The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **72**, 1476 (1980); https://doi.org/10.1063/1.439372

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Einstein *A* coefficients, oscillator strengths and lifetimes for some selected triplet–triplet transitions of N_2:A comparison between theory and experiment

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(Received 21 May 1979; accepted 17 October 1979)

Einstein *A* coefficients, oscillator strengths and lifetimes have been calculated by an asymptotic expansion method, introduced by Chang and Karplus, for the N_2, $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ (first positive), $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ (second positive), $W\,^3\Delta_u \rightleftarrows B\,^3\Pi_g$ (Wu–Benesch) and $B'\,^3\Sigma_u^- \rightarrow B\,^3\Pi_g$ (infrared afterglow) band systems, using theoretical electronic transition moments, $Re(r)$, of Yeager and McKoy. Whenever possible, comparison has been made with those calculated from the electric dipole moment functions, $Re(\bar{r})$, which are functions of $\bar{r}$ centroids, obtained from band intensity or lifetime measurements. Excellent agreement has been obtained in the case of the second positive band system of molecular nitrogen. However, for all other cases, conventional $Re(\bar{r})$ functions are found to be superior to the theoretical $Re(r)$ functions of Yeager and McKoy.

INTRODUCTION

Recently,[1] an expression has been derived for the calculation of band strengths for the Morse and the Morse-Pekeris oscillators when the electronic transition moment $R_e(r)$ can be expressed as

$$R_e(r) = a_0 + a_1 r + a_2 r^2 + \cdots \, . \tag{1}$$

Einstein *A* coefficients $A_{v'v''}$, oscillator strengths $f_{v'v''}$, and lifetimes for the upper vibrational levels $\tau_{v'}$ are related to the band strengths $S_{v'v''}$ by the following equations:

$$A_{v'v''} = 2.026\times 10^{18} S_{v'v''} g_u^{-1} \lambda_{v'v''}^{-3} \, , \tag{2}$$

$$\begin{aligned} f_{v'v''} &= 1.499\times 10^{-16} A_{v'v''} \lambda^2_{v'v''} g_u g_l^{-1} \\ &= 303.6974\; S_{v'v''} \lambda^{-1}_{v'v''} g_l^{-1} \, , \end{aligned} \tag{3}$$

$$\tau_{v'} = \Big(\sum_{v''} A_{v'v''}\Big)^{-1} \, , \tag{4}$$

where $A_{v'v''}$ are in $\sec^{-1}$, $\lambda_{v'v''}$ are in Å, $S_{v'v''}$ are in atomic units, and $\tau_{v'}$ are in sec. g_u and g_l are the degeneracy of the upper and the lower electronic levels, respectively. v' and v'' represent the upper and the lower vibrational levels, respectively. Oscillator strengths $f_{v'v''}$, are dimensionless quantities, often referred to as the numbers of dispersed electrons, or simply f values.

Equations (2)–(4) are often described in different forms in the literature, depending on the units of $S_{v'v''}$ and $\lambda_{v'v''}$. Readers are referred to Benedict and Plyer[2] and Tatum[3] for very useful conversion tables for intensity and transition probability parameters. Band strengths factors, without the vibration–rotation interactions, are given by

$$S_{v'v''} = \left| \int \psi_{v'} R_e(r) \psi_{v''} \, dr \right|^2 \, , \tag{5}$$

where $\psi_{v'}$ and $\psi_{v''}$ are the upper and the lower vibrational wave functions, respectively, and $R_e(r)$ is an average of electronic dipole moment with respect to upper and lower electronic wave functions. Derivation of $R_e(\bar{r})$ from the band intensity study has been explained elsewhere[4–6] and will not be repeated here. Actually, three different methods exist. The first and the most extensively used is one suggested by Turner and Nicholls.[4] The second method was suggested by Pearse,[5(a)] introduced by Seaton,[5(b)] and was improved by Pillow.[5(c)] The third method, called the regression method, was introduced by Jansson and Cunio[6] and appears to replace the former two methods by its advantages and merits. It also appears that the calculation of relative population levels $N_{v'}$ which is the key part of the derivation of the $R_e(\bar{r})$ function existed as early as the works of Tawde and Patankar.[7]

The derived electronic transition moments are fit with $\bar{r}$ centroids,[8] defined as $\bar{r}_{v'v''} = \int \psi_{v'} r \psi_{v''} \, dr / \int \psi_{v'} \psi_{v''} \, dr$, and is called the $R_e(\bar{r})$ function. In some of the literature, the $R_e(\bar{r})$ functions are often written as $R_e(r)$ functions. It is suggested that the electronic transition moment functions derived from the band intensity or lifetime measurements as a function of $\bar{r}$ centroids should clearly be written as $R_e(\bar{r})$ functions in order to avoid confusion with the actual $R_e(r)$ functions. It is granted that the $\bar{r}$ centroids are quantum mechanical averages of r; also, its importance in order to get a first hand idea of the dependence of electronic transition moment with $\bar{r}$ (r centroids) is unquestioned. Benesch *et al.*[9] also gave strong arguments in accepting $\bar{r}_{v'v''}$ as an effective value of r in much the same way as $\lambda_{v'v''}$ is the effective wavelength of any transition. Theoretical $R_e(r)$ functions, on the other hand, are not derived from the band intensity or lifetimes measurements. One needs to start with accurate wave functions for the electronic states considered. Lack of accurate molecular wave functions, particularly for the excited states, has always made it difficult to calculate molecular transition probability parameters.

Wolniewicz[10] studied the transition probability parameters of H_2 (B–X; E–X; E, F–B) systems elaborately.

0021-9606/80/031476-06$01.00

TABLE I. Selected transition moment functions for the N_2, triplet–triplet transition.

Transition	Method	$R_e(r)$ and $R_e(\bar{r})$ functions
$B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$	HRPA[a]	$0.7373 - 0.5181r + 0.1065r^2$
	TDA[a]	$0.4977 - 0.1443r - 0.0499r^2$
	This work[b]	$6.9985 - 7.9692\bar{r} + 2.3781\bar{r}^2$
$C\,^3\Pi_u \rightarrow B\,^3\Pi_g$	HRPA[a]	$0.3291 + 2.2010r - 0.9347r^2$
	TDA[a]	$0.3535 + 2.1519r - 0.9332r^2$
	Becker *et al.*[c]	$4.6145 - 2.3534\bar{r}$
	Nicholls[d]	$-14.537 + 33.80\bar{r} - 16.019\bar{r}^2$
$W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$	HRPA[a]	$0.2058 + 0.3334r - 0.2399r^2$
	TDA[a]	$0.6715 - 0.5204r + 0.1299r^2$
$B'\,^3\Sigma_u^- \rightarrow B\,^3\Pi_g$	HRPA[a]	$0.2562 + 0.2431r - 0.2053r^2$
	TDA[a]	$0.2183 + 0.3309r - 0.2561r^2$

[a] Absolute $R_e(r)$ functions obtained by a polynomial regression of data of Yeager and McKoy, Ref. 19.

[b] This study, see text.

[c] From Becker *et al.*, Refs. 30 and 31.

[d] From Nicholls, Ref. 33.

Wave functions used in their study and the method of computation are described in a series of papers by Kolos and Wolniewicz.[11] Huo[12] tried molecular Hartree–Fock wave functions for the calculation of theoretical transition probabilities of NH (A–X, c–a, c–b) and CH (A–X, B–X, C–X) band systems. Henneker and Popkie[13] reviewed briefly the present status of the theoretical calculation of transition probability parameters. They applied the single excited configuration interaction (SECI) method of Cade *et al.*[14] to generate the desired wave functions. Popkie[13(a)] later used multiconfiguration (MC) wave functions of Chan and Davidson[15] for the calculation of electronic transition probabilities for BeH and MgH (A–X) systems. Several methods currently used for the calculation of accurate molecular wave functions can be seen in a review paper by Wahl and Das.[16] Next came the random phase approximation (RPA), the higher random phase approximation (HRPA), and the Tamm–Dancoff approximation (TDA) in the equation of motion (EOM) method introduced by Rowe[17] and applied and developed by McKoy and his colleagues.[18,19]

A comparison between the conventional singly excited configuration interaction (SECI), random phase approximation (RPA), and a quasivariational method was done by Ho, Segal, and Taylor[20] with intermediate neglect of differential overlap, which they applied to polyatomic molecules H_2O, HCHO, CH_2N_2, and HCOOH. They concluded that the conventional SECI method was superior to the RPA method when static properties are calculated. Explanation of all the aforementioned methods and comparison is beyond the scope of this research. Yeager and McKoy,[19] however, were able to give electronic transition moments between the excited electronic states with RPA, HRPA, and TDA methods. In this research, we take their[19] data for the N_2, first positive, second positive, Wu–Benesch, and the infrared afterglow system and fit them with a transition moment $R_e(r)$ expressed in polynomials of r (internuclear distance). Next we apply an asymptotic expansion method already described elsewhere[1,21] and calculate Einstein A coefficients, oscillator strengths, and lifetimes for the band systems of N_2 using different $R_e(r)$ functions obtained by various approximations. We have also calculated the absolute transition probability parameters for some recent $R_e(\bar{r})$ functions obtained experimentally for the same band systems cited earlier.

RESULTS AND DISCUSSIONS

In Table I, we have summarized the absolute $R_e(r)$ and $R_e(\bar{r})$ functions used in this study along with the methods to generate these functions. The absolute $R_e(r)$ for all the systems studied were generated with the data of Ref. 19 by a standard least square fit technique.[22] The $R_e(\bar{r})$ functions were taken from the literature, and were derived either from the recent band intensity or from the lifetime measurements. Unless otherwise stated, all the spectroscopic data were taken from Benesch *et al.*[23] Calculated lifetimes have also been compared with those obtained from recent experimental measurements.

N_2, $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ system

Lifetimes calculated with HRPA and TDA $R_e(r)$ are greater than those of experiment by a factor of 8 to 10. For example, $\tau_{v'=0}(\mathrm{HRPA}) = 74.3$ μsec, $\tau_{v'=0}(\mathrm{TDA}) = 84.8$ μsec, $\tau_{v'=5}(\mathrm{HRPA}) = 38.4$ μsec, $\tau_{v'=5}(\mathrm{TDA}) = 47.1$ μsec; whereas the corresponding experimental values are about 8.0 and 6.2 μsec. Tables of calculated Einstein A coefficients and oscillator strengths are not given here. Franck–Condon factors and r centroids were recalculated by using recent spectroscopic constants.[23] They are in excellent agreement with those reported in Ref. 6. Jansson and Cunio[6] calculated A coefficients using relative $R_e(\bar{r}) = 1.0 - 1.1387\bar{r} + 0.3398\bar{r}^2$. However, the oscillator strength of the 0–0 band f_{00} was calculated with a $R^2_{e\,v'v''}$ dependence $R^2_{e\,v'v''} = R^2_{e\,00}(1 + a_1\bar{r}_{v'v''} + a_2\bar{r}^2_{v'v''})$. The first function was generated using the $\bar{r}$ centroids calculated by them and $(I_{v'v''}, \lambda^4_{v'v''})$ values of Joshi *et al.*,[24] based on the experimental intensity data of Turner and Nicholls[4] and the band head wavelengths of Dieke and Heath.[25]

We, however, calculate the A coefficients and oscillator strengths from the one and the same $R_e(\bar{r})$ function. The new absolute $R_e(\bar{r})$ function can be represented as $R_e(\bar{r}) = 6.9985 - 7.962\bar{r} + 2.3781\bar{r}^2$, which is a good fit for the lifetimes measured by Jeunehomme,[26] and absolute oscillator strength f_{00} measured by Wurster[27] and Bates and Witherspoon.[28] One more point to mention is that by definition oscillator strengths are proportional to the Einstein A coefficients. Therefore, the Einstein A coefficient A_{00} of Jansson and Cunio[6] should give the same oscillator strength f_{00} reported by them, when multiplied by a constant factor. We find that the value of f_{00} should be 2.169×10^{-3} and not 2.190×10^{-3} as reported by them when the conversion factor is taken as 1.499×10^{-16} and λ_{00} is 10 468.5 Å. The value of f_{00} will certainly change a little when the conversion factor and λ_{00} have slightly different values. For example, f_{00} becomes 2.170×10^{-3} when the conversion factor and λ_{00} are taken, respectively, as 1.5×10^{-16} and 10 469.0 Å. Use of λ_{00} given by Herzberg[29] did not improve the result.

TABLE II. Einstein *A* coefficients, oscillator strengths, and lifetimes for the N_2, $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ band system.[a]

	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$\tau_{v'}$ (μsec)
$v'=0$	6.6189 (+4) 2.1748 (−3)	4.0480 (+4) 1.8410 (−3)	1.3645 (+4) 9.0751 (−4)	3.2117 (+3) 3.3811 (−4)	5.4856 (+2) 1.0347 (−4)	6.1930 (+1) 2.6140 (−5)	3.0391 (+0) 4.8436 (−6)	8.1
$v'=1$	8.3965 (+4) 1.9865 (−3)	4.7794 (+2) 1.4846 (−5)	2.0871 (+4) 8.8278 (−4)	1.7879 (+4) 1.0810 (−3)	7.2843 (+3) 6.7409 (−4)	1.9013 (+3) 2.9847 (−4)	3.2512 (+2) 1.0298 (−4)	7.5
$v'=2$	3.8696 (+4) 6.9355 (−4)	5.9157 (+4) 1.3409 (−3)	1.2564 (+4) 3.6958 (−4)	3.0440 (+3) 1.2008 (−4)	1.2472 (+4) 6.8871 (−4)	9.2125 (+3) 7.5546 (−4)	3.6266 (+3) 4.8132 (−4)	7.2
$v'=3$	8.5082 (+3) 1.1998 (−4)	6.7173 (+4) 1.1649 (−3)	2.0920 (+4) 4.5483 (−4)	2.8639 (+4) 7.9915 (−4)	8.0841 (+2) 2.9818 (−5)	4.6049 (+3) 2.3322 (−4)	7.9226 (+3) 5.7982 (−4)	6.9
$v'=4$	9.7637 (+2) 1.1154 (−5)	2.4254 (+4) 3.3347 (−4)	7.2616 (+4) 1.2194 (−3)	1.6042 (+3) 3.3489 (−5)	2.9422 (+4) 7.8000 (−4)	8.2280 (+3) 2.8444 (−4)	2.4766 (+2) 1.1546 (−5)	6.7
$v'=5$	6.0378 (+1) 5.7200 (−7)	3.9165 (+3) 4.3890 (−5)	4.2242 (+4) 5.6654 (−4)	5.9565 (+4) 9.6924 (−4)	2.5464 (+3) 5.1090 (−5)	1.9037 (+4) 4.8018 (−4)	1.5939 (+4) 5.1756 (−4)	6.5
$v'=6$	2.0728 (+0) 1.6605 (−8)	3.1561 (+2) 2.9474 (−6)	9.3386 (+3) 1.0269 (−4)	5.7333 (+4) 7.5041 (−4)	3.8206 (+4) 6.0278 (−4)	1.3903 (+4) 2.6835 (−4)	7.1334 (+3) 1.7142 (−4)	6.4

[a] Calculated using $R_e(\bar{r}) = 6.9985 - 7.9692\bar{r} + 2.3781\bar{r}^2$. The final digit in parentheses indicates the power of 10 to which each entry should be raised: upper entry, Einstein *A* coefficients (sec^{-1}); lower entry, oscillator strengths (dimensionless).

In order to find the cause of this difference, we note that the way we define the band strength has not been defined in the same manner by them. The band strength factors $S_{v'v''}$ are given by

$$S_{v'v''} = \left| \int_0^\infty \Psi_{v'} R_e(r) \Psi_{v''}\, dr \right|^2 ,$$

and in cases when $R_e(r)$ is a slowly varying function of r or when its dependence to r is unknown, $S_{v'v''}$ can be taken as

$$S_{v'v''} = R_e^2 \times q_{v'v''} ,$$

where $q_{v'v''}$ are the well known Franck–Condon factors. With a little bit of algebra, we find that the band strength factors calculated by us can be related to Eq. (14) of Ref. 6 as

$$S_{v'v''} = q_{v'v''}(1.0 - 1.354\bar{r} + 0.4644\bar{r}^2) g_u \times 10^8/202.6K ,$$

where $K = 1.728\times10^5\ \mathrm{cm}^{-3}\,\mathrm{sec}^{-1}$, $\bar{r}$ is in Å, 202.6 and 10^8 are conversion factors (see Ref. 3). Again, the $R_e(\bar{r})$ dependence is different from the $R_e(\bar{r})$ dependence, used for the calculation of Einstein *A* coefficients. There are, therefore, two fundamental differences between our approach and the approach in Ref. 6. Firstly, $R_e(r)$ is the r dependence of the transition moment function which has been taken outside of the integral and, secondly, two different $R_e(\bar{r})$ functions have been used to calculate Einstein *A* coefficients and oscillator strengths.

We, on the other hand, suggest that oscillator strengths as well as the Einstein *A* coefficients should be calculated from the same electronic transition moment function. In this case, these parameters should be calculated from $R_e(\bar{r}) = 6.9985 - 7.9692\bar{r} + 2.3781\bar{r}^2$. Calculated absolute values of these parameters are presented in Table II. They are in excellent agreement with those in Ref. 6. The oscillator strengths are bound to differ a little, because of the reasons discussed earlier. For example, f_{00} calculated by our equation is 2.175×10^{-3} compared to their value of 2.190×10^{-3}. On the other hand, calculated Einstein *A* coefficients and oscillator strengths with the $R_e(r)$ functions obtained by the HRPA and TDA methods of McKoy *et al.* are less than by a factor of 10 to 8 from our values. Consequently, lifetimes are 8 to 10 times higher than those of our values, experimental values of Jeunehomme[26] and those that can be calculated from the Einstein *A* coefficients given by Jansson and Cunio.[6] For this band system, the authors of Ref. 19 calculated $R_e = 0.27$ a.u. at $R = 1.2$ Å and quote the corresponding experimental value to be equal to 0.31 a.u. In our opinion, the experimental value is about 0.86 a.u. [calculated from the $R_e(\bar{r})$ dependence obtained from this study] at $R = 1.2$ Å. It appears that the quoted experimental value at $R = 1.2$ Å in Ref. 19 for this band system was wrongly calculated from one of several $R_e(\bar{r})$ dependence given in Ref. 6. It is noted that the HRPA $R_e(r)$ function gave somewhat lower values of lifetimes than those obtained by the TDA $R_e(r)$. In any case, in our opinion, $R_e(r)$ functions obtained by HRPA and TDA methods failed to give reliable Einstein *A* coefficients, oscillator strengths, and lifetimes for the first positive band system of N_2.

N_2, $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ system

In Tables III and IV, we present the Einstein *A* coefficients, oscillator strengths, and lifetimes for the upper vibrational levels of the above mentioned band system, with the absolute HRPA and TDA $R_e(r)$ functions of Yeager and McKoy.[19] In Table V, the same transition probability parameters are given when calculated with the recent absolute $R_e(\bar{r})$ function of Becker, Engels, and Tartarczyk.[30] Actually, Becker *et al.*[30] gave the absolute $R_e(\bar{r})$ function as 4.79×10^{-18} $(1.0 - 0.51\bar{r})$ in cm esu, which should be read as 11.73×10^{-18} $(1.0 - 0.51\bar{r})$ in cm esu.[31] The latter equation, when converted to atomic units, becomes $4.6145\,(1.0 - 0.51\bar{r})$, and was used to calculate the parameters of

TABLE III. Einstein *A* coefficients, oscillator strengths, and lifetimes for the N_2, $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ band system.[a]

	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$\tau_{v'}$ (nsec)
$v'=0$	1.0911 (+7) 1.8579 (−2)	6.3057 (+6) 1.2086 (−2)	2.2623 (+6) 4.9066 (−3)	6.3618 (+5) 1.5704 (−3)	1.5203 (+5) 4.2993 (−4)	3.1951 (+4) 1.0425 (−4)	5.9745 (+3) 2.2677 (−5)	49.2
$v'=1$	1.1224 (+7) 1.6780 (−2)	8.4005 (+5) 1.4028 (−3)	4.3850 (+6) 8.2166 (−3)	3.2195 (+6) 6.8019 (−3)	1.3822 (+6) 3.3103 (−3)	4.4692 (+5) 1.2205 (−3)	1.1932 (+5) 3.7405 (−4)	46.2
$v'=2$	3.9851 (+6) 5.2894 (−3)	1.0794 (+7) 1.5899 (−2)	2.3152 (+5) 3.7990 (−4)	1.8991 (+6) 3.4859 (−3)	2.9641 (+6) 6.1135 (−3)	1.8629 (+6) 4.3388 (−3)	7.8506 (+5) 2.0761 (−3)	43.7
$v'=3$	5.2718 (+5) 6.2776 (−4)	7.7247 (+6) 1.0150 (−2)	7.7762 (+6) 1.1313 (−2)	1.5566 (+6) 2.5163 (−3)	4.8643 (+5) 8.7711 (−4)	2.1878 (+6) 4.4187 (−3)	1.9937 (+6) 4.5310 (−3)	41.8
$v'=4$	1.6344 (+4) 1.7645 (−5)	1.4013 (+6) 1.6614 (−3)	1.0313 (+7) 1.3468 (−2)	5.0179 (+6) 7.2399 (−3)	2.6218 (+6) 4.1933 (−3)	2.0887 (+4) 3.7167 (−5)	1.3784 (+6) 2.7395 (−3)	40.4
$v'=5$	6.5297 (+1) 6.4647 (−8)	4.1438 (+4) 4.4871 (−5)	2.3406 (+6) 2.7793 (−3)	1.1864 (+7) 1.5491 (−2)	3.1152 (+6) 4.4860 (−3)	3.0578 (+6) 4.8715 (−3)	7.0981 (+4) 1.2554 (−4)	39.7
$v'=6$	3.5530 (+1) 3.2668 (−8)	9.1174 (+2) 9.1383 (−7)	5.5630 (+4) 6.0924 (−5)	3.1152 (+6) 3.7371 (−3)	1.2676 (+7) 1.6701 (−2)	1.9694 (+6) 2.8578 (−3)	3.0012 (+6) 4.8110 (−3)	

[a] Calculated using $R_e(r) = 0.3291 + 2.2010r - 0.9347r^2$ (for explanation, see Tables I and II).

Table V of the text. Lifetimes of several vibrational levels of the $C\,^3\Pi_u$ state of this band have been studied extensively. Earlier studies have been reviewed in Ref. 30. $R_e(\bar{r})$ functions of this band system have also been summarized by Becker *et al.*[30] A list of other $R_e(\bar{r})$ functions of this band system along with those for several other diatomic molecules have been summarized by Kuznetsova, Kuzmenko, Kuzyakov, and Plastinin.[32] Nicholls[33] derived an absolute $R_e(\bar{r})$ function for this band system and calculated Einstein *A* coefficients, oscillator strengths, and absolute band strengths.

Lifetimes calculated by our method using the absolute $R_e(\bar{r})$ function of Nicholls[33] are less than those of experiment by a factor of about 3 (they are not presented here but are available on request). From a comparison of three (Tables III–V) tables, one sees that the absolute transition probability parameters calculated using HRPA $R_e(r)$ function are quite reasonable when compared with experimental values of lifetimes. Lifetimes calculated by both the HRPA $R_e(r)$ and TDA $R_e(r)$ functions are of the same order in magnitude with experiment, although they are higher than the experimental values by approximately 30% and 40%, respectively. Einstein *A* coefficients and oscillator strengths calculated by the absolute $R_e(\bar{r})$ function of Nicholls[33] are approximately three times higher than the values obtained using corrected absolute $R_e(\bar{r})$ function of Becker *et al.*[30,31] Consequently, lifetimes of the $C\,^3\Pi_u$ state of N_2, calculated using the absolute $R_e(\bar{r})$ function of Nicholls,[33] are smaller by approximately a factor of 3. It also appears that the absolute band strengths calculated by Nicholls[33] are in error because of a wrong conversion factor in Eq. (6) of Ref. 33.

However, Einstein *A* coefficients, given by Nicholls, are a good fit to the lifetime $\tau_0(C\,^3\Pi_u, N_2)$, which is 44.5 nsec according to Bennett and Dalby.[34(a)] We repeated our calculations using spectroscopic constants given by Herzberg.[29] The results did not improve. We think that

TABLE IV. Einstein *A* coefficients, oscillator strengths, and lifetimes for the N_2, $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ band system.[a]

	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$\tau_{v'}$ (nsec)
$v'=0$	1.0490 (+7) 1.7860 (−2)	6.0757 (+6) 1.1645 (−2)	2.1838 (+6) 4.7364 (−3)	6.1514 (+5) 1.5185 (−3)	1.4724 (+5) 4.1638 (−4)	3.0994 (+4) 1.0113 (−4)	5.8054 (+3) 2.2035 (−5)	51.2
$v'=1$	1.0762 (+7) 1.6089 (−2)	8.0620 (+5) 1.3463 (−3)	4.2229 (+6) 7.9128 (−3)	3.1066 (+6) 6.5636 (−3)	1.3360 (+6) 3.1997 (−3)	4.3269 (+5) 1.1817 (−3)	1.1571 (+5) 3.6272 (−4)	48.0
$v'=2$	3.8087 (+6) 5.0552 (−3)	1.0342 (+7) 1.5233 (−2)	2.2324 (+5) 3.6630 (−4)	1.8278 (+6) 3.3549 (−3)	2.8591 (+6) 5.8970 (−3)	1.8000 (+6) 4.1925 (−3)	7.5981 (+5) 2.0094 (−3)	45.5
$v'=3$	5.0144 (+5) 5.9710 (−4)	7.3768 (+6) 9.6934 (−3)	7.4428 (+6) 1.0828 (−2)	1.4972 (+6) 2.4203 (−3)	4.6766 (+5) 8.4325 (−4)	2.1095 (+6) 4.2606 (−3)	1.9258 (+6) 4.3768 (−3)	43.6
$v'=4$	1.5375 (+4) 1.6599 (−5)	1.3314 (+3) 1.5786 (−3)	9.8405 (+6) 1.2851 (−2)	4.7967 (+6) 6.9207 (−3)	2.5201 (+6) 4.0307 (−3)	1.9965 (+4) 3.5526 (−5)	1.3286 (+6) 2.6405 (−3)	42.2
$v'=5$	6.5528 (+1) 6.4876 (−8)	3.8833 (+4) 4.2051 (−5)	2.2212 (+6) 2.6375 (−3)	1.1310 (+7) 1.4768 (−2)	2.9727 (+6) 4.2807 (−3)	2.9380 (+6) 4.6808 (−3)	6.8546 (+4) 1.2123 (−4)	41.5
$v'=6$	3.3643 (+1) 3.0932 (−8)	8.9056 (+2) 8.9260 (−7)	5.1831 (+4) 5.6764 (−5)	2.9523 (+6) 3.5417 (−3)	1.2072 (+7) 1.5905 (−2)	1.8748 (+6) 2.7205 (−3)	2.8832 (+6) 4.6218 (−3)	

[a] Calculated using $R_e(r) = 0.3535 + 2.1519r - 0.9332r^2$ (for explanation, see Tables I and II).

TABLE V. Einstein A coefficients, oscillator strengths, and lifetimes for the N_2, $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ band system.[a]

	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$\tau_{v'}$ (nsec)
$v'=0$	1.3791 (+7)	8.7827 (+6)	3.4211 (+6)	1.0372 (+6)	2.6646 (+5)	6.0225 (+4)	1.2161 (+4)	36.5
	2.3482 (−2)	1.6833 (−2)	7.4199 (−3)	2.5604 (−3)	7.3550 (−4)	1.9651 (−4)	4.6160 (−5)	
$v'=1$	1.2583 (+7)	1.0051 (+6)	5.9941 (+6)	4.7952 (+6)	2.2211 (+6)	7.7172 (+5)	2.2132 (+5)	36.2
	1.8810 (−2)	1.6784 (−3)	1.1232 (−2)	1.0131 (−2)	5.3193 (−3)	2.1076 (−3)	6.9379 (−4)	
$v'=2$	3.8618 (+6)	1.1738 (+7)	3.1465 (+5)	2.5421 (+6)	4.3517 (+6)	2.9436 (+6)	1.3371 (+6)	36.0
	5.1256 (−3)	1.7290 (−2)	5.1630 (−4)	4.6660 (−3)	8.9755 (−3)	6.8793 (−3)	3.5362 (−3)	
$v'=3$	4.1129 (+5)	7.2533 (+6)	8.1518 (+6)	1.9659 (+6)	6.3171 (+5)	3.1685 (+6)	3.1225 (+6)	36.2
	4.8975 (−4)	9.5310 (−3)	1.1860 (−2)	3.1780 (−3)	1.1391 (−3)	6.3994 (−3)	7.0964 (−3)	
$v'=4$	7.3666 (+3)	1.0433 (+6)	9.3640 (+6)	5.0168 (+6)	3.2350 (+6)	2.3601 (+4)	1.9708 (+6)	36.7
	7.9534 (−6)	1.2370 (−3)	1.2228 (−2)	7.2383 (−3)	5.1740 (−3)	4.1995 (−5)	3.9168 (−3)	
$v'=5$	2.1513 (+2)	1.5123 (+4)	1.6553 (+6)	1.0391 (+7)	2.9193 (+6)	3.7173 (+6)	1.0030 (+5)	37.9
	2.1298 (−7)	1.6376 (−5)	1.9656 (−3)	1.3568 (−2)	4.2039 (−3)	5.9222 (−3)	1.7739 (−4)	
$v'=6$	1.9760 (+1)	1.5940 (+3)	1.4081 (+4)	2.0798 (+6)	1.0681 (+7)	1.6865 (+6)	3.6157 (+6)	40.2
	1.8168 (−8)	1.5976 (−6)	1.5422 (−5)	2.4950 (−3)	1.4073 (−2)	2.4473 (−3)	5.7960 (−3)	

[a] Calculated using $R_e(\bar{r}) = 4.6145 - 2.3534\bar{r}$ (for explanation, see Tables I and II).

the absolute $R_e(\bar{r})$ function of Nicholls should not be taken seriously, and we shall not reproduce his table of Einstein A coefficients and oscillator strengths. It is worthwhile to mention that the theoretical calculation of Stephenson[35] yielded $\tau_0 = 52.0$ nsec and $f_{00} = 3.3\times10^{-3}$ and Fraser[35] gave a value of 58 nsec (13 nsec with a correction for hybridization). The experimental[34] f value lies between 4.0×10^{-2} and 1.4×10^{-1}. The f_{00} values calculated with HRPA and TDA $R_e(r)$ functions and the absolute $R_e(\bar{r})$ function of Becker *et al.*[30,31] are, respectively, 1.86×10^{-2}, 1.79×10^{-2}, and 2.35×10^{-2}. $\tau_0(C\,^3\Pi_u, N_2)$ obtained by HRPA and TDA $R_e(r)$ agree extremely well with that measured by Bennett and Dalby[34(a)] and calculated by Stephenson.[35]

N_2, $W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$ system

Calculated lifetimes with HRPA and TDA $R_e(r)$ are approximately 16–20 times greater than those reported by Covey, Saum, and Benesch.[36] Spectroscopic constants of the $W\,^3\Delta_u$ state were taken from recently reported constants by Benesch and Saum.[37] The equilibrium internuclear distance for the upper state was taken from Suchard and Melzer.[38] We purposely did not use the spectroscopic constants and the band wavelengths given in Ref. 38 for the fear that they are wrong. We also note that the $\tau_0(N_2, W\,^3\Delta_u)$ given in Ref. 38 is in error. Covey, Saum, and Benesch[36] determined the Einstein A coefficients and lifetimes by measuring the intensity of 0–2 band relative to the 2–4 band of the first positive band system of molecular nitrogen.

We, however, do not repeat their values here. A coefficients calculated by HRPA $R_e(r)$ are smaller than those reported by Covey *et al.*[36] by approximately a factor of 16. Therefore, the lifetimes are greater than those by approximately a factor of 16. On the other hand, experimental A coefficients are 20 times greater than those obtained with TDA $R_e(r)$. Consequently, the lifetimes obtained by TDA $R_e(r)$ are greater by a factor of approximately 20. However, it should be noted that Covey *et al.* calculated transition probability parameters indirectly, from the knowledge of absolute transition probability of the first positive band system. In any case, transition probability parameters calculated using HRPA and TDA $R_e(r)$ show similar trends as reported by Covey *et al.* They are not given here, but are available on request.

N_2, $B'\,^3\Sigma_u^- \rightarrow B\,^3\Pi_g$ system

This transition, often called the Y band system, was first observed by Kistiakowsky and Warneck.[39] Gartner and Thrush[40] studied the kinetic behavior of the $B'\,^3\Sigma_u^-$ state and indirectly derived a value of $(3.7\pm1.5)\times10^4$ sec^{-1} for the Einstein A coefficient of the 0–0 transition, using the A_{24} value of Shemansky and Broadfoot[41] for the first positive band system of molecular nitrogen. They obtained $A_{00} = (4.1\pm1.7)\times10^4$ sec^{-1}, where the A_{24} value of Jansson and Cunio[6] for the first positive system was used. Otherwise, A coefficients for the Y bands are not shown. Earlier Covey, Saum, and Benesch[36] calculated transition probability parameters for the N_2, $W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$ system in a similar fashion. The A_{00} values obtained by HRPA and TDA $R_e(r)$ are, respectively, 5.26×10^3 and 4.93×10^3 sec^{-1}. Full tables are available on request.

CONCLUSIONS

It can be concluded from the above results and discussions that the overall performances of absolute $R_e(r)$ functions obtained by Yeager and McKoy, in calculating absolute transition probability parameters for the triple-triplet transitions of molecular nitrogen, are far from satisfactory. Closest agreement was obtained in the case of the second positive system of nitrogen, theoretical lifetimes being greater than those of experiments by over 30% to 40%. In other cases, theoretical values are quite far from those of experiments, differing by factors of 8 to 20. For all the cases considered here, lifetimes obtained by HRPA $R_e(r)$ function are found to be lower than those obtained by TDA $R_e(r)$ functions. We conclude that the conventional absolute $R_e(\bar{r})$

functions derived from lifetimes measurements or band intensity parameters are superior to HRPA or TDA $R_e(r)$ functions.

We also calculated Franck–Condon factors, r centroids, and band strengths for all the aforementioned bands for larger arrays, where $v', v''=12$. Except for the $W\,^3\Delta_u \rightleftharpoons B\,^3\Pi_g$ band, lifetimes are calculated for the sums $v''=0$ to 12. Transition probability parameters were calculated by asymptotic expansion, which is very simple to use and which gives quite accurate results for a wide range of vibrational quantum numbers. Transition probability parameters will differ very little from our values if a different vibrational model is used. However, that would hardly affect the conclusions of this study. Full arrays of these parameters calculated with HRPA and TDA $R_e(r)$ functions for the B–A, W–B, and B'–B bands along with those obtained with absolute $R_e(\bar{r})$ given by Nicholls for the C–B band are available on request from one of us (B. P. C.).

ACKNOWLEDGMENTS

Research grants obtained from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos (FINEP) are gratefully acknowledged. We are grateful to Professor Edemundo da Rocha Vieira for helpful and encouraging discussions, to Dr. Gautam Bandyopadhyay for sending us needed references, and we thank Mr. F. R. Volcato of the Centro de Processamento de Dados of this University for helping in computations. We also wish to thank Dr. John D. Gaffey, Jr. for reading the manuscript.

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