

# Electronic transition moment of the $N_2^+(A^2\Pi_u-X^2\Sigma_g^+)$ system

H. H. Wu\* and D. E. Shemansky\*

Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania 15260  
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The variation of the electronic transition moment of the  $N_2^+ A^2\Pi_u-X^2\Sigma_g^+$  system has been estimated using measured optical emission rates. The variation is nonlinear and may be described by the equation  $R_e(\bar{r})/R_e(1.0) = 33.3[1.00 - 1.80\bar{r} + 0.83\bar{r}^2]$ ,  $1.02 \text{ \AA} \leq \bar{r} \leq 1.14 \text{ \AA}$ . An accurate transition probability table cannot be established due to lack of emission rate data in the near infrared. The variation of  $R_e(\bar{r})$  cannot be obtained from lifetime measurements of the  $A^2\Pi_u$  state.

## INTRODUCTION

The  $N_2^+(A^2\Pi_u-X^2\Sigma_g^+)$  Meinel system ( $N_2^+M$ ) has been actively studied in recent years. This is possibly partly due to the peculiar behavior of the system in laboratory experiments, but perhaps mostly due to the fact that most ionizing transitions by photons and electrons impacting on  $N_2X$  enter the  $N_2^+A^2\Pi_u$  state.<sup>1,2</sup> The position of the  $N_2^+A^2\Pi_u$  potential curve relative to  $N_2X$  is such that the excited molecules are populated in a well developed vibrational distribution. In the upper atmosphere this is the dominant factor determining the distribution of energy in the  $N_2^+X$  state, and is thus a factor of importance to ionospheric physics.

There has been much disagreement among published measurements of both the extrinsic and intrinsic properties of the  $N_2^+A^2\Pi_u$  state.<sup>1-4</sup> Most of the difficulty appears to stem from the relatively small transition probabilities of the  $N_2^+M$  system. The particular property of the transition that we wish to discuss in this article is the dependence of the electronic transition moment,  $R_e(\bar{r})$ , on mean internuclear distance ( $r$ -centroid,  $\bar{r}$ ),<sup>5</sup> since this has been the most uncertain factor in the determination of the distribution of transition probabilities. We also discuss the relative merits of the methods of calculating  $R_e(\bar{r})$  in general. It appears that the method in this particular case may be a source of discrepancy among recent estimates of the  $R_e(\bar{r})$  variation. The discussion which follows is confined only to the variation of  $R_e(\bar{r})$ . We discuss absolute values in a following article.<sup>6</sup>

The variation of  $R_e(\bar{r})$  can be estimated from experimental data directly by emission or absorption measurements of the bands, or indirectly through measurements of the lifetimes of the upper state vibrational levels. Published estimates of  $R_e(\bar{r})$  for  $N_2^+M$ , have been gathered together and discussed in the recent Ref. 4 article. The remarkable feature in the comparison of the curves is that all of the  $R_e^2(\bar{r})$  estimates obtained from relative emission rates in the laboratory and auroral experiments display a positive slope in the  $1.08 \text{ \AA} < \bar{r} < 1.15 \text{ \AA}$  region, whereas the estimates from lifetime measurements calculated by Ref. 4 display a negative slope. The two sets of curves are thus distinctly different, and Ref. 4 has suggested that the latter should be accepted on the argument that  $R_e(\bar{r})$  must approach zero in the separate atom limit.

An analysis of recent careful measurements of the  $N_2^+M$  system in emission presented in this article, in

combination with other intensity measurements in the literature has produced a new measure of the variation of  $R_e^2(\bar{r})$ . The results do not differ significantly with earlier estimates using the same method in the  $1.08 \text{ \AA} < \bar{r} < 1.14 \text{ \AA}$  region. However, in the region,  $\bar{r} < 1.08 \text{ \AA}$ , where band emission rates are weak and generally ignored,  $R_e^2(\bar{r})$  takes on a negative slope.

The new results are thus nonlinear in  $\bar{r}$  and remain distinctly different from the estimate<sup>4</sup> based on lifetime measurements. We suggest in the discussion below that the new curve is unlikely to be far wrong. On the other hand there are uncertainties associated with computations of  $R_e(\bar{r})$  using lifetime measurements that render the method dangerous to apply in general and to the  $N_2^+M$  system in particular.

## THEORY

The transition probability of a band ( $A_{v',v''}$ ) can be determined through the relation

$$A_{v',v''} = \nu_{v',v''}^3 q_{v',v''} R_e^2(\bar{r}), \quad (1)$$

where  $\nu_{v',v''}$  is the wavenumber of the transition and  $q_{v',v''}$  the Franck-Condon factor. The calculation of  $A_{v',v''}$  through Eq. (1) has undergone much discussion in the literature and has been most recently reviewed in Ref. 4. One can define a single valued  $A_{v',v''}$  for a given  $v'$ ,  $v''$ , except in the case of some forbidden transitions (cf. Ref. 7).

The volume emission rate ( $I_{v',v''}$ ) of a band can be related to  $A_{v',v''}$  through the equation

$$I_{v',v''} = N_{v'} A_{v',v''}, \quad (2)$$

where  $N_{v'}$  is the population density of level  $v'$ .

The determination of relative  $A_{v',v''}$  values from emission rate measurements thus requires either some method of determining  $N_{v'}$  or sets of observations of more than one band in  $v''$  progressions. In practice one must nearly always make use of sets of measurements in  $v''$  progressions to eliminate the effects of an unknown distribution in  $N_{v'}$ . One may thus relate values of  $R_e(\bar{r})$  by the equation

$$\frac{R_e^2(\bar{r}_1)}{R_e^2(\bar{r}_2)} = \frac{I_{v',v_1}}{I_{v',v_2}} \frac{\nu_{v',v_2}^3 q_{v',v_2}}{\nu_{v',v_1}^3 q_{v',v_1}}, \quad (3)$$

where  $v' = v$  is a common upper state vibrational level, and  $v'' = v_1, v_2$  are differing lower state vibrational levels. Relative values of  $R_e(\bar{r})$  calculated in this manner are clearly independent of the production and deactiva-

tion modes of the excited state, spacial distribution of  $N_{v'}$ , and distribution of  $N_{v''}$  as a function of  $v'$ , provided the measurements of  $I_{v',v''}$  are not affected by resonance absorption. The variation of  $R_e(\bar{\nu})$  can be determined from Eq. (3) by iterative adjustment of assumed straight line segments as discussed in detail by Ref. 8. The data can then be fitted with a suitable analytic function. Alternatively one can assume a suitably high order polynomial dependence on  $\bar{\nu}$  and compute the parameters immediately. The latter method is applied in the analysis presented in this article.

The variation of  $R_e(\bar{\nu})$  can be calculated indirectly from lifetime measurements, since one can write

$$A_{v'} = 1/\tau_{v'} = \sum_{v''} A_{v',v''} = \sum_{v''} \nu_{v',v''}^3 q_{v',v''} R_e^2(\bar{\nu}), \quad (4)$$

where  $\tau_{v'}$  is the lifetime of level  $v'$ .

The solution requires that an analytic form be assumed for  $R_e^2(\bar{\nu})$ . A polynomial appears to be the most convenient form, and the solution can be exact if the number of parameters is chosen equal to the number of measured levels. However, in practice, using the upper limit in the number of parameters is generally not possible, since one would require lifetimes of impossibly high accuracy to avoid oscillations or negative values in  $R_e^2(\bar{\nu})$  due to noise in the data. The reason for this is that there is usually a substantial overlap of the  $R_e^2(\bar{\nu})$  function determining the distribution of  $A_{v'}$  values. A reasonably uniform distribution in the magnitudes of  $\nu_{v',v''}^3 q_{v',v''}$  could thus clearly result in very large oscillations in  $R_e^2(\bar{\nu})$  as a consequence of relatively small errors in lifetime measurement. Under these circumstances Eq. (4), with a given set of  $A_{v'}$  and  $\nu_{v',v''}^3 q_{v',v''}$  values, may provide several very different solutions for  $R_e^2(\bar{\nu})$  depending on the assumed number of parameters. It is even possible in some cases to obtain different linear functions in  $\bar{\nu}$  as equally valid solutions to the lifetime distributions. It is therefore generally necessary to obtain supporting band emission rate measurements, or to demonstrate that the resulting  $R_e(\bar{\nu})$  is essentially independent of the order of the assumed polynomial in the particular case.

## EXPERIMENTAL

Spectra of the  $N_2^+M$  transition were obtained using the laboratory system described by Ref. 9. The excitation source was an electrostatically focussed, differentially pumped, electron gun. Research grade  $N_2$  was excited by  $\sim 80$  eV electrons in a cylindrical stainless steel collision chamber of 20 cm length and 30 cm diameter. The chamber was evacuated with an ion pump system.

Spectra were observed with a  $\frac{3}{4}$  m Czerny-Turner Spex Industries vacuum spectrometer. The detector used for most of the observations was a cooled RCA C31034A photomultiplier tube. Observations longward of 8900 Å were obtained with a cooled ITT F4027 tube with S-1 type response. The data was gathered by counting pulses directly from the tubes with a computer controlled observational system.<sup>9</sup> The signal was integrated at a given grating position with a counter op-

erated in frequency mode. Compensation for instabilities in excitation rates was automatic; the emission rate of a selected band was monitored with a filter photometer, and the spectrometer signal was recorded as a ratio with the photometer signal. The noise background was also automatically measured, with the electron beam suppressed, and subtracted from the signal. The noise rate was not measureably different from dark noise of the tubes and had no dependence on grating position.

Chamber pressure was measured and controlled using an MKS Baratron capacitance manometer as transducer. Pressure was maintained within specified tolerances with a servo system connected to a computer interrupt facility. The observations were made at pressures of 1 mTorr–20 mTorr.

The spectra were placed on a uniform differential brightness scale through calibration with a standard tungsten ribbon lamp calibrated by the National Bureau of Standards.

## RESULTS

Spectra were obtained in the 5500 Å–10 000 Å region at resolutions of 10 and 20 Å. The  $N_2^+M$  spectrum is blended with  $N_2$  first positive (1P) emission and atomic lines to the extent that, for an accurate analysis, synthesized spectra must be used to separate the transitions. Figure 1(a) shows a spectrum obtained at 10 Å resolution. In an ordinary discharge in which low energy electrons abound, the  $N_2$ 1P system tends to dominate the spectrum, and is the main reason for the late discovery of the  $N_2^+M$  system. The present experimental apparatus tends to suppress scattered electrons and the  $N_2$ 1P bands are relatively weak.

The spectra were reduced to obtain relative band intensities by first placing the spectra on a uniform differential brightness scale through calibration with the standard source. Synthesized spectra of the  $N_2$ 1P system were then subtracted from the experimental spectra using a similar method to that described by Ref. 10. Bands of the  $N_2$ 1P system can be accurately synthesized as demonstrated by Ref. 11. Figure 1(b) shows the spectrum of Fig. 1(a) after subtraction of the  $N_2$ 1P system. The  $N_2^+M$  bands were then separated from the atomic lines and background emission by comparison with synthetic  $N_2^+M$  spectra. Figure 1(b) shows a superposed synthetic spectrum. The accuracy of synthesizing bands of the  $N_2^+M$  system is demonstrated in Fig. 2, which shows a comparison of experimental and calculated spectra at 2 Å resolution.

Table I shows the relative  $R_e(\bar{\nu})$  values normalized within each progression, calculated from the measured intensities and the Ref. 12 Franck-Condon factors. The table includes values calculated from previously published measurements.<sup>2,10,13,14</sup> The Ref. 2 data are regarded as particularly good as a result of an experimental method that eliminated emission from the neutral species. The Ref. 14 data are from auroral measurements which had been used previously by Nicholls<sup>15</sup> to establish the first estimate of  $N_2^+M$   $R_e(\bar{\nu})$  variation.

The averaged data given in the table, which includes the Ref. 15 value, was used to calculate the  $R_e(\bar{r})$  variation shown in Fig. 3. The red and infrared data including the auroral measurements all indicate a positive slope for  $R_e(\bar{r})$ . All of the previous estimates of the  $R_e(\bar{r})$  variation were based on the red and infrared data. Hence the consistent results from the emission rate measurements, as compiled and discussed in Ref. 4.

The curve drawn through the plotted points in Fig. 3 was calculated as a best fit function, second order in  $\bar{r}$ . The normalized result can be written as

$$R_e(\bar{r})/R_e(1.0) = 33.3(1.00 - 1.80\bar{r} + 0.83\bar{r}^2),$$

$$1.02 \text{ \AA} < \bar{r} < 1.14 \text{ \AA} . \quad (5)$$

A very similar result can be obtained by assuming a reciprocal dependence on  $\bar{r}$ ,

$$R_e(\bar{r})/R_e(1.0) = 29.41(1.00 - 2.104(\bar{r})^{-1} + 1.138(\bar{r})^{-2}),$$

$$1.02 \text{ \AA} < \bar{r} < 1.14 \text{ \AA} . \quad (6)$$

Equations (5) and (6) are designed to give three figure

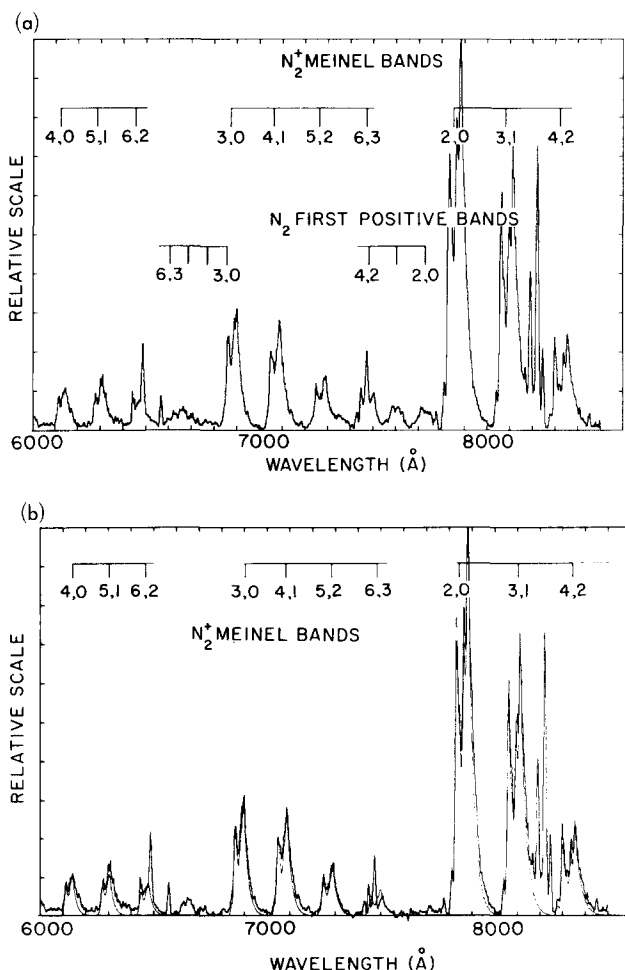


FIG. 1. (a) Experimental spectrum of the  $N_2$  first positive and  $N_2^+$  Meinel systems.  $P=1$  mTorr,  $E=100$  eV,  $I=20$   $\mu$ A,  $\Delta\lambda=10$   $\text{\AA}$ . (b) Experimental and synthetic spectra of the  $N_2^+$  Meinel system. Light trace: synthetic; Heavy trace: The experimental spectrum in Fig. 1(a), after the subtraction of  $N_2$  first positive system.

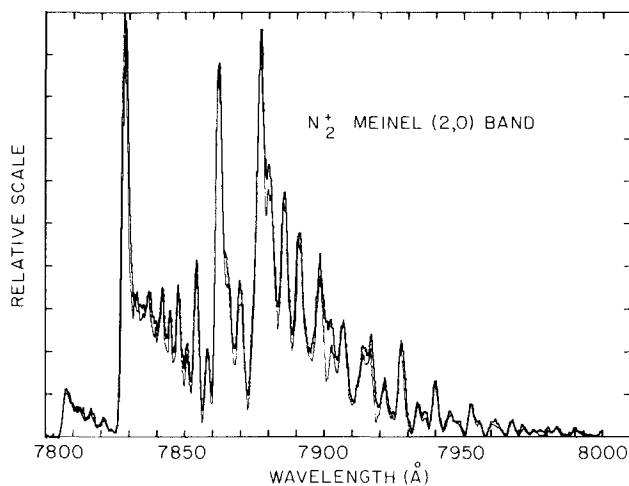


FIG. 2. Experimental and synthetic spectra of the  $N_2^+$  Meinel (2,0) band. Light trace: synthetic; Heavy trace: experimental.  $P=3$  mTorr,  $E=100$  eV,  $I=27$   $\mu$ A,  $\Delta\lambda=2$   $\text{\AA}$ .

accuracy in  $[R_e(\bar{r})]^2$ . An equally similar result is obtained by assuming a third order dependence on  $\bar{r}$ . The inclusion of the shorter wavelength data thus results in a nonlinear  $R_e(\bar{r})$  variation.

## DISCUSSION

The four sets of emission rate measurements used in the calculation of the  $R_e(\bar{r})$  variation shown in Fig. 3 are consistent with one another. Any single set of data would produce a similar curve.

Errors in the independent measurements would thus likely be systematic in nature and common to all of the groups. The method of reduction eliminates any dependence on production and deactivation of the excited levels. Errors could arise from significant resonance absorption of the bands, but the experimental conditions are such that this could not be a serious consideration. Spectral calibration in every case can probably be

TABLE I. Measured relative  $R_e(\bar{r})$  for bands of the  $N_2^+$  Meinel system.

Band	$\bar{r}(\text{\AA})$	$\nu^3 q(\text{cm}^{-3})$	$\lambda(\text{\AA})$	1 <sup>b</sup>	2 <sup>c</sup>	3 <sup>d</sup>	4 <sup>e</sup>	5 <sup>f</sup>	6 <sup>g</sup>
2,0	1.0766	2.6109+11	7853.6	10.0	...	10.0	10.0	...	10.0
2,1	1.1196	2.7823+11	9471.3	10.0	...	11.0	10.4	...	10.35
3,0	1.0460	1.2534+11	6874.4	10.3	11.0	11.0	10.0	8.5	10.37
3,1	1.0845	3.6678+11	8082.9	10.0	10.0	10.0	10.0	10.0	10.0
3,2	1.1311	9.9585+10	9775.5	10.6	...	...	...	...	10.6
4,0	1.0186	5.1539+10	6123.6	13.0	11.8	11.0	...	...	12.11
4,1	1.0535	2.7294+11	7064.5	10.0	10.0	10.0	10.0	10.0	10.0
4,2	1.0930	3.0706+11	8324.1	9.8	9.6	...	10.7	10.5	9.9
5,1	1.0257	1.5309+11	6285.8	12.6	10.6	10.25	10.0	...	11.11
5,2	1.0612	3.4970+11	7263.9	10.0	10.0	10.0	10.0	...	10.0
5,3	1.1027	1.8049+11	8579.1	...	9.1	...	...	...	9.1

<sup>a</sup>Relative values normalized within each  $\nu''$  progression.

<sup>b</sup>Present work.

<sup>c</sup>From Ref. 2 data.

<sup>d</sup>From Ref. 13 data.

<sup>e</sup>From Ref. 10 data.

<sup>f</sup>From Ref. 14 data.

<sup>g</sup>Average, estimated with greater weight placed on Col. 1, 2 data.

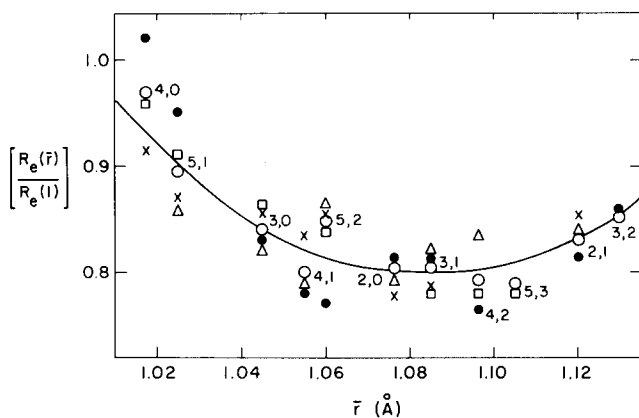


FIG. 3. Electronic transition moment of the  $N_2^+$  Meinel system. ● present result. □ Holland and Maier II (Ref. 2). X Stanton and St. John (Ref. 13). △ Shemansky and Broadfoot (Ref. 10). ○ Averaged, estimated with greater weight placed on ● and □ data.

traced to the National Bureau of Standards. This may result in some common systematic error, but it seems rather doubtful that the uncertainty would be significant compared to direct measurement error. We therefore suggest that the curve shown in Fig. 3 is unlikely to be far wrong.

The variation of Fig. 3 is distinctly different from that calculated from the time-of-flight lifetime measurements.<sup>4</sup> This does not necessarily suggest any large error in the lifetime measurements. The Deslandres matrix of Franck-Condon factors is such as

TABLE II. Calculated and measured damping constants  $N_2^+$  Meinel system.

$v'$	1 <sup>b,c,d</sup>	2 <sup>b,c,e</sup>	3 <sup>b,c,f</sup>	4 <sup>b,c,g</sup>	5 <sup>b,h</sup>	6 <sup>i</sup>
0	5.62 E4	5.88 E4	6.01 E4	7.00 E4	6.03 E4	...
1	7.19 E4	7.19 E4	7.19 E4	7.19 E4	7.20 E4	7.19 ± 0.5 E4
2	8.36 E4	8.33 E4	8.26 E4	7.48 E4	8.31 E4	8.40 ± 0.4 E4
3	9.32 E4	9.35 E4	9.26 E4	7.88 E4	9.35 E4	9.35 ± 0.35 E4
4	1.02 E5	1.02 E5	1.02 E5	8.37 E4	1.03 E5	1.03 ± 0.04 E5
5	1.11 E5	1.10 E5	1.10 E5	8.98 E4	1.13 E5	1.10 ± 0.05 E5
6	1.18 E5	1.17 E5	1.17 E5	9.66 E4	1.21 E5	1.19 ± 0.07 E5
7	1.25 E5	1.22 E5	1.24 E5	1.11 E5	1.30 E5	1.25 ± 0.08 E5
8	1.32 E5	1.27 E5	1.30 E5	1.13 E5	1.37 E5	1.37 ± 0.1 E5
$\kappa_{1-5}^a$	2.7 E-5	8.1 E-6	2.4 E-5	2.4 E-3	7.2 E-5	0
$\kappa_{1-8}^a$	1.1 E-4	4.1 E-4	1.5 E-4	1.4 E-3	4.8 E-5	0

<sup>a</sup>Cross-correlation coefficient  $\kappa = 1 - [\sum X_i Y_i / (\sum X_i^2 \sum Y_i^2)^{1/2}]$ . The  $Y_i$  are measured data of Col. 6 (Ref. 3) in each case.

$\kappa_{1-5}$  refers to cross-correlation of  $v' = 1-5$  values.  $\kappa_{1-8}$  refers to cross-correlation of  $v' = 1-8$  values. Perfect correlation results in  $\kappa = 0$ .

<sup>b</sup>Cols. 1-5 are normalized to the measured data of Col. 6.

<sup>c</sup>Cols. 1-4 calculated using Ref. 12 Franck-Condon factors.

<sup>d</sup>Col. 1:  $R_e^2(\bar{r})/R_e^2(1.0) = 1.756E3[1.03611\bar{r}^4 - 4.14438\bar{r}^3 + 6.17990\bar{r}^2 - 4.07103\bar{r} + 1.0]$ .

<sup>e</sup>Col. 2:  $R_e^2(\bar{r})/R_e^2(1.0) = 2.324E1[-0.92326\bar{r}^2 + 1.9663\bar{r} - 1.0]$ .

<sup>f</sup>Col. 3:  $R_e^2(\bar{r})/R_e^2(1.0) = -5.833[1.1714\bar{r}^2 - 2.3429\bar{r} + 1.0]$ .

<sup>g</sup>Col. 4: Extrapolated Eq. (5).

<sup>h</sup>Col. 5: Calculated by Ref. 4, based on the values of Col. 6.

<sup>i</sup>Col. 6: Measured values Ref. 3. We do not imply acceptance of these values as valid measures of the  $N_2^+M$  damping constants. An ongoing analysis of measurements in this laboratory indicates somewhat larger probabilities,<sup>6</sup> and that the  $A^2\Pi_u$  state may be affected by secondary excitation processes.

to introduce uncertainty in the calculated variation of  $R_e(\bar{r})$ , simply because the calculation involves an operation analogous to the unfolding of integral equations in overlapping regions of  $\bar{r}$ , as discussed above. This is demonstrated in Fig. 4 in which the distinctly different curves labeled 1, 2, and 3 all provide an accurate fit to the lifetime measurements. The curves were calculated using the most accurately measured lifetimes,  $v' = 1-5$ , of the levels, but the results still fit the data through  $v' = 8$ , within the estimated measurement uncertainty.  $R_e^2(\bar{r})$  in curve 1 is fourth order in  $\bar{r}$  and curves 2 and 3 are second order. Curve 4 is a plot of Eq. 5 obtained from the emission rate data and extrapolated beyond  $\bar{r} = 1.14 \text{ \AA}$  for the purpose of comparison. The damping constants ( $A_{v'}$ ) calculated with these functions are shown in Table II and compared with the measured values and Ref. 4 calculation. The  $A_{v'}$  calculated from curves 1, 2, and 3 of Fig. 4 and those of Ref. 4 cross correlate with the measured values with comparable degrees of accuracy as indicated in Table II. In theory it should be possible to produce an exact fit to the  $v' = 1-5$  lifetime data with an  $R_e^2(\bar{r})$  fourth order function. However, in this case it is not possible since the computed result leads to negative values of  $R_e^2(\bar{r})$  for  $\bar{r} \geq 1.06 \text{ \AA}$ . This does not necessarily suggest large errors in lifetime measurement, since the computed result is very sensitive to the relative  $A_{v'}$  values.

From our point of view the curves in Fig. 4 and those of Ref. 4 calculated from the measured lifetimes are equally valid measures of  $R_e(\bar{r})$  variation, provided no reference is made to the emission rate measurements. However, each of the curves provide different emission

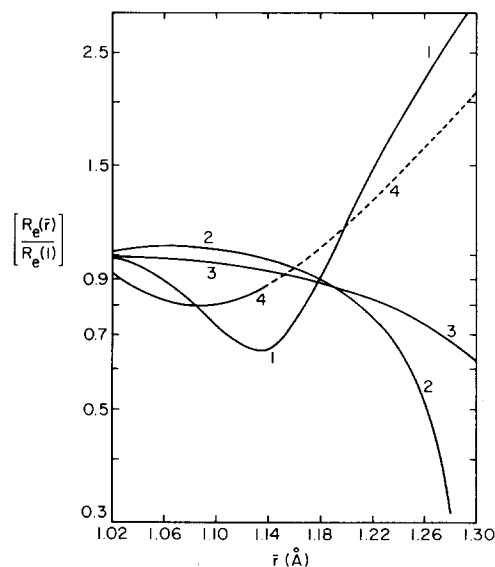


FIG. 4. Variation of  $R_e(\bar{r})$ . Curves 1-3 are calculated from the measured lifetimes<sup>3</sup> of the  $N_2^+ A$  state. These curves are equally valid solutions provided one ignores the measured relative band intensities. Curve 4 is the  $R_e(\bar{r})$  variation, Eq. (5), calculated from the averaged measured relative band intensities, extrapolated to  $\bar{r} = 1.30 \text{ \AA}$ . Curve 1:  $[R_e(\bar{r})/R_e(1.0)]^2 = 1.756E3(1.03611\bar{r}^4 - 4.14438\bar{r}^3 + 6.17990\bar{r}^2 - 4.07103\bar{r} + 1.0)$ , Curve 2:  $[R_e(\bar{r})/R_e(1.0)]^2 = 2.324E1(-0.92326\bar{r}^2 + 1.9663\bar{r} - 1.0)$ , Curve 3:  $[R_e(\bar{r})/R_e(1.0)]^2 = -5.833(1.1714\bar{r}^2 - 2.3429\bar{r} + 1.0)$ .

TABLE III. Measured and calculated relative emission rates of  $N_2^+M$  near infrared bands.

	1 <sup>c</sup>	2 <sup>d</sup>	3 <sup>e</sup>	4 <sup>f</sup>	5 <sup>g</sup>	6 <sup>h</sup>	7 <sup>i</sup>	8 <sup>j</sup>
$I(2, 1)^a$	107	...	128	115	114	98	114	112
$I(2, 0)$	100	...	100	100	100	100	100	100
$I(3, 2)$	85	...	...	...	85	68	92	81
$I(3, 1)$	278	242	244	292	272	254	313	265
$I(3, 0)$	100	100	100	100	100	100	100	100
$\kappa_2^b$	5 E-4	...	1.6 E-3	9 E-6	0	2.8 E-3	0	3.9 E-5
$\kappa_3^b$	3.6 E-5	...	...	...	0	1.1 E-3	9.3 E-4	5.6 E-5

<sup>a</sup>Emission rates, in photon units, are normalized within each  $v''$  progression.

<sup>b</sup>Cross-correlation coefficient, with respect to the Col. 5 values, is defined in Table II.  $\kappa_2$  refers to the  $v'=2$  data set.  $\kappa_3$  refers to the  $v'=3$  data set.

<sup>c</sup>Col. 1: Present data.

<sup>d</sup>Col. 2: Ref. 2 data.

<sup>e</sup>Col. 3: Ref. 13 data.

<sup>f</sup>Col. 4: Ref. 10 data.

<sup>g</sup>Col. 5: Mean of Cols. 1-4.

<sup>h</sup>Col. 6: From Ref. 4 probability tables.

<sup>i</sup>Col. 7: From Ref. 10 probability tables.

<sup>j</sup>Col. 8: Present values calculated with  $R_e(\bar{r})$ , Eq. (5).

rate distributions within the  $v''$  progressions of the system, and only one can be correct. If we follow the argument of Ref. 4, variations in  $R_e(\bar{r})$  such as those represented by curves 1 and 4 of Fig. 4 should be rejected since they suggest  $R_e^2(\bar{r})$  is an increasing quantity as one moves to larger values of  $\bar{r}$ . This argument is based on the premise that states with identical atomic structures in the separate atom limit should have  $R_e^2(\bar{r})$  tending to zero in that limit. However, the  $N_2^+(A^2\Pi_u - X^2\Sigma_g^+)$  transition probabilities are determined at values of  $\bar{r} \lesssim 1.35 \text{ \AA}$ . Larger values of  $\bar{r}$  correspond to the  $N_2^+(X^2\Sigma_g^- - A^2\Pi_u)$  transition, and the measured lifetimes of the  $N_2^+M$  system can therefore refer only to  $R_e(\bar{r})$  variation for  $\bar{r} \lesssim 1.35 \text{ \AA}$ . The value  $\bar{r} = 1.35 \text{ \AA}$  is actually far from the separate atom limit and corresponds to positions on the potential curves about 7 eV below the dissociation limit and  $\sim 1 \text{ eV} - 2 \text{ eV}$  above the potential minima.<sup>16</sup> Thus there is no reason to believe that a variation such as curve 1 of Fig. 4 would not eventually converge to zero in the separate atom limit. In other words it is our opinion that one cannot extrapolate with confidence over such an enormous range of atomic separation on the basis of measurements of a transition that does not occur within the range in question. Thus it appears from this argument that one cannot obtain a unique measure of  $R_e(\bar{r})$  variation for the  $N_2^+M$  system from lifetime measurements alone; there is simply no reasonable means of discrimination among the various solutions. It is clear that one cannot obtain a unique  $R_e(\bar{r})$  variation from lifetime measurements of any system with a reasonably uniform distribution of Franck-Condon factors within the Deslandres matrix.

Direct emission rate measurements thus appear to be the only practical means of determining the  $R_e(\bar{r})$  variation under conditions of the kind described above. Unfortunately the construction of a complete table of transition probabilities cannot be made without extrapolation over the  $1.14 \text{ \AA} < \bar{r} < 1.35 \text{ \AA}$  region, since measurements of progressions beyond  $\lambda = 10\,000 \text{ \AA}$  are not avail-

able. The relative  $A_{v'}$  values calculated with either Eqs. (5) or (6) show a systematic divergence with the quantities obtained from the lifetime measurements (Table II). However it is not certain that this indicates disagreement of the measurements since the shape of the  $R_e(\bar{r})$  curve can be manipulated in the extrapolated region to provide a reasonable fit to the lifetime data.

The transition probabilities calculated in Ref. 4 could not be used satisfactorily for measurements in the  $\lambda > 6800 \text{ \AA}$  spectrum. The divergence with observation in the  $6800 \text{ \AA} < \lambda < 10\,000 \text{ \AA}$  region is not large, but significant, 15%-25%, as indicated in Table III, and the use of such probabilities would lead to uncertainty in the estimation of relative population.

## CONCLUSIONS

The electronic transition moment,  $R_e(\bar{r})$ , of the  $N_2^+M$  system is nonlinear in  $\bar{r}$ , according to emission rate measurements, and has a dependence that may be described by

$$R_e(\bar{r})/R_e(1.0) = 33.3(1.00 - 1.80\bar{r} + 0.83\bar{r}^2) , \\ 1.02 \text{ \AA} \leq \bar{r} \leq 1.14 \text{ \AA} .$$

The range in  $\bar{r}$  over which the calculated  $R_e(\bar{r})$  is valid is too small to allow the calculation of a complete transition probability table. Extrapolation of  $R_e(\bar{r})$  over the necessary range in  $\bar{r}$  leads to a lifetime distribution systematically different from the recent time-of-flight lifetime measurements.<sup>2,3</sup> This does not necessarily imply large errors in the relative lifetime measurements.

Calculation of the  $R_e(\bar{r})$  variation from lifetime measurements of the  $N_2^+(A^2\Pi_u - X^2\Sigma_g^+)$  transition requires impossibly high accuracy in the measured quantities. Calculations with the more recent lifetime measurements do not lead to a unique estimation of  $R_e(\bar{r})$ . The most recently published transition probability table,<sup>4</sup> based on the lifetime measurements, is not consistent

with relative emission rate measurements in the  $\lambda > 6800 \text{ \AA}$  region of the spectrum.

The only practical means of determining the variation of  $R_e(\bar{r})$  for  $1.14 \text{ \AA} < \bar{r} \leq 1.35 \text{ \AA}$  appears to be through emission rate measurements in the near infrared.

Any molecular system of transitions with reasonably well developed  $v''$  progressions, such as the  $N_2^+M$  system, will not lend itself to transition moment analysis through lifetime measurements.

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\*Present address Kitt Peak National Observatory Tucson, AZ 85726. Kitt Peak National Observatory is operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation.

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