

## Franck-Condon Factors for Electronic Band Systems of Molecular Nitrogen

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Franck-Condon factors have been calculated for five electronic band systems of  $N_2$ :  $C^3\Pi_u-B^3\Pi_g$ ,  $B^3\Pi_g-A^3\Sigma_u^+$ ,  $A^3\Sigma_u^+-X^1\Sigma_g^+$ ,  $a^1\Pi_g-X^1\Sigma_g^+$ , and  $C^3\Pi_u-X^1\Sigma_g^+$ . Rydberg-Klein-Rees potentials were constructed for these electronic states, and exact vibrational wave functions were obtained by direct numerical solution of the radial Schrödinger equation. Calculated relative band intensities are compared with experimental data. In addition, radiative lifetimes are calculated from absolute absorption data for two of these band systems. Various proposals concerning the variation of the electronic transition dipole moment  $R_c(\bar{r})$  with internuclear distance are discussed, and it is suggested that  $R_c(\bar{r})$  is likely to vary most for forbidden transitions.

### INTRODUCTION

In recent years much work has been devoted to the calculation of Franck-Condon factors for electronic band systems.<sup>1</sup> Many of these calculations have employed Morse curves to represent the potentials of the upper and lower electronic states. However, this procedure has been shown to be often unreliable, especially for high vibrational quantum numbers (2).

This paper reports the calculation of Franck-Condon factors for five electronic band systems of  $N_2$  using a previously described procedure (2) based upon Rydberg-Klein-Rees (RKR) potentials. These potentials are constructed from the observed vibrational and rotational term values, and have been shown in the case of  $I_2$  to reproduce the spectroscopic data within the experimental error. From these potentials the vibrational wave functions (and hence the Franck-Condon factors), are then obtained by numerically solving the radial Schrödinger equation.

We have chosen to study  $N_2$  not only because of its great astrophysical interest, but also because it is one of the few molecules for which very accurate spectroscopic term values for several electronic states are available. Following a

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<sup>1</sup> An extensive review is given by Nicholls and Stewart (1).

brief review of the numerical procedure, we shall present calculated arrays of Franck–Condon factors for the Second Positive ( $C\ ^3\Pi_u-B\ ^3\Pi_g$ ), First Positive ( $B\ ^3\Pi_g-A\ ^3\Sigma_u^+$ ), Vegard–Kaplan ( $A\ ^3\Sigma_u^+-X\ ^1\Sigma_g^+$ ), Lyman–Birge–Hopfield ( $a\ ^1\Pi_g-X\ ^1\Sigma_g^+$ ) and Tanaka ( $C\ ^3\Pi_u-X\ ^1\Sigma_g^+$ ) band systems and potential energy curves for the  $X$ ,  $A$ ,  $B$ ,  $C$ , and  $a$  states of  $N_2$ . A critical comparison of observed and calculated intensities is given and various proposals concerning the variation of the electronic transition moment with internuclear distance are discussed. It is pointed out that the evidence available for other systems as well as for  $N_2$  suggests that the variation is generally small for strong transitions and may be large for weakly allowed transitions. Finally the utility of accurate Franck–Condon factors is illustrated by calculating radiative lifetimes for some of the excited states of  $N_2$ .

#### NUMERICAL PROCEDURE

The Franck–Condon factor  $q_{v'v''}$  associated with the ( $v'$ ,  $v''$ ) band is defined by the square of the vibrational overlap integral

$$q_{v'v''} = \left[ \int \psi_{v'} \psi_{v''} dr \right]^2, \quad (1)$$

where  $\psi_{v'}$  and  $\psi_{v''}$  are the upper and lower state vibrational wave functions which satisfy the radial Schrödinger equation

$$(d^2\psi_v/dr^2) + [E_v - U(r)]\psi_v = 0 \quad (2)$$

for the potential  $U(r)$  with vibrational energy eigenvalue  $E_v$ . To a first approximation, the integrated band intensity (energy/sec) of the ( $v'$ ,  $v''$ ) transition in emission is related to the Franck–Condon factor  $q_{v',v''}$  by

$$I_{v'v''} = KN_{v'}\nu^4\bar{R}_e^2q_{v',v''}. \quad (3)$$

Here  $K$  is a constant involving units and geometry,  $N_{v'}$  is the population of the upper state,  $\nu$  is the frequency characteristic of the ( $v'$ ,  $v''$ ) band (usually taken as the band origin) and  $\bar{R}_e$  is the average electronic transition moment assumed to be a constant or a slowly varying function of the internuclear distance.

Among the terms in Eq. (3) which control the intensity distribution in an electronic band system, the Franck–Condon factor usually exerts the dominant influence. The vibrational overlap integral is an extremely sensitive function of the relative phase of the two oscillatory vibrational wave functions, and the Franck–Condon factor may vary irregularly, often by more than three orders of magnitude, from band to band.

#### POTENTIAL ENERGY CURVES

The accuracy of the vibrational wave functions used to compute the Franck–Condon factors depends critically upon the accuracy of the potentials employed.

In the Rydberg(3)–Klein(4)–Rees(5) procedure, the potential is constructed from the observed vibrational and rotational spectroscopic term values rather than by imposing an analytic form on the potential. The turning points  $r_+$  and  $r_-$  for the vibrational level of energy  $U$  are derived from semiclassical expressions by evaluating numerically the Klein action integrals. This procedure has been described fully elsewhere (2). To extend the wings of the potential curve beyond the range covered by the spectroscopic data we join repulsive and attractive segments of the form

$$V_{\text{rep}} = a/r^{12} + b \quad (4)$$

and

$$V_{\text{att}} = a'/r^{b'}, \quad (5)$$

where the zero of energy refers to separated atoms. The four constants appearing in Eqs. (4) and (5) are determined from the last two turning points  $r_{\pm}$  on either extreme of the central region so that the repulsive and attractive segments are smoothly joined to the potential. These extrapolated portions of the potential give only minor contributions to the Franck–Condon factors for the highest observed levels, but are required to carry through the numerical procedures (2).

Tables I–V give the RKR potential curves <sup>2</sup> for the X, A, B, C, and a states of N<sub>2</sub>. The vibrational levels are labelled by the quantity  $I = v + \frac{1}{2}$ , which is the action variable for the linear momentum appearing in the Klein action integrals. The source of spectroscopic data used has been summarized below each table. Whenever possible we have employed the reported  $\Delta G(v)$  and  $B_v$  data rather than spectroscopic constants to generate the turning points.

#### FRANCK-CONDON FACTORS

Once the potential is constructed, vibrational wave functions are obtained by solving Eq. (2), the radial Schrödinger equation. We use a program due to Cooley (7), modified for our purposes (8), which replaces the one-dimensional second-order differential equation by an equivalent finite difference equation. This is iteratively solved for the eigenvalue  $E_v$  and the wave function  $\psi_v$  by employing a Numerov (9) method of integration, together with a second-order iteration-variation procedure due to Löwdin (10). This procedure has been reviewed in detail elsewhere (8, 11).

A comparison of the calculated and observed energy levels  $E_v$  shows that the RKR method reproduces the known vibrational energy spacings of the molecule to a high degree of accuracy, the average difference between the observed and

<sup>2</sup> Potential curves have been constructed previously for some of the electronic states of N<sub>2</sub> by Vanderslice, Mason, and Lippincott (6) and by Jain (6) using analytic approximations to the Klein action integrals. However, the errors introduced by this procedure result in correspondingly large uncertainties in the Franck–Condon factors (see Reference 2).

TABLE I  
 POTENTIAL ENERGY CURVE<sup>a</sup> FOR THE  $X^1\Sigma_g^+$  STATE<sup>b</sup> OF  $N_2$  ( $J = 0$  ROTATIONAL STATE)

$I = v + \frac{1}{2}$	$U(r)$ cm <sup>-1</sup>	$r_-(\text{Å})$	$r_+(\text{Å})$
0.0	0.00		1.0976
0.5	1161.22	1.0557	1.1469
1.5	3462.39	1.0260	1.1847
2.5	5735.00	1.0077	1.2137
3.5	7978.97	0.9934	1.2384
4.5	10 194.23	0.9816	1.2609
5.5	12 380.70	0.9715	1.2819
6.5	14 538.32	0.9626	1.3020
7.5	16 667.00	0.9546	1.3211
8.5	18 766.67	0.9472	1.3397
9.5	20 837.26	0.9405	1.3577
10.5	22 878.69	0.9342	1.3755
11.5	24 890.89	0.9284	1.3929
12.5	26 873.79	0.9229	1.4102
13.5	28 827.30	0.9178	1.4273
14.5	30 751.36	0.9130	1.4443
15.5	32 645.89	0.9085	1.4612
16.5	34 510.82	0.9042	1.4781
17.5	36 346.07	0.9002	1.4951
18.5	38 151.57	0.8963	1.5121
19.5	39 927.24	0.8927	1.5291
20.5	41 673.01	0.8891	1.5462

<sup>a</sup> The values of the constants in Eqs. (4) and (5) are:  $a = 9.1917 \times 10^3$ ,  $b = -7.4669 \times 10^4$ ;  $a' = -2.2609 \times 10^3$ ,  $b' = 4.1523$ .

<sup>b</sup> The potential was calculated from the combined spectroscopic data of several authors. The  $G(v)$  values were calculated from the vibrational constants of A. Lofthus, *Can. J. Phys.* **34**, 780 (1956). The  $B_v$  data was as follows:  $B_0$  and  $B_2$ - $B_9$  are from P. G. Wilkinson, *Astrophys. J.* **126**, 1 (1957);  $B_1$  is from B. Stoicheff, *Can. J. Phys.* **32**, 630 (1954);  $B_{10}$ - $B_{15}$  are from the work of Lofthus as recalculated by Wilkinson; and  $B_{16}$ - $B_{20}$  are from Lofthus' constants.

calculated  $G(v)$  values being about 1.5 wave numbers for the potential energy curves of  $N_2$  given in Tables I-V. The difference between the observed and calculated  $\Delta G(v)$  values is much less. As a further check on the accuracy of the RKR procedure, as well as a test of the vibrational wave functions, the  $B_v$  values for each vibrational level are calculated by computing the expectation value of  $\langle 1/r^2 \rangle$ . The observed and calculated  $B_v$  values are also found to be in close agreement, the average difference being five parts in ten thousand or less.<sup>3</sup>

The evaluation of the overlap integrals is accomplished by Simpson's rule using steps of 0.001 Å between the limits 0.500 and 2.200 Å for each band system

<sup>3</sup> The potential curves which most accurately reproduce the input  $G(v)$  and  $B_v$  data are those for the  $A^3\Sigma_u^+$  and  $B^3\Pi_g$  states. Those potential curves for which only a few states are known ( $a^3\Pi_g$  or  $C^3\Pi_u$ ), or those states ( $X^1\Sigma_g^+$ ) where we must combine spectroscopic data from different sources tend to be less accurate.

TABLE II  
 POTENTIAL ENERGY CURVE<sup>a</sup> FOR THE A  ${}^3\Sigma_u^+$  STATE<sup>b</sup> OF N<sub>2</sub> (*J* = 0 ROTATIONAL STATE)

$I = v + \frac{1}{2}$	$U(r)$ cm <sup>-1</sup>	$r_-(\text{Å})$	$r_+(\text{Å})$
0.0	0.00		1.2865
0.5	726.73	1.2328	1.3481
1.5	2159.63	1.1980	1.3992
2.5	3564.93	1.1759	1.4378
3.5	4942.33	1.1589	1.4715
4.5	6291.93	1.1450	1.5025
5.5	7613.73	1.1332	1.5319
6.5	8907.23	1.1230	1.5602
7.5	10 172.43	1.1137	1.5877
8.5	11 409.13	1.1055	1.6148
9.5	12 616.83	1.0981	1.6418

<sup>a</sup> The values of the constants in Eqs. (4) and (5) are:  $a = 4.8066 \times 10^4$ ,  $b = -3.1506 \times 10^4$ ;  $a' = -1.4243 \times 10^5$ ,  $b' = 4.4262$ .

<sup>b</sup> The potential was calculated from the  $G(v)$  and  $B_v$  data of G. H. Dieke and D. F. Heath, Johns Hopkins Spectroscopic Report No. 17, The Johns Hopkins University, Baltimore, Maryland (December, 1959).

TABLE III  
 POTENTIAL ENERGY CURVE<sup>a</sup> FOR THE B  ${}^3\Pi_g$  STATE<sup>b</sup> OF N<sub>2</sub> (*J* = 0 ROTATIONAL STATE)

$I = v + \frac{1}{2}$	$U(r)$ cm <sup>-1</sup>	$r_-(\text{Å})$	$r_+(\text{Å})$
0.0	0.00		1.2125
0.5	846.92	1.1627	1.2694
1.5	2523.32	1.1298	1.3159
2.5	4170.72	1.1089	1.3509
3.5	5789.02	1.0929	1.3813
4.5	7378.52	1.0796	1.4091
5.5	8938.72	1.0683	1.4353
6.5	10 469.82	1.0583	1.4605
7.5	11 971.62	1.0494	1.4849
8.5	13 444.02	1.0414	1.5088
9.5	14 886.72	1.0341	1.5323
10.5	16 299.82	1.0273	1.5556
11.5	17 682.92	1.0210	1.5788
12.5	19 036.22	1.0153	1.6019

<sup>a</sup> The values of the constants in Eqs. (4) and (5) are:  $a = 2.4830 \times 10^4$ ,  $b = -3.9951 \times 10^4$ ;  $a' = -1.7368 \times 10^5$ ,  $b' = 4.6678$ .

<sup>b</sup> Same source for spectroscopic data as Table II.

of N<sub>2</sub>. The Franck-Condon factor arrays found in this manner<sup>4</sup> are presented in Tables VI-X for the Second Positive, First Positive, Vegard-Kaplan (VK), Lyman-Birge-Hopfield (LBH) and Tanaka band systems, respectively. The

<sup>4</sup> All computer programs described in this paper have been documented and are available in a report by Zare (12).

TABLE IV  
 POTENTIAL ENERGY CURVE<sup>a</sup> FOR THE  $C^3\Pi_u$  STATE<sup>b</sup> OF  $N_2$  ( $J = 0$  ROTATIONAL STATE)

$I = v + \frac{1}{2}$	$U(r)$ cm <sup>-1</sup>	$r_-$ (Å)	$r_+$ (Å)
0.0	0.00		1.1485
0.5	1016.66	1.1030	1.2005
1.5	3010.96	1.0730	1.2438
2.5	4951.62	1.0540	1.2771
3.5	6825.46	1.0396	1.3076
4.5	8606.49	1.0282	1.3389

<sup>a</sup> The values of the constants in Eqs. (4) and (5) are:  $a = 2.0125 \times 10^4$ ,  $b = -7.8672 \times 10^4$ ;  $a' = -9.0066 \times 10^4$ ,  $b' = 1.1569$ .

<sup>b</sup> Same source for spectroscopic data as Table II.

TABLE V  
 POTENTIAL ENERGY CURVE<sup>a</sup> FOR THE  $a^4\Pi_g$  STATE<sup>b</sup> OF  $N_2$  ( $J = 0$  ROTATIONAL STATE)

$I = v + \frac{1}{2}$	$U(r)$ cm <sup>-1</sup>	$r_-$ (Å)	$r_+$ (Å)
0.0	0.00		1.2208
0.5	843.57	1.1707	1.2777
1.5	2509.91	1.1378	1.3244
2.5	4148.53	1.1169	1.3594
3.5	5759.43	1.1007	1.3898
4.5	7342.61	1.0874	1.4176
5.5	8898.06	1.0760	1.4437
6.5	10 425.80	1.0659	1.4686

<sup>a</sup> The values of the constants in Eqs. (4) and (5) are:  $a = 3.0769 \times 10^4$ ,  $b = -4.2125 \times 10^4$ ;  $a' = -9.2171 \times 10^4$ ,  $b' = 3.1171$ .

<sup>b</sup> The potential was constructed from spectroscopic constants given by P. G. Wilkinson *Astrophys. J.* **126**, 1 (1957).

negative number in each entry is the power of ten by which the entry has to be multiplied (e.g., 1.23 -4 stands for  $1.23 \times 10^{-4}$ ). All Franck-Condon factors are rounded to three figures. We have varied the input for these calculations taking into account the errors inherent in the numerical methods and the uncertainty present in the spectroscopic data. The strongest transitions ( $q_{v',v''} \sim 10^{-1}$ ) are constant to one part in the last figure, the weaker transitions ( $q_{v',v''} \sim 10^{-3}$ ) are uncertain to five parts in the last figure, and the weakest transitions ( $q_{v',v''} \sim 10^{-6}$ ) are only accurate to one or two significant figures. This illustrates the increasing sensitivity of the Franck-Condon factor to the shape of the potential when severe cancellation occurs in the calculation of the overlap integrals.

Another possible source of error in the application of these calculated Franck-Condon factors is the neglect of rotation-vibration interaction in summing over all the lines of a band in deriving Eq. (3). The Franck-Condon factors given

in Tables VI-X are calculated from rotationless ( $J = 0$ ) potentials and strictly obtain for the real or hypothetical  $Q(0)$  line of the band. If the population of each contributing rotational level of the upper electronic state is available, the rotation-vibration interaction may be taken into account exactly. In the absence of this information it is customary to neglect the effects of rotation-vibration interaction. The calculations (2) for I<sub>2</sub> indicate that this approximation may introduce a 5 to 10% error in calculations which employ these Franck-Condon factors as effective Franck-Condon factors for integrated band intensities.

#### COMPARISON OF CALCULATED AND OBSERVED RELATIVE INTENSITIES

Although many molecular spectra have been carefully assigned and analyzed, there have been relatively few studies whose sole purpose has been to record relative intensities. This is in part owing to the difficulty of accurate intensity measurements. Most modern intensity work is done with photoelectric detectors, which have the advantage over photographic plates of wider range of linear response. In either case, one must calibrate against a standard light source to correct for variation of sensitivity with frequency. Even when a photocell is used, the overlapping of bands and blending of rotational structure by the spectrometer produce an error which may be different for each band studied. Procedures have been developed to account for overlapping (13), but the limited precision of intensity measurements suggests caution in the use of results and the need to include spectrometer tracings in articles reporting experimental data whenever serious overlapping is encountered.

We present in Tables XI-XIV observed relative band intensities and those

TABLE VI  
FRANCK-CONDON FACTORS FOR THE N<sub>2</sub> SECOND POSITIVE ( $C^3\Pi_u-B^3\Pi_g$ ) BAND SYSTEM

$v''$	$v'$	0	1	2	3	4
0		4.55 -1	3.88 -1	1.34 -1	2.16 -2	1.16 -3
1		3.31 -1	2.29 -2	3.35 -1	2.52 -1	5.66 -2
2		1.45 -1	2.12 -1	2.30 -2	2.04 -1	3.26 -1
3		4.94 -2	2.02 -1	6.91 -2	8.81 -2	1.13 -1
4		1.45 -2	1.09 -1	1.69 -1	6.56 -3	1.16 -1
5		3.87 -3	4.43 -2	1.41 -1	1.02 -1	2.45 -3
6		9.68 -4	1.52 -2	7.72 -2	1.37 -1	4.70 -2
7		2.31 -4	4.68 -3	3.32 -2	9.93 -2	1.09 -1
8		5.36 -5	1.33 -3	1.23 -2	5.26 -2	1.04 -1
9		1.21 -5	3.57 -4	4.12 -3	2.31 -2	6.67 -2
10		2.61 -6	9.15 -5	1.27 -3	8.95 -3	3.40 -2
11		5.23 -7	2.25 -5	3.69 -4	3.16 -3	1.50 -2
12		9.10 -8	5.22 -6	1.03 -4	1.03 -3	5.97 -3

TABLE VII

FRANCK-CONDON FACTORS FOR THE  $N_2$  FIRST POSITIVE ( $B \ ^3\Pi_g-A \ ^3\Sigma_u^+$ ) BAND SYSTEM

$v'$ $v''$	0	1	2	3	4	5	6
0	4.06 -1	4.01 -1	1.58 -1	3.17 -2	3.47 -3	2.01 -4	5.72 -6
1	3.27 -1	3.71 -3	2.85 -1	2.77 -1	9.18 -2	1.41 -2	1.07 -3
2	1.64 -1	1.59 -1	6.59 -2	1.05 -1	3.06 -1	1.63 -1	3.41 -2
3	6.67 -2	1.93 -1	2.25 -2	1.50 -1	1.11 -2	2.59 -1	2.26 -1
4	2.44 -2	1.29 -1	1.22 -1	4.67 -3	1.53 -1	6.94 -3	1.76 -1
5	8.38 -3	6.57 -2	1.39 -1	4.09 -2	4.94 -2	1.00 -1	5.05 -2
6	2.80 -3	2.92 -2	9.94 -2	1.03 -1	2.04 -3	9.29 -2	4.02 -2
7	9.26 -4	1.20 -2	5.66 -2	1.08 -1	5.13 -2	8.81 -3	1.04 -1
8	3.07 -4	4.73 -3	2.83 -2	7.88 -2	8.85 -2	1.22 -2	3.92 -2
9	1.03 -4	1.83 -3	1.31 -2	4.78 -2	8.58 -2	5.37 -2	4.73 -5
$v'$ $v''$	7	8	9	10	11	12	
0	8.81 -8	8.28 -11	5.50 -10	1.42 -10	5.38 -12	6.27 -11	
1	3.70 -5	5.14 -7	8.52 -10	1.56 -9	1.80 -10	1.71 -10	
2	3.26 -3	1.35 -4	1.86 -6	1.59 -9	1.06 -9	4.29 -10	
3	6.36 -2	7.50 -3	3.64 -4	5.44 -6	6.79 -9	4.09 -11	
4	2.68 -1	1.01 -1	1.45 -2	8.19 -4	1.41 -5	2.84 -8	
5	9.30 -2	2.83 -1	1.43 -1	2.50 -2	1.63 -3	3.20 -5	
6	9.90 -2	3.20 -2	2.71 -1	1.86 -1	3.94 -2	2.96 -3	
7	5.00 -3	1.26 -1	2.86 -3	2.37 -1	2.26 -1	5.79 -2	
8	8.29 -2	2.75 -3	1.24 -1	3.86 -3	1.88 -1	2.60 -1	
9	6.71 -2	4.68 -2	2.43 -2	9.80 -2	2.61 -2	1.35 -1	

calculated from Eq. (3), assuming a constant  $\bar{R}_e^2$ , for the Second Positive, First Positive, LBH, and VK band systems. Experimental intensities reported in Tables XI, XII, and XIV were obtained photoelectrically. However, intensity data for the LBH system (Table XIII) are plate-blackenings reported by Birge and Hopfield (14), and are thus much less precise.

Within their accuracy, the experimental data of Tyte (15)<sup>5</sup> for the Second Positive system are in excellent agreement with the calculated intensities (Table XI). Tyte reports a variation of intensities in a  $v''$  progression with changes in discharge operating current; relative intensities of the strongest bands of the same  $v''$  progression change by as much as 30%. When the discharge current is

<sup>5</sup> Based on intensity measurements taken under forty different experimental conditions, Tyte suggested that some of the Morse Franck-Condon factors may be suspect: the  $q\hat{v}'$  for the (1-2), (2-1), (2-3), (3-2), (4-2), (4-3), (4-6) bands being too low; the  $q\hat{v}''$  for the (1-6), (2-2), (3-8), (4-9) bands being too high. In each case the Franck-Condon factors calculated from RKR potentials (Table XI) differ from those found from Morse potentials (Reference 35) in the direction Tyte indicated.

TABLE VIII

FRANCK-CONDON FACTORS FOR THE N<sub>2</sub> VEGARD-KAPLAN ( $A^3\Sigma_u^+ - X^1\Sigma_g^+$ ) BAND SYSTEM

$v''$	$v'$	0	1	2	3	4
0		1.06 -3	5.55 -3	1.57 -2	3.15 -2	5.07 -2
1		8.41 -3	3.27 -2	6.65 -2	9.31 -2	9.91 -2
2		3.34 -2	8.88 -2	1.15 -1	8.91 -2	4.00 -2
3		8.29 -2	1.33 -1	8.12 -2	1.35 -2	3.65 -3
4		1.44 -1	1.09 -1	9.45 -3	1.74 -2	6.05 -2
5		1.89 -1	3.67 -2	1.77 -2	7.36 -2	3.88 -2
6		1.92 -1	8.43 -5	8.13 -2	4.21 -2	1.05 -3
7		1.55 -1	4.26 -2	7.92 -2	1.22 -4	5.28 -2
8		1.02 -1	1.17 -1	1.76 -2	4.83 -2	5.01 -2
9		5.47 -2	1.53 -1	6.52 -3	8.10 -2	8.41 -4
10		2.46 -2	1.32 -1	7.06 -2	3.10 -2	3.70 -2
11		9.22 -3	8.48 -2	1.33 -1	1.11 -3	7.68 -2
12		2.89 -3	4.23 -2	1.36 -1	5.51 -2	3.14 -2
13		7.51 -4	1.68 -2	9.49 -2	1.24 -1	1.19 -3
14		1.62 -4	5.36 -3	4.90 -2	1.34 -1	5.71 -2
15		2.94 -5	1.38 -3	1.94 -2	9.39 -2	1.25 -1
16		4.50 -6	2.92 -4	6.04 -3	4.74 -2	1.30 -1
17		5.41 -7	5.02 -5	1.49 -3	1.79 -2	8.60 -2
18		4.55 -8	6.87 -6	2.95 -4	5.22 -3	4.03 -2
19		3.89 -9	7.47 -7	4.57 -5	1.18 -3	1.40 -2
20		7.87 -10	6.38 -8	5.44 -6	2.09 -4	3.70 -3
$v''$	$v'$	5	6	7	8	9
0		6.93 -2	8.38 -2	9.21 -2	9.38 -2	8.96 -2
1		8.35 -2	5.57 -2	2.78 -2	8.41 -3	3.66 -4
2		5.73 -3	1.92 -3	1.90 -2	3.87 -2	4.83 -2
3		3.44 -2	5.52 -2	4.64 -2	2.21 -2	3.65 -3
4		5.16 -2	1.45 -2	1.60 -4	1.52 -2	3.44 -2
5		4.23 -4	1.88 -2	4.41 -2	3.63 -2	1.19 -2
6		4.10 -2	4.70 -2	1.23 -2	1.06 -3	2.03 -2
7		4.21 -2	8.71 -4	1.90 -2	4.11 -2	2.51 -2
8		5.30 -5	3.71 -2	4.04 -2	5.56 -3	5.90 -3
9		4.56 -2	3.70 -2	8.28 -6	2.58 -2	3.73 -2
10		4.73 -2	5.09 -4	4.04 -2	3.06 -2	3.60 -4
11		5.46 -4	4.74 -2	2.72 -2	2.09 -3	3.45 -2
12		3.87 -2	3.89 -2	4.04 -3	4.48 -2	1.69 -2
13		7.29 -2	1.50 -4	5.23 -2	1.40 -2	1.12 -2
14		2.35 -2	4.83 -2	2.56 -2	1.43 -2	4.35 -2
15		4.59 -3	6.63 -2	4.83 -3	5.35 -2	2.44 -3
16		7.08 -2	1.14 -2	6.13 -2	9.98 -3	3.13 -2
17		1.31 -1	1.53 -2	5.25 -2	1.94 -2	4.41 -2
18		1.22 -1	9.26 -2	1.39 -3	6.97 -2	2.67 -4
19		7.28 -2	1.36 -1	3.78 -2	3.04 -2	4.26 -2
20		3.06 -2	1.08 -1	1.18 -1	2.95 -3	6.34 -2

TABLE IX  
FRANCK-CONDON FACTORS FOR THE  $N_2$  LYMAN-BIRGE-HOPFIELD  
( $a \ ^1\Pi_u-X \ ^1\Sigma_g^+$ ) BAND SYSTEM

$v''$	$v'$	0	1	2	3	4	5	6						
0	4.43	-2	1.18	-1	1.73	-1	1.85	-1	1.60	-1	1.20	-1	8.08	-2
1	1.51	-1	1.90	-1	9.44	-2	1.15	-2	6.67	-3	4.75	-2	8.52	-2
2	2.50	-1	8.02	-2	3.30	-3	7.51	-2	9.62	-2	4.70	-2	4.94	-3
3	2.53	-1	5.84	-4	1.08	-1	6.81	-2	4.43	-4	3.47	-2	7.32	-2
4	1.73	-1	9.22	-2	8.41	-2	4.39	-3	7.81	-2	5.51	-2	2.37	-3
5	8.61	-2	1.91	-1	3.19	-4	9.76	-2	3.47	-2	9.80	-3	6.39	-2
6	3.22	-2	1.76	-1	7.30	-2	6.18	-2	2.05	-2	7.84	-2	1.24	-2
7	9.17	-3	9.93	-2	1.73	-1	1.17	-3	9.90	-2	5.16	-3	4.47	-2
8	1.99	-3	3.87	-2	1.60	-1	9.17	-2	2.93	-2	5.50	-2	5.01	-2
9	3.37	-4	1.10	-2	8.76	-2	1.71	-1	1.64	-2	8.17	-2	5.19	-3
10	4.75	-5	2.33	-3	3.23	-2	1.38	-1	1.25	-1	3.08	-3	8.54	-2
11	5.64	-6	3.82	-4	8.50	-3	6.71	-2	1.66	-1	5.56	-2	4.09	-2
12	3.93	-7	4.90	-5	1.65	-3	2.19	-2	1.09	-1	1.55	-1	7.44	-3
13	8.72	-9	4.29	-6	2.37	-4	5.03	-3	4.45	-2	1.46	-1	1.09	-1
14	2.46	-9	1.85	-7	2.43	-5	8.35	-4	1.22	-2	7.55	-2	1.63	-1
15	5.58	-10	1.80	-8	1.62	-6	9.86	-5	2.34	-3	2.50	-2	1.11	-1
16	2.66	-10	6.22	-9	1.17	-7	7.93	-6	3.17	-4	5.62	-3	4.52	-2
17	2.83	-11	5.41	-10	1.31	-8	5.57	-7	3.09	-5	8.94	-4	1.22	-2
18	4.25	-11	3.25	-10	5.71	-10	6.06	-8	2.71	-6	1.08	-4	2.35	-3
19	1.42	-10	4.86	-10	8.40	-15	1.68	-9	3.47	-7	1.27	-5	3.66	-4
20	3.40	-11	1.24	-13	1.66	-9	6.11	-10	4.10	-8	2.03	-6	5.69	-5

TABLE X  
FRANCK-CONDON FACTORS FOR THE  $N_2$  TANAKA ( $C \ ^3\Pi_u-X \ ^1\Sigma_g^+$ ) BAND SYSTEM

$v''$	$v'$	0	1	2	3	4				
0	5.59	-1	3.03	-1	1.01	-1	2.76	-2	7.16	-3
1	3.36	-1	8.73	-2	2.71	-1	1.82	-1	7.88	-2
2	9.03	-2	3.64	-1	1.82	-3	1.30	-1	1.82	-1
3	1.33	-2	1.95	-1	2.44	-1	7.11	-2	2.42	-2
4	1.12	-3	4.47	-2	2.67	-1	9.92	-2	1.48	-1
5	6.28	-5	5.84	-3	9.52	-2	2.80	-1	9.47	-3
6	6.12	-6	5.13	-4	1.80	-2	1.58	-1	2.19	-1
7	6.77	-7	4.90	-5	2.27	-3	4.32	-2	2.13	-1
8	4.83	-9	5.17	-6	2.79	-4	8.06	-3	8.76	-2
9	1.44	-10	1.48	-7	4.21	-5	1.39	-3	2.40	-2
10	1.68	-8	9.72	-8	4.41	-6	2.59	-4	5.66	-3
11	1.64	-10	5.89	-8	6.62	-7	3.78	-5	1.26	-3
12	2.93	-9	1.38	-8	1.22	-7	3.95	-6	2.15	-4
13	1.09	-11	1.97	-9	3.58	-8	3.37	-7	2.44	-5
14	1.34	-9	3.67	-9	7.52	-10	1.43	-8	2.62	-6
15	1.37	-10	7.14	-12	1.71	-8	9.60	-9	2.00	-7

TABLE XI

COMPARISON OF CALCULATED AND OBSERVED<sup>a</sup> RELATIVE BAND INTENSITIES (ENERGY/SEC<sup>2</sup>) FOR THE SECOND POSITIVE ( $C^3\Pi_u-B^3\Pi_g$ ) SYSTEM. THE FIRST ENTRY IS CALCULATED; THE SECOND ENTRY IS OBSERVED. IN EACH  $v''$  PROGRESSION, THE ENTRIES HAVE BEEN SCALED TO TEN. ALL BLANK CALCULATED ENTRIES ARE 0.00

$v''$	$v'$	0	1	2	3	4
0		10.00	10.00	4.91	1.04	0.05
		10.00	10.00	4.91		
1		5.78	0.48	10.00	10.00	2.10
		5.99	0.47	10.00	10.00	
2		1.99	3.50	0.56	6.64	10.00
		1.63	3.67	0.77	7.91	10.00
3		0.53	2.65	1.34	2.34	2.85
		0.57	2.92	1.83	3.45	2.30
4		0.12	1.12	2.62	0.14	2.39
		0.13	1.30	3.08		2.55
5		0.02	0.35	1.73	1.75	0.04
				2.13	1.87	
6			0.09	0.74	1.88	0.64
			0.01	1.24		0.62
7			0.02	0.25	1.07	1.19
				0.32	1.29	1.90
8				0.07	0.44	0.90
					0.47	1.20
9				0.02	0.15	0.45
						0.36

<sup>a</sup> Reference 15.<sup>5</sup>

raised the rotational structure of each band may be altered, resulting in different recorded intensity measurements depending on the resolution of the spectrometer. In addition, the N<sub>2</sub><sup>+</sup> First Negative ( $B^2\Sigma_u^+-X^2\Sigma_g^+$ ) system is known to overlap the N<sub>2</sub> Second Positive system (15),<sup>5</sup> but without spectrometer tracings we cannot speculate further about the nature of this variation. In Table XI we have used only the relative band intensities reported by Tyte at lowest operating

TABLE XII  
 COMPARISON OF CALCULATED AND OBSERVED<sup>a</sup> RELATIVE BAND INTENSITIES (ENERGY/SEC)  
 FOR THE FIRST POSITIVE ( $B^3\Pi_g-A^3\Sigma_u^+$ ) SYSTEM. THE FIRST ENTRY IS CALCULATED;  
 THE SECOND ENTRY IS OBSERVED. IN EACH  $v''$  PROGRESSION, THE ENTRIES HAVE  
 BEEN SCALED TO TEN. ALL BLANK CALCULATED ENTRIES ARE 0.00

$v' \dots \dots 0$		1	2	3	4	5	6	7	8	9	10	11	12
$v''$													
0	10.00 10.00	10.00	8.84 8.34	1.73 1.70	0.25	0.02							
1	4.24 4.34	0.05	10.00 10.00	10.00 10.00	4.48 3.84	1.15 1.24	0.10 0.23						
2	1.01 1.54	1.25 2.07	1.38 2.48	2.42 3.66	10.00 10.00	9.25 8.54	2.14 2.03	0.24 0.33	0.01				
3	0.17	0.75 1.36	0.26 1.18	2.09 3.25	0.24 1.09	10.00 10.00	10.00 10.00	3.33 3.04	0.50 0.72	0.03			
4	0.02	0.22 0.78	0.73 1.46	0.04 1.22	2.01 2.89	0.18	5.36 6.61	10.00 10.00	4.96 4.73	1.00 1.23	0.08		
5		0.04	0.38 0.94	0.17 1.16	0.38	1.61 3.05	1.02 2.45	2.41 3.18	10.00 10.00	7.26 6.86	1.81 1.95	0.13	
6			0.11	0.21 1.20	0.01	0.90	0.52	1.74 3.28	0.80	10.00 10.00	10.00 9.95	2.33 2.17	0.20
7			0.02	0.09	0.11	0.05	0.84	0.06	2.15	0.08	9.33 10.00	10.00 10.00	2.95 3.08
8				0.02	0.08	0.04	0.18	0.60	0.03	2.26	0.11	6.17 6.24	10.00 10.00
9					0.03	0.07	0.00	0.29	0.34	0.30	1.96	0.62	3.89

<sup>a</sup> Reference 18.

current. We note that these are in reasonable agreement with the unpublished work of Wallace (16).<sup>6</sup>

In the First Positive system (Table XII) experimental intensities for the strong bands which lie on and near the (0-0) sequence are in good agreement with calculations. This agreement is also confirmed by comparing the calculated intensities with the careful photographic measurements of Elliott and Cameron

<sup>6</sup> We would like to thank Dr. Wallace for making available to us his intensity data worksheets.

TABLE XIII

COMPARISON OF CALCULATED AND OBSERVED<sup>a</sup> RELATIVE BAND INTENSITIES (ENERGY/SEC)  
 FOR THE LYMAN-BIRGE-HOPFIELD ( $a\ ^1\Pi_g-X\ ^1\Sigma_g^+$ ) SYSTEM. THE FIRST ENTRY IS  
 CALCULATED; THE SECOND ENTRY IS OBSERVED. IN EACH  $v''$  PROGRESSION, THE  
 ENTRIES HAVE BEEN SCALED TO TEN. ALL BLANK CALCULATED ENTRIES  
 ARE 0.00

$v''$	0	1	2	3	4	5	6
0	2.33 6	7.12 7	10.0 10	10.0 10	10.0 10	10.0 10	10.0 10
1	6.92 8	10.0 9	4.78 7	0.55 0	0.37 3	3.50 8	9.35 10
2	10.0 10	3.68 6	0.15 2	3.15 5	4.68 8	3.06 4	0.48
3	8.76 10	0.02 b	4.20 6	2.50	0.02 b	1.99 2	6.29 7
4	5.17 9	3.20 7	2.84 6	0.14 0	2.93 5	2.78 8	0.18 b
5	2.22 6	5.73 10	0.01 b	2.73 5	1.13 5	0.43 2	4.26 5
6	0.71 3	4.54 8	1.85 5	1.50 5	0.59	3.03 6	0.72 b
7	0.17	2.20 6	3.77 7	0.03 1	2.45	0.17 b	2.28 0
8	0.03	0.73 2	3.01 6	1.67 4	0.63 b	1.61	2.24 2
9		0.18 0	1.41 5	2.67 1	0.30	2.08	0.20 b
10		0.03	0.44 1	1.85 5	1.99 7	0.07 b	2.88
11			0.10	0.77 2	2.27 7	1.05 0	1.19 2
12			0.02	0.21 1	1.27 3	2.51 2	0.19 b
13				0.04	0.44	2.02	2.36
14				0.01	0.10	0.89	3.01
15					0.02	0.25	1.75
16						0.05	0.61
17						0.01	0.14
18							0.02

<sup>a</sup> Reference 14.<sup>b</sup> Reported "missing" by Reference 14.

TABLE XIV

COMPARISON OF CALCULATED AND OBSERVED<sup>a</sup> RELATIVE BAND INTENSITIES (QUANTUM/SEC) FOR THE VEGARD-KAPLAN ( $A \ ^3\Sigma_u^+ - X \ ^1\Sigma_g^+$ ) SYSTEM. THE FIRST ENTRY IS CALCULATED; THE SECOND ENTRY IS OBSERVED. ALL ENTRIES IN EACH  $v''$  PROGRESSION HAVE BEEN SCALED TO TEN

$v''$	$v' = 0$	$v' = 1$
0	0.12	0.64
1	0.83	3.30
2	2.85	7.77
3	6.08	10.00
4	9.01 3.69	7.02 1.79
5	10.00 7.64	2.03 1.52
6	8.57 10.00	0.00
7	5.78	1.67
8	3.13	3.83 7.24
9	1.38	4.13 10.00
10	0.50	2.93 8.62

<sup>a</sup> Reference 21.

(17) for the strong  $\Delta v = 3, 4,$  and  $5$  sequences. However, large deviations are present for the weak bands in the experimental data of Turner and Nicholls (18). The First Positive system is known to overlap itself as well as to be overlapped by the  $N_2$  ( $B' \ ^3\Sigma_u^- - X \ ^1\Sigma_g^+$ ) band system (19). In the absence of a spectrometer tracing we cannot estimate the effect of overlapping. However, the greatest disagreement occurs for the weak bands in the lower left hand corner of

Table XII. We note that these were observed in the wavelength region 10 000–16 000 Å, where dispersion of the prism spectrometer used by Turner and Nicholls is rapidly decreasing: 580 Å/mm at 10 000 Å and 920 Å/mm at 16 000 Å.

Comparison of observed and calculated relative intensities for the LBH system (Table XIII) shows that the visual estimates of Birge and Hopfield (14) follow the trend of the calculated band intensities, although the experimental data are too poor to allow more than a qualitative comparison. Similarly for the C-X band system, Tanaka (20) reports absorption intensities for the (0-0), (1-0) and (2-0) bands from photographic plate-blackenings which are in the ratio 4:3:2, respectively. The corresponding calculated absorption intensities from the Franck-Condon factors given in Table X are 5.6:3.0:1.0 on an arbitrary relative scale. In the absence of more accurate and extensive intensity data, the present agreement for the LBH and Tanaka band systems must be considered good.

For the VK band system (Table XIV), however, there is a significant disagreement between the calculated band intensities and the photoelectrically measured intensities of Carleton and Papaliolios (21). Although accurate intensity measurements for the VK system are complicated by the weak emission of the long-lived  $A^3\Sigma_u^+$  state of N<sub>2</sub>, the recent intensity work of Zipf (22) reported to one-figure-precision agrees with the more precise data of Carleton and Papaliolios and thus seems to confirm the latter. Moreover, the plate-blackenings reported by Bernard (23) for transitions from  $v' = 0$  and 1 of the  $A$  state to higher vibrational levels of the ground state show an increasing disparity between the observed and calculated relative intensities. Thus, within the combined experimental and calculational uncertainties, there is no way to reconcile the observed band intensities for the VK system with those calculated from Eq. (3).

#### VARIATION OF THE ELECTRONIC TRANSITION MOMENT

Once reliable intensity measurements are available it is possible in principle to improve upon Eq. (3) by determining the variation of the square of the electronic transition moment  $R_e^2(\bar{r}_{v'v''})$  in a Taylor series expansion in powers of the  $r$ -centroid  $\bar{r}_{v'v''}$ . The  $r$ -centroid method, proposed by Fraser (24), has been reviewed before (1, 2). Briefly, the  $r$ -centroid is a weighted value of the internuclear distance encountered in the ( $v'$ ,  $v''$ ) band. It is defined by

$$\bar{r}_{v'v''} = \int \psi_{v'} r \psi_{v''} dr / \int \psi_{v'} \psi_{v''} dr.$$

Observed band intensities (quanta/sec) may be used to determine the variation of  $R_e^2(\bar{r})$  with  $\bar{r}$  from the relation

$$R_e^2(\bar{r}_{v'v''}) = I_{obs}^{v'v''} / [KN_{v'}v''^2q_{v'v''}] \quad (6)$$

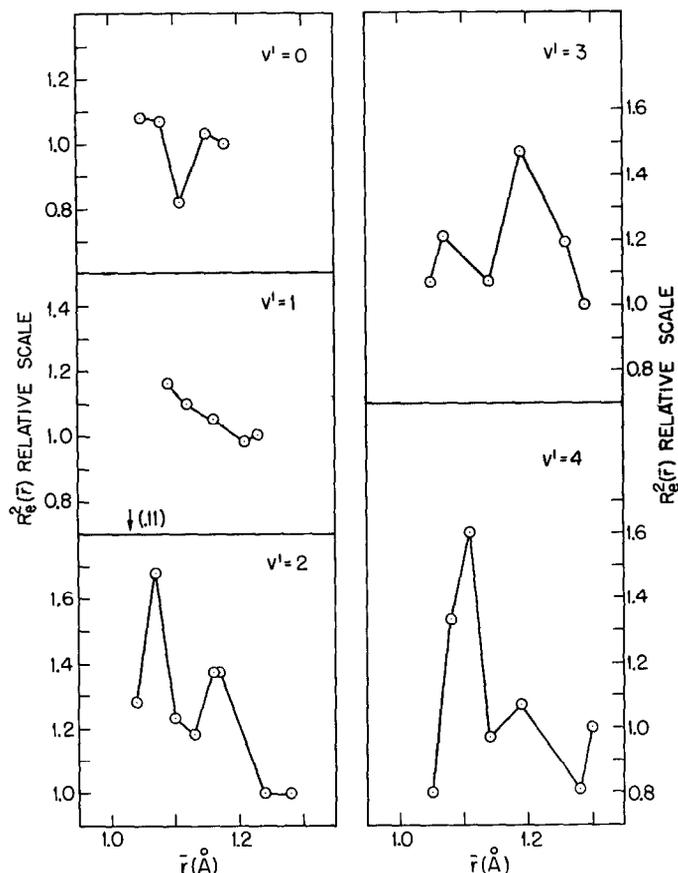


FIG. 1. Variation of the square of the electronic transition dipole moment with internuclear distance for the Second Positive band system of  $N_2$ . Relative ordinate scales for all  $v'$  progressions are independent. Points lying off scale are indicated by arrows.

using calculated values of  $r$ -centroids and Franck-Condon factors involved in each transition. Equation (6) may be shown to be exact for a linear variation.

The  $r$ -centroid method has been applied to a large number of molecular band systems.<sup>7</sup> Since it ascribes all discrepancies between the calculated and observed relative intensities to variation of the electronic transition moment, the results can only be valid if both the experimental intensity and calculated Franck-Condon factors are highly accurate.

In the past, significant variation of  $R_e^2(\bar{r})$  has been reported, a factor of two to four over the Second Positive system (15, 26)<sup>5</sup> and a factor of ten over the First Positive system (27). However, a large part of this variation was due to

<sup>7</sup> Reference to over twenty such band systems are found in Reference 25.

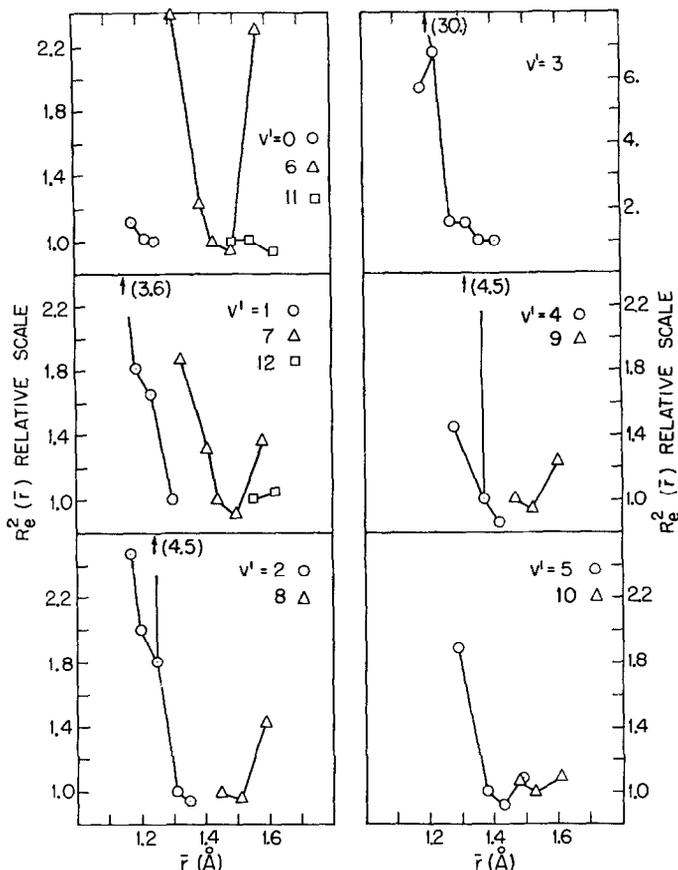


FIG. 2. Variation of the square of the electronic transition dipole moment with internuclear distance for the First Positive band system of N<sub>2</sub>. Relative ordinate scales for all  $v''$  progressions are independent; progressions are grouped together for convenience only. Points lying off scale are indicated by arrows.

the sizeable errors caused by the use of Morse Franck-Condon factors in Eq. (6). Plots of  $R_e^2(\bar{r})$  against  $\bar{r}$  for separate  $v''$  progressions of these two band systems, Figs. 1 and 2, show considerable scatter, and we cannot smoothly join the variation of  $R_e^2(\bar{r})$  found in one  $v''$  band progression to another. Thus we cannot determine any significant variation of  $R_e^2(\bar{r})$  for these band systems outside the combined sources of calculational and experimental error.

However, for the VK system there is a regular deviation between the experimental and calculated intensities beyond any reasonable uncertainties in the data. From Eq. (6)  $R_e^2(\bar{r})$  has been determined and its variation is shown in Fig. 3 to be linear; the data for the  $v' = 0$  and  $v' = 1$  progressions have been fitted to-

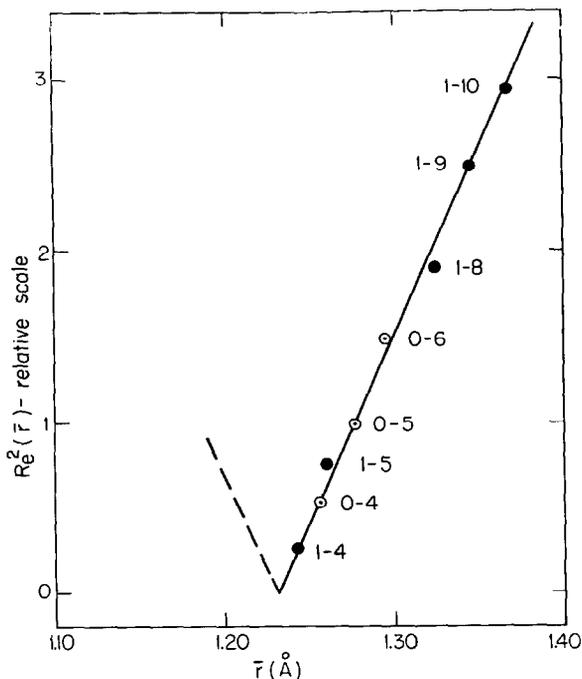


Fig. 3 Variation of the square of the electronic transition dipole moment with internuclear distance for the Vegard-Kaplan band system of  $N_2$ .

gether. The lack of scatter of the points in Fig. 3 reflects the excellence of the Franck-Condon factors and may also be taken to indicate high precision in the experimental data. In the range of  $r$ -centroid from 1.25 Å to 1.37 Å  $R_e^2(\bar{r})$  changes over an order of magnitude, approaching zero at the lower observed limit. Although  $R_e^2(\bar{r})$  must remain a positive quantity, the electronic transition dipole moment  $R_e(\bar{r})$  may change sign. The extrapolation of  $R_e^2(\bar{r})$  into the region of small  $\bar{r}$  may be obtained by reflecting the experimental curve as indicated by the dashed line of Fig. 3. When the less quantitative photographic data of Bernard (23) are included in Fig. 3,  $R_e^2(\bar{r})$  may be shown to be steeply rising for  $\bar{r} > 1.40$  Å in agreement with Fig. 3, but with a somewhat different slope.

#### RADIATIVE LIFETIMES

The distribution of intensity within an electronic band system given by the Franck-Condon factors is essential to calculations of radiative transition probabilities ( $A$ ) or lifetimes ( $\tau$ ) from absorption data. The following relation is used (28):

$$A = 1/\tau \sim 2.880 \times 10^{-9} \frac{g_l \langle \nu_e^3 \rangle_{av}}{g_u \langle \nu_a \rangle_{av}} \int \epsilon d\nu_a, \quad (7)$$

where  $\epsilon$  is the molar decadic extinction coefficient,  $g_l$  and  $g_u$  are the effective multiplicities of the lower and upper electronic states (see following discussion), and  $\nu$  is the frequency in wave numbers of absorption ( $\nu_a$ ) or emission ( $\nu_e$ ). In two cases lifetimes calculated from absorption data can be compared with those measured directly in emission.

Watanabe, Zelikoff and Inn (29) give approximate peak extinction coefficients for 11 bands, of observed width  $5 \text{ \AA}$  or less, for the LBH system in absorption from  $v'' = 0$ . The observed intensities are in rough agreement with those shown in Table XIII so that we might expect a reasonable value for the total absorption intensity. Assuming each band to be rectangular with peak extinction height and  $5 \text{ \AA}$  width, the sum  $\sum \epsilon \Delta\nu_a$  is 1773. By taking a maximum bandwidth of  $5 \text{ \AA} \sim 255 \text{ cm}^{-1}$  the calculated lifetime should be a minimum value. The average absorption frequency is at the (3-0) band,  $7.39 \times 10^4 \text{ cm}^{-1}$  and  $\langle \nu_e^3 \rangle$  from  $v' = 3$  is  $2.39 \times 10^{14} \text{ cm}^{-3}$ . The lifetime for the  $a \text{ } ^1\Pi_g(v = 3) - X \text{ } ^1\Sigma_g^+$  is calculated to be  $1.2 \times 10^{-4} \text{ sec}$ . This compares favorably with the measurement  $\tau = 1.7 \pm 0.3 \times 10^{-4} \text{ sec}$  obtained directly in emission by decay of a molecular beam (30). Our calculation thus serves to confirm that more accurate value; also, the disagreement is in the direction anticipated.

Wilkinson and Mulliken (31, 32) have surveyed the N<sub>2</sub> spectrum in absorption, presenting minimal optical paths (meter-atmospheres) required for the appearance of five band systems arising from the ground state, including the VK and LBH transitions. The optical paths are inversely proportional to the respective extinction coefficients. If it is assumed that all measured bands have the same width, Eq. (7) gives the functional form for the calculation of radiative lifetime of the VK transition from the known  $\tau$  of the LBH system (30). Since single bands were compared, their Franck-Condon factors must also be included. Table XV summarizes the pertinent data. The multiplicity factor  $g_l/g_u$  can be taken from the symmetry designations of the combining states provided that the rotational structure is not well resolved in the absorption spectrum. For the VK system, Wilkinson's text and microphotometer tracing (31) indicate that the four branches overlap.<sup>8</sup> We must also take into account the variation of  $R_e^2(\bar{r})$  shown in Fig. 3. However, there is no experimental data for the variation of  $R_e^2(\bar{r})$  in the region of the  $r$ -centroid for the (9, 0) band,  $\bar{r} = 1.105 \text{ \AA}$ , so that no correction to the Franck-Condon factor was made. This procedure is only reasonable if  $R_e^2(\bar{r})$  varies somewhat as indicated by the dashed line in Fig. 3.

The calculated lifetime,  $\tau = 0.1 \text{ sec}$  may be compared to the measurement of 1 sec obtained recently by Zipf (22) who observed the radiative decay directly. Zipf's result agrees with the previous work of Carleton and Oldenberg (33) who report  $\tau = 2.0 \pm 0.9 \text{ sec}$ ; the uncertainty in this earlier result largely reflects

<sup>8</sup> Similarly for the LBH system we have taken the value of  $g_l/g_u$  as  $1/2$ , corresponding to the full multiplicity of each state, since the maximum extinction measurements of Reference 29 were made at low dispersion and probably at the bandhead, where rotational structure is blended.

TABLE XV  
CALCULATION OF RADIATIVE LIFETIME OF THE  $A \ ^3\Sigma_u^+(v' = 0)$  STATE OF  $N_2$  FROM ABSORPTION DATA, AFTER WILKINSON AND MULLIKEN (31, 32)

Transition	Relative optical path (meter-atmospheres)	$\langle \nu_a \rangle_{av}$ (cm <sup>-1</sup> )	$\langle \nu_e^3 \rangle_{av}$ (cm <sup>-3</sup> )	$q_{v'v''}$	$g_l/g_u$	$\tau$ (sec)
$a \ ^1\Pi_g-X \ ^1\Sigma_g^+$ (3-0)	0.025	$7.39 \times 10^4$	$2.39 \times 10^4$	0.185	$\frac{1}{2}$	$1.7 \times 10^{-4}$
$A \ ^3\Sigma_u^+-X \ ^1\Sigma_g^+$ (9-0)	4	$6.16 \times 10^4$	$4.11 \times 10^{13}$	0.090	$\frac{1}{3}$	$1.0 \times 10^{-1}$

the uncertainty of the lifetime of the First Positive system since the ratio of the lifetimes of the First Positive to the VK system was determined. The comparison of 0.1 to 1 sec indicates no better than an order-of-magnitude accuracy for the technique of rapid survey of transition probabilities in absorption (31, 32).

It is of interest to note that radiative lifetimes are known, with varying accuracy, for seven electronic band systems in  $N_2$ : five connecting with the ground state (31, 32), and the First Positive (33) and Second Positive (34) systems. These account for a good deal of the total intensity of all known  $N_2$  transitions in the visible and near uv. Thus the radiative behavior of many of the upper states of  $N_2$  may be described from an overall viewpoint, as well as in the detailed picture provided by the Franck-Condon factors.

#### DISCUSSION

The comparison of Franck-Condon factors calculated from Rydberg-Klein-Rees potentials for the major band systems of  $N_2$  with those calculated from Morse potentials (35) shows that the latter often differ by as much as 20% for the strongest transitions ( $q_{v'v''} \geq 0.1$ ) and by as much as 40% for the less intense but significant transitions ( $q_{v'v''} \geq 0.01$ ). This result warrants caution in the use of Morse Franck-Condon factors, even for low vibrational quantum numbers.

In particular previous determinations of the variation of the electronic transition dipole moment with internuclear distance are open to re-examination. When we consider the uncertainties present in relative intensity measurements and take into account the errors introduced by inexact Franck-Condon factors we find that  $R_e^2(\bar{r})$  appears to be constant over the range of  $\bar{r}$  for the First and Second Positive systems of  $N_2$  (see Figs. 1 and 2). This is to be contrasted with the report of variation by a factor of ten for the First Positive (27), and a variation by a factor of two to four for the Second Positive system (15, 26).<sup>5</sup> A survey of calculations of  $R_e^2(\bar{r})$  for band systems of other molecules<sup>7</sup> shows that variations by a factor of two to four are commonly reported. We stress that these conclusions are only valid provided that the intensity data and the calculated Franck-Condon factors used are free from uncertainties of this magnitude.

For the Vegard-Kaplan system, however, we find (Fig. 3) an abnormally large<sup>9</sup> variation of  $R_e^2(\bar{r})$ , over a factor of ten, lying far outside the combined sources of error. Attempts have been made to explain this variation and predict the variation of  $R_e^2(\bar{r})$  for other cases. Carleton and Papaliolios (21) have noticed that a large change of equilibrium internuclear distance of the combining states is associated with the large variation of  $R_e^2(\bar{r})$  in the VK system; this is clearly a necessary requirement to have an appreciable spread in  $\bar{r}$ , but it is not sufficient to produce a change in  $R_e^2(\bar{r})$ .<sup>9</sup> Bates (39) has suggested that  $R_e^2(\bar{r})$  should vary more strongly with  $\bar{r}$  for perpendicular band systems ( $\Delta\Lambda = \pm 1$ ) than for parallel band systems ( $\Delta\Lambda = 0$ ) where the electron cloud is believed to change less drastically. While Nicholls<sup>7</sup> has presented some evidence to substantiate this effect, further comparisons of parallel and perpendicular transitions using accurate Franck-Condon factors are necessary to establish this point. Mulliken (40) and Mulliken and Rieke (41) have proposed that the variation of the electronic transition dipole moment might be related to the behavior of the transition in the united atom and separated atom limits. Thus for the  $B-X$  transitions of the halogens, they expected a significant variation of  $R_e^2(\bar{r})$  since the transition is forbidden for the separated atoms but enhanced by case  $c$  coupling in the united atom limit. However, the radiative lifetime ( $\tau = 7.2 \pm 1.0 \times 10^{-7}$  sec) of  $I_2(B^3\Pi_{0^+g}-X^1\Sigma_g^+)$  measured directly in emission (42) at an effective internuclear distance corresponding nearly to  $r_e' = 3.02$  Å agrees (2) within a factor of two with the results of absolute absorption measurements corresponding to  $r_e'' = 2.67$  Å. Finally we note that in the one instance where the variation of the radiative lifetime in emission was studied for different excited vibrational levels Bennett and Dalby (43) report for  $CO^+(A^2\Pi-X^2\Sigma^+)$  that  $\tau$  varies from 2.1– $2.8 \times 10^{-6}$  sec as  $v'$  decreases from 5 to 1 in accordance with the changing frequency of emission, assuming a constant electronic transition dipole moment.

Exact calculations (44, 45) have been done for the one-electron molecules  $H_2^+$  and  $HeH^{++}$  which have one bound state each. Transition probabilities vary smoothly in all cases, but we have noted (2) that the variation of  $R_e^2(\bar{r})$  is greatest for the weaker transitions. A careful review of the available data<sup>1,7,9</sup> indicates that  $R_e^2(\bar{r})$  is likely to be constant within about a factor of two for "allowed" electric dipole transitions ( $\tau \sim 10^{-6}$ – $10^{-9}$  sec) and is likely to be more strongly

<sup>9</sup> The only variation of  $R_e^2(\bar{r})$  which we could find larger than that of the VK system was that for the Schumann-Runge bands of  $O_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$  reported by Hébert and Nicholls (36) who indicate a change by a factor of 25 between  $\bar{r} = 1.44$  Å to  $\bar{r} = 1.76$  Å. This result is particularly interesting not only because of the magnitude of the variation but also the large separation of the equilibrium internuclear distances of the two combining states ( $\Delta r = 0.4$  Å). However, Jarman (37) has recalculated Franck-Condon factors for four of the strongest bands using RKR potentials and finds that the Morse Franck-Condon factors can deviate by as much as 30%. Moreover, the recent reviews by Krindach, Sobolev, and Tunitskii (38) and Marr (38) indicate that the maximum variation for this band system is very small, a factor of two at the most, within the uncertainties of the data, which show considerable scatter.

variable for "weak" electric dipole transitions ( $\tau > 10^{-6}$  sec) over the range of  $r$ -centroid corresponding to significant band intensities. This hypothesis is also in agreement with all the results presented above on intensities of the electronic band systems of  $N_2$  and indicates one direction for new experimental work.

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