Experimental determination of the Einstein coefficient for the
\( \text{N}(^2\text{P} - ^4\text{S}) \) transition

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Abstract

We have measured the Einstein coefficient for the forbidden atomic transition, \( \text{N}(^2\text{P} - ^4\text{S}) \), at 346.6 nm, by determining absolute photon emission rates at 346.6 nm when known number densities of \( \text{N}(^2\text{P}) \) are in the detector field of view. The \( \text{N}(^2\text{P}) \) is generated in a discharge-flow reactor and its number density is determined by vacuum ultraviolet resonance absorption at 174 nm. The absolute response of the monochromator is determined from measurements of the \( \text{O}/\text{NO} \) air afterglow. This first experimental determination, \((5.4 \pm 1.4) \times 10^{-3} \text{ s}^{-1}\), agrees well with published theoretical calculations.

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1. Introduction

Metastable \( \text{N}(^2\text{P}) \) nitrogen atoms are a source of bright auroral radiation at both 346.6 nm in the ultraviolet, from the \( \text{N}(^2\text{P} - ^4\text{S}) \) transition, and at 1040 nm in the near infrared, from the \( \text{N}(^2\text{P} - ^2\text{D}) \) transition [1–3]. Observations of \( \text{N}(^2\text{P}) \) emission intensities in comparison with intensities of \( \text{N}_2(\text{B} - \text{X}) \) or \( \text{N}_2(\text{C} - \text{B}) \) transitions have been used to estimate the depth of penetration of auroral electrons [2] and the altitude profiles of atomic oxygen number densities [3]. Both of these measurements rely on the fact that long-lived \( \text{N}(^2\text{P}) \) is quenched rather efficiently by atomic oxygen under auroral conditions, whereas the molecular emissions are not because of their short radiative lifetimes.

Proper analysis of \( \text{N}(^2\text{P}) \) emission measurements in aurorae require accurate knowledge of the \( \text{N}(^2\text{P} - ^2\text{D}, ^4\text{S}) \) transition probabilities and the rate coefficient for \( \text{N}(^2\text{P}) \) quenching by atomic oxygen. We determined the latter experimentally several years ago [4]. The former, however, is known only through two theoretical calculations published some 30 years apart [5,6]. Although the two calculations agree within 12%, our observations of \( \text{N}(^2\text{P}) \) excitation in the energy transfer reaction between \( \text{N}_2(\text{A}) \) and \( \text{N}(^4\text{S}) \) [7] suggested the calculation of the \( \text{N}(^2\text{P} - ^4\text{S}) \) transition probability could possibly be erroneous, and an experimental determination of that transition probability was warranted.

2. Experimental

The intensity of an electronic transition is given by the product of the number density of species in
the emitting state and the Einstein coefficient for spontaneous radiation:

\[ I = NA, \]

(1)

where \( I \) is the absolute photon emission rate in units of photons cm\(^{-3}\) s\(^{-1}\), \( N \) is the number density in species cm\(^{-3}\), and \( A \) is the Einstein coefficient in units of s\(^{-1}\). The basis of our measurement, therefore, is to determine absolute photon emission rates and number densities of emitting species simultaneously. The ratio of these two quantities, then, is the Einstein coefficient we seek.

Our experiments used the 5 cm diameter discharge-flow reactor shown schematically in Fig. 1. \( \text{N}(^2\text{P}) \) was generated in the upstream section of the reactor in a microwave discharge sustained in a flow of \( \text{N}_2 \) dilute in either helium or argon at total pressures between 0.3 and 1.5 Torr. The \( \text{N}(^2\text{P}) \) was then detected in emission at 346.6 nm using a 0.5 m monochromator equipped for photoelectric detection and also by vacuum ultraviolet resonance absorption at 174 nm. The absorption measurements are made across the central diameter of the flow reactor. The source of the resonance radiation was a microwave excited discharge in helium with a trace of added air. On the opposite side of the flow reactor, a 0.2 m vacuum monochromator and solar-blind photomultiplier detected the radiation. Normal to the diameter defined by the resonance absorption system, a 0.6 cm diameter fiber-optic bundle collected 346.6 nm radiation emanating from the center of the flow reactor and transported it to the 0.5 m monochromator.

The number density of the \( \text{N}(^2\text{P}) \) atoms varies radially across the flow reactor, being highest in the center and zero at the walls. The absorption and emission diagnostics, therefore, both sample average number densities in the reactor. Because the system and flows are cylindrically symmetric, however, and because the two diagnostics have similar fields of view across the flow reactor (narrow and collimated), the average number densities they monitor are the same. Thus, the non-uniform \( \text{N}(^2\text{P}) \) number densities have no effect on the experimental results.

The 0.5 m monochromator was calibrated for absolute photon emission rate measurements by ob-

![Fig. 1. Schematic view of discharge-flow reactor used in the experiments.](image-url)
serving the intensity of the O/NO air afterglow when known amounts of O and NO were added to the reactor. Titrating N atoms with NO, using procedures we have detailed previously [8,9], produced the O. Our air afterglow calibrations, made at 580 nm, used a chemiluminescence rate coefficient of $1.17 \times 10^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ nm$^{-1}$. This value is an average based upon our critical analysis [10] of the published literature [11–18] on the air afterglow. We think this value is accurate within ±10%.

We established the relative spectral response of the system in situ to extrapolate the calibration made at 580 to 346.6 nm. We used a branching ratio technique based upon measurements of NO($B'$-$X'$ II) band intensities and the NO($B$-$X$) transition probabilities we reported [tS] (which were confirmed theoretically by Langhoff et al. [20] and experimentally by Luque and Crosley [21]) to determine the response variation between 250 and 500 nm, and O/NO air afterglow intensity measurements to establish the relative spectral response between 400 and 850. The two techniques agreed to within ±5% in the region of spectral overlap.

We have discussed our use of VUV resonance absorption techniques to determine atomic number densities in a discharge-flow reactor previously [22,23]. The 174.3 nm transition that is absorbed by N($2p$) is actually a multiplet consisting of four separate transitions, two doublets separated by about 0.25 nm with a separation between the lines in each doublet of about 0.0008 nm or 0.26 cm$^{-1}$. The Doppler width of each line is about 0.17 cm$^{-1}$, small enough that the unresolved multiplet can be treated as a composite of four independent transitions.

Our measurements were made with a resolution of 1 nm to ensure that all lines of the multiplet were transmitted equally through the instrument. The equation describing the fractional absorption, $A = (I_0 - I)/I_0$, then becomes [24]

$$A = \frac{\sum C_i \int_{-\infty}^{\infty} (1 - e^{-x_0/e^{-x_0^2}}) e^{-(\omega_i/\alpha)^2} d\omega_i}{\sum C_i \int_{-\infty}^{\infty} e^{-(\omega_i/\alpha)^2} d\omega_i},$$

where $C_i$ is the relative intensity of each multiplet component, $k_{0i}$ the absorption coefficient at line center, $\omega_i$, the reduced frequency of the line, $\alpha$ is the ratio of the width of the line from the resonance lamp to that of the absorption line, and $l$ is the absorption path length. The reduced frequency, $\omega_i$, is given in terms of the separation from the center-line frequency, $\nu_0$, by

$$\omega = \frac{2(\nu - \nu_0)}{\Delta \nu_D} \sqrt{\ln 2},$$

where $\Delta \nu_D$ is the full width at half maximum of the line as determined by Doppler broadening:

$$\Delta \nu_D (s^{-1}) = \frac{2}{\lambda_0} \sqrt{\frac{2RT}{M}},$$

$\lambda_0$ being the center wavelength of the transition, $R$ the gas-law constant, $T$ the translational temperature, and $M$ the mass of the atom.

Doppler broadening is the only significant mechanism of line broadening in a low power, low pressure microwave discharge resonance lamp and of the absorption line as well (collision broadening contributes less than 1% to the total linewidth in 3 Torr of helium) [25]. As a result the ratio of the widths of the lamp line to the absorption line is just the square root of the ratio of translational temperatures in the lamp and the flow reactor. The translational temperature in the flow reactor is equal to the laboratory temperature, 300 K. We determined the translational temperature in the resonance lamp to be 500 K from measurements of the band profiles of $N_2(C^2\Pi_u - B^2\Pi_g)$ transitions. Fig. 2 shows a comparison between a fit of the observed $N_2(C-B)$ bands and band contours calculated assuming rotational temperatures of 400, 500, and 600 K. The rotational profile calculated from a 500 K temperature best reproduces the data. The uncertainty in this value, ±50 K, contributes to an uncertainty in the overall absorption measurement of only ±3%.

The absorption coefficient at line center is

$$k_0 = \frac{2}{\Delta \nu_D} \sqrt{\frac{\ln 2}{8\pi}} \frac{\lambda_0^2}{\alpha^2} \frac{d_u}{d_1} A_{ul} N,$$

where $d_u$ and $d_1$ are the degeneracies of the upper and lower states in each of the four transitions in the multiplet, $A$ the Einstein coefficient, and $N$ the number density of absorbing atoms. We used transition probabilities based upon the radiative lifetime...
Fig. 2. Comparison of the spectrum of $N_2(C^3Π_u - B^3Π_g)$ emission from the lamp used in the absorption measurements with synthetic spectra generated assuming different rotational temperatures for the $N_2(C)$ emission. The best fit rotational temperature, 500 K, corresponds to the kinetic temperature in the lamp.
for the upper state of the multiplet of 1.8 ns as measured by Hutchison [26]. Table 1 summarizes the relevant spectroscopic data.

### 3. Results

Fig. 3 shows typical results of measurements of the 346.6 nm intensity as a function of \( N(^2P) \) number density. The \( N(^1P) \) number densities were determined by measuring the fractional absorption at 174 nm and using the results of a numerical integration of Eq. (2) to relate the fractional absorption to \( N(^1P) \) number density. Since the absolute photon emission rate is the product of the number density of emitters and the Einstein coefficient for the transition, the Einstein coefficient for the 346.6 nm transition is just the slope of the line through the data in Fig. 3.

The average result from several measurements in both Ar and He carrier gas is \( 5.4 \times 10^{-3} \) s\(^{-1} \). We estimate the uncertainty in this value to be \( \pm 26\% \) based upon the square root of the sum of the squares of the various uncertainties in the experimental parameters: 5% in the raw data (ratio of intensity to number density), 12% in the number density diagnostic (lamp temperature and transition probabilities), 10% in the air afterglow rate coefficient, and 20% in the photometric calibration of the monochromator.

### 4. Discussion

This Einstein coefficient was first calculated by Garstang to be \( 5.4 \times 10^{-3} \) s\(^{-1} \) over 40 years ago [5]. More recently, Godefroid and Froese-Fischer [6] calculated a value of \( 4.8 \times 10^{-3} \) s\(^{-1} \). Both of these values agree well with our experimental determination. We had speculated these calculated values might be erroneous because we determined a rate coefficient for \( N(^2P) \) formation in the energy-transfer reaction between \( N_r(A) \) and \( N(^1S) \) to be five times larger than the rate coefficient for \( N_r(A) \) quenching by \( N(^1S) \) [7]. The most likely explanation for this discrepancy seemed to be that the Einstein coefficient used to determine either the \( N_r(A) \) or \( N(^2P) \) number density was in error. We have considered the issue of the \( N_r(A) \) Einstein coefficient [27], and determined that previously accepted values are not seriously in error [28]. The results of this investigation indicate that the same can be said for the \( N(^3P-^3S) \) transition. Thus the discrepancy in our previous measurements must result from an additional metastable in our flow reactor that we have so far been unable to...
detect. Evidence for this additional metastable has been found in other studies as well [29,30].

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