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Energy transfer collisions between vibrationally excited molecular nitrogen and atoms^{a)}

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Chemiluminescent reactions between metastable states of molecular nitrogen and atoms are used to determine the vibrational temperatures of these nonradiating molecular systems. The excitation rates of Na, Mg, Cd, and Zn are used to obtain the vibrational temperature of $N_2(X^1\Sigma)$ and $N_2(A^3\Sigma)$ states in a fast flowing nitrogen afterglow. The exponential dependence of the intensities of the emission from atoms excited by the energy transfer collisions on the energy of the level yields vibrational temperatures on the order of 3100 K. We also report the presence of apparent strong selection rules on the total spin of the system which effectively suppresses energy transfer to the singlet states of magnesium.

I. INTRODUCTION

Distributions of vibrational level populations of molecular states are of considerable interest. This interest has grown as the need for a better, more detailed understanding of the electrical properties of a gas discharge has progressed and as energy transfer from vibrationally excited molecules to other atomic or molecular systems is more and more utilized. In ion-molecule reactions, for example, vibrationally excited molecules can play a critical role in upper atmosphere chemistry.¹

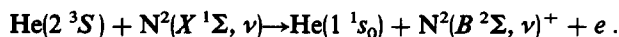
Determining the vibrational distributions of radiating states is generally simple enough; one simply measures the relative intensities of the various vibrational transitions and combines it with the Franck-Condon factors to obtain the relative densities. The situation is more difficult in the case of nonradiating levels; e.g., the ground electronic state and/or metastable states of the molecular system. In principle one can determine the densities of such nonradiating levels by using optical absorption. The difficulty here is that available optical sources are in general weak although a tunable laser may be used if one is fortunate enough.

A more generally useful method would be to somehow force the nonradiating levels to fluoresce. The equivalent process experimentally is to find a second species which will quench the vibrational state of interest and in a resonant energy transfer process cause the second species to be excited to a radiating level.

In this article we are concerned with the application of this method to the long-lived states of molecular nitrogen. Nitrogen is of great interest in atmospheric and plasma chemistry² and in laser plasmas.^{3,4} In particular the $N_2(A^3\Sigma)$ metastable state can be a very efficient system in which to store energy for subsequent transfer to other atomic and molecular systems.⁵

Milne had observed that the excitation temperature of the radiating levels of Na added to a flowing nitrogen afterglow (2–10 Torr) corresponded to the vibrational temperature of relaxing N_2 molecules.⁶ Energy transfer collisions between vibrationally excited ground electronic levels of

molecular nitrogen and sodium produced strong sodium excitation. This work suggested that the Na excitation temperatures corresponded to the vibrational temperatures of the ground $N_2(X^1\Sigma)$ state. Duthler and Broida⁷ examined the relative intensities of Hg, Zn, and Cd line emission which were generated in a flowing nitrogen afterglow (1–10 Torr). They concluded that the group IIb excitation resulted from energy transfer from electronically excited $N_2(A^3\Sigma)$ molecules. The Hg excitation was used to determine the vibrational temperature of the metastable molecular nitrogen system. Jolly *et al.*⁸ determined the vibrational level populations of $N_2(X^1\Sigma)$ in a pure nitrogen glow discharge by adding He(2^3S_1) metastable atoms to the discharge. The reaction in this case is



The fluorescent species in this case is the nitrogen molecular ion excited in the Penning collision between the metastable helium and the molecular nitrogen. Fahey *et al.*⁹ extended this technique to the excitation of Cd and Zn by a thermal energy beam of electronically excited $N_2(A^3\Sigma)$ metastable molecules. In the molecular beam, single collision conditions prevail so the experimental conditions are substantially different from those of Refs. 6 and 7 in which ground state N_2 densities were between 1 and 10 Torr. Nonetheless, the relative intensities of the Cd and Zn emission resulting from excitation in the molecular beam of metastable nitrogen which were extracted from a cold cathode discharge were in a Boltzmann distribution; the excitation temperature in this case being on the order of 4500 K.

We report here the use of energy transfer collisions between metastable molecular nitrogen and the atoms of Na, Mg, Cd, and Zn occurring in an afterglow of microwave-excited active nitrogen. The energy levels of Na are in near energy resonance with $N_2(X^1\Sigma, \nu)$ state and permit one to determine the vibrational level populations of that system as in Ref. 9. The excited states of the alkaline earths are in near resonance with the $N_2(A^3\Sigma, \nu)$ metastable state. Energy transfer from the $N_2(A)$ state to these species can thus be used to determine vibrational level populations in the $N_2(A)$ state as shown by Fahey *et al.*⁹ who utilized Zn and Cd to obtain vibrational temperatures of the metastable nitrogen

^{a)} Research supported by AFAWL Contract No. F33615-81-K-2081.

in a beam. The use of Mg extends the range over which useful vibrational temperatures may be obtained. With magnesium as a probe we are able to extend the vibrational measurements to lower excitation temperatures than can be obtained with Cd or Zn. For example, at a temperature of 3000 K, 99% of all the N₂(A³Σ) population is in vibrational states below $\nu = 8$. There is only one Cd or Zn optical transition whose upper level falls within the energy range represented by N₂(A) population at $\nu = 7$ or below. Magnesium, on the other hand, has six observable transitions in this range. The energy levels of Cd and Zn are primarily energy resonant with the higher vibrational levels of the molecular nitrogen.

The flowing, active nitrogen afterglow has been used by several workers^{3,10,11} to observe energy transfer from the active nitrogen species to the Hg-halides. In this case the fluorescence efficiencies of the HgX emission resulting from the energy transfer collision depends greatly on the vibrational populations of the N₂(A³Σ). There is thus interest in determining the effective vibrational temperature in this system.

II. EXPERIMENTAL APPARATUS

Molecular nitrogen is admitted at the entrance to the flow apparatus through a small expansion nozzle. The gas expands into a Pyrex cross of 10 in. diameter. A weak microwave discharge is established in the nitrogen gas, localized by a quarter-wave, foreshortened cavity. The atom probe, consisting of a small oven which contains the atom of interest (Na, Cd, Zn, or Mg), is located approximately 50 cm downstream from the excitation region. In this region the short-lived discharge products have decayed and remaining in the reaction zone are primarily N atoms and N₂ molecules both in their electronic ground state. N₂ metastable molecules, and small concentrations of atomic and molecular ions which may be further reduced by electric field heating of the afterglow to increase the ambipolar diffusion rate.

The background N₂ pressure at the location of the atom probe is on the order of 0.1 Torr or less. The pressure in this region is kept low in order to minimize collisional effects in the excited states of the atom probe system. With the 540 cfm pump, consisting of a large mechanical forepump and a Roots blower exhausting the Pyrex cross, the flow velocity is subsonic and on the order of 10³ to 10⁴ cm s⁻¹. The fluorescence produced by the interaction of the active nitrogen afterglow with the atom probe is observed at right angles to the flow direction through a quartz window by a 0.5 m monochromator fitted with a photomultiplier. The detection system is operated in the photon counting mode with the pulses being counted and displayed by a multichannel scaler.

The weak nitrogen afterglow is a pale blue color. If the microwave excitation is increased above a nominal 1 W, the afterglow assumes the characteristic orange glow associated with the recombination of atomic nitrogen. Since there is some evidence that the atomic nitrogen may quench the excited N₂(A³Σ) molecule,⁵ the system was generally operated at minimum excitation levels. With the addition of Na in the reaction zone a bright yellow flame appeared presumably resulting from transfer of energy from the vibrational system of the N₂(X¹Σ) molecules to the electronic states of the Na.

Magnesium produced a bright blue flame resulting from excitation by the N₂(A³Σ) system.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Energy transfer collisions

The excitation of the probe atom by the nitrogen is presumed to follow the reaction

$$\frac{dn_j}{dt} = -\frac{n_j}{\tau_j} + n_0 \sum_{\nu > \nu_j} N_2(\nu)k(\nu),$$

where the net rate of loss of excited state atoms from the probe source is equated to the loss rate by photon decay and excitation by energy transfer collisions between electronically and/or vibrationally excited molecular nitrogen and the probe atom. n_j is the excited probe atom density and τ_j is the lifetime of the excited state. n_0 is the ground state probe atom density, $N_2(\nu)$ is the population density of the ν th vibrational level, and $k(\nu)$ is the rate constant for energy transfer. $N_2(\nu)$ is either the N₂(X¹Σ, ν) or N₂(A³Σ, ν). The sum is carried out over all those vibrational levels whose energy is sufficient to excite the particular probe atom state. In general, except at high vibrational temperatures, it is sufficient to use only the vibrational populations of the level in closest energy coincidence with the n_j .

In steady state, we then have

$$\frac{n_j}{\tau_j} = n_0 \sum_{\nu > \nu_j} N_2(\nu)k(\nu),$$

n_j/τ_j , however, is directly proportional to the intensity of the fluorescence observed from the n_j state provided there are no collisional losses from this state.

$k(\nu)$ is the rate constant for the energy transfer from the N₂(A) molecule in the vibrational state, ν , to the atomic species. We make the explicit assumption that $k(\nu)$ does not depend on ν as was also assumed in Refs. 6, 7, and 9. The energy difference between the lowest lying vibrational state and the atomic state is generally within kT and rotational excitation of the molecular final state will further reduce any dependence of the transfer rate on energy. It is not clear whether the transfer rates depend on Franck-Condon factors. The experimental work of Nadler and Rosenwaks¹² involving energy transfer from vibrationally excited N₂(A) molecules to Cu suggests that Franck-Condon factors are important parameters in determining the energy transfer rates. In the cited work all Cu levels observed lie below $\nu = 0$ of the N₂(A) state. The work of Bauer *et al.*,¹³ however, suggests that energy transfer at least in the case of alkali atoms proceeds via a curve crossing, implying that Franck-Condon factors are not important. In any case, explicitly including the Franck-Condon factors in Eq. (2) does not materially alter the equilibrium excitation temperature of the Mg excited states. Fahey *et al.* also discuss this point in more detail.⁹

B. Sodium probe

The energy levels of atomic sodium are in near resonance with vibrationally excited N₂(X¹Σ, ν) molecules. Thus, sodium may be used as the probe atom for this system

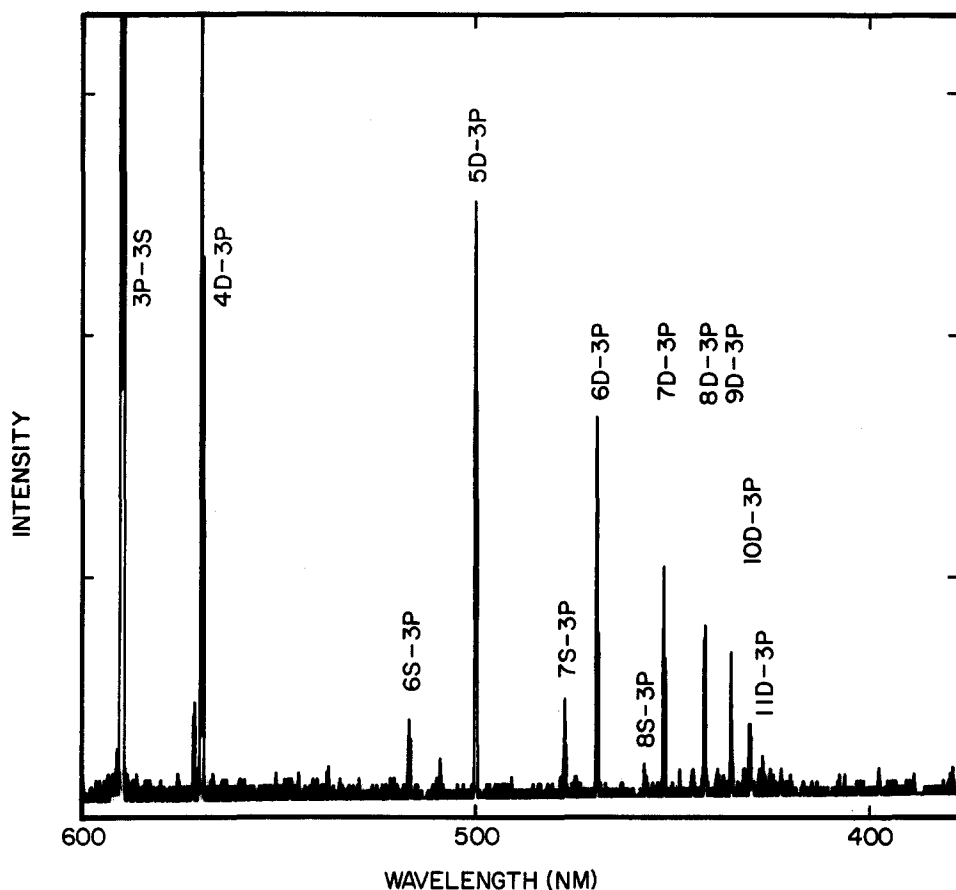


FIG. 1. Sodium spectrum from 600 to 400 nm. The gain has been increased to show the weakest lines. The doublet structure was well resolved. The $nD-3P$ series to $n = 11$ is clearly seen. The $3P-3S$ transition showed some evidence of radiation trapping. The spectrum is uncorrected for spectral response.

as shown by Milne.⁶ In Fig. 1 we show the emission spectrum of Na from 600 to 400 nm. Fluorescence from $nD-3P$ states up to $n = 12$ may easily be resolved. In Fig. 2 we plot the log of intensity, against the energy of the respective nD state. In

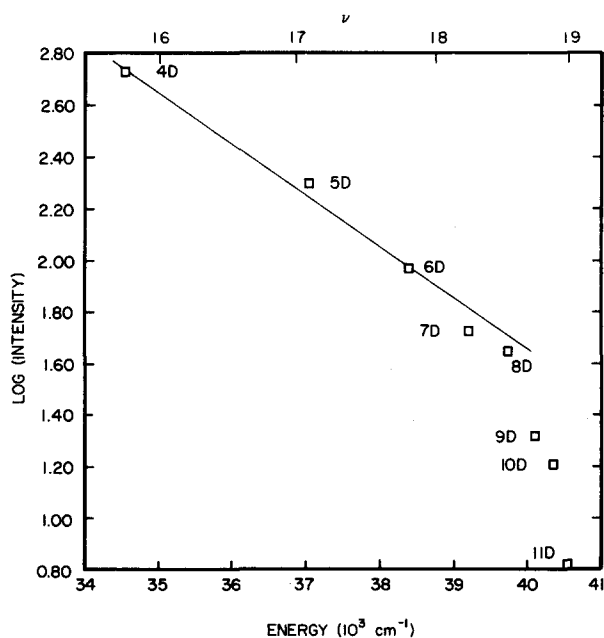


FIG. 2. The log of the absolute relative intensity of the $nD-3P$ emission lines vs energy of the level in cm^{-1} . The straight line shown represents an excitation temperature of 3100 K.

Fig. 2 the intensities have been corrected for the spectral response of the instruments.

The plot of $\log(I)$ vs energy lies along an approximate straight line for $n < 9$ ($E < 40\,000\,cm^{-1}$) suggesting that the vibrational populations of the $N_2(X^1\Sigma, \nu)$ system are in an equilibrium distribution. If the cross section for energy transfer is presumed not to vary significantly with vibrational level, as discussed above, we can infer the relative populations of the vibrational levels and obtain an equilibrium temperature of approximately 3100 K. Milne⁶ obtained temperatures near 4000 K in the Lewis-Raleigh afterglow region at pressures 50–100 times larger than those reported here. The departure of the data from linearity for $nD > 8$ is likely due to collisional ionization of the high lying Na states. The D states with $n > 8$ are within 0.2 eV of the ionization limit of sodium. This feature was also observed by Milne⁶ and Duthler and Broida⁷ and is further discussed therein.

C. Magnesium probe

Figure 3 shows the emission spectrum from 630 to 280 nm obtained when magnesium is used as the probe atom. The energy levels of magnesium are in near resonance with vibrationally excited $N_2(A^3\Sigma)$ molecules. A plot of the log of the intensity of the observed magnesium fluorescence lines terminating on the 3^3P level is shown in Fig. 4. Account has been taken of the differing statistical weights of the S and D levels. The straight line drawn reflects a vibrational temperature of 3100 K, identical to the results obtained for the ground vibrational temperature. This is to be expected since the hot electrons in the active microwave discharge provide

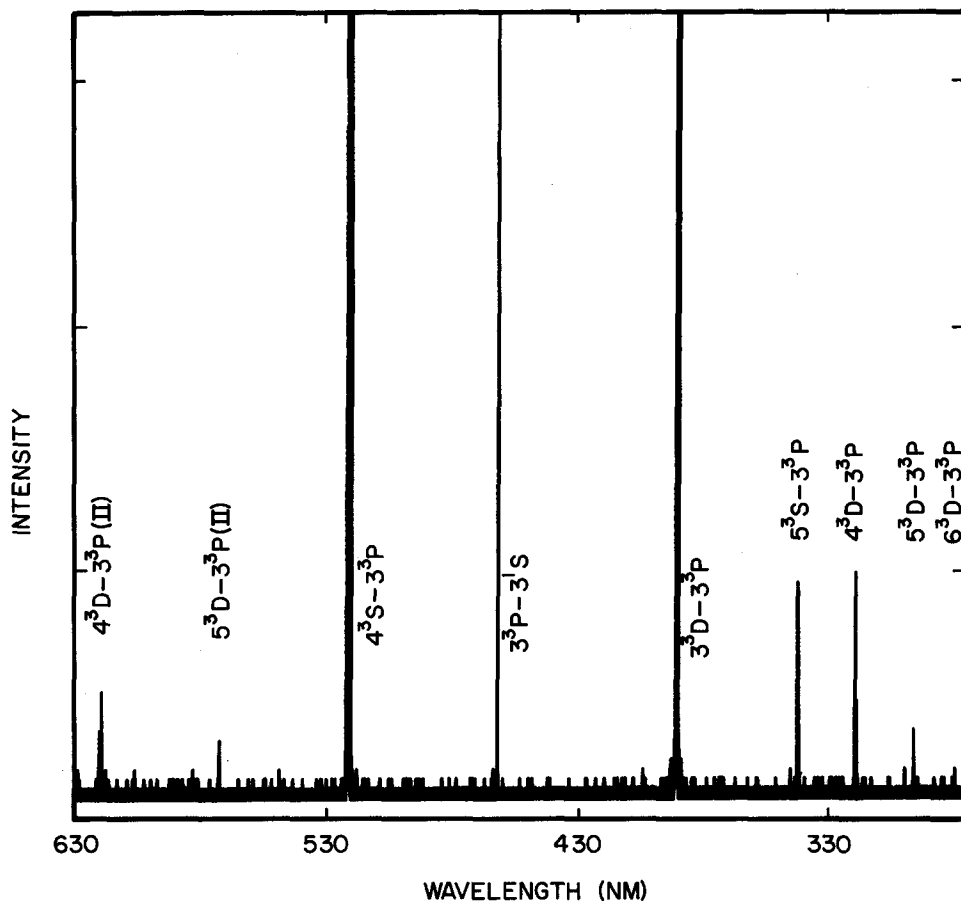


FIG. 3. Magnesium spectrum from 630 to 280 nm. The gain has been increased to show the weakest lines. The structure of the terminal 3^3P level was resolvable but not the structure in the n^3D level. The spectrum is uncorrected for spectral response.

the vibrational heating for both the ground and metastable molecular systems.

There are several interesting features to be noted in the spectrum of Fig. 3. The intercombination line at 457 nm

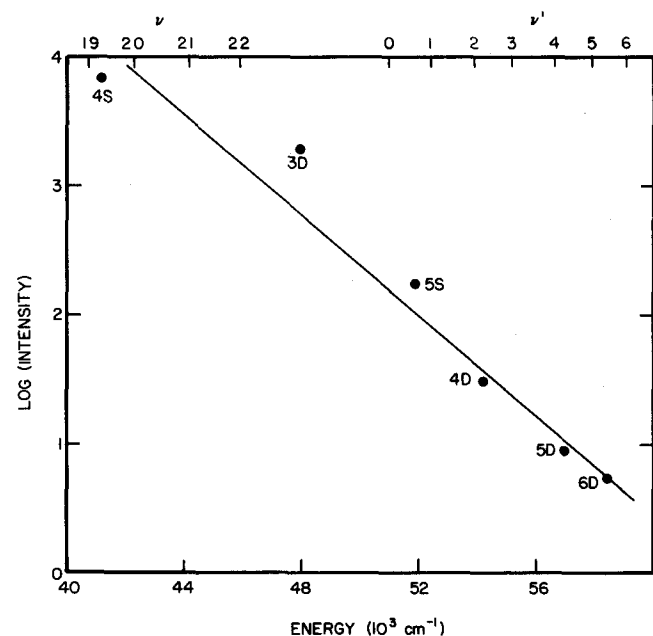


FIG. 4. The log of the absolute relative intensity vs energy of the observed magnesium transitions. The 4^3S and 5^3S to 3^3P transitions were weighted to account for the differing statistical weights of the upper levels. The straight line represents an excitation temperature of 3100 K.

($3^3P_1-3^1S_0$) is relatively intense. However, emission from the nearby $3^1P_1-3^1S_0$ resonance line at 285 nm is not observable nor is any other emission line originating on a singlet level. In a typical magnesium discharge the intercombination line intensity is generally negligible compared to the intensity of the singlet resonance line. The absence of any significant population of the magnesium singlet levels suggests that there are strong selection rules governing the excitation transfer from the $N_2(A)$ states to magnesium. Similar observations were noted by Lee and Martin¹⁴ in energy transfer from electronically excited CO molecules to Hg and by Duthler and Broida⁷ in the excitation of Hg by $N_2(A)$ molecules. The Wigner spin rule is evidently very effective in suppressing singlet excitation in these systems.

D. Cadmium probe

In Fig. 5 we show the fluorescence spectrum obtained when Cd is used as the probe atom. The energy levels of cadmium and zinc are energy resonant primarily with the higher vibrational levels of the metastable molecule. The transitions which appear in the spectrum are all from Cd levels which lie at or below the lowest vibrational state of the nitrogen; thus, in principle, all the vibrationally excited nitrogen is capable of energy transferring to the Cd. The results for Cd shown here are not useful for determining vibrational temperatures in the 3000 K range. In Ref. 9 both Cd and Zn were used to infer vibrational temperatures above 4000 K and the results here may be compared with that data.

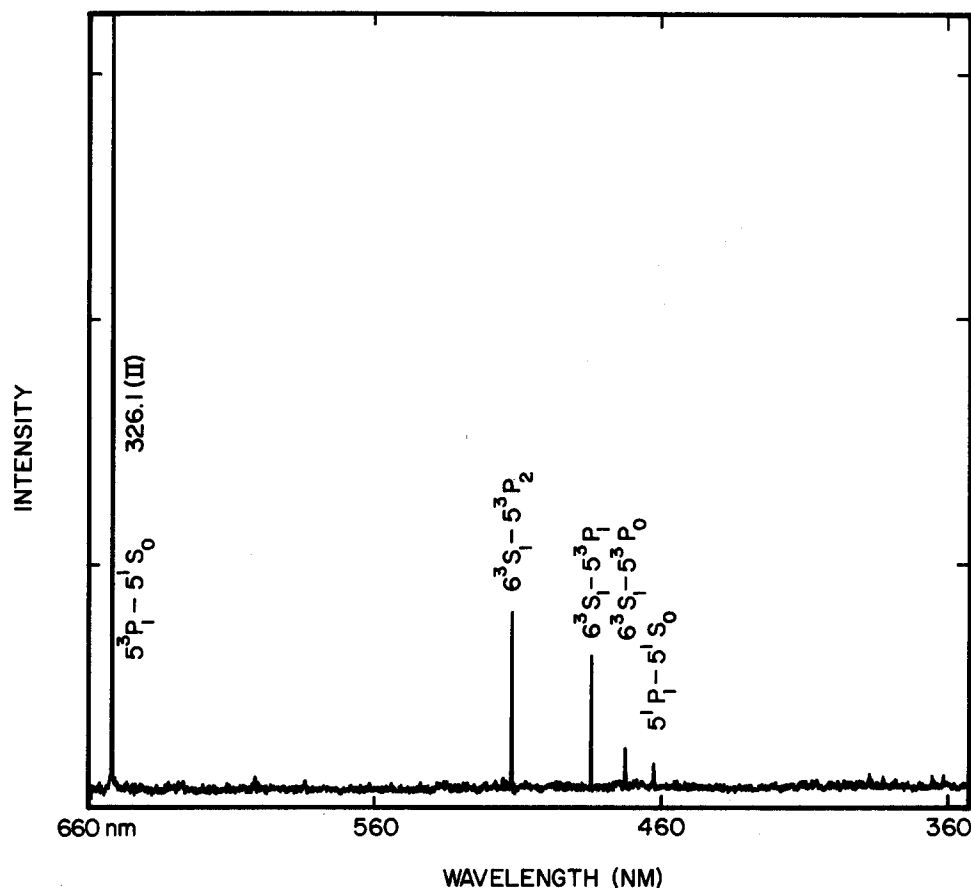


FIG. 5. Emission spectrum of cadmium from 660 to 360 nm. The gain was adjusted to show the weakest lines. The normally intense 5^1P_1 to 5^1S_0 resonance transition is relatively weak compared to the intercombination line. The 6^3S_1 level lies above the $\nu = 0$ level of the $N_2(A)$ state while both the 5^3P_1 and 5^1P_1 lie below the $\nu = 0$ level.

Of perhaps more interest is again the apparent significance of spin selection rules in a molecular system. Energetically both the intercombination line in Cd and the resonance 5^1P_1 - 5^1S_0 transition are capable of being excited by all the vibrational levels of the nitrogen. In a typical Cd discharge the resonance line is generally 2-3 orders of magnitude greater than the intercombination line. However, the energy transfer collisions do not populate significantly any of the Cd singlet levels.

Also, we observe no emission from higher lying Cd triplet levels. If there are significant concentrations of other energetic, long-lived states of molecular nitrogen present in the afterglow as suggested by Dreilung and Setser,¹⁰ we would expect to see emission associated with energy transfer from these populations. No such anomalous fluorescence is observed in either Mg, Cd, or Zn spectra and we thus conclude that under the operating conditions described above,

the metastable $N_2(A^3\Sigma)$ system is the only electronically excited species in our nitrogen afterglow.

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