Direct-potential-fit analysis for the $A^3\Pi_{1u} - X^1\Sigma^+_g$ system of Br$_2$

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Doppler-limited rovibrational absorption spectra of the $A^3\Pi_{1u} - X^1\Sigma^+_g$ electronic transition of Br$_2$ are measured in the 12072–14249 cm$^{-1}$ region by a tone burst modulation method using a Ti:sapphire ring laser. $P$, $Q$, and $R$-branch lines belonging to the $\nu' = 0$–26 bands of 79,81Br$_2$ and 79,79Br$_2$, and the $\nu' = 0$–26 bands of 81,81Br$_2$ are observed and assigned. Accurate analytic potential energy functions for the $A^3\Pi_{1u}$ and $X^1\Sigma^+_g$ states are determined from a combined-isotopologue direct-potential-fit analysis of these data together with all other available high quality data for the $A$ and $X$ states. This work also yields a slightly improved ground-state well depth $\Gamma(0)/C_0 = 16056.875(2)$ cm$^{-1}$ and dissociation energy $\Delta(0)/C_0 = 15894.49(2)$ cm$^{-1}$ for 79,79Br$_2$, and shows that the isotope shift of the $A-X$ electronic transition energy $\Gamma_1^{79} - \Gamma_1^{81} = -0.016(3)$ cm$^{-1}$ is likely mainly due to the isotopologue dependence of the $X$-state well depth.

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1. Introduction

The $A^3\Pi_{1u} - X^1\Sigma^+_g$ system of Br$_2$ has been studied by many researchers. It was first observed in 1926 by Kuhn [1] and Nakamura [2] who published vibrational analyses of its absorption spectrum in the 5117–6722 and 5130–7586 Å regions, respectively. In 1931 Brown extended their results by using a grating spectrometer to study Br$_2$ absorption in the 5100–7600 Å region, and reported vibrational assignments for band heads that he tentatively identified as being associated with $\nu = 0$–21 and $\nu = 1–5$ [3]. Five years later Darbyshire used a prism instrument to study high temperature samples in the 7600–8180 Å region [4]. This allowed him to extend the ground-state vibrational range to $\nu = 13$ and to observe two $A$-state vibrational levels lying below the lowest one that Brown had seen.

The first rotational analysis for the $A^3\Pi_{1u} - X^1\Sigma^+_g$ system was reported by Horsley in 1967 [5]. He measured the absorption spectrum of natural bromine in the 6400–7100 Å region, and assigned the $Q$-branch lines of bands identified as $\nu' = \nu'' = (13–19) – 2$ and (16, 17) = 3 of 79,81Br$_2$. However, the absolute vibrational numbering for the $A$ state remained unclear. In that same year Clyne and Coxon measured the band structure of Br$_2$ in the 6400–10000 Å region in emission, but again the absolute vibrational numbering in the $A$ state remained unsettled [6]. Finally, in 1970 Coxon and Clyne measured the absorption spectrum of a few bands of isotopically pure 79,79Br$_2$ with rotational resolution [7], and by comparing their results with the 79,81Br$_2$ measurements of Horsley [5], they confirmed Darbyshire’s hypothesis [4] that the tentative $A$-state vibrational labels proposed by Brown [3] should be increased by seven. Shortly after this, Coxon extended his rotational resolution studies of the $A^3\Pi_{1u} - X^1\Sigma^+_g$ system to span almost 50% of the $A$-state well ($\nu' = 7–24$) [8], and reported extended sets of Franck–Condon factors and $R$-centroids for this system [9]. These studies provided a good basic understanding of the $A^3\Pi_{1u}$ state of Br$_2$, and facilitated its use in studying a number of ion-pair states [10–15]. Moreover, one of these studies of ion-pair states reported a handful of observations of $A$-state levels $\nu = 30–35$ [10], and another reported observations of $R(A) = 0$ [15]. However, all of this early work has since been superseded by measurements of higher precision spanning an even wider range of levels. An overview of the data, on which the present analysis is based, is presented in Table 1. The average relative discrepancies shown in its second-last column are based on the final recommended potential energy function model of Section 4. The fact that all values of this average relative discrepancy are $< 1$ shows that there are no significant calibration error inconsistencies among the various data subsets.

In 1999 Boone used Doppler-limited magnetic rotation spectroscopy with a dye laser [16,17] to measure and assign some 3263 lines of 51 bands in the $A^3\Pi_{1u} - X^1\Sigma^+_g$ spectrum of 79,79Br$_2$, involving $A$-state vibrational levels $\nu = 13–37$. The highest
vibrational level he observed is bound by only 2 cm$^{-1}$. This is less than half the binding energy of the highest observed level of the $B^3\Pi_u$ state \cite{18}, and hence should allow an improved determination of the Br$_2$ dissociation energy. Boone performed both a conventional Dunham expansion analysis and a \textquoteleft Near-Dissociation-Expansion\textquoteright analysis, and those results can be found in his thesis \cite{16}. However, the lowest observed level of the A state was still $v(A)=7$ \cite{8}, which lies almost 1000 cm$^{-1}$ above the A-state potential minimum.

In the present work, rovibrational absorption spectra of the $A-X$ transition of Br$_2$ were measured in the 12072–14249 cm$^{-1}$ region, and $P$, $Q$, and $R$-branch progressions of 109 bands in this system were assigned. The observed vibrational levels of $79^{37}$Br$_2$ and $79^{35}$Br$_2$ in the A and X state are $v'=2$–16 and $v'=2$–8, respectively, and those of $81^{37}$Br$_2$ and $81^{35}$Br$_2$ are $v'=2$–5 and $v'=6$, while the associated rotational sublevels range up to $J=99$. Thus, the high-resolution data (uncertainties $<0.01$ cm$^{-1}$) for the A state used in the present analysis extend from $v(A)=2$–37, with the highest observed vibrational level lying less than 2 cm$^{-1}$ below the dissociation limit. A schematic overview of this system is presented in Fig. 1.

Unfortunately, the high-resolution A-X data described above only span a small portion of the $X^1\Sigma_g^+$ state potential well ($v'=0$–8). Since we wish also to obtain the best possible overall description of the $X^1\Sigma_g^+$ ground state, the present analysis also incorporated the laser-induced fluorescence Fourier Transform (FT) results of Focsia et al. \cite{19} for the $B-X$ system, which extend from $v(X)=2$–29 for $79^{37}$Br$_2$ and from $v(X)=3$–29 for $79^{35}$Br$_2$ and $81^{37}$Br$_2$. Following Focsia et al., our analysis also incorporates the 1515 synthetic term values for levels $v'=0$–14 of the ground state of $79^{37}$Br$_2$, which they had generated from the molecular constants of Gerstenkorn et al. \cite{18}, and treated as a synthetic fluorescence series. However, even with this inclusion, the data range only span 54% of the ground-state potential well.

More recently, Postell et al. performed laser-induced fluorescence measurements that extended this range to $v(X)=44$, which is 75% of the way to dissociation [20,21]. Although their data have relatively low precision ($\pm0.27$ cm$^{-1}$), since they include results for all three isotopologues and extend the range to cover 3/4 of the potential well, they are also used in our analysis (weighted appropriately). The final set of X-state data included in the present analysis were then the 12 VUV resonance fluorescence series reported in 1982 by Venketeswarlu et al. [22]. Although these data span the range $v'=0$–76, they were pointlessly omitted from the analysis of Focsia et al. because the 1982 molecular constants seemed inconsistent with their new higher accuracy ($\pm0.01$ vs. $\pm0.06$ cm$^{-1}$) FT results for $v'=2$–29 [19]. However, although the constants may be inconsistent, we find that within the reported uncertainties, the actual VUV data are entirely compatible with the higher resolution data. Hence, these VUV fluorescence series data were also utilized in the present analysis. As a result, our data for the $X^1\Sigma_g^+$ state span 99.2% of the ground-state potential well, with the highest observed level ($v'=76$) being bound by 129 cm$^{-1}$. However, since the $A^3\Pi_u$ and $X^1\Sigma_g^+$ states have the same asymptote, the present analysis should yield an improved estimate of the ground-state dissociation energy.

In the following, Section 2 describes our new laser absorption measurements for the three isotopologues of Br$_2$. Section 3 then describes our method of analysis and the models used for the potential energy and Born–Oppenheimer breakdown functions, while Section 4 presents our results.

2. Experimental

2.1. Methodology

Fig. 2 presents a schematic view of the experimental setup. A titanium sapphire ring laser (Coherent, 899–21) pumped by an
argon ion laser (Coherent, Innova 300) was used to obtain our Doppler limited absorption spectra. The absorption occurred in a White-type cell with an effective path length of 13.6 m that was Doppler limited absorption spectra. The absorption occurred in a argon ion laser (Coherent, Innova 300) was used to obtain our measurements at wavelengths shorter than 0.77 μm, were made with the cell at room temperature, while for those at longer wavelengths the cell was heated to 150 °C.

Tone burst modulation was adopted as the signal detection technique [23]. The laser source sidebands were produced using a balanced mixer using this 191 MHz source and square-wave technique [23]. The laser source sidebands were produced using a balanced mixer using this 191 MHz source and square-wave technique [23].

Fig. 2. Block diagram of the Ti:Sapphire ring laser spectrometer.

Here, the X-state $V_{\text{in}}^m$ values for different isotopologues ($\alpha_1$, $\alpha_2$) were related by conventional first-order semiclassical scaling by powers of the ratio of reduced masses, $V_{\text{in}}^m/V_{\text{in}}^0 = (\mu_{\alpha_2}/\mu_{\alpha_1})^{m+1/2}$. In the A state, the $e$ and $f$ parity sublevels are separated by the $\Omega$-doubling interaction characterized by the molecular constants $q_0$. In the A–X system, the $f$ and $e$ levels, respectively, are the upper levels of the Q- and R-transitions. To take the $\Omega$-doubling into account, independent values of the inertial rotational constant, $B'_0$, and $B''_0 = B'_0 + q_{0e}$, respectively, are used [25]. An empirical fit to Eq. (1) that was 'saturated' with respect to the number of parameters being used has a root mean square deviation of 0.003 cm$^{-1}$, and a histogram of those deviations shows the expected Gaussian shape. Hence 0.0030 cm$^{-1}$ is the uncertainty used to weight the present data in our fits.

2.2. Results

In contrast with some of the previous work on this system [16,18], the present experiments did not use isotopically purified Br$_2$ gas, so our absorption spectrum consists of overlapping series of P-, Q- and R-branch lines from all three species: 79$\text{Br}_2$, 79,81$\text{Br}_2$, and 81$\text{Br}_2$. Fig. 3 shows a recorder trace of the Doppler-limited absorption spectrum detected by our tone-burst technique for the interval 12711.0–12713.5 cm$^{-1}$. The approximately equal natural abundances of 79Br and 81Br give rise to intensity ratios of 1:2:1 for lines of 79,79$\text{Br}_2$, 79,81$\text{Br}_2$ and 81,81$\text{Br}_2$, respectively. Our analysis readily discerns the $\Omega$-doubling splitting in the A state. However, because the nuclear quadrupole coupling constants for both bromine isotopes are only half of that for iodine, our Doppler-limited spectrum could not resolve the nuclear-quadrupole-induced splitting of the P- and R-branch lines, although it was readily observed in the A–X systems of ICl, I$_2$ and IBr [24,26–28].

The present study observed transitions involving vibrational levels $\nu' = 2–16$ of the A state and $\nu'' = 2–8$ of the X state for 79,79$\text{Br}_2$ and 79,81$\text{Br}_2$, as well as $\nu' = \nu'' = (2–5) - 6$ transitions of 81$\text{Br}_2$. These 9334 assigned lines in 108 bands include the first ever readily observed of levels $\nu'(A) = 2–6$. As was outlined in Section 1, in order to obtain the most comprehensive description possible for the A and X states, the present analysis combines our new results.

$\nu'(A; J; \nu) = T_v + B'_0(J(J + 1) - Q^2) - D_p(J(J + 1) - Q^2)^2 + \cdots$

$- \sum_{\ell=1}^{\infty} a_{\ell} \nu^{2\ell}(\nu' + 1/2)^2(J(J' + 1))^{2\ell}$.  \hspace{1cm} (1)
99.2% of the data are presented in Fig. 4 and Table 1. These data span of Br2.

with the earlier data of Venkateswarlu et al. [22], Gerstenkorn et al. [18], Boone [16], Focsa et al. [19], and Postell [20,21]. Overviews of the BOB, and parameterized potential energy, Born–Oppenheimer breakdown (BOB), and \( \Omega \)-doubling strength functions, are compared with experiment, and the parameters \( \{ p \} \) are optimized by a standard non-linear least-squares-fit technique [29]. The partial derivatives of the eigenvalues with respect to the parameters of the Hamiltonian that were required by the least-squares procedure were generated from the Hellman–Feynman theorem expression

\[
\frac{\partial E_{j\ell}}{\partial p_i} = \left\langle \psi_{j\ell} \left| \frac{\partial H}{\partial p_i} \right| \psi_{j\ell} \right\rangle.
\]

where the eigenfunctions \( \psi_{j\ell}(r) \) are obtained when solving the radial Schrödinger equation for the level energies in order to simulate the spectra. The quality of a fit is characterized by the dimensionless root-mean-square deviations between the \( N \) simulated data \( y^{\text{calc}}_i \) and the corresponding experimental values \( y^{\text{obs}}_i \):

\[
\overline{dd} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{y^{\text{calc}}_i - y^{\text{obs}}_i}{u_i} \right)^2}^{1/2}
\]

in which \( u_i \) is the uncertainty associated with datum-\( i \). While most of these uncertainties are set at the characteristic value associated with a given data set (see Table 1), those associated with the highest \( J \) lines for a given branch are sometimes somewhat larger, and those for transitions in which the upper or lower level is 'quasibound', lying above the dissociation limit but below the top of a potential energy barrier, are defined as

\[
u^{\text{ad}}_i = \sqrt{(u^{\text{ad}}_i)^2 + (0.2 \Gamma_i)^2}
\]

in which \( \Gamma_i \) is the tunnelling predissociation width of quasibound level \( E_{j\ell}(i) \), which is calculated as described in Ref. [30], and the factor of 0.2 is based on the experience of Refs. [31,32].

3.2. The radial Hamiltonian

As in most DPF analyses reported to date, the present work uses a form of the effective radial Hamiltonian introduced by Watson in which BOB terms associated with the radial kinetic energy operator are incorporated into both an effective 'adiabatic' correction to the rotationless potential, and the non-adiabatic centrifugal BOB correction [33,34]. Following the convention of Ref. [35] for the mass-scaling of the BOB terms, and that of Ref. [30] for describing \( \Omega \)-doubling, the effective radial Hamiltonian used in the present work is defined by

\[
\tilde{H}(\psi_{j\ell})(r) = \left\{ \frac{\hbar^2}{2\mu_B} \frac{d^2}{dr^2} \left[ V^{\text{ad}}_{j\ell}(r) + \Delta V^{(\text{ad})}_{\ell\ell'}(r) \right] + \frac{J(J + 1) - \Omega^2}{2\mu_B\hbar^2} \left[ 1 + g^{(\text{ad})}_{\ell\ell'}(r) + s_{\ell\ell'}(e/f)\Delta V^{(\text{ad})}_{\ell\ell'}(r)[JJ + 1]^{1/2} \right] \right\} \psi_{j\ell}(r)
\]

Here, \( V^{(\text{ad})}_{\ell\ell'}(r) \) is the effective adiabatic potential for the selected reference isotopologue (labelled \( \alpha = 1 \)), and \( \Delta V^{(\text{ad})}_{\ell\ell'}(r) \) is the difference between the effective adiabatic potentials for isotopologue \( \alpha \) and that for the reference species \( \alpha = 1 \), while \( g^{(\text{ad})}_{\ell\ell'}(r) \) is the non-adiabatic correction to the effective centrifugal potential term. In addition, \( s_{\ell\ell'}(e/f) \) is a dimensionless numerical factor which is zero when there is no \( \Omega \)-doubling (i.e. for the \( \alpha \Sigma^+ \) state of Br2), and has numerical values of zero or \( \pm 1 \) for the \( e \)- and \( f \)-levels of states with \( \Omega = 0 \) [29,30,36]. For the \( \alpha \Pi_{1u} \) state we select the \( e \)-parity levels as the reference states, and hence \( s_{\ell\ell'}(e/e) = 0 \) and \( s_{\ell\ell'}(f/f) = 1 \). The potential energy and centrifugal BOB functions are each written as a sum of terms, one for each of atoms \( A \) and \( B \):

\[
\Delta V^{(\text{ad})}_{\ell\ell'}(r) = \frac{\Delta M_{\ell\ell'}^{(1)}}{M_A^{(1)}} \tilde{S}_{\ell\ell'}^{(1)}(r) + \frac{\Delta M_{\ell\ell'}^{(3)}}{M_B^{(3)}} \tilde{S}_{\ell\ell'}^{(3)}(r);
\]

\[
g^{(\text{ad})}_{\ell\ell'}(r) = \frac{M_A^{(1)}}{M_A^{(0)}} \tilde{R}_{\ell\ell'}^{(1)}(r) + \frac{M_B^{(3)}}{M_B^{(0)}} \tilde{R}_{\ell\ell'}^{(3)}(r).
\]
Here, $\Delta M_k^{(n)} = M_k^{(n)} - M_k^{(1)}$ is the difference between the atomic mass of atom $A$ in isotope-$\alpha$ ($M_k^{(n)}$) and in the reference isotope ($M_k^{(1)}$), and analogous definitions apply for atom $B$. The $\Omega$-doubling (or $A$-doubling) radial strength function is then written as the product [25,30,36]:

$$\Delta V^{(\Omega)}_\alpha(r) = \left( \frac{r^2}{2\mu_\alpha^2} \right)^{2n} f_\alpha(r).$$

(8)

3.3. Models for the potential energy, Born–Oppenheimer breakdown, and $\Omega$-doubling functions

The $X$ and $A$ state potential energy functions $V^{(X/A)}_{\text{ex}}(r)$ are represented by “Morse/Long-Range” (MLR) functions which have the form [37,38]:

$$V^{\text{MLR}}_{\text{ex}} = \frac{1}{\Xi} \left( 1 - \frac{u_{\text{ MLR}}(r)}{u_{\text{ MLR}}(r^*_{eq})} \right)^2.$$  

(9)

Here, $\Xi$ is the well depth, $r^*_\text{eq}$ is the equilibrium internuclear distance, $u_{\text{ MLR}}(r)$ defines the attractive long-range tail of the potential, and $u_{\text{ MLR}}(r^*_{eq})$ is the value of that function at $r = r^*_\text{eq}$. In the exponent of Eq. (9),

$$y_p(r; r^*_\text{eq}) = \frac{r^p - r^*_{eq}^p}{r^p + r^*_{eq}^p}$$  

(10)

is a dimensionless radial variable, with $p$ being a small positive integer (see below). The exponent coefficient function $\beta(r)$ is defined so that

$$\lim_{r \to \infty} \beta(r) = \beta_{\infty} = \ln \left( 2\Xi u_{\text{ MLR}}(r^*_{eq}) \right)$$  

(11)

and since $y_p(r; r^*_\text{eq}) \to 1$ as $r \to \infty$, this means that at very large distances

$$V^{\text{MLR}}_{\text{ex}}(r) \approx \Xi - u_{\text{ MLR}}(r) \cdots,$$

where $\Xi$ is the absolute energy at the dissociation limit. In order to impose the limiting behaviour of Eq. (11), the MLR exponent coefficient function is written as a constrained polynomial:

$$\beta(r) = \beta_{\infty} + \beta_1 y_p(r; r^*_\text{ref}) + \sum_{i=1}^{N_p} \beta_i y_p(r; r^*_\text{ref})^i$$  

(13)

in which the two radial variables $y_p(r; r^*_\text{ref})$ and $y_p(r; r^*_\text{ref})$ have the same dimensionless form as $y_p(r; r^*_\text{eq})$ in Eq. (10), except that they are expressed relative to a different expansion centre, $r = r^*_\text{ref}$, and they are defined in terms of separate (integer) powers, $p$ and $q$:

$$y_p(r; r^*_\text{ref}) = \frac{r^p - r^*_\text{ref}^p}{r^p + r^*_\text{ref}^p}; \quad y_p(r; r^*_\text{ref}) = \frac{r^p - r^*_\text{ref}^p}{r^p + r^*_\text{ref}^p}.$$  

(14)

As indicated by theory [39–44], the long-range potential tail can be written as a sum of damped inverse-power terms:

$$u_{\text{ MLR}}(r) = \sum_{i=1}^{\text{last}} D_{\alpha\beta}(r) \frac{C_i^{(n)}}{r^i}.  

(15)

Since ground-state atomic Br is not in an $S$ state, it has a permanent quadrupole moment. As a result, the leading term in the long-range potential for both the $X^{1S_g}$ and $A^{3P_u}_0$ states is the first-order quadrupole–quadrupole interaction energy corresponding to $m_1 = 5$ [39,42], and the next two are the leading second-order dispersion energy terms for which $m_2 = 6$ and $m_3 = 8$ [39–44]. Throughout this work $C_5$, $C_6$, and $C_8$ were fixed at the theoretical values of Sauter et al. [45], although in some of the later fits the $C_5$ coefficient for the $A$ state was treated as a free parameter. Damping functions $D_{\alpha\beta}(r)$ were introduced to take account of the weakening of the dispersion interaction at distances where the electron clouds on the interacting atoms overlap significantly [38,43,46]. The present work uses the modified Douketis-type [46] damping functions for $s = -1$ introduced in Ref. [38]:

$$D_{\alpha\beta}(r) = \left( 1 - \exp \left\{ -\frac{b \cdot (r^*_{eq})^2 - c \cdot (r^*_{eq})^2}{m} \right\} \right)^{m-1}$$  

(16)

in which $b = 3.30$ and $c = 0.423$, and $\rho$ is a system-dependent scaling parameter defined in terms of a ratio of atomic ionization energies [38,46] that has the value $\rho = 0.912$ for a pair of ground-state Br atoms. Damping function behaviour has not been studied for the first-order quadrupole–quadrupole interaction giving rise to the $m_1 = 5$ terms, but it is convenient to use Eq. (16) for that case too as it ensures physically sensible behaviour of the MLR potentials at very short distances [37,38].

As discussed in Refs. [47,38], the value of $p$ in Eqs. (13) and (14) must be larger than the difference between the powers of the first and last terms in Eq. (15), $p > (m_{\text{last}} - m_1)$, in order to prevent the long-range behaviour of the exponential term in Eq. (9) from changing the effective values of one or more of the $C_m$ coefficients defining the $u_{\text{ MLR}}(r)$ function. However, there is no analogous constraint on the value of $q$, although experience suggests that the best choice is usually $3 \leq q \leq p$. Similarly, the value of $r^*_\text{ref}$ has no physical significance, but setting it at an optimum distance (manually selected, see below) somewhere between $r^*_\text{eq}$ and the largest interatomic distance sampled by the data used in the analysis (the outer turning point of the highest observed vibrational level) allows us to obtain an optimum representation of the data with the smallest number of fitted $\beta_i$ exponent coefficients.\(^1\)

Physical arguments regarding the limiting asymptotic values of the BOB functions of Eqs. (6) and (7) [48] make it appropriate to write the associated radial strength functions in the same type of form used for Eq. (13):

$$S^{(X/A)}_{\text{ad}}(r) = S^{(X)}_{\text{ad}}(r; r^*_\text{eq}) + [1 - y_p(r; r^*_\text{ref})] \sum_{i=0}^{N_p} \gamma_i y_p(r; r^*_\text{ref})^i,  

(17)

$$\tilde{R}^{(X/A)}_{\text{ad}}(r) = \tilde{R}^{(X)}_{\text{ad}}(r; r^*_\text{eq}) + [1 - y_p(r; r^*_\text{ref})] \sum_{i=0}^{N_p} \gamma_i y_p(r; r^*_\text{ref})^i  

(18)

in which all of the radial $y$-variables have the form of Eq. (10). Since we choose to set the zero of energy at the energy of separated ground-state atoms, and neither of the Br atoms is charged, the limiting asymptotic values of these functions are $S^{(X)}_{\text{ad}} = \tilde{R}^{(X)}_{\text{ad}} = 0$, and the isotopic dependence of the well depths is defined by the value of $u^{(X)}_{\text{ad}}$ [48,49]. Since our molecule is comprised of two atoms of the same chemical species ($A = B = \text{Br}$), this leads to the result:

$$\delta S^{(X)}_{\text{ad}} = S^{(X)}_{\text{ad}}(r; r^*_\text{eq}) = \frac{\Delta M_{\text{Br}(1)} + \Delta M_{\text{Br}(2)}}{M_{\text{Br}(1)}^2} \left( S^{(X)}_{\text{ad}} - u^{(X)}_{\text{ad}} \right).$$

(19)

In order to ensure that the effective adiabatic potentials for different isotopologues all have the same limiting long-range behaviour, we would normally set $p_{\text{ad}} = m_1 = \text{last} (5 \text{ for Br}_2)$ [48]. For the $X$ state, however, the $C_5/r^5$ term is orders of magnitude weaker than the $C_6/r^6$ term for virtually the whole potential well. We therefore use $p_{\text{ad}} = 6$ for the $X$ state, while fixing $p_{\text{ad}} = 5$ for the $A^{3P_u}_0$ state. There is no physical basis for specifying particular values for $q_{\text{ad}}$, $p_{\text{ad}}$, or $q_{\text{ad}}$ [48], but in practice it is convenient to set $q_{\text{ad}} = p_{\text{ad}}$ and $q_{\text{ad}} = p_{\text{ad}}$, and we fix the latter two at $q_{\text{ad}} = p_{\text{ad}} = 3$. We also adopt the Watson convention of fixing $u_{\text{ad}}^{(X)} = 0$, since this parameter is expected to be indeterminable from transition energy data alone.

\(^1\) A good preliminary estimate for $r^*_\text{eq}$ is often the geometric mean of the inner and outer turning points of the highest observed level: $r^*_\text{eq} \approx 3.0 \text{ Å for the } X^{1S_g}_0 \text{ state and } 4.7 \text{ Å for the } A^{3P_u}_0 \text{ state.}
[33,34]. Finally, since we know of no physical constraints on the limiting asymptotic value or behaviour of the $\Omega$-doubling radial strength function, we write it as a simple polynomial in the dimensionless radial variable of Eq. (10):

$$f_{\Omega}(r) = \sum_{i,t} W_i^\Omega e_i(r).$$

(20)

Our earlier experience [48] indicated that use of very small values of the integer $\alpha_q$ tends to yield $\Omega$-doubling strength functions $\Delta V^\Omega_{\alpha_q}(r)$ with implausible oscillatory behaviour outside the data region, and so we fix $\alpha_q = 4$.

3.4. Procedures

A particular MLR model, is defined by the terms included in Eq. (15) for $u_{A,A}(r)$ and by the values chosen for $p, q, r_{ref}$ and the polynomial order $N_p$ in Eq. (13), and may be identified by the label $MLR_{p,q}^{N_p}(N_p)$. The optimum recommended model is then chosen in order to minimize $\bar{D}$ and the number of fitting parameters, together with the requirement that the resulting potential behave “sensibly” outside the data region, at both large and small $r$. Because we are dealing with a non-linear least-squares problem, in order to commence a particular DPF analysis it is necessary to have realistic initial trial estimates of the MLR parameters $\Delta_2, \Delta_3, \cdots, \Delta_p$, and the exponent polynomial expansion coefficients $[\beta_i]$ for each model considered. Fortunately, they are readily obtained by performing a preliminary empirical analysis using Dunham polynomial expressions for the level energies [50], generating RKR turning points from the resulting expressions [51,52], and then fitting the resulting turning points to Eq. (9). This last step was performed using computer program BETA-M, which is available (with a manual) on the wwww [53]. In later stages of an analysis, such fits can be performed on potential function points generated from some earlier DPF run. Since the BOB functions and the $\Omega$-doubling function are relatively weak, setting the initial trial values for all of the $u_i, t_i$ and $w_i$ coefficients equal to zero virtually always yields stable, convergent fits.

In the initial stage of a DPF analysis involving two (or more) electronic states, it is usually initially desirable to consider each state separately, so that correlations between the effects of parameters for the different states do not confuse the selection of the optimum model for each. This can be done readily with program DPF by requiring that the energy levels of all states other than the one of interest be represented by independent term values or band constants. In some cases this approach means that the fits involve a relatively large number of free parameters (more than 5600 when the $A^2\Pi_{u\text{av}}$ state of $Br_2$ is represented by term values), and hence they can be somewhat time consuming (requiring $\approx$1 CPU hour per cycle of fit in the above example), but they are otherwise robust and stable.

When one of the $X$ or $A$ states of $Br_2$ was represented by term values and the other by analytic potential energy, BOB and $\Omega$-doubling functions, the quality of fit was not affected significantly by the inclusion of adiabatic potential-energy BOB functions $\Delta V_{\text{ad}}(r)$. However, when potential functions were used for both states, the quality of fit improved significantly (by 20%) on allowing the first adiabatic BOB parameter, $u_{00}$, to be free for one or both states, although there was no significant further improvement when higher-order $u_{ij}$ were also allowed to vary. As is shown by Eq. (19), the value of $u_{00}$ determines the isotopologue-dependence of the well depth for a given state. The isotopologue-dependence of the electronic transition energy is therefore given by (since $\Delta E_{\text{ad}}(A) = \Delta E_{\text{ad}}(X) = 0$):

$$\Delta T^{(X)}(A - X) = \Delta T^{(X)}(X) - \Delta T^{(X)}(A),$$

(21)

$$= \left( \frac{\Delta M_{BR_{(1)}}^{(X)}}{M_{BR_{(1)}}} + \frac{\Delta M_{BR_{(2)}}^{(X)}}{M_{BR_{(2)}}} \right) (u_{00}^{(X)} - u_{00}^{(B)}).$$

(22)

Comparison of results for cases in which one or the other or both of $u_{00}^{(A)}$, $u_{00}^{(X)}$ were allowed to vary freely showed that while the fitted values of these parameters varied significantly from case to case (sometimes even changing sign), the value of the difference $u_{00}^{(A)} - u_{00}^{(X)}$ was model-independent (within the uncertainties). We therefore conclude that the present analysis is able to determine the electronic isotope shift $\Delta T^{(X)}(A - X)$, but that the isotope-dependence of the individual well depths is less well defined. This conclusion was found to hold independent of what models were used for the potentials, for the non-adiabatic (centrifugal) BOB functions, or for the $\Omega$-doubling radial strength functions, and our final recommended value for $\Delta T^{(X)}(A - X)$ is presented in Section 4.

When the energy levels of the $A$ state were treated as independent term values, the quality of fit showed no significant improvement when one or more of the non-adiabatic centrifugal BOB parameters $\gamma_i$ for the $X$ state was allowed to vary, and the resulting values of $\gamma_i$ always had uncertainties greater than 100%. We therefore conclude that the available data for the $X$ state of $Br_2$ are not able to discern a non-adiabatic centrifugal BOB correction function. For the $A^2\Pi_{u\text{av}}$ state, however, the situation is quite different, as both the centrifugal BOB correction and the $\Omega$-doubling splittings have substantial effects on the predicted transition energies.

4. Results

Our challenge now is to determine the optimum form and polynomial order for the functions used to represent the exponent coefficients of the two MLR potentials, and for the $A$-state centrifugal BOB and $\Omega$-doubling radial strength functions. Because fits in which one state or the other was represented by term values were relatively time consuming, we began with a cyclic approach of, in turn, optimizing the fit with regard to the parameters defining one of these states while holding the model for the other fixed, and then repeating the procedure for the other. However, in the end, all parameters for both states were fitted simultaneously.

The long-range tails $u_{00}(r)$ of all of the models used for both electronic states were three-term versions of the damped inverse-power sums of Eqs. (15) and (16) in which $m_5 = 5$, 6 and 8, and except where stated otherwise, the inverse-power coefficients $C_5$, $C_6$ and $C_8$ were held fixed at the theoretical values of Sautet et al. [45]. In view of the discussion of Section 3.3, this means that the integer $p$ defining the dimensionless radial variables $y_p(r, r_e)$ and $y_p(r, r_{ref})$ must be set to be $p > (m_{\text{max}} - m_5) + (8 - 5) = 3$. Further, since the leading contribution associated with the long-range behaviour of the exponential term in the MLR form of Eq. (9) is a term with the inverse power $m = m_5 + p$, and the power associated with the third dispersion energy term in the theoretically predicted long-range potential is $m_4 \approx 10$ [47], this exponent-variable power was fixed at $p = 5$ for all of the cases considered below.

In general, the quality of fit improves with increases in the order $N_p$ of the polynomial defining the potential function exponent coefficient $[\beta_i]$ of Eq. (13). However, it tends to converge at different rates for different values of the radial-variable expansion centre $r_{ref}$, and for different values of the power $q$ defining the second dimensionless radial expansion variable, $y_q(r, r_{ref})$. All else being equal, for larger values of $q$, larger values of $N_p$ tend to be required to achieve a good quality of fit. However, for small values of $q$, the extrapolation properties of the potential are sometimes poor (see below). Performing fits to a variety of different models for the $X$ state of $Br_2$ yielded the results shown in Fig. 5, and analogous results for the $A$ state are shown in Fig. 6. In both, the predicted improvement in the quality-of-fit parameter $\bar{D}$ with increasing $N_p$ for given values of $q$ and $r_{ref}$ is easily seen, and as expected, the range of $r_{ref}$ values that yields a “good” fit (i.e., minimum values
of BR) increases with \( N_p \). However, there are clearly still a number of different \( \{q, r_{\text{ref}}, N_p\} \) combinations that will give a ‘good’ fit for either state.

An important test of the validity of a given fitted potential is whether it behaves well in the extrapolation region between the outer turning point of the highest observed level and the asymptotic limit where \( r \to \infty \). This is a particularly relevant question for the \( X^1\Sigma_g^+ \) state, since the highest observed vibrational level \((v' = 76)\) is bound by 129 cm\(^{-1}\) and has an outer turning point of only 4.63 Å. While our long-range potential for this state consists of three inverse-power terms with \( m_i = 5, 6 \) and 8, the \( C_5 \) coefficient is very small (and repulsive), and so the long-range tail \( u_{LR}(r) \) consists mainly of inverse-power terms corresponding to \( m_i = 6 \) and 8. As a result, in the extrapolation region, a plot of \( C_{LR}^{opt}(r) \equiv r^p[\mathcal{E} - V(r)] \) vs. 1/r\(^2\) should approach an \( r \to \infty \) intercept of \( C_{LR}^{theory} \) with a limiting slope of \( C_{LR}^{theory} \). Fig. 7 shows plots of this type associated with the optimum \( r_{\text{ref}} \) values for a number of the families (cases with the same \( N_p \) and \( q \)) of models considered in Fig. 5. It is immediately clear that outside the data region, all of the potential function models for which \( q = 4 \) or 5 behave unphysically by showing implausible extrema, while those with \( q = 6 \) and 7 smoothly approach the limiting slope from above, which is the behaviour one would wish for, since the first theoretically-predicted long-range term omitted from our \( u_{LR}(r) \) model for the long-range potential is the attractive \( C_0/\sqrt{r} \) term. While the \( N_p = 5.5 \) model is also very good in this regard, its lack of positive limiting curvature away from the \( C_0 \) slope leads us to prefer the best \( q = 6 \) model. The fact that all of the curves for the fitted potentials in Fig. 7 dip below the dotted line for the nominal limiting slope at the \( 1/r^2 \to 0 \) intercept merely reflects the presence of the very weak \( C_5 \) term in the long-range tails of those potentials. On the basis of the results summarized in Figs. 5 and 7 we therefore conclude that our recommended model for the \( X^1\Sigma_g^+ \) state of \( \text{Br}_2 \) is a two-state potential with \( p = 5 \), \( q = 6 \), \( r_{\text{ref}} = 3.12 \) Å, and \( N_p = 11 \). The values of the parameters defining this potential are listed in Table 2.

For the \( A^3\Pi_{1u} \) state of \( \text{Br}_2 \), the highest observed vibrational level is bound by less than 2 cm\(^{-1}\) and has an outer turning point of approximately 9.2 Å. On an inverse-\( r \) scale this is relatively close to the limit \( r \to \infty \). Since the leading long-range terms for this state correspond to \( m_i = 5, 6 \) and \( C_5 \) coefficient is not very small (as it is for the \( X^1\Sigma_g^+ \) state), this means that the appropriate long-range extrapolation test would be a plot of \( C_{LR}^{opt} \equiv r^p[\mathcal{E} - V(r)] \) vs. 1/r, which should have an \( 1/r \to 0 \) intercept of \( C_{LR}^{theory} \) and a limiting slope of \( C_{LR}^{theory} \). Fig. 8 shows plots of this type for models associated with the optimum-\( r_{\text{ref}} \) values for a number of the cases considered in Fig. 6. It is immediately clear that all of these models behave sensibly in the long-range extrapolation region. We are therefore free to choose our recommended potential function model for the \( A^3\Pi_{1u} \) state so as to satisfy the objectives of minimizing the number of empirical potential function expansion parameters (i.e., minimizing \( N_p \)), and optimizing the quality of fit (i.e., minimizing \( \delta \)). This leads us to recommend an MLR potential with \( p = 5 \), \( q = 4 \) and \( N_p = 13 \) for representing the \( A^3\Pi_{1u} \) state of \( \text{Br}_2 \).

Our remaining challenge is to determine optimum models for representing the centrifugal BOB correction function \( R_{BOB}(r) \) and the \( \Omega \)-doubling radial strength function \( I_{\Omega}(r) \) for the \( A^3\Pi_{1u} \) state of \( \text{Br}_2 \).
Table 2
Parameters of the recommended models MLR_{20}^{\text{X}}(N_i) for the $A^{3}Π_{u}$ and $X^{1}Σ_{g}^{+}$ states of Br₂ with energies in cm$^{-1}$ and lengths in Å. Note that all $β, t_0^β$ and $w_c^β$ are dimensionless. Numbers in parentheses are 95% confidence limit uncertainties in the last digits shown. Uncertainties are omitted for parameters lacking direct physical significance. This description uses $^{79}$Br₂ as the reference isotopologue, and the $e'$ levels as the reference energies for the $Ω$-doubling in the $A$ state.

<table>
<thead>
<tr>
<th>Form</th>
<th>$A^{3}Π_{u}$ state MLR$^{20}_{1,1}(13)$</th>
<th>$X^{1}Σ_{g}^{+}$ state MLR$^{20}_{1,1}(11)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$</td>
<td>13909.011 (12)</td>
<td>0.0</td>
</tr>
<tr>
<td>$D_e$</td>
<td>2147.864 (9)</td>
<td>1605.875 (2)</td>
</tr>
<tr>
<td>$r_{ref}$</td>
<td>2.70432 (3)</td>
<td>2.2810272 (7)</td>
</tr>
<tr>
<td>$μ_{B^0}$</td>
<td>0.912</td>
<td>0.912</td>
</tr>
<tr>
<td>$C_5$</td>
<td>$3.2 \times 10^{4}$</td>
<td>$-3.3 \times 10^{2}$</td>
</tr>
<tr>
<td>$C_6$</td>
<td>$6.37 \times 10^{5}$</td>
<td>$6.274 \times 10^{5}$</td>
</tr>
<tr>
<td>$C_7$</td>
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<td>(5, 6)</td>
</tr>
<tr>
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<td>3.12</td>
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<td>1.04182773</td>
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<tr>
<td>$β_1$</td>
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<td>0.861027</td>
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<tr>
<td>$β_2$</td>
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<td>1.243753</td>
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<tr>
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<td>$-3.380$</td>
</tr>
<tr>
<td>$β_{11}$</td>
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</tr>
<tr>
<td>$β_{12}$</td>
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</tr>
<tr>
<td>$[p_{ad}, q_{ad}]$</td>
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<td>(6, 6)</td>
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<tr>
<td>$u_0^{ad}$</td>
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<td>0.371 (42)</td>
</tr>
<tr>
<td>$[p_{ad}, q_{ad}]$</td>
<td>(3, 3)</td>
<td>$-1.810$</td>
</tr>
<tr>
<td>$t_0^{β}$</td>
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<td>$-1.810$</td>
</tr>
<tr>
<td>$t_1^{β}$</td>
<td>0.00113</td>
<td>$-0.571$</td>
</tr>
<tr>
<td>$t_2^{β}$</td>
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<td>$-0.1809$</td>
</tr>
<tr>
<td>$t_3^{β}$</td>
<td>$-8.22$</td>
<td>$-0.571$</td>
</tr>
<tr>
<td>$t_4^{β}$</td>
<td>$-29.34$</td>
<td>$-0.1809$</td>
</tr>
<tr>
<td>$t_5^{β}$</td>
<td>49.9</td>
<td>$-0.571$</td>
</tr>
<tr>
<td>$t_6^{β}$</td>
<td>$-41.9$</td>
<td>$-0.1809$</td>
</tr>
<tr>
<td>$t_7^{β}$</td>
<td>14.</td>
<td>$-0.571$</td>
</tr>
<tr>
<td>$w_0^{β}$</td>
<td>0.00391</td>
<td>$-0.0126$</td>
</tr>
<tr>
<td>$w_1^{β}$</td>
<td>0.035</td>
<td>$-0.0126$</td>
</tr>
<tr>
<td>$w_2^{β}$</td>
<td>0.318</td>
<td>$-0.0126$</td>
</tr>
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</table>

Fig. 8. Test of the long-range extrapolation behaviour of a number of fitted MLR models for the $A^{3}Π_{u}$ state of Br₂. The labels for the various cases are $N_{ref}^{20}$, where $N = N_{ref}$.

Fig. 9. Test of convergence of the fits as a function of $N_{θ}$ for different choices of the order $N_{ref}$ of the polynomial function used to represent the centrifugal BOB radial function $R_{θ}(r)$ of Eq. (18). It is immediately clear that convergence with respect to the order of the $Ω$-doubling polynomial occurs at $N_{θ} = 3$, independent of the value of $N_{ref}$. Moreover, Fig. 10 shows that the resulting $Ω$-doubling radial strength function is well-behaved and model-independent. Note that the conventional “band constant” parameters used to describe $Ω$-doubling as a function of $r$ commonly represented as $q_{θ}$ may be generated as the radial expectation values of $ΔV_{θ}(r)$ for different vibrational levels.

Unfortunately, Figs. 9 and 11 show that convergence with respect to the order of the centrifugal BOB strength function polynomial order is not as rapid as was the case for the $Ω$-doubling radial strength function. Moreover, Fig. 12 shows that the centrifugal BOB radial strength function determined in this way is not so well-defined and model-independent as was the case for the $Ω$-doubling radial strength function seen in Fig. 10. Nonetheless, all of the functions shown in Fig. 12 have the same basic shape: a minimum near $r_{c}$, a broad maximum around 4–7 Å and gradual fall-off at larger distances, and those for $N_{θ} = 9$ and 10 are indistinguishable. Moreover, since it is the radial expectation value of this (very weak) function, weighted by the square of the vibrational wavefunction, that affects the actual level energies, the small oscillations and model-dependence seen in Fig. 12 are not too troubling. In any case, we select the $N_{θ} = 9$ function as our recommended model for the centrifugal BOB radial strength function.

The parameters defining our final recommended models for the $X^{1}Σ_{g}^{+}$ and $A^{3}Π_{u}$ states of Br₂ are summarized in Table 2. For the 16914 data for three isotopologues used in this study, these parameters yield a quality of fit corresponding to $Ω = 0.899$. The final fitted parameters shown in Table 2 were rounded off using the sequential rounding and refitting procedure of Ref. [54] that
minimizes the number of significant digits required to represent the parameters determined by a fit without reducing the precision with which they represent the data. Uncertainties are not listed for parameters other than \( D_e \) and \( r_e \) because, as is the case for higher-order Dunham coefficients in a conventional parameter-fit analysis, the individual parameters have no particular physical significance, so their uncertainties offer no insight. However, these parameters collectively provide a very accurate delineation of the two potential energy functions. Moreover, when those parameter uncertainties are combined with the correlation matrix from the fit, it is a straightforward matter to calculate the uncertainties in the resulting potential functions at any given distance (see Eq. (7) of Ref. [54]). Fig. 13 presents the 95% confidence limit uncertainties in our recommended \( X \) and \( A \)-state potential energy functions. AFORTRAN subroutine for generating the recommended potentials, together with lists of the band constants \( G_v, B_v, D_v, \ldots \), and (for the \( A^3P^1_u \) state) \( q_v \), for all bound levels of all three isotopologues, have been submitted to the Journal's online Supplementary data archive.

As discussed at the end of Section 3, we believe that the present analysis can determine the isotopologue-dependence of the \( A-X \) electronic transition energy more reliably than it can the isotopologue-dependence of the individual potential energy well depths \( \Delta_e \) of the two states. To justify this conclusion, Table 3 presents results obtained from fits to our final model in which either none, or one, or both of the leading adiabatic BOB parameters \( u_0(X) \) and \( u_0(A) \) was allowed to vary. The values of the quality-of-fit parameter \( \text{dd} \) clearly indicate that at least one of these parameters can be determined from the data, and there is a small (1%) preference for that being the \( u_0^{A} \) value for the \( X^1\Sigma^+ \) state. We choose the case in

<table>
<thead>
<tr>
<th>( u_0(X) )</th>
<th>( u_0(A) )</th>
<th>( \text{dd} )</th>
<th>( \delta \Delta_e )</th>
<th>( \delta \Delta_e (A^3\Pi_{1u}) )</th>
<th>( \delta \Delta_e (A^3\Pi_{3u}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 ( ^a )</td>
<td>0.0 ( ^a )</td>
<td>1.10941</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.0 ( ^a )</td>
<td>-0.356 (8)</td>
<td>0.90615</td>
<td>0.0</td>
<td>0.018</td>
<td>-0.018</td>
</tr>
<tr>
<td>0.0 ( ^a )</td>
<td>0.326 (7)</td>
<td>0.89874</td>
<td>-0.016</td>
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<td>-0.016</td>
</tr>
<tr>
<td>0.0 ( ^a )</td>
<td>0.372 (42)</td>
<td>0.89862</td>
<td>-0.018</td>
<td>-0.003</td>
<td>-0.016</td>
</tr>
</tbody>
</table>

\( ^a \) Value fixed at zero in the fit.
which both $u_0$ values are allowed to vary as our recommended model because it provides more realistic estimates of the uncertainties. However, the fact that the electronic isotope shift is virtually the same for all of the last three cases considered in Table 3 gives us confidence regarding its physical significance. Note that it has the same sign and magnitude as the $A$-X electronic isotope shift reported by Booth et al. ($-0.0129$ (20) cm$^{-1}$) [55].

Table 4 lists the values of the well depths and electronic transition energy for the three isotopologues implied by the recommended parameter sets of Table 2. Note that to generate a potential for one of the ‘minor isotopologues’ ($^{79,81}$Br$_2$ or $^{81,81}$Br$_2$) one should not replace the $\Sigma_v$ value in Table 2 by the associated value from Table 4, but rather one should add the appropriate adiabatic correction function $AV^{(X)}_{\Sigma_v}$ of Eq. (6) to the potential for the reference isotopologue $^{79,79}$Br$_2$. Since the radial strength function $S_{\Sigma_v}$ for each state has only a single non-zero term ($u_0^{\Sigma_v}$), this correction function is quite simple. For standard Franck–Condon factor and matrix element calculations, sample potential function input files for use in the standard program LEVEL can be found in the journal’s online Supplementary data archive.

5. Discussion

In many of the studies of the $B^3\Pi_{1u}$-state halogens, it became commonplace to use near-dissociation theory analyses [56–59] to obtain optimal estimates of the distance from the highest observed level to dissociation, of the number and energies of ‘missing’ levels, and of the leading long-range potential energy coefficient, $C_5$. However, the distance at which the $C_5/r^5$ term becomes the dominant contribution to the long-range potential is almost an order of magnitude larger for the $A^3\Pi_{1u}$ states [45,60], and so it is relatively much more difficult to determine values of their $C_5$ long-range coefficient from experimental data. Although most of the analyses reported herein were performed with all of the $C_n$ coefficients held fixed at the values of Sauter et al. [45], we also ran a couple of series of fits in which $C_2(A)$ was also treated as a free parameter. While the overall quality of fit improved slightly and the irregularity in the variation of $\Delta A$ with $r_{\text{ref}}$ was somewhat reduced (c.f., Fig. 6), the model-dependence of the fitted $C_5$ values was sufficiently large that it was clear that no reliable empirical estimate of this $C_5$ coefficient may be obtained in this way.

The best previous estimate of the dissociation energy of Br$_2$ was that which Gerstenkorn and Luc obtained in 1989 [61] based on 16914 Fourier Transform data for the $B^3\Pi_{1u}^\circ$$–$$X^3\Sigma_g^\circ$ system of $^{79,80}$Br$_2$ extending to $\nu = 53$, which is bound by only 5.3 cm$^{-1}$ [18]. They generated RKR turning points from Dunham $G_\nu$ and $B_\nu$ polynomials obtained from fits in which the first four centrifugal distortion constants were constrained to quantum-mechanical values calculated from the RKR potential in a self-consistent manner. A fit of their outermost RKR turning points to a simple (undamped) inverse-power sum then yielded values of $\Sigma$, $C_2$, $C_5$, $C_8$ and $C_{10}$ for the $B$-state. On combining their $\Sigma$ value with the accurately-known atomic spin–orbit splitting energy [62] and their value for the ground-state zero-point energy [61], we obtain $\Sigma(X) = 16056.925$ (10) and $\Sigma(A) = 15894.545$ (10) cm$^{-1}$. These values are 0.050 cm$^{-1}$ larger than those yielded by the present analysis: $\Sigma(X) = 16056.875$ (2) and $\Sigma(A) = 15894.495$ (2) cm$^{-1}$. However, the fact that the binding energy of the highest observed level of the $A$ state (1.90 cm$^{-1}$) is more than a factor of two smaller than that for the $B$ state gives us confidence in preferring the present results.

The lowest level of the $A^3\Pi_{1u}$ state used in the present analysis is the $\nu = 2$ level observed in the present work [63]. However, a number of years ago Hwang et al. [15] reported the determination of $\Sigma_A(A)$ values with estimated relative uncertainties of 0.05 cm$^{-1}$ and an absolute uncertainty of 0.3 cm$^{-1}$ for the three isotopologues of Br$_2$ from a study of $\beta \rightarrow A$ transitions in a free jet expansion. The reason for our neglect of their $\nu = 0$ observations was that we found them to be incompatible with any reasonable extrapolation from the present work. In particular when synthetic 0–0 band X–A transitions for $^{79,80}$Br$_2$ generated from the parameters reported in Ref. [15] and the ground-state constants of Gerstenkorn et al. [18] were included in our analysis, they were found to be consistently 0.5 cm$^{-1}$ larger than predictions yielded by the fit.

![Fig. 14](image-url) Values of $B_v$ (left-hand panel), and first differences $\Delta B_v = B_{v+1} – B_v$ (right-hand panel) between inertial rotational constants for the $A^3\Pi_{1u}$ state. The dotted blue curve shows results from the present fit to Eq. (1) and the solid black points come from the 1972 results of Coxon [8], while the (superimposed) solid red and broken green curves pass through values generated from potential-fit analyses that, respectively, did and did not allow for the centrifugal BOB correction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The original "parameter-fit" analysis of Boone [16] reported what appear to be an anomalous fluctuation in the $v$-dependence of the first differences $D_B^{v}/C_{17}^{B_{v}}/C_{0}^{B_{v}}$ between the values of the leading rotational constants for the $A_{3}^{3}P_{1}^{1}u$ state [16]. This behaviour is shown in the right-hand panel of Fig. 14, and the leading centrifugal distortion constants showed analogous behaviour. Since that behaviour was first discerned in a "parameter-fit" analysis, we were initially concerned that it might reflect non-mechanical perturbative effects. However, we found that it was fully accounted for by the analytic potential energy functions yielded by our DPF analysis, with the resulting potential curve(s) showing no anomalous behaviour in this region. We therefore conclude that this apparently anomalous behaviour of $D_B^{v}$ merely reflects some minor change in the shape of the $A$-state potential in this region. For the record, Fig. 15 compares values of the band constants for the $A_{3}^{3}P_{1}^{1}u$ state obtained from a conventional "parameter fit" analysis using Eq. (1) with those generated from the recommended MLR potential. Note that the potential-fit values of the $\Omega$-doubling parameter $q_{\Omega}(\text{Pot})$ shown here were calculated as expectation values of the function $\Delta V_{\Omega}^{\Delta}(r)$ of Eq. (8).

Finally, Fig. 16 shows the MLR potential curves for the $A_{3}^{3}P_{1}^{1}u$ (solid black curves) and $X_{1}^{1}R_{+}^{g}^{3}u$ (red curves) states yielded by our DPF analysis, together with an RKR potential for the $A_{0}^{3}P_{2}^{2}u$ state reported by Sur and Tellinghuisen [64] and Van Marter et al. [65]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Potentials tend to merge at internuclear distances $\gtrsim 4 \text{Å}$ and less than 300 cm$^{-1}$ from the dissociation limit. The outer turning points of vibrational levels $v(A) \gtrsim 20$ lie in this region. The $A_{3}^{3}P_{1}^{1}u$ state of a halogen dimer is able to be perturbed by the $A_{3}^{3}P_{2}^{2}u$ and the $B_{3}^{3}P_{0}^{3}u$ states through a type of spin–orbit interaction, as reported

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Fig. 15. Comparison of "parameter-fit" values of the band constants for the $A_{3}^{3}P_{1}^{1}u$ state of $^{79,81}\text{Br}_{2}$, all in cm$^{-1}$ (blue or black points, with error bars or boxes indicating uncertainties), with values generated from the recommended MLR potential (red curves). ‘Neg.’ and ‘Pos.’ mean that the values are negative and positive, respectively.

Fig. 16. The present MLR potentials for the $A_{3}^{3}P_{1}^{1}u$ and $X_{1}^{1}R_{+}^{g}^{3}u$ states of Br$_2$, together with the potential curve for the $A_{3}^{3}P_{2}^{2}u$–state reported by Sur and Tellinghuisen [64] and Van Marter et al. [65]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
by Ishiwata et al. in their analysis of the $A^3\Pi_{1u}$ state of Cl$_2$ [66].

The combination of this coupling with an accidental vibrational degeneracy may be the source of the strong perturbations that made the data for $\sigma(A) = 27$ sufficiently irregular that they could not be used in our analysis.

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Appendix A. Supplementary material

Supplementary data associated with this article consist of: (i) a listing of all of the experimental data used in the analysis, (ii) lists of the first 8 band constants for all vibrational levels of all 3 isotopologues, calculated from the recommended potential energy functions for the A and X states, (iii) sample data files for performing calculations with these potentials using the publicly available bound-state/Franck-Condon program “LEVEL” (see http://leroy.uwaterloo.ca/programs/), and (iv) a stand-alone Fortran subroutine for generating these potential energy functions. This material may be found in the online version at http://dx.doi.org/10.1016/j.jms.2012.12.006.

References