

## ELECTRONIC ENERGY TRANSFER FROM METASTABLE ARGON ATOMS TO GROUND-STATE NITROGEN ATOMS

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The excitation of ground-state nitrogen atoms by metastable argon atoms has been studied by vacuum ultraviolet spectroscopy in a discharge-flow reactor. Rate constants for excitation of the  $2s^2 2p^2 3s^2 P$ ,  $2s^2 2p^2 3s^4 P$  and  $2s 2p^4 4P$  states were determined to be  $(9.0 \pm 2.7) \times 10^{-11}$ ,  $(1.6 \pm 0.7) \times 10^{-11}$  and  $(6.8 \pm 2.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. These energy-transfer reactions involve energy defects of 0.6–1.2 eV. The results are discussed in terms of several types of curve crossings.

### 1. Introduction

In the past few years several studies have focussed on the transfer of electronic energy from metastable argon atoms to the atomic quenchers Kr [1,2], Xe [3], O [3–5], Cl [3,6] and H [7]. Energy transfer in quenching by the rare gases (Kr, Xe), is a near resonant process, and states of the acceptor atom differing significantly in energy from the metastable argon energy (11.548 eV for the  $^3P_2$  state and 11.723 eV for  $^3P_0$  state) are populated much less strongly, if at all, compared to the states of lower energy defect. For these two atoms, quenching is negligible into states with energy defects of more than 0.1 eV. In contrast, the excitation of O, Cl and H atoms by energy transfer from metastable argon occurs with large excitation rate constants, leading to product channels with large energy defects, being over 1 eV in the case of Cl and H.

To extend the scope of the studies, we have investigated the excitation of nitrogen atoms by energy transfer from metastable argon atoms. Nitrogen atoms, like O, Cl and H atoms show strong excitation

of states with large energy defects (0.6–1.2 eV). The experiments involve observations of N-atom emissions in the vacuum ultraviolet. Rate constants for excitation of the various states observed were determined by comparing the intensities of emission from these states with emissions of Cl lines excited when known amounts of  $\text{Cl}_2$  were added to the reactor. The excitation rate constants for the Cl emissions have been determined previously [6,8] by comparison with the Kr standard [1,2,4,8].

### 2. Experimental

The apparatus used in these experiments was a discharge flow reactor similar to those used previously in rare-gas metastable excitation studies [1,8]. Argon, purified by passage through a molecular sieve trap (Linde 5A) maintained at liquid nitrogen temperature, flows at a rate of ca.  $1000 \mu\text{mole s}^{-1}$  through a hollow cathode discharge (ca. 200 V, 1–5 mA) which converts a small fraction of the argon into metastables. The argon metastable flow and the reagent flow (Ar,  $\text{N}_2$  and N; about  $70 \mu\text{mole s}^{-1}$  in all) enter the reaction cell coaxially directly in front of the spectrometer observation window and are

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mixed there by diffusion. Spectral observations normal to the flow are made through a LiF window by a vacuum ultraviolet monochromator whose spectral response has been calibrated [8]. Nitrogen atoms are produced by flowing nitrogen ( $1-10 \mu\text{mole s}^{-1}$ ), diluted in argon (ca.  $70 \mu\text{mole s}^{-1}$ ), through a 2.45 GHz microwave discharge. The concentration of N atoms in the reactor was determined by titration [23] of the N with NO prior to mixing the reagents,  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ . The strong nitrogen line at 149.3 nm resulting from the  $\text{Ar}(^3\text{P}_{2,0}) + \text{N}$  reaction was observed to decay linearly as a function of added NO provided the initial number density of N atoms was  $\geq 5 \times 10^{12} \text{ atoms cm}^{-3}$ . Use of too low initial [N] and hence incomplete reaction would give overestimations of [N] and lead to an underestimate of the rate constant. A substantial flow of argon (ca. 8% of the total flow) passed through the microwave discharge tube to reduce the transit time from the discharge to the observation region, and thereby eliminate uncertainties introduced by atom recombination in the tube connecting the microwave discharge to the observation region. NO for the N-atom titration was used as a 10% mixture in argon (total flow,  $0.1-1.0 \mu\text{mole s}^{-1}$ ). Although microwave discharges are also sources of vibrationally excited nitrogen, the observations reported here cannot be attributed to dissociative excitation of vibrationally excited nitrogen. For such a process to occur, ca. 5% of the total nitrogen would have to have 8.5–9 eV of vibrational energy or an effective vibrational temperature ca. 30 000 K. Typical vibrational temperatures produced in laboratory microwave discharges are 5000–10 000 K [9], with the effective temperature downstream being reduced somewhat due to relaxation on the walls of the tube. Chlorine for rate constant measurements was diluted to 2% in argon (total flow  $0.1-1 \mu\text{mole s}^{-1}$ ) and was mixed with the reagents prior to entering the observation region. The total pressure in the cell was near 200 Pa (1.5 Torr). All measurements were made at room temperature, 296 K.

### 3. Results

Energy transfer from metastable argon excites three sets of states in atomic nitrogen:  $2s^2 2p^2 3s \ ^2\text{P}$  (10.68 eV),  $2s^2 2p^2 3s \ ^4\text{P}$  (10.34 eV) and  $2s 2p^4 \ ^4\text{P}$

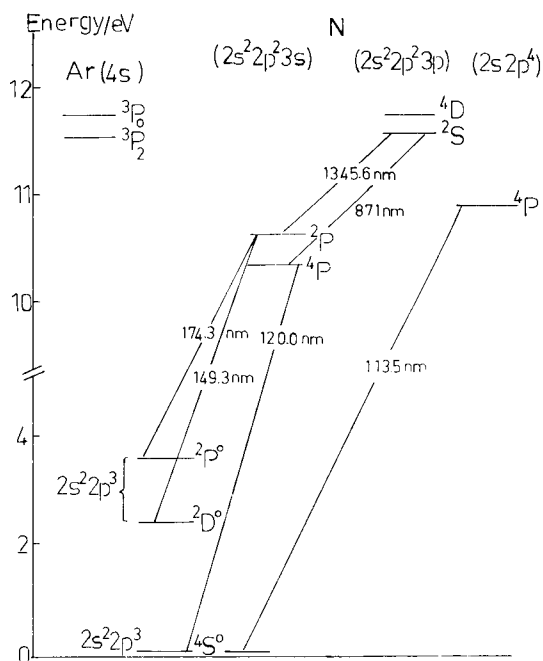


Fig. 1. Energy level diagram for the  $\text{Ar}^*(^3\text{P}_{2,0}) + \text{N}(^4\text{S})$  system showing the relevant states and transitions.

(10.93 eV). These energy levels are shown relative to those of metastable argon in fig. 1 along with the wavelengths of their transitions in the vacuum ultraviolet. The rate constant for excitation of the  $2s^2 2p^2 3s \ ^2\text{P}$  states was determined by comparing the emission from this state at 149.3 nm with the emission from Cl at 138.0 nm excited in the interaction between metastable argon and  $\text{Cl}_2$ . The sensitivity of the monochromator used to measure this rate constant fell off rapidly at wavelengths below 130 nm, so that the rate constants for the excitation of the  $2s^2 2p^2 3s \ ^4\text{P}$  and  $2s 2p^4 \ ^4\text{P}$  states could only be estimated from preliminary observations using a different monochromator in which the ratio of the intensities of the various states was determined at several different nitrogen atom number densities.

The basic technique of measuring excitation rate coefficients by comparison with a standard reaction has been discussed in detail previously [1,2,4,8]. The rate constant for the excitation of the line of interest,

in this case the 149.3 nm line, is given by

$$k_{149.3} = k_{138} I_{149.3} [\text{Cl}_2] q_{149.3} / (I_{138} [\text{N}] q_{138}), \quad (1)$$

where  $I_{149.3}$  and  $I_{138}$  are the measured intensities of the lines,  $q_{149.3}$  and  $q_{138}$  are the relative monochromator response correction factors, and  $k_{138}$  is the rate constant for excitation of the 138.0 nm line of Cl from the interaction between  $\text{Ar}^*$  and  $\text{Cl}_2$ . This rate constant has been measured previously in a comparison with the Kr standard [6,8]. The rate constant for excitation of the Cl ( $4s\ ^4P_{3/2}$ ) state is given by Gundel et al. [8] as  $7.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Correcting this number for the branching ratio for emission at 138.0 nm compared to all emission from this level (0.89) [6] and a small (5%) decrease to correct for the use of an incorrect Kr 123.6 nm excitation rate constant in their paper [10], gives  $k_{138} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Clyne and Nip [6] reported  $k_{138} = 8.45 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  but this value was obtained by using an incorrect value for the Kr 123.6 nm excitation coefficient. The value they report for the Kr 123.6 nm excitation coefficient is  $0.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is 24% high compared to the correct value of  $0.18 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ †. Correcting the rate constant of Clyne and Nip gives  $k_{138} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in agreement with the corrected value of Gundel et al.

The intensity of the 149.3 nm line of nitrogen was measured as a function of added NO. A typical run is shown in fig. 2. The slope of this plot gives the ratio  $I_{149}/[\text{N}]$  which is needed in eq. (1) to evaluate the excitation rate constant. The results of eight separate runs gave  $k_{149.3} = 6.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Multiplying this rate constant by 1.36 [11] to include emission from  $2s^2 2p^2 3s\ ^2P - 2s^2 2p^3\ ^2P$  at 174.3 nm gives  $k(2s^2 2p^2 3s\ ^2P) = (9.0 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

† The correction to the 123.6 nm excitation rate coefficient comes from using the correct branching ratio for 123.6 nm excitation compared to total Kr excitation (see ref. [2]) and a revised value for the rate constant for quenching metastable argon by Kr [10]. The proper branching ratio is 0.306; the revised rate constant is  $0.58 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Gundell et al. [8] used 0.30 and  $0.62 \times 10^{-12}$ , although 0.36 was the branching ratio quoted in their paper. Clyne and Nip used 0.36 and  $0.62 \times 10^{-12}$  for the branching ratio and excitation rate constant respectively.

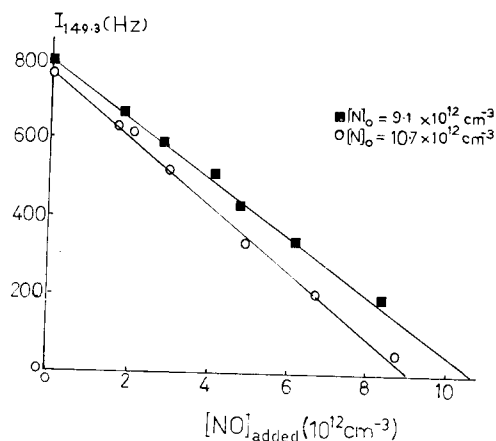


Fig. 2. The emission intensity of the  $\text{N}(2s^2 2p^2 3s\ ^2P) - \text{N}(2s^2 2p^3\ ^2D)$  line excited by the energy transfer reaction between  $\text{Ar}^*(^3P_{2,0})$  and  $\text{N}(^4S)$  as a function of added  $[\text{NO}]$ , hence  $[\text{N}(^4S)]$ .

$\text{cule}^{-1} \text{ s}^{-1}$ . The error limits represent one standard deviation from the average of the eight runs. The overall uncertainty, including the uncertainty in  $k_{138}$  (25%) and the uncertainty in the monochromator response function (10%) will be 30%.

Several measurements of the ratio of the 120.0 nm intensity to the total emission intensity from the  $2s^2 2p^2 3s\ ^2P$  states, i.e. the sum of the 149.3 and 174.3 nm intensities, gave a value at  $[\text{N}] \leq 1 \times 10^{12} \text{ atoms cm}^{-3}$  of  $0.18 \pm 0.05$ . Thus the rate constant for excitation of  $\text{N } 2s^2 2p^2 3s\ ^4P$  will be  $1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The ratio of the 113.5 nm line to the  $^2P$  lines was  $0.76 \pm 0.22$ , thus giving a rate constant for excitation of  $\text{N } 2s^2 2p^4\ ^4P$  of  $6.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The overall uncertainty in both of these values will be about 42%. Strictly speaking, these values should be considered lower limits since no attempts were made to make self-reversal corrections other than using only data for low  $[\text{N}]$ . We do not anticipate that such corrections could exceed 20–30%. The results are summarized in table 1.

#### 4. Discussion

The mechanism for the energy transfer will undoubtedly involve some type of curve crossing. There are three possibilities for the types of crossings which could explain the observed results. The excitation

Table 1  
Rate constants for nitrogen-atom excitation by metastable argon

Process a,b)	Rate constant ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Cross section <sup>c)</sup> ( $\text{\AA}^2$ )
$\text{Ar}^*(^3\text{P}_{2,0}) + \text{N}(^4\text{S}) \rightarrow \text{N}^*(2s^2 2p^2 3s^2 \text{P}) + \text{Ar}(^1\text{S}_0)$	$(9.0 \pm 2.7) \times 10^{-11}$	$11.6 \pm 3.5$
$\text{Ar}^*(^3\text{P}_{2,0}) + \text{N}(^4\text{S}) \rightarrow \text{N}^*(2s^2 2p^2 3s^4 \text{P}) + \text{Ar}(^1\text{S}_0)$	$(1.6 \pm 0.7) \times 10^{-11}$	$2.1 \pm 0.9$
$\text{Ar}^*(^3\text{P}_{2,0}) + \text{N}(^4\text{S}) \rightarrow \text{N}^*(2s 2p^4 \text{P}) + \text{Ar}(^1\text{S}_0)$	$(6.8 \pm 2.9) \times 10^{-11}$	$8.8 \pm 3.7$

a) All processes measured at 296 K.

b) No distinction has been made among the N-atom multiplet levels.

c) Derived by dividing the measured rate constant by the mean relative velocity.

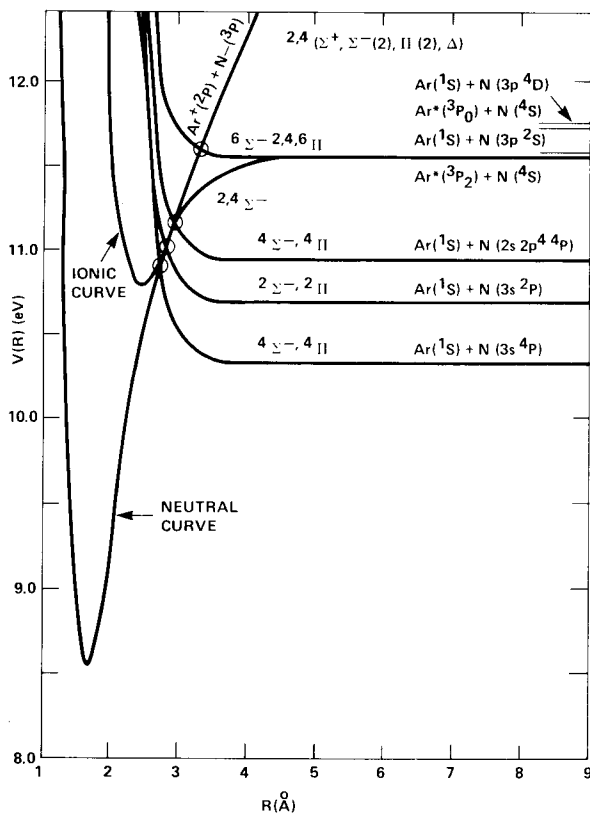


Fig. 3. Potential energy diagram for the interaction of  $\text{Ar}^*(^3\text{P}_2)$  with  $\text{N}(^4\text{S})$ . The  $\text{Ar}(^1\text{S}) + \text{N}$  potential curves are Lennard-Jones curves taken to be similar to  $\text{Ar}-\text{Na}$  ( $\epsilon = 6.24 \text{ meV}$ ,  $\sigma = 3.65 \text{ \AA}$  [12]). The attractive  $\text{Ar}^* + \text{N}(^4\text{S})$  curve is assumed similar to  $\text{ClN}$  [13], although slightly less bound. The curve displayed is a Morse potential with  $D_e = 3.0 \text{ eV}$ ,  $r_e = 1.7 \text{ \AA}$  and  $\omega_e = 800 \text{ cm}^{-1}$ . The ionic potential combines coulombic attraction with exponential repulsion  $A \exp(-r/\rho)$ .  $\rho$  was taken to be 0.31 which holds for the alkali halides [14];  $A = 2.27 \times 10^3$  was taken so that the potential minimum would fall at 2.5  $\text{\AA}$  (average  $r_e$  for  $\text{KF}$  and  $\text{KCl}$ ). Curve crossings which may be important are circled.

could occur as a result of direct crossing between attractive entrance channel states and exit channel states which dissociate to the observed nitrogen atom states. Alternatively, the curve crossing could be into nitrogen atom states different from those observed, with subsequent excitation of the observed emissions via radiative cascade. Finally, the coupling of entrance and exit channels could be affected by the intermediary of an ionic curve. Neither symmetry nor spin restrictions can be invoked to eliminate any of the three possibilities. Fig. 3 shows a set of qualitative potential curves which will aid in the subsequent discussion.

In order for the excitation to occur by a direct crossing of the entrance channel with exit channels dissociating to the observed nitrogen atomic states, the entrance-channel potential-energy curve must be more strongly bound than the exit-channel curve. The exit potentials will be Rydberg states of  $\text{Ar}-\text{N}^+$  while the entrance channel will be a Rydberg of  $\text{Ar}^+-\text{N}$ . The molecule  $\text{ArN}^+$  is isoelectronic with the molecule  $\text{ClN}$  which has two known bound states [13]  $^3\Sigma^-$  ( $D = 3.5 \text{ eV}$ ) and  $^1\Sigma^+$  ( $D = 4.0 \text{ eV}$ ), both of which correlate to a molecular orbital configuration of 2420 in the order  $\sigma \pi \pi^* \sigma^*$  [15]. For the molecule  $\text{ArN}^+$ , there are  $^3\Sigma^-$  states dissociating to both  $\text{Ar}(^1\text{S}) + \text{N}^+(^3\text{P})$  and to  $\text{Ar}^+(^2\text{P}) + \text{N}(^4\text{S})$ . One of these correlates to the bound 2420 configuration, the other to the less bound or unbound 2330 configuration. The open shell  $\text{Ar}^+-\text{N}$  is more like  $\text{ClN}$  than is  $\text{Ar}-\text{N}^+$  with its closed-shell  $\text{Ar}$ . Thus we would anticipate that the more strongly bound ionic state would be the one dissociating to the argon ion. If this be so, then the

entrance channel Rydberg states will indeed be more strongly bound than the exit channel states, and the crossings may be effected. The  $2s2p^4$   $^4P$  states will be Rydberg states of a highly excited nitrogen ion. Presumably, the curves for these states will be fairly repulsive.

Another possibility is that the primary exit channels are the  $2s^22p^23p^4D$  and  $2s^22p^23p^2S$  states at 11.75 and 11.60 eV respectively. Then the  $2s^22p^23s$   $^4P$  and  $^2P$  states would be excited via radiative cascade at 871 and 1350 nm respectively. These processes are slightly endoergic, but the excitation rate constants are similar to the excitation rate constants of endoergic xenon levels by metastable argon [3]. For this indirect excitation mechanism, the  $^4D$  states, would most likely be excited by Ar  $^3P_0$  and the excitation rate constant would be about seven times larger than reported to account for the difference in population of the two metastable species.

The third possibility is the ionic-intermediate curve crossing mechanism [16]. Calculations based upon this model have given an energy transfer cross section for the excitation of atomic oxygen by metastable argon which is in reasonable accord with experimental results [3,4]. However, it was not possible to show that the mechanism is unique to that system as other possibilities have been proposed [3]. The negative ion of nitrogen is unstable. However, the electron affinity of atomic nitrogen has been determined from resonances in electron scattering experiments, to be 0.07 eV [17]. In most instances crossing points may be simply calculated by considering only the ionic curve and assuming a flat neutral curve:  $r_c = e^2/\Delta E$ , where  $\Delta E$  represents the differences in energy between the asymptotic limits of  $Ar^+-N^-$  and the potential energy curve of interest. Application of this formula to the  $Ar-N^*$  system gives crossing points of 2.5 to 3.5 Å. These crossing points are sufficiently small, however, that it is no longer valid to ignore the repulsive part of either potential curve. The minimum of the ionic curve will be at about 2.5 Å by analogy with the  $Ar^+O^-$  systems [3], and the Lennard-Jones  $\sigma$ -values for the  $ArN^*$  potentials will be about 3.5–4 Å as in the case of the unbound  $ArO^*$  potential curves. Combining these two effects implies that the crossing will be on the repulsive wall of the  $ArN^*$  curves, but still at a distance of around 3 Å. The Hasted–Chong correlation [18] gives an interaction

matrix element of about 0.5 eV at this crossing distance. This will lead to total quenching probabilities [16] of about  $10^{-3}$  or less and total quenching cross sections less than  $1 \text{ Å}^2$ . However, the Hasted–Chong correlation is only good at best to a factor of two or three, so that even though the discussion above indicates that the ionic-intermediate mechanism is unlikely, the mechanism cannot be rejected conclusively. A factor of two in the interaction matrix element, will make more than an order of magnitude change in the overall quenching probability for the situation at hand. For the case of excitation of the  $2s^22p^23s^2P$  and  $^4P$  states by the ionic-intermediate mechanism, the exit channel crossing would involve a two-electron process. This does not in itself eliminate the mechanism, but it would reduce the probability of crossing at that point further from the probability calculated from the Landau–Zener formula [19,20]. Excitation of the  $2s2p^4$   $^4P$  state would not involve a two-electron process.

An obvious test of whether the excitation of the  $2s^22p^23s$   $^2P$  and  $^4P$  states of nitrogen is direct, or via radiative cascade would be to look for the cascade emission. To our knowledge, this has not been done.

Since large energy defects accompany the energy-transfer process, direct excitation implies that the electronically excited product nitrogen atoms will carry excess translational energy. Thus another test of the mechanism would be to measure the translational energy of the excited nitrogen atoms in the same way that it has been done in energy transfer studies between metastable argon and Kr [1], O [5], Cl [6] and Br [21] atoms. In these studies resonance absorption curves-of-growth were determined using the excited atoms from the energy transfer process as the emission source and a separate flow of thermal, ground-state atoms as the absorbers. The curves-of-growth are then compared to various models for the excited atoms' mean translational energy and their fluorescence line profile. Absorption of light from a translationally hot source by a given concentration of thermal absorbers is always less than absorption of light from thermal emitters. This translational energy probing has not been attempted. However, there is some evidence in the literature on this point. In their studies on the kinetics of metastable nitrogen atoms, Lin and Kaufman [22] noted that the absorbance of a given number density of nitrogen metastables (the

$2s^2 2p^3 \ ^2D$  and  $^2P$  states which absorb 149.3 and 174.3 nm respectively) was significantly less if they used a resonance lamp containing a trace of nitrogen in argon as opposed to a lamp using helium as the bath gas. This situation is similar to the one observed by Lin et al. [23] in their studies on the oscillator strength for absorption of the OI 130.4 nm resonance triplet. In that experiment, the apparent oscillator strength was a factor of two smaller using an argon resonance lamp. This discrepancy has been resolved successfully by us in studies on the excitation of atomic oxygen by metastable argon [4,5]. The abnormally low absorbance results from a poor match in line width between the translationally hot emitters, formed in an energy transfer process with metastable argon and the thermal absorber. Thus, the results of Lin and Kaufman suggest that the N  $2s^2 2p^2 3s \ ^2P$  states are excited directly, and not via radiative cascade.

Lin et al. [23] did not observe any difference between Ar or He resonance lamps in their absorption studies on ground state nitrogen atoms at 120 nm. This evidence does not necessarily imply an indirect excitation of the  $2s^2 2p^2 3s \ ^4P$  levels by metastable argon, however, as the metastable excitation of these levels is relatively weak and could be insignificant compared to electron excitation in the microwave lamps used by Lin et al.

The experimental evidence suggests that the excitation of the  $2s^2 2p^2 3s \ ^2P$  states of atomic nitrogen by metastable argon occurs via a direct curve crossing. Further experiments are necessary before definite conclusions may be made regarding the mechanism for excitation of the  $2s^2 2p^2 3s \ ^4P$  and  $2s 2p^4 \ ^4P$  states.

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