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N_2 Vegard–Kaplan System in Absorption*

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Seven bands (6, 0–12, 0), of the N_2 Vegard–Kaplan system have been observed in the absorption spectrum of 12 m·atm of gas. The measuring instrument was a 2-m scanning spectrometer with a resolution of about 30 000. Pulse-counting techniques, coupled with the use of a theoretical model based on a measured collision broadening coefficient, have allowed fairly accurate estimates of the transition probabilities of the observed bands. The electronic transition moment has been calculated from the measured transition probabilities and extrapolated with the aid of emission measurements, in order to determine the lifetimes of the system. It is shown that the system has a double lifetime for each vibrational level. The calculated lifetimes $[\tau^i(v')]$ for the $A\,^3\Sigma_u^+$ ($v=0$) state were $\tau^2(0)=1.27$ sec for the $\Sigma=0$ substate levels, and $\tau^1(0)=\tau^3(0)=2.5$ sec for the $\Sigma=1, -1$ substate levels.

I. INTRODUCTION

The N_2 Vegard–Kaplan (VK) system is important to both auroral studies and laboratory investigations involving active nitrogen. In the aurora, for example, one generally observes less than 5% of the energy developed in the $A\,^3\Sigma_u^+$ state, from one source alone [cascade through the very bright N_2 first positive system (1*PG*)], in the form of emission in the ($A\,^3\Sigma_u^+$–$X\,^1\Sigma_g^+$) transition. As a consequence, there have been a considerable number of attempts to determine the transition probability or lifetime of the long-lived $A\,^3\Sigma_u^+$ state.

Estimates of the lifetime have varied by more than a factor of 10^3, from the 30-sec figure given by Hunten[1] as a result of observation of an afterglow type of aurora, to the 26-msec figure given by Wilkinson and Mulliken,[2] from observations of the uv absorption spectrum. Later estimates have reduced this range, but the lifetime has remained rather uncertain. The majority of the estimates obtained from observations of laboratory afterglows (Noxon,[3] Zipf,[4] Phillips[5]) agree on a value of about ($\tau=$)1 sec. Dunford[6] estimated $\tau=0.08$ sec from measurements of the decomposition of ammonia by active nitrogen. However, it is not certain that N_2 molecules in the $A\,^3\Sigma_u^+$ state were the reacting species. Brömer and Spieweck,[7] in recent measurements of the decay of the (0, 6) band, estimated $\tau=10$ sec. Discrepancies of this magnitude are not unexpected in view of the long extrapolation to zero pressure and large corrections for diffusion to the walls of the container. Most of the remaining estimates of the lifetime (Wentink and Isaacson,[8] Brennen[9]) are based on a carefully conducted experiment by Carleton and Oldenberg[10] (see also Oldenberg *et al.*[11]) in which a measure of the relative lifetimes of the $B\,^3\Pi_g$ and $A\,^3\Sigma_u^+$ states was obtained. However, a reanalysis of the results of their experiment has been necessary (Shemansky and Carleton[12]) and the estimates of Refs. 8 and 9 ($\tau\approx12$ sec) must be reduced by an order of magnitude.

The fact that the lifetime has remained uncertain suggests that the usual methods of measurement are not adequate for the N_2 VK system. For example, there is no apparent divergence in procedure by which one might discriminate between the two very similar experiments of Zipf[4] and Brömer and Spieweck,[7] although they differ by a factor of 10 in their lifetime estimates. One must therefore resort to experiments such as that of Carleton and Oldenberg in which the transition probability is determined by the direct measurement of the excited-state population and the volume emission rate. In this type of experiment the processes which seriously affect the afterglow measurements, radiationless deactivation, repopulation, and diffusion of the excited-state molecules, can be ignored. The most direct method of determining the transition probability of a band is through the measurement of equivalent width in the absorption spectrum of a known amount of gas. The only observations of the N_2 VK absorption bands reported in the literature up to this point are the spectrographic measurements of Wilkinson.[13,14] The absorption bands are very difficult to observe; of the order of 10 m·atm of highly purified gas is required for a measurement in weak absorption. The presence of 1 or 2 parts in 10^6 of O_2 results in

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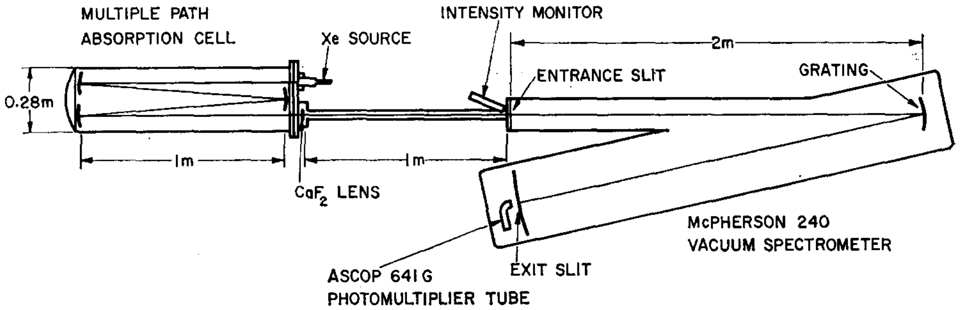

FIG. 1. Experimental arrangement.

contamination of the spectra. In spite of the advantages of the method, the lifetime estimate of Wilkinson and Mulliken, obtained from the observations of Ref. 13, cannot be considered reliable. This is due more to the crude approach to the analysis, than to the difficulty in making the observations or to contamination by O_2. The lifetime was estimated by comparison of the appearance path length of the N_2 VK bands with that of the N_2 Lyman–Birge–Hopfield (LBH) system. However, the appearance path length is very difficult to interpret because of differences in the rotational structure of the bands, and in the linewidths. In any case, the appearance path length for the N_2 LBH system given by Wilkinson and Mulliken appears to be in error by more than an order of magnitude. There are additional difficulties involving the determination of lifetime once the transition probability of a band has been estimated. These factors will be discussed in more detail below. However, it is clear that Wilkinson and Mulliken would have obtained better results by estimating equivalent widths directly, in spite of the difficulties involved in making measurements of this type from photographic spectra. The fact remains that transition probabilities of long-lived systems determined from absorption measurements are potentially more accurate than the various methods involving emission measurements; the former approach is direct, and avoids most of the serious difficulties which, in the case of the N_2 VK system, have made the laboratory afterglow measurements very uncertain.

This paper describes measurements of transition probabilities of seven bands, (6, 0)–(12, 0), from observations of the absorption spectrum of 12 m·atm of gas. The large dynamic range resulting from the use of pulse-counting techniques, coupled with the use of synthetic comparison spectra, has allowed the determination of the transition probabilities with little uncertainty. The determination of the lifetimes of the system from the measured transition probabilities is complicated by a strong variation of the electronic transition moment. The estimation of the lifetimes of the system requires the extrapolation of the electronic transition moment as a function of internuclear distance. The extrapolation is simplified by the fact that both the absorption measurements and the measurements in emission (which extend over the extrapolated region) indicate a linear variation. The extrapolated moment, modified slightly by the emission measurements, is very nearly a straight line, and goes through zero at a point between the equilibrium internuclear distances of the $A\ {}^3\Sigma_u{}^+$ and $X\ {}^1\Sigma_g{}^+$ states. The resulting lifetimes of the $v=0$ level, which is the level most sensitive to the extrapolation, are in very good agreement with the values determined from the reanalysis of the Carleton and Oldenberg experiment.

The characteristics of the $(A\ {}^3\Sigma_u{}^+\text{–}X\ {}^1\Sigma_g{}^+)$ transition are discussed below in detail from the point of view of deriving transition probabilities of the bands from the rotational structure. It will be shown that there are two distinct lifetimes associated with each vibrational level of the $A\ {}^3\Sigma_u{}^+$ state. Thus the calculated lifetime of the $v=0$ level is $\tau=1.27$ sec for the $\Sigma=0$ substate and double this value (2.5 sec) for the $\Sigma=1, -1$ substates.

II. EXPERIMENT

The experimental arrangement is shown schematically in Fig. 1. The absorption tube was a modified Perkin–Elmer multiple path cell. The path length was variable from 4 to 40 m in 4-m increments. It was discovered through experience that the experiment was very difficult to conduct using mechanical and oil diffusion pumps for evacuation, due to the presence of small amounts of oil vapor in the absorption cell. The uv transmitting and reflecting surfaces rapidly become opaque as a result of the deposition of photodissociated pump oil on the critical parts of the surfaces (see Taylor *et al.*[15]). The cell was therefore evacuated to about 10^{-7} torr using a sorption roughing pump, combined with a 50-liter/sec differential ion pump, and was filled with Matheson research-grade N_2 after several weeks of outgassing at about 150°C. The O_2 content of the gas was further reduced by adapting a technique introduced by Noxon.[16] The cell was filled by passing the gas through a discharge between nickel electrodes, followed by a liquid-nitrogen cold trap. The object of this procedure was to convert most of the O_2 to NO,

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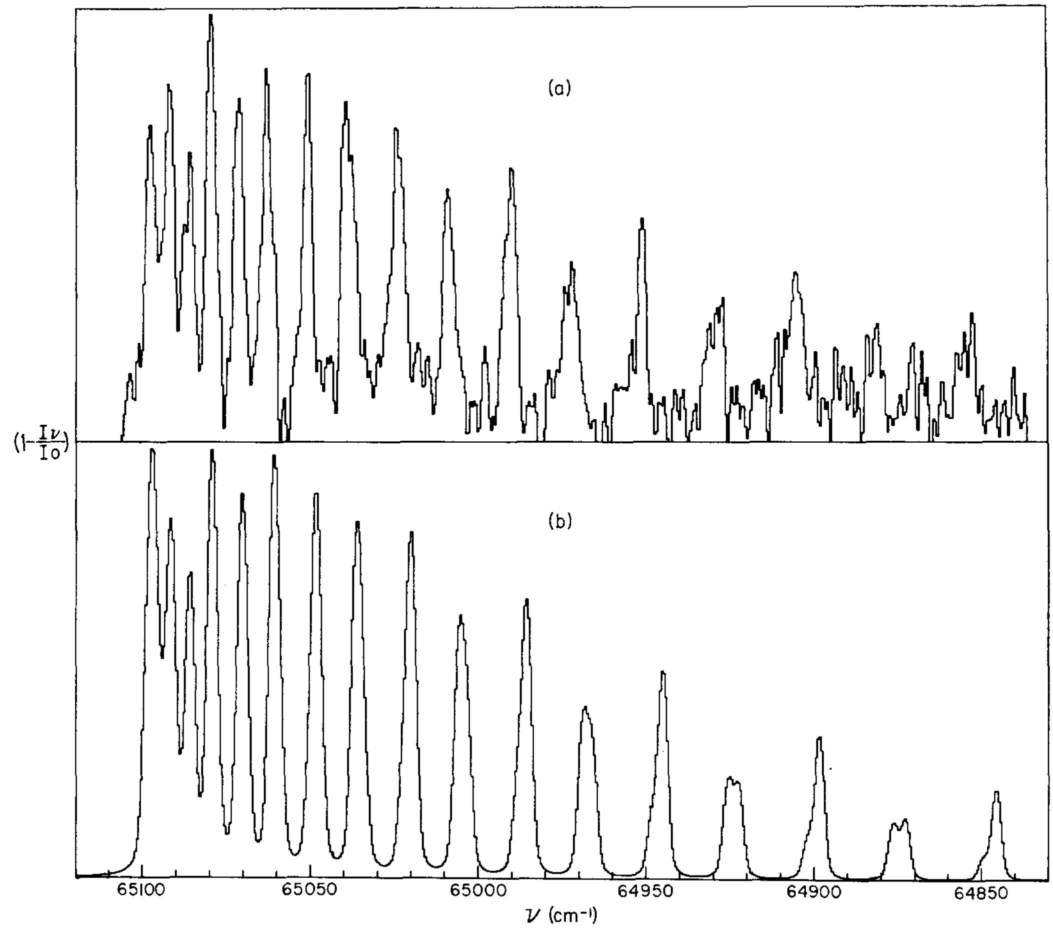

FIG. 2. Comparison of calculated and observed N_2 V–K (12, 0) band. (a) Observed spectrum #80. $W_{12,0}=4.76$ cm^{-1}, peak$=0.088$, $T=296.2$°K, $P=778.4$ torr, $l=1203$ cm. (b) Synthetic spectrum N_2 VK (12, 0) band. $W_{12,0}=4.70$ cm^{-1}, peak$=0.087$, $D_0^2=2.93\times10^{-45}$ erg·cm^3, $\alpha_L=1.07\times10^{-2}$ $P/T^{1/2}$ cm^{-1}, $T=296.2$°K, $P=778.4$ torr, $l=1203$ cm.

which would then be removed by the cold trap. The absorption cell filled in this manner to slightly above atmospheric pressure (measured with a Texas Instruments quartz Bourdon gauge) allowed the observation of the N_2 VK bands in the 1500–1700-Å region with no trace of the O_2 Schumann–Runge bands or continuum. The region was contaminated by one as yet unidentified band falling at about 1545 Å. However, the observed N_2 (VK) bands were not contaminated. The continuum source was a xenon-filled tube with an LiF window, excited by a 100-W microwave generator. The measuring instrument was a 2-m McPherson 240 vacuum spectrometer, with a 1200-lines/mm grating (blazed at 1500 Å in the first order). The design of the spectrometer was such that the grating could be used only in the first order; the resolution of the instrument was thus limited to about 30 000, with 10-μ entrance and exit slits. The detector was an EMR 641G photomultiplier tube, which was operated in the pulse-counting mode. The intensity of the source was monitored with a second photomultiplier tube at the entrance slit of the spectrometer. Instabilities in the source were compensated for by using a modified Hewlett–Packard 5214L preset counter in the ratio recording mode. The signal from the detector at the exit slit was integrated during a period determined by a preset integrated count from the detector at the entrance slit. A single scan of the grating was used to produce each spectrum, because the spectrometer drive train was not accurately repeatable. The grating drive, which was connected to a digital motor, was advanced (roughly four steps per spectral slitwidth) by a pulse generated by the preset counter at the end of each counting cycle. The signal was recorded in both analog form and on computer-compatible digital magnetic tape.

The path length of the absorption measurements was limited to a maximum of 12 m by the rather low reflectivity of the mirrors in the absorption cell, ~75% in the spectral region of interest. At this path length the signal at the exit slit was of the order of 100 count/sec, and about 20 000 count per spectral point were accumulated. A typical spectrum required 30 h of operation.

Seven bands of the $v''=0$ progression, $(6,0)\rightarrow(12,0)$, were observed at the 12-m·atm path length. The (12, 0) band was the strongest and most easily ob-

TABLE I. Equivalent widths and the corresponding transition probabilities of the observed N_2 Vegard–Kaplan bands.

Spect No.	Band	Path length (m·atm)	Observed $W_{v'v''}$ (cm^{-1})	Observed P [a]	Observed $W_{v'v''}/P$	Calculated $W_{v'v''}/P$	Calculated $A^2_{v'v''}$ (sec^{-1})	Calculated $A^1_{v'v''}=A^3_{v'v''}$ (sec^{-1})	Calculated ν (cm^{-1})	Calculated $^2R_e(\bar{r})$
80	12, 0	12	4.76	0.088	54.1	53.9	0.257	0.128	65 062	1.205-7
78	12, 0	12	4.67	0.083	56.3	53.9	0.251	0.126	65 062	1.191-7
77	11, 0	12	4.56	0.076	60.0	52.2	0.238	0.119	63 932	1.101-7
81	11, 0	12	3.48	0.070	49.5	52.2	0.181	0.0906	63 932	9.601-8
91	11, 0	8	3.25	0.056	57.9	52.2	0.253	0.127	63 932	1.135-7
92	11, 0	4	1.56	0.027	57.8	52.2	0.243	0.121	63 932	1.113-7
83	10, 0	12	4.46	0.078	57.2	50.8	0.226	0.113	62 830	1.038-7
85	9, 0	12	3.42	0.069	49.5	48.7	0.161	0.0805	61 651	8.663-8
87	8, 0	12	2.60	0.054	48.1	46.4	0.118	0.0589	60 444	7.640-8
95	8, 0	12	2.24	0.052	43.1	46.4	0.104	0.0520	60 444	7.173-8
103	7, 0	12	2.20	0.048	46.0	39.8	0.0977	0.0488	59 207	7.178-8
98	7, 0	12	2.25	0.056	40.2	39.8	0.0996	0.0498	59 207	7.247-8
89	6, 0	12	1.86	0.058	32.1	37.4	0.0787	0.0394	57 942	7.018-8
100	6, 0	12	1.35	0.029	46.5	37.4	0.0569	0.0285	57 942	5.967-8
99	6, 0	12	1.20	0.037	32.5	37.4	0.0508	0.0254	57 942	5.638-8
	5, 0	12	<0.60				<0.024	<0.012	56 649	4.38-8

[a] P is the peak value of $(1-I_\nu/I_0)$.

servable. Higher members of the progression are probably also measureable, but were not observed in this experiment due to the rapid decrease in source intensity below about 1520 Å. The (5, 0) band was not observable in 12 m·atm of gas. Figure 2 shows a spectrum $(1-I_\nu/I_0)$ of the 12, 0 band, smoothed with a 1:2:1 smoothing function, along with a synthetic spectrum. The equivalent width of each band was estimated by producing plots similar to the one shown in Fig. 2, in which the continuum background was approximated with one or two linear functions of wavenumber (ν). Errors in the background approximation were then removed by comparison with synthetic spectra. The synthetic spectra will be discussed in the following section.

In addition to the observations of 12 m·atm path length, the (11, 0) band was observed at 8 and 4 m·atm in order to confirm that the spectra were on the weak part of the curve of growth, as predicted by the theoretical model discussed below. At 4 m·atm, the signal level was increased to about 50 000 counts, in order to maintain a fair degree of accuracy in the measurement of total absorption.

The measured equivalent widths of the bands are given in Table I. The table includes an estimated upper limit for the (5, 0) band. Spectrum #81 appears to be a spurious measurement but is included in the table. There was no clear reason for rejecting the spectrum, although it was obtained at a lower signal level.

III. THEORY

A. Characteristics of the Transition

The $(A\ ^3\Sigma_u^+ - X\ ^1\Sigma_g^+)$ transition is an electric dipole transition although it is forbidden by the difference in total electron spin between the two states. The bands have four branches; P_{Q_1}, R_{Q_3}, R_{R_2}, P_{P_2} (see Fig. 3). The $A\ ^3\Sigma_u^+$ state deviates from Hund's coupling case (b), since the triplet levels are split and the branches are separable. The splitting is due to interactions resulting from vibration and rotation, along with a large contribution from electron spin–spin interaction (Schlapp[17,18]). The line-strength factors have been calculated theoretically by Schlapp,[18] and are given in Table II, along with the transition probabilities for the rotational levels. It should be noted that most of the line-strength factors used for the N_2 VK system in the literature (Petrie,[19] Wilkinson,[13] Broadfoot and Hunten[20]) have been in error due to the

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[20] A. L. Broadfoot and D. M. Hunten, Can. J. Phys. **42**, 1212 (1964).

TABLE II. Line-strength factors and transition probabilities for $({}^3\Sigma_u^+ \leftrightarrow {}^1\Sigma_g^+)$ transitions with (B_e/λ_e) values similar to that of the N_2 Vegard–Kaplan system.

${}^1\Sigma_g^+ - {}^3\Sigma_u^+$	${}^3\Sigma_u^+ - {}^1\Sigma_g^+$	S_J	$A^i{}_{J'J''}{}^{a}$	$B^i{}_{J''J'}{}^{a}$
$R_2(J)$	$P_2(J+1)$	(J)	$(C2)(D_0^2)({}^2\nu_{J'J''})^3[J/2J+1)]$	$(C2)(8\pi hc)^{-1}D_0^2[J/(2J+3)]$
$Q_1(J)$	$Q_1(J)$	$(J+\frac{1}{2})$	$(C2)(D_0^2)({}^1\nu_{J'J''})^3(\frac{1}{2})$	$(C2)(8\pi hc)^{-1}D_0^2(\frac{1}{2})$
$Q_3(J)$	$Q_3(J)$	$(J+\frac{1}{2})$	$(C2)(D_0^2)({}^3\nu_{J'J''})^3(\frac{1}{2})$	$(C2)(8\pi hc)^{-1}D_0^2(\frac{1}{2})$
$P_2(J)$	$R_2(J-1)$	$(J+1)$	$(C2)(D_0^2)({}^2\nu_{J'J''})^3[(J+1)/(2J+1)]$	$(C2)(8\pi hc)^{-1}D_0^2[(J+1)/(2J-1)]$

[a] D_0 is the vibronic matrix element, common to all the line-strength factors, which determines the absolute transition probability for a given band. $(C2)=64\pi^4/3h$.

fact that the factors given in Schlapp's table applied to a ${}^1\Sigma$–${}^3\Sigma$ transition rather than a ${}^3\Sigma$–${}^1\Sigma$ transition. The auroral rotational temperature measurements of Refs. 19 and 20 could consequently be in error. It is uncertain whether the auroral measurements of Wallace[21] would be affected.

The N_2 (VK) system has an unusual characteristic in that the $A\,{}^3\Sigma_u^+$ state possesses two distinct lifetimes, as will now be demonstrated. The transitions that compose a band of this system, unlike transitions between states having the same multiplicity, are asymmetric as a consequence of the difference in multiplicity between the upper and lower states. Figure 3 illustrates the nature of the asymmetry. The $K'=1$ level of the diagram is complete and shows the total of four allowed transitions; the F_1 and F_3 substate levels have only one Q-branch transition each, whereas the F_2 substate levels each have two, one P-branch and one R-branch transition. Qualitatively, one can expect very little difference in the eigenfunctions of the three substates, since the $A\,{}^3\Sigma_u^+$ state is very nearly in Hund's coupling case (b), and the substates are therefore almost degenerate. Thus one cannot expect significant differences in the transition probabilities of the four branches, other than those associated with $\Delta K=1$ and $\Delta K=-1$ transitions. Quantitatively this is the case, as Table II shows, and the F_2 substate levels must then have twice the transition probability of the F_1 and F_3 levels. This will now be considered in detail, and a comparison will be made with an observed band in emission.

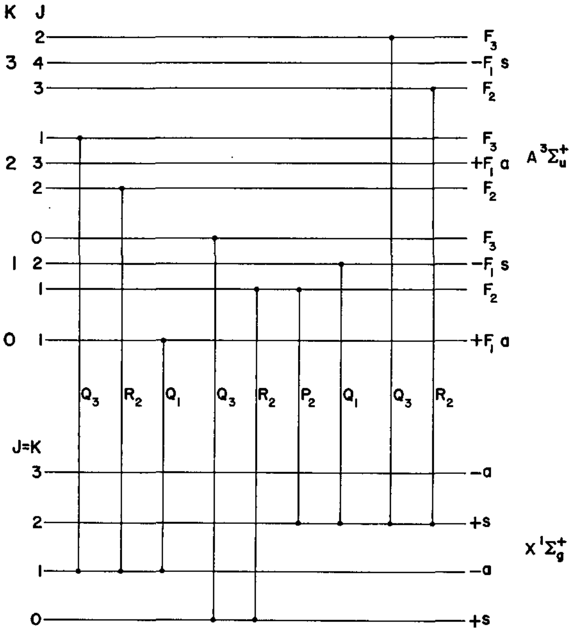

FIG. 3. Energy-level diagram for $({}^3\Sigma_u^+ – X\,{}^1\Sigma_g^+)$ transitions.

The intensity equation for the lines of a given N_2 (VK) band can be represented by the equation

$$I_{J'J''}{}^i = N_{J'}{}^i A_{J'J''}{}^i, \tag{1}$$

where $N_{J'}{}^i$ is the population of upper state level J', substate i, and $A_{J'J''}{}^i$ is the transition probability for upper state level J', substate i, to lower state level J''.

The lifetime $(\tau_{J'}{}^i)$ of a given level J' (if we assume for convenience that there is only one band in the progression) is determined by the total transition probability,

$$(1/\tau_{J'}{}^i) = A_{J'}{}^i = \sum_{J''} A_{J'J''}{}^i. \tag{2}$$

Since there is only one transition from each level of the $i=1$, and $i=3$ substates, the $A_{J'}{}^i$ function can be read directly from Table II. That is,

$$A_{J'}{}^1 \approx A_{J'}{}^3 = (C2)(D_0)^2({}^3\nu_{J'})^3(\tfrac{1}{2}), \tag{3}$$

since ${}^1\nu_{J'} \approx {}^3\nu_{J'}$. But the $i=2$ substate levels each have two transitions, $P_2(J+1)$ and $R_2(J-1)$; from Table II,

$$A_{J'}{}^2 \approx (C2)(D_0)^2({}^2\nu_{J'})^3, \tag{4}$$

where ${}^2\nu_{J'}$ is an average of the two transitions. Thus theoretically the $i=2$ levels have one-half the lifetime of the $i=1$ and $i=3$ levels.

Laboratory observations in emission (Miller[22]) in which the rotational structure of the bands was completely resolved, can be used to show that this is in fact the case. The long lifetime of the $A\,{}^3\Sigma_u^+$ state guarantees that the rotational structure would be in

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[21] L. Wallace, J. Atmospheric Terrest. Phys. **17**, 46 (1959).

[22] R. E. Miller, J. Chem. Phys. **43**, 1695 (1965).

TABLE III. Predicted line intensities for bands of the N_2 Vegard–Kaplan system, with the rotational structure of the $A\ ^3\Sigma_u{}^+$ state in thermal equilibrium.

Branch	Intensity
$P_2(J+1)$	$(N/3Q)(C2)(D_0)^2({}^2\nu_{J'J''})^3$ $\times(J)\exp[-F_2(J)/kT]$
$Q_1(J)$	$(N/3Q)(C2)(D_0)^2({}^1\nu_{J'J''})^3$ $\times(J+\frac{1}{2})\exp[-F_1(J)/kT]$
$Q_3(J)$	$(N/3Q)(C2)(D_0)^2({}^3\nu_{J'J''})^3$ $\times(J+\frac{1}{2})\exp[-F_3(J)/kT]$
$R_2(J-1)$	$(N/3Q)(C2)(D_0)^2({}^2\nu_{J'J''})^3$ $\times(J+1)\exp[-F_2(J)/kT]$

thermal equilibrium under laboratory conditions, as will be discussed below. The relative populations of the levels of the $A\ ^3\Sigma_u{}^+$ state would then be independent of the lifetimes of the levels, but would be determined entirely by collisions with ground-state molecules,

$$N_J{}^i=(N^i/Q_i)(2J+1)\exp(-F_i(J)/kT), \qquad (5)$$

where $N^i=\sum_J N_J{}^i$, $F_i(J)$ is the rotational energy of the level, and Q_i is the partition function. In addition, since the three substates are separated by only very small amounts of energy,

$$\tfrac{1}{3}N\approx N^1\approx N^2\approx N^3. \qquad (6)$$

Equations (1), (5), and (6) and the transition probabilities given in Table II combine to give the predicted relative line intensities of the N_2 VK bands. These are given in Table III. A comparison with Miller's experimental measurements of the (0, 5) band is given in Table IV. It is clear the predicted relative intensities are accurate, even at low K'' values where they are especially sensitive to the line-strength factors. Therefore, if one were to argue that the theoretical line-strength factors actually were erroneous, it would be necessary to present an argument for nonthermal equilibrium in the rotational levels of the $A\ ^3\Sigma_u{}^+$ state. But nonthermal equilibrium under laboratory conditions of observation would be highly unlikely. The Miller[22] observations were made at a pressure of 3 torr, implying a kinetic collision rate of the order of 10^8/sec. The effective lifetime should be of the order of 100 msec under these conditions, judging by the afterglow measurements of Refs. 4 and 7. The cross section for rotational relaxation, except for the lighter molecules, is generally of the order of the gas-kinetic cross section (Massey and Burhop[23]); thus even if one assumed an extremely short lifetime of 1 msec, there would still be roughly 10^5 collisions between excitation and emission. There is little doubt that thermal equilibrium would be maintained, even though emission in the VK bands, with the double lifetime, would tend to break down the detailed balance in the $A\ ^3\Sigma_u{}^+$ state levels.

For the same reason, one could not hope to observe a double lifetime in the observations of laboratory afterglows.

The lack of a single distinct lifetime appears to be a general characteristic of transitions involving states of different multiplicity. Another notable example is the CO Cameron system ($a\ ^3\Pi$–$X\ ^1\Sigma^+$). The ($a\ ^3\Pi$) state is intermediate in coupling between Hund's cases (a) and (b) (Budó[24,25]), and consequently has a multitude of lifetimes. Theoretically the lifetime is a strong function of the quantum number J, and in addition the Λ-doubling components of a given rotational level may differ in lifetime by a considerable factor. Of course, case (b) transitions such as $^1\Sigma$–$^3\Sigma$ would have a single, well-defined lifetime.

B. Transition Probabilities from Absorption Spectra

The absorption coefficient (k_ν) is defined by the equation

$$I_\nu=I_0\exp(-k_\nu l), \qquad (7)$$

where I_ν is the transmitted intensity, I_0 is the incident intensity, and l is the thickness of the absorbing gas. The absorption coefficient for a given line is related to the absorption probability $(B_{J''J'}{}^i)$ by the equation

$$k_\nu{}^{iJ''J'}=h({}^i\nu_{J''J'})(B_{J''J'}{}^i)(\delta N_{J''}/\delta\nu), \qquad (8)$$

where $B_{J''J'}{}^i$ is defined in terms of radiation density, and $(\delta N_{J''}/\delta\nu)$ is the differential population of lower state level J'', in which $\delta N_{J''}/N_{J''}$ is the fraction of the population in level J'' capable of absorbing radiation in the wavenumber interval $\nu+\delta\nu$ (Mitchell and Zemansky[26]). The integrated line strength is given by

$$S^{iJ''J'}=\int k_\nu{}^{iJ''J'}d\nu=h\nu B_{J''J'}{}^iN_{J''}. \qquad (9)$$

The equations (7)–(9) can thus be combined to relate the absorption coefficient to the equivalent width.

If the absorption is assumed to be weak, then the equivalent width for the band is independent of the shape of the absorption coefficient and can be written in the form

$$\begin{aligned} W_{v'v''}&=\sum_{J''}\sum_{J',i}\int 1-\left(\frac{I_\nu{}^{iJ''J'}}{I_0}\right)d\nu \\ &=\sum_{J''}\sum_{J',i}h({}^i\nu_{J'J''})(B_{J''J'}{}^i)N_{J''}l, \qquad (10)\end{aligned}$$

from Eqs. (7) and (9).

Equation (10) can be reduced to a good approximation for the N_2 (VK) system, to the form

$$W_{v'v''}\approx h\nu_{J'J''}B_{J''}Nl, \qquad (11)$$

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[23] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952), p. 454.

[24] A. Budó, Z. Physik **105**, 579 (1937).

[25] A. Budó, Z. Physik **98**, 437 (1936).

[26] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, New York, 1961).

TABLE IV. N_2 V-K (0, 5) band comparison of theoretical ($T=400$°K) and experimental[a] wavelengths and relative line intensities.

	Intensities						Wavelengths			
$J''=K''$	R_2	Q_3	P_2	Q_1	R_2/Q_3	P_2/Q_1	R_2	Q_3	P_2	Q_1
0	4.9[b]	1.3			3.8		4.502	4.323		
	4.3[c]	1.1			3.9		2604.48	2604.30		
1	4.0[b]						4.367			
	3.1[c]	1.6		1.6	1.9		2604.35	2604.22		2604.89
2	10.0[b]	5.5	2.0	8.5	1.8	0.23	4.295	4.178	5.277	5.212
	8.1[c]	5.0	2.1	5.3	1.6	0.40	2604.28	2604.16	2605.26	2605.19
3	4.9[b]		2.5	4.9		0.51	4.287		5.657	5.588
	4.8[c]	3.4	2.1	3.6	1.4	0.58	2604.27	2604.16	2605.64	2605.57
4	12.0[b]	6.8	6.2	11.0	1.8	0.56	4.337	4.231	6.103	6.028
	11.0[c]	8.2	6.1	9.0	1.3	0.68	2604.32	2604.21	2606.08	2606.01
5	6.2[b]	7.6	3.6	5.4	0.82	0.67	4.450	4.347	6.609	6.532
	6.1[c]	4.7	3.9	5.3	1.3	0.74	2604.43	2604.33	2606.59	2606.51
6	12.3[b]	7.9	8.5	12.9	1.6	0.66	4.626	4.524	7.178	7.099
	12.9[c]	10.4	9.2	11.9	1.2	0.77	2604.61	2604.51	2607.16	2607.08
7	6.0[b]	4.6	4.6	6.2	1.3	0.74	4.864	4.763	7.809	7.728
	6.7[c]	5.5	5.2	6.4	1.2	0.81	2604.85	2604.74	2607.79	2607.71
8	12.6[b]	9.3	9.8	12.9	1.4	0.76	5.163	5.064	8.502	8.421
	13.5[c]	11.4	11.2	13.5	1.2	0.83	2605.15	2605.05	2608.48	2608.40
9	5.8[b]	4.6	5.1	6.2	1.3	0.82	5.525	5.426	9.257	9.176
	6.7[c]	5.7	5.9	7.0	1.2	0.84	2605.51	2605.41	2609.24	2609.16
10	11.0[b]	8.1	9.6	14.1	1.4	0.68	5.949	5.851	0.076	9.993
	13.0[c]	11.3	12.1	14.0	1.2	0.86	2605.93	2605.83	2610.06	2609.98
11	4.6[b]	4.3	4.9	5.1	1.1	0.96	6.436	6.329	0.956	0.874
	6.2[c]	5.5	6.0	6.9	1.1	0.87	2606.42	2606.32	2610.94	2610.86
12	9.6[b]	7.6	8.5	10.2	1.3	0.83	6.984	6.886	1.900	1.817
	11.7[c]	10.4	11.8	13.4	1.1	0.88	2606.97	2606.87	2611.88	2611.80
13	4.3[b]	2.9		4.6	1.5		7.595	7.496		2.823
	5.4[c]	4.8	5.7	6.4	1.1	0.89	2607.58	2607.48	2612.89	2612.81
14	6.8[b]	5.1	6.2	7.8	1.3	0.79	8.269	8.171	3.976	3.892
	9.9[c]	8.9	10.7	11.9	1.1	0.90	2608.25	2608.16	2613.96	2613.88

[a] Reference 22.

[b] Experimental.

[c] Theoretical ($T=400$°K).

Table V. N_2 molecular constants.[a]

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	B_e	α_e	γ_e	r_e (Å)	D_e	β_e
$A\ {}^3\Sigma_u{}^+$	50 206.96	1460.6	13.851	6.25–3	1.72–3	1.4545	1.798–2	−8.44–5	1.2865	5.12–6	3.9–8
	b	c				d, e			d	f	
$X\ {}^1\Sigma_g{}^+$	0	2359.61	14.456	7.51–3	5.09–4	1.9992	1.760–2		1.0973	5.73–6	4.6–9
		g				b			b	f	

[a] Units are cm^{-1} unless otherwise designated.

[b] Recalculated by author from Miller[22] data.

[c] From G. H. Dieke and D. F. Heath, *Johns Hopkins Spectroscopic Report* #17 (Johns Hopkins University, Baltimore, Md., 1959).

[d] Calculated by author from Dieke and Heath data (Footnote c).

[e] $\lambda_v = -1.335+(7\times10^{-3})v, \gamma = -3\times10^{-3}$ (see Schlapp[18]).

[f] Theoretical values.

[g] From G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950).

since $B_{J''}(=\sum_{J',i}B_{J''J'}{}^i)$, the total absorption probability of the J'' levels is a constant independent of J'', except for $J''=0$ (see Table II and Fig. 3). $B_{J''}$ is related to the vibronic matrix element (D_0, from the notation of Chiu[27]) by the equation

$$B_{J''}=(C2)(4\pi hc)^{-1}D_0{}^2, \tag{12}$$

where $(C2)=64\pi^4/3h$. Thus Eqs. (11), (12), (3), and (4) combine to determine the transition probability of a band in weak absorption, from a measurement of $W_{v'v''}$.

The curve of growth for a given band can be predicted as a function of $(D_0{}^2)$ provided one has a measure of k_ν as a function of ν. The determination of k_ν in this case is complicated by the fact that collision broadening must be taken into account. The Lorentz broadening coefficient for the calculations was taken from a measurement of broadening in the N_2 Lyman–Birge–Hopfield system (Shemansky[28]). The rather large broadening cross section (1.6×10^{-14} cm^2) results in lines of about 1-cm^{-1} half-width, at 1 atm, more than half the width of the instrumental function. The synthetic spectra were calculated using the computational methods of Armstrong[29] for the Voigt function. Figure 2 shows a synthetic spectrum of the (12, 0) band convolved with a triangular instrumental function. The molecular constants used in the computation are given in Table V. A comparison of the ratios of equivalent width to peak height of the spectrum (Table I) suggests that the broadening coefficient in the computed spectrum could not be far wrong. The deviation from weak absorption in the computed spectrum was about 3%, an amount that would not be measurable experimentally.

The differences in shape of the experimental and synthetic spectra near the bandhead could possibly be due to a minor (~10%) deviation from the theoretical line-strength factors at low K values, but the noise figures of the experimental spectra are not high enough to establish a deviation of this magnitude.

IV. DISCUSSION

The equivalent widths of the observed bands and the calculated transition probabilities are given in Table I. The accuracy of the measurements is difficult to estimate, but should be roughly ±10% for most of the probabilities given in the table; the open structure of the bands, and the use of synthetic comparison spectra facilitated a reasonably accurate determination of the relative intensity of the continuum. The identification of the (5, 0) band in the absorption spectrum was uncertain, and only an upper limit estimate of the equivalent width is given in Table I.

In order to estimate the lifetimes of the system, one must predict the transition probabilities of the remaining significant members of the Deslandres table. The calculation of these remaining transition probabilities would be an uncomplicated procedure but for the fact that the electronic transition moment (R_e) of the system has a marked variation as a function of internuclear distance. A number of measurements of the variation of R_e, on a relative scale, have been made from observations of emission spectra (see Broadfoot and Maran[30]). Most of the measurements are in good agreement, and indicate a linear variation which would pass through zero at an internuclear distance in the region of 1.2 Å. The measurements of the present work which cover a region of internuclear distance below that of the emission measurements, also indicate a linear variation with an intercept at virtually the same internuclear distance. Although the two sets of measurements, absorption and emission, cover almost the entire range of internuclear distance required to fill the Deslandres table, the lifetime must still be determined by extrapolation of the absorption measurements; the emission measurements of the variation of R_e are not on an absolute basis. However, the emission measurements are compatible with an almost straight-line extrapolation of the transition moment as determined

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[27] Y.-N. Chiu, J. Chem. Phys. **42**, 2671 (1965).

[28] D. E. Shemansky, "Transition Probabilities and Collision Broadening Cross Section of the N_2 Lyman–Brige–Hopfield System," J. Chem. Phys. (to be published).

[29] B. H. Armstrong, J. Quant. Spectry. Radiative Transfer **7**, 61 (1967).

[30] A. L. Broadfoot and S. P. Maran, J. Chem. Phys. **51**, 678 (1969), this issue.

by the absorption measurements, since in the two cases, the ratios of the constants in the linear equations for R_e are very nearly equal. This will now be discussed in detail.

The N_2 VK system falls into that class of band systems, according to the criteria established by Fraser,[31] for which the equation

$$A_{v'v''}{}^{i}=({}^{i}\nu_{v'v''})^3[{}^{i}R_e{}^2(\bar{r})]q_{v'v''} \tag{13}$$

may be written, where $q_{v'v''}$ is the Franck–Condon factor, $R_e(\bar{r})$ is a measure of the variation of the electronic transition moment as a function of internuclear distance, and $\bar{r}$ is the "r centroid" as defined by Fraser. The transition probability of the band $A_{v'v''}{}^{i}$, is equal to $A_{J'}{}^{i}$ as defined in Eq. (2), provided the summation over J'' takes place for a specific vibrational level, v''. $A_{J'}{}^{i}$ is of course, apart from a small dependence on ν, independent of J'; $A_{v'v''}{}^{i}$ could not be defined if this were not the case.

The values of ${}^2R_e(\bar{r})$ calculated from the measured transition probabilities are given in Table I and are plotted against $\bar{r}$ in Fig. 4. The recent measurements of relative $R_e(\bar{r})$ by Broadfoot and Maran[30] are also plotted on the figure. The Franck–Condon factors and $\bar{r}$ values used in the calculations are from Albritton and Zare.[32] The $q_{v'v''}$ values given by Ref. 32 are similar to those calculated by Benesch *et al.*[33] The variation of $R_e(\bar{r})$ has a rather steep slope, but there appears to be no indication of anything other than a linear relationship with $\bar{r}$. If one assumes a linear relationship, the best-fit equation for $R_e(\bar{r})$ can be written,

$${}^{i}R_e(\bar{r})=a[\bar{r}+(b/a)], \tag{14}$$

where, for $i=2$, $b/a=-1.173$ (Å), and $a=\pm1.32\times10^{-6}$ $(\text{cm}^3\,\text{sec}^{-1})^{1/2}$ Å^{-1}. The experimental data, strictly speaking, limit the validity of Eq. (14) to the region $1.08<\bar{r}<1.14$ Å, whereas one would require values of $R_e(\bar{r})$ for $\bar{r}$ as large as 1.4 Å. However, the measurements in emission of v'' progressions for $v'=0$, 1 can be taken into account to reduce the risk in extrapolating $R_e(\bar{r})$. The emission measurements do not yield absolute values of $R_e(\bar{r})$, but there are two factors to consider in comparing the emission and absorption measurements: (1) The emission measurements represent a relatively large range of $\bar{r}$ (1.23→1.44), and give no indication of a departure from a linear variation of $R_e(\bar{r})$. (2) The ratio of intercept to slope ($b/a=-1.206$ Å), differs by less than 3% from the value obtained from the absorption measurements.

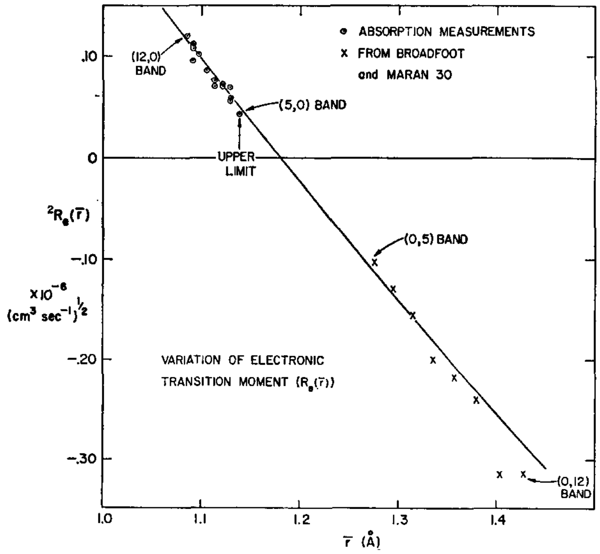

FIG. 4. Variation of electronic transition moment.

The above two points, coupled with the fact that the gap between the two sets of measurements is relatively small (0.1 Å) compared to the region over which the measurements are valid, suggest that $R_e(\bar{r})$ passes through zero and deviates only slightly from a straight line in the region of interest. Thus, assuming the best-fit linear equations to be tangent to a curve with a slowly changing slope, one can write $R_e(\bar{r})$ in the form of a second-order polynomial that fits both the absorption and emission data reasonably well,

$${}^{i}R_e(\bar{r})=\gamma(\alpha\bar{r}^2+\beta\bar{r}+1), \tag{15}$$

where, for $i=2$,

$$\alpha=0.1167\ (\text{Å})^{-2},$$

$$\beta=-0.9850\ (\text{Å})^{-1},$$

$$\gamma=\pm1.69\times10^{-6}\ (\text{cm}^3\,\text{sec}^{-1})^{1/2}.$$

This is the curve shown in Fig. 4.

The possibility that the electronic transition moment could change sign has been mentioned by Bates (see Fraser[31]). The N_2 VK system appears to be the only system for which there is experimental evidence indicating the occurrence of this phenomenon.

The transition probabilities of the bands and the lifetimes of the vibrational levels, calculated using eqs. (15) and (13), are given in Table VI. It was necessary to extrapolate the totals $(\sum_{v''}A_{v'v''})$ of the levels beyond $v'=5$, due to a lack of calculated Franck–Condon factors for $v''>20$. The extrapolation was made by assuming a constant second rate of change of $A_{v'}$, determined from the $v'=0$→5 levels. The lifetimes vary by about 13% over the levels $v'=0$–13.

It is difficult to estimate a probable error for the calculated lifetimes since they are determined by extrapolation. The use of Eq. (14) in Eq. (13) would result in lifetimes for the $v'=0$ level about 25% lower than those given in Table VI. The difference would be progressively less for higher levels. If one were to choose the transitions from the $v'=13$ level that did not require extrapolation of $R_e(\bar{r})$, an upper limit of

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[31] P. A. Fraser, Can. J. Phys. **32**, 515 (1954).

[32] D. L. Albritton and R. N. Zare (unpublished).

[33] W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. **143**, 236 (1966).

$\tau^2(13)\approx2.5$ sec would be obtained, whereas the extrapolated value is $\tau^2(13)\approx1.4$ sec. Thus one would not expect a gross error in the estimated lifetimes.

The only other estimate of lifetime obtained from absorption measurements (Wilkinson and Mulliken[2]) disagrees with the present estimate by two orders of magnitude. However, the Wilkinson and Mulliken estimate was obtained by an indirect method, and involved a gross error in one of the quantities used in the calculation. The lifetime was estimated by comparing the appearance path lengths of bands of the N_2 VK and N_2 LBH systems. The known lifetime of the N_2 LBH system was then used to calculate the lifetime of the VK system. The greatest error in this computation stems from the appearance path-length estimates. The difficulty in comparing the appearance path lengths for the two systems arises in the differences in linewidths and band structures. The N_2 LBH path-length measurements were made at pressures in the 1 torr region with no pressure broadening of the lines, while the N_2 VK measurements were made at 760 torr or greater with a large effect due to pressure broadening. The gross difference in linewidths coupled with differences in the structure of incompletely resolved bands could clearly lead to large errors in the relative appearance path lengths. The appearance path length of the N_2 LBH system given by Wilkinson and Mulliken was 2.5×10^{-2} m·atm, from a measurement by Wilkinson[34] at 1.5 torr. This combination of path length and pressure places the absorption of the stronger bands far into the region of strong absorption (Shemansky[28]). One quantitative measurement, reported in Ref. 28, has in fact been made from an observation in a path length of 5.6×10^{-3} m·atm at 1 torr. Tanaka *et al.*[35] reported an appearance path length of 2.6×10^{-3} m·atm at 0.5 torr. Both of these measurements are still on the nonlinear part of the curve of growth. This suggests that one should use an appearance path length of about 10^{-3} m·atm for the purpose of comparison with the N_2 VK system. The Wilkinson and Mulliken lifetime of 2.6×10^{-2} sec should then be increased by a factor of 25 to about 0.6 sec. An additional factor enters into the comparison of appearance path lengths; it is erroneous to assume that the relative path lengths give a direct measure of relative transition probabilities of bands of different systems. In this case there are more transitions contributing to the transition probability of an LBH band than there are to a VK band. As a result the LBH bands are more difficult to observe, per unit transition probability. A very rough measure of this factor can be obtained by comparing the ratio $D^2/A_{v'v''}$ for the two systems. Bands of the LBH system have a ratio $D_1^2/A_{v'v''}=3.6\times10^{-45}$, and for the VK system, $D_0^2/A_{v'v''}{}^2=1.4\times10^{-44}$. Thus the Wilkinson and Mulliken lifetime must be raised by

TABLE VI. Absolute transition probabilities of the N_2 Vegard–Kaplan system.

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	$A^2_{v'}$	Extrapolated	
																							$A^2_{v'}$	$\tau^2(v')$
0	2009.525 4.1-6	2108.264 6.0-4	2215.790 6.51-3	2333.302 2.92-2	2462.225 7.57-2	2604.266 1.308-1	2761.498 1.634-1	2936.442 1.538-1	3132.212 1.126-1	3352.691 6.53-2	3602.786 3.05-2	3888.781 1.15-2	4218.882 3.6-3	4604.003 8.9-4	5059.958 1.8-4	5604.368 3.0-5	6269.863 --	-- --	-- --	-- --	-- --	.784	.784	1.27
1	1953.289 3.1-5	2046.451 6.5-4	2147.613 9.79-3	2257.825 3.29-2	2378.329 4.53-2	2510.602 2.23-2	2656.411 --	2817.904 3.53-2	2997.704 1.141-1	3199.044 1.661-1	3425.967 1.539-1	3683.585 1.022-1	3978.465 5.12-2	4319.171 1.99-2	4717.141 6.10-3	5197.930 1.5-3	5753.257 2.9-4	6444.387 4.5-5	-- --	-- --	-- --	.762	.762	1.31
2	1901.116 7.5-4	1989.255 --	2084.709 5.14-3	2188.404 1.23-2	2301.426 2.83-3	2425.061 8.30-3	2560.841 5.21-2	2710.599 6.49-2	2876.563 1.88-2	3061.457 4.87-3	3268.648 7.25-2	3502.343 1.485-1	3767.878 1.578-1	4072.115 1.105-1	4424.007 5.58-2	4835.549 2.12-2	5323.089 6.18-3	5909.526 1.40-3	6627.897 2.5-4	7527.951 3.4-5	-- --	.744	.744	1.34
3	1852.608 4.33-3	1936.208 1.69-3	2026.524 5.9-4	2124.375 8.7-4	2230.720 3.96-3	2346.594 2.75-2	2473.599 2.33-2	2613.054 --	2766.955 3.81-2	2937.609 7.98-2	3127.855 3.72-2	3341.195 3.4-4	3582.016 5.60-2	3855.888 1.352-1	4169.983 1.481-1	4533.689 1.019-1	4959.578 4.91-2	5464.854 1.74-2	6073.678 4.66-3	6821.039 4.67-3	7759.779 6.5-4	.735	.735	1.36
4	1807.424 1.41-2	1886.908 7.92-3	1972.581 1.6-4	2065.173 2.2-4	2165.534 7.98-3	2274.653 1.03-2	2393.699 4.3-4	2524.053 3.13-2	2667.363 3.95-2	2825.611 1.42-3	3001.194 3.35-2	3197.065 8.41-2	3416.875 4.12-2	3665.200 2.4-4	3947.859 5.53-2	4272.359 1.282-1	4648.548 1.319-1	5089.619 8.39-2	5613.696 3.69-2	6246.297 1.18-2	7024.530 2.80-3	.723	.723	1.38
5	1765.261 3.37-2	1841.003 1.62-2	1922.468 3.7-4	2010.311 1.6-4	2105.287 3.07-3	2208.275 3.3-5	2320.304 1.39-2	2442.582 2.14-2	2576.544 --	2723.902 3.57-2	2886.716 4.70-2	3067.484 1.48-3	3269.274 3.79-2	3495.898 8.46-2	3752.134 3.34-2	4044.066 2.02-3	4379.557 6.36-2	4768.953 1.221-1	5226.107 1.102-1	5770.137 6.20-2	6428.025 2.40-2	.722	.712	1.40
6	1725.659 6.23-2	1798.187 2.05-2	1875.828 5.7-5	1959.367 2.9-4	2049.483 1.4-4	2146.957 2.32-3	2252.701 1.13-2	2367.782 3.7-4	2493.454 2.05-2	2631.206 2.80-2	2782.819 --	2950.436 4.43-2	3136.663 4.54-2	3344.689 --	3578.499 4.94-2	3843.083 7.90-2	4144.812 1.89-2	4491.929 8.94-3	4895.302 7.53-2	5369.528 1.116-1	5934.762 8.46-2	.663	.704	1.42
7	1688.982 9.96-2	1758.193 1.71-2	1832.347 3.38-3	1911.977 2.20-3	1997.690 --	2090.139 2.29-3	2190.285 1.70-3	2298.923 5.96-3	2417.209 1.91-2	2546.448 4.8-5	2688.187 3.05-2	2844.278 2.72-2	3016.953 2.56-3	3208.929 5.53-2	3423.539 3.44-2	3664.933 2.57-3	3938.341 6.33-2	4250.435 6.37-2	4609.867 5.07-3	5028.064 2.30-2	5520.428 8.40-2	.543	.698	1.43
8	1654.430 1.361-1	1720.782 8.20-3	1791.753 1.36-2	1867.871 3.12-3	1949.537 5.0-5	2037.532 3.63-4	2132.534 2.1-4	2235.384 9.06-3	2347.063 2.06-3	2468.721 1.24-2	2601.714 2.21-2	2747.651 1.12-3	2908.461 4.21-2	3086.471 1.79-2	3284.514 1.21-2	3506.079 6.16-2	3755.493 1.68-2	4038.240 1.45-2	4361.315 7.13-2	4733.810 3.96-2	5167.756 --	.484	.696	1.44
9	1622.022 1.786-1	1685.751 7.5-4	1753.804 2.77-2	1826.619 1.24-3	1904.697 1.55-3	1988.605 3.2-5	2078.997 1.05-3	2176.630 3.31-3	2282.377 2.04-3	2397.257 1.66-2	2522.466 3.1-4	2659.415 2.54-2	2809.780 1.68-2	2975.571 9.08-3	3159.214 4.81-2	3363.671 5.08-3	3592.588 3.04-2	3850.501 4.40-2	4143.146 2.35-3	4477.876 3.46-2	4864.253 6.48-2	.514	.696	1.44
10	1591.599 2.108-1	1652.915 2.66-3	1718.291 3.83-2	1788.129 1.3-4	1862.883 4.97-3	1943.072 --	2029.285 3.4-4	2122.200 9.3-5	2222.603 6.03-3	2331.401 4.07-3	2449.655 8.31-3	2578.610 1.90-2	2719.734 1.58-3	2874.776 3.63-2	3045.831 5.65-3	3235.435 2.63-2	3446.682 4.01-2	3683.389 --	3950.319 4.94-2	4253.477 3.36-2	4600.598 2.12-3	.490	.699	1.43
11	1563.019 2.322-1	1622.111 1.91-2	1685.027 3.94-2	1752.135 5.39-3	1823.850 6.98-3	1900.644 2.2-4	1983.053 2.8-5	2071.693 2.9-4	2167.268 3.87-3	2270.591 1.7-4	2382.609 1.39-2	2504.426 9.9-4	2637.337 2.07-2	2782.875 1.19-2	2942.865 1.29-2	3119.494 3.56-2	3315.414 --	3533.863 3.61-2	3778.842 1.94-2	4055.347 1.21-2	4369.697 5.41-2	.525	.705	1.42
12	1536.155 2.426-1	1593.196 5.04-2	1653.847 3.02-2	1718.447 1.87-2	1787.376 5.0-3	1861.067 2.5-3	1940.010 3.3-4	2024.761 2.5-4	2115.960 6.8-4	2214.341 3.3-3	2320.749 5.9-3	2436.170 4.4-3	2561.753 1.73-2	2698.852 1.2-3	2849.066 3.07-2	3014.299 1.6-3	3196.842 3.14-2	3399.468 1.62-2	3625.571 1.11-2	3879.348 4.64-2	4166.051 1.9-3	.522	.713	1.40
13	1510.894 2.414-1	1566.041 9.25-2	1624.604 1.56-2	1686.896 3.57-2	1753.269 1.08-3	1824.119 6.97-3	1899.894 1.2-4	1981.103 --	2068.327 1.0-5	2162.230 3.55-3	2263.577 1.7-4	2373.250 1.09-2	2492.272 2.23-3	2621.847 1.62-2	2763.386 1.01-2	2918.560 1.33-2	3089.362 2.60-2	3278.190 2.61-3	3487.951 4.08-2	3722.205 2.42-3	3985.364 3.27-2	.554	.725	1.38

v''

v' | λ (Å) R_2 Head

$A^2_{v'v''} = 2A^1_{v'v''} = 2A^3_{v'v''}$ (sec^{-1})

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another factor of 4 to $\tau^2=2.4$ sec. Other minor factors involving relative transition probabilities within each band system bring this figure down to a final value of $\tau^2 \approx 1.6$ sec. The remarkable agreement with the present work must be considered accidental; the computational method does not warrant an accuracy better than a factor of 2 or 3. However, the recalculation does indicate that the disparity in lifetime estimates lies entirely in an erroneous appearance path length for the LBH system coupled with analytical errors by Wilkinson and Mulliken. Wilkinson's observations of the VK bands appear to be in good agreement with the present work; the appearance path length of 4 m·atm estimated by Wilkinson[13] is in accord with the figures given in Table I. The method of appearance path lengths for the determination of transition probabilities clearly has little to recommend it.

Most of the lifetime measurements of the VK system stem from observations of laboratory afterglows. Phillips[5] measured a lifetime of 1.1 sec from observations of the decay of emission from I_2, excited by active nitrogen. Dunford[6] estimated $\tau=0.08$ sec using ammonia as a reactant. These measurements are uncertain because the reacting species in the active nitrogen were not directly identified as molecules in the $A\ ^3\Sigma_u^+$ state. Noxon[3] estimated $\tau \approx 1$ sec from the decay of VK bands from $v'=0$, 1 levels in a high-pressure afterglow ($\sim$1 atm). His observations ruled out a shorter lifetime, but the possibility of a lifetime longer than 1 sec could not be excluded. The mean lifetime of the observed decay was about 1 sec, and Noxon concluded that this was mostly due to the natural lifetime of the state. Zipf[4] obtained $\tau=0.9$ sec from observations of the decay of the (0, 6) band in pure N_2 at pressures between 10 and 0.1 torr. Brömer and Spieweck[7] repeated the Zipf experiment with a larger diffusion length, and obtained $\tau=10$ sec. The disparity of these two estimates illustrates the difficulty in making such measurements. Fundamental mode diffusion to the walls of the container dominates the measured lifetime at these pressures. The measured diffusion coefficient was exactly the same in both cases. The order-of-magnitude difference in lifetime estimates must therefore stem from obscure minor differences in experimental conditions; there appears to be no way of discriminating between the measurements. The estimate of the natural lifetime could depend critically on the minor processes assumed to be affecting the decay of the metastable molecules; the dominance of diffusion relegates the decay by emission to a minor role in determining the effective lifetime. The afterglow measurements thus appear to be rather uncertain, due to the competing effects of diffusion, radiationless deactivation, and reactivation.

The measurements of greatest importance are those of Carleton and Oldenberg,[10] from which a direct estimate of the transition probability of the (0, 6) band has been obtained, with an accuracy comparable to the measurements given in Table I. Since the band lies within the appropriate region of internuclear distance, the transition probability can be used to place the emission measurements of $R_e(\bar{r})$ on the absolute scale. Thus a comparison can be made with the $R_e(\bar{r})$ extrapolated from the absorption measurements. Carleton and Oldenberg originally estimated a lifetime of 2.0 sec for the $v'=0$ level. However, this value has been subject to revision. The transition probability of the (0, 6) band was calculated from direct measurements of the volume emission rate and the population of the $v'=0$ level. The population was determined from a measurement of the fractional self-absorption of the (1, 0) first positive band. The accuracy of the calculated lifetime of the $A\ ^3\Sigma_u^+$ state therefore depends on the accuracy of the measured lifetime of the $B\ ^3\Pi_g$ state. The lifetime of the $B\ ^3\Pi_g$ state used in the original calculation was inaccurate and consequently the lifetime of the $A\ ^3\Sigma_u^+$ state was raised to about 12 sec (Wentink and Isaacson,[8] Brennen[9]). An erroneous assumption in the original analysis, which involved the coupling of the ($B\ ^3\Pi_g$–$A\ ^3\Sigma_u^+$) transition has led to a further recalculation, giving a final value of $\tau^2(0)=1.36$ sec (Shemansky and Carleton[12]). This is in excellent agreement with the value given in Table VI, $\tau^2(0)=1.27$ sec. The accuracy of the lifetimes given in Table VI would otherwise have been rather uncertain. This is especially true of the lower vibrational levels, which are the most sensitive to the extrapolation of $R_e(\bar{r})$. There is no reason to doubt the carefully conducted experiment of Carleton and Oldenberg; the reanalysis of their work (Ref. 12) does not question the experimental measurements, but involves only the calculation of the lifetimes from the measured quantities.

V. CONCLUSION

Measurements of the N_2 VK system in absorption have allowed the calculation of the lifetimes of the $A\ ^3\Sigma_u^+$ state. Although the measurements themselves are reasonably accurate, the accuracy of the calculated lifetimes is difficult to estimate without the aid of other independent measurements. The uncertainty stems from the necessity of extrapolating the measured electronic transition moment in order to calculate the lifetime. However, measurements in emission of relative $R_e(\bar{r})$ in the extrapolated region tend to support a near linear extrapolation. An $R_e(\bar{r})$ curve modified slightly by these measurements was used in the calculation. The calculated lifetimes for the higher vibrational levels are on firmer ground since a large fraction of the total transition probability of the levels is determined within the measured region of $R_e(\bar{r})$. Thus the calculated lifetime of the $v'=13$ level is estimated to have an accuracy of better than 50%. One cannot expect a large variation in lifetime as a function of v'; the Franck–Condon factors are rather evenly scattered in magnitude throughout the Deslandres table, and a large variation in lifetime would require a wildly varying transition moment. The lifetimes of the lower vibrational levels, although less certain, are therefore estimated to be of the same order of accuracy.

Most of the earlier estimates of lifetime appear to be rather uncertain. Although a number of the afterglow measurements indicate a mean lifetime within a factor of 2 of the values in Table VI, the agreement could quite possibly be accidental. However, Noxon[3] does present a convincing argument for a mean lifetime of roughly 1 sec, based on his measurements at 1 atm pressure. The lifetime estimate of greatest importance is that derived from the Carleton and Oldenberg experiment, since the measurements are not affected by the competing processes that control the population of the excited state. The lifetimes calculated from this experiment, for the $v'=0$ level, differ by only 7% with the values given in Table VI. The remarkable agreement may be accidental since the estimated probable errors of both sets of measurements are substantially larger than 7%. However, it should be safe to reduce the probable error of the lifetimes given in Table VI to the value estimated for the Carleton and Oldenberg measurements, about 20%.

It has been shown that the N_2 $A\,{}^3\Sigma_u^+$ state has two distinct lifetimes, resulting from asymmetry in the transitions forming the bands. The calculated lifetimes for the $v'=0$ level are $\tau^2(0)=1.27$ sec for the $\Sigma=0$ substate levels, and $\tau^1(0)=\tau^3(0)=2.5$ sec for the $\Sigma=1, -1$ substate levels, with a probable error of about 20%.

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Microwave Spectra of Nitrogen-Containing Molecules. IV. Conformation, Dipole Moment, and Quadrupole Coupling Constants of Cyclopropylamine

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The microwave spectra of three isotopic species of cyclopropylamine have been investigated. The *A*, *B*, and *C* rotational constants in megahertz for $C_3H_5NH_2$ are, respectively, 16269.95, 6723.00, and 5795.33; for C_3H_5NHD they are 15957.12, 6382.01, and 5504.06; and for $C_3H_5ND_2$ they are 15592.62, 6091.39, and 5246.56. Quadrupole coupling constants have been measured and have the values $\chi_{aa}=2.288$, $\chi_{bb}=1.841$, and $\chi_{cc}=-4.129$ MHz for the normal isotopic species. The dipole-moment components are found to be $\mu_a=0.43$ D and $\mu_c=1.11$ D which lead to a total moment of 1.19 D. The molecular structure of cyclopropylamine has been discussed, and in addition to other structural parameters, we have found C–C=1.520, C–N=1.428, and amino H···H=1.631 Å.

INTRODUCTION

Recently we have undertaken microwave studies of a variety of nitrogen-containing molecules[1–3] in order to obtain a clearer understanding of the nature of the chemical bonding and electron distribution of nitrogen in different environments. Cyclopropylamine was especially interesting because of the conformational problem that it presented and because of the possibility of observing internal rotation and inversion motions and determining their respective potential barriers, as was done for methylamine[4] and dimethylamine.[5] Another factor of special interest here was the nature of the bonding of the nitrogen to the cyclopropyl ring and the extent to which the nitrogen lone-pair electrons might interact with the electrons of the cyclopropyl ring.[6,7]

In this study we report the microwave spectrum, structure, dipole moment, and quadrupole coupling constants of cyclopropylamine ($C_3H_5NH_2$). While a complete structural determination was not attempted,

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