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Excitation of Cd, Zn, and Sr by a beam of active nitrogen[a]

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Excitation of the electronic levels of Cd, Zn, and Sr is observed when these metal vapors collide with a thermal-energy, active nitrogen beam. The beam is extracted from a glow discharge in pure N_2. The active beam component is inferred to be vibrationally excited N_2 in the $A\,^3\Sigma_u^+$ electronic state. The absolute relative intensity of the emission lines in each element was measured. The excitation rates of the Cd and Zn target levels were found to depend exponentially on their energies indicating an effective temperature of approximately 4000°K. We believe that this temperature is related to the vibrational temperature of the $N_2(A\,^3\Sigma_u^+)$ states that excite Cd and Zn in energy transfer collisions. The excitation rates of the Sr levels did not show an exponential energy dependence, which is a result consistent with $N_2(A\,^3\Sigma_u^+)$ as the active species. The potential of such an emission study as a sensitive beam diagnostic is noted.

I. INTRODUCTION

Excitation transfer between constituents of long-lived nitrogen afterglows and heavy metal impurities was observed as early as 50 years ago.[1] At that time neither the identity of the constituents nor the mechanism was well understood. Since that time the energies of the vibrational and electronic states of molecular nitrogen have been identified and the excitation transfer between these states and other atomic and molecular species has been well studied.[2]

Recent measurements have shown that excitation transfer between vibrationally excited $N_2(X^1\Sigma_g^+)$ molecules and Na atoms occurs as well as the inverse process involving excited Na atoms. Thus, excited Na atoms are quenched by ground state $N_2(X^1\Sigma_g^+)$ molecules[3] and vibrationally excited $N_2(X^1\Sigma_g^+)$ molecules are quenched by ground state Na atoms.[4] In an afterglow experiment, it was demonstrated by using absolute intensity measurements that the steady-state populations of the Na atomic levels were created by collisions with $N_2(X^1\Sigma_g^+,\ \nu \ge 7)$ and were related by a Maxwell–Boltzmann distribution.[5] It was found that the Na excitation temperature was in good agreement with the $N_2(X^1\Sigma_g^+)$ vibrational temperature, indicating a direct correlation of these temperatures in general.

In the experiment reported here, we have observed the following reaction:

$$N_2(A\,^3\Sigma_u^+,\ \nu') + A \rightarrow A^* + N_2(X^1\Sigma_g^+,\ \nu'')\ , \tag{1}$$

$$A^* \rightarrow A + h\nu\ , \tag{2}$$
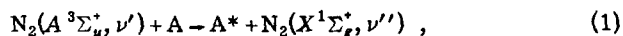
where A is the target species of Cd, Zn, or Sr. In reaction (1), heavy metal vapor targets are excited by collisions with N_2 molecules that are both electronically and vibrationally excited. The reaction is monitored by observing the respective photons produced in (2). From absolute relative intensity measurements, we find that the excitation rates of the Cd and Zn electronic states depend exponentially on energy indicating an effective temperature near 4000 °K. The excitation rates for Sr do not exhibit this exponential energy dependence.

The excitation of the Cd, Zn, and Sr targets is a result of energy-transfer collisions with high vibrational states of the $N_2(A\,^3\Sigma_u^+)$ molecule. In the case of Cd and Zn, we believe that the resulting energy dependence is due to the exponential populations in the vibrational states of the molecule and to the fact that only a subset of all the vibrational states are sufficiently energetic to excite a given target level. In the Sr target, all excited neutral levels, and hence the ground ion level, lie below the lowest vibrational level of the $N_2(A\,^3\Sigma_u^+)$ state. Thus, the populations of all the vibrational levels are sufficiently energetic to excite any Sr neutral level. In this case, an exponential energy dependence would not be expected.

II. EXPERIMENTAL APPARATUS

The experimental apparatus consisted of a N_2 beam source, a target collision region, and an optical detection system.

The N_2 beam source design is identical to that of a rare-gas metastable source design that has been described elsewhere.[6] The source is essentially a glow discharge maintained in pure N_2 gas undergoing nozzle expansion. The expansion is across a 0.015 cm hole supporting a 50 Torr pressure gradient. The discharge current is maintained at 5 mA by an applied voltage of 700 VDC. A cone-shaped skimmer mounted on a differentially pumped wall defines the beam. The beam tranverses a 61 cm diameter cylindrical vacuum chamber that serves as a collision region and is maintained at a pressure below 10^{-6} Torr. A pair of electric-field sweep plates mounted behind the skimmer insured that any charged particles were removed from the beam prior to the collision.

The discharge sidelight was straw yellow in appearance, characteristic of a Lewis–Rayleigh-type afterglow. A monochromator observing the discharge emission directed along the beam axis revealed that the second positive system ($C\,^3\Pi - B\,^3\Pi$) produced the most intense emission in the visible region. The absence of any significant emission at the 391.4 nm nitrogen molecular ion line or the 346.6 nm nitrogen atomic

metastable line was also noted. This absence indicated the "weak" nature of the source discharge.

The beam was characterized in part by the use of time-of-flight (TOF) measurements and particle detectors. These measurements showed that the beam contained excited neutral species with kinetic energies several times thermal. When a rotating mechanical chopper wheel interrupted the beam, a conventional copper–beryllium multiplier revealed two peaks separated in time. The first peak was demonstrated to be a signal due to photons from the discharge by making TOF measurements at two multiplier positions. The second peak had an integrated intensity more than 100 times the photon peak and corresponded to a beam component with a mean velocity of 1.1×10^5 cm/s. This velocity corresponds to a N_2 kinetic energy of 180 meV. An estimate of the absolute flux of the particle peak was made using a shielded secondary electron detector similar to the gas cell used by Dunning et al.[7] Using a detection efficiency of unity at a chemically clean stainless-steel surface, a lower limit value for the flux was determined to be 10^{14} particles/s sr.

The identity of the active species in the beam can only be inferred by utilizing both the data from the TOF measurements and the data from the optical emission which is produced in collisions with the target species. From the former we can require the active species to have a lifetime on the order of or larger than the flight time to the detectors, to have sufficient internal energy to produce secondary emission in a multiplier, and to have no net charge. The mean flight time to the multiplier during TOF measurements was as large as 900 μs. We also note here that the lowest electronic N_2 molecular state, the $A\,^3\Sigma_u^+$ state, is known to be able to activate copper–beryllium multipliers.[8] However, vibrationally excited ground state nitrogen is not expected to activate such multipliers.

In the collision region, the beam was collimated by an aperture to fill a solid angle of 3.2×10^{-4} sr. The heavy-metal target was titrated into the beam path by resistively heating a boron nitride crucible that contains the solid metal. This arrangement produced estimated number densities of 10^{14} cm^{-3} to 10^{15} cm^{-3} along a 1 cm path length of the beam.[9] Any optical emission produced in the target vapor by the N_2 beam is directed through a window in the chamber wall and analyzed by a 1/4-m monochromator equipped with a cooled S-19 photomultiplier. The photomultiplier signal was input to a photon counting unit that provided photon pulse rates. In order to make accurate relative intensity measurements, the detection system response was calibrated in the region of 250–700 nm by a quartz–iodine lamp referenced to NBS standards.[10]

III. RESULTS AND DISCUSSION

A. Target excitation and emission

In collision process (1) it is assumed that single collision conditions prevail and that the excited target state then is only quenched by radiative decay.

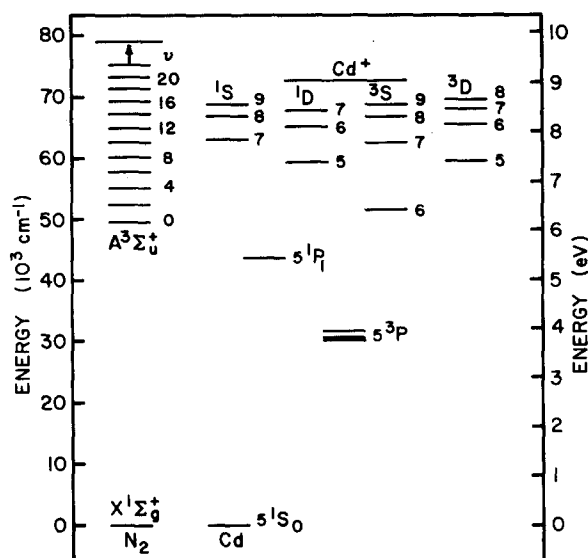In the case of Cd and Zn in which an excited state A^*

FIG. 1. Energies for the vibrational states of $N_2\,(A\,^3\Sigma_u^+)$ and for the observed multiplets in Cd. The same multiplets occur in Zn but are shifted to slightly higher energies.

is nearly coincident in energy with a vibrational level ν' of the $N_2(A\,^3\Sigma_u^+)$ exciting species, all the vibrational levels for which $\nu \geq \nu'$ are energetically available for excitation transfer. We can thus express the time rate of change of the density of target atoms in a particular excited state, N_A^*, as

$$\frac{dN_A^*}{dt} = -\frac{N_A^*}{\tau} + N_A v \sum_{\nu=\nu'}^{\infty} \sigma(\nu)N(\nu) \, , \tag{3}$$

where τ is the radiative lifetime of the excited state of Cd or Zn, v is the beam velocity, N_A is the density of ground state target atoms, $N(\nu)$ is the density of the νth vibrational level, and $\sigma(\nu)$ is the cross section for the process of Eq. (1). The sum is carried over all the molecular levels for which $\nu \geq \nu'$.

For steady state excitation as is present in this beam experiment, Eq. (3) then reduces to

$$\frac{N_A^*}{\tau} = N_A v \sum_{\nu=\nu'}^{\infty} \sigma(\nu)N(\nu) \, . \tag{4}$$

This expression thus equates the photon emission rate from the state A^* with the rate of excitation of this state by the active N_2 beam. By comparing the intensities of the Cd and Zn emission lines on an accurate relative scale, Eq. (4) allows one to observe the change in the quantity $\sum_{\nu=\nu'}^{\infty} \sigma(\nu)N(\nu)$ as a function of ν'.

Accurate relative emission spectra were taken for the Cd, Zn, and Sr targets in the spectral region of 250–600 nm. Some of the relevant energy levels in the N_2 and Cd species are shown in Fig. 1. The Zn multiplets are similar to those of Cd but shifted to slightly higher energies. A summary of the observed emission lines in Cd and Zn is shown in Table I, where the observed multiplets are identified by their principal quantum number n. In each case the $n'\,^3P_1^\circ - n'\,^1S_0$ and $n'\,^1P_1^\circ - n'\,^1S_0$ transitions were also observed, with the former being the most intense emission line. The intensity of individual lines

TABLE I. Summary of the observed multiplet transition in the Cd and Zn targets.

Transition	Cd ($n' = 5$) n	Zn ($n' = 4$) n
$n\,^3S - n'\,^3P^0$	6, 7, 8, 9	5, 6, 7
$n\,^3D - n'\,^3P^0$	5, 6, 7, 8	4, 5, 6, 7
$n\,^1S - n'\,^1P^0$	7, 8, 9	6, 8
$n\,^1D - n'\,^1P^0$	5, 6, 7	4, 5, 6, 7

varied over more than 3 orders of magnitude.

The relative intensity I of a multiplet was determined by first folding in the detection response for each spectral line, then summing to obtain the total line intensity of the multiplet, and finally dividing this total intensity by a statistical weight factor. This factor was the product $(2S + 1)(2L + 1)$, where L and S are the angular momentum quantum numbers of the upper state. The statistical weight includes only the upper state since the excitation rate of a given state is independent of the lower state reached by radiative decay. No account was taken of branching ratios since the transitions observed are the most probable one of those with a given upper state. The relative intensity data, I, plotted versus the energy of the upper state for Cd and Zn is shown in Figs. 2 and 3, respectively. The straight line drawn in each figure is the result of a least-squares fit to a straight line for the total emission. In terms of room temperature kT, the straight line slopes for the Cd and Zn data are 13 kT and 14 kT, respectively. The combined uncertainty in the data points ranged from approximately 10% for the most intense emission to near 30% for the weakest emission. The relative intensity scales of Figs. 2 and 3 are related by an unknown constant and hence cannot be used to determine ratios of emission cross sections for the Cd and Zn multiplets.
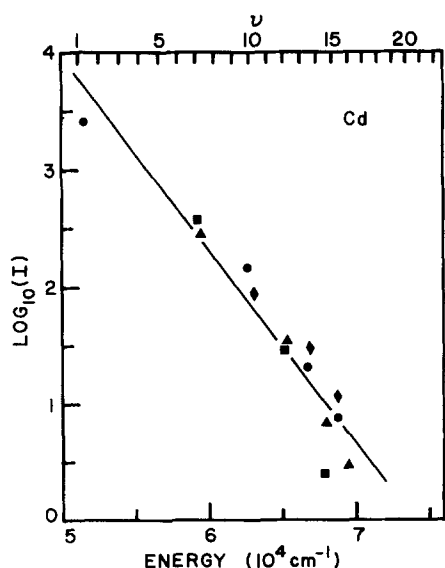

FIG. 2. Plot of the relative multiplet intensities I observed in Cd as a function of energy. The energies of the N_2 ($A\,^3\Sigma_u^+$) vibrational levels are plotted on the upper scale. The symbols identify the series as ● for ^3S, ▲ for ^3D, ◆ for ^1S, and ■ for ^1D. The solid line represents a least-squares fit to all the points.
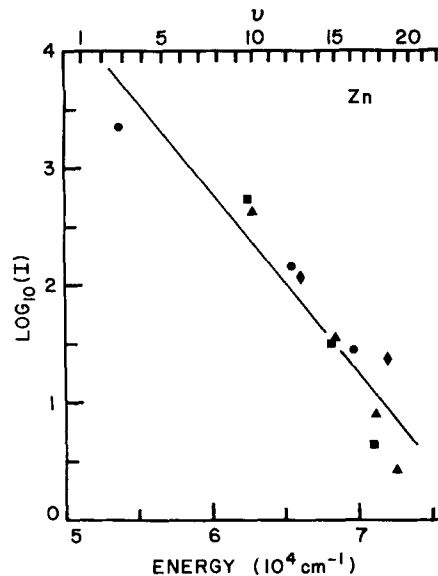

FIG. 3. Plot of the relative multiplet intensities I observed in Zn as a function of energy. The energies of the N_2 ($A\,^3\Sigma_u^+$) vibrational levels are plotted on the upper scale. The symbols identify the series as ● for ^3S, ▲ for ^3D, ◆ for ^1S, and ■ for ^1D. The solid line represents a least-squares fit to all the points.

In the case of Sr, similar emission was observed with the ^3F and ^1F multiplet series also appearing. The intensity data for the strontium could *not* be fit to a straight line on a plot similar to those of Figs. 2 and 3.

B. Active species

In light of the combined data from the beam diagnostics and the optical emission measurements, the active beam component can be deduced with reasonable certainty. From the data, emission is observed from target states which lie as high as 72 000 cm^{-1} (8.9 eV) above the ground state. For all three targets, no emission from ion levels was observed. Possible candidates for the active beam component are the vibrationally excited $B\,^3\Pi_g$, $a\,^1\Pi_g$, $a'\,^1\Sigma_u^-$, $X\,^1\Sigma_g^+$, and $A\,^3\Sigma_u^+$ levels of the nitrogen molecule. The nitrogen atomic metastables are not sufficiently energetic to excite the observed target states and hence are not considered as possible candidates.

The $B\,^3\Pi_g$ and $a\,^1\Pi_g$ states have radiative lifetimes of 1–8 μs[11] and 115 μs,[12] respectively. The flight time to the vapor target is 220 μs, while the flight time to the particle multiplier ranged up to 900 μs. When the particle multiplier was displaced along the beam, no variation in the multiplier signal compatible with these short lifetimes was observed. The $a'\,^1\Sigma_u^-$ state has a lifetime of 40 ms and therefore its population is not appreciably reduced by the time of flight.[13] Since the energy of the $\nu' = 0$ state of N_2 ($a'\,^1\Sigma_u^-$) is near 68 000 cm^{-1}, we would expect more excitation of higher lying target levels than is observed. In Sr, no ion emission is observed even though vibrational levels above $\nu' = 3$ are sufficiently energetic to excite the 5 ^2P ion levels which radiate in the visible region. Thus we exclude these three states from being the active beam component.

Excitation transfer from the $X\,^1\Sigma_g^+$ state must proceed

from vibrationally excited molecules with $25 \le \nu \le 35$. Large populations in these states seem unlikely because of the relatively weak source discharge producing these states. In nitrogen afterglows, populations of vibrational states with $\nu \ge 25$ are not in general observed. Further, we note that one can compute the ratio of cascade population to direct population in the n' $^3P_1^\circ$ state of Cd and Zn by adding the appropriate emission line intensities and comparing this sum to the n' $^3P_1^\circ-^1S_0$ emission intensity. This ratio is found to be 0.43 and 0.45 for Zn and Cd, respectively, with the smallest cascade contribution being 0.3% of the total. If the Cd and Zn excitation occurred via the $X^1\Sigma_g^+$ state, one would expect this ratio to be near 10^{-3} since the n' $^3P_1^\circ$ states near 40 000 cm^{-1} are coincident in energy with a much lower and therefore more highly populated vibrational state. We also note that the Sr emission would also be expected to show the same exponential dependence if the $X^1\Sigma_g^+$ state were the exciting species.

The above discussion leaves the $A^3\Sigma_u^+$ state as the most probable candidate for the active beam component. The $N_2(A^3\Sigma_u^+)$ state has a sufficient lifetime on the order of 1 s.[14] The observed Cd and Zn levels are in near coincidence with specific vibrational levels of the $A^3\Sigma_u^+$ state, and by Eq. (4) one expects a variation in the excitation rate with ν'. However, for Sr all the observed levels lie below $\nu' = 0$ and thus we must set $\nu' = 0$ in the sum in Eq. (4) for all A^* of Sr. Experimentally, we observe an exponential dependence of the Cd and Zn emission intensities on the energy of the levels. However, no such dependence exists for the Sr levels. We are led then to conclude that the vibrationally excited $A^3\Sigma_u^+$ state of nitrogen is the dominant active species in the beam.

C. Vibrational temperature

Figures 2 and 3 summarize the results obtained for Cd and Zn, respectively. The straight-line fit to all the data points indicates that the quantity $\sum_{\nu=\nu'}^{\infty} \sigma(\nu)N(\nu)$ of Eq. (4) depends exponentially on energy and hence on ν'. If the dependence of $\sigma(\nu)$ on ν could be accounted for, the relative populations of the vibrational states, $N(\nu)$, could be determined. Or, conversely, if $N(\nu)$ were known, then the dependence of $\sigma(\nu)$ on ν could be determined.

In this experiment, we cannot measure $\sigma(\nu)$ or $N(\nu)$ directly. From the data, however, we see that σ does not significantly depend on the L or S quantum numbers of the upper state because the weighted relative excitation of the different multiplet series is approximately equal. Further, other experiments which have observed excitation transfer from $N_2(X^1\Sigma_g^+, \nu > 0)$ to K and Na have observed that σ does not depend on the closeness of the match in energy between the vibrational levels and the traget electronic levels.[4,15]

In σ is assumed to vary in some reasonable manner, e.g., with ν or with the Franck–Condon factors for the N_2 transition, a good straight-line fit can still be made

to the data. In both the Cd and Zn data, the lowest ^3S multiplet falls significantly below the least-squares fit to the other data points. A σ dependence on ν or the Franck–Condon factors could account for the apparent reduced excitation of these low lying levels.

The measured effective temperature of near 4000 °K for the total emission is a reasonable temperature to expect from the weak source discharge and is comparable to that measured in microwave afterglow sources.[5] Thus, from the above discussion, we conclude that the vibrational distribution is directly related to this effective temperature. Indeed, if the cross section, σ, does not depend on ν, this effective temperature would equal the vibrational temperature.

The importance of measuring the vibrational temperature of the nitrogen excited state is suggested by the study of ion–neutral reaction rates.[16] For example, in the case of the reaction of $O^+ + N_2(X^1\Sigma_g^+)$, the rate constant at thermal kinetic energies was found to increase by a factor of 50 over the vibrational temperature range of 300–6000 °K.[17] In general, it is very difficult to measure the reactant vibrational temperature in an accurate, nonperturbing fashion. The target emission measurements with Cd and Zn reported here promise to furnish such a method for the $N_2(A^3\Sigma_u^+)$ state if one can simply "calibrate" the method by measuring the cross-section dependence.

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