Diatom potential curves and transition moment functions from continuum absorption coefficients: Br$_2^*$†

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A program for calculating diatomic molecule absorption coefficients using "exact" numerically computed radial wavefunctions was developed and used to examine critically a number of approximations which are frequently used in absorption coefficient calculations. These tests showed that both use of the delta function approximation, and fixing the rotational quantum number in the radial overlap integrals at $J = 0$, introduce errors of slightly less than 6% of the absorption coefficient maximum $e^{\inf}$. Similarly, errors of slightly less than 8% of $e^{\inf}$ are introduced by either fixing the initial state $J$ at the average value for the ground temperature, or by using Giauque's Airy-function approximation for the unbound state wavefunction. A simple procedure for shrinking the sum over initial state $J$'s without significant loss of accuracy was therefore devised. These techniques were then applied to the analysis of the visible absorption continuum of Br$_2$, and a nonlinear least-squares fitting procedure used to determine optimized final state potential curves and transition moment functions for the two overlapping electronic transitions. In the region to which the data are sensitive, 2.105 $\leq R \leq 2.55$ Å, the transition moments so obtained (in debyes, lengths in angstroms) are $M(1\Pi_g^u)-X(\Sigma_g^+)$ and $M(1\Pi_u^g)-X(\Sigma_u^+)$ transitions $M(1\Pi_g^u)-X(\Sigma_g^+)$ and $M(1\Pi_u^g)-X(\Sigma_u^+)$ transitions. The concomitant repulsive potential curves for the $B(1\Pi_u^g)$ and $1\Pi_g^u$ states are, respectively (in cm$^{-1}$, expressed relative to the ground state dissociation limit; lengths in angstroms): $V_0(R) = -11744.594$ $\exp[-5.807(R-2.3)]$ and $V_0(R) = 7654$ $\exp[-4.637(R-2.3)-0.879(R-2.3)]$, where the former expression applies only to the region inside the B-state inner turning point for $\nu = 8$, $R(8) = 2.4485$ Å. Comparisons with experimental relative intensities in the discrete portion of the $B-X$ spectrum, and with molecular beam photofragment spectroscopy measurements of the relative strengths of the two electronic transitions, are also reported.

I. INTRODUCTION

The dependence of the continuous absorption and emission intensities of diatomic molecules upon their potential energy curves and transition moment functions has been understood in principle almost since the birth of wave mechanics. The foundation was laid by Condon's quantum-mechanical restatement of Franck's proposed mechanism for photodissociation. Condon's procedure, now known as the reflection or delta-function method, was immediately used to explain the absorption continua of a number of systems. A wave mechanical treatment was then introduced by Steckelberg and Gibson, Rice, and Bayliss, who used it to determine repulsive potential curves from the absorption data for O$_2$ and Cl$_2$, respectively. Since that time, analogous studies have been performed on a number of systems, with a variety of approximations being used for the radial wavefunctions, the transition moment function, and the summation over the populated levels of the absorbing species.

To date, this type of analysis has not gained general acceptance as a practical and reliable method of determining transition moment functions and repulsive potential curves. This is somewhat surprising, since information of this type is much sought after, and is difficult to obtain even using much more sophisticated methods. This neglect may partly be attributed to the use of computational approximations which often limit the accuracy of the potentials obtained in this way. However, computer technology removed the need for most such approximations more than a decade ago. The main obstacle now is the dearth of experimental data which are sufficiently accurate and extensive to justify the trouble and expense of a proper analysis. However, with present techniques, accurate experimental data of this type could be readily obtained for many systems. Combining such results with appropriate computational methods, such as those described below, should routinely yield accurate information about repulsive potential curves and transition moment functions, thus reopening an important field of spectroscopy for exploitation.

One case for which appropriate experimental data are already available is the visible and near infrared absorption continuum of Br$_2$ vapor. This spectrum is due to transitions from levels of the ground $X(\Sigma_g^+)$ state into both the purely repulsive $1\Pi_u^g$ state and the continuum of unbound levels above the dissociation limit of the bound $B(1\Pi_u^g)$ state. The potential energy curves which we determined for this system are shown in Fig. 1, together with the corresponding calculated room temperature absorption continuum and its decomposition into the $1\Pi_u^g-X(\Sigma_g^+)$ and $B(1\Pi_u^g)-X(\Sigma_u^+)$ transitions. Since the low frequency end of the $B-X$ spectrum (transitions to levels below the $B$-state dissociation limit) is discrete rather than continuous, data in this region are not considered in the present analysis. This presents no difficulties, since Barrow et al. have determined an accurate potential curve for the bound portion of this potential from an analysis of the discrete spectrum. Furthermore, this restriction to frequencies $\nu > 20000$ cm$^{-1}$ means that the weak absorption associated with transi-
FIG. 1. Potential energy curves and (insert) room temperature decadic absorption coefficients associated with the visible absorption spectrum of Br₂, the latter being decomposed into (dashed curves) the separate contributions due to the two contributing electronic transitions. Horizontal dashed lines indicate the dissociation limits of the B (upper line) and the X and 1Π₁ₓ (lower line) states.

lations into the A(Π₁ₓ) state may be completely neglected, since it occurs at lower frequencies.

Section II of this paper summarizes the present method of calculating absorption coefficients using “exact” numerical unbound state wavefunctions, and describes a convenient new way of taking account of the J dependence of the radial overlap integrals. This is followed in Sec. III by a critical examination of the validity of a coupled set of approximate ways of performing such calculations: Gisselenson’s⁴⁵ Airy-function method, and the Sulzer and Wielandt² procedure. Section IV then describes a procedure for performing nonlinear least-squares fits of absorption coefficients calculated from trial potential curves and transition moment functions, to experimental data. Finally, in Sec. V this method of analysis is applied to the visible absorption spectrum of Br₂ and used to determine repulsive potential curves for the 1Π₁ₓ and B(Π₁ₓ) states, and the transition moment functions connecting these states to the ground (X¹Σ⁺) state.

II. CALCULATION OF CONTINUUM ABSORPTION COEFFICIENTS

A. General theory

The photodissociation cross section (continuum absorption coefficient) for transitions from the vibration—rotation levels (ν, J) of an initial electronic state into unbound levels with angular momentum Ω’ of the final electronic states [ν’], caused by absorption of light of frequency ν (in cm⁻¹) is

\[ \sigma(\nu) = \frac{8}{3h^2c} \sum_{\Omega} \sum_{J} g(\nu) \sum_{J’} S(J’)(2J + 1)^{-1} \times \left| \int_{0}^{\infty} \Psi_{\nu J’}(R)M_{\nu J’}(R)\Psi_{\nu J}(R)\,dR \right|^2. \]  

Here, Fν,J is the fraction of the absorbing molecules in vibration—rotation state (ν, J), g(ν) the electronic degeneracy factor for electronic state “n,” ρ(Eν) the “density of states” normalization factor associated with the unbound level energy Eν, above the dissociation limit of state ν, S(J’) is the appropriate Hön–London factor,²⁷⁻²⁹ M(J)(R) the transition moment function for absorption into electronic state ν, and Ψν,J(R) and Ψν,J’(R) are the effective radial wavefunctions of the initial (bound) and final (unbound) states of the transition. The value of Eν is related to the absorption frequency ν, the energy of the initial level E(ν, J), and energy of the dissociation limit of state ν, D(ν), by the expression³⁰

\[ \nu = E_{\nu} + D(\nu) - E(\nu, J). \]

While the sums over ν and J include all populated levels of the initial state, that over J’ is restricted by the rotational selection rule appropriate to the given type of electronic transition.

If the absorbing species are in thermal equilibrium, Fν,J is simply the normalized Boltzmann population factor for the different vibration—rotation levels of the initial electronic state:

\[ F_{\nu J} = F_{\nu J}(T) = (2J + 1)e^{-E_{\nu J}/kT}/Q(T), \]

where

\[ Q(T) = \sum_{\nu J} (2J + 1)e^{-E_{\nu J}/kT} \]

is the usual internal motion partition function for a diatomic molecule. This effectively introduces a temperature dependence into the cross section of Eq. (1).

In practice it is usually convenient to replace the internuclear distance R by the dimensionless variable

\[ z = R/R_0, \]

where R₀ is some arbitrarily chosen scaling length. This transforms the radial Schrödinger equation into the form

\[ \{d^2/dz^2 + B_ν(E - V(z)) - J(J + 1)/z^2\}\phi_ν(z) = 0, \]

where V(z) is the potential energy function (in cm⁻¹), and Bν = 8μc(πR₀)²/ℏ. The unit spatial normalization required of bound state wavefunctions,

\[ \int_{0}^{\infty} \Psi_\nu(r)^*\Psi_\nu(r)\,dr = \int_{0}^{\infty} \phi_\nu(z)^*\phi_\nu(z)\,dz = \delta_{\nu J}, \]

and the analogous “density of states” normalization of the continuum wavefunctions,³¹

\[ \int_{0}^{\infty} \Psi_\nu(r)^*\Psi_\nu(r)\,dr = \int_{0}^{\infty} \phi_\nu(z)^*\phi_\nu(z)\,dz = \frac{2(E - E^*)}{\rho(E)}, \]

mean that

\[ \phi(z) = \sqrt{R_0} \Psi(R). \]

In the present work, the normalization of the continuum wavefunctions was defined by the asymptotic behavior,

\[ \lim_{z \to \infty} \{\phi_{\nu J}(z)\} = \sin(kz + \eta_{\nu J})/k, \]

\[ \eta_{\nu J}(E) = \eta_{\nu J}(E_{\nu}) + \frac{\sqrt{2\pi}}{2} \int_{0}^{\infty} \frac{Q(T)\,d\nu}{\sqrt{2\pi}} \left( \frac{1}{\rho(E_{\nu})} \right)^{1/4} \left( \frac{1}{\rho(E)} \right)^{1/2} \left( \frac{E - E_{\nu}}{E_{\nu}} \right)^{-1/4}, \]

\[ k = \sqrt{\frac{2E_{\nu} - E^*}{\rho(E_{\nu})}}. \]
where \( \eta(E) \) is the phase shift, and \( k = (E_0E_v)^{1/2} \). This corresponds to a density of states of (in units 1/cm\(^{-1}\), for \( R_0 \) in cm and \( E_v \) in cm\(^{-1}\))

\[
\rho(E_v) = R_0^2 \left( \frac{\mu c}{\hbar E_v} \right)^{1/2}.
\]

(11)

Utilization of (5), (9), and (11) transforms (1) to the form

\[
\sigma_T(v) = \frac{16\pi R_0^2}{3} \left( \frac{2\mu}{c^2h} \right)^{1/2} \sum_{v_i j} \sum_{w} F_{v j}(T) \left( E_w \right)^{1/2} \times \sum_{j'} \Phi_{v_i j'} \Phi_{w j} \left( 2J + 1 \right) \left( 2J' + 1 \right) \left( \Phi_{v_i j'} \Phi_{w j} \right)^2.
\]

(12)

If we set \( R_0 = 1 \AA, \) express \( M_w(R) \) in D, and define \( \mu' = \mu N_c \) to be the reduced mass in amu, the absorption cross section, in units \( \text{Å}^2/\text{molecule} \), is given by

\[
\sigma_T(v) = 3.22691 \times 10^{-4}(\mu'v)^{1/2} \sum_{v_i j} \sum_{w} F_{v j}(T) \left( E_w \right)^{1/2} \times \sum_{j'} \Phi_{v_i j'} \Phi_{w j} \left( 2J + 1 \right) \left( 2J' + 1 \right) \left( \Phi_{v_i j'} \Phi_{w j} \right)^2.
\]

(13)

The analogous expression for the decadic molar absorption coefficient, \( \epsilon_T(v) \text{ mole} \cdot \text{cm}^{-1} \), is the same as (13), except that the numerical factor on the right hand side becomes \( 8.43946 \).

**B. Approximations required for practical calculations**

For species with small reduced masses (e.g., hydrides), the rotation–vibration levels are sufficiently spaced that relatively few levels are populated, even at quite high temperatures. In this case the sums over \( v, J \) and \( J' \) in (13) may be evaluated with virtually no approximations. On the other hand, for heavy (large reduced mass) species the initial state population usually involves hundreds of levels, so that these sums must be at least partially truncated if the calculations are to be at all manageable. Since the absorption coefficients associated with different vibrational levels are very different in character, the \( v \) summation cannot be readily simplified. However, the contributions for the different \( J \) and \( J' \) values associated with a given \( v \) all have a similar frequency dependence. As a result, most previous calculations simply neglected the \( J \) and \( J' \) dependence of the radial overlap integral in (13), and collapsed these two summations by setting \( J = J' \) equal to either zero or \( J \) (most probable). In the following, these approximations are examined, and a new way of treating the \( J \) summation is introduced.

The procedures considered below are tested by performing calculations on a model problem involving absorption into a single repulsive state. For the sake of convenience, the potential curves and transition moments determined in Sec. V for the \( X^1\Sigma_g^+ \rightarrow X^1\Pi_w \) transitions of Br\(_2\) are used to define this model problem, and calculations are performed for the highest and lowest temperatures associated with the Br\(_2\) data of Paschier et al.\(^ {24} \) However, the conclusions reached are believed to be quite generally valid, and to be only weakly dependent on the features of this particular system. Segment A of Fig. 2 shows the calculated decadic absorption coefficients for this model problem at the two temperatures considered.

**FIG. 2.** A: Calculated model–problem absorption coefficients at \( T = 298^\circ \text{K} \) (solid curve) and \( 713^\circ \text{K} \) (dashed curve). B: Scaled differences between absorption coefficients calculated in the \( P \)– or \( R \)–branch approximation, and those yielded by the \( Q \)–branch (\( J' = J \)) approximation, at the same two temperatures considered in segment A. C: Scaled differences between absorption coefficients calculated using various approximate treatments of the sum over \( J \), and those obtained using \( NJ = 15 \). D: Scaled errors in calculated absorption coefficients caused by early truncation of the sum over \( v \).

1. **Collapse of the sum over \( J' \)**

An almost universal approximation in previous absorption coefficient calculations has been a neglect of the \( (J–J') \) dependence of the overlap integral in (13).\(^ {7–19} \)

Since the Hön–London factors \( S_{J'} \) have the normalization property that

\[
\sum_{J'} S_{J'} = (2J + 1),
\]

(14)
fixing $J' = J$ in all the overlap integrals effectively collapses the sum over $J'$. The justification usually given for this step is the assumption that for the range of $(J' - J)$ allowed by the rotational selection rules, the approximation

$$
\int_{0}^{\infty} \Phi_{e_{J',J}M_{e_{J',J}}} \Phi_{v',J} dz \approx \int_{0}^{\infty} \Phi_{e_{J,J}M_{e,J}} \Phi_{v,J} dz \tag{15}
$$

is fairly accurate. However, this assumption does not appear to have been quantitatively tested. In the case of discrete spectra it is known to be a poor approximation even for relatively heavy species. For example, Brown et al.\textsuperscript{33} showed (see their Table III) that the Franck-Condon factors for $P$ and $R$ branches of transitions in the visible spectrum of $I_4$ could differ by as much as 39%. However, in continuous absorption the magnitude of this type of effect may be partially damped by the averaging associated with the sums over $v$ and $J$.

We have examined this question by comparing model problem absorption coefficients calculated while assuming, in turn, that all transitions were $P$ branch ($J' = J - 1$), $Q$ branch ($J' = J$), or $R$ branch ($J' = J + 1$). The differences between the values obtained using the "Q-branch approximation" and those obtained using the $P$-branch or $R$-branch approximations, scaled to the calculated room temperature absorption coefficient maximum $\epsilon_{\text{max}} = 158.72 \text{ l/mole} \cdot \text{cm}$, are plotted in segment B of Fig. 2. These differences show that the error associated with the approximation (15) is of the order of a few tenths of a percent of the absorption coefficient maximum.

In spite of the above, fixing $J' = J$ in the overlap integrals and collapsing the sum over $J'$ using (14) (the $Q$-branch approximation) introduces very little error into the calculated absorption coefficients. This occurs because the average of $P$- and $R$-branch overlap integrals is very close to the corresponding $Q$-branch value. This is demonstrated by the fact that the $P$- and $R$-branch deviations seen in Fig. 2(B) are approximately equal in magnitude, but opposite in sign. Since the rotational intensity factors associated with $P$ and $R$ transitions are nearly equal, the residual discrepancies between the $Q$-branch results and the appropriately weighted (by $S_{J}$) sums of $P$, $Q$, and $R$ intensities are quite small. For the model problem, these residual discrepancies have the same qualitative behavior as the $P$-branch curves in Fig. 2(B), but their amplitude is smaller by a factor of $\approx 0.006%$ of $\epsilon_{\text{max}}$. Thus, unless one requires calculated absorption coefficients of extremely high accuracy (better than 0.006% of $\epsilon_{\text{max}}$), the $Q$-branch approximation (fixing $J' = J$) should yield satisfactory results at a cost of only $1/2$ or $1/3$ (depending on the rotational selection rule) of the computation time required by the full sum over $J'$.

Use of the $Q$-branch approximation allows molar absorption coefficients to be calculated from the simplified expression

\begin{equation}
\epsilon_{\text{F}}(\nu) = 8.49346(\mu)^{1/2} \sum_{v,J} F_{e_{J},J}(T) \sum_{n} (E_{n})^{1/2} \times \left| \int_{0}^{\infty} \Phi_{e_{J,J}M_{e,J}} \Phi_{v,J} dz \right|^{2} \tag{16}
\end{equation}

It should be pointed out that this collapse of the $J'$ summation to the $Q$-branch term will be a relatively poorer approximation for species with small reduced mass, since the wavefunction displacement associated with a given change in $J'$ would be relatively larger. Thus, the reliability of the $Q$-branch approximation should be quantitatively tested if one wishes to use it in calculating absorption coefficients for light species such as hydrides.

2. Simplifying the sum over $J$

In the past, many absorption coefficient calculations simply neglected the $J$ dependence of the radial overlap integral in (16) and fixed $J = 0, 1, 2, 3$. However, Doyle\textsuperscript{12} showed that this approximation causes an apparent shift of the calculated absorption continuum to shorter wavelengths, and that this displacement introduced errors of up to 50% in his calculated absorption coefficients for $H_2\left(\Sigma^+_g\right)$. The errors associated with this approximation are just as serious for heavy diatomics as for light ones.\textsuperscript{13,14}

A less drastic approximation, which effects the same collapse of the sum over $J$, consists of fixing the value of $J$ appearing in the overlap integral at its average (or most probable) value for the particular vibrational level at the given temperature.\textsuperscript{15,16,17} Since this characteristic $J$ (for each $v$) increases with temperature $T$, this approach takes account of the overall displacement of the spectrum with increasing $T$. However, it ignores the broadening due to the existence of contributions from a range of populated rotational levels.

A simple new procedure for taking account of both the displacement and broadening of the absorption continuum due to a thermal rotational population distribution is presented here. It is based on a division of the rotational population distribution for each initial vibrational level into a chosen number ($N_J$) of equally populated segments. The average value of $J$ for each segment is then determined, and the sum of the equally weighted contributions from these $N_J$ selected $J$ values is used to approximate the sum over all $J$. For $N_J = 1$, this approach is identical to the average-$J$ method described above, but in the limit of large $N_J$ it becomes virtually equivalent to the exact sum over all $J$.

Before dividing the total population $F_v(T)$ associated with a given vibrational level into $N_J$ equal segments, one must first determine how big this population is. According to (3)

\begin{equation}
F_v(T) = \sum_{J} F_{e_{J},J}(T) = Q_{e_{J},J}(T) e^{E_v/RT} \sum_{v'} Q_{e_{J},J}(v', T) e^{E_v'/RT}, \tag{17}
\end{equation}

where $E_v = E(v, 0)$, and $Q_{e_{J},J}(v, T)$ is the rotational partition function associated with level $v$:

\begin{equation}
Q_{e_{J},J}(v, T) = e^{E_v/RT} \sum_{v' J} (2J + 1) e^{E_v'(v, J)/RT}. \tag{18}
\end{equation}

Assuming that

\begin{equation}
E(v, J) = E_v + B_v [J(J + 1)], \tag{19}
\end{equation}

that the rotational levels are sufficiently dense that the sum
over \( J \) may be replaced by an integral, and that the upper bound of the sum in \( (18) \) may be set at \( J = \infty \), one obtains

\[
Q_R(v, T) = kT/B_e .
\]  
(20)

Results analogous to (20) are obtained when centrifugal distortions terms are included in the eigenvalue expression \( (19) \), but the small improvement in accuracy is overshadowed by the increased complexity of the result.

Consider the \( M \)th of the \( NJ \) equally populated segments of the rotational population distribution for vibrational level \( v \). Its lower and upper bounds are denoted by the rotational quantum numbers \( J_s(M) \) and \( J_s(M) \), respectively. The fact that this segment contains \( 1/NJ \) of the total population of level \( v \) means that

\[
\frac{Q_R(v, T)}{NJ} = e^{E_p/kT} \sum_{J(J+1)} \frac{J(J+1)}{e^{E(v,J)/kT}} .
\]

Use of (19) and (20) and the approximation that the sum over \( J \) may be replaced by an integral yields

\[
1/NJ = e^{-E_p/3kT} \int_0^{\infty} \frac{J(J+1)}{e^{E_vJ/kT}} .
\]

Since \( J_s(1) = 0 \), this yields

\[
J_s(M) = \left( kT/B_e \right) \ln[NJ/(NJ - M)]
\]

where, of course, \( J_s(M) = M(M+1) \).

In the \( M \)th of the \( NJ \) segments, the average value of \( J \) is defined as

\[
\overline{J}^M_s(v, T) = NJ e^{E_p/kT} \sum_{J(J+1)} \frac{J(J+1)}{e^{E_vJ/kT}} Q_R(v, T) .
\]

Making use of (19) and (20), replacing the sum over \( J \) by an integral, and utilizing the approximation

\[
J = \left[ J(J+1) \right]^{1/2} = \frac{1}{2} + \left[ J(J+1) \right]^{1/2} ,
\]

then yields the desired result

\[
\overline{J}^M_s(v, T) = -\frac{1}{2} + \frac{4(kT/B_e)^{1/2} + (kT/B_e)^{1/2}(\alpha^{1/2} \theta/NJ)}{4} \times \left\{ \text{erf}(a(M, NJ)) - \text{erf}(a(M - 1, NJ)) \right\}
\]

\[
-\frac{(kT/B_e)^{1/2}(NJ - M)a(M, NJ)}{-\frac{(NJ - M + 1)a(M - 1, NJ)}},
\]

where

\[
a(M, NJ) = \left[ \frac{NJ}{(NJ - M)} \right]^{1/2} .
\]

For the case \( NJ = M = 1 \), (21) readily reduces to the usual expression for the average value of \( J \) for a given \( v \) and \( T \):

\[
\overline{J}^1_s = -\frac{1}{2} + \frac{(\alpha^{1/2}/2)(kT/B_e)^{1/2} + (kT/B_e)^{1/2}/4 \theta}{4} .
\]

One noteworthy feature of (21) is the fact that all of the dependence on the particular temperature or vibrational level is contained in the multiplicative factors \((kT/B_e)^{1/2}\). This helps make (21) particularly easy to use. As an illustration of the nature of the results obtained from (21), Table I presents \( \overline{J}^M_s(v = 0, T) \) values for ground state \( ^7\text{H}_7\text{Br}_2 \) (the model problem) at the lowest and highest temperatures associated with the data of Passchier et al.\(^{24} \). The \( \overline{J}^M_s \) values yielded by (21) are in general nonetheless, so they are always rounded off to the nearest integer.

<table>
<thead>
<tr>
<th>( M )</th>
<th>( T = 298 \text{K} )</th>
<th>( T = 713 \text{K} )</th>
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<td>8, 16, 21, 26, 30, 34, 38, 42</td>
<td>13, 25, 33, 40, 46, 52, 58, 63</td>
</tr>
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</table>

Table I. \( \overline{J}^M_s(v = 0, T) \) values for \( ^7\text{H}_7\text{Br}_2 \).

Replacement of the complete sum over \( J \) by a sum over the average \( J \) characterizing \( NJ \) equally populated segments of the rotational population distribution transforms (16) into the form

\[
\epsilon_f(v) = 8.43946 \left[ \mu(v) \right]^{1/2} \sum_{\nu} F_\nu \left( \sum_{\nu} (E_\nu)^{1/2} \right) \times \int_0^{\infty} \Phi_{\nu s} \overline{J}^M_s v \Phi_{\nu v} \overline{J}^M_s d\nu .
\]

(22)

Here, the \( F_\nu \) (T) is defined by (17), and \( \overline{J}^M_s \) is the average \( J \) in the \( M \)th of the \( NJ \) equally populated segments of the rotational population distribution. Use of (19) and (20) and related approximation allows \( \overline{J}^M_s(v, T) \) and the rotational partition function \( Q_R(v, T) \) appearing in (17) to be generated by the simple expressions (21) and (20), respectively.

As an illustration of the utility of the present approach, segment C of Fig. 2 plots the relative errors in the model-problem absorption coefficients calculated using both various small values of \( NJ \) and the \( J = 0 \) approximation. The reference values used in the comparisons correspond to \( NJ = 15 \), for which case the absorption coefficients were shown in Fig. 2(A). While the discrepancies for the \( NJ = 1 \) case are fairly large, the errors die off quite rapidly with increasing \( NJ \). Going beyond the results shown in Fig. 2(C), we find that the maximum errors associated with analogous \( NJ = 6 \) and 10 calculations are, respectively, 0.0003 and 0.00015 of \( \epsilon_{\text{max}}^M(NJ = 15) \). This shows that the present approach provides an accurate and relatively inexpensive way of properly accounting for the sum over \( J \) in an absorption coefficient calculation.

Since the complete sum over many \( J \)'s can be accurately represented by a short sum over values characterizing the various segments of the rotational population, the validity of this approach should not be particularly sensitive to the precise manner in which these characteristic \( J \)'s are determined. Therefore, the approximations (such as 19) implicit in the derivation of (21) should not restrict the utility of this expression for generating \( \overline{J}^M_s \) values for use in (22).

3. Truncation of the sum over \( V \)

While the sum over \( v \) in (22) should include all vibrational level which are "significantly" populated, mini-


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mization of computational expense requires this sum to be truncated as early as possible. In practice this sum is simply truncated as soon as some specific fraction of the vibrational population, denoted VSUM, has been accounted for. Segment D of Fig. 2 shows how the error associated with this truncation procedure decreases as VSUM is increased from 0.90 to 0.98; for VSUM = 0.998 the analogous relative discrepancies have maximum absolute values of 0.00025 and 0.00040 at 286 and 713 °K, respectively. In all cases, the reference values used in the comparisons corresponded to VSUM = 0.9996. As might be expected, the discrepancies seen in Fig. 2(D) are qualitatively similar to the shape of the function $|\phi_0(R)|^2$ for the first vibrational level omitted from consideration. For example, the five extrema in the dashed curve for VSUM = 0.90 correspond to the fact that the $n = 4$ level was the first one omitted from that calculation. This behavior makes it virtually impossible to find a simple way of compensating for the effect of the neglected levels.

**C. Numerical methods**

Unless explicitly stated otherwise, the radial wavefunctions used throughout this work were always obtained by numerical integration of (8). The eigenvalues $E(v, J)$ and eigenfunctions $\phi_{vJ}(z)$ for bound vibration-rotation levels were calculated using a standard program based on those of Cooley5,5 Cashmore, and Cashmore.36 The radial wavefunctions for the unbound states, $\phi_{vJ}(z)$, were obtained using the same (Numerov) integration procedure and were subjected to the normalization requirement of (10). The latter could be imposed by integrating outward from $z = 0$ all the way to the asymptotic region where the wavefunction becomes a sine function. However, this approach is very expensive computationally, since this asymptotic sinusoidal behavior is not usually achieved until $z$ becomes very large.

The present work utilized a procedure for determining the correct asymptotic amplitude from the wavefunction at relatively small $z$. This technique is based on the first-order WKB wavefunction,

$$\psi_E, J(z) = A[z(k(z))^{1/2}] \sin \left( \int k(x) dx + \eta \right),$$

where

$$k(z) = \left[ B_0 \left( E_u - V_0(z) \right) - J(J + 1) / z^2 \right]^{1/2}.$$  

At values of $z$ significantly larger than the classical turning point, (23) should be an excellent approximation to the exact wavefunction. The local amplitude $A(z)$ determined by fitting the numerical wavefunction to (23) therefore determines an "apparent asymptotic amplitude" of

$$A_{\infty}(z) = A(z)[k(z)/k(\infty)]^{1/2} = A(z) \left[ E_u - V_0(z) - J(J + 1)/B_0 z^2 \right]^{1/4}.$$  

Values of $A_{\infty}(z)$ were evaluated at each maximum of the numerically calculated wavefunction, and convergence was assumed to have been achieved when the relative values at three successive maxima agreed to within a chosen criterion. Tests showed that requiring $A_{\infty}(z)$ to be two parts in $10^{8}$ yielded values of the overlap integrals which were accurate to better than one part in $10^{9}$. Hence, the present calculations assumed that $A_{\infty}(z)$ was converged when the relative differences between three successive values were less than $2 \times 10^{-6}$.

In the $B_2$, problem considered herein, the numerical integration was performed on an interval starting at 1.9 Å, using a mesh size of 0.0015 Å. This step size is small enough to ensure a minimum of 11 (and an average of ~20) mesh points between the closest adjacent nodes of any of the wavefunctions considered. Tests showed that further decreases in this step size change the calculated absorption coefficients by less than $10^{-5}$ of the largest value considered. For this case, the average computing time required for determining the absorption at a single frequency from a single initial $(v, J)$ state into a single final $(E_u, J^f)$ state, using an IBM 360–75 computer, is $0.00036$ min.

A Fortran listing of the computer program used in this work is available from the authors on request.

**III. APPROXIMATE METHODS OF CALCULATING ABSORPTION COEFFICIENTS**

**A. Gislason's Airy-function approach**

One of the most widely used approximate methods for calculating continuum absorption coefficients is Condon's reflection or delta–function method.14,16,25 In it, the continuum wavefunction $\Psi_{vJ}(R)$ is assumed to be proportional to a delta function $\delta(R - R_f)$ centered at $R_f = R_f(E_u, J)$, the turning point at energy $E_u$ on the effective upper state potential

$$U_u(R) = V_u(R) + J(J + 1)/R_u(R/R_0)^2,$$

where $B_0$ and $R_0$ are as in (6). This assumption means that the overlap integral appearing in Eq. (1) is simply proportional to $|M_u(R_f)|^2$. The conceptual and computational simplicity associated with this result have led to its widespread use in absorption coefficient calculations and analyses.

In a recent paper, Gislason25 introduced a much better type of approximation for the unbound state wavefunctions. At each energy $E_u$ the exact potential is approximated by a linear function passing through the turning point and having the correct slope there. For this approximate potential, the exact eigenfunctions are Airy functions of the first kind, $Ai(x)$. If the other factor in the integrand in (1), $|M_u(R)|^2$, is expanded as a Taylor series about the upper state turning point $R_f$, then the resulting integrals may be evaluated analytically and the overlap integral expressed as a simple sum. In Gislason's formulation,25 the density of states factor $\rho(E_u)$ is incorporated into the wavefunction normalization, so that the quantity of interest is [see (1)]

$$q(E_u) = \rho(E_u) \left| \int_0^\infty M_u \Psi_{vJ}(R) dR \right|^2.$$  

Utilizing the dimensionless variable $z$ from (5) and defining

$$W(z) = M_u(z) \Psi_{vJ}(z)$$

transforms Gislason's result into the form

---

\[ q_u(E_u) = \left( \frac{U_0^{(1)}}{z_t} \right)^2 \left( \sum_{i=0}^{\infty} \frac{W_{z_t}^{(i)}}{E_{z_t}} \right)^2, \tag{24} \]

where
\[ a = 3B_u U_0^{(1)} = 0.177961 \mu (t_0^{(1)}), \]
(for \( R_0 = 1.0 \times 10^{-4} \text{ cm}, \) as in Sec. II.A), and the superscript “(i)” denotes the \( i \)th derivative with respect to \( z_t \), evaluated at \( z_t = R_t^v / R_0 \). Thus, the evaluation of the overlap integral is reduced to a problem of determining the slope of the unbound state potential \( U_0^{(1)} \) and the value and derivatives of \( \Phi_{sv}(z) \) and \( M_u(z) \), all evaluated at the turning point \( z_t \).

For \( M = 0 \) this result (24) is precisely equivalent to the delta-function approximation, and Glisason pointed out that this probably explains the good qualitative success of the latter. Moreover, the use of (24) with \( M > 0 \) is in principle a straightforward procedure, requiring only a knowledge of \( M_c(z) \), \( \Phi_{sv}(z) \), and their derivatives. However, the utility of the higher-order (\( M > 0 \)) versions of (24) has not previously been examined.

Consideration of (6) shows that any of the derivatives of \( \Phi_{sv}(z) \) at \( z_t \) may be expressed in terms of \( \Phi^{(0)} \), \( \Phi^{(1)} \), and the value and derivatives of the effective bound-state potential,
\[ U_b(z) = V_b(z) + J(J + 1)/B_b z^2 \]
evaluated at \( z_t \). For example,
\[ W^{(2)} = M_u^{(0)} B_u U_0^{(1)} \Phi_{sv}^{(0)} + [U_0^{(1)} - E_{sv}] \Phi_{sv}^{(1)} \]
\[ + 3M_u^{(2)} B_u [U_0^{(0)} - E_{sv}] \Phi_{sv}^{(0)} + 3M_u^{(2)} \Phi_{sv}^{(1)} + M_u^{(3)} \Phi_{sv}^{(2)} \]
and analogous expressions are readily obtained for the higher derivatives (\( k > 1 \)). The necessary values of \( \Phi_{sv}^{(1)} \) and \( U_0^{(1)} \) are readily obtained by numerical interpolation, as are \( U_0^{(1)} \) and \( z_t \) itself. From a computational viewpoint, use of (24) effectively replaces the numerical integration to determine the exact wavefunction \( \Phi_{sv, l}(z) \), by these simple interpolations. With the present computer programs, this cuts the computation time by a factor of 5, and there is virtually no difference between the computation times for the \( M = 0 \) (delta-function), \( M = 1 \) or 2 versions of (24).

The reliability of (24) was examined by applying it to the same model problem considered in Sec. II.B, and comparing the results with “exact” numerical calculations for \( T = 0^\circ \), 298, and 713 \( ^\circ \)K. Both types of calculations were performed with \( N_{J} = 15 \) (except at \( T = 0^\circ \)K where only the \( v = 0 \), \( J = 0 \) level is populated). The solid curves labeled \( A(M) \) in Figs. 3–5 illustrate the relative
errors in the approximate Airy-function absorption coefficients obtained using (24). The lower segment of each figure plots these discrepancies as a fraction of the absorption coefficient maximum at that temperature, while the upper segment plots the fractional deviation from the numerical absorption coefficient at each frequency. For the sake of comparison, the dashed curves show the analogous errors in calculations which involve the numerical upper state wavefunctions, but use the \( J = 0 \) or \( N J = 1 \) approximations. The absence of dashed curves in Fig. 3 reflects the fact that \( v = 0, J = 0 \) is the only populated level at \( T = 0 \) K.

It is clear that while the \( M > 0 \) results are significantly better than those corresponding to the delta-function approximation \((M = 0)\), they are less accurate than even the \( N J = 1 \) results obtained using the exact upper state wavefunctions. Moreover, there is no reason to expect that results obtained from (24) using \( M > 2 \) will be better than those for \( M = 1 \) or 2, since the limit \( M \rightarrow \infty \) merely represents convergence to a wrong final state wavefunction. Thus, it appears that Gillason's appealingly simple result (24) should not be used if one desires results accurate to better than \( 1\% - 2\% \) of the absorption coefficient maximum.

**B. The Sulzer and Wieland equation**

Some years ago Sulzer and Wieland\(^{16}\) (SW) devised a simple three-parameter expression for describing the temperature and frequency dependence of the absorption coefficients of simple molecules. Using a number of plausible simplifying approximations, they obtained

\[
\varepsilon_T(v) = \varepsilon_T^{\text{max}} e^{\nu_0(v-u)/\Delta
u_T^2},
\]

where \( \nu_0 \) is the (temperature-independent) position of the absorption coefficient maximum, and the temperature dependence of the maximum \( \varepsilon_T^{\text{max}} \) and natural half-width \( \Delta
\nu_T \) of the absorption coefficient peak are given by

\[
\varepsilon_T^{\text{max}} = \varepsilon_T^{\text{max}} \left[ \tanh(k c_0/2kT) \right]^{1/2},
\]

\[
\Delta
\nu_T = \Delta
\nu_0 \left[ \tanh(k c_0/2kT) \right]^{-1/2},
\]

where \( c_0 \) is the (known) vibrational frequency of the absorbing molecule. If the parameters \( \nu_0, \varepsilon_T^{\text{max}}, \) and \( \Delta
\nu_0 \) are determined from the data at one temperature, (25) and (26) may be used to predict the absorption spectrum at other temperatures.

In spite of the fairly drastic approximations associated with their derivation, the appealing simplicity of Sulzer and Wieland's expressions has encouraged their use.\(^{12,13,16,37}\) However, we are unaware of any quantitative comparisons between their predictions and the results of "exact" numerical calculations. The model problem considered above and in Sec. III was therefore used for testing these expressions.

The three SW parameters characterizing this spectrum, \( \nu_0 = 24230 \text{ cm}^{-1}, \varepsilon_T^{\text{max}} = 196, 9 \text{ 1/mole cm}, \) and \( \Delta
\nu_0 = 1963 \text{ cm}^{-1} \) were determined from the properties of the numerically calculated spectrum at \( T = 0 \) K. However, even under these conditions the spectrum is not symmetric [as required by (25)], so the natural half-width given above is a simple average of the half-widths 1831 and 2059 cm\(^{-1}\), respectively, for the low and high frequency wings of the spectrum. The resulting relative errors in the SW predictions at \( T = 0 \), 298 and 713 K appear as the dotted curves in Figs. 3-5. These results show that the semiempirical SW equation makes predictions of roughly the same quality as those obtained from the delta-function approximation [curves A(0) in Figs. 3-5], and hence that it is not reliable to better than a few per cent. Much of this difficulty is certainly due to the inherent asymmetry of the actual absorption spectrum.

**IV. LEAST SQUARE FITTING OF CONTINUUM ABSORPTION COEFFICIENTS**

**A. The fitting procedure**

The attractive wells of the initial and final state potential energy curves associated with an absorption continuum are usually readily obtainable from an inversion of their observed vibration-rotation energy levels. However, both the repulsive part of the final state potential and the transition moment function are generally unknown, and must be determined from an analysis of experimental continuum absorption coefficients. In practice, one represents these unknowns by parametrized functions, and determines optimum values of the parameters by performing least squares fits of calculated absorption coefficients to experimental data. Since the calculated values are not linear functions of the various parameters, an iterative approach is required. In each cycle, the selection of trial parameter values \( \rho(a = 1, \ldots, m) \) is followed by the calculation of predicted absorption coefficients \( \varepsilon_T(v) \) at appropriate frequencies and temperatures. Corrections \( \Delta \rho(a) \) to these trial parameters which approximately minimize the weighted sum of squares of deviations

\[
\sum_{\nu} w(\nu, T) |\varepsilon_T^{\text{ex}}(\nu) - \varepsilon_T^{\text{cal}}(\nu)|^2
\]

from the experimental values \( \varepsilon_T^{\text{ex}}(\nu) \) are then obtained as solutions of the set of \( m \) linear equations (\( \beta = 1, \ldots, m \))

\[
\sum_{\nu} w(\nu, T) \left( |\varepsilon_T^{\text{ex}} - \varepsilon_T^{\text{cal}}| \right) \frac{\partial \varepsilon_T^{\text{cal}}}{\partial \rho_{\beta}} = \sum_{\nu} w(\nu, T) \frac{\partial \varepsilon_T^{\text{cal}}}{\partial \rho_{\alpha}} |\varepsilon_T^{\text{ex}} - \varepsilon_T^{\text{cal}}| = 0.
\]

(28)

The ensuing improved parameters \( \rho(a) = \rho(a) + \Delta \rho(a) \) may then be used to generate a new set of computed absorption coefficients. This cycle is repeated until \( |\Delta \rho(a)| \) becomes smaller than \( 1\% \) of the predicted statistical uncertainty in \( \rho(a) \), for all \( \alpha \). The weights \( w(\nu, T) \) appearing in (27) and (28) should vary as the squared inverse of the uncertainties in the individual experimental absorption coefficients, and are normalized such that their average value is unity.

For the parameters \( \rho(a) \) characterizing the transition moment functions \( M(R) \), the partial derivatives \( \partial \varepsilon_T^{\text{cal}}/\partial \rho_{\alpha} \) are easily obtained. The partial derivatives of the radial overlap integrals in (22) are

\[
\int_0^\infty \Phi_{\rho(a)} \Psi_{\rho(a)} \Phi_{\rho(a)} dz,
\]

and hence can readily be evaluated from the numerically calculated wavefunctions at the same time as the
overlap integral itself. The sums over \( \nu, M, \) and \( \nu \) in (22) may then concurrently accumulate values of both the absorption coefficient and its partial derivatives with respect to these parameters. This approach yields exact values of these partial derivatives at minimum computational expense.

The analogous partial derivatives of \( \varepsilon^p(\nu) \) with respect to the parameters of the final state potential are more difficult to determine using the type of approach described above.\(^{38}\) Hence, they were approximated by the finite difference expression

\[
\frac{\delta \varepsilon^p}{\delta \psi} \approx \frac{\varepsilon^p(\nu; \psi_0 + \delta \psi) - \varepsilon^p(\nu; \psi_0)}{\delta \psi},
\]

where \( \psi_0 \) is one of the final state potential parameters, and the increments \( \delta \psi \) were chosen so that the RMS value of \( \delta \varepsilon^p \) was the same for all parameters. In the present work this mean value of \( \delta \varepsilon^p \) was set at 0.50 \( \text{[1/mole \cdot cm]} \), which is \( 0.3\% \) of the absorption coefficient maximum; decreasing it further had no significant effect on the fits.

\textbf{B. Form of the potential energy and transition moment functions}

The fact that bound state wavefunctions decay rapidly outside the classically allowed region ensures that the integrand of the radial overlap integral in (22) will be negligibly small, except in the relatively narrow region between the inner and outer turning points of the populated initial-state vibrational levels. This means that absorption coefficient data can only provide information about the nature of the transition moment function \( M_s(R) \) on this interval (in the case of \( \text{Br}_2 \), it ranges from \( \approx 2.10 \) to 2.55 \( \text{Å} \)). In such a restricted region \( M_s(R) \) is unlikely to change greatly, and hence should be able to be accurately represented by a power series. We therefore chose to represent it by a Taylor series expansion centered at a distance \( R_s \), which is close to the initial-state equilibrium distance:

\[
M_s(R) = \sum_{l=0}^{\infty} b_{l}^s (R - R_s)^l.
\]

For the \( \text{Cl}_2 \) and \( \text{F}_2 \) analogs of the electronic transition of \( \text{Br}_2 \) considered in Sec. V, Mulliken and Reike\(^{46}\) calculated the transition moments and found them to be smooth functions which monotonically decrease with increasing \( R \). While (30) does not have the correct behavior as \( R \rightarrow \infty \), over the narrow region to which the absorption coefficient data are sensitive it can provide an arbitrarily exact representation of \( M_s(R) \). Since it is precisely the value and shape of \( M_s(R) \) near \( R_s \) which determines its effect on the calculated absorption coefficients, (30) is a natural parametrization whose use in the fits should minimize the effect of correlation between the different transition moment parameters. Moreover, if the results of an absorption coefficient analysis are expressed in terms of the value and derivatives of \( M_s(R) \) at a particular point, they will be relatively easy to combine with the results of \( R \)-centroid type analyses\(^{41}\) of bound-bound transition intensities.

As with \( M_s(R) \), the overlap integral in (22) only depends on values of the continuum wavefunction \( \Phi_{\nu_1 \nu_2}^p \) in the narrow region between the inner and outer turning points of the populated vibrational levels of the initial state. However, determination of the correct normalization for these wavefunctions implicitly requires knowledge of the corresponding potential curves over the whole region from their inner turning points out to the asymptote at \( R \rightarrow \infty \). On the other hand, the WKB method for accelerating determination of the correct normalization factors (see Sec. VIC above) implies that the absorption coefficients are not very sensitive to the details of the potential curve beyond the overlap region, as long as it approaches the correct asymptote. This insensitivity is confirmed by the qualitative success of the delta-function method of approximating the unbound state wavefunctions involved in such transitions.\(^{21,26,41}\)

In view of the above, it seems best to characterize the repulsive final state potential curve explicitly in terms of its value and shape in the narrow region of wavefunction overlap centered at \( R_s \), while using a potential form which approaches the correct asymptote as \( R \rightarrow \infty \). In the present work, the form of the purely repulsive final-state potential was chosen to be

\[
V_s(R) = A_w \exp \left\{ -\left[ a_1^f (R - R_s)^2 + a_2^f (R - R_s) + \ldots \right] \right\}.
\]

Since the absorption coefficients depend mainly on the behavior of \( V_s(R) \) in a narrow interval about \( R_s \), the independent parameters used in the fits were not \( A_w, a_1^f, a_2^f, \ldots \), etc., but rather were \( V_s(R_s), V_s'(R_s), V_s''(R_s), \ldots \), etc., where primes denote differentiation with respect to \( R \), and

\[
\begin{align*}
A_w &= V_s(R_s), \\
a_1^f &= -V_s''(R_s)/V_s'(R_s) = -V_s''(R_s)/A_w, \\
a_2^f &= \frac{1}{2} \left( [a_1^f]^2 - V_s'(R_s)/A_w \right), \\
&\vdots \\
&\text{etc.}
\end{align*}
\]

The advantage of parametrizing the potential in terms of the values of \( V_s(R) \) and its derivatives at \( R_s \) was demonstrated by fits to the \( \text{Br}_2 \) absorption coefficient data which constrained \( a_2^f = 0 = a_3^f = \ldots \), etc. When the values being fitted were \( A_w \) and \( a_1^f \), the statistical correlation coefficient between these variables was found to be greater than 0.999, and the fits converged very slowly and unreliably. In contrast, when exactly the same potential form and initial conditions were used, but \( V_s(R_s) \) and \( V_s''(R_s) \) were treated as the independent variables, the corresponding correlation coefficient was only \( 0.4 \) and the fit converged quite rapidly. In addition to increasing the stability of the fits, use of \( V_s(R_s), V_s'(R_s), \ldots \), etc., as the fitted variables also makes the results of the absorption coefficient analysis largely independent of the analytic form chosen for the potential.

\textbf{V. APPLICATION: AN ANALYSIS OF THE VISIBLE ABSORPTION CONTINUUM OF} \( \text{Br}_2 \)

\textbf{A. Outline of the problem}

The continuous absorption spectrum of \( \text{Br}_2 \) vapor in the visible and near infrared is due to transitions from
discrete levels of the ground \(X^1\Sigma^+_g\) state into both the purely repulsive \(1\Sigma^+_u\) state and unbound levels above the dissociation limit of the \(B^3(1\Sigma^+_u)\) state (see Fig. 1). The essential nature of this spectrum was explained in 1936 by Acton, Alickin, and Bayliss, \(^{23}\) and the next year, Bayliss\(^{24}\) reported upper state potential curves determined from an analysis of their data. However, Bayliss's analysis ignored the \(R\) dependence of the transition moment functions, and his method of calculation involved approximations which are now (thanks to modern computers) unnecessary. Additional uncertainties in his results arise from the fact that modern photoelectric absorption coefficient measurements\(^{25,27}\) differ significantly from the data\(^{24}\) he used. Further interest in this problem is raised by the apparent discrepancy between molecular beam photofragment spectroscopy measurements and conclusions obtained from previous absorption coefficient analyses regarding the relative strengths of the two competing electronic transitions in the region near \(21450\) cm\(^{-1}\). \(^{45}\)

In the following, the techniques described in Secs. II and IV are used to analyze the \(\text{Br}_3\) absorption coefficients of Passchier et al. \(^{24}\) At seven temperatures ranging from 25 to 440°C, these authors measured absorption coefficients at 48 wavelengths in the range 750–300 nm, which span virtually the whole of the observed spectrum. Unfortunately, the continuum in the region \(\lambda \geq 511\) nm is overlapped by discrete transitions into bound levels lying below the dissociation limit of the \(B^3(1\Sigma^+_u)\) state. Therefore, only the data for \(\lambda < 500\) nm are used in the present analysis. In addition, the reliability of the reported absorption coefficients for \(\lambda < 310\) nm seems questionable for two reasons. The first is that their very small magnitude would make these results most sensitive to the presence of small amounts of impurities; the second is the implausible nonmonotonic temperature dependence of the reported values. As a result, the present analysis only utilized the data corresponding to the 26 wavelengths in the region \(500 < \lambda \leq 320\) nm.

The discussion in Sec. IV indicated that the statistical weight associated with any datum used in a fit should vary as the squared inverse of its experimental uncertainty. Unfortunately, while Passchier et al. \(^{24}\) reported an “average deviation from the mean” for each of their data, it is not clear how these relate to the actual confidence limits on the experimental values, since they did not state the number of independent measurements considered in each case. Moreover, the nonmonotonic temperature dependence of the results at \(\lambda = 300\) nm imply the existence of errors at least five times as large as the reported deviations. However, the most troublesome point is the fact that these mean deviations imply that the absorption coefficients at shortest wavelengths, those which the above arguments suggest are least reliable, should be weighted several thousand times heavier than values at the absorption maximum. We found this unreasonable, and chose to weight all of the data equally.

In spite of the preceding discussion, it would seem reasonable to use the reported average deviations from the mean to indicate the order of magnitude of the uncertainties in the experimental data. This leads to an estimated uncertainty of \(\pm 0.1\%–1.0\%\) of the 298 K absorption coefficient maximum. Comparing this quantity with the results in Figs. 3–5 shows that the Sulzer and Wieland and Airy-function approximations should not be used in this analysis, and that the calculations should be performed using “exact” numerical continuum wavefunctions. On the other hand, these uncertainties are some two orders of magnitude larger than the errors associated with the \(Q\)-branch approximation \([\text{fixing } J' = J \text{ in Eq. (1)}]\), so this approximation was used throughout the computations reported below. The results in segment C of Fig. 2 show that the calculations must be performed using \(NJ > 1\) in order to ensure that the error introduced on simplifying the \(J\) summation is smaller than the experimental uncertainties. In practice, the calculations were performed using a wide range of \(NJ\) values in order to ascertain the effect of this approximation on the results of the fits. Finally, the use of \(VSUM \approx 0.998\) insured that truncation of the sum over \(v\) introduced no error into the present analysis.

In general, it is virtually impossible to determine both the final state potential curve(s) and the \(R\) dependence of the transition moment function(s) from absorption coefficient data for a single temperature. This occurs because at any one temperature, the effect of the variation of the transition moment function can be largely compensated for by an appropriate displacement and distortion of the apparent final state potential curve. However, if data for (significantly) different temperatures are analyzed simultaneously, the effects of the shape of the final-state potential and the \(R\) dependence of the transition moment function become distinguishable. Therefore, all of the fits reported below utilized data for more than one temperature. In order to conserve computation time, preliminary calculations included only the absorption coefficients at the highest and lowest experimental temperatures, and 25 and 440°C. However, the final fits also utilized data for intermediate temperatures.

Since the experimental data were obtained for normal \(\text{Br}_3\), the calculated absorption coefficients should be a sum of values for \(^{79}\text{Br}_3\), \(^{79}\text{Br}_3\), \(^{81}\text{Br}_3\), and \(^{81}\text{Br}_3\), each weighted by the appropriate relative isotopic abundance (0.255, 0.500, and 0.245, respectively). Trial calculations showed that the absorption coefficients for the \((79, 81)\) isotope differed from those for the \((79, 79)\) and \((81, 81)\) species by as much as 0.15 1/mol·cm. However, since the results for the two homonuclear isotopes are roughly equidistant above and below those for \((79, 81)\), the appropriately weighted sum of contributions from all three species will differ very little from the \((79, 81)\) results. The maximum error associated with this “pure \((79, 81)\)” approximation was found to be 0.005 1/mol·cm. Since this is 2 orders of magnitude smaller than the uncertainties in the experimental data, the \((79, 81)\) absorption coefficients were used to approximate the true average throughout the present analysis.

In the fits reported below, the two transition moment functions were represented by polynomials of the form
of (30), where the reference length $R_x = 2.3$ Å (quite close to the ground-state equilibrium distance of 2.2810 Å). In order to distinguish between the parameters for the two electronic transitions, the label $u = 0$ corresponds to absorption into the $B(3\Pi_{u})$ state, while $u = 1$ labels the absorption into the $1\Pi_{u}$ state.

As above, the potential energy curves of the $B(3\Pi_{u})$ and $1\Pi_{u}$ states are labelled $u = 0$ and 1, respectively. The latter was treated strictly in the manner described in Sec. IV B; $V_{u}(R)$ was represented by (31), with $R_x = 2.3$ Å, while the parameters actually varied in the fits were $V_{1}(R_{c})$, $V'_{1}(R_{c})$, $V''_{1}(R_{c})$, etc. On the other hand, since the attractive well of the $B$-state potential has been independently determined from an analysis of the discrete absorption spectrum, the $u = 0$ potential curve must be treated differently. The repulsive part of the $B$-state potential was represented by a slightly modified form of (31):

$$V_u(R) = B_0 + A_0 \exp\left\{-\left[\frac{a_1^2(R - R_x) + a_2^2(R - R_x)^2}{R_x} + \ldots\right]\right\}. \quad (33)$$

The constants $A_0$ and $B_0$ were then defined by requiring this function to pass through the two innermost accurately known turning points, while $a_1^2$, $a_2^2$, etc., were the parameters varied in the fits.

B. Known potentials for $X(1\Sigma_g^+)$ and $B(1\Pi_{u})$ state $Br_2$.

Barrow et al. have reported a thorough analysis of the discrete $B-X$ absorption spectra of $^{77}$Br$_2$ and $^{81}$Br$_2$. They concluded that the potential energy curves for these isotopes were essentially identical, and presented RKR turning points, calculated for the $(79, 79)$ case, for levels $v = 0-10$ of the ground ($X(1\Sigma_g^+)$ state and for $v = 0-44$ of the $B(3\Pi_u)$ state. These were used to generate the turning portions of the $B$- and $X$-state potentials used in the present calculations. The $X$-state potential was obtained by performing six-point Lagrangian interpolation over the given turning points, and extrapolating beyond them with exponentials.

Since the repulsive part of the $B$-state potential [represented by (33)] is required to join smoothly to the calculated inner turning points, the behavior of the latter was examined carefully. Coxon pointed out that the computed inner turning points for $v > 41$ are unreliable, and that the reported values in this region were obtained from an extrapolation based on turning points for $v < 41$. However, further scrutiny showed that the second derivatives of their potential in the inner wall region were somewhat irregular for $v > 9$, and actually had negative values at $v = 25$ and 29. In order to minimize the effect of any such anomalies on the absorption coefficient analysis, the inner turning points for $v > 9$ were ignored, and the constants $A_0$ and $B_0$ in (33) defined by requiring this function to pass through the inner turning points for $v = 8$ and 9:

$$R_0(8) = 2.4484689 \text{[Å]}, \quad G(8) = 1300.635 \text{[cm}^{-1}] \right).$$

$$R_0(9) = 2.4386671 \text{[Å]}, \quad G(9) = 1436.505 \text{[cm}^{-1}] \right). \quad (34)$$

Equation (33) was then used to represent the $B$-state potential for $R < R_0(8)$, while six-point Lagrangian interpolation over the remaining turning points generated the required potential for $R > R_0(8)$.

The energies associated with RKR turning points are usually expressed relative to the potential minimum. A complete description of the potential curves therefore requires us to record the values assumed for the distance between the $B$- and $X$-state potential minima, $T_0 = 15902.47$ cm$^{-1}$, the distance between their dissociation limits, 3685.15 cm$^{-1}$, and the ground state dissociation energy $D_0 = 16057.00$ cm$^{-1}$. These quantities were taken from the paper of Barrow et al.

C. Results

The results presented below were obtained from fits to the data of Passchier et al. for the 26 wavelengths in the range $500 \approx \lambda \approx 320$ nm, and the four temperatures: 25, 150, 300, and 440 °C. However, very similar results were obtained from fits to the data at half of these wavelengths and only the two extreme temperatures, 25 and 440 °C. This agreement justified neglect of the experimental data for the intermediate temperatures 75, 225, and 375 °C, on ground that its inclusion would have increased the computation time while providing no new information. Figure 6 illustrates the ex-

---

**FIG. 6.** Comparison of experimental decadic absorption coefficients for Br$_2$ (points) with the predictions yielded by the present analysis (solid curves).

---

TABLE II. Potential curve and transition moment parameters determined from the visible absorption spectrum of Br₂; energies are in cm⁻¹, lengths in Å, and transition moments in D.

<table>
<thead>
<tr>
<th>N, J</th>
<th>ERR</th>
<th>b₀</th>
<th>b₁</th>
<th>b₂</th>
<th>a₁</th>
<th>a₂</th>
<th>V₁</th>
<th>10⁻²V₁′</th>
<th>10⁻²V₁″</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.137</td>
<td>0.3971</td>
<td>⋯</td>
<td>0.4969</td>
<td>⋯</td>
<td>5.878</td>
<td>7779</td>
<td>-348.7</td>
<td>⋯</td>
</tr>
<tr>
<td>0</td>
<td>0.982</td>
<td>0.3799</td>
<td>⋯</td>
<td>0.5084</td>
<td>⋯</td>
<td>5.605</td>
<td>7890</td>
<td>-356.8</td>
<td>14.52</td>
</tr>
<tr>
<td>1</td>
<td>0.863</td>
<td>0.3798</td>
<td>⋯</td>
<td>0.5059</td>
<td>-0.326</td>
<td>5.366</td>
<td>7594</td>
<td>-349.3</td>
<td>⋯</td>
</tr>
<tr>
<td>0</td>
<td>0.666</td>
<td>0.4109</td>
<td>0.411</td>
<td>0.4956</td>
<td>⋯</td>
<td>6.266</td>
<td>7768</td>
<td>-349.6</td>
<td>⋯</td>
</tr>
<tr>
<td>1</td>
<td>0.651</td>
<td>0.4025</td>
<td>0.354</td>
<td>0.4997</td>
<td>-0.103</td>
<td>6.016</td>
<td>7710</td>
<td>-350.0</td>
<td>⋯</td>
</tr>
<tr>
<td>0</td>
<td>0.556</td>
<td>0.3986</td>
<td>0.377</td>
<td>0.5034</td>
<td>⋯</td>
<td>6.054</td>
<td>7712</td>
<td>-355.1</td>
<td>14.96</td>
</tr>
<tr>
<td>1</td>
<td>0.527</td>
<td>0.3910</td>
<td>0.313</td>
<td>0.5066</td>
<td>-0.107</td>
<td>5.822</td>
<td>7654</td>
<td>-355.3</td>
<td>15.11</td>
</tr>
</tbody>
</table>

*Calculations using only J = 0.

TABLE III. Correlation matrix for the final (N, J = 15) fit to the Br₂ data.

<table>
<thead>
<tr>
<th></th>
<th>b₀</th>
<th>b₁</th>
<th>b₂</th>
<th>a₁</th>
<th>V₁(R₁)</th>
<th>V₁′(R₁)</th>
<th>V₁″(R₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b₀</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b₁</td>
<td>0.652</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b₂</td>
<td>-0.923</td>
<td>-0.362</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a₁</td>
<td>0.613</td>
<td>0.566</td>
<td>-0.412</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a₂</td>
<td>0.955</td>
<td>0.719</td>
<td>-0.836</td>
<td>0.746</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V₁</td>
<td>0.884</td>
<td>0.524</td>
<td>-0.792</td>
<td>0.854</td>
<td>0.892</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V₁′</td>
<td>0.532</td>
<td>0.045</td>
<td>-0.685</td>
<td>-0.033</td>
<td>0.303</td>
<td>0.415</td>
<td></td>
</tr>
<tr>
<td>V₁″</td>
<td>0.028</td>
<td>-0.045</td>
<td>-0.069</td>
<td>-0.376</td>
<td>-0.141</td>
<td>-0.092</td>
<td>0.480</td>
</tr>
</tbody>
</table>

The excellent agreement between the experimental data (points) and the absorption coefficients calculated from the parameters determined here. The latter are also available in tabulated form. The parameters obtained on fitting calculated absorption coefficients to these 104 data are summarized in Table II. There, N, J is the number of segments into which the rotational population is divided (see Sec. II.B), and ERR is the standard error (in units 1/mole cm) associated with the converged fit. The final recommended parameter values are those in the last row of this table, and the quantities in parentheses there are the predicted 95% confidence limit uncertainties (= two standard errors) in the last digits shown. The uncertainties associated with the parameters obtained from the other fits are quite similar to those for N, J = 15. The fits were performed with all of the parameters being varied simultaneously, so these uncertainties include the effects of correlation. The correlation matrix for the final (N, J = 15) fit is shown in Table III. Large values (near ±1) of the off-diagonal elements of this matrix indicate that correlation effects are probably a dominant source of the predicted uncertainties in the associated parameters. The number of digits quoted for each parameter was chosen so that a change of 5 in the next place would affect the predicted absorption coefficients by less than 0.05 l/mole cm.

The results in the first row of Table II correspond to a case in which b₀ = b₂ = a₁ = 0, while those in the next six rows show how the quality of the fit improves as more potential-curve and transition-moment parameters are allowed to vary. However, including any of the additional parameters b₁, a₂, or V₁″(R₂) (i.e., a₂) led to no further decreases in ERR, while the relative uncertainties in the estimates obtained for these quantities were much greater than 100%. We therefore con-
included that the eight parameters considered in Table II are all that may be determined from the existing data for this system, and that the uncertainty associated with the experimental data is $\approx 0.5$ l/mole · cm.

The results in the lower half of Table II show the effect on the fits of increasing the value of $NJ$. The fitted parameters appear to converge smoothly as $NJ$ is increased from 1 to 15. However, the standard error of the fit (ERR) does not change significantly, and the changes in the parameters are smaller than the predicted uncertainties in the $NJ = 15$ (or $NJ = 1$) values. In view of the magnitude of the $NJ$ dependence shown in Fig. 2, the latter observations are somewhat surprising. We believe that they reflect the relatively large errors in the experimental data. In any case, large $NJ$ values certainly correspond to a better analysis, so the present best estimates of the parameters characterizing the Br$_2$ absorption continuum are those in the last row of Table II.

The final transition moment functions yielded by the present work are (in D, with lengths in Å)

$$M_0(R) = 0.3905 + 0.265 \ (R - 2.3) \quad (35)$$

for the $X(\Sigma^+_g) - B(\Pi_{1u})$ transition, and

$$M_1(R) = 0.5060 - 0.154 \ (R - 2.3) \quad (36)$$

for the $X(\Sigma^+_g) - 1\Pi_{1u}$ transition. The magnitude of the correlation coefficient between $b_0^2$ and $b_1^2$ is fairly large ($0.927$), but the fits had no difficulty in distinguishing between the two transition moments, and were able to determine their magnitudes quite precisely. Although the uncertainties in the slopes of the two transition moment functions are relatively large, it is clear that they are of opposite sign over the region being sampled. Moreover, the results in the bottom half of Table II show that these transition moment slopes are the parameters which are most sensitive to the approximations used in performing the sum over $J$. In particular, use of the "$J = 0$ approximation" yields a value of $b_1^2$ which even has the wrong sign.

According to Table II, the purely repulsive $^1\Pi_{1u}$ potential is given by

$$V_1(R) = 7654 \ e^{-14.637(R-2.3)} + 0.879(R-2.3)^2 \quad (37)$$

while the repulsive part of the $B(\Pi_{1u})$ state potential for $R < R_0(\theta)$ [see (34)] is

$$V_0(R) = -1174 + 5494 \ e^{-15.407(R-2.3)} \quad (38)$$

where lengths and energies are in Å and cm$^{-1}$, respectively, and the zero of energy in the ground-state dissociation limit. The differences between the predictions of (38) and the reported inner turning points for $B$-state levels $\nu > 9$, are shown in Fig. 7. The error bars seen there correspond to the $\pm 0.1561/\text{Å}$ uncertainty in the fitted $a_1^2$ value.\(^{46}\)

Note that all of the expressions (35)–(38) should be fairly accurate in the region

$$2.10 \leq R \leq 2.55 \ \text{Å} \quad (39)$$

between the turning points of the populated initial-state levels, but they may not be very reliable beyond this range. This caveat applies particularly to the transition moment expressions (35) and (36), since these functions do not have the correct limiting behavior at either $R = 0$ or $R = \infty$.

The present results indicate that there are two points of intersection between the $B(\Pi_{1u})$ and $^1\Pi_{1u}$ potential energy curves. The one at larger distance is located at $R = 2.893$ (± 0.009) Å, $E = 396$ (± 39) cm$^{-1}$ above the ground-state dissociation limit, a point lying between the outer turning point of levels $\nu = 2$ and 3 on the $B$-state curve. The other crossing point lies at $R = 2.03$ (± 0.03) Å and $E = 25000$ (± 3400) cm$^{-1}$. Although outside the region specified by (39), these predictions should be accurate within the stated uncertainties.

Using the optimized potential energy and transition moment functions reported here, 76,86Br$_2$ absorption coefficient functions have been calculated in the "$NJ = 15$ approximation" at 5 nm intervals across the range 500 ≤ $\lambda$ ≤ 300 nm, at the Br$_2$ melting point (266 °K) and at 50 °K intervals for temperatures in the range 300 ≤ $T$ ≤ 1000 °K. The contributions due to the individual $X - B$ and $X - ^1\Pi_{1u}$ transitions are also tabulated with the wavelengths for the latter extending to 600 nm. Copies of these tables can be obtained from the authors on request.

D. Discussion and comparisons

One interesting feature of the present results is the fact that the transition moment functions for the two electronic transitions are found to have slopes of opposite sign. This contradicts the simplest molecular orbital descriptions of these transitions, which predict that these functions should be identical.\(^{40}\) Early calculations for the corresponding transitions of F$_2$ and Cl$_2$ yielded transition moments which were monotonically decreasing functions of $R$ in the neighborhood of the ground-state equilibrium distance.\(^{40}\) This is true for the present $X(\Sigma^+_g) - 1\Pi_{1u}$ transition moment function, but
TABLE IV. Percent deviations between predicted $v''(B^3\Pi_u^0) = 40 - v''(X^1\Sigma_g^+)$ relative fluorescence intensities and the experimental results of Holzer et al.$^{47}$

<table>
<thead>
<tr>
<th>$v''$</th>
<th>FCFA</th>
<th>$v''$ FCF</th>
<th>$I(\nu'; v'')$b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-7</td>
<td>+7</td>
<td>+4</td>
</tr>
<tr>
<td>2</td>
<td>-10</td>
<td>-2</td>
<td>-4</td>
</tr>
<tr>
<td>3</td>
<td>-15</td>
<td>-11</td>
<td>-12</td>
</tr>
<tr>
<td>4</td>
<td>-3</td>
<td>-3</td>
<td>-3</td>
</tr>
<tr>
<td>5</td>
<td>-5</td>
<td>-6</td>
<td>-2</td>
</tr>
<tr>
<td>6</td>
<td>+4</td>
<td>-2</td>
<td>+9</td>
</tr>
<tr>
<td>7</td>
<td>+8</td>
<td>-2</td>
<td>+5</td>
</tr>
</tbody>
</table>

a As in Ref. 23.
b"Best" predicted values.

not for that associated with $X^1\Sigma_g^+ \rightarrow B^3\Pi_u^0$ transitions. However, the positive slope of the latter is in qualitative accord with the positive transition moment slope which Tellinghufen determined from the discrete spectra for the analogous electronic transition of $I_2$. $^{41}$

The $B \rightarrow X$ transition moment function obtained here may be combined with previously reported Franck–Condon factors (FCF) and $R$ centroids ($\overline{R}_{\nu, \nu''}$) and used to predict integrated emission intensities $I(\nu'; v'')$ in the discrete portion of this spectrum, since

$$I(\nu'; v'') \propto v^3 \text{FCF}(\nu'; v'') | \overline{R}_{\nu, \nu''}'|^2.$$  \hspace{1cm} (40)

Relative intensities in the fluorescence series ($\nu' = 40, J' = 16 \rightarrow 0 \rightarrow 10$) have been observed by Holzer et al.$^{47}$ If they are normalized so that the average of the intensities for $\nu'' = 0$ is $1.0$, and then compared with similarly normalized predicted intensities, one finds the percentage deviations shown in Table IV. The column labeled "FCF" shows the differences obtained if the predicted intensities are based only on the factor FCF ($\nu', v''$) (as in Barrow et al.$^{51}$); the next shows the results obtained when the frequency factor $v''$ is included in the predicted intensity, and the last column shows the discrepancies obtained when the $R$ dependence of the transition moment function is also taken into account. These results show that the systematic differences which Barrow et al.$^{51}$ found between the observed and calculated relative intensities arise from their neglect of the $v^3$ factor in (40). However, it appears that these experimental intensities$^{47}$ are not sufficiently accurate to be able to discern the $R$ dependence of the transition moment function.

Figure 8 compares the present recommended transition moment functions (solid lines), and their predicted uncertainties (shaded region), with the values obtained by Bayliss$^{10}$ in 1937 (horizontal dotted lines): $M_0 = 0.325$ and $M_4 = 0.514$ [D]. Also shown (dashed lines) are the transition moment functions obtained from analyses utilizing the $N_J = 1$ and $J = 0$ approximations. The error in Bayliss's value of $M_0$ probably reflects difficulties associated with determination of the appropriate normalization factors for his continuum wavefunctions.

Figure 9 compares the upper state potential energy functions determined here (solid curves), and their uncertainties (shaded regions), with the curves reported by Bayliss$^{10}$ (dashed curves). The solid points are B-state inner turning points for $v'' = 2 \rightarrow 9$. This figure indicates that Bayliss's potential energy curves are not particularly reliable beyond the immediate neighborhood of the ground-state equilibrium distance. On the other hand, Table V shows that the values

FIG. 8. Comparison of transition moment functions obtained here [solid and dashed lines; see (35) and (38) and Table II] and those reported by Bayliss$^{10}$ (horizontal dotted line).

FIG. 9. Comparison of potential curves obtained here (solid curves), and their uncertainties (shaded regions), with those reported by Bayliss$^{10}$ (dashed curves). Solid points are the B-state inner turning points for $v'' = 2 \rightarrow 9$. The zero of energy is the dissociation limit of the ground ($X^1\Sigma_g^+$) and $1\Pi_u^0$ states, while the horizontal dashed line indicates the $B^3\Pi_u^0$-state dissociation limit.

TABLE V. Comparison of Bayliss-potentials$^{10}$ with those determined here, at $R_e = 2.30$ Å, energies in cm$^{-1}$ and lengths in Å.

<table>
<thead>
<tr>
<th>(v(R_e))</th>
<th>(V_0(R_e))</th>
<th>(10^4 \cdot V_0'(R_e))</th>
<th>(10^4 \cdot V_0''(R_e))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1\Pi_u^0) present</td>
<td>7554</td>
<td>-354, 9</td>
<td>15, 11</td>
</tr>
<tr>
<td>(\text{Bayliss})</td>
<td>7566</td>
<td>-414, 4</td>
<td>5, 41</td>
</tr>
<tr>
<td>(B^3\Pi_u^0) present</td>
<td>4320</td>
<td>-319, 0</td>
<td>18, 52</td>
</tr>
<tr>
<td>(\text{Bayliss})</td>
<td>4391</td>
<td>-291, 5</td>
<td>3, 80</td>
</tr>
</tbody>
</table>
ues and derivatives of Bayliss's potentials at $R_s = 2.3 \text{ Å}$ are in remarkably good agreement with the present results. This implies that the differences seen in Fig. 9 are partially due to the fact that Bayliss's potentials were not constrained to have the correct long-range behavior.

In a recent paper, Oldman et al. used photofragment spectroscopy to measure the relative intensities of the two types of electronic transitions contributing to the absorption spectrum at $\nu = 21450 \text{ cm}^{-1}$ and $T \approx 300$–400°C. They found that the absorption intensity into the $B$ state was some 1.28 times more intense than that into the $\Pi_{1u}$ state, and pointed out that this disagreed with some earlier absorption coefficient analyses which predicted that the $B$-state absorption should be the weaker component under these conditions. However, both the present work and that of Bayliss (see his Fig. 1) agree with the conclusion of Oldman et al. that the absorption into the $B$-state provides the dominant contribution there. The two contradictory absorption coefficient analyses referred to by Oldman et al. utilized the Sulzer and Weidmann equation to describe the frequency and temperature dependence of the absorption profile. The work in Sec. IIIIB showed that these equations are not quantitatively reliable. Hence, the apparent discrepancy referred to by Oldman et al. should be attributed to breakdown of the Sulzer–Wieland expressions.

There remains a significant difference between the ratio of the $B(\Pi_{1u})$ and $\Pi_{1u}$ absorption coefficients at 21450 cm$^{-1}$ found in the molecular beam work, 1.28, and that obtained here. Since Oldman et al. report beam temperatures of 300–400 K, their ratio should be compared to present predictions of 2.06 at 300 K and 1.60 at 400 K. We believe that this disagreement is much too large to be due to error in the present results. In the absence of other explanations, we speculate that it may reflect either error in the reported beam temperature (our calculated ratio drops to 1.28 at 510 K), or to nonthermal vibration–rotation population distribution in the beam.

Systematic fitting procedures of the type described in Sec. IV (and applied in Sec. V) have not previously been applied to the analysis of experimental absorption coefficients. However, the ease with which the present approach extracted distinct transition moment and potential curve parameters for the two overlapping transitions contributing to the Br$_2$ spectrum convincingly demonstrates its utility. In the application to Br$_2$, the quality of the existing data is barely sufficient to justify use of the more sophisticated version of the present procedure (e.g., calculations with $N^2 > 2$). However, the broad frequency and temperature ranges for which these results are available, and the fact that this spectrum consists of two overlapping transitions made it a particularly interesting system to study. Moreover, Figs. 8 and 9 show that the present analysis greatly improves our knowledge of the transition moment and potential energy functions for this molecule, while the predicted absorption coefficients should be of practical value.

ACKNOWLEDGMENTS

We are grateful to J. A. Coxon for helpful discussions about the bound state potential energy curves and discrete transition intensities for the $B$–$X$ spectrum, to J. Tellinghuisen for his comments on the use of the delta function approximations, and to J. E. Grabenstetter for his comments on the manuscript.

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†This work was initiated in the M.Sc. dissertation of R. J. Le Roy (University of Toronto, 1967); see also the Ph.D. dissertation of R. G. Macdonald (University of Toronto, 1973).
‡ Alfred Sloan Foundation Fellow 1974–76.
§ Present address: Department of Chemistry, University of California, Berkeley, California 94720, USA.
20 K. M. Sando, Mol. Phys. 23, 413 (1972), and references therein.
26 The photodissociation cross section $\sigma$, in $\text{Å}^2$/molecule, is simply related to the decay absorption coefficient $\epsilon$, in $1/\text{molecule} \cdot \text{cm}$, by the expression $\sigma = 10^3 (\text{cm} \cdot \text{molecule}^{-1})/\epsilon / N_0$, where $N_0$ is Avogadro's number.
30 Unless explicitly indicated contrary (as in $\epsilon = 2\text{cm}^{-1}$/273 K), the units of energy and frequency are always assumed to be wave-numbers, cm$^{-1}$.\n
This contrasts the collapse of the J' summation, discussed above, which is a relatively better approximation for heavy species than for light ones.

37While partial derivatives with respect to potential function parameters of the wavefunction's asymptotic phase shift $\eta_{0}(R)$ are readily obtained, accurate wavefunction derivatives are more difficult to determine in the neighborhood of the classical turning point.

42To facilitate reliable interpolation, the present calculations used the actual eight-digit turning points rather than the five-digit values reported in the paper. 31
45Note that since $\eta_{0}(R)$ is required to pass through the two turning points of (34), the upper and lower bounds of $a^{2}_{b}$ correspond to (all in cm$^{-1}$): $A_{b} = 5471$, $B_{b} = -1112$, and $A_{g} = 5521$, $B_{g} = -1240$, respectively.