

Improved Spectroscopic Data Synthesis for $I_2(B^3\Pi_{0u}^+)$ and Predictions of J Dependence for $B^3\Pi_{0u}^+ - X^1\Sigma_g^+$ Transition Intensities¹

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Some new techniques are introduced in a reanalysis of the spectroscopic data for $I_2(B^3\Pi_{0u}^+)$ to obtain a more complete and internally consistent set of molecular constants, and an RKR potential curve. In particular, attention is focussed on the determination of reliable high-order rotational constants (D_v , H_v , etc.) for highly excited vibrational levels. The ensuing intermolecular potential for this state is then used together with a known ground-state curve in a study of the J dependence of Franck-Condon factors for discrete $B^3\Pi_{0u}^+ - X^1\Sigma_g^+$ transitions over a wide range of v and J . It is concluded that at the temperatures 1000–2000 °K routinely achieved in shock-tube experiments, the intensity of most vibrational bands will vary drastically as J ranges across the half-width of the thermal rotational population distribution.

De nouvelles techniques sont utilisées pour reprendre l'analyse des données spectroscopiques concernant $I_2(B^3\Pi_{0u}^+)$ afin d'obtenir un ensemble de constantes moléculaires plus complet et plus cohérent, ainsi qu'une courbe de potentiel RKR. Une attention particulière est apportée à la détermination de valeurs fiables pour les constantes rotationnelles d'ordre élevé (D_v , H_v , etc.) des niveaux vibrationnels hautement excités. Le potentiel intermoléculaire résultant pour cet état est alors utilisé, conjointement avec une courbe d'état fondamental connue, dans une étude de la façon dont J dépend des facteurs Franck-Condon pour les transitions discrètes $B^3\Pi_{0u}^+ - X^1\Sigma_g^+$, dans un vaste domaine de valeurs de v et J . On conclut qu'aux températures de 1000–2000 °K habituellement obtenues dans les expériences de tube de choc, l'intensité en pratique de n'importe quelle bande vibrationnelle variera drastiquement lorsque J passe par les valeurs correspondant à la demi-largeur de la distribution de la population rotationnelle thermique. [Traduit par le journal]

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I. Introduction

Molecular iodine has long been used as a prototype system for studying diverse physical and chemical phenomena². In many of these problems, the visible absorption or emission spectrum of the $B^3\Pi_{0u}^+ - X^1\Sigma_g^+$ electronic transition is used to monitor the events of interest. Thus, it is desirable to have an accurate knowledge of the frequency and temperature dependence of these transition intensities. In

cases for which the relevant intermolecular potentials are well known, the calculation of such intensities is by now a routine procedure (see, e.g.: Zare 1964; Coxon 1971; Jarman 1971). However, most calculations of this sort have tended to assume that the intensity of a given vibrational band, or the continuum absorption from a given vibrational level were independent of the rotational quantum number J . This approximation becomes increasingly invalid at high temperatures where a very wide range of J levels will be populated. In particular, at the 1000–2000 °K, routinely achieved in shock-tube studies of I_2 dissociation, a significant fraction of even the $v = 0$ B -state molecules have rotational energies as large as the dissociation energy. Thus, a knowledge of the J dependence of the transition intensities is required for a proper analysis of the experimental data.

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²In particular, I_2 has become almost a "model system" for studies of the rate and mechanism of diatomic dissociation and recombination (see, e.g.: Rabinowitch and Wood 1936; Christie *et al.* 1955; Ip and Burns 1972), and for studies of intermolecular and intramolecular energy transfer (see e.g.: Steinfeld 1970; Tellinghuisen 1972a; Wong and Burns 1973).

In the present paper, we will examine the J dependence of intensities of the $B(^3\Pi_{0u}^+)$ - $X(^1\Sigma_g^+)$ vibrational bands of I_2 . The calculation of such effects requires a knowledge of the potential energy curves of the two states. For the ground ($X(^1\Sigma_g^+)$) state, reliable molecular constants and RKR turning points are known (Le Roy 1970b) for the region from the potential minimum to within $0.04 D_e(X)$ of the dissociation limit.³ However, for the $B(^3\Pi_{0u}^+)$ state, the situation is not so good. In large part this is due to the incompleteness and limited accuracy of the presently available experimental data. In his recent analysis of this system, Tellinghuisen (1973a) corrected most of the inadequacies of earlier treatments. However, he did not make full use of the available data for levels near dissociation, and also did not attempt to extrapolate beyond the highest observed level to predict energies and rotational constants for the *ca.* 15 as-yet-unobserved highest bound levels (lying within 20 cm^{-1} of dissociation). Furthermore, while his analysis yielded fairly reliable $G(v)$ and B_v expressions, no estimates of the higher-order rotational constants D_v and H_v were reported. Since the experimental B_v values are only weakly coupled to these higher-order constants, it is unlikely that this introduced significant errors into his rotational constants or RKR potential. However, in addition to giving a generally more complete picture of the B -state energy level spectrum, a knowledge of these constants is necessary when one is attempting to predict laser line coincidences which may be used to populate highly excited B -state levels. Such predictions would greatly facilitate energy transfer studies of these levels.

In the following, we present a reanalysis of the currently available spectroscopic data for B -state I_2 to obtain an improved set of molecular constants and RKR potential for it. The imminent publication of new data for this species⁴ should lead to improvements in these results in the near future. However, the new techniques introduced in the present data

³ $D_e(X) = 12\,548.0\text{ cm}^{-1}$ is the ground-state $I_2(X(^1\Sigma_g^+))$ dissociation energy (Le Roy 1970a; Le Roy and Bernstein 1971).

⁴K. K. Yee and J. Tellinghuisen (1972, private communications). Preprints by Singh and Tellinghuisen (1973), and by Barrow, Broyd, Pederson, and Yee (1973) describing these new data were received after completion of the present work.

synthesis should be of more enduring value. These are largely concerned with the question of determining reliable values of the higher-order rotational constants (D_v , H_v , etc.) from data which are weakly (or negligibly) sensitive to them. Three ways of calculating such constants from a known potential are described and compared, and it is demonstrated that such results may be readily incorporated in the data analysis to yield optimized self-consistent sets of molecular constants. The constants thus obtained for B -state I_2 are then used to generate an RKR potential for this state. This curve is in turn used in calculations which predict marked J dependence for B - X transition intensities of I_2 .

II. Improved Molecular Constants and Internuclear Potential of I_2 ($B(^3\Pi_{0u}^+)$)

A. Selection of Data

Although it is one of the most frequently studied molecular states, the spectroscopic data for $B(^3\Pi_{0u}^+)$ I_2 are currently rather incomplete. In particular, virtually all the reliable rotational constants come from the analysis of 17 bands of the main visible absorption spectrum involving B -state levels between $v' = 3$ and 30 (Brown and Klemperer 1964; Steinfeld *et al.* 1965, 1969; Richardson and Powell 1967)⁵. Steinfeld *et al.* (1969) also reported analyses of band absorption into the $v' = 43$ and 49 B -state levels. However, later studies showed that inconsistencies in the vibrational and rotational assignments of these data make them unreliable (Le Roy 1970a; Yee and Miller 1972), and hence (following Tellinghuisen (1973a)), they are omitted from consideration. As a result, for the *ca.* 57 bound vibrational levels above $v' = 30$, the only available experimental rotational datum was a B_v value extracted from Halldorsson and Menke's (1971) measurements of fluorescence emission from $v' = 43$. The only other known rotational constant is the theoretically predicted (Le Roy 1972) result that $B_{v'} = 0$ at $v' = v_D = 87.75$, the effective vibrational quantum number at the dissociation limit.

In general, the frequencies in a vibrational band may be represented by (Herzberg 1950)

⁵The additional band origins and B_v values for levels $v' = 15$ and 17-19 used by Steinfeld *et al.* (1965) were ignored here since the accuracy and extent of the data on which they are based is unknown.

$$\begin{aligned}
 [1] \quad v(v', J'; v'', J'') &= E(v') + B_{v'}[J'(J' + 1)] \\
 &- D_{v'}[J'(J' + 1)]^2 + \dots - E(v'') \\
 &- B_{v''}[J''(J'' + 1)] \\
 &+ D_{v''}[J''(J'' + 1)]^2 - \dots
 \end{aligned}$$

where single primes denote the upper (here *B*-state) levels and double primes the lower (ground-state). Since reliable ground-state constants are known (Le Roy 1970*b*), only the *B*-state parameters needed to be determined using fits to eq. 1. While the derived coefficients will be sensitive to the degree of the $J(J + 1)$ polynomial, the magnitude of the resulting $D_{v'}$ constants and insensitivity to the addition of higher-power terms showed that eq. 1 could be treated here as a quadratic. The magnitude of the coefficients $H_{v'}$ calculated later shows that this assumption is valid.

In addition to the $v' \leq 30$ band absorption measurements, Halldorsson and Menke's (1970) observation of *R*(15)–*P*(13) splittings in resonance fluorescence from $v' = 43$ into ground-state levels $6 \leq v'' \leq 11$ yields a value of B_{43} . These splittings $\Delta(v'')$ generate the expression:

$$B_{43} = [\Delta(v'') + 58B_{v''} - 24476D_{v''}]/116 + 428D_{43}$$

Substituting the known ground-state constants, observed $\Delta(v'')$ values, and a plausible D_{43} value produces an estimate of B_{43} . Since the method of analysis described below yields highly accurate $D_{v'}$ constants, this B_{43} value should be quite reliable. Combining these rotational constants with the frequency of the laser-coincident line exciting this fluorescence (Yee and Miller 1972) then yields the vibrational energy of $v' = 43$.

Aside from this $v' = 43$ eigenenergy, the only reliable observation of levels above $v' = 30$ appear to be Brown's (1931) band-head measurements for levels $48 \leq v' \leq 72$. In his analysis, Tellinghuisen (1973*a*) chose to ignore the data for $v' > 67$ and $v' < 55$. However, the internal consistency of Brown's (1931) data suggests that he was excessively cautious, and hence all 25 of the reported band heads were used in the present analysis.

While no experimental data are currently available for the interval between $v' = 72$ and the dissociation limit, in the interest of obtaining the most complete possible set of

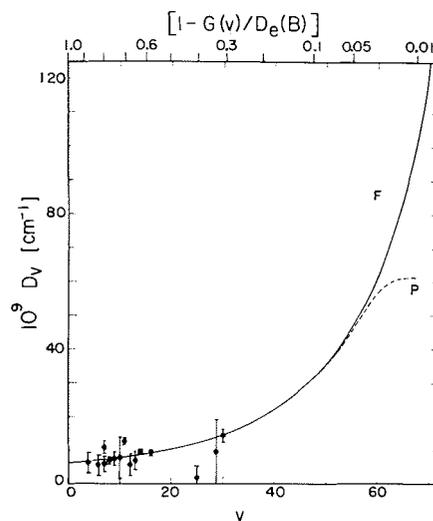


FIG. 1. Comparison of experimental $D_{v'}$ values (points) with those calculated by perturbation theory (curve P) and from fits to eqs. 3, 5, and 6 (curve F).

vibrational constants we chose to utilize theoretical predictions for the level energies in this region. Le Roy and Bernstein (1970, 1971) derived an expression for the "natural" distribution of vibrational eigenvalues in the neighborhood of a molecular dissociation limit. On applying this result to *B*-state I_2 they obtained an improved estimate of its dissociation energy, concluded that the dissociation limit semiclassically corresponds to a quantum number $v' = v_D = 87.75(\pm 0.4)$, and predicted the energies of the 15 unobserved levels $73 \leq v' \leq 87$. These "data" were also used in the present analysis. Of course any subsequent developments which show that their predictions were in error will have no effect on the accuracy with which the present constants represent levels $v' \leq 72$.

B. Method of Analysis

A major difficulty in determining the molecular constants of *B*-state I_2 is the fact that the band absorption measurements are only slightly sensitive to the rotational constant $D_{v'}$. Thus, relatively small experimental errors can give rise to anomalously large errors and statistical uncertainties in $D_{v'}$ values obtained on fitting data to eq. 1. This is the source of the rather erratic v' dependence of the "experimental" $D_{v'}$ values shown in Fig. 1. On the other hand, the relative insensitivity of these data to $D_{v'}$,

means that the errors in the corresponding fitted $E(v')$ and $B_{v'}$ values will be fairly small. As a result, an RKR potential curve calculated from the latter will be fairly accurate, and hence so will $D_{v'}$ values computed as properties of such a potential function. Such *calculated* $D_{v'}$ constants may then be *held fixed* in fits of the data to eq. 1 to yield improved experimental $E(v')$ and $B_{v'}$ values. The latter will in turn yield a better RKR potential, and thence better calculated $D_{v'}$ values. This iterative procedure will necessarily converge quite rapidly, since the small changes in the potential with each step will have relatively little effect on the calculated $D_{v'}$ values. Of course, this type of self-consistent procedure for optimizing molecular constants is of quite general utility, and is by no means restricted to use with band absorption data of the type considered here.

C. Calculating Diatomic Rotational Constants

B_v, D_v, \dots etc. From a Known Potential Energy Function

The procedure described above requires an ability to determine values of the rotational constant D_v from a given potential energy function. While in principle relatively straightforward, the calculation of such higher-order rotational constants received little attention in the past. Very recently, however, new methods of doing this have been presented by Albritton *et al.* (1973a) and by Tellinghuisen (1973b). These are briefly described below and critically compared to the somewhat older "eigenvalue-fitting" procedure (see, *e.g.*, Moody and Beckel 1970). In this assessment, particular attention is paid to the utility of these methods in the immediate neighborhood of the dissociation limit. The potential function used in these comparisons is that obtained below (see Sect. IIE) for $I_2(B^3\Pi_{0v}^+)$.

Perturbation Theory

It has long been known (Kemble 1937) that the effect of rotation on the levels of a vibrating diatomic molecule could be predicted by simply treating the centrifugal potential as a perturbation and applying perturbation theory in a straightforward manner. This approach yields the familiar (Herzberg 1950) quantum-mechanical definition of the lowest-order rotational constant:

$$[2] \quad B_v = (\hbar^2/2\mu) \langle v, 0 | R^{-2} | v, 0 \rangle$$

However, its implications with respect to the higher-order constants were largely overlooked until Albritton *et al.* (1973a) demonstrated that the higher-order constants in the rotational term-value expression

$$[3] \quad G(v, J) = G(v, 0) + B_v[J(J+1)] - D_v[J(J+1)]^2 + H_v[J(J+1)]^3 + \dots$$

could be accurately calculated using the appropriate perturbation-energy expressions. The second-order energy yields

$$[4] \quad D_v = (\hbar^2/2\mu)^2 \sum_{v' \neq v} \frac{|\langle v, 0 | R^{-2} | v', 0 \rangle|^2}{G(v', 0) - G(v, 0)}$$

while third- and higher-order energies yield analogous expressions for H_v, L_v, \dots etc. (Albritton *et al.* 1973a).

The matrix elements

$$\langle v, 0 | R^{-2} | v', 0 \rangle = \int_0^\infty R^{-2} \psi_{v,0}(R) \psi_{v',0}(R) dR$$

appearing in these expressions may be readily evaluated using the exact numerically calculated radial eigenfunctions $\psi_{v,0}(R)$ of the non-rotating molecule. However, the second- and higher-order expressions contain summation(s) over v' which implicitly include the continuum of unbound levels above the dissociation limit. While the evaluation of matrix elements involving continuum wave functions introduces no great difficulties, performing the summation (integration) over all energies from the dissociation limit to infinity may be quite tedious. Fortunately, $\langle v, 0 | R^{-2} | v', 0 \rangle$ tends to be very small for large $|v - v'|$, and the energy differences in the denominators (see eq. 4) further de-emphasize the contribution of coupling to "distant" levels. On the other hand, the number of neighboring levels to which coupling is significant increases sharply with v . For the ground state of CO, Albritton *et al.* (1973a) found that, while four-digit accuracy in D_v required only 3 terms in eq. 4 at $v = 0$, sixteen terms were necessary at $v = 28$, and the latter is only halfway to dissociation. Thus, even neglecting the continuum, the calculation of high-order rotational constants for highly excited levels necessarily requires very large numbers of matrix elements.

In most of the trial D_v and H_v calculations for B -state I_2 reported below, the summations

over v' included all bound levels below $v = 71$, but neglected contributions from the continuum and from the 7 highest bound levels ($v = 81-87$). Since the latter all lie within *ca.* 24 cm^{-1} of dissociation, this truncation of the discrete eigenvalue spectrum will merely slightly exaggerate the importance of the (omitted) continuum. In practical calculations, some truncation of this sort will always be necessary and its nature will affect the range of utility of this method for the case under consideration.

Eigenvalue Fitting

This approach involves solving the radial Schrödinger equation at a number of J 's for each v , and then fitting the resultant $G(v, J)$ values to eq. 3 to obtain the desired values of B_v , D_v , H_v , ... etc. For each v , the upper limit to this range of J was taken as $J_D(v)$, the largest value for which $G(v, J)$ lies below the dissociation limit, and the energies were obtained at *ca.* $30 J$ values between $J = 0$ and $J_D(v)$. Although $J_D(v)$ decreases approximately linearly with increasing v (Dickinson and Bernstein 1970), the concomitant growth in the magnitudes of D_v , H_v , ... etc. tempers the decreasing sensitivity to these higher-order constants.

Of course, constants obtained in this way will be somewhat dependent on the degree of the polynomial used in the fit. Errors associated with this choice may be minimized by use of some systematic statistical rule such as a sequential F-test for the highest-order coefficient. A somewhat simpler, and perhaps more persuasive test of the significance of any particular coefficient is its stability under changes in the degree of the fitting polynomial. This latter criterion was used in present applications of both the eigenvalue-fitting procedure, and of the energy-derivative method described below.

Energy-Derivative Fitting

This technique is related to those described above in that it uses perturbation theory in its derivation, and fits to a polynomial in $J(J+1)$ for actually determining the constants. The effect of a small change in the centrifugal potential on any given level energy $G(v, J)$ can be accurately represented by the first-order perturbation energy, and hence one obtains

$$\begin{aligned}
 [5] \quad B_{\text{eff}}(v, J) &\equiv \frac{\partial G(v, J)}{\partial [J(J+1)]} \\
 &= (\hbar^2/2\mu) \langle v, J | R^{-2} | v, J \rangle \\
 &= B_v - 2D_v[J(J+1)] \\
 &\quad + 3H_v[J(J+1)]^2 \\
 &\quad + 4L_v[J(J+1)]^3 + \dots
 \end{aligned}$$

The second line of eq. 5 shows how $B_{\text{eff}}(v, J)$ is obtained from the calculated radial expectation value, while the third line shows that fits of such results to a power series in $J(J+1)$ should yield the desired rotational constants. Tellinghuisen (1973*b*) preferred not to consider eq. 5 itself and instead chose to use the derived expression (Tellinghuisen's actual expression contained an addition factor of 2):

$$\begin{aligned}
 [6] \quad D_{\text{eff}}(v, J) &\equiv \frac{B_{\text{eff}}(v, 0) - B_{\text{eff}}(v, J)}{2J(J+1)} \\
 &= D_v - \frac{3}{2}H_v[J(J+1)] \\
 &\quad - 2L_v[J(J+1)]^2 - \dots
 \end{aligned}$$

While better suited to graphical presentation than eq. 5, eq. 6 implicitly distorts the relative uncertainties in the ordinates at different J , and in addition, fits to it would be especially sensitive to inaccuracies in the calculated $B_{\text{eff}}(v, 0)$ ($= B_v$) values. On the other hand, by removing a variable from the fits, use of eq. 6 permits the use of lower-order polynomial expressions, which in turn leads to a somewhat more reliable determination of the higher-order rotational constants.

When Tellinghuisen (1973*b*) proposed this approach, he focussed attention on the use of semiclassical phase integral techniques for evaluating the expectation values in eq. 5. Of course, quantal expectation values obtained from the exact numerically calculated wave functions are equally suitable, and somewhat more precise. On the other hand, the semiclassical calculation requires less computation time, and in addition, the phase integrals only depend on the nature of the potential *between* the classical turning points. This latter consideration is particularly important for levels very near dissociation. However, the results in his Table I (and the scatter in Fig. 3 of the

paper by Singh and Tellinghuisen (1973)) indicate that Tellinghuisen's (1973*b*) approach may have some difficulty in achieving very high precision, particularly for highly excited vibrational levels. This may explain why, in contrast to the present results, his $D_{\text{eff}}(v, J)$ curves appeared to display only a linear dependence on $J(J+1)$ even when virtually the same range of J values is spanned (e.g., for $v' = 40$ of B -state I_2).

Throughout the present work, expectation values of R^{-2} were evaluated quantumly using the appropriate exact (numerically calculated using double-precision arithmetic) radial wave functions. The subsequent fits to eqs. 5 and 6 utilized *ca.* 30 different $B_{\text{eff}}(v, J)$ (or $D_{\text{eff}}(v, J)$) values uniformly distributed between $J = 0$ and $J_D(v)$. In the fits to eq. 6, steps were taken to circumvent difficulties due to any inordinate dependence on the accuracy of $B_{\text{eff}}(v, 0)$. To this end, the fits were repeated as the $D_{\text{eff}}(v, J)$ values for smallest J were successively dropped, until these omissions yielded no further improvement in the "goodness" of the fit.

Comparisons

When the divers methods described above were applied to B -state I_2 , they gave virtually identical D_v values over the lower part of the potential well. In addition, their (extrapolated) values at the potential minimum ($v = -1/2$) were in good agreement with a value obtained from the "Dunham" expression given by Herzberg (1950) (his eq. III-118). However, as is shown in Fig. 1, the D_v values calculated by perturbation theory (curve P) drop below those obtained by the other techniques (coinciding to yield curve F) for $v \gtrsim 55$. This falloff is precisely the type of error which neglect of coupling to the continuum is expected to introduce to perturbation-theory calculations of D_v .

Although the perturbation theory D_v 's are apparently reliable for levels lying more than *ca.* 200 cm^{-1} ($\approx 0.05D_e(B)$) below dissociation, one third of all the vibrational levels lie above this point. Furthermore, a perturbation-theory calculation of higher-order rotational constants will be *increasingly* affected by coupling to "distant" levels (Albritton *et al.* 1973*a*). An examination of the perturbation-theory H_v expression also shows that error due to ignoring coupling to levels (and the continuum) lying

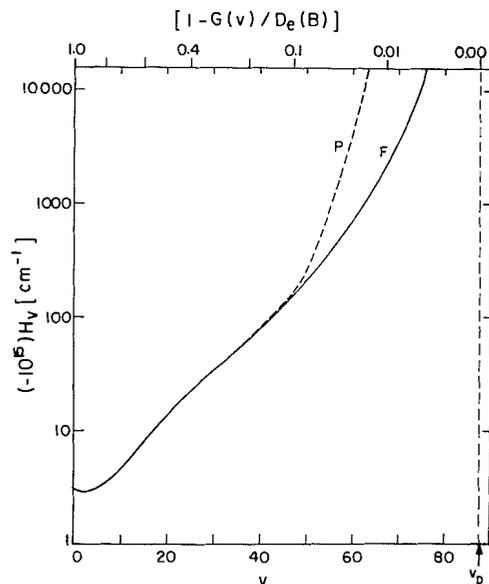


FIG. 2. Comparison of H_v values calculated by perturbation theory (curve P) with those obtained from fits to eqs. 6 and 7.

above the level in question should make the calculated constant too large. This result was verified by calculations which progressively omitted more and more of the highest bound levels from consideration. Thus, the discrepancies seen in Fig. 2 between the perturbation-theory H_v 's (for B -state I_2) and values calculated by other techniques are readily attributable to the inadequacy of the former. The perturbation-theory approach is therefore probably the least generally useful of the methods considered here.

As implied above, D_v values obtained from eigenvalue fitting and from both versions of the energy-derivative method were in good agreement over virtually the whole potential well.⁶ Similar agreement was found for the H_v values thus calculated for the lower levels, and their extrapolated values at the potential minimum were also in good agreement with the "Dunham" H_e value (Herzberg 1950, eq. III-127). However, as v increased, the eigenvalue-fitting H_v estimates displayed an increasingly capricious dependence on the degree

⁶For computational ease these calculations were not extended to levels above $v' = 75$, which is within 10 cm^{-1} ($\approx 0.002D_e(B)$) of dissociation.

TABLE 1. $I_2(B^3\Pi_{0u}^+)$ parameters obtained on fitting band absorption data to eq. 1 with $D_{v'}$ held fixed at the calculated value ^a

Band ($v'-v''$)	$E(v')$ ^b	$10^4 B_{v'}$	$10^9 D_{v'}$
3-6	16 092.65(-1.08)	284.24(+3.10)	6.57(+22.)
4-7	211.96(0.0)	282.93(+0.02)	6.71(+0.4)
5-4	329.88(-0.01)	281.13(+0.38)	6.86(+33.)
6-3	446.10(-0.02)	279.43(+0.07)	7.01(+1.5)
7-3	561.10(-0.19)	277.80(+0.32)	7.17(+1.2)
7-5	560.83(+0.01)	277.94(-0.14)	7.17(-3.6)
8-4	673.86(-0.01)	275.94(+0.05)	7.34(+0.5)
9-4	785.58(-0.02)	274.20(+0.02)	7.52(+0.1)
10-5	894.83(0.0)	272.44(0.0)	7.71(0.0)
11-1	17 002.66(+0.12)	271.00(-0.59)	7.91(-4.8)
12-2	108.80(-0.01)	269.30(+0.12)	8.12(+2.5)
13-2	213.19(-0.02)	267.40(+0.28)	8.35(+1.5)
14-1	315.81(+0.03)	265.62(-0.13)	8.59(-0.9)
16-2	515.73(+0.01)	261.47(-0.03)	9.11(-0.22)
25-0	18 320.68(-0.02)	241.65(+0.36)	12.30(+10.4)
29-0	626.43(0.0)	231.24(+0.10)	14.23(+4.7)
30-0	18 697.692	228.26	14.58(0.33)
43-0	19 433.61	187.0	25.25

^aQuantities in parentheses are the differences with the results of the original fits in which $D_{v'}$ was a fitting parameter.
^bEnergies expressed relative to the ground-state $v'' = 0, J'' = 0$ level.

of the polynomial [3] used in the fit, and for the higher levels⁶ this approach became totally unreliable. Thus, while satisfactory for $D_{v'}$'s, the eigenvalue-fitting procedure apparently cannot readily yield reliable values of H_v or higher-order rotational constants.

Similarly to the above, while fits to eqs. 5 and 6 yielded essentially equivalent H_v values for all cases considered here, for highly excited levels the former increasingly displayed a noticeable dependence on the degree of the fitting polynomial. Thus, it appears that performing fits to Tellinghuisen's (1973b) eq. 6 is the most reliable of the methods considered here for calculating values of $D_{v'}$ and H_v from a known potential energy curve. However, the linear graphical plots used by Tellinghuisen (1973b) and by Singh and Tellinghuisen (1973) provide a rather inadequate analysis of the $D_{\text{eff}}(v, J)$ results obtained here, since our fits to eq. 6 required polynomials of degree between 4 and 6 (depending on v). For $v' = 40$, for example, a linear fit to our $D_{\text{eff}}(v, J)$'s yields $H_{40} = 111.4 \times 10^{-15} \text{ cm}^{-1}$, which appears to be in good agreement with the value of Singh and Tellinghuisen (1973). However, the higher-order fits show that a more accurate value for this constant is $78.1 \times 10^{-15} \text{ cm}^{-1}$, which is some 30% smaller.

D. Rotational Constants of $I_2(B^3\Pi_{0u}^+)$

Initial estimates of the B -state rotational constants were obtained by fitting the band absorption data to eq. 1 with no constraints other than that (as throughout this analysis) the ground-state molecular constants were held fixed at known (Le Roy 1970b) values. The $D_{v'}$ constants thus obtained are the points shown in Fig. 1. While Richardson and Powell's (1967) data for the 30-0 band were not available for such reanalysis, the high precision of their measurements and reasonableness of their experimental D_{30} value justify acceptance of their constants.

When combined with the theoretical datum $B_{87.75} = 0$, the $v' = 43$ parameters obtained from the fluorescence measurements, and the observed and predicted vibrational energies for levels $48 \leq v' \leq 87$, the above results yielded an initial RKR potential for this state. $D_{v'}$ constants were then calculated from this curve and used in fits to eq. 1 to generate improved level energies and $B_{v'}$ constants, which in turn yield a new RKR curve and improved $D_{v'}$ values. This procedure converged after only three iterations. The final calculated $D_{v'}$ constants (corresponding to curve F in Fig. 1) are given in Table 1 together with the corresponding optimized level energies and

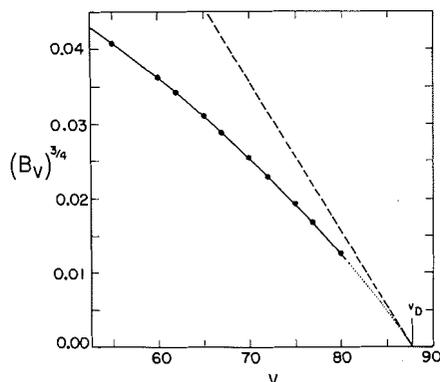


FIG. 3. Comparison of calculated B_v 's near dissociation (points and solid curve) with the limiting theoretical behavior (dashed line) predicted by Le Roy (1972).

$B_{v'}$ values. The numbers in parentheses are their differences with the results of the initial fits in which the $D_{v'}$ constants were allowed to vary (yielding the points in Fig. 1). It is evident that the present procedure yields significantly improved molecular parameters for these levels.

The dearth of experimental rotational data for levels above $v' = 30$ introduces uncertainties into the RKR curve in this region which manifest themselves as small anomalies in the shape of the (very steep) inner wall of the potential. Fortunately, these errors may be readily removed (see Sect. III E), and such corrections were applied at each step of the iterative procedure

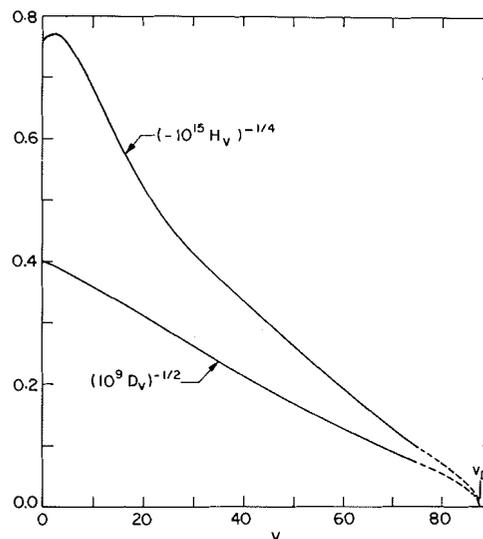


FIG. 4. Simplified plots of D_v and H_v which remove the essential singularities at $v = v_D$.

described above. However, while the adjusted potential is "better" in that anomalies in the slope of the inner wall are removed, it no longer precisely corresponds to the purely experimental (*i.e.* interpolated) B_v expression for levels above $v' = 30$. To remove this inconsistency, corrected B_v values for $v' > 30$ were calculated from eq. 2 using the optimized RKR potential. Combining these results with those in Table 1 yields our final expression

$$\begin{aligned}
 [7] \quad B_v = & 2.904741 \times 10^{-2} - 1.833819 \times 10^{-4}(v + \frac{1}{2}) + 3.303907 \times 10^{-6}(v + \frac{1}{2})^2 \\
 & - 2.301969 \times 10^{-7}(v + \frac{1}{2})^3 + 4.432396 \times 10^{-9}(v + \frac{1}{2})^4 \\
 & - 4.309644 \times 10^{-11}(v + \frac{1}{2})^5 + 1.724098 \times 10^{-13}(v + \frac{1}{2})^6
 \end{aligned}$$

which should be valid for *all* vibrational levels.

Figure 3 shows how the actual B_v constants obtained here approach the limiting near-dissociation behavior predicted by Le Roy (1972). The dashed line there corresponds to the "upper bound" prediction of his eq. 10. It is clear that this asymptotic functionality is achieved only for the very highest levels.

While reliable *experimental* D_v 's and H_v 's are not yet available for this system, values were readily calculated using the techniques described above.⁶ The most striking feature of these results is the rapidly accelerating growth (faster than exponential) in the magnitudes of both parameters with increasing v . As is suggested by curves F in Figs. 1 and 2, both quantities approach infinity as the levels approach dissociation. It will be shown elsewhere that this limiting behavior is theoretically expected.

In view of the singular behavior as $v \rightarrow v_D$, the customary $(v + \frac{1}{2})$ polynomials analogous to eq. 7 do not offer accurate or compact representations of the D_v 's and H_v 's. In addition, they would be useless for making predictions in the interval between the highest level for which results are calculated, and dissociation. On the other hand, Fig. 4 shows that $(D_v)^{-1/2}$ and $(-H_v)^{-1/4}$ are

well-behaved functions of v , and that their extrapolation to the known intercept (singularity) at $v = v_D = 87.75$ is quite well defined. Thus, polynomial fits to the latter should yield much more useful representations of these rotational constants. Fitting the calculated constants in this manner yielded

$$[8] \quad D_v = 10^{-9}/[0.40294 - 3.1913 \times 10^{-3}(v + \frac{1}{2}) - 1.3200 \times 10^{-4}(v + \frac{1}{2})^2 \\ + 5.0270 \times 10^{-6}(v + \frac{1}{2})^3 - 1.0406 \times 10^{-7}(v + \frac{1}{2})^4 \\ + 1.1386 \times 10^{-9}(v + \frac{1}{2})^5 - 4.936 \times 10^{-12}(v + \frac{1}{2})^6]^2$$

and

$$[9] \quad H_v = -10^{-15}/[0.7513 + 1.5549 \times 10^{-2}(v + \frac{1}{2}) - 3.56071 \times 10^{-3}(v + \frac{1}{2})^2 \\ + 1.807046 \times 10^{-4}(v + \frac{1}{2})^3 - 4.559987 \times 10^{-6}(v + \frac{1}{2})^4 \\ + 6.202624 \times 10^{-8}(v + \frac{1}{2})^5 - 4.34774 \times 10^{-10}(v + \frac{1}{2})^6 + 1.23202 \times 10^{-12}(v + \frac{1}{2})^7]^4$$

This D_v expression is accurate to within $\pm 0.5\%$ for levels $0 \leq v \leq 75$, and should also be reasonably reliable for the 12 levels above $v = 75$. On the other hand, the H_v expression is somewhat less precise, representing the calculated values with an uncertainty of 1–3%. This uncertainty is due to both the relatively larger uncertainty in the calculated H_v 's, and to the difficulty of obtaining a precise fit to their values. In any case, it is apparent that simple manipulations of eqs. 8 and 9 will yield the familiar Dunham rotational constants (Herzberg 1950) D_e, H_e, β_e , etc.

It should perhaps be emphasized that this inherent singularity of D_v and H_v constants near dissociation will be common to *all* molecular states whose potentials have no barrier at long range.⁷ Thus, expressions of the form of the present eqs. 8 and 9 should prove useful *whenever* one is attempting to describe these quantities for highly excited levels.

E. Vibrational Constants and RKR Potential for $I_2(B^3\Pi_{0u}^+)$

The optimized vibrational energies obtained from the absorption and resonance fluorescence data are given in Table 1. Fitting them by least squares to a polynomial in v yielded a standard error of 0.04 cm^{-1} . The fact that analogous smoothing fit of Brown's (1931) results for $48 \leq v' \leq 72$ had a standard error of 0.16 cm^{-1} led to use of a relative weighting of 16:1 in the least-squares fit which yielded the final $G(v)$ polynomial. Since the predicted energies of the highest bound levels (Le Roy and Bernstein 1971) depend only on Brown's (1931) data, they were also given a statistical weight of 1/16 relative to the energies in Table 1. The final vibrational term value expression obtained from these results is

$$[10] \quad G(v) = 126.1044(v + \frac{1}{2}) - 0.833184(v + \frac{1}{2})^2 + 3.41741 \times 10^{-3}(v + \frac{1}{2})^3 \\ - 2.684084 \times 10^{-4}(v + \frac{1}{2})^4 + 4.651628 \times 10^{-6}(v + \frac{1}{2})^5 \\ - 2.966643 \times 10^{-8}(v + \frac{1}{2})^6 + 6.69103 \times 10^{-11}(v + \frac{1}{2})^7$$

It corresponds to a B -state electronic energy of $\bar{\nu}_0 = 15\,724.10 \text{ cm}^{-1}$ (or $T_e = 15\,768.38 \text{ cm}^{-1}$). As with eqs. 7–9, this expression should be valid for levels all the way to dissociation.

Once $G(v)$ and B_v expressions are known for any given species, a reliable RKR potential curve may be generated using standard numerical methods (Zare 1964; Coxon 1971; Dickinson 1972; Fleming and Rao 1972; Tellinghuisen

⁷More precisely, this is true for D_v if the attractive long-range intermolecular potential dies off faster than R^{-2} , and for H_v if it dies off faster than R^{-3} .

1972b). The present calculations utilized a double precision version of Zare's (1964) computer program. However, we chose to omit the Y_{00} correction described by Kaiser (1970), since the lack of data for levels below $v = 3$ necessarily precludes a precise determination of its magnitude.

As is often the case (Ginter and Battino 1965; Le Roy and Burns 1968), the available experimental rotational data were insufficiently complete to allow a reliable direct calculation of the turning points of the higher levels. This

gave rise to anomalies in the curvature and slope of the inner branch of the potential in the region above $v' = 30$. These difficulties were removed in the usual way (Verma 1960; Ginter and Battino 1965; Le Roy 1970*b*; Coxon 1971). The inner branch of the potential in the offending region was smoothed with an analytic extrapolation from the region $v' \leq 30$, and concomitant small adjustments were made in the corresponding outer turning points. For the final optimized potential, this extrapolation function (determined by a fit to the calculated inner turning points for $v' = 28, 29$, and 30) was

$$[11] \quad V(R) = 140.302 + \frac{3.932448 \times 10^{12}}{R^{21.328125}}$$

where the units of energy and length are cm^{-1} and \AA , and the zero of energy is taken as the B -state potential minimum. The concomitant shifts of the turning points for levels above $v' = 30$ are -0.00001 , -0.0013 , -0.0053 , -0.010 , $+0.0038$, and $+0.18 \text{ \AA}$ at $v = 40, 50, 60, 70, 80$, and 87 respectively. These shifts correspond to adjustments of the B_v values for these levels by $0.0005, 0.06, 0.22, 0.32, -0.08$, and -1.1% respectively, changes which are totally inconsequential in view of the dearth of data in this region. Note that the final B_v expression (eq. 7) corresponds to these adjusted values.

To conserve space (and because results based on more complete experimental data should be forthcoming shortly⁴), the present optimized RKR potential is not listed; however, it is readily available from the authors.

A perturbation-theory treatment of intermolecular forces shows that the long-range potential of B -state I_2 is given by (see, *e.g.*, the review by Le Roy 1973)

$$[12] \quad V(R) = D - C_5/R^5 - C_6/R^6 - C_8/R^8 - \dots$$

where D is the dissociation limit, and the constants C_5, C_6 , and C_8 are all positive (attractive). Since an analysis of the energies of the highest observed levels (Le Roy and Bernstein 1971) yielded apparently reliable values of D and C_5 , the turning points obtained above may be used to yield the coefficients C_6 and C_8 . This is done using a type of plot suggested by Cummings (1972). Since $G(v) = V(R_2(v))$ at the (known) outer turning points, he proposed

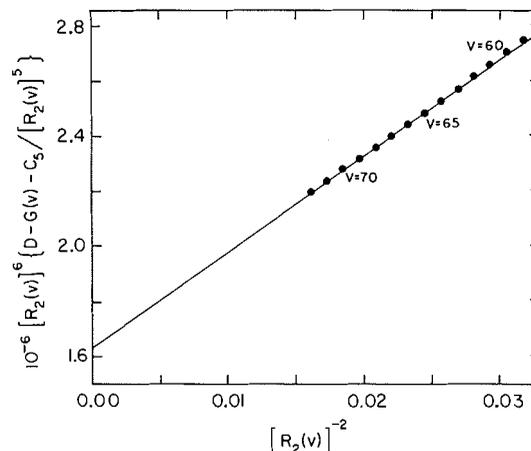


FIG. 5. RKR turning points for B -state I_2 plotted according to eq. 13; the intercept and slope yield the values of C_6 and C_8 given in Table 2.

a rearrangement of eq. 12 to yield

$$[13] \quad [R_2(v)]^6 \{D - G(v) - C_5/[R_2(v)]^5\} = C_6 + C_8/[R_2(v)]^2 + \dots$$

in which both the parameters on the left-hand side are known. The plot suggested by this expression is seen in Fig. 5; it utilizes Le Roy and Bernstein's (1971) values of $C_5 = 3.10_6 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$ and of D .

Since the long-range potential expansion eq. 12 breaks down at small distances, Le Roy's (1973) criterion (his eq. 5) was used to delineate its range of validity. As a result, only turning points for levels $v \geq 59$ were used in eq. 13. Furthermore, to avoid incorporating extrapolation error into these results, the plot was cut off at the point for the highest observed level, $v = 72$. Fitting the 14 points shown in Fig. 5 to eq. 13 then yields the "experimental" values of C_6 and C_8 given in Table 2, where they are compared to theoretical values recently obtained by Cummings (1972).

III. J Dependence of Intensities of Discrete $B(^3\Pi_{0u^+}) - X(^1\Sigma_g^+)$ Transitions of I_2

A. Nature and Method of Calculations

The intensity of a given line in a discrete absorption or emission spectrum depends on (see, *e.g.*: Herzberg 1950; Zare 1964) the frequency of the light (the factor ν for absorption and ν^4 for emission), and

TABLE 2. Long-range potential coefficients for $I_2(B^3\Pi_{0u}^+)$

	$10^{-6} C_6$ ($\text{cm}^{-1} \text{\AA}^6$)	$10^{-6} C_8$ ($\text{cm}^{-1} \text{\AA}^8$)
Experimental ^a	1.63(± 0.01)	35.1(± 0.4)
Theoretical ^b	1.85(± 0.2)	19. (± 4)

^aFrom a fit to the points on Fig. 5.^bFrom Cummings (1972).

$$[14] \quad I(v', J'; v'', J'') = N(v', J') S(J', J'') (\bar{R}_e)^2 \\ \times \left[\int_0^\infty \psi_{v'', J''}(R) \psi_{v', J'}(R) dR \right]^2$$

Here, $N(v', J')$ is the population of the initial vibrational-rotational level, $S(J', J'')$ the rotational intensity factor, $R_e(R)$ is the transition moment function characterizing the particular electronic transition, and $\psi_{v, J}(R)$ is the radial wave function of the initial (v', J') or final (v'', J'') state. In this expression we have already exploited the usually valid assumption that $R_e(R)$ is relatively slowly varying, by taking this function out of the integral and replacing it by an average value \bar{R}_e . For $B-X$ state halogen transitions, the factors $S(J', J'')$ are effectively independent of J' except at very small J' . Thus, the intensity of a given line depends mainly on the population of the initial level, and the square of the overlap integral between initial and final state wave functions (the Franck-Condon factor).

In the present work we chose to examine relative line intensities using the Franck-Condon amplitude (*i.e.* the overlap integral)

$$[15] \quad FCA(v', J'; v'', J'') = \\ \int_{-\infty}^\infty \psi_{v'', J''}(R) \psi_{v', J'}(R) dR$$

rather than the customary Franck-Condon factor

$$q(v', J'; v'', J'') = [FCA(v', J'; v'', J'')]^2$$

While this choice lends itself to a more convenient graphical presentation of the results, one should remember that the actual intensities vary as the square of FCA , and hence they will vary even more dramatically than do the results presented below. Of course the use of this amplitude introduces an arbitrary choice of sign, in regard to which we adopt the con-

TABLE 3. Franck-Condon amplitudes $FCA(v', J'; v'', J'')$ for emission from B -state level $v' = 5$ into X -state level $v'' = 10$

J'	Amplitudes ($\times 10^{-2}$)		
	P branch	Q branch ^a	R branch
0	4.851	4.850	—
50	4.497	4.464	4.431
100	3.366	3.300	3.234
150	1.403	1.303	1.204
200	-1.462	-1.594	-1.726
250	-5.268	-5.427	-5.585
300	-9.929	-10.10	-10.27
350	-15.04	-15.19	-15.35

^aForbidden.

vention that the factor $FCA(v', J'; v'', J'')$ must always be positive at $J = 0$.

In $B(^3\Pi_{0u}^+) - X(^1\Sigma_g^+)$ halogen spectra only the P - and R -branch rotational transitions corresponding to $J'' = J' \pm 1$ are allowed. While the intensities of P and R lines originating in a given level will in general be different, they will be systematically related. This fact is illustrated in Table 3 which compares Franck-Condon amplitudes for P , R , and (the forbidden) Q lines corresponding to emission from B -state level $v' = 5$ into ground-state level $v'' = 10$. These results show that the intensities of the three types of transitions have very similar J dependence, the differences being roughly equivalent to small shifts of the J' scale. Since the Q -branch intensities lie right in the middle of the P and R results, the ensuing calculations were performed only for this case ($\Delta J = 0$).

In computing the exact radial wave functions required by eq. 15, the RKR potential obtained above was used for the B state while that reported by Le Roy (1970b) was used for the ground state. While the latter was obtained using slightly less accurate values of the physical constants and reduced mass than were used here, it may be made consistent with the present

results by simply multiplying the reported X -state turning points by the factor⁸

$$\left(\frac{16.85803}{16.85749} \times \frac{63.43770}{63.437697} \right)^{1/2} = 1.0000160$$

The wave functions $\psi_{vJ}(R)$ were obtained by exact numerical solution of the radial Schrödinger equation using a (double-precision) computer program based on that of Cashion (1963). The integration increment (of 0.002 Å) was chosen so that there would be a minimum of 20–27 mesh points between any pair of adjacent wave-function nodes. The resulting vibrational wave functions for the different levels of a single potential curve were orthogonal to better than 0.5 parts in 10^7 . In Jarman's (1971) terminology this corresponds to a "noise factor" of 2.5×10^{-15} . The overlap integrals in eq. 15 (and in eqs. 2, 4, and 5) were all evaluated using Simpson's rule.

B. J Dependence of the Franck–Condon Amplitudes

Figures 6 and 7 contain the essence of the present results. Each segment of the former presents the Franck–Condon amplitudes for emission from a given B -state level (labelled v') into a range of ground-state levels (labelled v''), as functions of J . To put these results into perspective, each segment also contains values of $\Delta J(T)$, the full width at half maximum of the B -state rotational population distribution at four temperatures. The three higher temperatures are typical of those occurring in emission intensity studies of shock-heated iodine-inert gas mixtures (Brown 1973). Recalling that the actual intensity will vary as the *square* of the amplitude shown here, it is evident that the J dependence of these factors *must* be considered in any serious attempt to interpret such intensities.

Each segment of Fig. 7 presents Franck–Condon amplitudes for absorption from a given ground-state level (v'') into a range of

B -state levels (v'), as functions of J . In this case $\Delta J(T)$ represents the width at half maximum of the rotational population of the given X -state level (v''). It is again evident that at the higher temperatures, the band absorption intensities would be very inadequately represented by the $J = 0$ amplitudes.

In both Figs. 6 and 7 the curves were cut off when J reached $J_D(v)$, the value for which the appropriate B -state vibrational level crossed the dissociation limit. This range of J and the range of vibrational quantum numbers up to $v = 35$ should include most important contributions to the visible B -state emission spectrum. Note that in the ground electronic state $v'' = 35$ is just over halfway to dissociation, while the B state's $v' = 35$ level is more than 3/4 of the way.

It appears that little of general import may be extracted from the patterns of J dependence seen in Figs. 6 and 7 other than the trivial conclusion that the intensities of transitions involving the least excited vibrational levels (e.g., $v' = 0$ and/or $v'' = 0$) will show the least J dependence. Villarejo (1968) has presented a simple model for predicting when such effects will be important. However, it is based on a harmonic-oscillator approximation to the potential and hence is useful only if the levels of both states lie relatively close to the respective potential minima. Note that the change in sign of a Franck–Condon *amplitude* in Figs. 6 and 7 corresponds to the Franck–Condon factor in this region passing quadratically through a minimum value of zero.

J -dependent Franck–Condon factors have been examined previously in a number of systems (Learner 1962; Villarejo 1968; Villarejo, Stockbauer, and Inghram 1969; Generosa and Harris 1970; Balfour and Whitlock 1972). However, the magnitude of the changes seen here over a thermal range of J are as large as or larger than any reported previously. For the (v' , v'') vibrational bands with both v' and v'' ranging from 0 to 25, Franck–Condon amplitudes and R centroids have been calculated at $J = 0, 80, 160, 240,$ and 320 . The results seen in Figs. 6 and 7 indicate that interpolation over this range of values should be capable of yielding highly accurate results in the intermediate region. Hence, the results for each band were fitted to a polynomial in J and the

⁸Of course, if one believes the *atomic* reduced mass should be used rather than the reduced mass of the nuclei, the 63.437697 used here should be replaced by 63.452235. In practice, the exact value assumed for the reduced mass is irrelevant as long as precisely the same value used in the RKR calculation is also used in the subsequent solution of the Schrödinger equation for this potential.

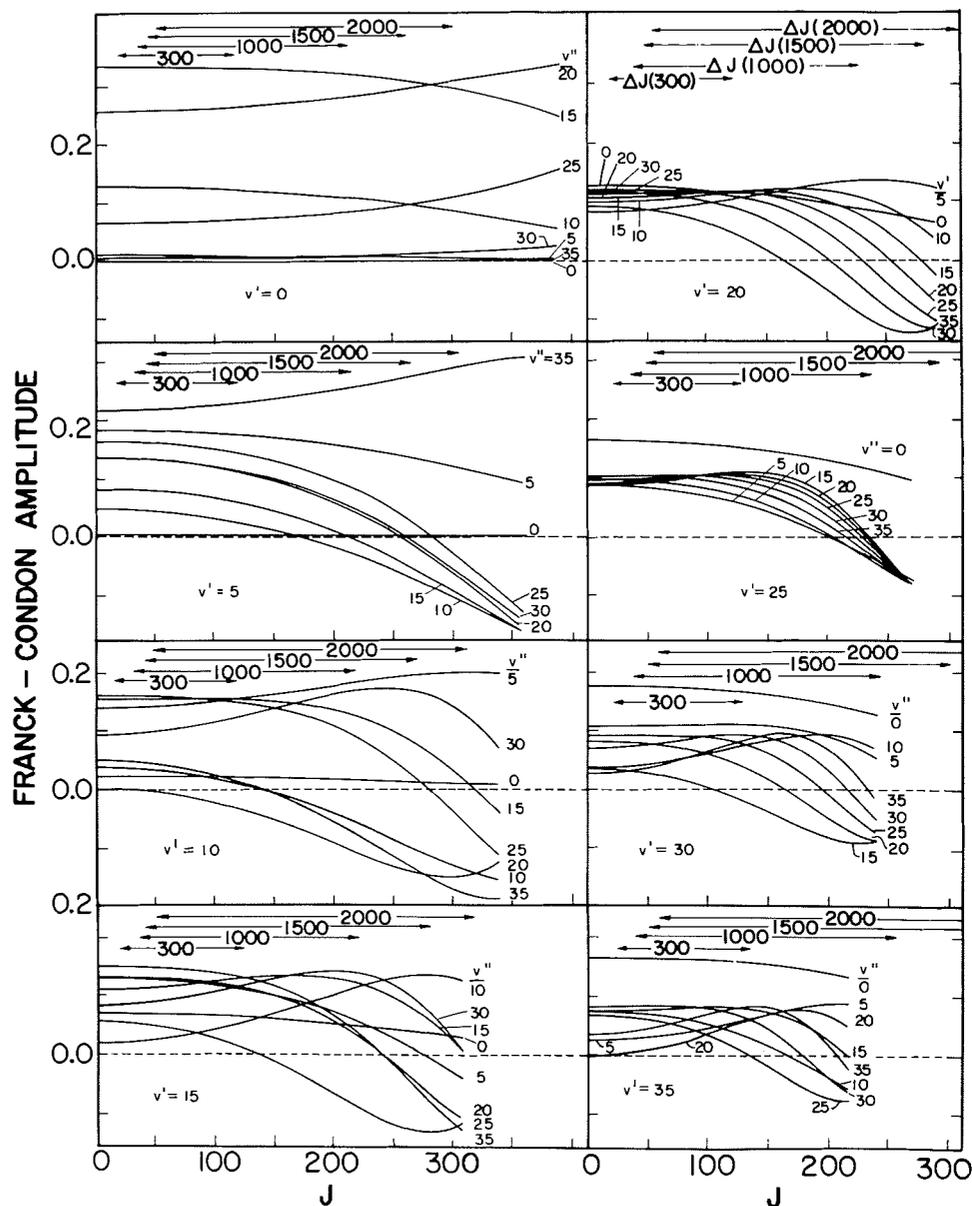
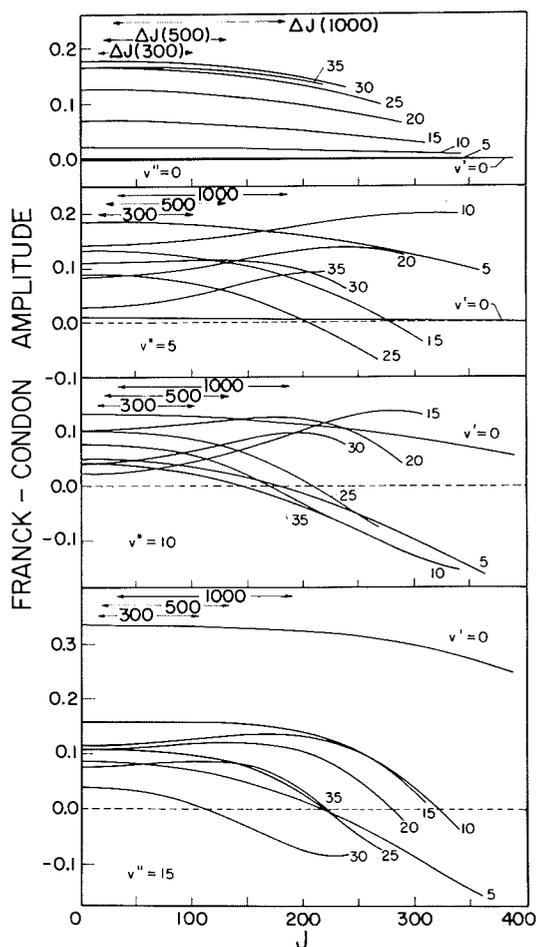


FIG. 6. Franck-Condon amplitudes for emission from particular B -state levels (labelled v') into a range of ground (X -state) levels (labelled v'') as functions of J . $\Delta J(T)$ designates the full width at half maximum of the rotational population of the initial state at temperature T .

coefficients were tabulated. These results are available from the authors upon request.

NOTE ADDED IN PROOF: In a recent paper, Albritton *et al.* (1973*b*) independently introduced an iterative data-fitting procedure utilizing calculated D_v values, which is similar to that described in Sect. II B above. In addition, S. M.

Kirschner and J. K. G. Watson (to be published in *J. Mol. Spectrosc.*) have recently derived another method of calculating centrifugal distortion constants (D_v and H_v) which is very similar to one of Klein's (1932) methods of obtaining potential curves from spectroscopic data.

FIG. 7. As in Fig. 6, for $B \leftarrow X$ absorption.

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