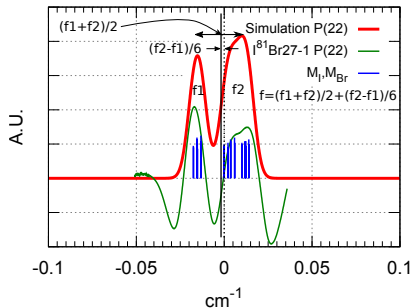
$$Y(J, I, F) = \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)} \quad (5)$$

$$C(J, I, F) = F(F+1) - I(I+1) - J(J+1) \quad (6)$$

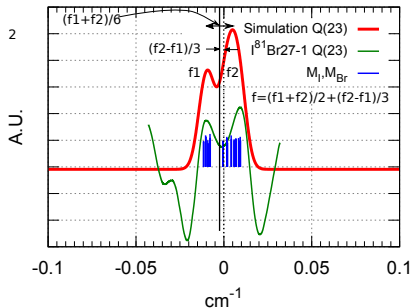
Hyperfine Structure of the A – X System



Simulation of Line Profiles of the A – X System



$I^{81}Br\ 27 \leftarrow 1\ P22$



$I^{81}Br\ 27 \leftarrow 1\ Q23$

	X state		A state		
$eQq_0''(I)$	-0.0918469	$eQq_0'(I)$	0.008	$\frac{a(I)}{2} \frac{C(J,I_1,F_1)}{J(J+1)}$	~ 0.0
$eQq_0''(Br)$	0.0194037569	$eQq_0'(Br)$	0.01	$\frac{a(Br)}{2} \frac{C(J,I_2,F_2)}{J(J+1)}$	~ 0.0
		$eQq_2'(I)$	-0.045		
		$eQq_2'(Br)$	-0.001		

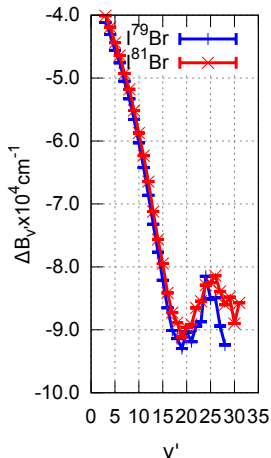
in cm^{-1}

Bands constants of the A state

The Band Constants for the A State of $I^{79}Br$

v'	T_v'	B_v'	$q_v' \times 10^5$	$D_v' \times 10^7$	$H_v' \times 10^{11}$
3	12821.6070 (63)	0.0408630(97)		-0.195 (39)	0.000 (44)
4	12943.1777 (23)	0.0404513(27)	0.290(55)	-0.2050(85)	-0.0050(74)
5	13061.1858 (15)	0.0400206(17)	0.430(30)	-0.2183(49)	-0.0050(37)
6	13175.5142 (11)	0.0395647(14)	0.490(25)	-0.2277(39)	-0.0080(29)
7	13286.0096 (11)	0.0390890(14)	0.530(30)	-0.2476(38)	-0.0070(29)
8	13392.5331 (10)	0.0385841(13)	0.550(21)	-0.2645(37)	-0.0100(29)
9	13494.9272 (10)	0.0380512(11)	0.580(18)	-0.2886(30)	-0.0110(22)
10	13593.0308 (11)	0.0374855(11)	0.640(19)	-0.3158(32)	-0.0130(24)
11	13686.68470(98)	0.0368827(11)	0.670(19)	-0.3473(31)	-0.0150(23)
12	13775.7277 (10)	0.0362405(11)	0.750(19)	-0.3846(30)	-0.0180(22)
13	13860.00360(99)	0.0355543(11)	0.770(21)	-0.4213(32)	-0.0270(24)
14	13939.3800 (13)	0.0348221(15)	0.930(28)	-0.4666(41)	-0.0330(31)
15	14013.7552 (13)	0.0340455(15)	1.000(25)	-0.5212(41)	-0.0410(31)
16	14083.0736 (12)	0.0332243(15)	1.110(27)	-0.5835(42)	-0.0480(32)
17	14147.3464 (20)	0.0323593(24)	1.280(56)	-0.6420(70)	-0.0610(52)
18	14206.6730 (27)	0.0314582(36)	1.440(62)	-0.686 (13)	-0.090 (12)
19	14261.2329 (16)	0.0305442(22)	1.170(64)	-0.7630(69)	-0.0850(55)
20	14311.3247 (13)	0.0296145(18)	1.410(58)	-0.8200(53)	-0.0920(41)
21	14357.2652 (29)	0.0287110(42)	1.820(76)	-0.953 (16)	-0.010 (17)
22	14399.4522 (36)	0.0277921(51)	1.810(61)	-0.935 (20)	-0.100 (22)
23	14438.2590 (35)	0.0268982(57)	2.30 (14)	-0.942 (22)	-0.150 (23)
24	14474.0440 (49)	0.026011 (13)	1.80 (21)	-0.830 (97)	-0.50 (20)
25	14507.0540 (43)	0.0251960(97)	2.00 (13)	-1.065 (55)	-0.160 (87)
26	14537.5910 (52)	0.024345 (14)	2.00 (14)	-0.98 (11)	-0.70 (24)
27	14565.8110 (62)	0.023496 (27)	1.20 (29)	-0.98 (30)	-2.00 (97)
28	14591.8720 (84)	0.022602 (35)	1.10 (33)	-0.80 (41)	-6.90 (140)
29	14615.8820 (91)	0.021678 (33)	0.60 (31)	-1.50 (33)	-11.90 (98)

in cm^{-1} and σ in parentheses



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

Schrödinger equation and Potential Function

Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + [V_{ad}^1(r) + \Delta V_{ad}^{(\alpha)}(r)] + \frac{\hbar^2[J(J+1) - \Lambda^2]}{2\mu_\alpha r^2} [1 + g^{(\alpha)}(r)] + sg_\Lambda(e/f)\Delta V_{\Omega}^{(\alpha)}(r)[J(J+1)]^\Lambda \right\} \psi_{v,J}(r) = E_{v,J} \psi_{v,J}(r)$$

Potential Function For the A and X state (Morse Long Range)

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

$$u_{\text{LR}}(r) = \sum_{i=1}^{\text{last}} D_{m_i}(r) \frac{C_{m_i}}{r^{m_i}}, \quad D_m(r) = \left(1 - \exp \left\{ -\frac{b \cdot (\rho r)}{m} - \frac{c \cdot (\rho r)^2}{\sqrt{m}} \right\} \right)^m$$

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

$$y_p(r; r_{\text{ref}}) = \frac{r^p - r_{\text{ref}}^p}{r^p + r_{\text{ref}}^p}, \quad y_q(r; r_{\text{ref}}) = \frac{r^q - r_{\text{ref}}^q}{r^q + r_{\text{ref}}^q}$$

Robert J. Le Roy et al. "Long-range damping functions improve the short-range behaviour of 'MLR' potential energy functions", Mol. Phys. **109**, p435(2011)

Born–Oppenheimer Breakdown Correction Functions and Λ –Doubling

Λ –Doubling for the A state

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

$$f_{\Omega}(r) = \sum_{i=0}^{N_{\Omega}} \omega_i^{\Omega} y_{q_{\Omega}}(r, r_e)^i$$

Born–Oppenheimer Breakdown Correction Functions

$$\Delta V_{ad}^{(\alpha)}(r) = \frac{\Delta M_A^{(\alpha)}}{M_A^{(\alpha)}} \tilde{S}_{ad}^A(r) + \frac{\Delta M_B^{(\alpha)}}{M_B^{(\alpha)}} \tilde{S}_{ad}^B(r), \quad g^{(\alpha)}(r) = \frac{\Delta M_A^{(1)}}{M_A^{(\alpha)}} \tilde{R}_{na}^A(r) + \frac{\Delta M_B^{(1)}}{M_B^{(\alpha)}} \tilde{R}_{na}^B(r)$$

$$\tilde{S}_{ad}^A(r) = \tilde{S}_{\infty}^A y_{pad}(r; r_e) + [1 - y_{pad}(r, r_{\text{ref}})] \sum_{i=0}^{N_{ad}^A} \mu_i^A y_{q_{ad}}(r, r_{\text{ref}})^i$$

$$\tilde{R}_{na}^A(r) = \tilde{R}_{\infty}^A y_{p_{na}}(r; r_e) + [1 - y_{p_{na}}(r, r_{\text{ref}})] \sum_{i=0}^{N_{na}^A} t_i^A y_{q_{na}}(r, r_e)^i$$

$$\Delta M_A^{(\alpha)} = M_A^{(\alpha)} - M_A^{(1)}$$

Condition of the Calculating Potential Function Parameter

○ For the X state:

\mathcal{D}_e of the X state is constrained as 14797.9 cm^{-1} reported by Wrede(2000).

the Coefficients C_5 , C_6 , C_8 of the X state			
	I_2	Br_2	$I\text{Br}$
$C_5 \text{ cm}^{-1} \text{ \AA}^5$	$0.045 \times 10^5 \text{ (a)}$	$0.0033 \times 10^5 \text{ (b)}$	0.0122×10^5
$C_6 \text{ cm}^{-1} \text{ \AA}^6$	$-2.11 \times 10^6 \text{ (a)}$	$-0.6274 \times 10^6 \text{ (b)}$	-1.1565×10^6
$C_8 \text{ cm}^{-1} \text{ \AA}^8$	$-3.8 \times 10^7 \text{ (c)}$	$-1.55 \times 10^7 \text{ (b)}$	-2.42×10^7

○ For the A state:

the Coefficients C_5 , C_6 , C_8 of the A state			
	I_2	Br_2	$I\text{Br}$
$C_5 \text{ cm}^{-1} \text{ \AA}^5$	$-5.95 \times 10^4 \text{ (a)}$	$-3.2 \times 10^4 \text{ (b)}$	-4.36×10^4
$C_6 \text{ cm}^{-1} \text{ \AA}^6$	$-2.01 \times 10^6 \text{ (a)}$	$-6.37 \times 10^5 \text{ (b)}$	-1.13×10^6
$C_8 \text{ cm}^{-1} \text{ \AA}^8$	$-3.8 \times 10^7 \text{ (c)}$	$-1.55 \times 10^7 \text{ (b)}$	-2.42×10^7

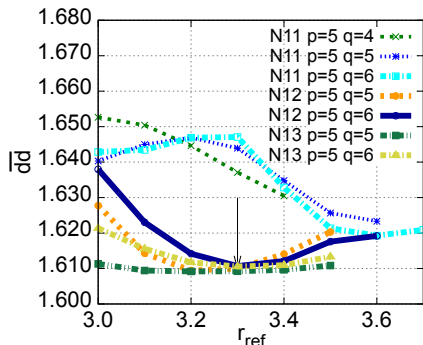
a M. Saute, M. Aubert-Frécon, J. Chern. Phys. 77(11),1 (1982)

b M. Saute, B. Bussery, M. Aubert-Frécon, Mol.Phys, 51, No.6, 1459-1474(1984)

c F. Martin, R. Bacis, S. Churassy, J. Vergès, J. Mol.Spectrosc 116, 71-100(1986)

DPotFit¹ is used in this calculation.

Relation of Rref and Dimensionless RMS

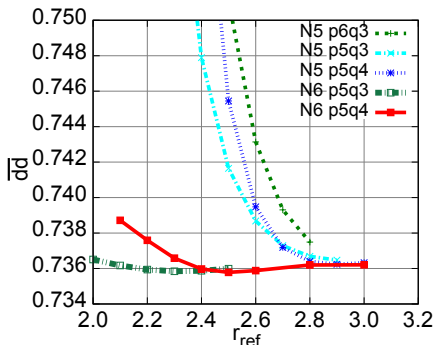


The $A^3\Pi_1$ State

The uncertain of the lines belonging to the $v(A)=27,28$ and 29 of $I^{79}\text{Br}$ are given 1.0cm^{-1} . Those of the $v(A)=28-32$ of $I^{81}\text{Br}$ are given 1.0cm^{-1} .

$$\overline{dd} = \left\{ \frac{1}{N} \sum_{i=1}^N \left[\frac{y_{\text{calc}}(i) - y_{\text{obs}}(i)}{\text{unc}(i)} \right]^2 \right\}^{1/2}$$

$$w(i) = 1/\text{unc}^2(i)$$



The $X^1\Sigma^+$ State

$y_{\text{obs}}(i)$:measured value

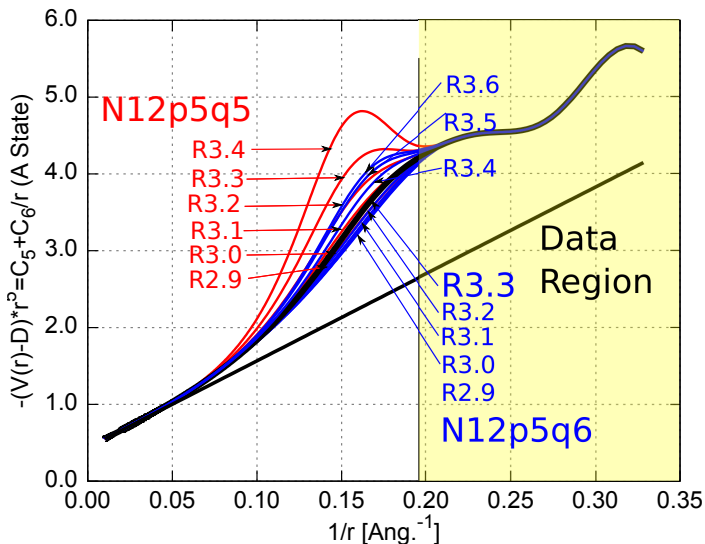
$y_{\text{calc}}(i)$:calculated value

$\text{unc}(i)$:The estimated
uncertainty of datum

N :The total number of data

$w(i)$:the normal data weights

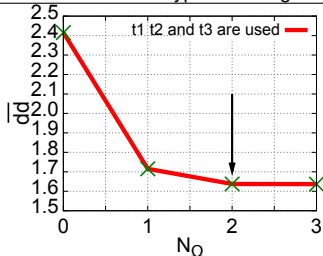
Long-Range Extrapolation behavior of the Potential



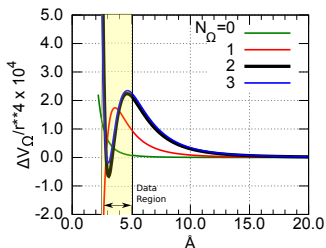
The long-range extrapolation behaviour of a number of fitted MLR models for the $A^3\Pi_1$ state of IBr

Number of Λ -Type Doubling Constants / Centrifugal Born – Oppenheimer Breakdown Terms

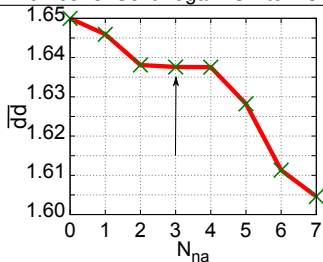
Number of Lambda-Type Doubling terms



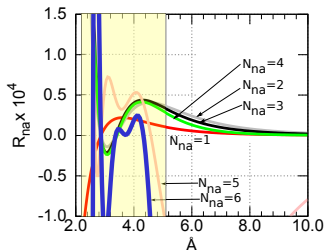
$\Delta V_\Omega(r)$ function



Number of Centrifugal BOB terms



Centrifugal BOB function



Potential Function Parameters for the A and X state

For the A-State: MLR N=12, p=5, q=6, $R_{ref}=3.3$

Values	Error	Values	Error	Values	Error
T_e 12369.5635	0.017	D_e 2428.3379	0.015	R_e 2.8655932	6.4×10^{-5}
C_5 4.3635×10^4	—	C_6 1.132×10^6	—	C_8 2.42×10^7	—
$D_e(X)$ 14797.90135	0.0014	$u_0^{Br}(X)$ 0.225	0.0080		
β_0 1.097556	0.0006	β_1 0.95356	0.00063	β_2 -0.5309	0.001
β_3 -1.7735	0.0055	β_4 -0.642	0.023	β_5 0.52	0.096
β_6 2.66	0.12	β_7 7.520	0.56	β_8 -11.7749	0.69
β_9 -20.249	1.4	β_{10} 28.300	1.6	β_{11} 16.5	1.3
β_{12} -24.3960	1.4				
t_0^{Br} 0.0	—	t_1^{Br} -0.0042	0.001	t_2^{Br} 0.0203	0.0052
t_3^{Br} -0.012	0.0059				
ω_0 0.0015	1.2×10^{-4}	ω_1 -0.115	0.0085	ω_2 0.452	0.018

UNC of the lines belonging to the $v(A)=27, 28$ and 29 of $I^{79}Br$ are given 1.0cm^{-1} .

Those of the $v(A)=28 - 32$ of $I^{81}Br$ are given 1.0cm^{-1} .

The constants $\beta_0 \sim \beta_6$ of the X are constrained into below values.

For the X-State: MLR N=6, p=5, q=4 $R_{ref}=2.5$

Values	Error	Values	Error	Values	Error
C_5 -1.21×10^3	—	C_6 1.156×10^6	—	C_8 2.42×10^7	—
D_e 14797.9*		R_e 2.46898596	6.1×10^{-8}		
β_0 0.32025489	1.0×10^{-6}	β_1 -1.132183	5.5×10^{-5}	β_2 -0.652405	5.2×10^{-4}
β_3 0.262	7.3×10^{-3}	β_4 1.519	0.045	β_5 3.41	0.28
β_6 5.6	0.79				
u_0^{Br} 0.202	0.17				

D_e was constrained into the value reported by E. Wrede.

All level of the A state were independent term values in this calculation.

Overall

For the A State

No. of Data: 23951

No. of Param.: 31

\overline{dd} : 1.6376

$v_{\min}(A)$: 3

$v_{\max}(A)$: 32

$D-v_{\max}(A)$: -126cm^{-1}

For the X State

No. of Data: 12103

No. of Param.: 6

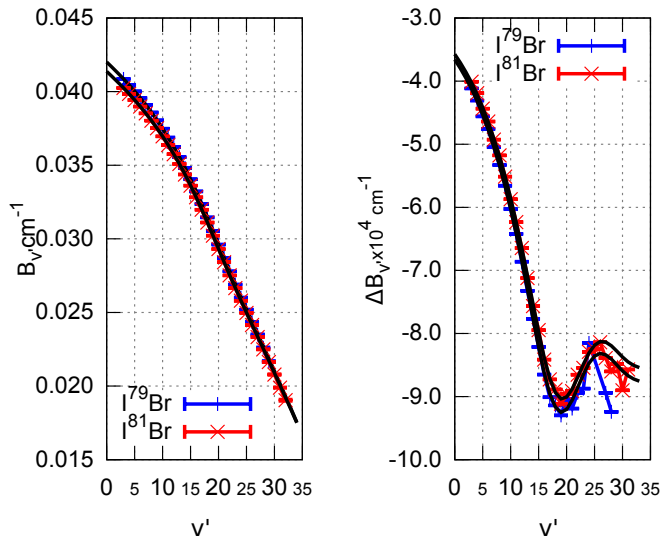
\overline{dd} : 0.735

$v_{\min}(X)$: 0

$v_{\max}(X)$: 19

$D-v_{\max}(X)$: 9880.7cm^{-1}

$B_{v'}$ and the first differences for the A state



Black lines indicate the parameter generated by DPotFit.

Conclusion

- Absorption lines of the A – X system in the 14000 – 14300 cm^{-1} region have been measured.
- The spectrum belonging to $v(A) = 30 - 32$ of the A state for ^{81}Br have been newly assigned.
- The bands of $v(A) \leftarrow v(X) = (20 - 29) \leftarrow 0, 1$ have been assigned. (3300 lines)
- Center of line positions have been estimated considering the electric quadrupole interaction.
- Potential function parameters are determined for the A and X state.
- First differential of the B_v of the A state which is calculated by potential fit are compared with parameters calculated by parameter fitting.
- There are a lot of unassigned absorption lines yet....

