

# The Fundamentals of the 3914Å and 3371Å Emissions for N<sub>2</sub> and Air Plasma Diagnostics

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October 25, 1982

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><b>A review is made of the basic physics of emission at 3914A and 3371A. The excita-<br/>tion cross section, the quenching coefficient and other mechanisms that affect these<br/>emissions are discussed in detail.</b> |                                          |                                                                                              |

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# THE FUNDAMENTALS OF THE 3914Å AND 3371Å EMISSIONS FOR N<sub>2</sub> AND AIR PLASMA DIAGNOSTICS

## 1. INTRODUCTION

The interaction of an electron beam with gaseous elements generates a plasma and characteristic emission spectra which are unique to each element. The emission is over a wide range of the electromagnetic radiation, from extreme ultraviolet to long wave infrared, consisting of band, line, and continuum emissions. Such a spectrum provides important information for measuring various plasma parameters without perturbing the state of the plasma.

Emission from an air plasma, is a complex phenomena arising from a host of excitation mechanisms. These mechanisms are numerous and are reviewed briefly. However, the main emphasis will be on two molecular bands at 3371Å and 3914Å. Their excitation mechanisms and other processes that affect their intensities are discussed in detail. The basic understanding of these mechanisms provides the tools for the plasma modelling and its diagnostics.

## 2. EMISSION PROCESSES IN AIR

Emission from air falls into bands, lines and continuum emissions. The processes that lead to the band emissions are

### 1. Simultaneous Excitation and Ionization



Examples are: the First Negative and Meinel Bands of N<sub>2</sub><sup>+</sup>

### 2. Direct Excitation



Examples of this excitation are the First and Second Positive Band Systems of  $N_2$ .

### 3. Ground State Vibrational Excitation



Examples are infrared bands of NO and  $NO^+$ .

### 4. Atom - Atom Interchange or Chemiluminescence



Examples are infrared emissions from NO.

In the preceding equations  $K^*$  and  $M_2^*$  indicate excited atoms and molecules, respectively.  $M_2^*$  is a vibrationally excited molecule. It should be noted, however, that the electronically excited molecules in reactions 1 and 2 can be vibrationally excited as well.

The line emissions arise when an excited atom or atomic ion is generated and that the excitation energy or part of it is emitted as radiation. These excited states are produced by

1. Dissociative Excitation and Dissociative Ionization With  
Excitation



Examples for the first process is the emissions at 8447Å from the dissociation of O<sub>2</sub>. Emissions at 8210Å from N and 5003Å from N<sup>+</sup> due to dissociative and ionization excitation of N<sub>2</sub> illustrate emission processes in reactions 7 and 8, respectively.

2. Direct Excitation



3. Dissociative Recombination



#### 4. Radiative and Collisional Recombination



The continuum emission, on the other hand, results from free - free transitions of the thermal electrons in the field of the atomic and molecular ions as well as in the field of the atoms and molecules e. g.



#### 3. SELECTED BANDS FOR PLASMA DIAGNOSTICS

The nitrogen molecule,  $N_2$  and its ion,  $N_2^+$  have numerous bands which emit radiation in the ultraviolet, visible and infrared. Many of these bands can be used for diagnostics of  $N_2$  and air plasmas. However, two specific bands shown in Figure 1, the first negative and the second positive, have often been utilized for plasma diagnostics <sup>2-8</sup> and as a measure of electron and x-ray energy deposition in  $N_2$  and Air. Therefore, a review of the basic

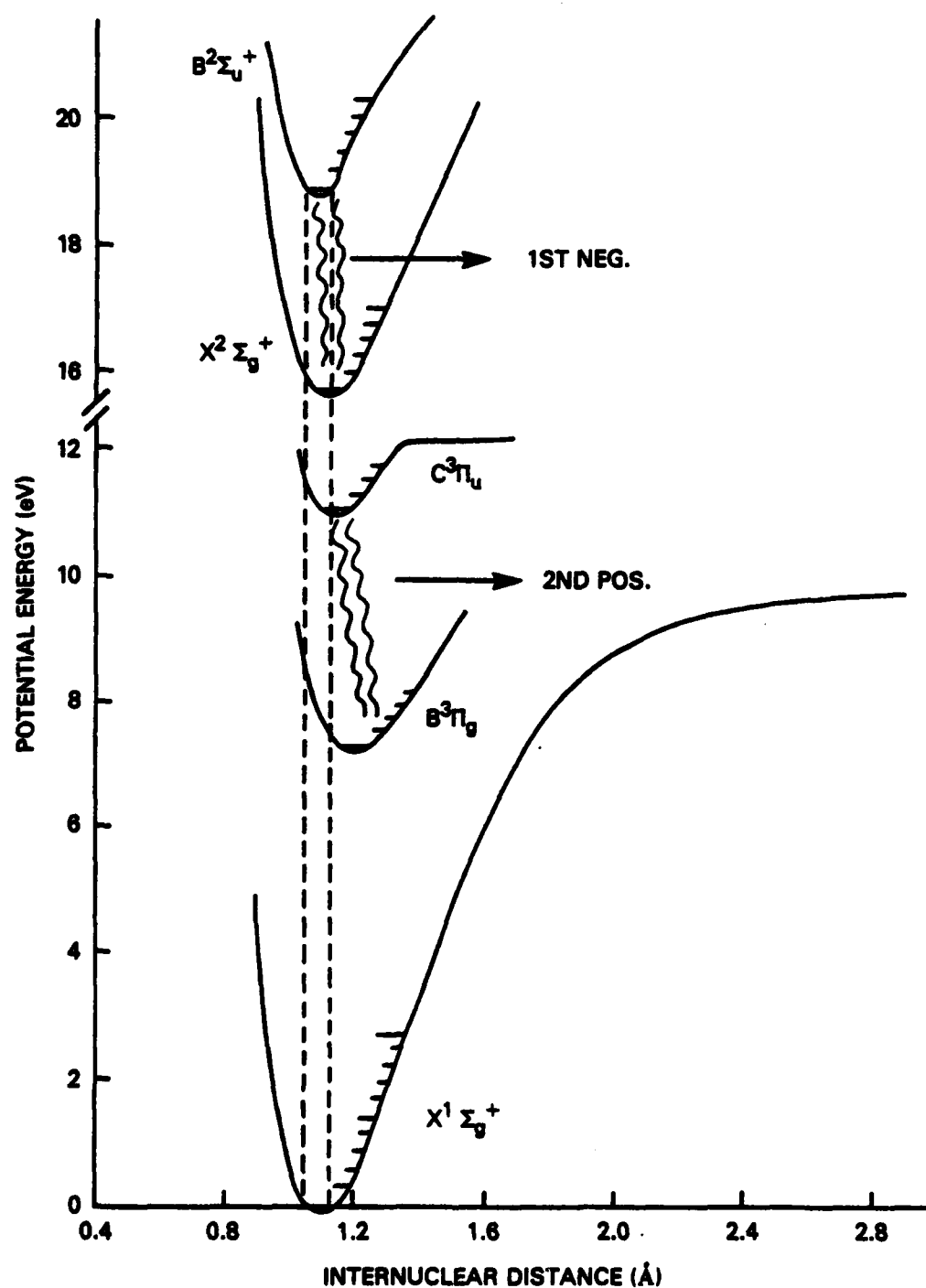


Fig. 1 — The partial potential energy diagram of  $N_2$  and  $N_2^+$ . Partial emissions in the second position and first negative bands are indicated.

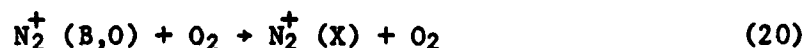
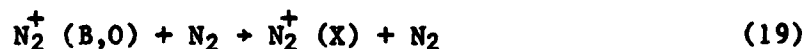
physical processes affecting their excitations and decays is in order.

### 3.1 THE (0,0) BAND OF THE FIRST NEGATIVE BANDS SYSTEM OF $N_2^+$

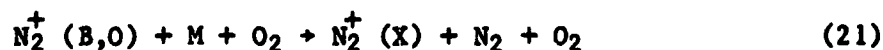
The first negative bands system of  $N_2^+$  corresponds to the  $B^2 \Sigma^+ (\bar{v}) \rightarrow X^2 \Sigma^+ (\bar{v}')$  transitions. The transition rates from various B-state vibrational levels have been calculated<sup>10,11</sup> and measured<sup>12,13</sup>. The transitions from  $\bar{v}=0$  have strong emissions at 3914Å, 4278Å and 4708Å which correspond to the (0,0), (0,1) and (0,2) bands, respectively. The lifetime of the B ( $\bar{v}=0$ ) state has been measured by many investigators and a weighted average<sup>14</sup> is  $62.5 \times 10^{-9}$  sec. using the Franck-Condon factor<sup>11</sup> for the (0,0) transition and the weighted average for the lifetime of the  $\bar{v}=0$  state, one obtains a rate of  $1.04 \times 10^7$  sec.<sup>-1</sup> for the (0,0) transition at 3914Å.

#### 3.1.1 THE QUENCHING OF THE $N_2^+ (B, \bar{v}=0)$

The  $N_2^+ (B, \bar{v}=0)$  state is quenched in collisions with  $N_2$  and  $O_2$  according to the following two body processes:



There is evidence<sup>15</sup> that the (B,0) state is also quenched by the following three body process



where M indicates  $N_2$  and/or  $O_2$ , i.e. the third body in this reaction must be  $O_2$ .

The rate coefficient for Reactions (19) and (20) have been measured by

Mitchell<sup>15</sup>, Brucklehurst and Downing<sup>16</sup>, Hirsh et al<sup>17</sup>, and Mackay and March<sup>18</sup>. The last measurement<sup>18</sup> which measures the quenching by N<sub>2</sub> only gives two different values which differ by 40% and thus are not included in Table 1 where the other measurements are summarized.

Table 1:  
The Quenching Coefficient for the  $B^2\Sigma(\bar{\nu}=0)$  State (in Torr<sup>-1</sup>)

|                | <u>Ref. 15</u>             | <u>Ref. 16</u> | <u>Ref. 17</u> |
|----------------|----------------------------|----------------|----------------|
| N <sub>2</sub> | 0.96 ± 0.09                | 0.85 ± 0.3     | 0.95 ± 0.05    |
| O <sub>2</sub> | 1.56 ± 0.15 <sup>(*)</sup> | 0.84 ± 0.3     | 1.5 ± 0.6      |

A weighted average for the quenching rate coefficients of the ( $\bar{\nu}=0$ ) state by N<sub>2</sub> and O<sub>2</sub> are  $4.6 \times 10^{-10}$  cm<sup>3</sup>/sec and  $6.5 \times 10^{-10}$  cm<sup>3</sup>/sec, respectively.

As for the three body quenching process given by Equation (21), Mitchell<sup>15</sup> gives a value of  $3.1 \times 10^{-29}$  cm<sup>3</sup>/sec for both O<sub>2</sub> and N<sub>2</sub>.

### 3.1.2 THE EXCITATION PROCESSES OF N<sub>2</sub><sup>+</sup>(B, $\bar{\nu}=0$ )

The N<sub>2</sub><sup>+</sup>(B) state is excited by the direct ionization and excitation process (See Eq. 1) whenever the incident electron has an energy above the threshold energy for the process (>18.8eV). Since the (0,0) transition at 3914Å is a well known auroral emission<sup>19</sup>, it has attracted considerable interest and its cross section has been measured by many investigators. The emission cross section at 3914Å, for the direct excitation and ionization of N<sub>2</sub>, is shown in Figure 2, based mainly on the data of reference 27.

(\*) Data for O<sub>2</sub> was obtained from air and N<sub>2</sub> data

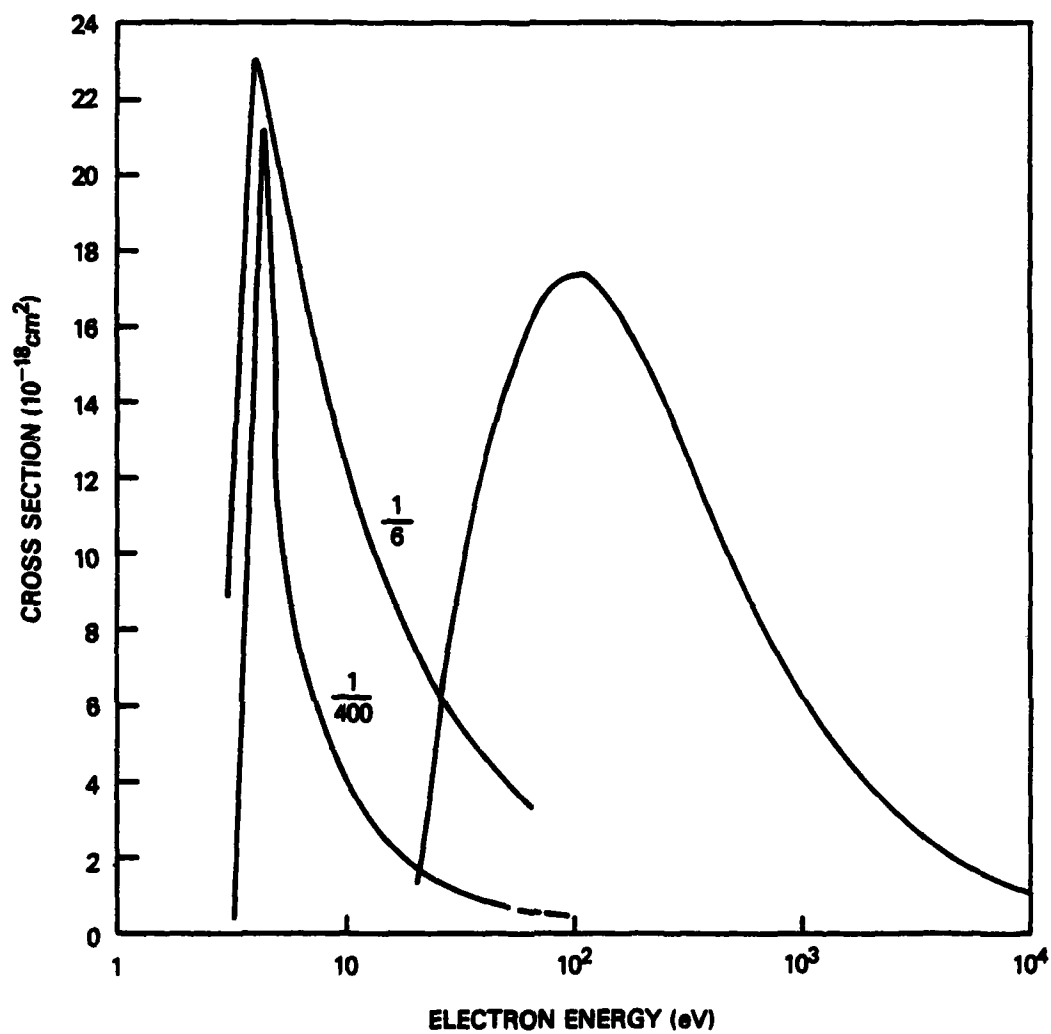


Fig. 2 — The 3914Å emission cross section due to electron impact with  $\text{N}_2$  (curve 1) and  $\text{N}_2^+$  (curves  $\frac{1}{6}$  and  $\frac{1}{400}$ ). The last two curves, from reference 28 and 29, are reduced for comparison by factors of 6 and 400, respectively.

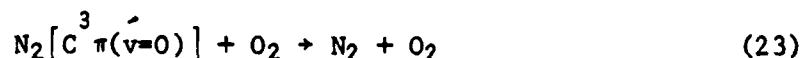
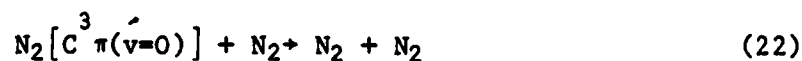
However, the  $B^2\Sigma(\bar{\nu})$  state can be excited by electron impact from the ground state of the nitrogen ion,  $N_2^+(x,\bar{\nu})$ , where the excitation threshold is .16 eV. The cross section for this process has been measured by Lee and Ton<sup>28</sup> and by Grandall, et al<sup>29</sup>. These two measurements are also shown in Figure 2, one of these<sup>23</sup> may be too large as indicated by McLean, et al<sup>30</sup>.

#### THE (0,0) BAND OF THE SECOND POSITIVE BANDS SYSTEM OF $N_2$

The second positive system of  $N_2$  corresponds to the  $C^3\Pi(\bar{\nu}) \rightarrow B^3\Pi(\bar{\nu})$  transitions. The life times of the various  $C^3\Pi$  vibrational levels have been measured<sup>12,13</sup> and calculated<sup>10,11</sup>. A weighted average<sup>14</sup> of many measurements gives a life time of 36.6 nsec for the  $\bar{\nu}=0$  state. The transition's from the  $(\bar{\nu}=0)$  state have strong emissions at 3371Å, 3577Å and 3805Å which correspond to the (0,0), (0,1) and (0,2) bands, respectively. Using the Franck-Condon Factors<sup>31</sup> for the (0,0) transitions and the life time of the (0) state one obtains a transition rate of  $1.22 \times 10^7 \text{ sec}^{-1}$  for the (0,0) transitions at 3371Å.

#### 1 THE QUENCHING OF $N_2(C,\bar{\nu}=0)$

The  $C^3\Pi(\bar{\nu}=0)$  state is quenched in collisions with  $N_2$  and  $O_2$  according to the following two processes.



Rate coefficients for these reactions have been measured in nitrogen and by Mitchell<sup>15</sup>, Millett, et al<sup>32</sup>, Albugues, et al<sup>33</sup> and Brocklehurst and Ing<sup>16</sup>. These measured data are summarized in Table II.

Table II:  
Quenching Coefficient for  $C^3\pi(\bar{\nu}=0)$  in Units of  $10^{-11}\text{cm}^3/\text{sec}$ .

|       | <u>Ref. 15</u>    | <u>Ref. 16</u>     | <u>Ref. 32</u>    | <u>Ref. 33</u>     |
|-------|-------------------|--------------------|-------------------|--------------------|
| $N_2$ | $(1.12 \pm .143)$ | $(1.17 \pm 0.137)$ | $(1.15 \pm .062)$ | $(1.15 \pm 0.062)$ |
| $O_2$ | $31.2 \pm 0.96$   | -                  | $(29 \pm 1.8)$    | 27.9               |

A recommended value for quenching of  $C^3\pi(\bar{\nu}=0)$  is  $1.12 \times 10^{-11} \text{ cm}^3/\text{sec}$ . As for quenching by  $O_2$  we recommend a value of  $2.9 \times 10^{-10} \text{ cm}^3/\text{sec}$  after lowering the values of Ref. 15 by 1.2 and raising the values of Ref. 32 and 33 by 1.2 because of the different life-times utilized in these references compared to an average life time of 36.5 nsec.

### 3.2.2 THE EXCITATION PROCESSES OF $N_2(C, \bar{\nu}=0)$

The upper level of the second positive band system,  $C^3\pi$ , is excited by electron impact from the ground state of  $N_2$ . The cross section for the excitation of the C-state has been measured and calculated by numerous investigators, see Ref. 34 for details. Since the excitation is a transition from a singlet,  $^1\Sigma$ , to a triplet,  $^3\pi$ , state, it is sharply peaked near the excitation threshold and varies as  $\sim E^{-3}$  where E is the energy of the incident electron. In Figure 3 we show the emission cross section for the (0,0) transition at 3371Å as measured by Imami and Borst<sup>35</sup>.

The excitation threshold for the  $C^3\pi(\bar{\nu}=0)$  is  $\sim 11\text{eV}$  and in a plasma it is generally excited by the secondary and the plasma electrons which also excite other triplet status of  $N_2$ , e.g.  $A^3\Sigma$  and  $B^3\pi$  states. Therefore, the effects of excitations from the  $A + B + C$  state should be investigated and may become appreciable, depending on the state of the plasma. Furthermore, collisions with excited states i.e.  $N_2(C)$  with  $N_2(C)$ ,  $N_2(B)$  and  $N_2(A)$  may

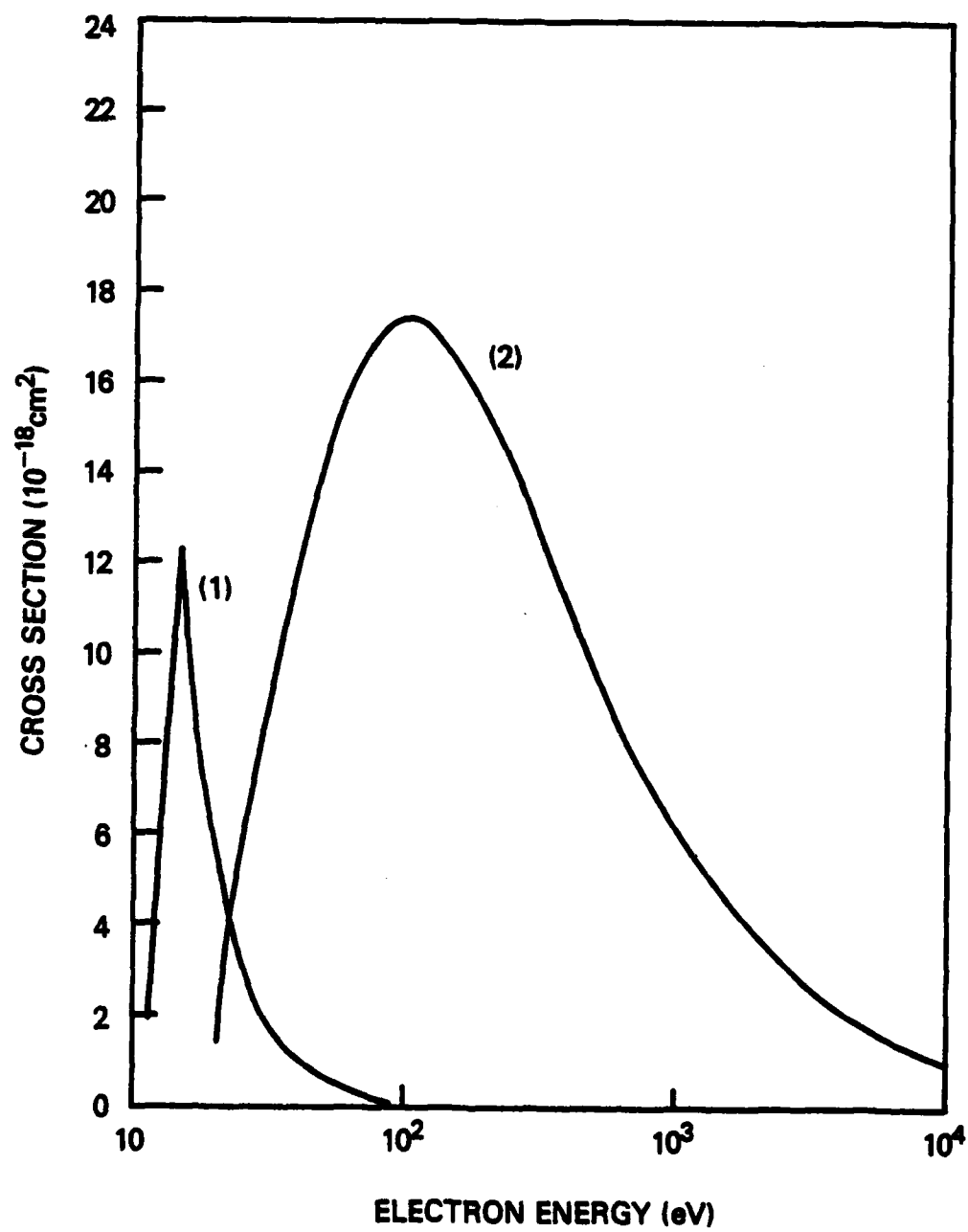


Fig. 3 — The emission cross sections of 3371Å (curve 1) and 3914Å (curve 2)

deplete the C-state as do the superelastic collisions with low energy electrons. In a cold plasma and at pressures where  $N_4^+$  predominates, the dissociative recombination of  $N_4^+$  may lead to the population of the C-state. R. Hill<sup>36</sup> has reported that 3% of this dissociative recombination results in the population of the C ( $\dot{v}=0$ ) .

In terms of what other processes may affect the emission at 3371Å, it should be noted that this band is a well known laser. It was first discovered by Heard (1963) and has been investigated thoroughly in pure nitrogen, where excitation occurs by electron beams<sup>38</sup> and in electric discharges with a fast current rise time<sup>39,40</sup>. Lasing action has also been observed in air<sup>41,42</sup> and under atmospheric conditions. Since this laser is a superradiant, stimulated emission also affects the population density of the  $\dot{v}=0$  state and hence its emission.

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