Radiative Lifetime of the $^5S_2$ Metastable State of N^+

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(Received 3 December 1981)

The radiative lifetime of metastable $N^+(^5S_2)$ has been measured to be 4.2 ± 0.6 msec, a value generally in agreement with theory, by direct monitoring of the spontaneous emission from $\sim 10^6$ N^+ ions stored in a radio-frequency ion trap. Additional measurements were made of the quenching rate coefficient (2.5×10^{-9} cm^3 sec^{-1}) and the production cross section ($\geq 10^{-18}$ cm^2) of $N^+(^5S_2)$ in N_2. This work supports the interpretation of the 2145-Å feature in the spectrum of aurorae as being due to $N^+(^5S_2)$ emission.

PACS numbers: 32.70.Fw, 94.10.Fa

Spin-forbidden electric dipole transitions (intersystem transitions) occur as a consequence of the breakdown of pure L-S coupling in atoms. For highly ionized atoms (e.g., Ar^{+16}), transition rates can exceed 10^6 sec^{-1} and are amenable to measurement in beam-foil experiments.[1] For light elements in low charge states, however, intersystem transitions are typically 6 orders of magnitude weaker than allowed transitions, and radiative lifetimes for states which can decay only by intersystem transitions generally exceed 1 msec. Calculated values of intersystem transition rates are sensitive to configuration interaction, and experimental tests are needed. Previously published lifetimes for $O(2p^3 3s\ ^5S_2)$ (Ref. 2) and $Mg(3s3p\ ^3P_1)$ (Refs. 3 and 4) were determined indirectly. This Letter reports on ion trap experiments with metastable $N^+(2s2p^3\ ^5S_2)$ ions which decay via spin-forbidden electric dipole transitions (2139.68 and 2143.55 Å) to the $2s^2 2p^2\ ^3P_{1,2}$ ground state. Observation of the spontaneous-emission decay curve has provided the first direct measurement of an intersystem transition rate in a light, low-charge-state atom. This rate is important for solar density determinations, since interpretation of the observed emissions from isoelectronic $O^{2+}(^5S_2)$ has been difficult because of uncertainties in the atomic physics data.[5] Measurements are also reported for the $N^+(^5S_2)$ quenching rate coefficient in N_2 and the cross section for $N^+(^5S_2)$ production by electron impact on N_2.

Emission from $N^+(^5S_2)$ is now thought to be responsible for the prominent but enigmatic feature near 2145 Å in the ultraviolet spectrum of aurorae,[6] and auroral intensity measurements[7] indicate an excitation cross section $\gtrsim 2 \times 10^{-18}$ cm^2. A recent laboratory study by Erdman, Espy, and Zipf[8] of the electron-impact excitation of N_2 detected only weak emission from the $N^+(^5S_2)$ decay. By using a lifetime of 4.4 μsec, erroneously derived by Sharp[9] from a tabulation of oscillator strengths by Kurucz and Peytremann[10] (proper evaluation gives 150 μsec), they infer a $N^+(^5S_2)$ production cross section $\sim 3 \times 10^{-21}$ cm^2, clearly inconsistent with auroral observations. The results presented in this Letter should clarify some of the present uncertainty regarding this auroral feature.

Theoretical studies of the $N^+(^5S_2)$ radiative lifetime have recently appeared. Dalgarno, Victor, and Hartquist[7] extrapolated along the carbon isoelectronic sequence, using previously calculated transition rates for higher ionization states, and obtained $\tau = 5.8$ msec. *Ab initio* calculations by Hibbert and Bates[11] and by Cowan, Hobbs, and York[12] arrived, respectively, at $\tau = 6.4$ and 3.2 msec. These are all substantially different from Kurucz and Peytremann's value, and laboratory results are clearly desirable.

The ion storage technique can be used to confine a group of ions in a perturbation-free environment for times greatly exceeding the expected radiative lifetime of a few milliseconds. Details of this technique are discussed elsewhere.[13] A cylindrical, radio-frequency ion trap, operating at 930 kHz, was used for this experiment. The trap, with diameter and height of 3.3 cm, was machined from stainless steel, and a 1.25-cm-diam, mesh-covered hole in the ring electrode permitted observation of radiative decays. The trap was operated with spherical potential wells up to a maximum well depth of 25 eV. N^+ ions, in both metastable and ground states, were created in the trap by electron-impact ionization of N_2 gas. The operating point of the trap was generally chosen to exclude N_2^+ ions from storage, and the number of stored N^+ ions was estimated at 10^6. Ions were detected at the end of a cycle by pulsing them through a mesh in the lower end-cap electrode onto an electron multiplier. With gas pressures in the 10^{-7}-Torr range, ion storage times were around 100 msec. A decreased storage time was observed at higher pressures, but in all cases the storage time exceeded the metastable lifetime by at least a factor of 10.

Photons spontaneously emitted from $N^+(^5S_2)$ were detected by a solar-blind photomultiplier tube and gated into a multichannel scaler. An interference filter, 200-Å bandpass centered on 2140 Å, was used to attenuate light from the electron-gun cathode. Signal rates of 0.3 count per cycle were typical, and a decay curve with good signal-to-noise ratio could be obtained in 15 min. A cycle consisted of a 4-msec fill period, a 1-msec delay, and an 8-msec observation period. A fast decay ($\tau < 0.3$ msec) was seen and attributed to emission in the N_2 Lyman-Birge-Hopfield bands. The 1-msec delay avoided this decay, allowed any metastable neutrals to drift out of the trap, and provided time for any cascading from higher levels to have finished. The remaining decay signal could be ascribed to $N^+(^5S_2)$ since it vanished if either the N_2 was removed or the ion trap was detuned to prevent N^+ storage. Estimates of trapping and detection efficiencies can be combined with the observed counting rate of $N^+(^5S_2)$ decay photons to obtain the cross section for producting $N^+(^5S_2)$ by dissociative ionization of N_2. An optimistic estimate of efficiencies implies a cross section near 10^{-18} cm, and we take this as a lower bound and report $\sigma \geqslant 1 \times 10^{-18}$ cm^2 for electron energies of 100–500 eV. This result is consistent with the auroral intensity measurements described above.

A nonlinear least-squares routine was used to fit the data with a function of the form $C\exp(-At)+B$. The reduced χ^2 showed that this single-exponential decay fits the data well. An example is shown in Fig. 1. Every measurement of the radiative transition rate required collecting several decay curves as the N_2 pressure was varied, all other parameters being held fixed. Each decay curve was analyzed to obtain the $^5S_2$ total decay rate A, and the results were then extrapolated to zero N_2 pressure. The slope of the curve of decay rate versus pressure gives the quenching rate coefficient for $N^+(^5S_2)$ in N_2. This curve was found to be linear, as expected, up to N_2 pressures of order 10^{-5} Torr, where the curve began leveling off. No clear explanation for this behavior emerged, though poor signal-to-noise ratios at these pressures made accurate investigations impossible. N_2 pressures used for the radiative lifetime measurements were kept in the linear region below 5×10^{-6} Torr. A representative measurement is shown in Fig. 2.

Consistent results for the radiative lifetime were obtained for potential well depths $D \geqslant 12$ eV, but an apparent increase in the lifetime was observed for depths $D \leqslant 10$ eV. This behavior can be explained if an initially large ion cloud is re-

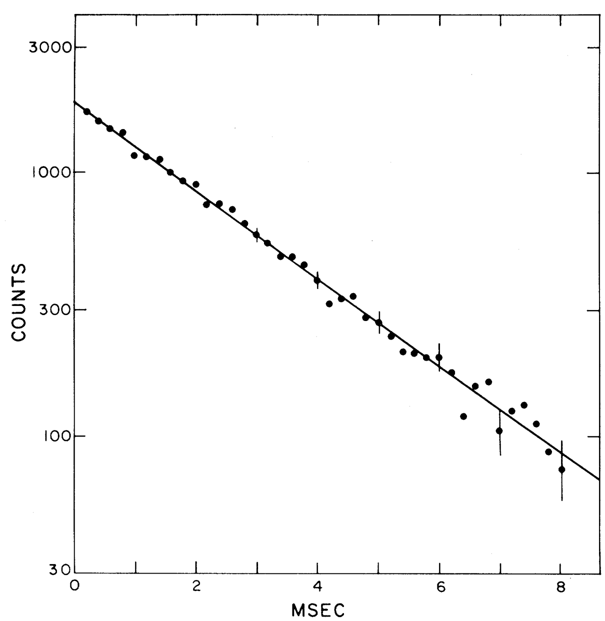

FIG. 1. Typical $N^+(^5S_2)$ decay curve. The straight line is the least-squares analysis of this decay.

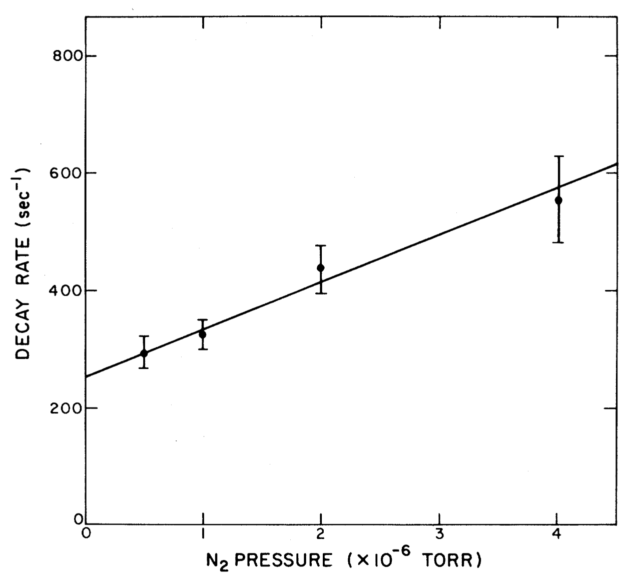

FIG. 2. Measurement of decay rate vs N_2 pressure for $D = 25$ eV. The zero-pressure extrapolation gives $A = 253 \pm 27$ sec^{-1} and the slope implies a quenching rate coefficient of 2.5×10^{-9} cm^3 sec^{-1}.

laxing on a time scale comparable to the metastable lifetime. It has been previously shown[14] that the ion cloud in a radio-frequency trap assumes a Gaussian density distribution with an average energy roughly 10% of the well depth. This work also cited evidence that the relaxation time required for Li^+ ions to reach the steady state was approximately 30 msec. In the trap used for the N^+ experiment, the steady-state ion cloud would be expected to have a radius (e^{-1} point) of roughly 0.4 cm, and the entire ion cloud would be well inside the 1-cm-radius field of view of the detection optics. Time-of-flight measurements of ion velocities following dissociative ionization of N_2 suggest that $N^+(^5S_2)$ is formed with an initial kinetic energy around 3 eV.[8,15] If the well depth $D \gg 3$ eV, then metastable ions created near the trap center, and thus most likely to be successfully stored, will have initial orbits totally inside the field of view. Well depths $D \sim 3$ eV, on the other hand, will result in an initial cloud of metastable ions which extends to the edges of the trap and is partially outside the field of view. Ground-state N^+ ions, created with less average kinetic energy, probably form a less extended cloud. As the metastable ions relax to a smaller steady-state distribution, the fraction of detectable photons increases and gives an apparent lengthening to the lifetime. Support for this model was obtained by reducing the field of view to 0.5 cm radius and observing a 30% increase in the apparent lifetime for $D = 10$ eV. This type of relaxation was numerically modeled, and it was found that the distorted decay curves are, with the addition of noise, indistinguishable from exponential decays with longer-than-natural lifetimes. A steady-state radius of 0.4 cm and a relaxation time of 10 msec produced results which were generally consistent with observations.

Ten sets of measurements, taken at potential well depths ranging from 12 to 25 eV, were used to obtain the final results. The mean value of the slope of decay rate versus pressure gives a quenching rate coefficient of 2.5×10^{-9} cm^3 sec^{-1}. Since the N_2 pressure measurements were made with an uncalibrated ion gauge, the quenching rate coefficient could be in error by as much as a factor of 2. The lack of calibration does not affect the decay rate, which depends only upon relative pressures. While various quenching mechanisms are possible, the substantial amount of energy (20.4 eV) possessed by $N^+(^5S_2)$ makes the charge transfer process $N^+(^5S_2) + N_2 \rightarrow N_2^+ + N$ most likely. The measured rate coefficient implies that the quenching rate in aurorae will equal the radiative decay rate, thus reducing the emission intensity by a factor of 2, at a height $h = 135 \pm 9$ km.[16] This is consistent with reports[8,17] of significant deactivation below 130 km of the auroral 2145-Å feature. These results also suggest that the observations of Erdman, Espy, and Zipf[8] can be explained on the basis of rapid quenching of $N^+(^5S_2)$.

The mean value of the $N^+(^5S_2)$ decay rate, extrapolated to zero N_2 pressure, is 255 ± 10 sec^{-1}. This must be corrected for quenching due to residual gas in the vacuum chamber. The residual gas, whose average pressure was 1.8×10^{-7} Torr with only minor daily fluctuations, was of unknown composition, but it is reasonable to assume a composition common in high-vacuum systems of mostly H_2, CO, and H_2O. Data for charge transfer and quenching of metastable ions are rare, but some observations on $Li^+(2\,^3S_1)$ (Ref. 18) and $N^+(2\,^1D_2)$ (Ref. 19) indicate that rates for H_2 are generally lower than for N_2, while those for CO and H_2O are generally higher. Consequently, we adopt an average quenching rate coefficient for the residual gas equal to the measured value for N_2. In view of the uncertainties in both the composition and the rate coefficients, the assigned possible error is chosen equal to the correction itself. The corrected decay rate is 240 ± 18 sec^{-1}.

Possible systematic errors were searched for by altering various parameters, including the electron beam energy, the timing sequence, and the ion-trap operating point. No likely sources of error were discovered other than the previously discussed dependence on the well depth for $D \leq 10$ eV. Although no well-depth dependence was discernible in the data used for final analysis, small effects due to ion-cloud motion cannot be ruled out. Consequently, we adopt a possible systematic error of 10%, or 24 sec^{-1}, a value chosen since it represents the approximate accuracy of a single measurement. The measured value for the radiative decay rate of $N^+(^5S_2)$ is then $A_{rad} = 240 \pm 30$ sec^{-1}, or, equivalently, the radiative lifetime is $\tau_{rad} = 4.2 \pm 0.6$ msec.

In summary, the radiative lifetime of $N^+(^5S_2)$ has been measured and is in general agreement with recent theoretical values. This result suggests that the tables of Kurucz and Peytremann be used with caution for intersystem lines. The experimentally determined quenching rate coefficient and excitation cross section in N_2 provide laboratory support for the interpretation of the 2145-Å auroral feature as being due to $N^{+}(^{5}S_2)$ emission.

The author gratefully acknowledges the able assistance of Ms. Carol Johnson and discussions with Dr. G. Victor regarding the theoretical and atmospheric aspects of this work. This work was supported in part by the Center for Astrophysics Postdoctoral Fellowship Program and by NASA under Grant No. NGL 22-007-006.

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Unifying Degenerate Four-Wave Mixing and Coherent Anti-Stokes Raman Scattering in Rare Media

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(Received 19 January 1982)

The degenerate and counterpropagating waves of the degenerate four-wave mixing process will appear nondegenerate and noncounterpropagating to a moving observer. A Lorentz-transformed degenerate four-wave mixing is seen to be indistinguishable from coherent anti-Stokes Raman scattering. Inverse transformations which render any given coherent anti-Stokes Raman scattering the appearance of a degenerate four-wave mixing are also presented.

PACS numbers: 42.65.Bp, 42.65.Cq

Coherent anti-Stokes Raman scattering (CARS)[1] and degenerate four-wave mixing[2] (DFWM) have some features in common, but differ in other ways. Both CARS and DFWM are four-wave mixing processes where the interaction of three waves leads to the generation of a fourth wave. In both processes, the energy and momenta are conserved among the four waves with no net transfer of energy or momentum to or from the medium in which the interaction occurs. On the other hand, whereas in DFWM all four waves are of the same frequency, in CARS no more than two of the waves can be degenerate and all four may be different. The phase-matching geometries in the case of DFWM are all simple and coplanar, consisting of two pairs of counterpropagating wave vectors. By contrast, phase-matching geometries[1] in the case of CARS can be quite complex and may even be three-dimensional. A variety of practical geometries has been reported in the literature where they have been given such names as BOXCARS,[3] bent[4] CARS, folded[5] BOXCARS, ARCS,[6] and COPCARS.[1,7]

The areas of CARS and DFWM have remained essentially isolated from each other in the literature. Recently, however, the distinction between

