1968

Electronic transitions in diatomic molecules

James O. Hornkohl

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ELECTRONIC TRANSITIONS IN
DIATOMIC MOLECULES*

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JAMES O. HORNKOHL, 1939

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(advisor) B. Ken Robertson
ELECTRONIC TRANSITIONS IN
DIATOMIC MOLECULES*

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ABSTRACT

The electronic transition moments of many band systems have been found to be linear functions of the internuclear distance. However, some band systems exhibit a quadratic variation of the transition moment. In these quadratic cases, the plots from which the variation of the transition moment is determined are based upon the approximation of the second r-centroid by the square of the first r-centroid. The square of the first r-centroid does closely approximate the second r-centroid but a simple error analysis shows that the small difference between the two is not a quantitative measure of the error introduced into the transition moment when the exact equality of the two is assumed. For the first positive bands of $N_2$ and the first negative bands of $N_2^+$, the error in the transition moment is about an order of magnitude larger than the error in the second r-centroid.
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INTRODUCTION

The use of the Franck-Condon factors and r-centroids in the interpretation of intensities resulting from electronic transitions in diatomic molecules has been investigated by many. In several of the band systems studied, the electronic transition moment, $R_e(r)$, has been found to be a linear function of $r$, the internuclear distance (e.g., 1-6). However, other band systems exhibit quadratic variations of $R_e(r)$ with $r$ (e.g., 1,7-10). The form of these electronic transition moments has been determined from plots of

$$\left[ \frac{I(n',v',m''v'' \bar{\lambda}(n,m)^4}{q(v',v'')N(n'v')} \right]^{1/2}$$

versus $\bar{r_1}(v',v'')$, the first r-centroid, where $I(n',v',m''v'')$ is the measured relative band intensity, $\bar{\lambda}(n,m)$ the average wavelength of the rotational lines observed in the band, $q(v',v'')$ is the Franck-Condon factor, and $N(n'v')$ is the population of the excited level. Because the square of the first r-centroid closely approximates the second r-centroid, $\bar{r_2}(v',v'')$, it has been thought that only a negligible error in a non-linear $R_e(r)$ results when its form is determined from such plots. The content of the present paper is a simple error analysis which demonstrates that this is not the case. Using the first positive system of $N_2$ and the first negative system of $N_2^+$ as examples, it is shown that the error is about an order of magnitude larger than $\bar{r_1}(v',v'')^2 - \bar{r_2}(v',v'')$.

A brief review of the equations required in the interpretation technique precedes the discussion of errors in a quadratic $R_e(r)$. 

1
In the Born-Oppenheimer approximation \( (11) \) the electrons adiabatically follow the nuclei with the result being that the total diatomic eigenfunction separates into electronic and nuclear eigenfunctions where the electronic eigenfunction is a parametric function of the internuclear distance. In the absence of a significant vibration-rotation interaction, the nuclear eigenfunction further separates into vibrational and rotational eigenfunctions but the electronic eigenfunction remains a parametric function of \( r \).

Let \( i \) designate an upper state where \( i \) represents the collection \( i', v', J', \Lambda', \) and \( M' \) where in turn \( i' \) represents the upper state electronic quantum numbers and the other symbols have their usual meanings as given, for example, in Herzberg \( (12) \). Letting \( j \) similarly designate a lower state, one may write for the transition moment of a transition from one vibrationally and rotationally perturbed electronic configuration to another

\[
M(i,j) = \langle i'v'J'\Lambda'M' | \mathbf{r}_e | j''v''J''\Lambda''M'' \rangle
\]

(1)

where \( \mathbf{r}_e \) is the position of the eth electron in a fixed system of axes whose origin rests at the center of mass. The molecular rotations are described by the three Euler rotations \( (\alpha, \beta, \gamma) \) of the fixed axes to a system of axes (primed coordinates) attached to the molecule such that the \( z' \)-axis lies along the internuclear axis. If the molecule were at a fixed \( \alpha, \beta, \) and \( \gamma \) orientation with respect to the space axes,
orthogonal transformations of internal molecular coordinates from one set of axes to the other could be accomplished using the Euler matrix, $D(\alpha \beta \gamma)$. However, in the adiabatic approximation, the rotations are much slower than the vibrational or electronic motion and the non-inertial nature of the two coordinate system may be ignored in the calculation of the electronic transition moment. The resulting simplification is that the transformation $\mathbf{r}'_e = D(\alpha \beta \gamma) \mathbf{r}_e$ leaves the rotational contribution in Eq. (1) separable.

$$M(i,j) = \left< \mathbf{J}'\Lambda'\mathbf{M}' \mid D(\alpha \beta \gamma) \mid \mathbf{J}''\Lambda''\mathbf{M}'' \right> \left< i'v' \mid \mathbf{r}'_e \mid j''v'' \right>$$

the absolute square of the rotational term is summed over $M'$ and $M''$ giving the rotational strength factor or Hönli-London factor, $S(J'\Lambda',J''\Lambda')$, whose evaluation will not be considered here. The vibrational strength factor or band strength, $S(n'v',m''v'')$, is the sum over electronic degeneracies of the absolute square of the electronic-vibrational term where $n'$ and $m''$ are the electronic quantum numbers remaining after summation. That is, the transition strength is the product of two strength factors.

$$S(n,m) = S(n'v',m''v'') S(J'\Lambda',J''\Lambda')$$

Symmetric top eigenfunctions are good approximations for the rotational eigenfunctions and the $S(J'\Lambda',J''\Lambda')$ can be directly calculated (e.g., see Rubin (13). For values of $v'$ and $v''$ not too large, Morse eigenfunctions (14-16) are satisfactory approximations of the vibrational eigenfunctions. The empirical eigenfunctions resulting from numerical
solution of the vibrational Schrödinger equation in which the Rydberg-Klein-Rees potential is employed (1,2,17, and 18) are still better approximations. In short, the vibrational and rotational eigenfunctions can be considered known. This is not the usual circumstance for the electronic eigenfunctions although the simplest are known and progress is being made for the more complex diatomic molecules. For example, Cade, Sales, and Wahl (19) have made significant progress with certain states of N$_2$ and N$_2^+$. The interpretation technique being described here in an approximation which is used when $\langle i'v' | \hat{r}_e^i | j''v'' \rangle$ cannot be directly calculated. In this case, the electronic integrations are performed in principle.

$$\langle i'v' | \hat{r}_e^i | j''v'' \rangle = \langle v' | R_e(r) | v'' \rangle$$ \hspace{1cm} (4)

The result is a parametric function of $r$. The form of $R_e(r)$ is to be empirically determined and it is assumed that

$$R_e(r) = C_0 + C_1 r + C_2 r^2 \ldots$$ \hspace{1cm} (5)

Through relative intensity measurement the values of the constants $C_0$, $C_1$, $C_2$, ... are to be determined. $R_e(r)$ is called the electronic transition moment but, of course, $M(i,j)$ is the electronic transition moment and $R_e(r)$ only the most purely electronic part of $M(i,j)$.

Substitution of Eq. (5) into Eq. (4) gives

$$S(n'v',m''v'') = q(v',v'') [C_0 + C_1 r_1 (v',v'') + C_2 r_2 (v',v'') \ldots]^2$$ \hspace{1cm} (6)

in which the Franck-Condon factor is defined as the square of the
The equation which defines the Einstein probability, $A(n,m)$, in terms of the line strength is now written,

$$A(n,m) = \frac{64\pi^4 \nu(n,m)^3}{3hc g_n (2J' + 1)} S(n,m),$$

where $\nu(n,m)$ is the line frequency and $g_n$ is the electronic degeneracy ($g_n = 2S' + 1$ for $\Lambda' = 0$ and $2(2S' + 1)$ for $\Lambda' \neq 0$). The equation for spontaneous emission, $I(n,m) = h\nu(n,m) A(n,m) N(n)$, where $N(n)$ is the population of the excited level, becomes

$$I(n,m) = \frac{64\pi^4 \nu(n,m)^4}{3c g_n (2J' + 1)} S(n'\nu',m''\nu'') S(J'\Lambda',J''\Lambda'') N(n).$$

Equation (10) is now summed over all rotational lines in the $\nu'\nu''$-band in order to obtain the total band intensity. An average frequency, $\bar{\nu}(n,m)$, is defined for the rotational lines in the band and a Maxwellian distribution of the rotational levels in each excited vibrational level is assumed. The absence of a significant vibration-rotation interaction has already been assumed. Hence, the total term value can be written as the sum of electronic, $T_e$, vibrational, $G(v)$, and rotational, $F(J)$, term values and the Maxwell-Boltzmann factor separates into independent
electronic, vibrational, and rotational factors. Then use of the rotational sum rule

$$\sum_{J''} S(J' \Lambda', J'' \Lambda'') = 2J' + 1 \quad (11)$$

and summation of Eq. (10) over $J'$ and $J''$ gives the total band intensity.

$$I(n'v', m''v') = \frac{64\pi^4}{3c^4g_n^3} \frac{\nu(n,m)^4}{v(n',v'')} S(n'v', m''v') N(n') \quad (12)$$

Using Eq. (6), ignoring all unnecessary constants, and converting to the experimentally more convenient wavelength, one arrives at the equation which relates the measured intensity to the unknown constants $C_0$, $C_1$, ..., 

$$\left[ \frac{I(n'v', m''v')}{q(v',v'')} \frac{\tilde{\nu}(n,m)^4}{N(n'v')} \right]^{1/2} = C_0 + C_1 \tilde{r}_1(v',v'') + C_2 \tilde{r}_2(v',v'') \ldots \quad (13)$$

If some number $L$ of the constants in Eq. (13) are significant, their values can be determined from $L$ measured $I(n'v', m''v')$ and the solutions to $L$ simultaneous equations. The $N(n'v')$ are rarely known, and the process is restricted to bands with the same $v'$ (i.e., $v''$-progressions). In what is apparently the first use of the $r$-centroids, Turner and Nicholls (20) found (as noted in the companion paper by Fraser (21)) that experimental scatter in $I(n'v', m''v')$ produced very large scatter in the values of the constants when they were determined as the solutions of simultaneous equations. Therefore, Turner and Nicholls plotted the term on the left of Eq. (13) versus $\tilde{r}_1(v',v'')$ and then scaled the values of $N(n'v')$ until all $v''$-progressions best fitted a single curve. The resultant curve for the first positive system of $N_2$ was found to be non-linear but since $\tilde{r}_1(v',v'')^2$ closely approximates...
\( \bar{r}_2(v',v'') \), the error introduced into the constants \( C_0, C_1, \) and \( C_2 \) was considered negligible. As shown below, the small difference between \( \bar{r}_2(v',v'') \) and \( \bar{r}_1(v',v'')^2 \) is not a quantitative measure of the error resulting in \( R_e(r) \) when the curve is non-linear.

**ERROR IN A QUADRATIC \( R_e(r) \)**

In the manner described above, Wallace and Nicholls (7) found that for the first negative system of \( N_2^+ \)

\[
R_e(r) = \text{const.} \ (14.473 - 23.497r + 10.134r^2) \tag{14}
\]

for the following range of the first \( r \)-centroid.

\[0.974 \text{ \AA} < \langle \bar{r}_1(v',v'') \rangle < 1.265 \text{ \AA}\]

It is convenient to define \( \Delta \bar{r}_2(v',v'') = \bar{r}_1(v',v'')^2 - \bar{r}_2(v',v'') \), \( \bar{R} = \langle v' | v'' \rangle \ [C_0 + C_1 \bar{r}_1(v',v'') + C_2 \bar{r}_1(v',v'')^2] \), and \( \Delta R \) as the approximate error produced in \( \langle v' | R_e(r) | v'' \rangle \) when one incorrectly assumes that \( \Delta \bar{r}_2(v',v'') \) is negligibly small. Then

\[
\frac{\Delta R}{R} = \frac{C_2 \langle v' | v'' \rangle}{\bar{R}} \Delta \bar{r}_2(v',v''). \tag{15}
\]

The Franck-Condon factors and the first two \( r \)-centroids were calculated by numerical integration of Morse eigenfunctions in the manner described by Nicholls (16). Table 1 is the result of applying Eq. (15) to Eq. (14). It is seen that the error in \( \langle v' | R_e(r) | v'' \rangle \), which is also an estimate of the error in \( R_e(r) \), is approximately an order of magnitude larger than the difference between the second \( r \)-centroid and the square
Jain and Sahni (1) have recently reapplied the plotting procedure to the \text{N}_2 first positive data of Turner and Nicholls (20). Using RKR eigenfunctions, Jain and Sahni found

\[
R_e(r) = \text{const.} \left(1.0 - 1.2550r + 0.4063r^2\right),
\]

\[
1.16 \text{ A}^\circ < \bar{r}_1(v',v'') < 1.61 \text{ A}^\circ.
\]

At the suggestion of James (22) they calculated \(S(n',v',m''v'')\) by two different methods. In their method (i), they directly substituted the constants of Eq. (16) into Eq. (6). In their method (ii), they calculated \(S(n',v',m''v'') = \left\langle v' | R_e(r) | v'' \right\rangle^2\) by numerical integration. Their methods (i) and (ii) would be nothing but a computational check if \(\bar{r}_1(v',v'')^k = \bar{r}_k(v',v'')\) held. In the present study, the differences between methods (i) and (ii) were computed from the table given by Jain and Sahni (this could not be done precisely) and compared with the errors predicted by Eq. (15). The error in \(S(n',v',m''v'')\) is just twice the error in \(\left\langle v' | R_e(r) | v'' \right\rangle\). Because the present study employed Morse eigenfunctions and because of the inprecision with which the difference between methods (i) and (ii) could be taken from the table of Jain and Sahni, the comparison is not entirely successful but it is clear that approximately the same errors result regardless of the eigenfunctions used. In each instance the signs of the errors agree.

Method (ii) of Jain and Sahni and Eq. (15) would yield identical results if identical eigenfunctions were used. However, instead of using their method (ii) it would appear to be more to the point to simply...
calculate the second r-centroids while the Franck-Condon factors and
first r-centroids are being calculated. One can then attempt to replace
the plotting procedure with, for example, a least squares determination
of $R_e(x)$ in which the plot versus the first r-centroids is used only as
a starting point.
CONCLUSIONS

To reiterate, the values of the necessary constants were taken from the literature and the quantity $\langle v' | R_e(r) | v'' \rangle$ was calculated according to the much used approximation,

$$\langle v' | R_e(r) | v'' \rangle = \langle v' | v'' \rangle \left[ C_0 + C_1 \tilde{R}_1(v',v'') + C_2 \tilde{R}_2(v',v'') \right]$$  \hspace{1cm} (17)

Then the same values of the constants were used in the exact equation

$$\langle v' | R_e(r) | v'' \rangle = \langle v' | v'' \rangle \left[ C_0 + C_1 \tilde{R}_1(v',v'') + C_2 \tilde{R}_2(v',v'') \right]$$  \hspace{1cm} (18)

The result given by Eq. (18) was subtracted from that given by Eq. (17) and this difference was then divided by the result of Eq. (17). Equation (15) is a convenient way of expressing this procedure. The procedure can be fairly described as simple and obvious. It demonstrates that the approximate equation predicts values of $\langle v' | R_e(r) | v'' \rangle$ which differ significantly from those predicted by the exact equation. The error figures given in Tables 1 and 11 cannot be used as correction factor to be applied to values obtained from the approximate equation because the correct values of the constants are not known. Indeed, a conclusion of this paper is that the constants reported in the literature are in error.

Jain and Sahni made a correct test of Eq. (17) when they computed their (ii) band strengths for the first and second positive systems of $N_2$ \hspace{1cm} (1). In their earlies CO$^+$ comet-tail study \hspace{1cm} (8), they did not compute band strengths according to method (ii). Using the values of the constants they report, one finds that the error in $S(n',v',m''v'')$ is typically 120 times larger than the difference $\tilde{R}_1(v',v'')^2 - \tilde{R}_2(v',v'')$ simply
because $C_2$ is typically 60 times larger than $\bar{R}$. A method (ii) calculation for this band system would give band strengths which differ from the method (i) strengths given in Table 4 of Reference (8) by 50 percent or more for about 25 of the 63 bands listed in the table.

The work criticized has not been redone correctly because the writer has only Morse eigenfunctions available at the present time. However, a preliminary study has been done for the $N_2^+$ first negative system and a determination of the constants by the solution of simultaneous equations was found to work reasonably well. If, with a particular set of intensity data, one finds that no successful substitute for the plotting procedure can be found, one can only conclude that the data or the eigenfunctions are unacceptable.

The writer wishes to acknowledge Dr. R. A. Anderson, Dr. J. L. Rivers, and Dr. J. W. L. Lewis for their many helpful suggestions.
Errors introduced into the values of <v' | R(r) | v''> by the assumption that the square of the first r-centroid equals the second r-centroid: First Negative System of N₂⁺. Constants in R(r) taken from Wallace and Nicholls (7). Only observed bands (according to Tyte (23)) are listed.

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\[
a_q(v', v'') = \frac{v''}{v'}
\]

\[
b_{v''} = \frac{v'}{v''}
\]

\[
c_{v'} = \frac{v''}{v'} - 2 \frac{v''}{v'} = \frac{v''}{v'}
\]

\[
d_{v''} = \frac{v'}{v''} = \frac{v'}{v''}
\]
TABLE II

Errors introduced into $S(n', v', m'' v'')$ by the assumption that the second $r$-centroid is well approximated by the square of the first $r$-centroid: Comparison for the first positive system of $N_2$ between the work of Jain and Sahni (1) and the present work.

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\[ a = \text{method (ii)} - S(\text{method (i))} \]

\[ b = 2\Delta R/R \]
REFERENCES

17. W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, 


(1966).

p. 475.


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