Accurate Analytic Potentials for the $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ states of Br$_2$ by Direct Potential Fitting using VUV, UV, VIS and NIR Data

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Abstract Doppler-limited rovibrational absorption spectra of the $A\,^3\Pi_{1u} \leftarrow X\,^1\Sigma_g^+$ electronic transition of Br$_2$ are measured in the $12\,072$–$14\,249$ cm^{-1} region by a tone burst modulation method using a Ti:sapphire ring laser and Br$_2$ with natural isotopic abundance. P-, Q-, and R-branch lines belonging to the $v' \leftarrow v'' = (2-16) \leftarrow (2-8)$ bands of ^{79}Br$_2$ and ^{79,81}Br$_2$, and the $v' \leftarrow v'' = (2-5) \leftarrow 6$ bands of ^{81}Br$_2$ are observed and assigned. A combined-isotopologue direct-potential-fit (DPF) analysis is used to determine accurate analytic potential energy functions for the $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ states from a combination of our new results with fluorescence data for the X state in the UV and VUV regions, magnetic rotation spectrum data for the $A - X$ system, and X state term values obtained from FT-IR results for the $B - X$ system in the VIS region. The $A - X$ electronic isotope shift and centrifugal Born-Oppenheimer breakdown (BOB) effects in the $A\,^3\Pi_{1u}$ state are also determined from his analysis. Band constants of the $A\,^3\Pi_{1u}$ state obtained from the recommended analytic potential energy function are compared with those obtained from a 'traditional' parameter-fit analysis.

Introduction: The first observations of the $A\,^3\Pi_{1u}$– $X\,^1\Sigma_g^+$ system of the bromine dimer were reported by Kuhn and Nakamura in 1926 [1, 2]. Since then there have been numerous studies of these states. In 1982, Venkteswarlu *et al.* measured fluorescence series transitions into $v''= 0$ – 76 of the $X\,^1\Sigma_g^+$ state in the Vacuum UV region [3]. Gerstenkorn *et al.* observed the $B\,^3\Pi_{0+u}$– $X\,^1\Sigma_g^+$ system using a Fourier Transform Spectrometer and reported an accurate Dunham expansion description for the lower portion of the $X\,^1\Sigma_g^+$ state well in 1987[4]. Accurate Laser-Induced fluorescence transitions into to $v''(X)=2$–29 were reported by Focsa *et al.* in 2000 [5], and analogous lower resolution (± 0.27 cm^{-1}) transitions into $v''(X) = 28 - 44$ were obtained by Postell in 2005 [6].

For the $A\,^3\Pi_{1u}$ state, Clyne and Coxon determined the absolute vibrational quantum numbering of the $A\,^3\Pi_{1u}$ state in 1970[7]. Shortly afterwards, Coxon observed absorption into $v' = 7 - 24$ of the $A\,^3\Pi_{1u}$ state in the visible and near infrared regions [8]. In 1999 Boone used Doppler-limited magnetic rotation spectroscopy with a dye laser [9, 10] to measure some 2975 lines of 55 bands in the $A\,^3\Pi_{1u} \leftarrow X\,^1\Sigma_g^+$ spectrum of ^{79,79}Br$_2$ for which $13 \leq v' \leq 37$. His highest vibrational level is bound by only 2 cm^{-1}.

While most vibrational levels of the A state have been measured by then, poor Franck-Condon factors had prevented the observation of levels $v'(A) = 0 - 6$. In the present study, we have measured the absorption spectrum belonging to $v'(A) = 2 - 16$ for the $A\,^3\Pi_{1u}$ state using a Ti:Sapphire ring laser, and analytic potential functions for the $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ states of Br$_2$ have been determined using a combined-isotopologue direct-potential-fit (DPF) analysis of these data together with all other available high quality data for the $A\,^3\Pi_{1u}$ and $X\,^1\Sigma_g^+$ states.

Experiment: Figure 1 presents a schematic view of the experimental setup. A Ti:Sapphire ring laser (Coherent, 899–21) was used to obtain Doppler limited absorption spectra. A White-type cell (path length 8 m) was filled with Br$_2$ gas containing all three isotopologues in natural abundance at 10 Torr. At wavelengths shorter than 0.77μm, the absorption lines were measured at room temperature, while the cell was heated to $150°$C when absorption lines in the $0.77-0.83\,\mu$m region were measured.

Figure 1: Block diagram of the Ti:Sapphire ring laser spectrometer

Tone burst modulation was adopted as a signal detection technique. The laser source having a sideband was produced using an electro–optical modulator (EOM 191MHz). A Burst signal generated using a 191MHz source and a pulse signal (at 100KHz) generated by a mixer were input into the EOM. The absolute and relative wavelengths of the laser were measured using a wavelength meter (Burleigh WA-1500) and a confocal cavity (F.P.I) having a free spectral range (FSR) of 0.01 cm^{-1}.

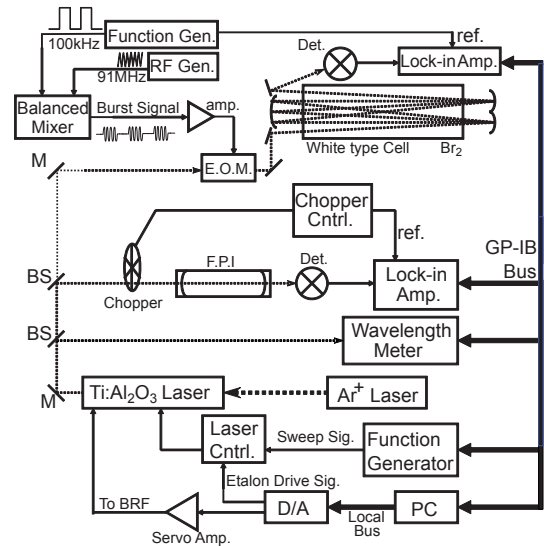**Analysis:** A direct-potential-fit analysis may be used to determine the molecular parameters $\mathfrak{D}_e$ and

r_e, and sometimes also long-range inverse-power potential coefficients. In this work, program DPotFit was used to determine these quantities and the associated potential energy functions from experimental line positions [11]. Since Br_2 has three isotopologues and there is Λ-type doubling in the $A\,^3\Pi_{1u}$ state, the radial Schrödinger equation is:

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

where $V_{\mathrm{ad}}^{(1)}(r)$ is the effective adiabatic potential for the reference isotopologue ($\alpha=1$), $\Delta V_{\mathrm{ad}}^{(\alpha)}(r)$ is the difference between the effective adiabatic potentials of isotopologue-α and the reference isotopologue, $g^{(\alpha)}(r)$ is the centrifugal Born-Oppenheimer breakdown (BOB) radial function, $sg_\Lambda(e/f)$ is a dimensionless numerical factor for the e and f levels, and $\Delta V_\Lambda^{(\alpha)}(r)$ is the Λ-doubling radial strength function [11–13]. The Morse/Long-Range (MLR) form is used for the potential energy functions of the A and X states:

$$
V_{\mathrm{MLR}}(r) \;=\; \mathfrak{D}_e\left\{ 1 - \frac{u_{\mathrm{LR}}(r)}{u_{\mathrm{LR}}(r_e)}\mathrm{e}^{-\beta(r)\cdot y_p(r,r_e)} \right\}^2, \qquad u_{\mathrm{LR}}(r) \;=\; \sum_{i=1}^{\mathrm{last}} D_{m_i}(r)\frac{C_{m_i}}{r^{m_i}} \tag{2}
$$

where r is the internuclear distance, $\beta(r)$ is the exponent coefficient function, $y_p(r,r_{\mathrm{ref}}) = \frac{r^p - r_{\mathrm{ref}}^p}{r^p + r_{\mathrm{ref}}^p}$ is a dimensionless radial variable, C_{m_i} are long range coefficients and $D_{m_i}(r)$ are damping functions [14, 15].
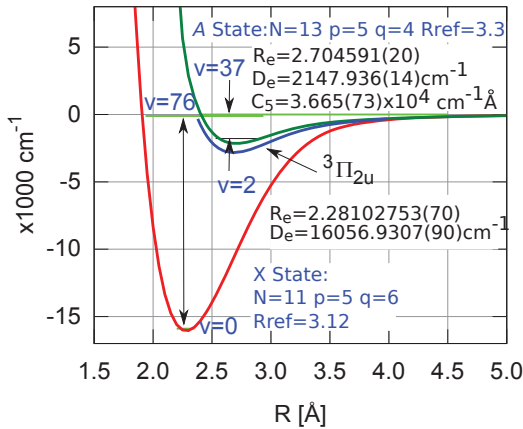

Figure 2: MLR Potentials of the A and X States of Br_2, and Potential curve of the A' state reported by Sur and Van Marter [16, 17].

Results: The data reported by Venkteswarlu *et al.*, Boone, Focsa *et al.*, Postell *et al.* and Gerstenkorn *et al.* were combined with those obtained here, and analysed using program DPotFit [11]. This X state data set spans 99.2% of the ground-state potential well, with the highest observed level being bound by only 129 cm^{-1}. The observed A state levels are $v'(A) = 2 - 37$, with the highest observed vibrational level lying less than 2 cm^{-1} from the dissociation limit. Figure 2 shows the well depths $\mathfrak{D}_e$, equilibrium internuclear distances r_e, and potential energy curves determined for the A and X states, where the integer N is the power of the polynomial defining the exponent coefficient function $\beta(r)$ while p, q and r_{ref} are non-physical parameters defining the dimensionless radial variables $y_{p/q}(r,r_{\mathrm{ref}})$. Experimental values for the long-range inverse-power C_5 constant of the A state and for the $A-X$ electronic isotope shift are also determined. The $A'\,^3\Pi_{2u}$ state potential is also plotted in this Figure. The A and A' state potentials become very close at $r \approx 4\,\text{Å}$.

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