N$_2^+$ Meinel band quenching

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We have measured the rate coefficients for quenching the $A\ ^2\Pi_u$ state of N$_2^+$ by air to be (7.0 ± 0.4), (7.5 ± 1.0), and $(7.0\pm1.0)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} for vibrational levels 2–4, respectively. Rate coefficients for quenching vibrational level 2 by molecular nitrogen and oxygen are (7.5 ± 0.8) and $(6.2\pm0.6)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively. Our results show that Meinel-band quenching becomes significant at altitudes below 100 km.

I. INTRODUCTION

The N$_2^+(A\ ^2\Pi_u)$ state is one of the major radiators in auroras[1-4] and the air glow[5] giving rise to the prominent nitrogen Meinel bands $(A\ ^2\Pi_u-X\ ^2\Sigma_g^+)$ in the red and near infrared region of the spectrum (500–2000 nm). In addition the production of substantially vibrationally excited N$_2^+$ through the ionization of N$_2$ by energetic electrons predominantly involves the $A\ ^2\Pi_u$ state. Thus, the excitation[6] and relaxation of N$_2^+(A\ ^2\Pi_u)$ determines the distribution of vibrational excitation of N$_2^+(X\ ^2\Sigma_g^+)$ in an aurora or disturbed atmosphere.

The deexcitation of N$_2^+(A\ ^2\Pi_u)$ can occur either by radiative or collisional relaxation. Because the lifetime of the $A\ ^2\Pi_u$ state is about 10 μs and the collisional relaxation rate is sufficiently large, this state collisionally quenches readily at pressures above a millitorr. The failure to discriminate collisional from radiative relaxation confounded early laboratory attempts to measure the lifetime of N$_2^+(A\ ^2\Pi_u)$.[7,8] Recent ion beam time-of-flight measurements, however, have determined unambiguously the lifetime of the N$_2^+(A\ ^2\Pi_u)$ state.[9,10] The collisional quenching of this state is still not well understood. Laboratory values for the rate coefficient for quenching N$_2^+(A\ ^2\Pi_u)$ by molecular nitrogen span a range of more than a factor of 2.[8,11-13] The systematic investigation of the quenching of the Meinel bands by molecular oxygen at room temperature has not been reported although Pendleton and Weaver estimated an O$_2$ quenching-rate coefficient based upon a single measurement in a nitrogen/oxygen mixture. Sheridan et al.[14] also published a value for O$_2$ quenching of N$_2^+(A\ ^2\Pi_u, v' = 4)$ but at collision energies of 6–11 keV.

The rate coefficients for quenching N$_2^+(A\ ^2\Pi_u)$ by molecular oxygen and nitrogen have now been determined using a Stern–Volmer analysis. The absolute magnitude of the quenching rates is obtained from the measured N$_2^+(A\ ^2\Pi_u)$ lifetimes of Peterson and Moseley.[10]

II. EXPERIMENTAL

These measurements were made using the LABCEDE facility[15,16] at the Air Force Geophysics Laboratory. The LABCEDE chamber is a cylindrical vacuum tank, 3.4 m long and 1 m in diameter, in which an electron beam has been used to irradiate a variety of gases of atmospheric interest. In nitrogen or nitrogen/oxygen mixtures, fluorescence from a number of neutral and ionic electronic bands is observed, including the Meinel bands.[17] The gas mixture to be irradiated enters the reaction chamber at one end through a large porous-tube array, flows under essentially plug-flow conditions along the longitudinal axis of the chamber and out through a 32 in. diffusion pump backed by a Roots blower/fore pump combination (effective pumping speed = 2.6 × 10^4 l s^{-1}). This flow pattern limits the residence time of gaseous species in the electron beam volume to only a few milliseconds at most, so that quenching by electron-beam-created species is negligible. The electron beam enters the chamber through one side, a little over a meter from the upstream end of the tank. The electron gun provides currents up to 20 mA at energies up to 6 kV.

Fluorescence is observed through one of two observation ports containing BaF$_2$ windows. One port views the excitation region from the upstream end of the tank, perpendicular to the electron beam, and about 1.2 m from it. The other observation port is at an angle of about 19° from the intersection of the electron beam with the longitudinal axis of the tank and about 0.7 m from this junction. A 5 cm diam, 10 cm focal length suprasil lens collects the fluorescence and focuses it upon the entrance slit of a 0.3 m monochromator (McPherson 218) equipped with a 1200 groove/mm grating blazed at 500 nm. An HTV R955 photomultiplier operated at a gain of 5 × 10^6 detects the photons, and a picoammeter/recorder combination displays the photomultiplier output.

The image of the monochromator slit at the excitation region determines the detector's field of view. This image is about 4 × 0.4 cm for viewing from the end of the tank, and 3 × 0.28 cm for viewing from the side port. The field of view of the detector, therefore, is a rectangular slice through the electron beam whose height is comparable to the diameter of the beam but whose width is narrow compared to the length of the irradiated volume. Because the mean molecular velocity of nitrogen at 300 K is 4.8

$\times 10^4$ cm s^{-1}, the N$_2^+(A)$ molecules can travel 5 mm or less during the molecule's effective lifetime. This distance is too short to allow significant diffusive losses out of the field of view along its longer dimension. Experiments in which the length of the field of view was varied by a factor of eight verified this assumption. Diffusion out of the field of view along the axis of the irradiated volume is balanced by diffusion into the field of view along the e-beam axis from species excited outside the monochromator field of view.

A Corning 3-71 colored glass filter rejects second-order spectra for measurements made to the red of 500 nm. In order to ensure that second-order leakage of the very strong nitrogen First Negative band at 391 nm (N$_2^+$ $B\ ^2\Sigma_u^+$, $v' = 0$—$X\ ^2\Sigma_g$, $v'' = 0$) did not contaminate the intensity measurements of the Meinel 2, 0 band at 782 nm; this filter's second-order rejection ratio was checked by scanning several strong UV mercury lines emitted from a pen lamp. The rejection ratio was about 10^{-6} compared to a ratio of the intensities of the Meinel 2, 0 band to the first-order 391 nm band of $\sim 5 \times 10^{-3}$. Concentrations of N$_2^+$ X ground state are sufficiently low that self-absorption of both fluorescence bands is completely negligible.

Most of the Meinel bands are spectrally overlapped with nitrogen First Positive $B\ ^3\Pi_g \rightarrow A\ ^3\Sigma_u^+$ emissions. The degree of overlap depends on pressure and the Meinel (2, 0), (3, 1), and (4, 2) bands are less overlapped at low pressures where the excitation of the Meinel bands is stronger relative to the excitation of the First Positive bands. This difference in apparent excitation results from two factors. At higher pressures the Meinel bands are quenched more efficiently. Also, the flux of secondary electrons increases with pressure and the secondary electrons excite the First Positive bands more efficiently than the primary electrons do. A number of procedures, described below, were used to minimize interference from underlying First Positive emissions.
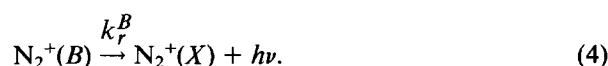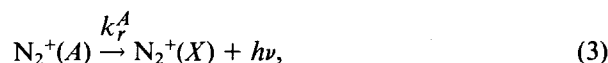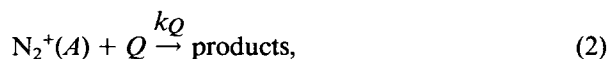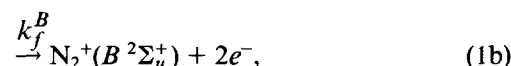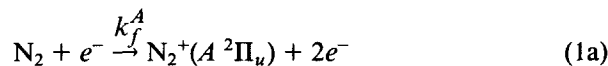
III. MEASUREMENT TECHNIQUE

A classical Stern–Volmer analysis[18] was used to extract the quenching rate coefficients of the Meinel bands, using the ionic nitrogen First Negative band at 391.4 nm ($B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+$) as the reference transition for the case of no quenching. Except near threshold, the relative cross sections for electron-impact excitation of the N$_2^+$ $A\ ^2\Pi_u$ and $B\ ^2\Sigma_u^+$ states as a function of energy are proportional.[19] In addition, the ratio of creation of both states by primary electrons to that by secondary electrons is identical (about 4/1).[20] Thus, measurements of the intensity of the 391.4 nm transition as a function of pressure will reflect accurately the relative changes in the Meinel band intensities if quenching were absent. Several groups have determined a Stern–Volmer quenching coefficient (defined below) for the 391.4 nm band of ≈ 1 Torr^{-1}.[8,21–23] Thus, at pressures below 10 mTorr, the 391.4 nm intensity is diminished by less than 1% which is negligible in the case of the present experiments.

The range of the primary electrons is so great[24,25]

(>10 m) at the pressures of these experiments (<10 mTorr), that production of significant number densities of such potentially reactive species as oxygen or nitrogen atoms in the observation region is unlikely. Thus, these species are ignored.

The quenching analysis is based upon the following series of reactions:

$$N_2 + e^- \xrightarrow{k_f^A} N_2^+(A\ ^2\Pi_u) + 2e^- \qquad (1a)$$

$$\xrightarrow{k_f^B} N_2^+(B\ ^2\Sigma_u^+) + 2e^-, \qquad (1b)$$

$$N_2^+(A) + Q \xrightarrow{k_Q} \text{products}, \qquad (2)$$

$$N_2^+(A) \xrightarrow{k_r^A} N_2^+(X) + h\nu, \qquad (3)$$

$$N_2^+(B) \xrightarrow{k_r^B} N_2^+(X) + h\nu. \qquad (4)$$

Processes producing vibrationally excited N$_2^+(A)$ by cascade from higher lying electronic states of N$_2^+$ are negligible both due to decreased production cross sections of those more highly excited states and Franck–Condon factors which favor cascade into the lowest vibrational levels of the $A\ ^2\Pi_u$ state. Steady-state conditions prevail in the observation volume so that

$$\frac{d[N_2^+(A)]}{dt} = k_f^A(p) - \{k_r^A + k_Q[Q]\}[N_2^+(A)] = 0, \qquad (5)$$

where the formation rate k_f is a function of pressure (p).

The Meinel band emission intensity is $I_A = k_r^A[N_2^+(A)]$, and Eq. (5) therefore gives

$$I_A = \frac{k_f^A(p)}{1 + (k_Q[Q]/k_r^A)}. \qquad (6)$$

Similarly, the emission intensity of N$_2^+(B)$ is

$$I_B = k_r^B[N_2^+(B)] = k_f^B(p). \qquad (7)$$

Because the ratio of the electron excitation cross sections for the N$_2^+$ (A and B) states is constant except near threshold,

$$k_f^A(p) = \alpha k_f^B(p), \qquad (8)$$

where α is the constant of proportionality between the curves of electron excitation cross section as a function of energy for the A and B states. As a result, the intensities of the First Negative and Meinel emission are related to the quencher density by

$$\frac{I_B}{I_A} = \frac{1}{\alpha} + \frac{k_Q}{\alpha k_r^A}[Q]. \qquad (9)$$

Plots of the ratio of the intensities of the 391.4 nm band to a Meinel band vs number density of quencher should be linear, and the ratio of the slope to intercept from those plots (the Stern–Volmer quenching coefficient) gives the ratio of k_Q to k_r^A. Holland and Maier[9] and Peterson and Moseley[10] have established values for k_r^A, so that k_Q can be determined.

In order to isolate the effects of quenching by molecular nitrogen from those of quenching by molecular oxygen, a series of runs in O_2/N_2 mixtures were performed with mole fraction ratios X_{O_2}/X_{N_2} ranging from 0 to 1.7. Each run consisted of series of measurements of the ratio I_B/I_A as a function of pressure with a fixed X_{O_2}/X_{N_2}. Analysis according to Eq. (9) then yields a value for k_Q/k_r^A of

$$k_Q/k_r^A = K_{\mathrm{mix}} = \frac{k_{N_2}}{k_r^A} X_{N_2} + \frac{k_{O_2}}{k_r^A} X_{O_2}, \qquad (10)$$

and

$$\frac{K_{\mathrm{mix}}}{X_{N_2}} = \frac{k_{N_2}}{k_r^A} + \frac{k_{O_2}}{k_r^A} \frac{X_{O_2}}{X_{N_2}}. \qquad (11)$$

Thus from a linear plot of K_{mix}/X_{N_2} vs X_{O_2}/X_{N_2} the molecular oxygen quenching-rate coefficient can be extracted from the slope, and the molecular nitrogen quenching-rate coefficient from the intercept.

IV. RESULTS

A. Quenching rates

Plots of the ratio of the intensity of the nitrogen First Negative band to the intensity of the Meinel bands as a function of pressure for the initial data showed distinct curvature. Experiments showed that this problem was not related to diffusion of the Meinel band emitters out of the field of view because, in a series of measurements in which the detector field of view was varied by a factor of 8, all the measurements gave identical results. Contamination of the Meinel spectrum by underlying nitrogen First Positive radiation seemed to be the most likely source of the curvature.

At pressures on the order of a millitorr, most of the emission observed in the tank is excited by the high-energy, primary electrons in the beam. As the pressure in the chamber rises, secondary electrons created from ionization of the gas in the chamber by the primary electron beam begin to become appreciable. These secondary electrons can collide with and excite the gas in the chamber within the detector's field of view. While the primary electron-beam flux is relatively constant over the range of pressures of this investigation, the secondary-electron flux increases rapidly as the chamber pressure is increased.

Almost 90% of the nitrogen First Positive band excitation is due to secondary electrons, whereas nearly 80% of the Meinel and First Negative band excitation arises from primary electrons.[20] Thus, at the lowest pressures, where the number of secondary electrons created is small and where the mean free path of these secondaries is relatively great, the nitrogen First Positive excitation will be negligible compared to the Meinel band excitation. As the pressure increases, however, the number of secondary electrons rapidly increases, and their mean free path decreases so that the effects of secondary excitation within a restricted field of view increases at a rate much greater than linear, while the growth in the nitrogen First Negative band intensity is essentially linear with pressure.

If the Meinel bands were not quenched, the Meinel band intensity would grow linearly with pressure, like the First Negative bands. Because they are quenched, however, they grow more slowly than linearly. When the Meinel bands are overlapped by other bands which grow much more rapidly than linearly with pressure, the effect of Meinel quenching on the total intensity within a given band pass around the Meinel bands will be underestimated due to the growing underlying radiation.

Several measures were employed to reduce the effects of underlying First Positive radiation to the point where the measurements of the Meinel band intensities were free from the interference of underlying First Positive radiation. The measurements were made with a field of view restricted to the central portion of the primary electron beam, were restricted to pressures below 7.5 mTorr, and used a monochromator to restrict the detector bandpass to narrow regions of the spectrum over which the Meinel band intensities are strongest compared to neighboring First Positive emissions.

Restricting the detector's field of view to the central portion of the electron beam discriminated against regions of the apparatus in which emissions are excited predominantly by secondary electrons. The primary electrons are confined to a fairly narrow, and well defined field of view. The secondary electrons on the other hand are scattered almost isotropically out of the primary beam so that excitation events involving secondary electrons are more likely to occur outside the primary beam. The field of view was maintained sufficiently large, however, that no effects of diffusion of the $N_2^+(A)$ out of the field of view prior to radiation could be observed.

The data in Fig. 1 are used to define an upper limit to the pressure below which the effects of underlying radiation are negligible. Figure 1 is a plot of the fraction of the total integrated intensity under the Meinel 2, 0 band which can be attributed to emission from the First Positive 7, 6 band as a function of pressure in air and in nitrogen. The integrated intensity of the 7, 6 band was calculated by scaling the intensity of the First Positive 7, 4 band by the appropriate transition probability[26] and monochromator response function. An interesting feature of the plot is that the presence of the oxygen in the air seems to reduce the importance of secondary electron excitation at least with respect to excitation of the nitrogen First Positive bands. Note also the point taken in air at 10 mTorr with the monochromator's field of view set to look somewhat above the central portion of the primary electron beam. The First Positive excitation for this setting has almost doubled in relation to the Meinel band intensity. This figure shows that if interference by the 7, 6 band of as much as 10% can be tolerated, then measurements in air can proceed up to 10 mTorr, whereas in nitrogen, the maximum pressure must be kept below 5 mTorr. In practice, the pressure limitation will not be so severe because the monochromator bandpass can be restricted to a region of the spectrum where the contribution of the First Positive band emission in that bandpass is somewhat less than its contribution to the observed emission over the whole emission band. For example,
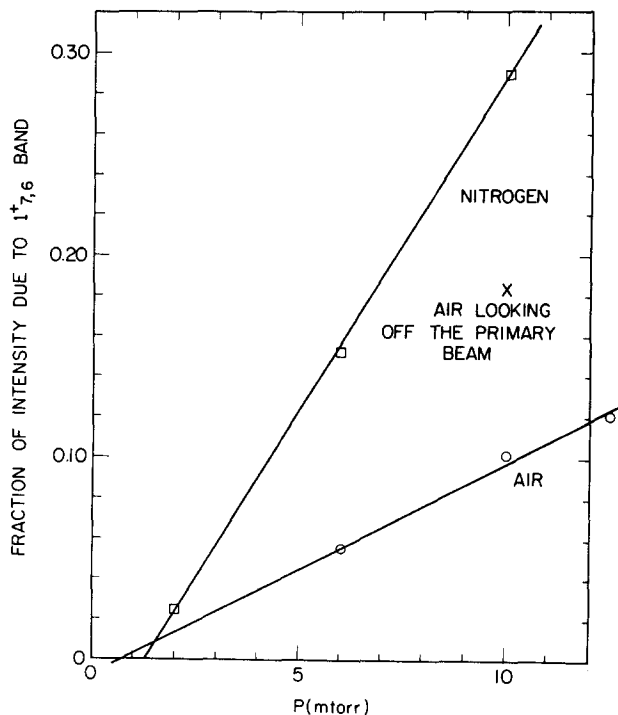
FIG. 1. The fraction of total integrated intensity in the 780–795 nm region that can be attributed to N$_2$(B $^3\Pi_g$, 7–A $^3\Sigma_u^+$, 6), 1$^+$, band.

one of the most intense portions of the Meinel 2, 0 band is the region around the R_2 head at 782.6 nm. The 7, 6 First Positive band on the other hand is strongest in the region between 785 and 790 nm and is falling off to the blue of 785 nm.

The effect of varying the bandpass on the ratio of the intensity of the First Negative band at 391.4 nm to the Meinel 2, 0 band at 782.5 nm as a function of pressure of air is shown in Fig. 2. The data taken with bandpasses between 0.25 and 1.0 nm all match up quite well at all pressures up to 10 mTorr. The data taken with a 2.0 nm bandpass, however, deviates markedly from linearity above 5 mTorr, and the effect of this deviation from linearity is even worse when the data are taken with a 2 nm bandpass which is centered at 785 nm, right in the center of the band where the First Positive contribution will be stronger. Although the data in Fig. 2 indicate that the safe region for measurements extends up to 10 mTorr with a 1 nm bandpass, most of the measurements were restricted to pressures below 7.5 mTorr.

Several series of quenching measurements consistent with these limitations on operating pressure were made. In Fig. 3 a representative quenching plot for laboratory air is shown. Runs with air at a number of different electron-beam currents and beam energies determined the independence of the quenching parameter upon these variables. The results are summarized in Fig. 4.

The experimental quenching parameters—ratio of slope to intercept—are 0.272 ± 0.014, 0.261 ± 0.017, and 0.222 ± 0.017 mTorr^{-1} for vibrational levels 2, 3, and 4, respectively, when quenched by air. These translate to rate coefficients of (7.0 ± 0.4) × 10^{-10}, (7.5 ± 1.0) × 10^{-10}, and (7.0 ± 1.0) × 10^{-10} cm^3 molecule^{-1} s^{-1} for vibrational levels 2–4, respectively.
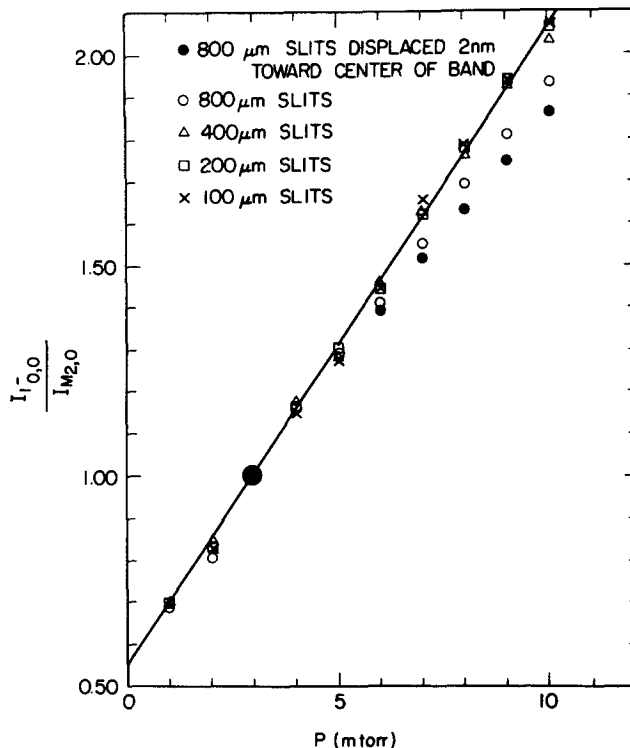

FIG. 2. Variation in the ratio of the First Negative, 1$^-$, (0, 0) 391.4 nm intensity to that for the Meinel 2, 0 band as a function of pressure of air. All data sets have been normalized to a value of 1.0 at 3 mTorr.

The quenching plots relevant to the measurements in the O$_2$/N$_2$ mixtures are shown in Figs. 5 and 6. In reducing the raw data from these runs, some small corrections were made for underlying oxygen radiation. Measurements of the ratio of the radiation intensity at 782.5 nm to that from the atomic oxygen line at 844.6 nm in pure oxygen, determined correction factors which were assumed valid for O$_2$/N$_2$ mixtures. These corrections generally were small, ≲10%, but were necessary to obtain
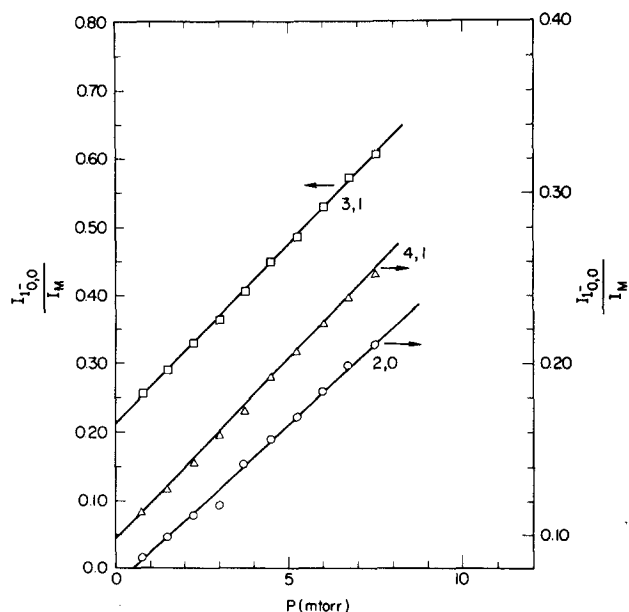

FIG. 3. Stern–Volmer quenching plot for the Meinel bands in air as ratioed to First Negative 1$^-$(0, 0) emission at 391.4 nm.
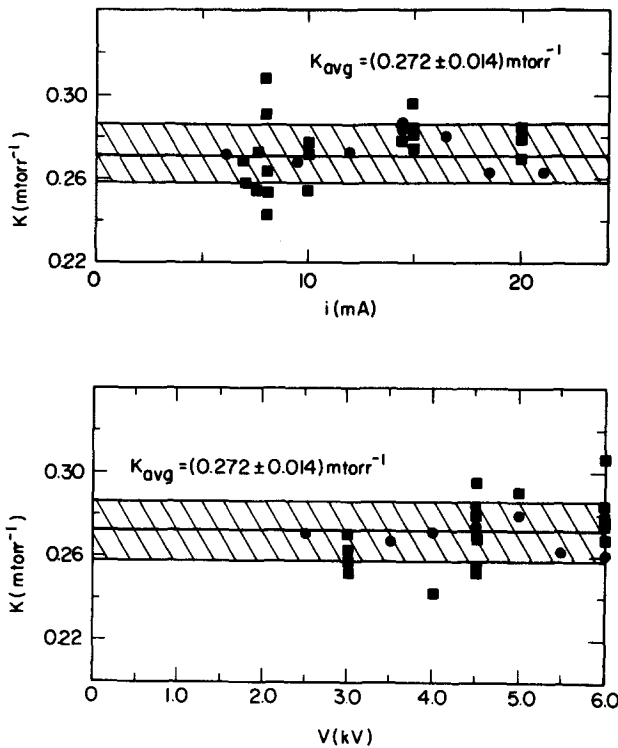
FIG. 4. Current and voltage dependence of quenching constant of Meinel 2, 0 band in air.
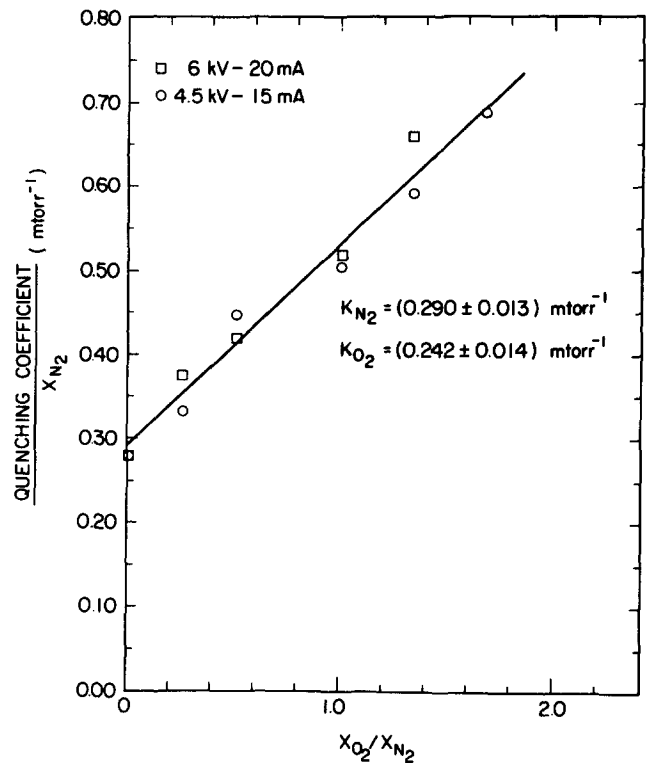

FIG. 6. Quenching of Meinel 2, 0 band in N$_2$/O$_2$ mixtures.

linear quenching plots. These measurements give quenching parameters of (0.242 ± 0.013) and (0.290 ± 0.014) mTorr^{-1} for oxygen and nitrogen, respectively, or quenching-rate coefficients of (6.2 ± 0.6) and $(7.5 \pm 0.8) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively.

FIG. 5. Meinel 2, 0 quenching by N$_2$/O$_2$ mixtures. ζ is offset added to ordinate for clarity.

Peterson and Moseley's[10] lifetime measurements (11.9, 10.7, and 9.7 μs for levels 2–4, respectively) were used to provide absolute quenching-rate coefficients. These lifetime measurements agree well with those of Holland and Maier[9] and, in addition, give relative transition probabilities fully consistent with band-intensity measurements of Wu and Shemansky[27] and Gattinger and Vallance Jones.[4] Peterson and Moseley claim an accuracy of better than 4% for their measurements.

The error limits quoted for these quenching-rate coefficients are two standard deviations from the average of all the data. These are probably reasonably accurate representations of the total uncertainty in the results because the major experimental uncertainties, the Meinel band lifetimes, and the pressure-gauge calibration are both less than 5%. Table I summarizes these results and compares them with available literature values.
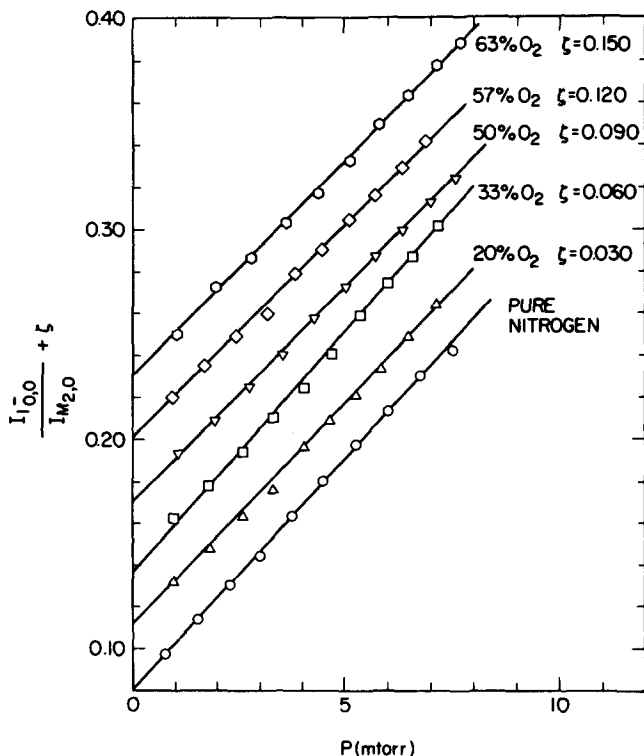
V. DISCUSSION

The present results indicate that the Meinel band quenching rates in N$_2$ and O$_2$ are slightly less than that predicted by the Langevin model, 8.3 and 7.7 $\times$ 10^{-10} cm^3 molecule^{-1} s^{-1}, respectively. Within the limits of experimental error, no variation in quenching-rate coefficient with vibrational level was seen for the measurements made with room air. Because of the absence of a significant vibrational-level dependence, only one vibrational level was investigated in varying N$_2$/O$_2$ mixtures. Although the results of the other investigations in nitrogen which are listed in Table I do show an apparent increase in quenching rate coefficient with vibrational level, none of the three

TABLE I. Meinel band quenching-rate coefficients.[a]

Quencher	Reference	Vibrational level		
		2	3	4
Air	Present results	7.0 ± 0.4	7.5 ± 1.0	7.0 ± 1.0
Nitrogen	Present results	7.5 ± 0.8		
	Gray, Roberts, Morack	3.4 ± 1.7	5.3 ± 2.7	5.2 ± 2.6
	O'Neil, Davidson	3.0	4.0	4.4
	Pendleton, Weaver	8.6 ± 0.9	9.6 ± 1.3	10.5 ± 1.7
Oxygen	Present results	6.2 ± 0.6		
	Pendleton, Weaver	16.4^{b}		
	Sheridan, Merlo, Enzweiler			13.0^{c}

[a] Units are 10^{-10} cm³ molecule⁻¹ s⁻¹.
[b] Estimated from one measurement in 80/20 N₂/O₂ mixture.
[c] At collision energies of 6–12 keV.

studies shows an unequivocal trend given the fairly large error bars of the measurements.

This measurement for the quenching of vibrational level 2 by nitrogen lies between the values reported by Gray, Roberts, and Morack[11] and O'Neil and Davidson[8] on the one hand, and by Pendleton and Weaver[12] on the other. Given the limits of uncertainty of each of the measurements, the current result is in accord with them all, although it agrees more closely with the measurement of Pendleton and Weaver. However, the rate for the quenching of vibrational level 2 by molecular oxygen is in substantial conflict with that of Pendleton and Weaver and the measurement at 6–12 keV by Sheridan, Merlo, and Enzweiler.[14] Pendleton and Weaver's measurement was basically an estimate based upon one measurement in an 80/20, N₂/O₂ mixture and is therefore rather uncertain due to extrapolating from small differences between two fairly large quantities. There is no reason to expect that results for high energy should be identical to those at thermal energies.

The measurements reported here are essentially global disappearance-rate coefficients and can provide no information on the microscopic mechanism for the removal of the observed levels. The studies of Katayama *et al.*[28] suggest likely pathways for the energy flow. They performed a double-resonance experiment in which they pumped N₂⁺($A_{v=4}$) with a laser, and then probed the populations of high vibrational levels of the ground electronic state of the ion with a second laser, operating on the $B\ ^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition, which was triggered after the A-state pumping laser had shut off. Nitrogen was a trace species in a bath of He for those studies. They noticed significant enhancement in the populations of vibrational levels 4–6 of the ground electronic state subsequent to pumping $A_{v=4}$. In a second series of experiments they observed emission from N₂⁺($A_{v=3}$) after pumping vibrational level 4 with a laser. The rise time of the $v' = 3$ fluorescence trace was equal to the decay time of the $v' = 4$ fluorescence trace. The latter showed essentially prompt emission followed by a single exponential decay. The results of those two experiments suggested that high lying levels of the X state are collisionally coupled with levels of the A state, with $v' = 4$, 3, and 2

of the A state being coupled to $v'' = 8$, 7, and 6 of the X state. It was also suggested that collisional relaxation out of $A_{v=4}$, for example, proceeds into the X state manifold at $v'' = 8$ and then either back to lower levels of the A state, e.g., $v' = 3$, or perhaps down to $X_{v''=7}$ from whence some of the energy crosses back over into the A-state manifold into $v' = 3$. An alternative might be cross relaxation between $A_{v=4}$ and X with a rapid coupling between $X_{v''=7}$ and $A_{v=3}$ being responsible for the observed emission at $A_{v=3}$. Katayama *et al.* did not make detailed measurements of all of the cross relaxation rates. They presumed that the mixing between the X and A states with energy defects less than kT happens on a per collision basis, and that the slow processes are then due to the larger energy-defect transitions, $X_{v''=8}$ or $A_{v=4}$ to either $X_{v''=7}$ or $A_{v=3}$.

A second, slightly different, alternative is suggested by the work of Dobler *et al.*[29] who have determined the total removal-rate coefficients of vibrationally excited ground-state N₂⁺ by nitrogen and oxygen to be 5 and 1.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, respectively. The rate coefficient for nitrogen, which is entirely a vibrational-quenching rate, is close to the A state removal rate determined here, and suggests that perhaps the A state crosses into the X state manifold and is quenched from there. Dobler *et al.* contend that the vibrational quenching of $X_{v'>0}$ is essentially a charge transfer reaction to molecular nitrogen, producing $X_{v'=0}$.

Whichever picture is correct, the present results indicate that vibrationally excited N₂⁺A and N₂⁺X are removed at essentially identical rates in nitrogen. This may result from the rapid cross coupling of the N₂⁺(A) and N₂⁺(X) states proposed by Katayama *et al.*[28] However, the data are entirely consistent with the kinetic reaction model described in Sec. III. There is no evidence that significant amounts of excitation in vibrational level $v = 4$ of the A state are transferred to the $v = 3$ A state level. If such collisionally indicated transfers occurred, the ratio I_B/I_A given in Eq. (9) would not scale with the first power of the quencher pressure.

The results for molecular oxygen quenching differ quite significantly from those of Dobler *et al.*[29] on the quenching of $X_{v'>0}$. This might result from actual differ-

ences in the quenching rates for the two different states, or it may be an indication that the higher levels of the X state are quenched by or react more rapidly with oxygen than is the case for lower vibrational levels. Dobler *et al.*'s experiment can only distinguish between $v'' = 0$ and higher vibrational levels. Most of the vibrationally excited nitrogen in their reactor, however, will be in the first two or three vibrational levels, whereas the cross coupling in the present experiment would be into levels 6–8. Only quite detailed laser experiments similar to those of Kata-yama *et al.*[28] can unravel these microscopic differences in behavior.

Vallance Jones and Gattinger[30] noted that the intensities of the Meinel bands relative to those of the nitrogen First Positive bands were somewhat weaker in a bright aurora than was the case in an aurora of medium intensity. Since brighter aurorae tend to penetrate deeper into the earth's atmosphere, they speculated that the reduction in Meinel band emission resulted from quenching of the Meinel bands at the lower altitude. The magnitude of the reduction was about 20%. The quenching data reported here, combined with the U.S. Standard Atmosphere,[31] would indicate a 20% reduction in Meinel band emission at about 95 km. This result roughly agrees with the estimate of Vallance Jones and Gattinger which was based upon estimates of Meinel band quenching-rate coefficients by Cartwright *et al.*[32] Those estimates for N$_2$ and O$_2$ differ significantly from the present measurements, but give an effective quenching rate for air which is similar to the value determined here.

VI. SUMMARY

The absolute quenching coefficients for various levels of N$_2^+A$ state in electron-irradiated N$_2$/O$_2$ have been determined experimentally. The effect of interfering species was eliminated by spectrally and spatially resolved observations of the Meinel band emissions. These results are important for understanding the aurorally disturbed upper atmosphere where the N$_2^+A$ state is a major pathway for excitation.

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