

Periodicity of the Oscillatory J Dependence of Diatomic Molecule Franck–Condon Factors¹

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Numerical calculations have shown that vibration–rotation interaction often contributes significantly to the J dependence of transition intensities of diatomic molecules. This occurs because centrifugal displacements of the vibrational wave functions cause the Franck–Condon amplitudes (radial overlap integrals) to behave as oscillating functions of $J(J+1)$. The present paper discusses the origin of this behavior and derives and tests a simple formula for predicting the periodicity of such oscillations. This procedure requires only a knowledge of the rotational constants and vibrational spacings of the initial and final states. It utilizes the result that the average centrifugal displacement rate of a diatomic molecule's radial wave function is approximately $(\hbar^2/2\mu)^{1/2}D_v/(B_v)^{3/2}$, where B_v and D_v are the usual diatomic rotational constants.

Des calculs numériques ont montré que l'interaction vibration–rotation contribue souvent de façon importante à la variation en fonction de J des intensités de transition dans les molécules diatomiques. Ceci se produit parce que les déplacements centrifuges des fonctions d'onde vibrationnelles font que les amplitudes de Franck–Condon (intégrales radiales de superposition) se comportent comme des fonctions oscillantes de $J(J+1)$. Dans le présent article, on discute l'origine de ce comportement; on dérive et on met à l'essai une formule permettant de prédire la périodicité de telles oscillations. Cette méthode requiert seulement la connaissance des constantes rotationnelles et de l'espacement des niveaux de vibrations dans l'état initial et l'état final. Elle utilise le résultat suivant lequel le taux de déplacement centrifuge de la fonction d'onde radiale d'une molécule diatomique est approximativement égal à $(\hbar^2/2\mu)^{1/2}D_v/(B_v)^{3/2}$, B_v et D_v étant les constantes rotationnelles usuelles d'une molécule diatomique.

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I. Introduction

The unknown importance of vibration–rotation interaction raises serious questions about the utility of many of the reported arrays of Franck–Condon factors for diatomic molecules. Since most such results are only tabulated for the case $J' = J'' = 0$, their use involves the rigid rotor assumption that Franck–Condon factors are identical for all lines in a given vibrational band. Although sometimes approximately valid, this assumption is often grossly incorrect. However, no reliable general criterion for predicting when it should be trusted has been reported. This is the problem with which the present paper is concerned.

Previous work on the J dependence of diatomic transition intensities has included both numerical and analytic studies. Most of the

latter were concerned with pure vibration–rotation transitions among the lower levels of a single potential energy curve. Early work in this vein was summarized by Tipping and Herman (1970) while more recent developments are described by Tipping and Forbes (1971) and Tipping (1973). These analytic studies require a simple analytic form for the potential function; in practice parabolic, Morse, or Dunham (a power series in $(R - R_e)/R_e$) functions are usually used. Expressions for transition intensities are then derived as analytic functions of the potential parameters and the rotational quantum number J . However, parabolic or Morse functions cannot accurately describe a real interaction potential over a wide energy range, while the analytic matrix elements associated with a several term Dunham potential become almost intolerably complicated if any but the lowest vibrational levels are being considered.³ Even

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³See, for example, the wave function expressions given in Table 1 of Herman *et al.* (1970).

for transitions involving only the lowest levels, the complexity of these expressions³ tends to obscure both the nature of the vibration-rotation interaction and any simple estimate of its importance. Analytic techniques have also been used in studies of J dependent band intensities in electronic transitions (Learner and Gaydon 1959; Learner 1962; James 1960; Villarejo 1968; Chakraborty *et al.* 1971; Chakraborty and Pan 1972). However, the difficulties described above are merely compounded by the existence of independent potential curves for the initial and final states.

Numerical studies of the J dependence of diatomic transition intensities, performed utilizing exact radial wave functions calculated from RKR or *ab initio* potential curves, have been reported for a number of systems.⁴ However, as informative as such calculations may be regarding the particular cases considered, fundamental physical conclusions are not readily extracted from the resulting arrays of numbers or sets of curves. On the other hand, such results do illustrate typical behavior and provide a convenient foil for any method devised for predicting the importance of vibration-rotation interaction.

The property of Franck-Condon factors most clearly illustrated by the numerical calculations⁴ is their oscillatory dependence on the rotational quantum number J . This behavior is particularly evident in the results of Balfour and Whitlock (1972) for the $A \leftrightarrow X$ transitions of Mg_2 and in those of Brown *et al.* (1973) for the $B \leftrightarrow X$ transitions of I_2 . In the following, we present a simple method for predicting the periodicity of such oscillations. The importance of vibration-rotation interaction is then readily ascertained from a comparison of the range of J 's involved in a given problem to this oscillation period. However, the present techniques are only applicable to cases in which there is substantial overlap between the radial wave functions of the initial and final states.

II. Vibration-Rotation Interaction in Diatomic Transition Intensities

A. Theoretical Background

The intensity of a given line in a discrete absorption or emission spectrum depends on (Herzberg 1950; Zare 1964; Whiting and Nicholls 1974) the frequency of the light, a factor of ν^4 for emission or ν for absorption, and

$$[1] \quad I(v', J'; v'', J'') = N(v', J') S(J', J'') \left| \int_0^\infty \Psi_{v'', J''}(R) M_e(R) \Psi_{v', J'}(R) dR \right|^2$$

Here, $N(v', J')$ is the population of the initial vibration-rotation level, $S(J', J'')$ the rotational intensity factor, $M_e(R)$ the electronic transition moment function, and $\Psi_{v, J}(R)$ the radial wave function of the initial (v', J') or final (v'', J'') state. Within the rigid rotor approximation, all of the J dependence of $I(v', J'; v'', J'')$ is contained in the factors $N(v', J')$ and $S(J', J'')$; the former being defined by the experimental conditions, while the latter are known functions of J', J'' , and the type of electronic transition (Hönl and London 1925; Kovács 1969; Hougen 1970; Whiting and Nicholls 1974). It is the breakdown of this approximation, the additional J dependence of the remaining factor, which is considered here. The calculations referred to in footnote 4 show that this breakdown is often very important and we wish to understand its origin in order to be able to predict when it will arise.

The wave functions $\Psi_{v, J}(R)$ are the solutions of the radial Schrödinger equation:

$$[2] \quad -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \Psi_{v, J}(R) + \left(V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} - G(v, J) \right) \Psi_{v, J}(R) = 0$$

When J increases, the attractive bowl of the effective interaction potential $U_J(R)$, defined as

$$[3] \quad U_J(R) = V(R) + (\hbar^2/2\mu) J(J+1)/R^2$$

shifts upward to higher energy and outward to larger R . Thus, as the energy $G(v, J)$ of a given vibrational level increases with J , its radial wave function $\Psi_{v, J}(R)$ is displaced to larger R . Since wave functions for different vibrational levels shift at different rates, increasing J will clearly displace

⁴See Haycock (1963); Cashion (1964); Halmann and Laulicht (1968); Hubisz (1968); Villarejo (1968); Villarejo *et al.* (1969); Fink *et al.* (1969); Generosa and Harris (1970); Balfour and Whitlock (1972); and Brown *et al.* (1973).

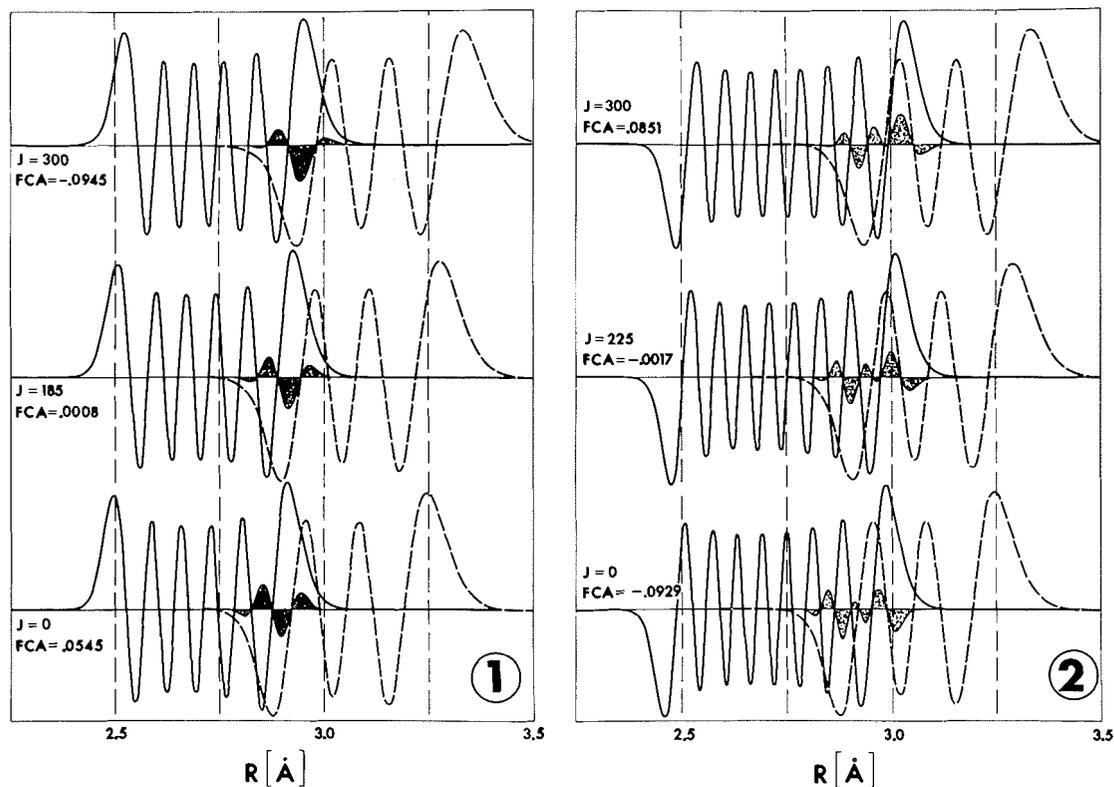


FIG. 1. Radial wave functions for the $v'' = 10$ level of X state I_2 (solid curve) and $v' = 5$ level of B state I_2 (dashed curve), the integrand of their overlap integral (shaded region, scaled down by a factor of 0.1), and the resulting FCA, all at three different values of J .

FIG. 2. For the ($v'' = 15, v' = 5$) band in the $B-X$ spectrum of I_2 , as in Fig. 1.

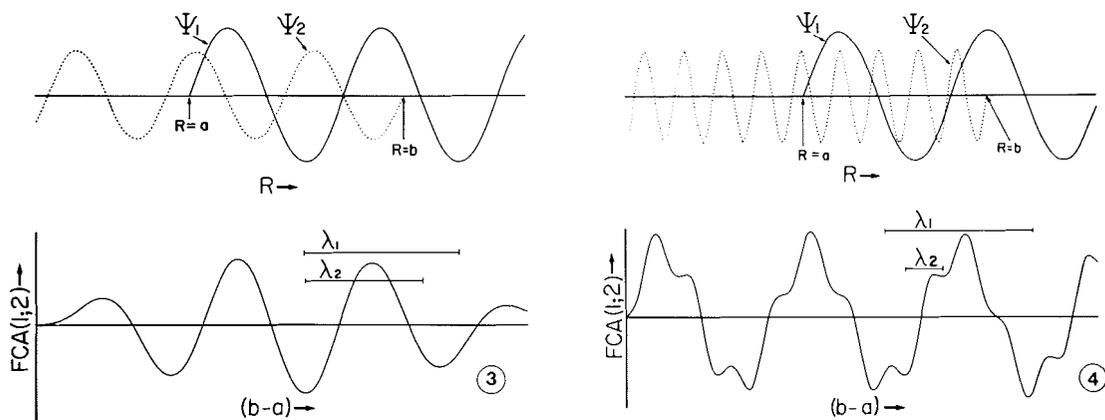


FIG. 3. Upper: model wave functions of [5] and [6] for $\lambda_1 = 1.3\lambda_2$. Lower: their overlap integral ([17]) as a function of the relative displacement ($b - a$).

FIG. 4. For $\lambda_1 = 3.8\lambda_2$, as in Fig. 3.

the oscillating functions $\Psi_{v',J'}(R)$ and $\Psi_{v'',J''}(R)$ relative to one another. If this relative shift is a significant fraction of their characteristic de Broglie wavelengths, it will cause a significant change in the overlap integral in [1].

For two of the bands in the visible spectrum of I_2 , Figs. 1 and 2 illustrate the effect of changes in J (where $J = J' = J''$) on the initial and final state eigenfunctions and on their product, $[\Psi_{v'',J''}(R)\Psi_{v',J'}(R)]$. The relative amplitudes of the positive and negative lobes of these product functions are significantly affected by changes in J , while the corresponding net radial displacement of these functions is relatively small. It is, therefore, reasonable to replace the transition moment function $M_e(R)$ by $\bar{M}_e(v',v'')$, an effective average value for the vibrational transition under consideration, and then to remove it from the integral. Except for pathological cases in which $M_e(R)$ changes significantly in a range comparable to the node spacing of the vibrational eigenfunctions, this approximation does not affect the ensuing discussion since it is the *relative* displacement of the vibrational wave functions which is the dominant source of vibration-rotation interaction.

In view of the above, the remainder of this paper will focus attention on the J dependence of the Franck-Condon amplitude (FCA):

$$[4] \quad \text{FCA}(v',J';v'',J'') = \int_0^\infty \Psi_{v'',J''}(R)\Psi_{v',J'}(R) dR$$

Since its square is the familiar (Herzberg 1950; Zare 1964) Franck-Condon factor, the actual intensities depend on the square of the FCA's and, hence, vary much more dramatically than the FCA itself. Intriguing pictures of the J dependence of FCA values for a wide range of vibrational transitions appear in Figs. 6 and 7 of the paper by Brown *et al.* (1973).⁵ For two of the cases considered there, the present Figs. 1 and 2 show how small relative shifts of the eigenfunctions can have rather drastic effects on the FCA's and, hence, on the transition intensities.

B. Characteristic Behavior of the FCA

The numerical results referred to in footnote 4 indicate that the FCA tends to be an oscillating function of $J(J+1)$. This behavior is readily explained using a simple model in which the two vibrational wave functions are approximated by sine functions,

$$[5] \quad \begin{aligned} \Psi_1 &= A_1 \sin(2\pi(R-a)/\lambda_1) & \text{for } R \geq a \\ &= 0 & \text{for } R < a \end{aligned}$$

$$[6] \quad \begin{aligned} \Psi_2 &= A_2 \sin(2\pi(R-b)/\lambda_2) & \text{for } R \leq b \\ &= 0 & \text{for } R > b \end{aligned}$$

For this case, the FCA is

$$[7] \quad \text{FCA}(1;2) = \frac{A_1 A_2 \lambda_1 \lambda_2}{2\pi(\lambda_2^2 - \lambda_1^2)} \{ \lambda_1 \sin(2\pi(b-a)/\lambda_1) - \lambda_2 \sin(2\pi(b-a)/\lambda_2) \}$$

A relative displacement of the wave functions [5] and [6] clearly corresponds to a change in $(b-a)$. Equation 7 shows that this would cause the FCA to oscillate as a sum of two sine functions whose amplitudes and wavelengths are defined by those of the original wave functions. This result displays the two types of limiting behavior shown in Figs. 3 and 4. If $\lambda_2 \simeq \lambda_1$, as in Fig. 3, the FCA has simple periodic oscillations with a frequency intermediate between those of the original wave functions. In this case, therefore, the displacement associated with one complete oscillation of the FCA is given by:

$$[8] \quad \bar{\lambda}(v',v'') = (1/2)(\lambda_{v'} + \lambda_{v''})$$

On the other hand, for $\lambda_2 \gg \lambda_1$ (see Fig. 4), the behavior of the FCA is dominated by the slower frequency term, with a small amplitude rapidly oscillating contribution superimposed on it. For this case, a more appropriate estimate of the 'displacement wavelength' associated with the FCA would be:

⁵For the sake of simplicity, these I_2 results all correspond to Q branch ($J' = J''$) transitions. Brown *et al.* (1973) showed that this restriction does not affect the characteristic J dependence of these quantities.

$$[9] \quad \bar{\lambda}(v', v'') = \max \{ \lambda_{v'}, \lambda_{v''} \}$$

The change in $J(J + 1)$ required to shift the radial wave functions, $\Psi_{v'}$ and $\Psi_{v''}$, relative to one another by one displacement wavelength, $\bar{\lambda}(v', v'')$, is given by

$$[10] \quad \Delta[J(J + 1)] = \bar{\lambda}(v', v'') \left/ \left| \frac{\partial \bar{R}(v'')}{\partial [J(J + 1)]} - \frac{\partial \bar{R}(v')}{\partial [J(J + 1)]} \right| \right.$$

Here, $\bar{R}(v)$ is a distance characterizing the position of the radial wave function for level v and $\partial \bar{R}(v)/\partial [J(J + 1)]$ is the centrifugal displacement rate of this eigenfunction. It is this quantity, $\Delta[J(J + 1)]$, which determines the importance of vibration-rotation interaction in any given case. In order to facilitate the utilization of [10], simple methods for estimating the characteristic wavelength and centrifugal displacement rate of a vibrational eigenfunction are devised below.

III. Centrifugal Displacement Rate of a Vibrational Eigenfunction

A. Average R Approach

In order to discuss the centrifugal displacement of a vibrational wave function, we must first select a means of characterizing its position. This can be done using either the eigenfunction's node or extremum positions or some average of the internuclear distance,

$$[11] \quad \bar{R}_m(v, J) \equiv [\langle v, J | R^m | v, J \rangle]^{1/m}$$

Most of these choices involve the tedious, though straightforward, procedure of: (i) determining the interaction potential $V(R)$; (ii) solving the resulting radial Schrödinger equation ([2]) to obtain the appropriate eigenfunction $\Psi_{v, J}(R)$ (represented in [11] by $|v, J\rangle$); and (iii) performing the quadrature of [11] or locating the appropriate nodes or extrema of $\Psi_{v, J}(R)$. However, there is one characteristic distance which is known experimentally, the quantity $\bar{R}_{-2}(v, J)$ defined by [11] when $m = -2$, and its use obviates the need for any numerical calculations.

It is well known (see Tellinghuisen 1973; Albritton *et al.* 1973) that:

$$[12] \quad B_v(J) \equiv \partial G(v, J) / \partial [J(J + 1)] = (\hbar^2 / 2\mu) \langle v, J | R^{-2} | v, J \rangle = \hbar^2 / 2\mu (\bar{R}_{-2}(v, J))^2$$

where $B_v(0)$ is the familiar diatomic rotational constant, B_v . Thus, a knowledge of the rotational level spacings yields an average value of R for each observed level:

$$[13] \quad \bar{R}_{-2}(v, J) = (\hbar^2 / 2\mu B_v(J))^{1/2}$$

The centrifugal displacement rate of this average R is

$$\partial \bar{R}_{-2}(v, J) / \partial [J(J + 1)] = -((\hbar^2 / 8\mu)^{1/2} / (B_v(J))^{3/2}) \partial^2 G(v, J) / \partial [J(J + 1)]^2$$

and for $J = 0$, this result takes on the particularly simple form:

$$[14] \quad \partial \bar{R}_{-2}(v, 0) / \partial [J(J + 1)] = (\hbar^2 / 2\mu)^{1/2} D_v / (B_v)^{3/2}$$

where D_v is the usual centrifugal distortion constant for the given vibrational level.

This result, [14], is extremely convenient since it expresses the centrifugal displacement rate directly in terms of the standard experimental parameters, B_v and D_v . The appropriate B_v values would certainly be available in any case for which transition intensity calculations could be undertaken, since such calculations presume a knowledge of the intermolecular potential, and B_v values are essential to its determination from spectroscopic data. Values of D_v are somewhat more difficult to determine experimentally, par-

ticularly for the highly excited vibrational levels for which their values are largest. However, D_v 's also depend on the intermolecular potential (and, hence, implicitly on the $G(v, 0)$ and B_v values) and a recent flurry of activity has yielded a number of different ways of calculating them from any given potential function (Tellinghuisen 1973; Albritton *et al.* 1973; Brown *et al.* 1973; Kirschner and Watson 1973; Barwell 1975).

Before proceeding to use [14], there are two questions which must be examined. The first concerns whether or not this derivative at $J = 0$ provides a realistic estimate of the centri-

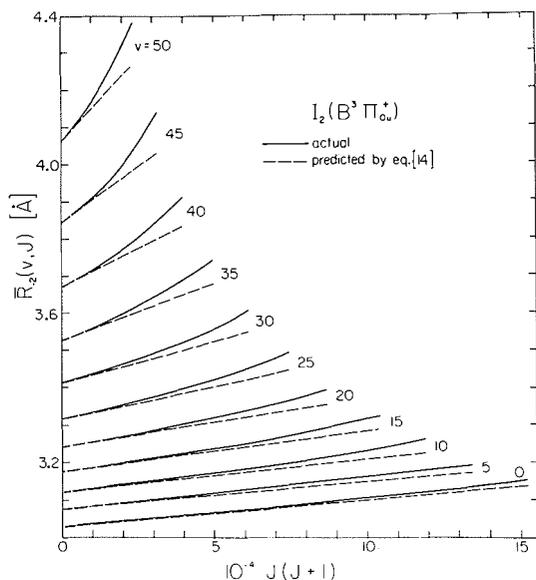


FIG. 5. Comparison of the actual centrifugal displacements of $\bar{R}_{-2}(v, J)$ values for levels of B state I_2 (solid curves) with the shifts predicted by [14] (dashed lines).

fugal displacement of $\bar{R}_{-2}(v, J)$ for all J . For a number of vibrational levels of B state I_2 ,⁶ Fig. 5 presents calculated values of \bar{R}_{-2} (solid curves) for J 's in the range $0 \leq J \leq J_D(v)$, where $J_D(v)$ is the largest J for which $G(v, J)$ lies below the dissociation limit. The dashed lines in this figure correspond to the derivative given by [14]. Comparisons between the solid and dashed curves indicate that except for highly excited vibrational levels at relatively high J , this expression provides a fairly realistic picture of the centrifugal displacement of the \bar{R}_{-2} values. Further confirmation of this conclusion is provided by examination of the $\bar{R}_m(v, J)$ values for $m = -2, 1$, and 2 which were reported for all bound and quasibound levels of ground state H_2 , HD , and D_2 (Le Roy 1971). For these species, increasing J from $J = 0$ to $J_D(v)$ led to changes in $\partial \bar{R}_m(v, J) / \partial [J(J+1)]$ of only 10–20%. Relative to the changes in these derivatives with increasing v , such discrepancies are negligible.

The second question considered is whether the use of some other type of average R would yield significantly different centrifugal shift rates. For a given level, it is clear that $\bar{R}_m(v, J)$ in-

⁶The present calculations on the $B(^3\Pi_{0u^+})-X(^1\Sigma_g^+)$ band system of I_2 were performed using the same potentials and numerical methods employed by Brown *et al.* (1973).

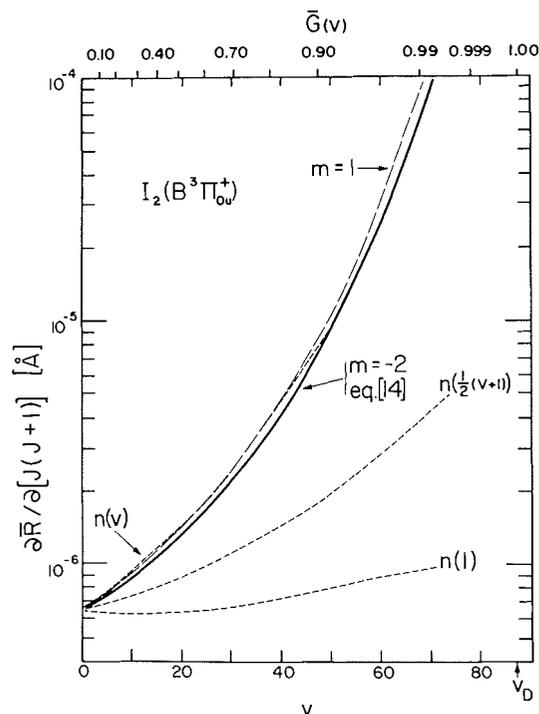


FIG. 6. Centrifugal displacement rates (note logarithmic scale) at $J = 0$ for levels of B state I_2 , based on different definitions of the characteristic distance $\bar{R}(v)$; curves $n(k)$ correspond to $\bar{R}(v)$ being the position of the k th node of the radial wave function, while $m = +1$ and -2 denote definitions based on [11]. $\bar{G}(v)$ is the vibrational energy scaled by the well depth.

creases monotonically with m . While this growth is also reflected in the corresponding derivatives, its magnitude is heavily damped. For example, for ground state H_2 the ratio $[\bar{R}_2(v, 0) / \bar{R}_{-2}(v, 0)]$ increases from 1.03 for the lowest vibrational level to 1.45 for the highest, while the ratio of the corresponding derivatives with respect to $J(J+1)$ increases from 1.00 to only 1.09 (Le Roy 1971). This 9% difference is virtually negligible when compared to the factor of 30 increase in the displacement rates over the same interval.⁷ Similarly, the near coincidence of the solid ($m = -2$) and long dash ($m = 1$) curves in Fig. 6 provides further evidence that

⁷This factor of 30 increase in the centrifugal displacement rate between the first and last vibrational levels is anomalously small compared to the situation for other diatomics. It reflects both the relative weakness of the long range dispersion forces for H_2 and the fact that the low density of levels results in a lack of vibrational levels lying very close to the dissociation limit.

the centrifugal displacement rates of the \bar{R}_m values defined by [11] are quite similar for any reasonable choice of m , particularly when compared on a scale which illustrates their strong dependence on v .

While different characteristic distances defined by [11] all have virtually the same centrifugal displacement rate, the rates associated with other definitions of the characteristic R may be drastically different. In particular, if node or extremum positions are used to characterize this position, the corresponding displacement rates may be both very different from those discussed above and very sensitive to which node or extremum is being considered. This fact is illustrated in Fig. 6 where the short dash curves labelled $n(k)$ represent the centrifugal displacement rates of the k th node of the particular vibrational wave function.⁶ While the outermost node (corresponding to $k = v$) shifts at virtually the same rate as the various \bar{R}_m values, the middle [$k = (1/2)(v + 1)$] and innermost ($k = 1$) nodes are displaced more slowly, particularly for the higher vibrational levels. On the other hand, for the high vibrational levels, for which the nodal displacement rate changes most drastically with k , the amplitude of the radial wave function is very small except in the neighborhood of the outer turning point. As a result, this 'large amplitude' part of the wave function will tend to provide the dominant contribution to the

FCA values whenever there is a sufficiently broad region of wave function overlap.

B. Inner Turning Point Approach

The derivatives appearing in [10] refer to the centrifugal displacement rates of the wave functions in their region of 'significant overlap'. Thus, use of [14] is justified in all cases where the overlap integral depends significantly on the outer part of the wave function. Furthermore, for the lower vibrational levels of a given state, the displacement rates of the different parts of the wave function are fairly similar both to [14] and to each other. However, Fig. 6 clearly shows that when an overlap integral for a high vibrational level involves only the innermost part of its wave function, use of [14] is quite inappropriate. A centrifugal displacement rate better suited to this situation must therefore be devised.

If curves representing the centrifugal displacement rates of the inner and outer classical turning points were added to Fig. 6, they would be virtually superimposed on the $n(1)$ and $n(v)$ curves respectively. Thus, it appears reasonable to use the inner turning point displacement rate to approximate the centrifugal shift rate of the innermost part of the wave function. For a given vibration-rotation level, the inner turning point $R_v^-(J)$ on the effective potential [3] is defined as the solution of the equation:

$$V(R_v^-(J)) + (\hbar^2/2\mu) J(J+1)/(R_v^-(J))^2 = G(v,0) + B_v[J(J+1)] - D_v[J(J+1)]^2 + \dots$$

Differentiating this expression with respect to $J(J+1)$ and setting $J = 0$ then yields:

$$[15] \quad \partial R_v^-(0)/\partial [J(J+1)] = (B_v - \hbar^2/2\mu [R_v^-(0)]^2)/(dV/dR)_{R=R_v^-(0)}$$

The inner turning points of the rotationless potential, $R_v^-(0)$, and hence the potential derivatives there, are readily calculated from experimental vibrational energies and B_v values. Hence, [15] is virtually as simple as the 'average R ' derivative expression, [14].

As with [14], it is desirable to ask how well the derivative at $J = 0$, given by [15], represents the centrifugal displacement of $R_v^-(J)$ for all J . For the $B(3^3\Pi_{0u}^+)$ state of I_2 ,⁶ this question is examined in Fig. 7; the solid curves seen there represent the exact $R_v^-(J)$ values, while the dashed lines are the tangents at $J = 0$ defined by [15]. These results show that this derivative at $J = 0$ provides a highly satisfactory estimate of the centrifugal displacement of $R_v^-(J)$ for virtually any J .

IV. De Broglie Wavelength Associated with a Vibrational Eigenfunction

According to the WKB approximation, a vibrational wave function in the classically allowed region between the turning points is given by (see *e.g.*, Merzbacher (1961)):

$$\Psi_{v,0}(R) = [k(R)]^{-1/2} \sin \left(\int_{R_v^-(0)}^R k(x) dx + \delta \right)$$

where $k(x) = \{2\mu[G(v,0) - V(x)]/\hbar^2\}^{1/2}$. The local de Broglie wavelength at any point, $\lambda(R)$, is

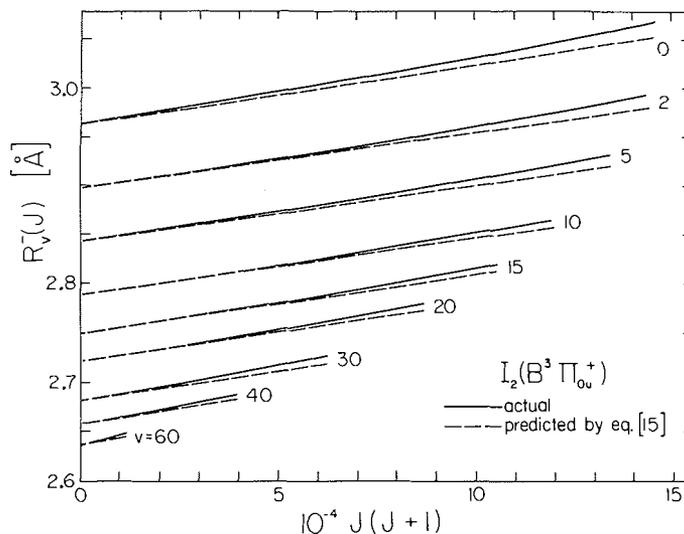


FIG. 7. Comparisons of the actual centrifugal displacements of inner turning points $R_v^-(J)$ for levels of B state I_2 (solid curves), with the shifts predicted by [15] (dashed lines).

therefore defined in terms of the value of the kinetic energy at that point:

$$\lambda(R) = h/(2\mu[G(v,0) - V(R)])^{1/2}$$

Thus, it seems reasonable to define the average wavelength associated with a given vibrational eigenfunction in terms of the expectation value of the kinetic energy for that state. This definition is convenient because this expectation value is known to be related to the vibrational level spacings (Stwalley 1973) by the expression

$$[16] \quad \langle v,0|[G(v,0) - V(R)]|v,0\rangle = (1/2) \partial G(v,0)/\partial \ln(v + (1/2))$$

The characteristic wavelength associated with any given vibrational wave function may therefore be expressed directly in terms of experimentally observed level spacings

$$[17] \quad \lambda_v(\bar{T}_v) = h/(\mu \partial G(v,0)/\partial \ln(v + (1/2)))^{1/2} \simeq h/((1/2) \mu(v + (1/2))[G(v+1,0) - G(v-1,0)])^{1/2}$$

The characteristic behavior of $\lambda_v(\bar{T}_v)$ is illustrated by the solid curve in Fig. 8. It approaches infinity at the dissociation limit because the localization of the wave function's probability amplitude near the outer turning point makes the average kinetic energy go to zero in this limit. In particular, Stwalley (1973) showed that for vibrational levels approaching the dissociation limit, the expectation value of the kinetic energy approaches zero as $(v_D - v)^{(n+2)/(n-2)}$,⁸ where for B state I_2 , $n = 5$.

In the present context, use of [17] is circumscribed by essentially the same conditions associated with [14] since both are based on a

⁸Here, v_D is the effective vibrational quantum number at the dissociation limit, while n is the inverse power of the asymptotically dominant term in the long range intermolecular potential for the state in question (Le Roy and Bernstein 1970; Le Roy 1973).

complete average of a property of the given state. However, if the region of overlap involves only the inner part of the wave function, say that lying between the inner turning point $R_v^-(0)$ and the potential minimum R_e , [17] becomes increasingly inappropriate for highly excited levels. In this interval, a more reasonable average kinetic energy is the harmonic oscillator value, $\langle v|[G(v,0) - V(R)]|v\rangle_{HO} = (1/2)G(v,0)$. The wavelength associated with this approximation is therefore given by

$$[18] \quad \lambda_v(HO) = h/(\mu G(v,0))^{1/2}$$

This expression gives rise to the dashed curve in Fig. 8. Since the λ_v estimates associated with [17] and [18] are both readily obtained from the experimental level energies, questions of convenience do not influence the choice of which should be used in any given case.

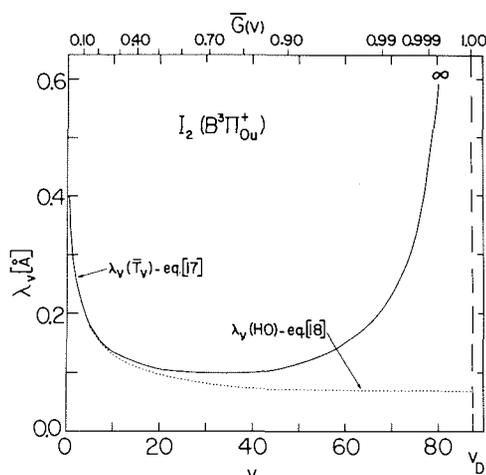


FIG. 8. Comparison between $\lambda_v(\bar{v})$ and $\lambda_v(\text{HO})$ for levels of B state I_2 , with $\bar{G}(v)$ as in Fig. 6.

V. Results and Applications

A. Summary of the Method

The preceding discussion implies that for any given vibrational band (v', v''), the period of the oscillations in the FCA caused by changes in $J(J+1)$ is given approximately by [10], where $\partial \bar{R}(v)/\partial [J(J+1)]$ is the centrifugal displacement rate of the wave function for level v and $\bar{\lambda}(v', v'')$ is a wavelength characteristic of the two overlapping eigenfunctions. The decision about whether $\bar{\lambda}(v', v'')$ should be represented by [8] or by [9] depends on whether or not the ratio of the two characteristic wavelengths is significantly different from unity. Consideration of Figs. 3 and 4 suggests that a wavelength ratio of 3 (or 1/3) would be an appropriate place to switch from one approximation to the other. This gives rise to the 'rule' in Table 1.

In general, the wavelength and centrifugal displacement rate associated with a given level can be represented by either the fully averaged 'expectation value' estimates of [14] and [17] or by the 'inner region' estimates given by [15] and [18]. These two possibilities are hereafter de-

TABLE 1. Rule governing the determination of $\bar{\lambda}(v', v'')$ from the de Broglie wavelengths of a pair of overlapping vibrational wave functions

Condition	Approach
$\max\{\lambda_{v'}, \lambda_{v''}\} / \min\{\lambda_{v'}, \lambda_{v''}\} < 3$	use [8]
$\max\{\lambda_{v'}, \lambda_{v''}\} / \min\{\lambda_{v'}, \lambda_{v''}\} \geq 3$	use [9]

noted 'EV(v)' and 'IR(v)' respectively (see Table 2). The approximations associated with their derivation imply that the EV(v) estimates should be used whenever the region of overlap includes the outer part of the wave function under consideration. Similarly, the IR(v) estimates are most appropriate when the overlap integral utilizes only the innermost part of the wave function in question. Consideration of the nature of wave function overlap (see Figs. 1 and 2) shows that for any vibrational band, the EV(v) estimates should always be used for the level (say v'') which has the smaller outer turning point, $R_{v''}^+$. For the other state, level v' , the choice between the EV(v') and IR(v') estimates depends on the precise definition of the 'outer' and 'innermost' parts of a wave function.⁹

The region between the potential minimum and the inner turning point is certainly a reasonable definition of the 'innermost' part of a radial wave function. Thus, condition (iii) in Table 2 provides an appropriate definition of the situations in which $\Delta[J(J+1)]$ should be calculated in the 'IR(v') and EV(v'')' approximation. Similarly, requiring that $R_{-2}(v'')$ be larger than the equilibrium distance of the potential curve with which level v' is associated seems a reasonable way of ensuring that the region of significant wave function overlap includes the 'outer' part of the v' wave function. This corresponds to condition (i) in Table 2. Unfortunately, for the intermediate situation described by condition (ii) in Table 2, neither of these limiting approximations is really appropriate. However, for reasons discussed later, it turns out to be safest to use the EV(v') and EV(v'') approximation in this intermediate case.

The rules summarized in Tables 1 and 2 describe how [10] should be used for predicting the oscillation period of the FCA for a given vibrational band. Since the actual absorption or emission intensity varies as the square of the FCA, a change of $J(J+1)$ by 1/4 of this period would be sufficient to shift the intensity from a maximum down to zero. Therefore, unless the range of $J(J+1)$ involved in the problem under consideration is *much less* than $(1/4)\Delta[J(J+1)]$, vibration-rotation interaction will significantly affect the observed transition intensities.

⁹The two vibrational levels associated with a given band (v', v'') are assumed to be labelled such that level v'' is the one with the smaller outer turning point ($R_{v''}^+ < R_{v'}^+$).

TABLE 2. Rules governing the choice of wavelengths and centrifugal displacement lengths to be used in [8]–[10]. R_e' is the equilibrium distance of the potential curve with which level v' is associated (see footnote 9)

Condition	Approach
(i) $R_e' \lesssim \bar{R}_{-2}(v'') < R_{v'',+} < R_{v',+}$	EV(v') and EV(v'') . . . use [14] and [17] for both levels
(ii) $\bar{R}_{-2}(v'') < R_e' < R_{v'',+} < R_{v',+}$	EV(v') and EV(v'') . . . use [14] and [17] for both levels
(iii) $\bar{R}_{-2}(v'') < R_{v'',+} \lesssim R_e' < R_{v',+}$	IR(v') and EV(v'') . . . $\left\{ \begin{array}{l} \text{use [15] and [18] for level } v' \\ \text{use [14] and [17] for level } v'' \end{array} \right.$

TABLE 3. For $A(v'')-X(v' = 0)$ bands of Mg_2 , comparison of fitted values of the FCA oscillation period, $\Delta[J(J+1)]$, with various predictions generated from [10], all quantities being multiplied by 10^{-3} . Preferred predictions (as per Tables 1 and 2) are presented in italic type

$v''-v'$	Δ_f fitted	$\bar{\lambda}(v',v'')$ from [9]		$\bar{\lambda}(v',v'')$ from [8]	
		EV(v') and EV(v'')	IR(v') and EV(v'')	EV(v') and EV(v'')	IR(v') and EV(v'')
10-0	46.3(± 5.5)	48.3	70.4	27.0	39.4
12-0	32.6(± 0.3)	48.5	70.8	27.0	39.4
14-0	28.7(± 1.0)	48.8	71.4	26.9	39.4
16-0	28.4(± 1.9)	49.0	72.0	26.9	39.6
18-0	31.9(± 4.0)	49.3	72.5	27.0	39.7
20-0	47.7(± 17.5)	49.6	73.2	27.1	40.0

B. Application to the $A(^1\Sigma_u^+) - X(^1\Sigma_g^+)$ Band System of Mg_2

For transitions between X state level $v' = 0$ and levels $v'' = 10, 12, 14, 16, 18$, and 20 of the A state of Mg_2 ,⁹ Balfour and Whitlock (1972) calculated FCA values at several different J 's using exact numerical wave functions calculated from RKR potential curves. Using standard non-linear least squares fitting techniques, their results were fitted to the expression

$$[19] \quad \text{FCA}(v', J; v'', J) = A \sin(2\pi J(J+1)/\Delta_f + \delta)$$

to yield values of the actual amplitude, period, and phase for these bands. The fitted oscillation periods obtained in this way (Δ_f in [19]) are presented in Table 3 where they are compared with various predictions based on [10].

For both the $A(^1\Sigma_u^+)$ and $X(^1\Sigma_g^+)$ states of Mg_2 , the vibrational spacings, turning points, and B_v values required for predicting $\Delta[J(J+1)]$ are given by Balfour and Whitlock (1972). While these authors did not report values of the centrifugal distortion constant D_v , these quantities were readily calculated from their potential curves using the method of Barwell (1975). The values of $\max\{\lambda_{v'}, \lambda_{v''}\} / \min\{\lambda_{v'}, \lambda_{v''}\}$ for all of the Mg_2 bands considered here lie between 8.3 and 10.9; thus, the corres-

ponding $\bar{\lambda}(v', v'')$ values should be obtained from [9]. Moreover, comparison of the $\bar{R}_{-2}(v'')$ and $R_{v'',+}$ values for the A state levels with the X state equilibrium distance of $R_e = 3.89 \text{ \AA}$ shows that while the $(v' - v) = (10 - 0)$ band corresponds (barely) to case (iii) in Table 2, all of the other bands correspond to the intermediate case (ii) situation.

In Table 3, the 'preferred' predictions associated with the rules in Tables 1 and 2 are printed in italic type. The fact that the predictions in the last column of this table are often more accurate than the preferred predictions is believed to be an accident and is probably associated with the fact that the present techniques are least reliable for bands corresponding to Table 2's condition (ii). In any case, in view of the approximations associated with the present method, the agreement of these two sets of predictions with each other and with the fitted oscillation periods is really quite good.

C. Application to the $B(^3\Pi_{0u}^+) - X(^1\Sigma_g^+)$ Band System of I_2

Using exact numerical wave functions computed from RKR potential curves, Brown (1973) calculated values of the FCA at several J 's for a number of bands in the $B(v') - X(v'')$ system of I_2 .⁹ The oscillation periods determined from fits of his results to [19] are presen-

TABLE 4. For $B(v')-X(v'')$ bands of I_2 , comparison of fitted values of $\Delta[J(J+1)]$ (middle entry for each band) with $EV(v')$ and $EV(v'')$ (upper entry, in parentheses) and $IR(v')$ and $EV(v'')$ predictions (lower entry, in brackets) generated from [10], all quantities multiplied by 10^{-3} . Preferred predictions (as per Tables 1 and 2) are printed in italic type

$v' \backslash v''$	5	10	15	20	25	30
5	(388) 2041 <i>[704]</i>	(363) ^a <i>[690]</i>	(368) ^a <i>[748]</i>	(389) 392 <i>[885]</i>	(430) 445 <i>[1186]</i>	(506) 410 <i>[2158]</i>
10	(249) 816 <i>[579]</i>	(225) 549 <i>[553]</i>	(220) 368 <i>[588]</i>	(226) 358 <i>[684]</i>	(239) 316 <i>[894]</i>	(263) 352 <i>[1529]</i>
15	(172) 494 <i>[498]</i>	(152) ^a <i>[466]</i>	(152) 311 <i>[488]</i>	(146) 270 <i>[554]</i>	(150) ^a <i>[698]</i>	(158) 272 <i>[1089]</i>
20	(122) 422 <i>[446]</i>	(106) 294 <i>[410]</i>	(100) 245 <i>[424]</i>	(98) 219 <i>[472]</i>	(100) 202 <i>[578]</i>	(102) 191 <i>[846]</i>
25	(87) 303 <i>[414]</i>	(76) 233 <i>[378]</i>	(70) 199 <i>[387]</i>	(68) 178 <i>[427]</i>	(68) 165 <i>[515]</i>	(69) 158 <i>[728]</i>

^aFits to calculated FCA's not reliable for this case, see text.

ted in Table 4 as the *middle* entry for each case. The four bands for which these 'true' oscillation periods are not given, $(v', v'') = (5, 10)$, $(5, 15)$, $(15, 10)$, and $(15, 25)$, are cases for which the fits either did not converge or yielded statistical uncertainties in the resulting oscillation periods of $\geq 100\%$.¹⁰ The reliability of the fitted periods for the other 26 bands is attested to by the fact that their statistical uncertainties were all less than ca. 10%.

The $B(^3\Pi_{ou}^+)$ state rotational constants, vibrational spacings, and turning points required for making predictions using [10] were taken from Brown *et al.* (1973). The analogous turning points, vibrational spacings, and B_v values for the ground state levels (denoted⁹ v'') are those of Le Roy (1970). However, since his empirical D_v values have been shown to be unreliable (Tellinghuisen 1973; Kirschner and Watson 1973; Wei and Tellinghuisen 1974), the required values of this quantity were calculated using the method of Brown *et al.* (1973).

For the bands considered in Table 4, the ratio $\max\{\lambda_{v'}, \lambda_{v''}\} / \min\{\lambda_{v'}, \lambda_{v''}\}$ is always less than 3, so all of the predictions considered here used [8] to generate $\bar{\lambda}(v', v'')$. Moreover, the criteria in

¹⁰These difficulties merely reflect the very high correlation between the different parameters in [19] which arose during the fits to the 4 or 5 calculated FCA's for each of these cases.

Table 2 imply that predictions for bands involving $v'' \leq 15$ should utilize the $IR(v')$ and $EV(v'')$ approximation, while for $v'' > 15$, the $EV(v')$ and $EV(v'')$ estimates should be used. Predictions for both these approaches are given in Table 4; the lower entry for each band corresponds to the former and the upper entry to the latter. The 'preferred' (as in Table 2) prediction for each case is printed in italic type. Their generally reasonable agreement with the actual (fitted) oscillation periods attests to the utility of the present approach.

D. Discussion

A difficulty with [10] is the fact that there may be situations in which the two centrifugal displacement rates appearing in its denominator are equal. This is relatively unlikely to occur in the $EV(v')$ and $EV(v'')$ approximation since the level with the larger outer turning point will also tend to have the larger centrifugal displacement rate predicted by [14]. On the other hand, it is almost certain to occur if the $IR(v')$ and $EB(v'')$ approximation is used for a wide range of v'' levels. For low v'' ,⁹ the $EV(v'')$ displacement rate should be smaller than the $IR(v')$ value since the outer part of the v'' wave function just overlaps the innermost part of that for level v' . However, as v'' increases, the $EV(v'')$ displacement rate of [14] grows rapidly,

approaching ∞ at the dissociation limit (see below). Thus, it must cross the relatively constant $IR(v')$ displacement rates of the other potential curve, yielding a (near) singularity in [10]. It is the onset of this behavior which is responsible for the increasing error in the $IR(v')$ and $EV(v'')$ predictions in Table 4 (lower entries, in brackets) for high v'' ; there, the near singularity would occur at $v'' \simeq 40$.

The preceding discussion makes it clear that the $IR(v')$ and $EV(v'')$ approximation should only be used when absolutely essential. This is the reason that it is not recommended for use in the intermediate case (ii) of Table 2, in spite of the fact that the $EV(v')$ and $EV(v'')$ approximation is not likely to be particularly accurate there either.

VI. Concluding Remarks

In view of the gross simplifications associated with the present method, the accuracy of the 'preferred' predictions (in italics) in Tables 3 and 4 is rather good. The oscillation periods involved differ by more than an order of magnitude, while the errors are usually less than a factor of 2 and often much less than that. Moreover, since most of the Mg_2 bands and half of those for I_2 fall into the intermediate case (ii) of Table 2, these systems provide a rather harsh test of the present techniques. Thus, the agreement which is found attests to the semiquantitative reliability of the present procedure for predicting the oscillation period of an FCA.

In general, bands described by condition (i) in Table 2 should be most suited for application of the present techniques (*none* of the Mg_2 or I_2 bands considered above fall into this category). Transitions between vibrational levels of a single potential curve fall into this category. More generally, the fact that the region of overlap includes the large amplitude outer parts of both wave functions means that vibronic bands of this type will be relatively intense, and hence will be the more prominent features of the spectrum. The $EV(v')$ and $EV(v'')$ approximation appropriate here is also the most easily used, since it requires knowledge only of experimentally observable vibrational spacings and rotational constants, and not of derived quantities such as turning points and their derivatives.

An important qualitative result associated with the centrifugal displacement rate of [14] is the fact that vibration-rotation interaction most

strongly affects the intensities of transitions involving highly excited vibrational levels. This occurs because the B_v in its denominator decreases and the D_v in its numerator increases with increasing v . Indeed, for levels approaching the dissociation limit, the characteristic near dissociation behavior of the rotational constants (Le Roy 1972, 1973; Barwell 1975) causes this displacement rate to approach infinity as $(v_D - v)^{-2(n-1)/(n-2)}$.⁸ This behavior overcomes the singularity in $\lambda_v(\bar{T}_v)$ arising from the analogous near dissociation behavior of the expectation value of the kinetic energy, so that the ensuing predicted oscillation period will approach zero for a vibrational level at dissociation. Of course, Franck-Condon overlap considerations will tend to prevent this limiting behavior from appearing in real cases. However, the trend toward shorter oscillation periods, $\Delta[J(J+1)]$, with increasing vibrational excitation should be generally valid.

If the absorbing or emitting vibrational level is in thermal equilibrium, the characteristic width of its rotational population distribution may be approximately represented by twice the J value of the most populated rotational level. This means that the quantity to be compared with the predicted $(1/4)\Delta[J(J+1)]$ is:

$$\delta[J(J+1)]_T \simeq 2kT/B_v$$

where B_v refers to the initial state, k is Boltzmann's constant, and T is the temperature. This result tends to further exaggerate the relative importance of vibration-rotation interaction for highly excited vibrational levels since the decrease of B_v with increasing v will tend to populate a wider range of J values.

While the present method is only semiquantitative, it does provide a simple picture of the essential nature of vibration-rotation interaction in diatomic transition intensities. It also provides a unifying generalization of previously suggested criteria for ascertaining when such interaction is expected to be important. In view of the extensive use of relative transition intensities for determining the temperature in many astrophysical and kinetics applications, the present techniques should prove fairly useful.

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- ALBRITTON, D. L., HARROP, W. J., SCHMELTEKOPF, A. L., and ZARE, R. N. 1973. *J. Mol. Spectrosc.* **46**, 25.
- BALFOUR, W. J. and WHITLOCK, R. F. 1972. *Can. J. Phys.* **50**, 1648.
- BARWELL, M. G. 1975. M.Sc. Thesis, University of Waterloo, Waterloo, Ontario.
- BROWN, J. D. 1973. Ph.D. Thesis, University of Toronto, Toronto, Ontario.
- BROWN, J. D., BURNS, G., and LE ROY, R. J. 1973. *Can. J. Phys.* **51**, 1664.
- CASHION, J. K. 1964. *J. Chem. Phys.* **41**, 3988.
- CHAKRABORTY, B. and PAN, Y. K. 1972. *J. Chem. Phys.* **56**, 3722.
- CHAKRABORTY, B., PAN, Y. K., and CHANG, T. Y. 1971. *J. Chem. Phys.* **55**, 5147.
- FINK, E. H., AKINS, D. L., and MOORE, C. B. 1969. *Chem. Phys. Lett.* **4**, 283.
- GENEROSA, J. I. and HARRIS, R. A. 1970. *J. Chem. Phys.* **53**, 3147.
- HALMANN, M. and LAULICHT, I. 1968. *J. Quant. Spectrosc. Radiat. Transfer*, **8**, 935.
- HAYCOCK, S. A. 1963. M.Sc. Thesis, University of Western Ontario, London, Ontario.
- HERMAN, R. M., TIPPING, R. H., and SHORT, S. 1970. *J. Chem. Phys.* **53**, 595.
- HERZBERG, G. 1950. *Spectra of diatomic molecules* (D. Van Nostrand Co., Princeton, N.J.).
- HÖNL, H. and LONDON, F. 1925. *Z. Phys.* **33**, 803.
- HOUGEN, J. T. 1970. N.B.S. Monograph 115 (U.S. Government Printing Office, Washington, D.C.).
- HUBISZ, J. L., JR. 1968. Ph.D. Thesis, York University, Toronto, Ontario.
- JAMES, T. C. 1960. *J. Chem. Phys.* **32**, 1770.
- KIRSCHNER, S. M. and WATSON, J. K. G. 1973. *J. Mol. Spectrosc.* **47**, 234.
- KOVÁCS, I. 1969. *Rotational structure in the spectrum of diatomic molecules* (Adam Hilger Ltd., London).
- LEARNER, R. C. M. 1962. *Proc. R. Soc. (Lond.) A*, **269**, 311, 327.
- LEARNER, R. C. M. and GAYDON, A. G. 1959. *Nature*, **183**, 242.
- LE ROY, R. J. 1970. *J. Chem. Phys.* **52**, 2683.
- 1971. *J. Chem. Phys.* **54**, 5433.
- 1972. *Can. J. Phys.* **50**, 953.
- 1973. *In* *Molecular spectroscopy 1* (Specialist periodical report of the Chemical Society of London), ed. by R. F. Barrow, D. A. Long, and D. J. Millen, Chap. 3, p. 113.
- LE ROY, R. J. and BERNSTEIN, R. B. 1970. *J. Chem. Phys.* **52**, 3869.
- MERZBACHER, E. 1961. *Quantum mechanics* (John Wiley and Sons, Inc., New York).
- STWALLEY, W. C. 1973. *J. Chem. Phys.* **58**, 3867.
- TELLINGHUISEN, J. 1973. *Chem. Phys. Lett.* **18**, 544.
- TIPPING, R. H. 1973. *J. Chem. Phys.* **59**, 6443.
- TIPPING, R. H. and FORBES, A. 1971. *J. Mol. Spectrosc.* **39**, 65.
- TIPPING, R. H. and HERMAN, R. M. 1970. *J. Mol. Spectrosc.* **36**, 404.
- VILLAREJO, D. 1968. *J. Chem. Phys.* **49**, 2523.
- VILLAREJO, D., STOCKBAUER, R., and INGRAM, M. G. 1969. *J. Chem. Phys.* **50**, 1754.
- WEI, J. and TELLINGHUISEN, J. 1974. *J. Mol. Spectrosc.* **50**, 317.
- WHITING, E. E. and NICHOLLS, R. W. 1974. *Astrophys. J. Suppl. Ser.* **27**, 1.
- ZARE, R. N. 1964. *J. Chem. Phys.* **40**, 1934.