

On the Lifetime of $N_2 C^3 \pi_u$ State*

JASON A. C. GALLAS**

*Instituto de Física, Universidade Federal do Rio Grande do Sul,
90000 Porto Alegre, RS, Brasil*

Recebido em 10 de Janeiro de 1980

The radiative lifetime of the $N_2 C^3 \pi_u$ electronic state and the absolute transition probabilities for the $N_2 C^3 \pi_u - B^3 \pi_g$ system have been calculated by assuming Morse potentials for the involved electronic states and then evaluating the resulting integrals analytically. The lifetimes are computed using several electronic transition moment functions given in the literature and comparisons are made. The present method of calculation does not involve the usual \bar{r} -centroid approximation, however it is found that, for the $N_2 C^3 \pi_u - B^3 \pi_g$ system studied here, this approximation gives very good results.

O tempo de vida radiativo do estado eletrônico $C^3 \pi_u$ do nitrogênio molecular e as probabilidades absolutas de transição para o sistema $C^3 \pi_u - B^3 \pi_g$ do N_2 foram calculados representando-se os estados eletrônicos através de potenciais de Morse e resolvendo-se as integrais envolvidas analiticamente. Os tempos de vida são calculados usando-se várias funções momento de transição eletrônica disponíveis na literatura e comparados entre si. O presente método de cálculo não envolve a usual aproximação da centróide \bar{r} . Entretanto, observa-se que, para o sistema $N_2 C^3 \pi_u - B^3 \pi_g$ estudado aqui, esta aproximação dá resultados muito bons.

* Part of the paper was presented in the 31st Annual Meeting of the Brazilian Society for the Progress of Science, Fortaleza, Ceará, 1979, July 11-18.

** Present address: Universidade Federal de Santa Catarina, Departamento de Física, Campus da Trindade, 88000 Florianópolis, SC - Brasil.

1. INTRODUCTION

Since the pioneering work of Bennett and Dalby¹ many experiments have been done in order to measure the lifetime of the $C^3\pi_u$ state of molecular nitrogen. These values, obtained under different experimental conditions², vary between 27 and 49 nsec as can be seen e.g. in Table 1 of the paper by Imhof and Read³, which gives a list of references to earlier experiments. In principle, as noted by Loftus and Krupenie in their review paper², the experiment of Imhof and Read³ is the cleanest for determining the lifetimes $\tau_{v,f}$. By using the electron-photon technique they have found³ $\tau_0 = 35.6 \pm 0.5$ nsec, $\tau_1 = 34.9 \pm 1.8$ nsec and $\tau_2 = 34.5 \pm 2.3$ nsec. Recently, Becker, Engels and Tatarczyk⁴, using selective excitation by laser radiation, obtained $\tau_0 = 36.6 \pm 0.5$ nsec and $\tau_4 = 36.51 \pm 0.1$ nsec. The value $\tau_0 = 36.6$ nsec of Becker, Engels and Tatarczyk⁴, coincidentally, is the same recommended value given by Loftus and Krupenie², which was obtained from the weighted average of measurements obtained by several workers².

From the theoretical point of view, the earliest available lifetime calculations seems to be the ones by Stephenson and by Fraser as referred by Imhof and Read³. Stephenson and Fraser have found 52 and 58 nsec respectively. Recently Loftus and Krupenie² rescaled the relative band strengths of Jain and Sahni⁵ using the average value $r_0 = 36.6$ nsec to obtain $\tau_1 = 36.3$ nsec, $\tau_2 = 36.6$ nsec, $\tau_3 = 37.5$ nsec and $\tau_4 = 40.0$ nsec.

In the theoretical calculation of the lifetime as well as the intensity distribution in the electronic spectra of diatomic molecules the most important quantities are the Einstein A coefficients, also known as the electronic-vibrational transition probabilities. To calculate these one needs to know the so-called electronic transition moment function. The electronic transition moment function can be derived from direct lifetime measurements, from the intensity distribution of the second positive bands or from *ab initio* calculations. There are several expressions available in the literature⁴⁻⁸ for the electronic transition moment function connecting the $C^3\pi_u$ and $B^3\pi_g$ electronic states N_2 . Since the available electronic transition moment functions are quite different from each other, we decided to investigate their reli-

ability in predicting the lifetimes of the $N_2C^3\Pi_u$ vibrational states. This was done by calculating the coefficients $A_{v',v''}$, using a recently published method⁹, which will be described in more detail in the next section. The used method allows one to calculate the Einstein A coefficients without the usual \bar{r} -centroid approximation¹⁰. Since the \bar{r} -centroid approximation is commonly used, we also repeated the calculations in this approximation and compared the results.

2. THEORY

The theoretical calculation of the radiative lifetime for the vibrational levels of an excited electronic state of a diatomic molecule is basically the calculation of the probabilities of the electronic-vibrational transition $A_{v',v''}$ (Einstein A coefficient). The lifetime $\tau_{v'}$ of the v' excited level is related to the probabilities by the equation

$$\frac{1}{\tau_{v'}} = \sum_{v''=0}^{v''_{\max}} A_{v',v''} \quad (1)$$

In the Born-Oppenheimer approximation for an electric dipole transition, the probabilities of electronic-vibrational transition are given^{10,11} by

$$A_{v',v''} = \frac{2.026 \cdot 10^{18}}{g_{v'}} \frac{S_{v',v''}}{\lambda_{v',v''}^3} \quad (2)$$

where the $A_{v',v''}$ are in sec^{-1} , the $S_{v',v''}$ are in atomic units and the wavelengths $\lambda_{v',v''}$ are in Angstroms. The factor $g_{v'} = (2 - \delta_{0,\Lambda'}) (2S' + 1)$ is the upper electronic level degeneracy due to the A-type doubling and spin multiplicity. Since $g_{v'}$ is known and the $\lambda_{v',v''}$ are all measured quantities, the problem of calculation of the electronic-vibrational transition probabilities $A_{v',v''}$ reduces to the calculations of the band strength factors

$$S_{v',v''} = \left| \int_0^{\infty} \psi_{v'}^* R_e(r) \psi_{v''} dr \right|^2 \quad (3)$$

where $R_e(r)$ is the electronic transition moment, ψ_v are the vibrational wavefunctions and r is the internuclear separation of the diatomic mo-

lecule. The electronic transition moment $R_e(r)$ appearing in Eq. (3) is usually obtained in two ways: from *ab initio* calculations, or from an analysis of the experimental band intensities using the empirical \bar{r} -centroid method of Fraser¹². The majority of the available $R_e(r)$ functions are given in terms of the \bar{r} -centroid and not in terms of the real internuclear separation. Only now have *ab initio* electronic transition moments, expressed as a function of the internuclear separation, become common in the literature.

For the evaluation of Eq. (3) one needs wavefunctions to describe the vibrational states. There are two types of commonly used wavefunctions to calculate band strengths¹³: the ones obtained by the RKR techniques, and Morse wavefunctions. The profusion of RKR techniques makes the choice of the right one doubtful. Besides that, the recent review work of Kuznetsova *et al.*¹³ shows that results obtained by using RKR and Morse wavefunctions are similar. In the present paper Morse wavefunctions are used. With this the integration in Eq. (3) can be performed analytically. This fact reduces the required computational time by a large amount compared to the RKR techniques.

If the electronic transition moment is represented by

$$R_e(r) = a_0 + a_1 r + a_2 r^2 \quad (4)$$

then the band strength factors are given for the case of no vibration-rotation interactions ($J' = J'' = 0$) by⁹

$$S_{v',v''} = I_{v',v''}^2 \quad (5)$$

where

$$I_{v',v''} = \frac{(-1)^{v'+v''} N_{v'} N_{v''}}{a'} \xi^{(k-1)/2} \times \\ \times \sum_{i=0}^{v'} \sum_{j=0}^{v''} (-1)^{i+j} \xi^{-j} B(b', v', i) B(b'', v'', j) I_j^i(\xi, \gamma, p), \quad (6)$$

$$N_v^2 = \frac{ab}{v! \Gamma(k-v)}, \quad \gamma = \frac{\alpha''}{\alpha'}, \quad \xi = \frac{k''}{(k')^\gamma} \exp(\alpha'' r_e'' - \gamma \alpha' r_e'),$$

$$b = k - 2v - 1, \quad k = \frac{\omega_e}{\omega_e^x}, \quad B(b, v, x) = \binom{v}{x} \frac{\Gamma(b+v+1)}{\Gamma(b+v+1-x)},$$

$$p = (k' + \gamma k'')/2 - (1 + \gamma)/2 - i - \gamma j,$$

$$I_j^i(\xi, \gamma, p) = p^{p+1/2} \left[\frac{\pi}{-b_2} \right]^{1/2} \exp(p g_0) R_e(\rho_0) [1 + (E_0 + E_1)/p], \quad (7)$$

$$E_0 = 3b_4/4b_2^2 - 15b_3^2/16b_2^3, \quad (8)$$

$$E_1 = - \left[a_1 \left(\frac{3b_3}{4b_2} + \frac{1}{4t_0} \right) + a_2 \left(\frac{3b_3 \rho_0}{2b_2} + \frac{\rho_0}{2t_0} + \frac{1}{2a't_0} \right) \right] / \left[a't_0 b_2 R_e(\rho_0) \right], \quad (9)$$

$$\rho_0 = r'_e + \ln [k'/(pt_0)]/a'$$

and all other symbols have the same meaning as in Ref.9. Note that the expressions for E_0 and E_1 in Ref. 9 have been corrected¹⁴.

3. RESULTS AND DISCUSSION

To evaluate Eq. (5) a double precision program in ALGOL has been implemented on a Burroughs B-6700 computer. The inputs of this program are the spectroscopic constants for both electronic states, the reduced mass of the molecule, the electronic weights and the $R_e(r)$ function; the wavelengths, Franck-Condon factors and \bar{r} -centroids are given as output. The program also calculates the band strength factors with and without making use of the \bar{r} -centroid approximation. With these, the Einstein A coefficients are easily obtained, through Eq. (2).

In the present work the spectroscopic constants of Benesch *et al.*¹⁵ are used to describe both electronic states. The wavelengths are calculated using the usual polynomial representation¹⁶ up to the $\omega_e^z z_e$ term. The values agree well with those given by Benesch *et al.*¹⁷ in their Table 3. In principle, the summations indicated in Eq. (1) should be performed over all vibrational levels of the lower electronic state. In practice, however, the summation rule $\sum_{q, v''} = 1$, obeyed by the Franck-

-Condon factors, is used to find the ν''_{\max} value up to which the summation must be performed in order to include all the relevant transitions. We assume $\nu''_{\max} = 9$. The summation of the Franck-Condon factors will be shown later.

Table I summarizes the electronic transition moment functions used in this work to calculate the band strength factors. The $R_e(r)$ functions obtained from experimentally measured band intensities by Jain⁶ and by Hartmann and Johnson⁷ can not be used to calculate the absolute transition probabilities and lifetimes, since they are only relative functions. In order to put them on an absolute scale we have multiplied these $R_e(r)$ functions by a constant factor, k_0 , such that one gets $\tau_0 = 36.6$ nsec for the $\nu' = 0$ level, the value recommended in the review paper of Loftus and Krupenie². These k_0 factors are also given in Table I. In a recent paper Becker, Engels and Tatarczyk⁴ have given the absolute transition moment function as $R_e(\bar{r}) = 4.79 \cdot 10^{-18} (1 - 0.51 \bar{r})$ cm esu. This function should be read¹⁸ as $11.73 \cdot 10^{-18} (1 - 0.51 \bar{r})$ in the same units. The k_0 factor listed in Table I for this $R_e(\bar{r})$ function is the one needed to express the last $R_e(\bar{r})$ expression in atomic units. All the aforementioned functions are given in terms of the \bar{r} -centroid variable.

Recently Yeager and McKoy⁸, have derived the electronic transition moments between the excited states of molecular nitrogen using the equations of motion method. In particular, they have calculated the electronic transition moment for the $N_2 C^3\Pi_u - B^3\Pi_g$ transition in terms of the real internuclear separation using three different approximations: the Tamm-Dancoff approximation (TDA), the random phase approximation (RPA) and the higher random phase approximation (HRPA). Yeager and McKoy⁸ believe the HRPA to be the most reliable one. We used HRPA and TDA electronic transition moments to calculate the absolute transition probabilities. Yeager and McKoy⁸ have given the electronic transition moment at 6 points for r between 0.9 and 1.4 Å. These six values are used to get a continuous $R_e(r)$ function in this range by fitting to them a polynomial in the variable r by least-square techniques¹⁹. In both cases the best fit polynomial was found to be of the second degree. The polynomials obtained by least-square fit to the TDA and HRPA values given in Table I of Ref. (17) are (for r in Ångstrom)

Table I - Coefficients of $R_e(r) = k_0(a_0 + a_1r + a_2r^2)$, with $R_e(r)$ given in a.u. for r in Å.

A u t h o r s	Method	k_0	a_1	a_2	a_3
Jain (1972) ⁶ (I)	intensities	16.6489 ^a	-1	1.9583	-0.8602
Jain (1972) ⁶ (II)	intensities	10.3902 ^a	-1	2.1047	-0.9357
Becker, Engels and Tatarczyk (1977) ⁴	lifetime	4.61	1	-0.51	
Hartmann and Johnson (1978) ⁷	intensities	17.732 ^a	1	-1.336	0.487
Yeager and McKoy (1977) ⁸	TDA	1.1822 ^a	0.3535	2.1519	-0.9332
Yeager and McKoy (1977) ⁸	HRPA	1.1598 ^a	0.3291	2.2010	-0.9347

^a Scaling factor to give $\tau_0 = 36.6$ nsec. See text

$$R_e^{\text{TDA}}(x) = 0.3535 + 2.1519x - 0.9332x^2 \text{ a.u.} \quad (10)$$

and

$$R_e^{\text{HRPA}}(x) = 0.3291 + 2.2010x - 0.9347x^2 \text{ a.u.} \quad (11)$$

In Table II we give the Einstein A coefficients calculated with the electronic transition moment given as a function of the \bar{x} -centroid variable. These coefficients show a quite reasonable agreement among themselves. It should be mentioned that since the calculation using the \bar{x} -centroid approximation coincides with the real calculations for a linear electronic transition moment function, the Einstein A coefficients presented for the $\text{BET}^4 R_e(r)$ function are exact. Also these coefficients are in good agreement with the RKR values given in Table 95 of Ref. 2.

Table III gives the absolute transition probabilities calculated with the *ab initio* electronic transition moment of Yeager and McKoy. These values are smaller than the ones given in Table II, a fact which, according to Eq. (1), will result in longer lifetimes. As expected in view of the similarity of Eq. (10) and (11), both arrays are nearly the same, however as stated by Yeager and McKoy⁸ the results obtained with the HRP A $R_e(r)$ function should be considered more reliable.

Finally, in Table IV we give the lifetimes computed from Eq. (1) for $v''_{\text{max}} = 9$ for all the electronic transition moments of Table I. In the first column of Table IV the sum of Franck-Condon factors is given in order to see the fraction of relevant transitions considered in calculating the lifetimes. Since much of the previous work in the calculation of band strengths has been done using the spectroscopic constant of Herzberg, we repeated the lifetime calculations using the aforementioned constants, which are given in Table IV in parenthesis. In order to check the reliability of the \bar{x} -centroid approximation, we also calculated the \bar{x} -centroids and used the approximate equation¹⁰

$$S_{v',v''} = \left[R_e(\bar{x}_{v',v''}) \right]^2 q_{v',v''}$$

where $q_{v',v''}$ are the Franck-Condon factors, to compute the $A_{v',v''}$ coefficients and lifetimes. These results are almost the same as the ones obtained without using the \bar{x} -centroid approximation, and for this reason

Table II - Absolute transition probabilities (in sec^{-1}) for the $N_2 C^3\Pi_u - B^3\Pi_g$ band system.

$R_e (P)$	v'	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$v''=7$	$v''=8$	$v''=9$
Jain (1972) ¹⁴ I	0	1.4270+7 ^a	8.7471+6	3.1755+6	8.7886+5	2.0204+5	3.9900+4	6.8089+3	9.9457+2	1.1345+2	8.7214+0
	1	1.3666+7	9.0592+5	5.8998+6	4.4705+6	1.9067+6	5.9741+5	1.5104+5	3.1910+4	5.6335+3	7.9942+2
	2	4.1205+6	1.2340+7	4.6081+5	2.4253+6	4.0647+6	2.5690+6	1.0575+6	3.3230+5	8.4801+4	1.7872+4
Jain (1972) ¹⁴ II	0	1.4301+7	8.6926+6	3.1758+6	8.9223+5	2.0991+5	4.2820+4	7.6459+3	1.1817+3	1.5182+2	1.4576+1
	1	1.3841+7	9.6474+5	5.9126+6	4.4797+6	1.9337+6	6.1842+5	1.6103+5	3.5449+4	6.6409+3	1.0347+2
	2	4.3498+6	1.2743+7	4.0808+5	2.4712+6	4.0890+6	2.6052+6	1.0918+6	3.5238+5	9.3360+4	2.0756+4
Becker, Engels and Tatarczyk (1977) ¹	0	1.3784+7	8.7773+6	3.4188+6	1.0365+6	2.6633+5	6.0226+4	1.2173+4	2.2013+3	3.5125+2	4.7684+1
	1	1.2584+7	1.0052+6	5.9941+6	4.7953+6	2.2216+6	7.7225+5	2.2167+5	5.4823+4	1.1877+4	2.2493+3
	2	3.8755+6	1.1781+7	3.1577+5	2.5521+6	4.3704+6	2.9682+6	1.3453+6	4.7615+5	1.4077+5	3.5829+4
Hartmann and Johnson (1978) ¹⁵	0	1.3345+7	8.8006+6	3.6023+6	1.1561+6	3.1618+5	7.6515+4	1.6669+4	3.2831+3	5.8059+2	9.0206+1
	1	1.1644+7	1.0482+6	3.0407+6	5.0341+6	2.4586+5	9.0693+5	2.7782+5	7.3814+4	1.7342+4	3.6155+3
	2	3.5616+6	1.1108+7	2.4191+5	2.6182+6	4.5867+6	3.2661+6	1.5656+6	5.8967+5	1.8672+5	5.1334+4

^a 1.4270 + 7 means 1.4270×10^7 .

Table III - Absolute transition probabilities (in sec^{-1}) for the $N_2 C^3\Pi_u - B^3\Pi_g$ band system, calculated with electronic transition moment from Yeager and McKoy⁸

	v'	$v'' = 0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$	$v''=7$	$v''=8$	$v''=9$
TDA ^a	0	1.0490+7 ^c	6.0757+6	2.1839+6	6.1523+5	1.4730+5	3.1023+4	5.8167+3	9.6675+2	1.3915+2	1.6365+1
	1	1.0768+7	8.0664+5	4.2255+5	3.1089+6	1.3374+6	4.3336+5	1.1600+5	2.6670+4	5.3306+3	9.1712+2
	2	3.8229+6	1.0382+7	2.2417+5	1.8360+6	2.8734+6	1.8104+6	7.6506+5	2.5278+5	6.9612+4	1.6399+4
	3	5.0828+5	7.4826+6	7.5553+6	1.5212+6	4.7566+5	2.1486+6	1.9651+6	1.0579+6	4.2228+5	1.3675+5
	4	1.5924+4	1.3813+6	1.0228+7	4.9957+6	2.6308+6	2.0899+4	1.3952+6	1.8851+6	1.2731+6	6.0385+5
	5	7.0600+1	4.1980+4	2.4100+6	1.2320+7	3.2525+6	3.2305+6	7.5794+4	8.0578+5	1.6848+6	1.4133+6
HRPA ^b	0	1.0911+7	6.3058+6	2.2624+6	6.3627+5	1.5209+5	3.1981+4	5.9862+3	9.9301+2	1.4258+2	1.6711+1
	1	1.1230+7	8.4050+5	4.3877+6	3.2219+6	1.3826+6	4.4761+5	1.1962+5	2.7458+4	5.4781+3	9.4041+2
	2	4.0000+6	1.0837+7	2.3249+5	1.9077+6	2.9789+6	1.8735+6	7.9048+5	2.6077+5	7.1697+4	1.6861+4
	3	5.3437+5	7.8354+6	7.8937+6	1.5815+6	4.9476+5	2.2283+6	2.0343+6	1.0934+6	4.3576+5	1.4090+5
	4	1.6928+4	1.4538+6	1.0719+7	5.2262+6	2.7369+6	2.1864+4	1.4476+6	1.9520+6	1.3162+6	6.2331+5
	5	7.0352+1	4.4797+4	2.5396+6	1.2924+7	3.4085+6	3.3621+6	7.8487+4	8.2628+5	1.7451+6	1.4615+6

^a Calculated using Eq. (10). ^b Calculated using Eq. (11). ^c 1.0490 + 7 means 1.049×10^7

Table IV - Lifetimes (in sec) for the N_2 $\sigma^3\pi$ vibrational levels.

v'	$\sum_{v''=0}^q q_{v'v''}$	Jain 72 ^a	Jain 72 ^a	BET 77	HJ 78 ^a	YM 77 ^a	YM 77 ^a	YM 77 ^b	YM 77 ^c	EXPERIMENT	
		I	II			TDA	HRPA	TDA	HRPA		
0	1.000	36.60 ^d (36.86) ^e	36.60(36.85)	36.55(36.70)	36.60(36.66)	36.60(36.90)	36.60(36.91)	51.15(51.57)	49.24(49.65)	36.6	0.5 ^f
1	1.000	36.19(36.72)	35.77(36.33)	36.15(36.53)	36.36(36.60)	34.34(35.04)	34.31(35.01)	48.01(48.97)	46.16(47.09)	36.8	1.0 ^g
2	0.999	36.40(37.14)	35.43(36.24)	35.89(36.57)	36.00(36.58)	32.44(33.50)	32.36(33.43)	45.35(46.82)	43.54(44.97)	37.0	1.8 ^g
3	0.992	37.14(38.30)	35.45(36.77)	35.73(37.09)	35.53(36.94)	30.74(32.39)	30.62(32.28)	42.97(45.27)	41.20(43.42)	34.5	1.9 ^h
4	0.961	38.60(41.03)	35.99(38.62)	35.93(39.02)	35.29(38.77)	29.29(32.12)	29.13(31.96)	40.93(44.90)	39.19(43.00)	36.5	1.0 ^f

^a Calculated with $R_e(x) = k_0(\alpha_0 + \alpha_1x + \alpha_2x^2)$, as given in Table I. ^b Calculated with Eq.(10). ^c Calculated with Eq.(11). ^d Values calculated using spectroscopic constants of Benesch *et al.*¹⁵. ^e Values calculated using spectroscopic constants of Herzberg²⁰. ^f From Ref. 4. ^g From Ref. 21. ^h From Ref. 22.

are not repeated here. A detailed computer print out with all results is available from the author on request.

As can be seen in Table IV the lifetimes obtained from the $R_e(r)$ functions of Table I show quite different behaviors: whereas the function labeled Jain 72 (1) predicts increasing values with the quantum number v' , the ones reported by Yeager and McKoy (TDA and HRP) show decreasing behavior. Also, one can see that the lifetimes are affected by changing the spectroscopic constants. The situation is extreme for the lifetimes calculated with the $R_e(r)$ functions of Jain 72 (11), Ref. 4 and Ref. 7: when using the spectroscopic constants of Benesch et al., the lifetime is predicted to decrease with increasing vibrational level whereas when using the older Herzberg constants the reverse is true. The last two columns of Table IV labeled TDA and HRP) show the lifetimes obtained using the electronic transition moments given by Eqs. (10) and (11) respectively. These values seem to be too high when compared with the presently accepted experimental values of the vibrational lifetimes of the $C^3\Pi_u$ state. However, it is worth mentioning that the existing experimental values of the lifetime cover a quite large range and that usually the range for single lifetimes do not overlap within the limit of error as can be seen, e.g., in Table 1 of Ref. 4.

4. CONCLUSIONS

In the present paper the Einstein A coefficients for the $N_2 C^3\Pi_u - B^3\Pi_g$ system and the vibrational lifetimes of the $C^3\Pi_u$ state are calculated. This is done by representing the involved electronic states by Morse potentials, which allows one to analytically compute the needed band strength factors, using electronic transition moment functions available in the literature. In general the lifetimes calculated with different $R(r)$ functions show some discrepancies among themselves, which are, however, within the experimental uncertainties. We also calculate the lifetimes using the *ab initio* TDA and HRP) electronic transition moment functions of Yeager and McKoy and which seem to be too high by approximately a factor of 1.18 and 1.16, respectively. This conclusion is based on the experimental lifetime of the ground vibrati-

onal level using $\tau_0 = 36.6$ nsec. We repeated all the above calculations using the usual \bar{x} -centroid approach and found this approach to be fully justified in the present case which uses up to second order polynomial $R_e(x)$ functions.

The author thanks Dr. John D. Gaffey, Jr. for critically reading the manuscript and the computer center of UFRGS for granting computer time. This work was partially supported by the Brazilian agencies CNPq and FINEP.

REFERENCES

1. R.G. Bennett and F.W. Dalby, *J. Chem. Phys.* **31**, 434-41 (1959).
2. A. Loftus and P.H. Krupenie, *J. Phys. Chem. Ref. Data* **6**, 113-307 (1977).
3. R.E. Imhof and F.H. Read, *J. Phys. B* **4**, 1063-69 (1971).
4. K.H. Becker, H. Engels and T. Tatarczyk, *Chem. Phys. Lett.* **51**, 111-5, (1977).
5. D.C. Jain and R.C. Sahni, *J. Quant. Spectrosc. Radiat. Transfer* **7**, 475-82 (1967).
6. D.C. Jain, *J. Quant. Spectrosc. Radiat. Transfer* **12**, 759-62 (1972).
7. G. Hartmann and P.C. Johnson, *J. Phys. B* **11**, 1597-612 (1978).
8. D.L. Yeager and V. McKoy, *J. Chem. Phys.* **67**, 2473-7 (1977).
9. J.A.C. Gallas, H.P. Grieneisen and B.P. Chakraborty, *J. Chem. Phys.* **69**, 612-4 (1978).
10. J.B. Tatum, *Astroph. J. Suppl. Series* **14**, 21-56 (1967).
11. A. Schadee, *J. Quant. Spectrosc. Radiat. Transfer.* **19**, 451-3 (1978).
12. P.A. Fraser, *Can. J. Phys.* **32**, 515-21 (1954).
13. L.A. Kuznetsova, N.E. Kuz'menko, Yu. Ya. Kuzyakov and Yu. A. Plastinin, *Sov. Phys. Usp.* **17**, 405-23 (1974).
14. J.A.C. Gallas, E.R. Francke, H.P. Grieneisen and B.P. Chakraborty, *Astrophys. J.* **229**, 851-5 (1979).
15. W. Benesch, J. Vanderslice, S.G. Tilford and P.G. Wilkinson, *Astrophys. J.* **142**, 1227-40 (1965).

16. G.Herzberg, Molecular Spectra and Molecular Structure, Vol. I, Spectra of Diatomic Molecules (Van Nostrand, New York, 1950), page 151.
17. W.Benesch, J.Vanderslice, S.G.Tilford and P.G.Wilkinson, Astrophys. J. 144, 408-18 (1966).
18. Private Communication between K.H.Becker and B.P.Chakraborty. The author thanks Dr. B.P.Chakraborty for making this result available,
19. P.R.Bevington, Data Reduction and Error Analysis for the Physical Sciences (McGraw-Hill, New York, 1969), page 237.
20. Ref. 16, page 552.
21. A.L.Osherovich and V.N.Gorshkov, Opt.Spectrosc. 41, 92-3 (1976).
22. A.Pochat, M.Doritch and J.Peresse, J.Chim.Phys. 70, 936-40 (1973).