

DIRECT POTENTIAL FITTING FOR THE $A\ ^3\Pi_{1u}$ and $X\ ^1\Sigma_g^+$ STATES OF Br_2

T.YUKIYA*, N. NISHIMIYA*, M.SUZUKI*, and R. J. LE ROY**

*Dept. of Electronics and Information Technology, Tokyo Polytechnic University, liyama 1583,
Atsugi City, Kanagawa 243-0297, Japan

** Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

June 21, 2012

Our Research

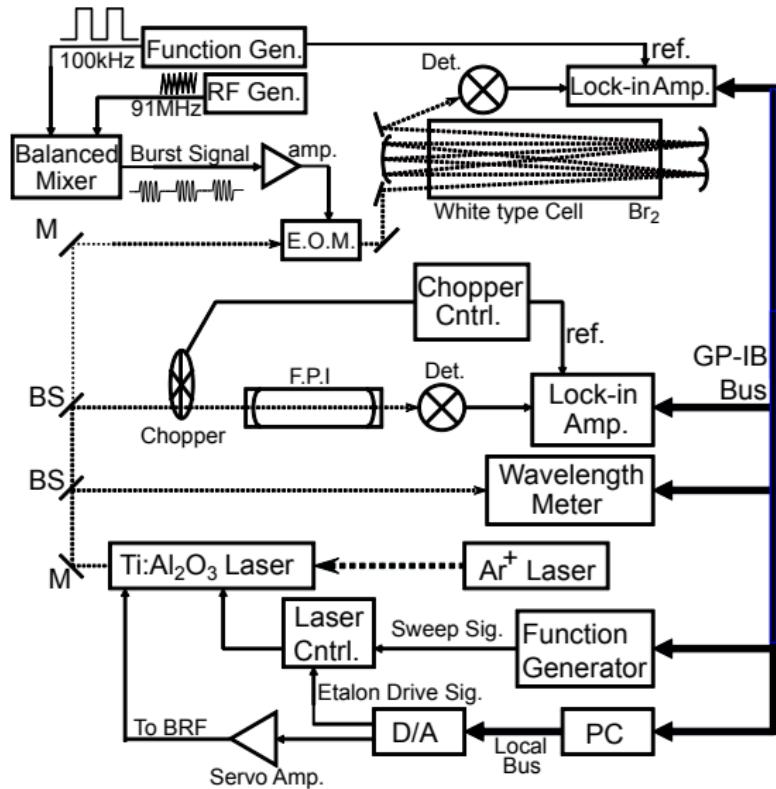
- The $A - X$ system of $\text{ICl}^{(1),(2)}$, $\text{IBr}^{(3),(4)}$, $\text{I}_2^{(5)}$ and $\text{Br}_2^{(6),(7)}$ have been studied in the $0.8\mu\text{m}$ region.
- The line positions of these spectra were determined in order to establish a frequency standard.
- Potential energy curves and spectroscopic constants of the A and X state are determined.

- (1) N. Nishimiya et al., "Nuclear Quadrupole Coupling Effect in the A-X System and Spectroscopic Constants for $v=2'-4''$, $3'-5''$ and $4'-5''$ Progressions of ICl ", JMS, 163, 43(1994).
- (2) T. Yukiya et al., "Doppler-limited spectroscopy of the $A^3\Pi_1 - X^1\Sigma^+$ system of ICl in the $0.8\mu\text{m}$ region using a Ti:sapphire ring laser", JMS 269, 193(2011).
- (3) N. Nishimiya et al., "Laser Spectroscopy of the $A^3\Pi_1 - X^1\Sigma^+$ System of IBr ", JMS, 173, 8(1995).
- (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) T. Yukiya et al., "High-Resolution Laser Spectroscopy of the $A^3\Pi_{1u} - X^1\Sigma_g^+$ System of I_2 with Ti: Sapphire Ring Laser", JMS, 182, 271(1997).
- (6) N. Nishimiya et al., "High-Resolution Laser Spectroscopy of the $A^3\Pi_1 - X^1\Sigma^+$ of Br_2 ", OHIO Columbus Meeting (2005).
- (7) N. Nishimiya et al., "Improvement of Spectroscopic Constants for the $A^3\Pi_1 - X^1\Sigma^+$ System of Br_2 ", OHIO Columbus Meeting (2011).

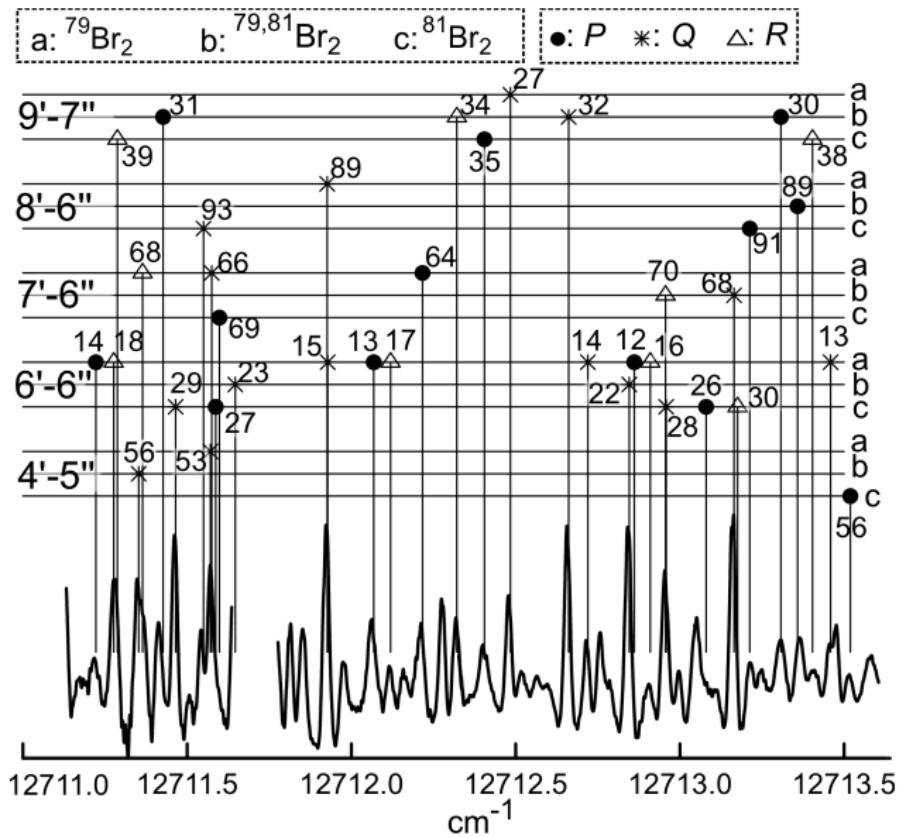
Previous Work

- M.A.A.Clyne and J.A.Coxon, "The Emission Spectra of Br₂ and IBr Formed in Atomic Recombination Processes", J.Mol.Spectroscopy, 23, 58 (1967).
- P.Venkateswarlu, V.N.Sarma, and Y.V.Rao, "Resonance series of Br₂ in the vacuum ultraviolet", J.Mol.Spectrosc., 96, 247 (1982).
- M. Saute, et. al., "Coefficients d'interaction à grande distance C_5 et C_6 pour les 23 états moléculaires de Cl₂ et de Br₂", Mol. Phys., 51, 1459 (1984).
- S. Gerstenkorn and P. Luc, "Analysis of the long range potential of ⁷⁹Br₂ in the $B^3\Pi_{0+u}$ state and molecular constants of the three isotopic bromine species ⁷⁹Br₂, ⁷⁹Br⁸¹Br₂ and ⁸¹Br₂", J. Phys. (France), 50, 1417 (1989).
- C. D. Boone, " Magnetic rotation study of the $A^3\Pi_{1u} - X^1\Sigma_g^+$ system of Br₂", Thesis (PhD), British Columbia (1999).
- C. Focsa, H. Li, and P. F. Bernath, "Characterization of the Ground State of Br₂ by Laser-Induced Fluorescence Fourier Transform Spectroscopy of the $B^3\Pi_{0+u} - X^1\Sigma_g^+$ system", J.Mol.Spectroscopy, 200, 104 (2000).
- D.J.Postell, "Laser Induced Fluorescence Spectroscopy of Br₂: Observations of Emission to High Vibrational Levels in the Ground X($^1\Sigma_g^+$) State", Thesis(Master of Science), Wright State University, 2005.

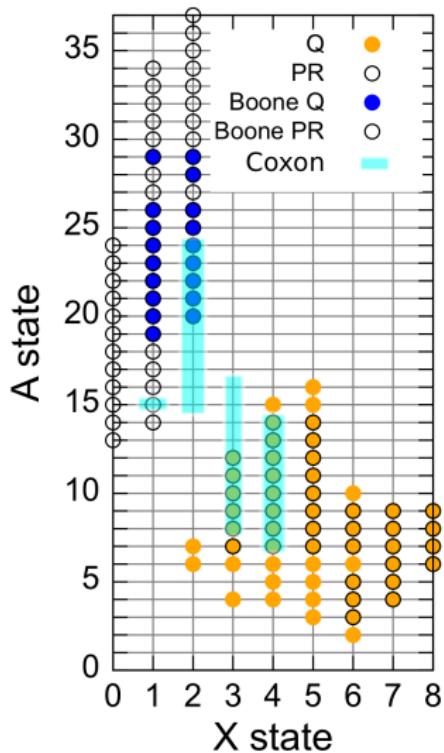
Block diagram of Ti:sapphire ring laser spectrometer.



Example of Br₂ Spectrum



Assigned Bands for the A State



A-X

Boone $^{79,79}\text{Br}_2:(13-37)' \leftarrow (0-2)''$ (Including Quasi Bound) $\pm 0.003\text{cm}^{-1}$

Coxon $^{79,79}\text{Br}_2:(7-24)' \leftarrow (1-4)'' \pm 0.02\text{cm}^{-1}$

This Work $^{79,79}\text{Br}_2, ^{79,81}\text{Br}_2::(2-16)' \leftarrow (2-8)''$
 $^{81,81}\text{Br}_2:(2-5)' \leftarrow 6'' \pm 0.0033\text{cm}^{-1}$

B-X

Gerstenkorn $\text{Br}_2:(0-52)' -(0-14)'' \pm 0.002\text{cm}^{-1}$

B-X (Laser Induced)

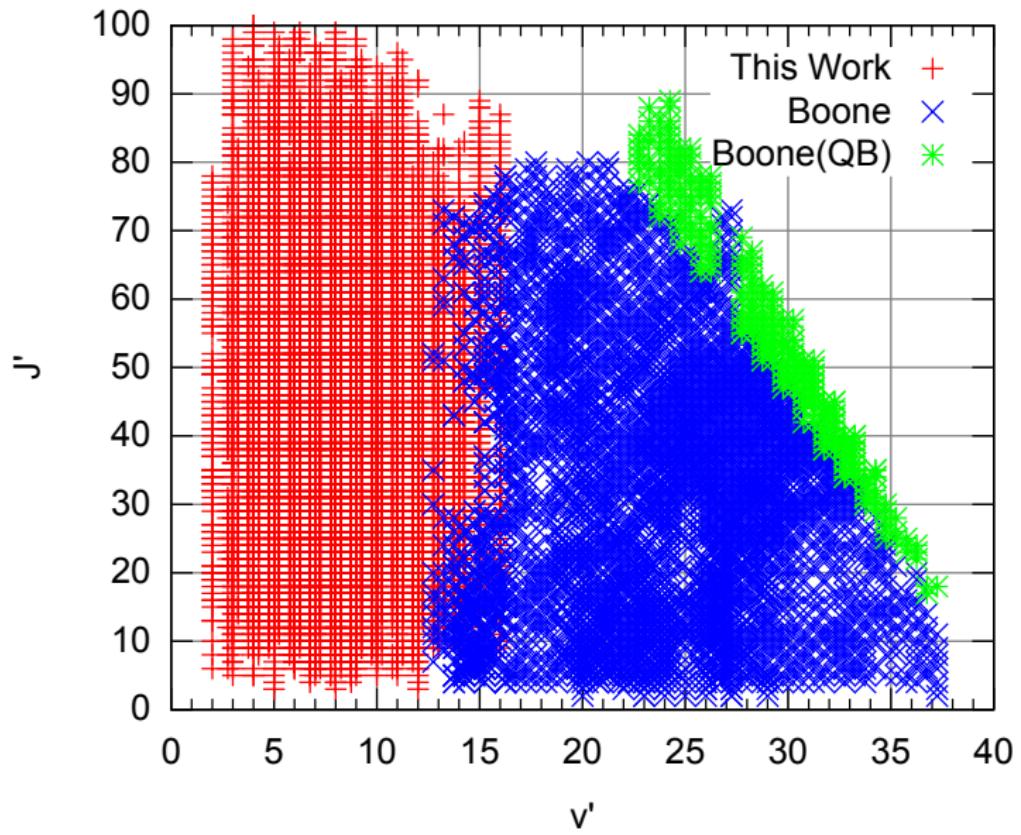
Focsa $\text{Br}_2:(10-22)'-(2-29)'' \pm 0.01\text{cm}^{-1}$

Postell $\text{Br}_2:(25,26,29,31,32,33)'-(28-44)'' \pm 0.27\text{cm}^{-1}$

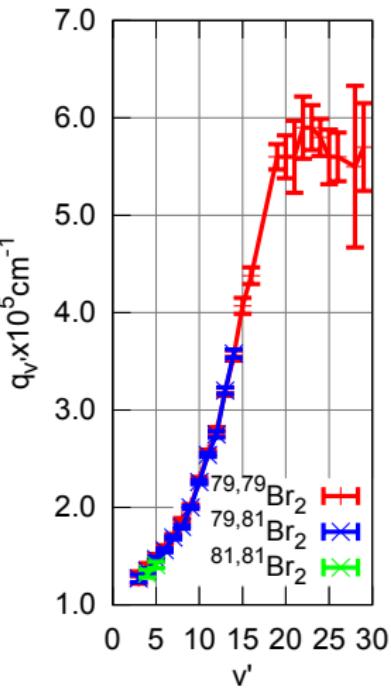
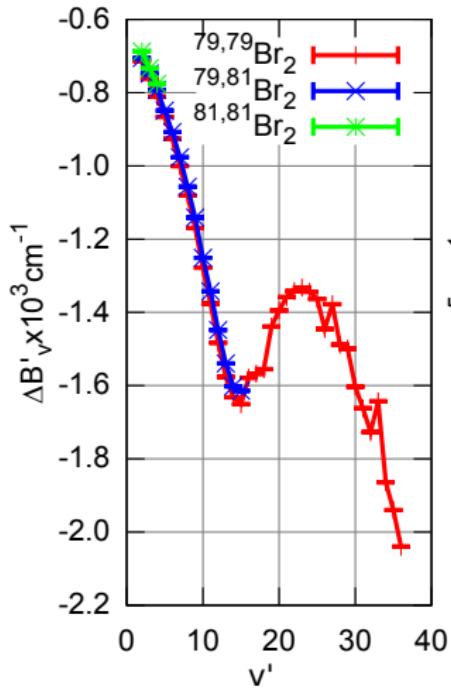
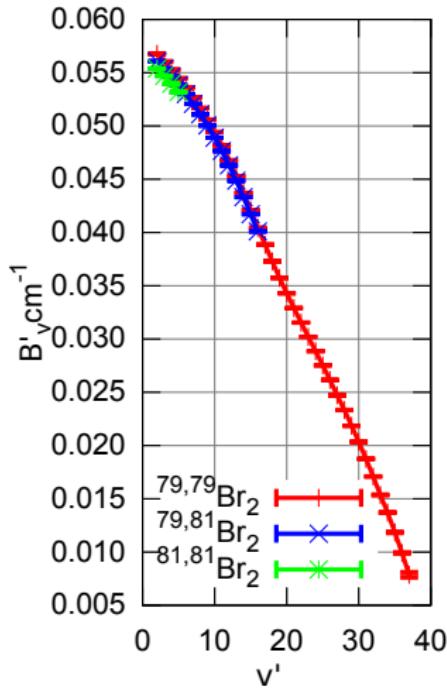
X State

Venkateswarlu: $\text{Br}_2: (0-76)'' \pm 0.8\text{cm}^{-1}$

Assigned Ro-vibrational Levels in the A State



$B_{v'}$ and the First Differences for the A State



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(Morse Long Range)

$$V_{MLR}(r) = \mathcal{D}_e \left\{ 1 - \frac{\mu_{LR}(r)}{\mu_{LR}(\mathbf{r}_e)} e^{-\beta(r) \cdot y_p(r; \mathbf{r}_e)} \right\}^2$$
$$\mu_{LR}(r) = \sum_{i=1}^{last} D_{m_i}(r) \frac{C_{m_i}}{r^{m_i}}, \quad D_m(r) = \left(1 - \exp \left\{ -\frac{b \cdot (\rho r)}{m} - \frac{c \cdot (\rho r)^2}{\sqrt{m}} \right\} \right)^m$$
$$\beta(r) = \beta_{MLR}(y_p(r; \mathbf{r}_{ref})) = y_p(r; \mathbf{r}_{ref}) \beta_\infty + [1 - y_p(r; \mathbf{r}_{ref})] \sum_{i=0}^{N_S, N_L} \beta_i \cdot y_q(r; \mathbf{r}_{ref})^i$$
$$y_p(r; \mathbf{r}_{ref}) = \frac{r^p - \mathbf{r}_{ref}^p}{r^p + \mathbf{r}_{ref}^p}, \quad y_q(r; \mathbf{r}_{ref}) = \frac{r^q - \mathbf{r}_{ref}^q}{r^q + \mathbf{r}_{ref}^q}$$

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 and Λ –Doubling Functions

Born–Oppenheimer Breakdown Correction

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

$$\tilde{S}_{ad}^A(r) = [1 - y_{p_{ad}}(r; \mathbf{r}_e)] \sum_{i=0}^{N_{ad}^A} u_i^A y_{q_{ad}}(r; \mathbf{r}_e)^i + u_\infty^A y_{p_{ad}}(r; \mathbf{r}_e)$$

$$\tilde{R}_{na}^A(r) = [1 - y_{p_{na}}(r; \mathbf{r}_e)] \sum_{i=0}^{N_{na}^A} t_i^A y_{q_{na}}(r; \mathbf{r}_e)^i + t_\infty^A y_{p_{na}}(r; \mathbf{r}_e)$$

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

Λ –Doubling Functions

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

$$f_\Omega(r) = \sum_{i=0}^{N_\Omega} \omega_i^\Omega y_{q\Omega}(r; \mathbf{r}_e)^i$$

Dimensionless Root-Mean-Square Deviation(\overline{dd})

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

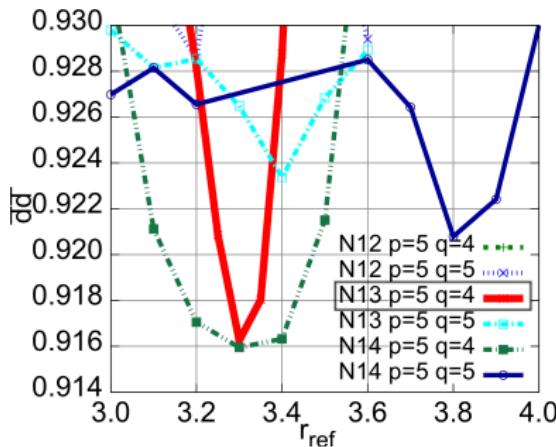
$y_{obs}(i)$: measured value

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

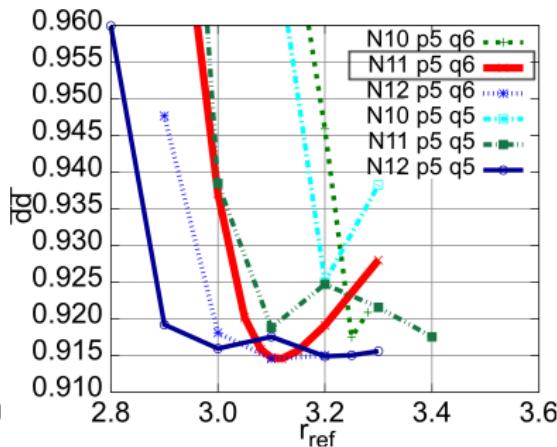
$unc(i)$: The estimated uncertainty of datum

N : The total number of data

Choosing of a Potential Model minimizing DRMS and Number of Parameters.



(a) A State



(b) X State

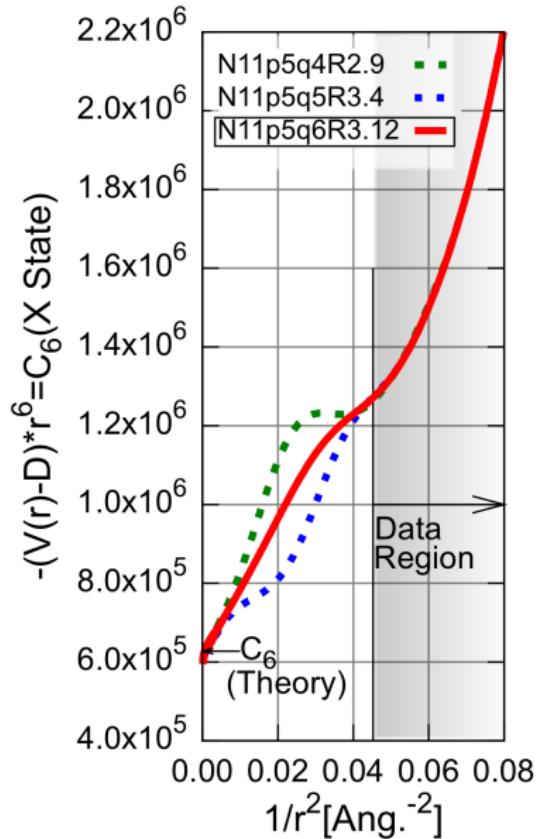
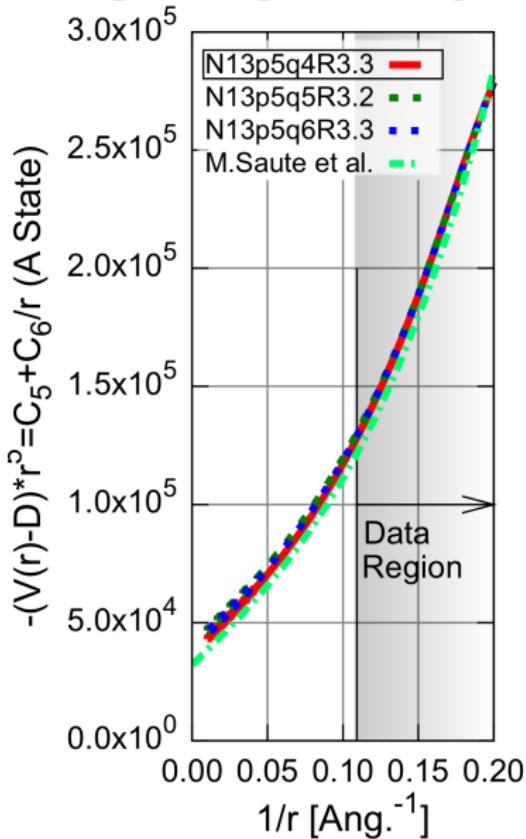
Number of β terms, p and q values of Morse Long Range (MLR) potential function in the A and X state were changed in this calculation. C_5, C_6 and C_8 of the X state and C_6 and C_8 of the A state are constrained at values reported by M. Saute. T_e and C_5 of the A state, D_e , R_e and β were computed by DPotFit^a. In the A state, Born – Oppenheimer Breakdown term $t_1 \sim t_6$ and Λ doubling term $\omega_0 \sim \omega_3$ were used. The lines of the $v'=27$ in A state were not included in this calculation.

X-State	$C_5 \text{ cm}^{-1}\text{\AA}^5:$	-0.0033×10^5
	$C_6 \text{ cm}^{-1}\text{\AA}^6:$	6.274×10^5
	$C_8 \text{ cm}^{-1}\text{\AA}^8:$	1.55×10^7
A-State	$C_5 \text{ cm}^{-1}\text{\AA}^5:$	0.32×10^5
	$C_6 \text{ cm}^{-1}\text{\AA}^6:$	6.37×10^5
	$C_8 \text{ cm}^{-1}\text{\AA}^8:$	1.55×10^7

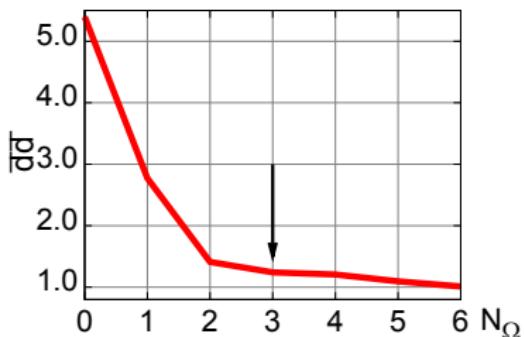
M. Saute (Mol. Phys., 51, 1459(1984)).

^a<http://scienide2.uwaterloo.ca/~rlroy/dpotfit/>

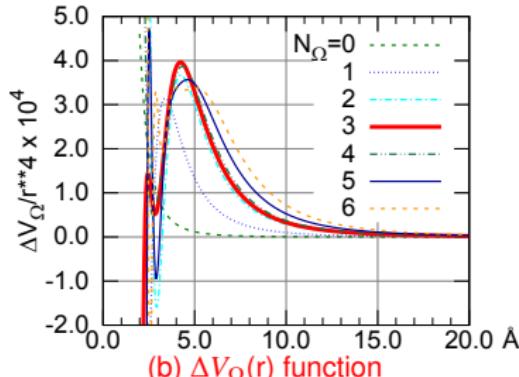
Long-Range Extrapolation behavior of the Potential



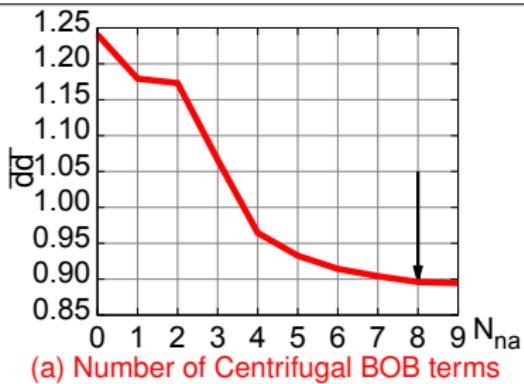
Number of Λ -Type Doubling Constants and Centrifugal Born–Oppenheimer Breakdown Terms



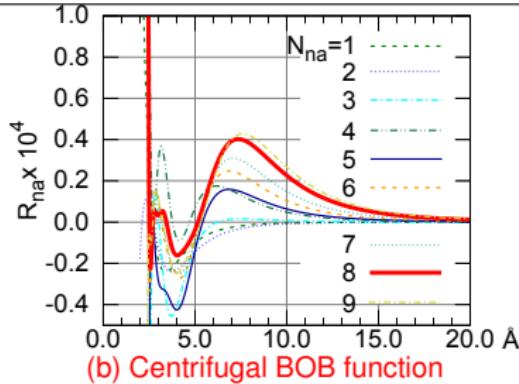
(a) Number of Lambda-Type Doubling terms



(b) $\Delta V_\Omega(r)$ function



(a) Number of Centrifugal BOB terms



(b) Centrifugal BOB function

Potential Function Parameters for the A and X state

For the A-State: MLR N=13, p=5, q=4, $R_{ref}=3.3$

Values		Error	Values		Error	Values		Error
T_e	13909.01274	0.023	D_e	2147.9239	0.014	R_e	2.7046951	2.1×10^{-5}
C_5	3.72212×10^4	720	C_6	6.37×10^5	—	C_8	1.55×10^7	—
β_0	1.1604	6.2×10^{-4}	β_1	0.60688	0.0028	β_2	-3.12787	0.005
β_3	-3.4697	0.012	β_4	10.3542	0.025	β_5	14.758	0.081
β_6	-42.133	0.31	β_7	-47.605	0.54	β_8	142.91	1.9
β_9	64.24	2.2	β_{10}	-295.0	5.6	β_{11}	42.8	3.8
β_{12}	260.0	7.0	β_{13}	-147.0	4.7			
t_0	0.0	—	t_1	0.00171	6.4×10^{-4}	t_2	-0.0174	0.00545
t_3	-0.036	0.025	t_4	1.205	0.24	t_5	-5.99	0.93
t_6	12.84	1.7	t_7	-12.9	1.6	t_8	5.0	0.55
ω_0	0.00386	5.0×10^{-5}	ω_1	-0.0122	0.0042	ω_2	0.037	0.011
ω_3	0.312	0.0084						

The lines of the $v'=27$ in A state were not included in this calculation.

For the X-State: MLR N=11, p=5, q=6, $R_{ref}=3.12$

Values		Error	Values		Error	Values		Error
D_e	16056.93664	0.0088	R_e	2.28102682	6.9×10^{-7}			
C_5	-3.3×10^2	—	C_6	6.274×10^5	—	C_8	1.55×10^7	—
β_0	1.0418061	3.8×10^{-5}	β_1	0.860947	1.7×10^{-4}	β_2	1.24355	7.4×10^{-4}
β_3	0.16568	0.0035	β_4	1.48566	0.0076	β_5	-1.9265	0.025
β_6	0.5507	0.043	β_7	3.806	0.061	β_8	2.972	0.12
β_9	-1.523	0.048	β_{10}	-3.38	0.11	β_{11}	-1.43	0.057
u_0	0.323	0.0068						

Overall

No. of Data: 16916
 $v'=27$ is not included

No. of Param.: 45

dd : 0.896

$v_{\min}(A)$: 2

$v_{\max}(A)$: 37

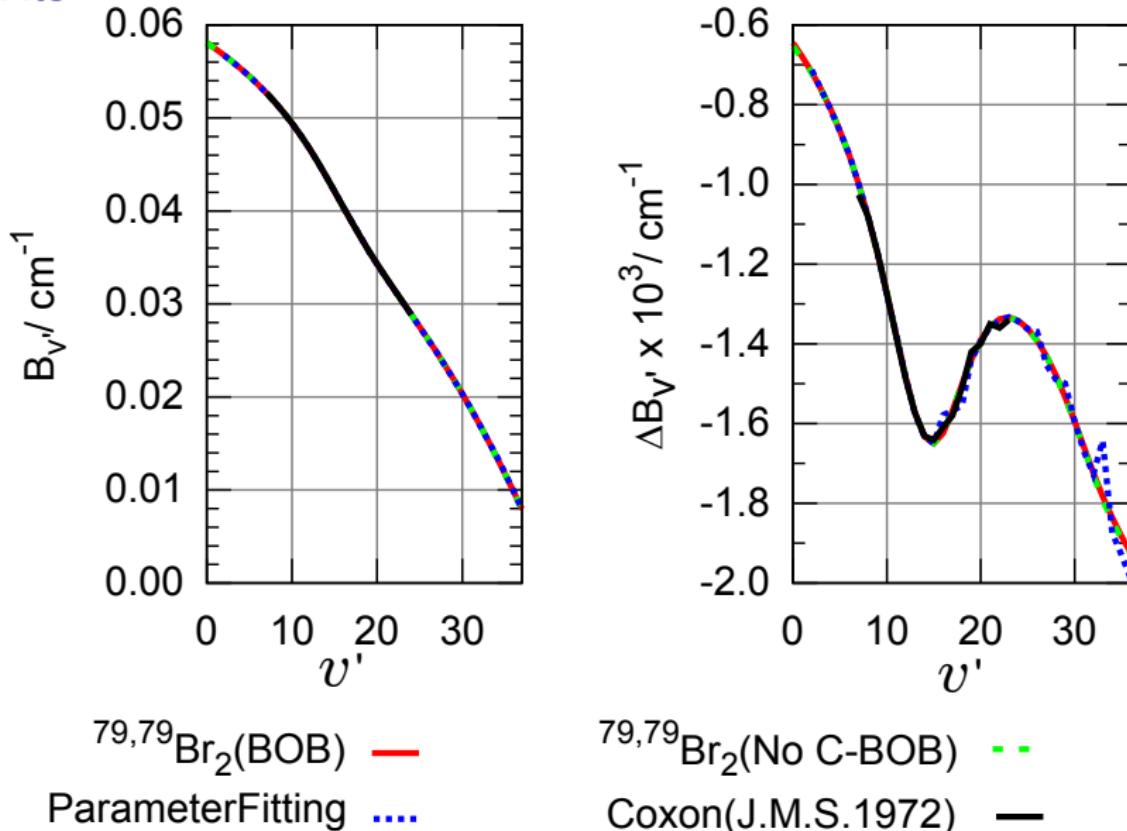
$D - v_{\max}(A)$: 2.0 cm^{-1}

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

$v_{\max}(X)$: 76

$D - v_{\max}(X)$: 116 cm^{-1}

Band Constant Calculated by Parameter Fits and by Direct-Potential Fits



Conclusion

- Spectra in the new bands were measured and assigned in 0.71 – 0.83 μm region.
- Irregular behavior of $B_{v'}$ for the A state were confirmed.
- Electronic isotope shift and centrifugal Born – Oppenheimer breakdown terms were determined for the first time.
- Accurate MLR potential function for the A and X state were determined.

