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TRANSITION PROBABILITIES FOR THE MEINEL BAND SYSTEM OF N_2^+

D. C. Cartwright

Aerospace Corporation

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Prepared by D. C. CARTWRIGHT
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Laboratory Operations
THE AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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Newly measured natural lifetimes for vibrational levels 1-8 and 10 of the A $^2\Pi_u$ state of N_2^+ have been analyzed by a weighted, non-linear, least squares technique to extract the absolute transition moment and its dependence on internuclear distance. Both are considerably different from previous results and lead to different transition probabilities and oscillator strengths. Transition probabilities for both v' = 0 and 9 are obtained by interpolation of the "electronic" portion of the band strength and result in predicted values for the lifetimes of the v' = 0 and 9 levels.

14 KEY WORDS
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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04701-72-C-0073.

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This report, which documents research carried out from 1 November 1971 through 30 June 1972, was submitted for review and approval on 20 October 1972 to Lt Col Elliott W. Porter, DYX.

Approved

GA Paulikas

G. A. Paulikas, Director
Space Physics Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Elliott W Porter

ELLIOTT W. PORTER, Lt Col, USAF
Asst Dir, Development Directorate
Deputy for Technology

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I. INTRODUCTION

The Meinel band system of N_2^+, $A\,^2\Pi_u - X\,^2\Sigma_g^+$, was first identified in auroral spectra[1] and has since been the subject of numerous studies[2] of auroral emission features because of its strength and possible population by $O^+(^2D)$ charge exchange[2a, 3] with $N_2(X\,^1\Sigma_g^+)$. Accurate measurements of the lifetimes for vibrational levels v' = 2-5 have recently been reported by Holland and Maier[4], for v' = 9 by Maier and Holland,[5] and for levels v' = 1-8 by Peterson and Moseley[6] (preceding paper). There is excellent agreement between the two sets of measurements for those levels which were measured in both experiments. The papers by Holland and Maier,[4] and by Peterson and Moseley[6] contain a discussion of the earlier lifetime measurements and the comparison with their new results. The recent theoretical paper on electronic transition probabilities by Popkie and Henneker[7] contains an excellent bibliography of the other experimental work which has been done on the Meinel band system. However, many of the basic properties relating to the Meinel system such as the population mechanisms and quenching cross sections are still unknown, which makes the interpretation of atmospheric processes involving this N_2^+ system somewhat uncertain.

Most of the previous attempts to extract the internuclear dependence of the band strength[8] of the Meinel system from auroral intensities[9] or laboratory relative intensities[10] have been unsuccessful because of the long lifetimes for the levels of the A-state and the presence of overlapping bands from the N_2 First-Positive band system. Holland and Maier[4] obtained some information about the internuclear dependence over a small wavelength interval from their molecular beam measurements. Popkie and Henneker[7] combined the lifetime measurements of O'Neil and Davidson,[11] and of Hollstein et al,[12] with the intensity measurements of Stanton and St. John[13] to estimate the transition moment dependence on internuclear distance. However, the lifetimes of the levels of the A-state were not well enough known at the time they did their work for them to establish the correct absolute value or the dependence over an extended range in the internuclear distance. Popkie and Henneker also reported *ab initio* calculations of the transition moments[8b] obtained by employing Hartree-Fock wave functions.

In this paper, the new lifetime measurements of Holland and Maier,[4] Maier and Holland[5] and Peterson and Moseley,[6] have been used to extract the transition moment and its dependence on internuclear distance. The data were analyzed by expanding the electronic portion of the molecular dipole strength as a polynomial in the internuclear distance, rather than applying the r-centroid method to the square of the transition moment. This procedure results in a non-linear relationship between the lifetime data and the parameters characterizing the transition moment, but is necessary in order to obtain results which can be compared to theory The resulting band strengths are considerably different from those obtained previously by others. In addition to providing accurate transition probabilities and oscillator strengths for the Meinel band system, these results can be used to obtain reliable values for transition probabilities from levels v' = 0 and 9, and hence their lifetimes, for which no experimental data exists.

II. THEORY

A thorough discussion of the theory of molecular electronic-vibrational transition probabilities is given by Henneker and Popkie[14] in paper I of their series dealing with the calculation of transition probabilities in diatomic molecules, and the relationship of these molecular properties to absolute rotational line intensities is discussed by Tatum[8a] and by Schadee.[15, 16] As the latter authors point out, there have been inconsistencies in some of the previous work with regard to the normalization of the rotational line strength factors. The derivation of the band transition probability from that for the individual rotational lines is therefore summarized below using the normalization recently suggested by Schadee,[16] and the form of the band strength for the case of electronic-vibrational coupling is discussed.

The transition probability describing a spontaneous transition from an upper (Γ') to a lower (Γ'') single rotational state can be written (atomic units) as[14, 16]

$$A_{\Gamma'\Gamma''} = \frac{4e^4}{3c^3 a_o^3 m_e^3} \Delta E^3_{\Gamma'\Gamma''} \frac{\mathcal{S}_{\Gamma'\Gamma''}}{(2J' + 1)} . \qquad (1)$$

In Eq. (1), the energy separation, $\Delta E_{\Gamma'\Gamma''}$, and the line strength, $\mathcal{S}_{\Gamma'\Gamma''}$, are in atomic units.[17] By convention, the upper state quantities are denoted by single prime and those for the lower state by double primes. The quantity a_o is the Bohr radius, and the others have their usual meaning.[17b] Denoting the electronic, vibrational and rotational quantum numbers by n, v and J, respectively, and the spin and parity substates[8a, 16] by Σ and p, then $\mathcal{S}_{\Gamma'\Gamma''}$ is the dipole-length form for the line strength of the transition between single rotational states[16] $\Gamma' \equiv n'v'\Sigma' p'J'$ and $\Gamma'' \equiv n''v''\Sigma'' p''j''$. It is usually a good approximation to neglect the interaction of the rotational motion with the electronic-vibrational motions, in which case the total line strength can be factored into

$$\mathcal{S}_{\Gamma'\Gamma''} = \mathcal{S}^{\Sigma''p''J''}_{\Sigma'p'J'} \frac{\sum_{\Sigma'\Sigma''}\sum_{p'p''}\left|\mathcal{R}^{n''v''\Sigma''p''}_{n'v'\Sigma'p'}\right|^2}{(2-\delta_{0,\bar{\Lambda}})(2S'+1)} \equiv \mathfrak{S}^{\Sigma''p''J''}_{\Sigma'p'J'} \frac{S^{n''v''}_{n'v'}}{(2-\delta_{0,\bar{\Lambda}})(2S'+1)} \quad (2)$$

The first factor on the right-hand side of Eq. (2) is the Hönl-London factor, normalized so that[16]

$$\sum_{J''}\sum_{\Sigma'\Sigma''}\sum_{p'p''} \mathfrak{S}^{\Sigma''p''J''}_{\Sigma'p'J'} = (2-\delta_{0,\bar{\Lambda}})(2S'+1)(2J'+1) \quad . \qquad (3)$$

The symbol $\bar{\Lambda}$ is the least of the quantities Λ' and Λ'' involved in the transition, and has been defined this way to insure that the line strength has the desired properties. If the transition involves a Σ-state, $(2-\delta_{0,\bar{\Lambda}}) = 1$, but it equals 2 for all other transitions. The second factor in Eq. (2) is the electronic-vibrational band strength, summed and averaged over the final and initial degenerate levels, respectively. The degeneracies have been taken to be the parity and spin substates, which is termed by Schaddee[16] the "electronic-vibrational degeneracy concept," in which the transitions are between (nv Σ p) substates, irrespective of the specific rotational transitions involved. The quantity $S^{n''v''}_{n'v'}$, appearing in the second factor in Equation (2), is customarily called the band strength[8a]. Because of the factorization in Equation (2) and the normalization of the Honl-London Factors, the transition probability between two electronic-vibrational states simplifies to[15] (atomic units)

$$A^{n''v''}_{n'v'} = \frac{4e^4}{3c^3 a_o^3 m_e^2} \Delta E^3_{v'v''} \frac{S^{n''v''}_{n'v'}}{(2 - \delta_{0,\Lambda'})(2S' + 1)} \qquad (4)$$

and in cgses units, is

$$A^{n''v''}_{n'v'} = \frac{64\,\pi^4}{3h} \nu^3_{v'v''} \frac{S^{n''v''}_{n'v'}}{(2 - \delta_{0,\Lambda'})(2S' + 1)} , \qquad (5)$$

where $\nu_{v'v''}$ is the energy separation between (n'v') and n"v") in wavenumbers (cm^{-1}). These transition probabilities are independent of the initial rotational state because of the assumption stated earlier of no coupling between the rotational and the electronic-vibrational motions.

The band strength, $S^{n'v''}_{n'v''}$, defined here in Equation (2) to include the summation over the parity and spin substates, is the fundamental quantity that characterizes the electronic-vibrational transition. It can be written in many equivalent forms[14] by using the commutation relations between the position coordinates and their conjugate momenta. The approach employed here, however, utilizes just the dipole-length formulation because that is the form most frequently employed[18] in the interpretation of experimental data.

The natural lifetime, $\tau_{v'}$, of any particular vibrational level, v', of the excited electronic state is related to the decay constant, $A^{n''}_{n'v'}$, by

$$\frac{1}{\tau_{v'}} = A^{n''}_{n'v'} \equiv \sum_{v''} A^{n''v''}_{n'v'} \quad . \tag{6}$$

and the absorption band oscillator strength is given by[16]

$$f^{n''v''}_{n'v'} = \frac{2}{3} \Delta E_{v'v''} \, S^{n''v''}_{n'v'} \qquad \text{(atomic units)} \tag{7}$$

$$= \frac{8\pi^2 m_e}{3he^2} \, \nu_{v'v''} \, \frac{S^{n''v''}_{n'v'}}{(2 - \delta_{0,\Lambda''})(2S'' + 1)} \qquad \text{(cgses units)} \tag{8}$$

The analysis of experimental data to obtain information about the electronic-vibrational interaction has been the subject of a good deal of research the past few years, with the majority of the discussion centered around the use of the r-centroid approximation.[18,19] This approximation was introduced to quantitatively account for the fact that the electronic portion of the transition moment[8b] varies with internuclear distance for many transitions in diatomic molecules. This method of dealing with electronic-vibrational coupling is generally successful[19] from an empirical standpoint, but has been criticized[20] because of its weak theoretical foundation and the difficulty of interpreting the r-centroid as an average internuclear distance. Employing the matrix notation and suppressing the summation over the degenerate substates, the band strength can be written in terms of the transition moment as (cgses units)

$$S_{n'v'}^{n''v''} = \left| \langle v' \| M(R) \| v'' \rangle \right|^2 \tag{9}$$

$$= \left| \langle v'n' \| -\sum_{\ell} e\, \vec{r}_{\ell} \| v''n'' \rangle \right|^2 , \tag{10}$$

where $\vec{r}_{\ell}$ denotes the coordinates of the electrons in a molecular-fixed reference frame, e is the electron charge, and the integration is taken over all electron coordinates, but only the radial coordinates of the nuclei. The customary r-centroid approximation writes Eq. (9) as

$$\begin{aligned} S_{n'v'}^{n''v''} &= (\alpha + \beta r_{v'v''} + \gamma r_{v'v''}^2 + \ldots)^2 q_{v'v''} \\ &= R_e^2 (r_{v'v''})\, q_{v'v''} , \end{aligned} \tag{11}$$

where $q_{v'v''}$ is the Franck-Condon factor[18] and $r_{v'v''}$ is the r-centroid, defined in terms of the internuclear distance by

$$r_{v'v''} = \frac{\langle v' \mid R \mid v'' \rangle}{\langle v' \mid v'' \rangle} . \tag{12}$$

Rather than employing the r-centroid approximation, one may simply expand the electronic portion of the transition moment in Eq. (9) as a power series in the internuclear distance

$$M(R) = \sum_{i=0} a_i R^i , \tag{13}$$

in which case Eq. (9) becomes

$$S_{n'v'}^{n''v''} = \left[a_0 <v'|v''> + a_1 <v'|R|v''> + a_2 <v'|R^2|v''> + \ldots\right]^2 \quad (11)$$

As emphasized by Klemsdal,[20e] this latter approach not only is free of the assumptions incorporated into the r-centroid approximation, which have been shown[20] to fail in some cases, but also permits a direct comparison of the obtained transition moment with that predicted by theory.

This approach of utilizing an expansion in terms of matrix elements rather than the r-centroid has been employed by Jain and Sahni[20b, d] and by Popkie and Henneker[7] in their analyses of intensity data to obtain the internuclear dependence of the transition moment, and has also been used in the present analysis of the lifetime data.

III. NUMERICAL TECHNIQUES

The extraction of the internuclear distance dependence of the transition moment from lifetime data requires the solution of a nonlinear problem when using either the r-centroid approximation or the matrix approach. This is because the lifetime is related to a sum of transition probabilities, Eq. (6), which are proportional to the square of the transition moment, and hence not linearly related to the unknown coefficients. This is in contrast to intensity data, which are proportional to a single transition probability, and which allow the construction of a linear relationship between the data and the transition moment itself by taking the square root of both sides of the appropriate equation. The method employed in this study to determine the transition moment was the following. Combining Eqs. (14), (5) and (6), the relationship between the lifetime and the transition moment becomes

$$\frac{1}{\tau_{v'}} = \frac{64\pi^4}{3h} \frac{1}{(2-\delta_{0,\Lambda'})(2S'+1)} \sum_{v''} \nu^3_{v'v''} \; x$$

$$\left[a_0 \langle v' | v'' \rangle + a_1 \langle v' | R | v'' \rangle + a_2 \langle v' | R^2 | v'' \rangle + \ldots \right]^2 . \qquad (15)$$

The unknown parameters, a_i, were determined by minimizing the weighted sum of the squares of the residuals, χ^2, defined by[21]

$$\chi^2 = \sum_{j=1}^{N} \left\{ \frac{1}{\sigma_j^2} \left[\frac{1}{\tau_j} - A_j^c \right] \right\} , \qquad (16)$$

where the σ_j are the uncertainties (standard deviations) in the data $(1/\tau_j)$, N is the number of data points, and the A_j^c are the calculated decay constants.

It is noted that because of the inverse relationship between the lifetime and the decay constant, equal uncertainties in all the measured lifetimes become unequal uncertainties in the decay constants and therefore vary from one vibrational level to another.

The solution of the nonlinear equation (15) to obtain the parameters (a_k) from the measured lifetimes was accomplished by using the differential corrector, or linearization procedure.[22] The essence of this method is the Taylor's series expansion of the function which contains the parameters, in the unknown parameters, and the retention of terms through the first derivatives. This approach results in one equation for each unknown parameter, which is still nonlinear in that parameter, but is now linear in the *change* in that parameter. If there are B parameters to be determined, then the resulting equations for the *change* in the parameters can be rearranged[23] into the matrix form

$$\underset{\sim}{C}\ \underset{\sim}{\delta a} = \underset{\sim}{b} \tag{17}$$

or

$$\begin{bmatrix} \sum_{v'} \frac{1}{\sigma_{v'}^2}\left(\frac{\partial A_{v'}}{\partial a_0}\right)^2 & + \cdots + & \sum_{v'} \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_0}\frac{\partial A_{v'}}{\partial a_B} \\ \sum_{v'} \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_0}\frac{\partial A_{v'}}{\partial a_1} & + \cdots + & \sum_{v'} \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_1}\frac{\partial A_{v'}}{\partial a_B} \\ \vdots & & \vdots \\ \sum_{v'} \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_0}\frac{\partial A_{v'}}{\partial a_B} & + \cdots + & \sum_{v'} \frac{1}{\sigma_{v'}^2}\left(\frac{\partial A_{v'}}{\partial a_B}\right)^2 \end{bmatrix} \begin{bmatrix} \delta a_0 \\ \delta a_1 \\ \vdots \\ \delta a_B \end{bmatrix} = \begin{bmatrix} -\sum \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_0} D_{v'} \\ -\sum \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_1} D_{v'} \\ \vdots \\ -\sum \frac{1}{\sigma_{v'}^2}\frac{\partial A_{v'}}{\partial a_B} D_{v'} \end{bmatrix}$$

where $\underset{\sim}{C}$ is a symmetric matrix, $A_{v''}$ is the decay constant for level v'', calculated with the assumed values for the parameters, δa_i is the change in the i^{th} parameter, and $D_{v''} = \frac{1}{\sigma_{v''}}\left[A_{v''} - \frac{1}{\tau_{v''}}\right]$ is the weighted residual calculated for level v'' with the assumed parameters. The solutions of the matrix equation (17) are the changes in the parameters (δa_i), and from these, a new improved estimate for the parameters can be calculated using

$$a_i = a_i + \delta a_i \; (i = 1, \ldots, N) \; . \tag{18}$$

These improved estimates for the parameters can again be inserted into Eq. (17) and the procedure of solving for the change in the parameters repeated until the magnitude of the changes in the parameters has decreased to an acceptably low level. Some care must be exercised in the choosing of the initial guesses for the unknown parameters to insure convergence to the true, rather than a local, minimum in χ^2. It was found that reasonable initial guesses for the nonlinear parameters were obtained by first solving the <u>linear</u> problem formed by expanding the band strength itself (i.e., the <u>square</u> of the transition moment) according to the r-centroid approximation

$$S_{n'v'}^{n''v''} = q_{v'v''}(\alpha_0 + \alpha_1 r_{v'v''}) \; , \tag{19}$$

where $q_{v'v''}$ is the Franck-Condon factor, $r_{v'v''}$ is the r-centroid, and α_0 and α_1 were determined. In this case the unknown parameters (α_i) are linearly related to the data points and can be obtained by a straightforward application of the least squares method. Initial estimates for the unknown parameters (a_i) in the nonlinear problem were obtained from the values of c_0 and c_1 in Eq. (19) according to

$$a_0 = \sqrt{c_0} \quad , \quad a_1 = \frac{c_1}{2\,a_0} \quad , \quad a_2 = 0 \quad . \tag{20}$$

The Franck-Condon factors and r-centroids were calculated numerically[24] from RKR potential energy curves obtained from spectroscopic data on N_2^+ provided by Albritton *et al.*[25] The matrix elements were obtained by making the appropriate modifications in Zare's[24] original programs.

By the use of matrix methods, which return the inverse of the curvature matrix $\underset{\sim}{C}$,

$$\underset{\sim}{\epsilon} = \underset{\sim}{C}^{-1} \quad , \tag{21}$$

where $\underset{\sim}{C}$ is defined by Eq. (17), the uncertainties in each of the parameters a_i due to the uncertainties in the basic data and the quality of the fit can be obtained from[26]

$$\sigma_{a_i} = \epsilon_{ii} \tag{22}$$

IV. RESULTS FOR THE MEINEL SYSTEM OF N_2^+

A. The Transition Moment

The method described in the previous section has been applied to the analysis of the new lifetime measurements of Holland and Maier,[4] of Peterson and Moseley,[6] and of Maier and Holland[5] which include levels $v' = 1$–8 and $v' = 10$. Although the lifetime is the measured quantity, it is the inverse of the lifetime that is directly related to the band strength. Figure 1 summarizes the experimental measurements[27] on the lifetimes for the vibrational levels of the Meinel band system, in which the decay constant (inverse lifetime) is plotted as a function of the vibrational quantum number. Also shown in the figure (right-hand ordinate) is the quantity $\sum_{v''} \nu^3_{v'v''} \, q_{v'v''}$ because some indication as to the variation of the transition moment with internuclear distance can be obtained by comparing this quantity with $1/\tau_{v'}$. That is, if there were no variation of the transition moment with internuclear distance, these two curves would be parallel. This qualitative comparison can be made more quantitative by plotting the ratio of $1/\tau_{v'}$ to $\sum_{v''} \nu^3_{v'v''} \, q_{v'v''}$, as a function of v', as has been done in Fig. 2. As seen from the figure, except for the data of Shemansky and Broadfoot,[10b] this ratio increases with increasing vibrational quantum number (v'). One might expect that those data whose ratio in Fig 2 increases with increasing v' would result in a transition moment with a different functional dependence on R from those which generally decrease. This indeed turns out to be the case.

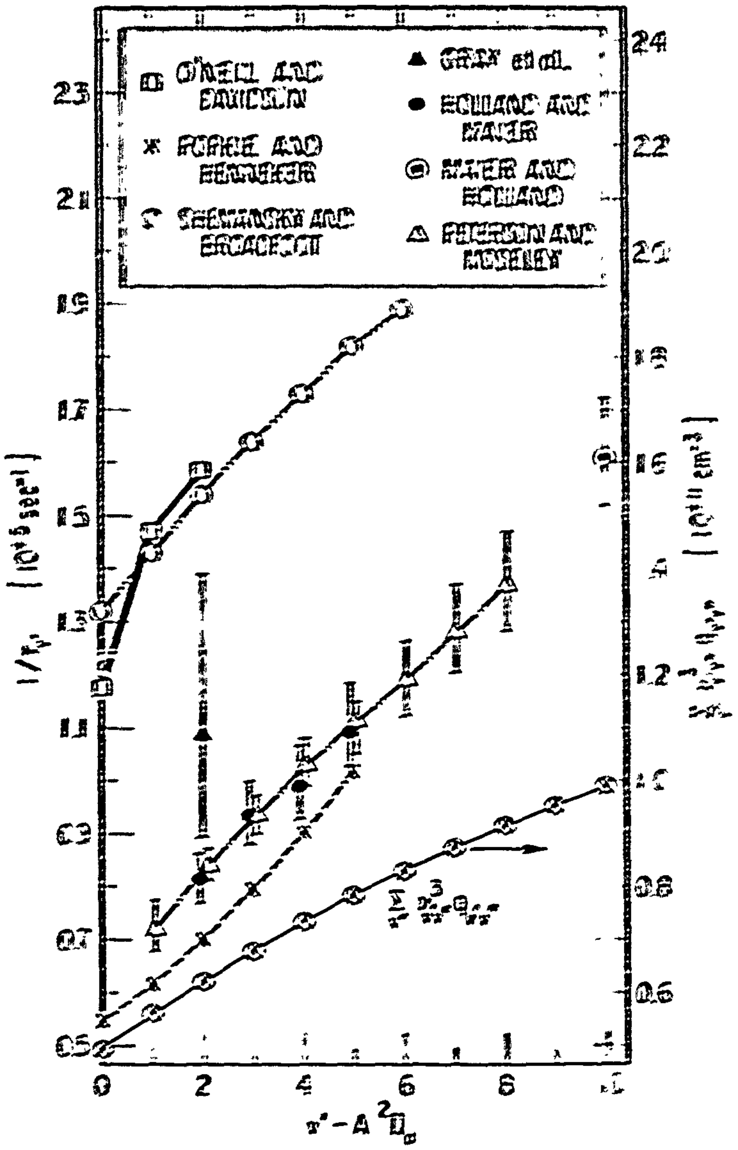

Fig. 1 Inverse of the measured natural lifetimes for the Meinel band system of N_2^+, as a function of the vibrational quantum number (v'). The data were taken from: □ - O'Neil and Davidson[11]; x - Popkie and Henneker[7], O - Shemansky and Broadfoot[10b]; ▲ - Gray et al[27a]; ● - Holland and Maier[4]; ⊖ - Maier and Holland[5]; △ - Peterson and Moseley[6]. The lower most curve is a plot (right-hand coordinate) of $\sum_{v''} \nu^3_{v'v''} q_{v'v''}$ as a function of v'.

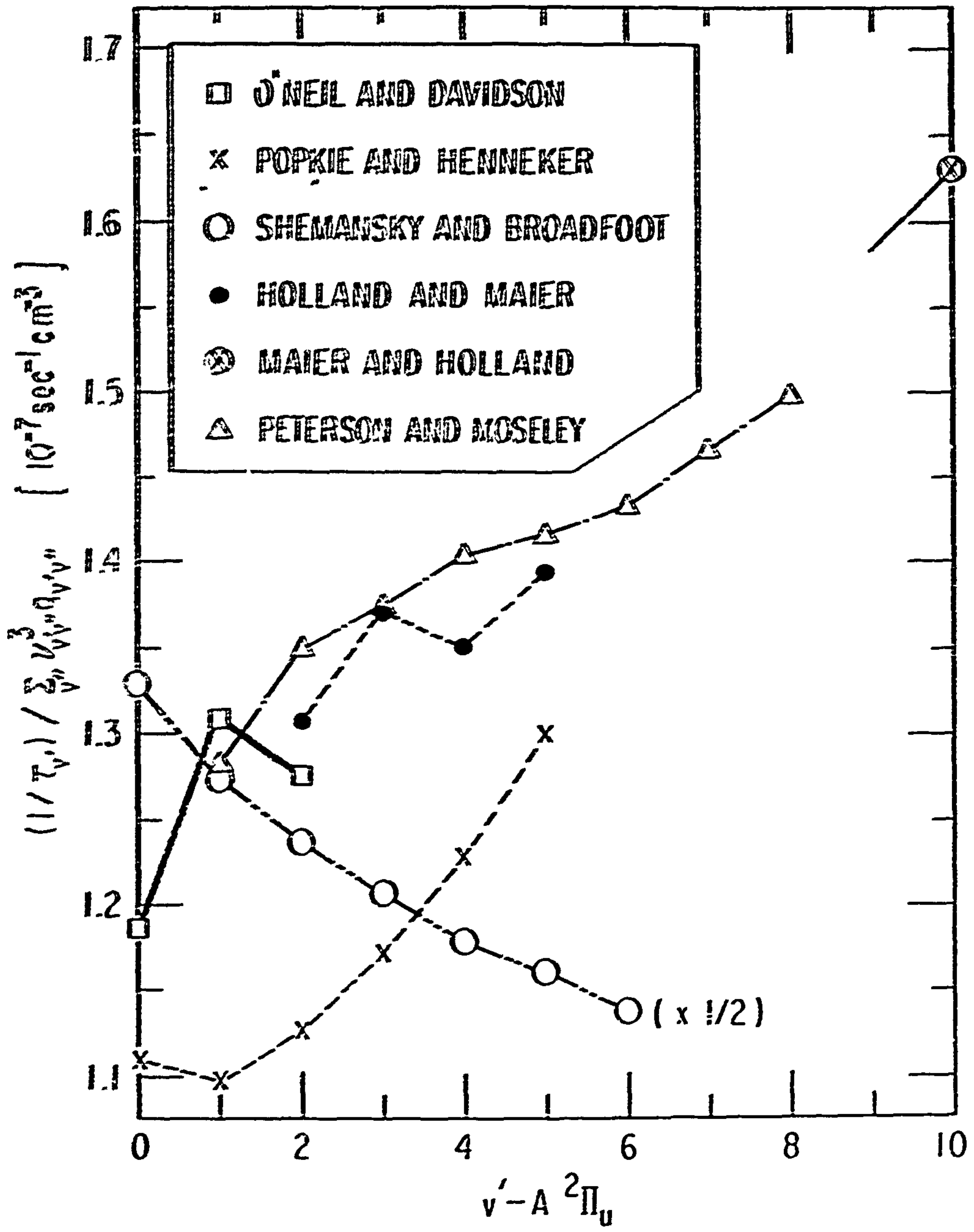

Fig. 2 The ratio of the inverse of measured natural lifetimes to the quantity $\sum_{v''} \nu^3_{v'v''} q_{v'v''}$ as a function of v'. The symbols used for the data are the same as in Fig. 1. The results from the data of Shemansky and Broadfoot[10b] have been reduced by a factor of two before plotting.

In the analysis of the new lifetime measurements,[4-6] the data were divided into two groups. The first group, called Case I, was taken to be the lifetimes for levels $v' = 1-8$ determined by Peterson and Moseley.[6] The lifetimes for levels $v' = 2-5$ determined by Holland and Maier[4] are so close to the values assumed in Case I, that their usage in Case I made no substantial difference[28] in the results obtained for the parameters The second group, called Case II, was formed from Case I by adding the lifetime for $v' = 10$ reported by Maier and Holland.[5] Cases I and II were analyzed assuming both a linear (two parameter) and a quadratic (three parameter) dependence of the transition moment on internuclear distance [Eq. (13)] . The linear dependence was concluded to be superior to the quadratic form for both cases on the basis of a combined statistical and physical argument. The statistical basis is that both the chi-square and the "F" test [29] indicate that the linear dependence is better than the quadratic. That is, the chi-square value was smallest for the linear form, and the "F" test indicates that termination of the expansion [Eq. (13)] at the linear term has a probability of about 65% of being correct. The physical reason is based on the fact that both the $X^2\Sigma_g^+$ and $A\ ^2\Pi_u$ states dissociate into the same atomic states and therefore the transition moment must vanish at sufficiently large internuclear distance. The linear dependence monotonically decreases over this range of R-values, but the quadratic form has a minimum near the center of this range and then begins to increase at the larger R-values. These two considerations clearly indicate that the linear form for the transition moment is the better representation of the true moment over this internuclear range.

The parameters determined for the linear transition moment for both Case I and Case II are given in Table I along with their standard deviation uncertainties. These parameters were determined using the uncertainties in the lifetime reported for each vibrational level (converted into an uncertainty in the decay constant) as the weights in Eq. (16).

Table I
Optimum Parameters in Eq (13) Determined From Case I and II Data

	a_o (Debye)†	a_i (Debye $\mathring{A}^{-1}$) †
Case I [v' = 1-8 (Ref. 6)]	2.412 ± .0417	- 0.9912 ± .0383
Case II [v' = 1-8 (Ref. 6), v' = 10 (Ref. 5)]	2.675 ± .0365	- 1.231 ± .0336

† 1 Debye = 10^{-18} cgsesu

The transition moment for Cases I and II is shown in Fig. 3 as the heavy solid lines. The shaded region around the solid line for Case I indicates the uncertainty in the transition moment due to the one standard deviation uncertainty in the parameters (Table I). The uncertainty range in the transition moment for Case II is similar to that for Case I, but has been omitted from the figure for clarity. The dashed curve labeled PH(T) is the theoretical dipole-length transition moment calculated by Popkie and Henneker[7] using Hartree-Fock wavefunctions. The shape of the theoretical curve is very similar to that for the present results, but it is a factor of about 2.4 smaller

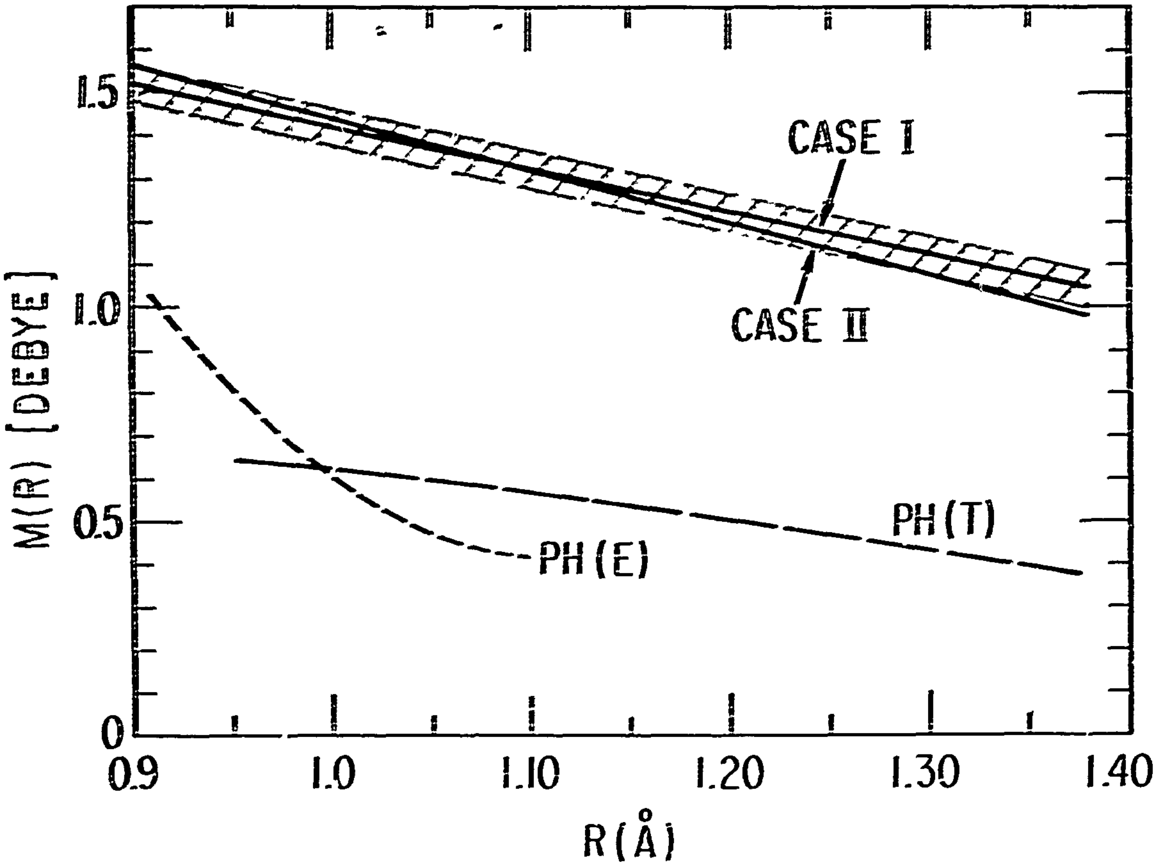

Fig. 3 Dipole-length transition moment (Debye) for the Meinel band system of N_2^+ as a function of the internuclear distance (Å). The two parameter results obtained for the Case I and Case II data sets are the solid lines. The shaded region around the Case I line denotes the uncertainty in the transition moment due to one standard deviation uncertainties in the parameters. The curve labeled PH(E) is the dipole-length result obtained by Popkie and Henneker[7] from earlier data. The curve labeled PH(T) is the theoretical dipole-length moment calculated by Popkie and Henneker[7] using Hartree-Fock wave functions.

in magnitude. The curve labeled PH(E) is the "experimental" transition moment obtained by Popkie and Henneker[7] by using the relative intensities for the Meinel system obtained by Stanton and St. John[13] in a laboratory electron impact excitation experiment, and the preliminary lifetime measurements for levels v' = 3-5 by Hollstein et al.[12] for absolute normalization. This transition moment was limited to R-values less than about 1.1 A because there were not sufficient experimental data available at that time to allow determination of the transition moment at larger R. There does not appear to have been any other experimental or theoretical determination of the internuclear dependence of the transition moment.

If the transition moment depends linearly on R, then the band strength can be written, without approximation, in terms of the Franck-Condon factor times a function of the r-centroid only. That is, Eq. (14) can, in this case, be rewritten as

$$S_{n'v'}^{n''v''} = \langle v'|v''\rangle^2 \left[a_o + a_1 \frac{\langle v'|R|v''\rangle}{\langle v'|v''\rangle} \right]^2 \equiv q_{v'v''} R_{el}^2 (r_{v'v''}) . \tag{23}$$

The quantity R_{el}^2 is sometimes called the electronic band strength although that term is misleading since any dependence of R_{el}^2 on the r-centroid represents a coupling between the vibrational and electronic motions. Except for the work done by Popkie and Henneker,[7] the previous analyses of experimental Meinel band intensity data have all utilized the r-centroid approximation, so the present results need to be written in that form [Eq. (23)] for purposes of comparison. Figure 4 compares the present results for R_{el}^2, as a function of the r-centroid, with the previous determinations. The heavy solid lines repre-

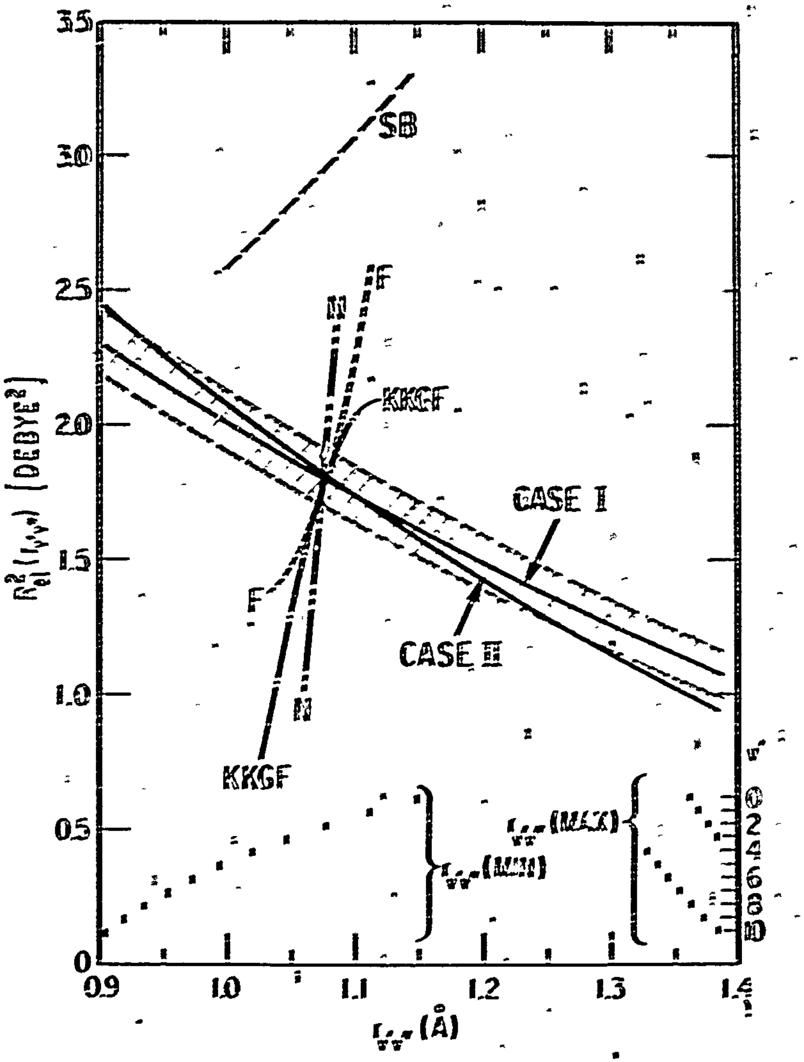

Fig. 4 The "electronic" portion of the band strength, R_{el}^2 in Debye,^{2} as a function of the r-centroid (Å). The solid curves are the two parameter results for the Case I and Case II data sets and the shaded region is the uncertainty due to one standard deviation uncertainties in the parameters. The curves labeled N, F, KKGF and SB are, respectively, Nicholls,[9a] Fedorova,[9b] Koppe *et al.*[10a] and Shemansky and Broadfoot[10b]. The short vertical lines at the bottom of the figure are the minimum and maximum values in the range of the r-centroid for fixed v'. See text for discussion of these results.

sent the two parameter results obtained for Case I and Case II data as labeled and the shaded region around the Case I line represents the one standard deviation uncertainty in R_{el}^2 due to a one standard deviation uncertainty in the parameters a_0 and a_1. The dashed curve labeled SB is the result obtained recently by Shemansky and Broadfoot[10b] using relative intensities of the Meinel bands excited by electron impact in a laboratory experiment. They found it necessary to normalize their results to the lifetimes determined by O'Neil and Davidson[11] for levels v' = 0-2 rather than the more recent beam experiment results of Hollstein et al.[12] in order to insure that their excitation cross section for the Meinel band system did not exceed the total electron-impact ionization cross section for N_2. Their R_{el}^2 then clearly represents an upper limit to the true value. However, it also demonstrates an incorrect dependence on the r-centroid. That is, R_{el}^2 increases with increasing r-centroid while the present results decrease as they should according to the physical argument stated above. The curves labeled N and F are results obtained from the analysis of auroral relative intensities by Nicholls[9a] and Fedorova,[9b] respectively, and have been normalized to the present result at the r-centroid corresponding to the (2, 0) band. The curve labeled KKGF is the laboratory result obtained by Koppe *et al.*[10a] from relative intensities of the Meinel bands excited by electron impact in the laboratory. This result has also been normalized to the present result at the (2, 0) band. The R_{el}^2 obtained in these three determinations all increase with increasing r-centroid rather than decrease as in the present results. The short vertical lines at the bottom of Fig. 4 represent the minimum (at the left) and maximum (at the right) values of the r-centroid for each v'' and the usefulness of this information will be discussed in the next section.

Some estimates of the quantity R_{el}^2 have also been obtained[30] using absolute intensity measurements of the near infrared emissions produced by shock wave through N_2 and air. Krupriyanova et al.[30b] obtained an estimate of the average value of R_{el}^2 for emissions in the wavelength region 0.9-1.1 μm which agrees fairly well with an upper limit estimate by Wurster.[30a] However these estimates are somewhat more than a factor of two larger than the present results.

B. Transition Probabilities and Oscillator Strengths

Once the transition moment has been determined, it is straightforward to calculate the band strengths, transition probabilities and oscillator strengths for the Meinel band system of N_2^+. The transition moment determined by using the Case II data was used to generate these quantities which are tabulated in the form of a matrix in Table II. The rows of this matrix are v' and the columns are v''. Each "element" of this matrix is composed of three numbers. The uppermost is the band oscillator strength, the middle one is the band transition probability, and the lowermost is the band origin wavelength in angstroms. The two columns at the far right are, from left to right, the experimental lifetimes and those calculated from the tabulated transition probabilities. These results are significantly different from previously tabulated results,[9b,10b] not only in absolute magnitude, but also in relative magnitude for different (v', v'') pairs. The results obtained using the transition moment from the Case I data differ only very slightly from those tabulated here.

Table II. [‡]
Transition Probabilities, Oscillator Strengths, and Band Origin Wavelengths for the Meinel Band System of N_2^+

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	τ_v (μsec) Expt [θ]	τ_v (μsec) Calc
0	1.68-3 [φ] 4.55+4 11086.9	8.71-4 1.36+4 14609.8	1.62-4 1.19+3 21261.9	1.24-5 2.79+1 38560.8	1.91-7 1.70-2 193.4+3											16.58
1	1.40-3 5.53+4 9181.5	1.39-4 3.52+3 11472.4	7.74-4 1.12+4 18210.5	3.01-4 2.02+3 22395.7	3.55-5 6.75+1 41860.3	5.42-7 8.16-2 289.1+3									[illegible]	13.87
2	6.90-4 3.73+4 7852.5	9.87-4 3.67+4 9409.9	4.43-5 1.05+3 11879.8	4.32-4 5.73+3 15851.9	3.66-4 2.19+1 23628.7	6.20-5 9.92+1 45679.6	7.12-7 7.07-3 550.5+3								11.9 ± 1	12.36
3	2.68-4 1.89+4 6873.6	1.01-3 5.17+4 8081.8	3.68-4 1.28+4 9774.0	2.82-4 6.21+3 12312.2	1.52-4 1.86+3 16540.5	3.49-4 1.86+3 24982.6	8.48-5 1.12+2 50168.0	1.36-7 1.41-5 567.4+4							10.7 ± 1	10.70
4	9.18-5 8.17+3 6123.0	6.08-4 4.07+4 7063.7	8.85-4 4.26+4 8323.1	4.27-5 1.40+3 10095.4	4.32-4 8.82+3 12772.5	1.84-5 2.05+2 17282.1	2.79-4 1.33+3 26477.2	9.88-5 1.07+2 55519.8							9.7 ± 1	9.68
5	2.94-5 3.20+3 5529.4	2.84-4 2.39+4 6285.2	8.13-4 5.14+4 7263.1	5.42-4 2.46+4 8577.1	1.72-5 5.58+2 10135.5	4.16-4 7.90+3 13263.1	6.38-6 6.51+1 18088.5	1.91-4 8.06+2 28133.0	1.02-4 8.85+1 61995.2						9.1 ± 1	8.89
6	9.07-6 1.19+3 5048.3	1.15-4 1.19+4 5671.0	5.06-4 4.05+4 6455.1	8.04-4 4.80+4 7472.6	2.17-4 9.27+3 8844.8	1.41-4 4.05+3 10795.6	2.95-4 5.18+3 13786.3	5.94-5 5.52+2 18946.9	1.09-4 4.05+2 29972.8	9.33-5 6.35+1 69963.1					8.4 ± .5	8.25
7	2.77-6 4.26+2 4650.7	4.32-5 5.38+3 5174.1	2.56-4 2.52+4 5819.0	6.70-4 5.08+4 6633.2	6.26-4 3.53+4 7692.6	3.41-5 1.37+3 9127.0	2.73-4 7.28+3 11176.9	1.53-4 2.48+3 14344.4	1.25-4 1.06+3 19881.4	4.80-5 1.56+2 32022.6	8.12-5 4.24+1 79957.8				7.6 ± .5	7.72
8	8.43-7 1.51+2 4316.7	1.55-5 2.28+3 4761.0	1.15-4 1.36+4 5305.4	4.20-4 3.93+4 5974.0	7.17-4 5.15+4 6819.9	3.78-4 2.01+4 7923.9	5.06-6 1.90+2 9424.2	3.12-4 8.02+3 11380.9	4.78-5 7.14+2 14940.2	1.69-4 1.29+3 20892.9	1.27-5 3.61+1 34315.0	6.33-5 2.45+1 92018.8			7.1 ± .5	7.29
9	2.59-7 5.31+1 4032.5	5.43-6 9.27+2 4420.1	4.79-5 6.70+3 4882.4	2.23-4 2.51+4 5442.9	5.59-4 4.95+4 6136.4	6.40-4 4.34+4 7016.0	1.61-4 8.08+3 8167.5	7.86-4 2.69+3 9139.0	3.07-4 7.10+3 12009.9	2.42-6 3.33+1 15577.7	1.79-4 1.23+3 21991.1	3.12-7 7.65-1 36893.7	4.50-6 1.24+0 110.0+3			6.91
10	8.04-8 1.87+1 3787.8	1.88-6 3.68+2 4127.9	1.91-5 3.10+3 4528.3	1.07-4 1.43+4 5006.5	3.52-4 3.78+4 5587.3	6.31-4 5.29+4 6307.2	4.79-4 3.06+4 7228.6	3.17-5 1.49+3 8424.8	1.76-4 5.78+3 10078.3	2.24-5 4.81+2 12467.1	1.01-4 1.28+3 16222.8	1.59-4 9.86+2 23190.1	3.87-6 1.07+1 34622.5	2.89-6 5.35-1 134.0+3	6.2 ± .4	6.16

[‡] $f_{v'v''}$
$A_{v'v''}$
$\lambda_{v'v''}$ (Å)

[φ] 1.68-3 = 1.68 x 10^{-3}

[θ] Ref. 9 (v' = 1-8), Ref. 5 (v' = 10)

The maximum and minimum range of the r-centroid for fixed v'' shown near the bottom of Fig. 4 leads to the following useful result. The range of the r-centroid variation for both $v'' = 0$ and $v'' = 9$ is contained within the ranges for the other v''-levels for which the lifetimes have been measured. As a consequence, the R_{el}^2 determined the v'' levels 1-8 and 10, which is an analytic function of the r-centroid, can be interpolated to provide reasonably accurate values for the transition probabilities and oscillator strengths for transitions from $v'' = 0$ and 9. These interpolated values are the ones shown in Table III and should be as accurate as the entries involving the other v''-levels. Since the transition probabilities connecting levels $v'' = 0$ and 9 with all lower v'''-levels are known, they can be summed to provide reasonably accurate life-times for levels $v'' = 0$ and 9, and the resulting values are given in the right-hand column in Table III. These are useful results because the wavelength region of the fluorescent processes from $v'' = 0$ are in the experimentally difficult near infrared region.

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