Radiative lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+

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The natural radiative lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+ has been measured by counting for equal time intervals the 214-nm photons emitted when the metastable ions decay to the $2s^22p^2(^3P_{2,1})$ levels of N^+. Although forbidden to decay by the LS selection rule $\Delta S = 0$, the $^5S_2$ state decays primarily as a consequence of spin-orbit mixing with other levels of the $2s2p^3$ configuration. The metastable N^+ ions are produced inside a cylindrical electrostatic ion trap by electron bombardment of a parent N_2 vapor maintained at pressures ranging from 5 to 25×10^{-8} Torr. The ion trap consists of a 5.0-cm-diam, 7.5-cm-long outer cylinder with end caps and a concentric 0.003-cm-diam central wire maintained at a negative potential of about 140 V. Some of the photons emitted by the decaying $^5S_2$ ions are focused onto a 12-nm-bandwidth interference filter in front of a photomultiplier tube and counted. The mean lifetime is obtained from the slope of a straight-line least-squares fit to the appropriate region of a logarithmic plot of the decay counts. Our result, extrapolated to zero N_2 pressure, for the natural radiative lifetime of the $N^+(^5S_2)$ metastable state is 5.4 ± 0.3 msec.

I. INTRODUCTION

We have employed an ion trapping technique to measure the natural radiative lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+. The six lowest-lying levels of singly ionized nitrogen are shown in the partial energy-level diagram of Fig. 1. Except for the $^5S_2$ state, all levels shown in Fig. 1 arise from the $2s^22p^2$ ground configuration of N^+. Since the $^5S_2$ state is the lowest-lying level of the $2s2p^3$ configuration, it is an example of a relatively long-lived metastable state whose radiative decay via an electric dipole ($E1$) transition is forbidden by the $\Delta S = 0$ spin-selection rule. Spin-orbit mixing is small for low-charge-state–low-atomic-weight ions and radiative lifetimes of spin-forbidden states can range from microseconds [1] to more than a second [2, 3].

In addition to its $E1$ decay at 214 nm to the $2s^22p^2(^3P_{2,1})$ levels, the $^5S_2$ state can decay via a magnetic quadrupole ($M2$) transition to the levels of the ^3P term. However, a calculation by Hibbert and Bates [4] indicates that the $M2$ transition probabilities are approximately five orders of magnitude less than the intercombination $E1$ transition probabilities.

During the 1970s, auroral spectra from satellite [5, 6] and rocket [7] observations revealed a feature near 214 nm which was originally assigned to the (1,0) band of NO. Later, Beiting and Feldman [8] excluded NO as the source of this feature, which was subsequently assigned [9, 10] to the ($^5S_2 \rightarrow {}^3P_{2,1}$) transitions of N^+ plus weak emissions of the Lyman-Birge-Hopfield and Vegard-Kaplan bands of N_2. Three theoretical studies and one measurement of the $N^+(^5S_2)$ state's radiative lifetime have since been published that support this state's role in the auroral emission. Cowan, Hobbs, and York [11] and also Hibbert and Bates [4] reported *ab initio* calculations of the $^5S_2$ state's lifetime, while Dalgarno, Victor, and Hartquist [12] extrapolated along the carbon isoelectronic sequence to obtain a value for the lifetime. These calculations established a value of about 5 msec for the radiative lifetime. Although the calculated lifetimes helped reconcile the origin of the 214-nm auroral feature, the theoretical results differ by as much as 70%. The only measurement

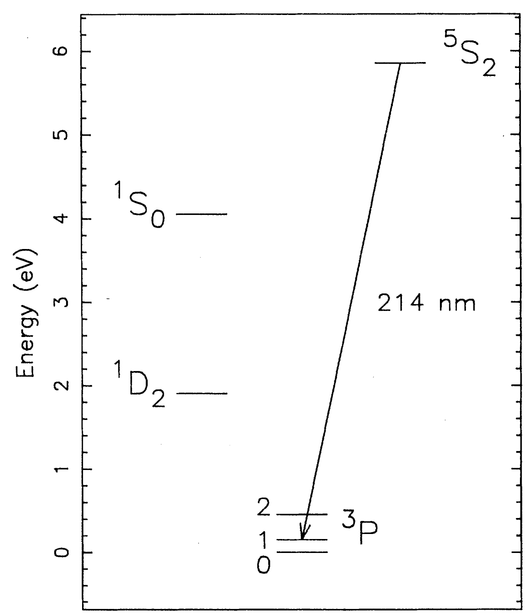

FIG. 1. Partial energy-level diagram showing the six lowest levels of N^+. The five lowest levels arise from the $2s^22p^2$ configuration, whereas the $^5S_2$ state is the lowest-lying level of the $2s2p^3$ configuration. The arrow indicates one of the intersystem transitions monitored for the measurement of the lifetime of the $^5S_2$ metastable state.

[13] of the lifetime, aside from a preliminary report [14] by the present authors, confirmed the order of magnitude of the calculations. However, there remains a significant uncertainty in the radiative lifetime of the $^5S_2$ metastable state of N^+.

II. EXPERIMENTAL METHOD

A population of N^+ ions was confined to a volume of approximately 25 cm^3 using a cylindrical electrostatic ion trap, sometimes referred to as a Kingdon [15] trap. Details concerning our ion storage apparatus and its application to the measurement of radiative lifetimes of metastable states of atomic ions have been discussed previously [16, 17]. The electrostatic ion trap is located in a vacuum chamber where the residual background pressure, as measured by an uncalibrated Baynard-Alpert ionization gauge, is approximately 10^{-9} Torr. Two circular ports, located on the outer cylindrical electrode of the trap, are covered with tungsten wire cloth so that the stored ion cloud can be observed. The trap's end cap electrodes are also constructed using tungsten wire cloth so that electrons from a dispenser cathode can pass through the trap. These electrons, accelerated to about 200 eV just before entering the trap, travel parallel to the trap's axis and produce both atomic and molecular nitrogen ions inside the trapping region by electron bombardment of a parent N_2 vapor.

The electrons are pulsed on during a trap fill period to produce ions in the $2s2p^3(^5S_2)$ metastable state of N^+ that have the appropriate initial conditions [16] for storage. The observed $N^+(^5S_2)$ signal asymptotically approached a maximum as the period of the fill pulse exceeded the predicted lifetime of the metastable state. After the trap is filled, some of the photons emitted by the decaying metastable ion population pass through a port in the outer cylindrical electrode and are focused onto a narrow bandwidth interference filter positioned in front of an EMI 9635QB photomultiplier tube operating in photon counting mode. The interference filter preferentially transmits photons emitted by the N^+ metastable state while rejecting unwanted background radiation from the hot dispenser cathode operating at $\sim 950\,°C$. The interference filter used in the $N^+(^5S_2)$ lifetime measurement had a full width at half maximum bandwidth of about 12 nm with its 14% peak transmittance centered at 214 nm. Assuming an estimated photon collection efficiency of 0.1%, the observed signal indicates a maximum of approximately 5000 ions are created in the N^+ $(^5S_2)$ metastable state per fill pulse.

By counting as a function of time the number of photons emitted by the decaying metastable ion population, radiative lifetimes ranging from about 1 msec to a few 100 msec can be measured using the present apparatus. Counts associated with the decay of the metastable population are collected through a cycle consisting of five events: a fill pulse, two photon counting periods, and two trap dumps. The trap dump uses a positive voltage pulse applied for 1 msec to the central electrode of the trap to empty the trap of ions. During the lifetime measurement of the $2s2p^3(^5S_2)$ state of N^+, each photon counting period consisted of 50 channels which were 0.4 msec in duration. The width of each channel and all other timing aspects of a data collection cycle were synchronized by an external clock with a period of 0.1 msec.

At the beginning of each channel, an on-line computer zeros and then gates on a 32-bit counter to register the number of photons detected as the metastable ion population inside the trap radiatively decays. Counts accumulated during a channel's dwell time are read by the computer and stored in a separate memory location for each channel. Signal averaging with background subtraction is accomplished by using two photon counting periods per cycle and repeating the cycle many times. The first photon counting period, which is preceded by a fill pulse, contains a record of both signal and background counts, while the second photon counting period, which is preceded by a trap dump, corresponds to only background counts. The counts collected in the second photon counting period are subtracted from the number detected

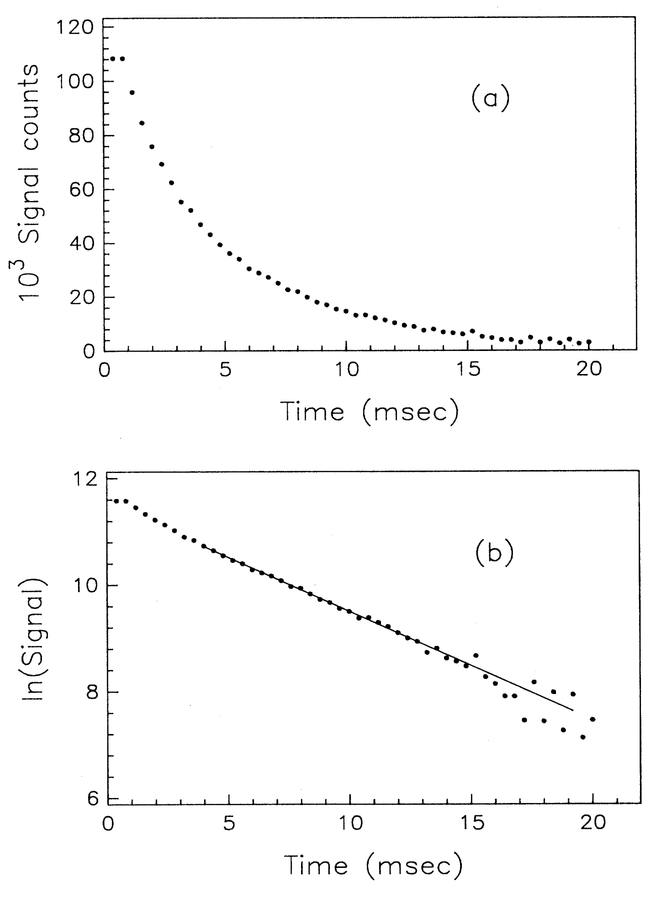

FIG. 2. (a) Fifty-channel decay curve of signal counts vs time as the $2s2p^3(^5S_2)$ metastable state population of N^+ decays. An interference filter centered at 214 nm was used to monitor the photons emitted as a result of the $(^5S_2 \rightarrow {}^3P_{1,2})$ intersystem $E1$ transitions. (b) Natural logarithm of the decay curve. The slope of a straight line (solid line) least-squares fit to the data gives the decay rate of the $N^+(^5S_2)$ state.

during the first period on a channel-by-channel basis and the result is added to that of the previous cycles. Therefore the signal level of each channel accumulates, and the background is minimized. At the conclusion of a data collection run, the signal emitted by the trapped ions has been recorded versus time and predominately consists of counts arising from the stored metastable ion population. A run of 5×10^5 data collection cycles produced a good signal-to-noise ratio for the $N^+(^5S_2)$ lifetime measurement.

The radiative lifetime measurement commenced with a few preliminary runs for diagnostic purposes where parameters affecting signal quality were varied. Results of the diagnostic runs were analyzed in order not only to ascertain whether or not more than one decay component existed in the decay curve but also to choose run parameters that would simultaneously maximize signal quality while minimizing total run time. Except for a small fast decay in the early channels of the decay curve, which is attributed to ion cloud stabilization, the decay curves collected for the $^5S_2$ state of N^+ consist of one component. Once an approximate value for the lifetime of the $^5S_2$ state was known, the channel dwell time was chosen so that the total photon counting interval spanned approximately four mean lifetimes. Then the number of data collection cycles, and therefore the total time for a run, was chosen so that the signal in the last few channels was about the same size as the background noise. A representative decay curve for the $2s2p^3(^5S_2)$ metastable state of N^+ is shown in Fig. 2(a).

III. DATA ANALYSIS

Since the initial population N_0 of $N^+(^5S_2)$ ions decays according to the exponential $N_0e^{-\gamma t}$, the natural logarithm of the decay counts versus time is a straight line whose slope is the decay rate γ. Thus the decay rate γ is obtained from the slope of a straight line fit to the appropriate region of the natural logarithm of the decay counts using a weighted least-squares fitting procedure [18]. Neglecting the first 3 msec of the decay where the ion cloud stabilizes and allowed cascades occur, Fig. 2(b) shows the expected straight-line behavior for a logarithmic plot of the decay counts shown in Fig. 2(a).

The total decay rate γ consists of two parts: the radiative decay rate γ_0 plus a pressure-dependent decay rate γ_p that represents loss of ions in the metastable state as a consequence of collisions with parent N_2 molecules present in the trapping volume. To first order in the N_2 pressure P, the decay rate is

$$\gamma = \gamma_0 + \gamma_p = \gamma_0 + k\, n_p ,$$

where k is the collision rate coefficient and n_p is the number of N_2 molecules per unit volume at a particular pressure P. We accumulated several decay curves at various parent N_2 pressures. Then the zero pressure intercept of a straight line least-squares fit to a plot of the decay rate versus pressure is the radiative decay rate γ_0, and the natural radiative lifetime τ_0 of the $^5S_2$ metastable state of N^+ is $\tau_0 = 1/\gamma_0$. Futhermore, the slope of the straight line gives the collision rate coefficient k.

IV. DISCUSSION

A major concern when making a direct radiative lifetime measurement of a metastable state is the possibility of a time-dependent background luminescence with a spectral distribution overlapping the bandpass of the interference filter used to monitor the decay. A time-dependent background could occur in our apparatus by either of two predominant mechanisms: (1) another metastable state of the stored atomic or molecular ions has a transition wavelength within the bandpass of the interference filter, and/or (2) radiation can be produced by collisions between the stored ions and the neutral parent vapor. Previous work [19, 20] indicates that electronic metastable states of the molecular ions ${N_2}^+$ and ${N_2}^{2+}$ do not have emission spectra within the bandpass of the interference filter used to monitor the decay of the N^+ $(^5S_2)$ state. Also, an analysis of the energy levels [21] corresponding to the first four ionization states of atomic nitrogen did not reveal other long-lived states whose radiative decay would contribute undesired counts to the observed decay curves. Thus, decay radiation from other metastable states should not produce systematic effects in the present lifetime measurement.

The average kinetic energy of the ions stored in our electrostatic trap is approximately 10 eV, which is more than sufficient to produce excited atomic or molecular states. Therefore radiation as a consequence of collisions between stored ions and neutral parent molecules could result in a substantial systematic error in the measured lifetime. In particular, there are a number of N_2 emission features within the 12-nm bandpass of the 214-nm interference filter; most notable is the Lyman-Birge-Hopfield system from 100 to 260 nm. The intensity of any collisionally induced background radiation is determined by the number of stored ions, and the time dependence should reflect the characteristic trapping time of the stored ion population. A separate measurement of the trapping time [16] for loss of nitrogen ions from the trap indicates a trapping time, at a parent N_2 pressure of 25×10^{-8} Torr, of approximately 50 msec; this value is about ten times longer than the measured radiative lifetime of the $N^+(^5S_2)$ metastable state.

In order to determine the influence of collisionally induced luminescence, decay curves were collected using very long signal integration times and a sequence of narrow bandwidth ($\sim$ 10 nm) interference filters covering the wavelength range from 190 to 340 nm. Although the signal-to-noise ratio was insufficient to allow an accurate determination of the decay rates, the observed decay curves did have decay rates that were consistent with the ion trapping time. More importantly, the size of these background signals was approximately $\frac{1}{100}$ the size of the signal for the $^5S_2$ metastable state. Thus, since the collisionally induced background signals were statistically unimportant relative to the $^5S_2$ signal at 214 nm, we conclude that systematic effects associated with collisionally induced radiation do not influence significantly the present lifetime measurement.

As an additional check for undesired decay radiation, the same 190 to 340 nm wavelength range was investigated again but without any background N_2 pressure in the vacuum chamber. No decay signals were observed, just a constant flat background noise. Other experimental parameters — such as the trapping potential, electron bombardment energy, trap fill time, and trap dump time — were varied also to explore for possible systematic errors. The measured decay rates were always the same to within the statistical errors of the theoretical fits.

V. RESULTS

Our final measured value for the lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+ is based on a total of 30 runs, each requiring approximately 7 h to achieve a signal-to-noise ratio similar to that of Fig. 2(a). Six runs were taken at each of five separate background N_2 pressures ranging from 5 to 25 $\times$ 10^{-8} Torr in 5 $\times$ 10^{-8} Torr increments. The experimental parameters for all these runs were as follows: trapping potential, 140 V; electron bombardment energy, 200 eV; trap fill time, 20 msec; trap dump time, 1 msec; 50 channels per cycle with a channel dwell time of 0.4 msec; and 5 $\times$ 10^5 total data collection cycles per run. The last few channels of each decay curve are used to determine the small residual background that was not removed by the real-time background subtraction technique discussed in Sec. II. One-half the average of the counts in the last few channels is taken as a constant background and subtracted from all channels. The solid line shown in Fig. 2(b) represents the straight line fit to the natural logarithm of the data using a weighted least-squares-fitting procedure; the decay rate at this particular N_2 pressure is obtained from the slope of the straight line. The time interval from 4.0 to 19.2 msec spanning approximately three mean lifetimes is included in the fit and neglects the slightly nonlinear portion of the logarithmic decay curve attributed in part to ion cloud stabilization. Excluding the early channels from the fit also minimizes the influence of cascades from higher-lying states of both atomic and molecular ions.

The six decay rates at each N_2 pressure are averaged, and the mean decay rates are plotted versus pressure as shown in Fig. 3. The extrapolation to zero N_2 pressure, again using a straight-line least-squares fit, is also shown in Fig. 3 and yields the radiative decay rate γ_0 and thus the natural radiative lifetime τ_0. Our result for the natural radiative lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+ is $\tau_0 = 5.4 \pm 0.3$ msec.

The major source of error for our experimental lifetime value is an uncertainty associated with knowledge of the N_2 pressure and consequently the extrapolation of the measured decay rates to zero N_2 pressure. There is also some uncertainty associated with the particular choice of time interval for the theoretical fit and of the small amount of residual background that is subtracted. Combining these uncertainties, all considerably larger than the statistical errors, we estimate an error of 5% for the lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+.

The collision rate coefficient of the $2s2p^3(^5S_2)$ state of N^+ is obtained from the slope of the straight line shown in Fig. 3 where the decay rates are plotted versus N_2 pressure. Actually, the pressure-dependent part γ_p of the total decay rate γ includes all pressure-dependent losses of ions from the metastable state and has at least two contributions. The first is the collisional quenching of the $^5S_2$ state; the second is the loss of the $^5S_2$ state ion from the trap when a kinetic collision sufficiently perturbs its trajectory about the central cylinder. A separate measurement of the trapping time [16] for loss of nitrogen ions from the trap indicates that collisional quenching is the major contribution to γ_p. However, the trapping time measurement is essentially for ground-state N_2^+ ions since they are the dominant trapped species. Nevertheless, our measured collision rate coefficient k for stored $N^+(^5S_2)$ ions is 3.1 $\times$ 10^{-9} cm^3/sec, which is approximately 21% larger than the result [13] reported by Knight. However, this is quite good agreement since the uncalibrated ionization gauge used to measure the N_2 pressure could give a large error ($\sim$ 100%) for the absolute value of the rate coefficient.

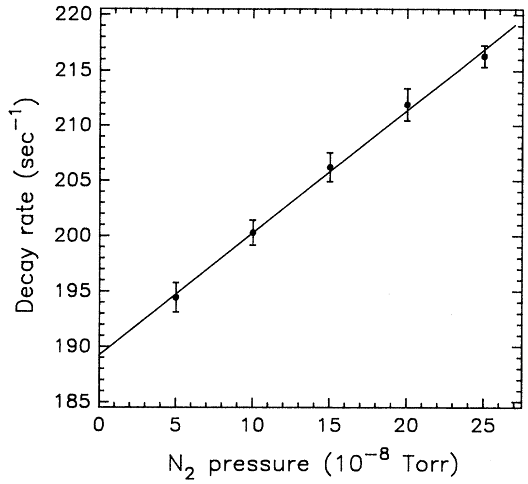

FIG. 3. Decay rates vs parent N_2 pressure for the $2s2p^3(^5S_2)$ metastable state of N^+. The natural radiative lifetime is obtained from the zero pressure intercept of the straight-line fit, whereas the collision rate coefficient is deduced from the slope.

TABLE I. Comparison of the values for the natural radiative lifetime τ_0 of the $2s2p^3(^5S_2)$ metastable state of N^+.

Authors	τ_0 (msec)	
Hibbert and Bates[a]	6.4	Theory
Dalgarno, Victor, and Hartquist[b]	5.8	Theory
Cowan, Hobbs, and York[c]	3.2	Theory
Knight[d]	4.2 $\pm$ 0.6	Experiment
Johnson, Smith, and Parkinson[e]	5.7 $\pm$ 0.6	Experiment
This work	5.4 $\pm$ 0.3	Experiment

[a]Reference [4].
[b]Reference [12].
[c]Reference [11].
[d]Reference [13].
[e]Reference [22].

VI. SUMMARY

Table I summarizes the theoretical and experimental values for the radiative lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+. The theoretical values include two *ab initio* calculations [4, 11] as well as an extrapolation [12] along the carbon isoelectronic sequence. The experimental results obtained at the Harvard-Smithsonian Center for Astrophysics (CfA) used two different cylindrical rf traps. The first measurement [13] employed a trap consisting of solid electrodes with small ports on the ring electrode. Thus the possibility of an erroneous zero for the N_2 pressure extrapolation exists for that work. After the cylindrical trap was modified to use mesh electrodes, a longer value [22] of the lifetime was measured. Our experimental result for the lifetime of the $2s2p^3(^5S_2)$ metastable state of N^+ is approximately 25% longer than Knight's measurement [13] but agrees well not only with the unpublished measurement [22] of the group at CfA but also with the extrapolation [12] by Dalgarno, Victor, and Hartquist.

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