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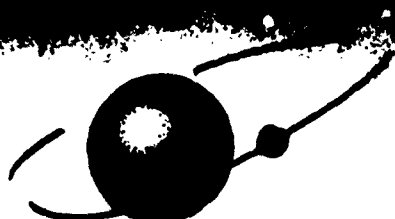
No. 66

THE FORMATION OF IONS IN THE UPPER ATMOSPHERE

Robert E. Huffman

November 1961

GRD



GEOPHYSICS RESEARCH DIRECTORATE  
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES  
OFFICE OF AEROSPACE RESEARCH  
UNITED STATES AIR FORCE  
BEDFORD, MASSACHUSETTS

**AFCRL 851**

**GRD Research Notes**

**No. 66**

**THE FORMATION OF IONS IN THE UPPER ATMOSPHERE**

**Robert E. Huffman**

**November 1961**

**Project 7635**

**Task 76367**

**Photochemistry Laboratory  
GEOPHYSICS RESEARCH DIRECTORATE  
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES  
OFFICE OF AEROSPACE RESEARCH  
UNITED STATES AIR FORCE  
Bedford, Massachusetts**

## **Foreword**

In March 1961, W. W. Hunt and R. E. Huffman presented an invited paper, "The Formation and Reactions of Ions in the Upper Atmosphere," at the National Meeting of the American Chemical Society in St. Louis. This note reviews the literature studies of ion formation and electron attachment processes in the upper atmosphere made in preparation of the paper. A separate report covering the reactions of ions in the upper atmosphere is to be published by W. W. Hunt.

It is hoped that this note accurately describes the present state of knowledge concerning this important area of GRD in-house and contractual research.

## **Abstract**

The present state of our knowledge concerning the formation of positive and negative ions in the earth's normal ionosphere will be reviewed. The main process by which positive ions and electrons are formed in the ionosphere is photoionization of neutral constituents by solar vacuum ultraviolet radiation. Negative ions are formed primarily by direct attachment of electrons to certain neutral constituents. Existing values of the cross sections and rate coefficients of these processes will be presented and gaps in the present knowledge will be discussed.

## **Contents**

|                             |            |
|-----------------------------|------------|
| <b>Foreword</b>             | <b>iii</b> |
| <b>Abstract</b>             | <b>v</b>   |
| <b>Introduction</b>         | <b>1</b>   |
| <b>1. Formation of Ions</b> | <b>5</b>   |
| <b>Photoionization</b>      | <b>5</b>   |
| <b>Electron Attachment</b>  | <b>15</b>  |
| <b>2. Conclusions</b>       | <b>22</b>  |
| <b>References</b>           | <b>24</b>  |

## Illustrations

| Figure |                                                                                                                                                                                                       | Page |
|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 1      | Electron densities in the ionosphere                                                                                                                                                                  | 3    |
| 2      | Distribution of the major positive ions above Fort Churchill, Canada (reproduced, with permission, from <u>J. Geophysical Research</u> )                                                              | 4    |
| 3      | Total absorption cross section (solid curve) and photoionization cross section (dots) of nitric oxide in the region 1100 to 1350 Å (reproduced, with permission, from <u>Advances in Geophysics</u> ) | 10   |
| 4      | Absorption cross section of NO in the region 200 to 1000 Å (reproduced, with permission, from <u>Advances in Geophysics</u> )                                                                         | 11   |
| 5      | Absorption cross sections of N <sub>2</sub> in the region 150 to 850 Å (reproduced, with permission, from <u>Advances in Geophysics</u> )                                                             | 12   |
| 6      | Oxygen total absorption and photoionization cross section from 100 to 1050 Å                                                                                                                          | 13   |
| 7      | Absorption cross section curve for atomic oxygen, nitrogen, and carbon (reproduced, with permission from <u>Monthly Not. Roy. Astronom. Soc.</u> )                                                    | 16   |
| 8      | Absorption coefficient (curve I) and ionization coefficient (curve II) of NO <sub>2</sub> in the region 1080-1300 Å. Rydberg bands and ionization potentials are indicated.                           | 17   |
| 9      | O <sub>2</sub> <sup>+</sup> and O <sup>+</sup> yield per incident photon from photoionization of O <sub>2</sub>                                                                                       | 18   |
| 10     | N <sub>2</sub> <sup>+</sup> and N <sup>+</sup> yields per incident photon from photoionization of N <sub>2</sub> . Solid curve obtained with Air-He, dashed curve with argon in the light source.     | 19   |



## **Illustrations (Cont)**

| <b>Figure</b> |                                                 | <b>Page</b> |
|---------------|-------------------------------------------------|-------------|
| 11            | Electron affinities of atmospheric constituents | 21          |
| 12            | Electron attachment process                     | 21          |

## Tables

| Table |                                                             | Page |
|-------|-------------------------------------------------------------|------|
| 1     | Neutral and Electron Concentrations in the Upper Atmosphere | 2    |
| 2     | Ionization Potentials of Atmospheric Atoms and Molecules    | 6    |
| 3     | Photon Absorption Processes                                 | 8    |

# THE FORMATION OF IONS IN THE UPPER ATMOSPHERE

## Introduction

The result of interpreting field observations of atmospheric phenomena in the light of laboratory observations is a recognition of the main processes occurring in the charged gas regions of the upper atmosphere. The recognition of the important reactions enables future laboratory effort to be channeled in the most fruitful directions. This review covers information available in the literature concerning laboratory investigation of the processes which are considered most important, and indicates the areas in which the greatest priority for additional research exists. Wherever it is possible, presently accepted rate coefficients or cross sections will be given. However, it must be emphasized that this general area of investigation is receiving much attention, primarily because of space science implications, and that revised numbers and concepts may be expected at frequent intervals. Since this review will concern only reactions in which charged species are created, many important atmospheric chemical reactions among neutral atoms and molecules will not be discussed here.

After a brief description of the general parameters of the upper atmosphere and the ionosphere, the processes yielding positive and negative ions in the ionosphere will be described. These processes are photoionization by solar vacuum ultraviolet radiation, yielding positive ions and electrons, and attachment of electrons to neutral atoms and molecules, producing negative ions. Areas of greatest priority for further effort will be indicated.

This review is concerned with the normal ionosphere formed in the altitude range from 50 to 500 kilometers. Special effects connected with the auroral zones and solar storms are not of concern here. The main neutral chemical species over this region include nitrogen and oxygen molecules ( $N_2$  and  $O_2$ ) and nitrogen and oxygen atoms (N and O). The energies of neutral and ionized atoms, molecules, and electrons are mainly the thermal values at the altitude in question, and, therefore, only this energy range is considered here. The temperature varies from about  $200^\circ K$  to an estimated value over  $1000^\circ K$ ; the pressure varies from 1 mm to  $10^{-8}$  mm Hg. The average day and

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night values of the electron concentration are shown in Figure 1, taken from the Handbook of Geophysics.<sup>18</sup> In all cases the electron concentration is smaller than the ion concentration, as approximate values in Table 1 illustrate.

Table 1 illustrate.

Table 1. Neutral and Electron Concentrations in the Upper Atmosphere

| Altitude | $\log_{10}$ (neutrals/cm <sup>3</sup> ) | $\log_{10}$ (electrons/cm <sup>3</sup> ) |
|----------|-----------------------------------------|------------------------------------------|
| 100      | 12.8                                    | 4.2                                      |
| 200      | 9.9                                     | 5.8                                      |
| 500      | 7.8                                     | 6.1                                      |

The electron concentration decreases considerably at night at the lower altitudes, but quite significant equilibrium concentration levels are maintained in the F region. The atmospheric neutral densities in this altitude region are subject to considerable revision at the moment, especially at the higher altitudes.

The composition of the ionosphere has been measured by Johnson, Heppner, Holmes, and Meadows with rocket-borne radio frequency mass spectrometers.<sup>20</sup> The results of three flights are shown in Figure 2, where the percentage of each specie as a function of altitude is recorded. It is apparent that the most abundant positive ions are  $\text{NO}^+$ ,  $\text{O}_2^+$ , and  $\text{O}^+$ . Other flights by this group examined the negative ion species and found, surprisingly, that almost the entire negative ion spectrum was obtained at mass 46, which has been interpreted to be  $\text{NO}_2^-$ , the negative ion of nitrogen dioxide. More complete information concerning theories, techniques, and older data on the ionosphere may be found in the book by Mitra<sup>22</sup>. The physical model for ionospheric "layer" formation, first proposed by Chapman<sup>10</sup> for the related problems of the atomic oxygen and ozone layers, is also summarized in Mitra.

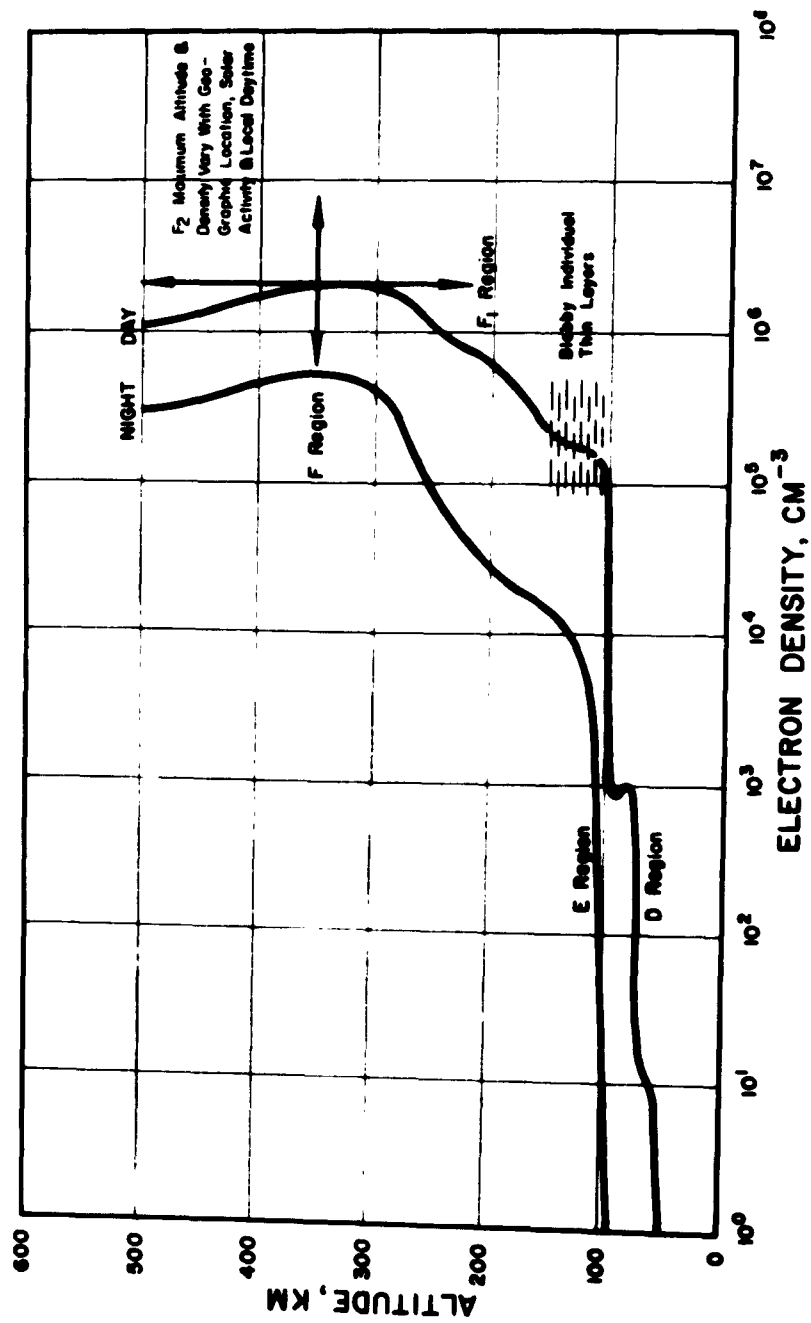


Figure 1. Electron densities in the ionosphere

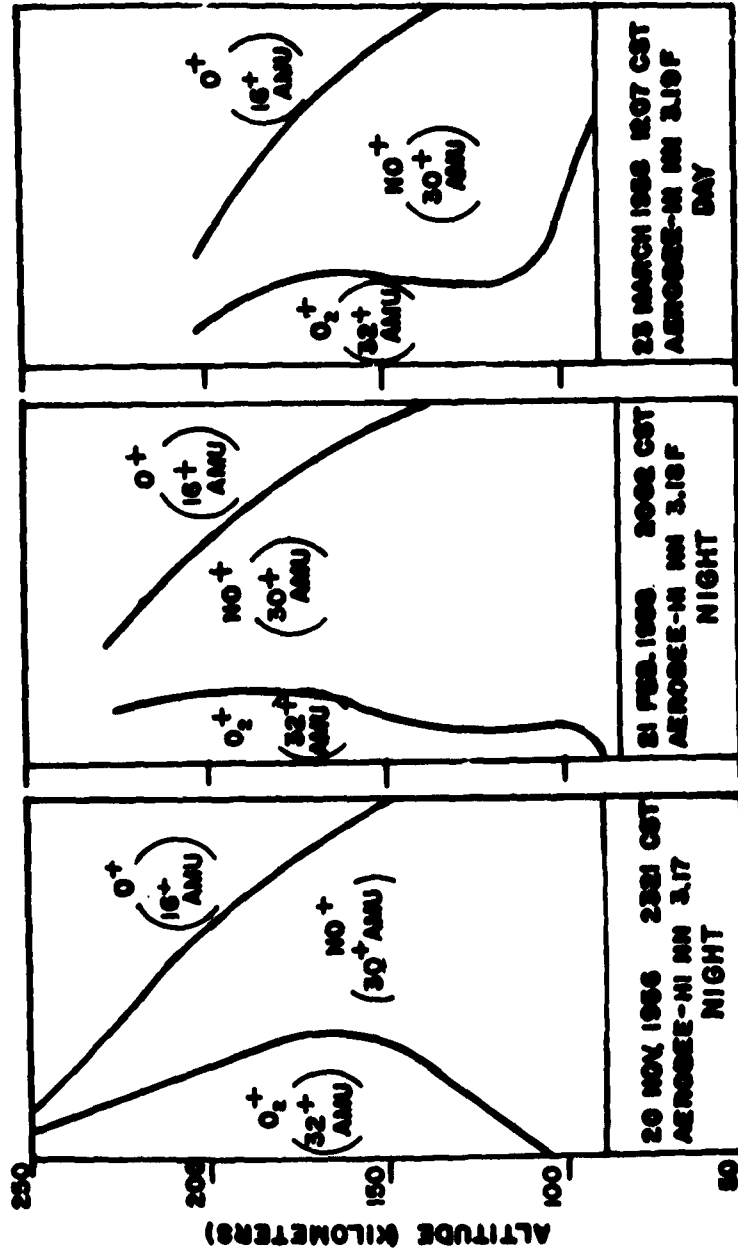


Figure 2. Distribution of the major positive ions above Fort Churchill, Canada (reproduced, with permission, from J. Geophysical Research)

## 1. Formation of Ions

### PHOTOIONIZATION

Photoionization of the neutral atoms and molecules of the atmosphere to yield positive ions and electrons is the most important process by which the normal ionosphere is maintained. Although auroral and solar storm effects are produced in part by other means, solar electromagnetic radiation in the vacuum ultraviolet portion of the spectrum is primarily responsible for the ionization processes, as discussed by Bates<sup>4</sup>, Watanabe<sup>32</sup>, and Mitra<sup>22</sup>. The present discussion will therefore be restricted to wavelengths between about 1400 and 100 Å (9 to 120 electron volts), where the energy of the photon is sufficient to ionize the atmospheric constituents and there is known to be sufficient solar radiation flux to cause measurable effects.

The first ionization potentials of atmospheric atoms and molecules are listed in Table 2. This energy must be supplied by a photon to separate an electron from the neutral atom or molecule. The methods of obtaining the ionization potential are beyond the scope of this review.<sup>32</sup> It should be pointed out that the major atmospheric atoms and molecules, N<sub>2</sub>, O<sub>2</sub>, O and N, require photon wavelengths below 1050 Å (11.8 ev). Nitric oxide (NO) requires wavelengths below 1340 Å (9.25 ev) for photoionization, making it the easiest atmospheric diatomic molecule to ionize. Therefore, its large abundance as a positive ion, compared to its low abundance as a neutral specie, is made plausible.

As solar radiation passes through the earth's atmosphere, all wavelengths below about 3000 Å are removed by absorption processes of various types. The ionization processes of most importance at any given altitude may be determined from the absorption laws by use of the solar flux incident at this altitude, the particle concentration of the specie of interest, and the photoionization cross section. The radiation flux and the particle concentration must be determined in the atmosphere itself, while the photoionization cross section is best determined in the laboratory. The solar flux at an

Table 2. Ionization Potentials of Atmospheric Atoms and Molecules

| Specie          | Wavelength (A) | Energy (ev) | Reference                        |
|-----------------|----------------|-------------|----------------------------------|
| O               | 910.7          | 13.614      | Moore, N. B. S. <sup>23</sup>    |
| N               | 852.7          | 14.54       | Moore, N. B. S. <sup>23</sup>    |
| N <sub>2</sub>  | 795.7          | 15.580      | Worley and Jenkins <sup>36</sup> |
| O <sub>2</sub>  | 1026.7         | 12.075      | Watanabe, et al. <sup>31</sup>   |
| NO              | 1340.3         | 9.25        | Watanabe, et al. <sup>30</sup>   |
| NO <sub>2</sub> | 1270.3         | 9.76        | Watanabe, et al. <sup>24</sup>   |

altitude within the sensible atmosphere is dependent upon all of the absorption processes occurring above this altitude. Therefore, the solar flux at a given altitude and wavelength is a function of the solar flux incident upon the earth's atmosphere, the number of molecules from the "top" of the atmosphere to the given altitude, and the total absorption cross section for each atmospheric specie of interest. Laboratory measurements, therefore, are most concerned with the total absorption and the photoionization cross sections.

The total absorption cross section is defined by the expression:

$$I(\lambda) = I_0(\lambda) \exp(-\sigma(\lambda) n_0 l)$$

where  $I_0(\lambda)$  and  $I(\lambda)$  are the incident and transmitted radiation intensities,  $\sigma(\lambda)$  is the total absorption cross section,  $n_0$  is the number of gas molecules per cm<sup>3</sup> at standard conditions (Locksmit's number), and  $l$  is the radiation path length reduced to the equivalent distance at standard conditions of temperature and pressure. The ionization cross section is defined by the relation:

$$\sigma_i(\lambda) = f(\lambda) \sigma(\lambda)$$

where  $f(\lambda)$  is the ionization efficiency, or the fraction of absorbed photons which produce ionized particles of any type, and  $\sigma_i(\lambda)$  is the ionization cross section. Other cross sections may, of course, be defined for processes



leading to specific ionized fragments or excited states.

As intimated in the last paragraph, photons of the typical energies considered here may react through a number of different processes following absorption. The most important possibilities for the present purposes are summarized in Table 3, using the oxygen molecule as an example. All of these processes except dissociation, ion-pair formation, and dissociative ionization, are possible with atomic species as well. Excitation processes (a.) occur at specific wavelengths, as seen in the typical molecular vibration-rotation bands and atomic lines. Preionization (g.) occurs in absorption bands or lines which are abnormally broadened. All of the other dissociation and ionization processes [(b.), through (f.)] yield absorption continua which occur over wide wavelength intervals. Ionization continua typically rise, as a step function at the ionization potential, to a plateau value which decreases slowly at still lower wavelengths. More typically, however, the threshold energies of other electronic configurations are exceeded, and their contributions are superimposed upon the first ionization continuum. In addition, other lines or bands extrapolating to higher ionization potentials, and in some cases broadened by preionization, are superimposed on the ionization continua. Although values for individual atoms and molecules vary widely, the absorption processes are listed in Table 3 in order of the photon energy typically required, with the least energetic processes being listed first. The experimental and theoretical techniques used to understand the absorption processes occurring in atmospheric gases are beyond the scope of this review<sup>32, 34</sup>.

In the following paragraphs, photoionization and total absorption cross sections for atmospheric gases are summarized. In order to present a useful treatment of the data, the wavelengths of interest are limited to values between the first ionization potential and the lowest wavelengths which have been investigated. In addition, data is presented only for nitric oxide (NO), nitrogen molecule ( $N_2$ ), oxygen molecule ( $O_2$ ), oxygen atom (O), nitrogen atom (N), and nitrogen dioxide ( $NO_2$ ), although many other atmospheric gases occurring in minor amounts have been studied. The values of the photoionization and/or the total absorption cross sections are given as a function of wavelength, so that the present status of the available data and

Table 3. Photon Absorption Processes

|                                  |                                  |
|----------------------------------|----------------------------------|
| (a.) Excitation                  | $O_2 + h\nu = O_2^*$             |
| (b.) Dissociation                | $O_2 + h\nu = O + O$             |
| (c.) Ionization (ground state)   | $O_2 + h\nu = O_2^+ + e$         |
| (d.) Ionization (excited states) | $O_2 + h\nu = O_2^{*+} + e$      |
| (e.) Ion pair formation          | $O_2 + h\nu = O^+ + O^-$         |
| (f.) Dissociative ionization     | $O_2 + h\nu = O^+ + O + e$       |
| (g.) Preionization               | $O_2 + h\nu = O_2^* = O_2^+ + e$ |

the approximate values of these cross sections can be evaluated. It must be mentioned that more weight has been given to photoelectric than to photographic data, since the latter technique is difficult even with the most painstaking attention to detail. These processes have been reviewed by Watanabe,<sup>32</sup> Weissler<sup>34</sup>, Inn<sup>19</sup>, and Ditchburn<sup>13</sup>.

Nitric oxide (NO) ionization and absorption measurements are shown in Figure 3, which contains the results of ionization cross-section measurements by Watanabe<sup>30</sup> and absorption cross-section measurements by Marmo<sup>21</sup>. Although present in extremely small concentrations in the atmosphere, this molecule has been very carefully studied, since it may be ionized by hydrogen Lyman alpha solar radiation and thereby form the D layer of the ionosphere at about 90 km altitude. The great amount of data resulting from its low ionization potential makes it a useful example of the detailed study which should be given to all atmospheric species. The ionization cross section rises sharply at the ionization potential and increases in a series of steps which have been interpreted as vibrational structure of the nitric oxide ion. Below wavelengths of about 1220 Å, the ionization and absorption cross sections have about the same value, indicating that the ionization efficiency is near unity. With other molecules this may not be the case. The situation below 1000 Å is shown in Figure 4, which shows the work of Granier and Astoin<sup>16</sup>, and Sun and Weissler<sup>26</sup>. It can be observed that the cross sections

are not as well established in this region and more work is necessary. Rough agreement of the cross section and the general shape in overlapping wavelength regions indicate the data give satisfactory preliminary information.

Nitrogen ( $N_2$ ) cross sections are shown in Figure 5, which contains data of Astoin and Granier<sup>2</sup>; Curtis<sup>11</sup>; Weissler, Lee, and Mohr<sup>33</sup>; and Wainfan, Walker, and Weissler<sup>28</sup>. Nitrogen is quite transparent to wavelengths above about 1000 Å, but at lower wavelengths it absorbs in strong bands and a strong ionization continuum beginning near 800 Å. The curves shown were obtained as the envelope of the lowest absorption cross sections found at a number of discrete atomic lines produced by the light source used. Absorption data obtained with a wavelength continuous (continuum) light source will be needed to resolve the detailed shape of the nitrogen continuum. The absorption data available indicate a cross section of about  $1$  or  $2 \times 10^{-17}$  cm<sup>2</sup> in the plateau above the first ionization potential.

Oxygen ( $O_2$ ) absorption and ionization cross-section data below the wavelength of the first ionization potential is shown in Figure 6, which is a plot of averaged results given by Watanabe<sup>29</sup> from data of Aboud, Curtis, Mercure, and Rense<sup>1</sup>; Watanabe and Marmo<sup>31</sup>; and Wainfan, Walker, and Weissler<sup>28</sup>. Oxygen absorbs strongly between 1000 and 2000 Å and has been studied many times in this region; however, below 860 Å, where the hydrogen many-lined spectrum ends, the data is quite sparse. The oxygen ionization continuum, beginning at 1027 Å, rises more slowly than the nitrogen continuum. It rapidly becomes larger below 800 Å and is more intense than the nitrogen continuum at its plateau level, rising to cross-section values of about  $3 \times 10^{-17}$  cm<sup>2</sup>. Over the 800-400 Å wavelength region, where the strongest absorption occurs, detailed information showing the structure of the continuum is not available.

Atomic oxygen (O) and atomic nitrogen (N) cross-section measurements are much more difficult because these species are not stable chemically, but rapidly recombine at atmospheric pressures to form the molecular gases  $O_2$  and  $N_2$ . However, the data are quite important for upper atmosphere problems, because above some altitude near 110 km the atmosphere consists

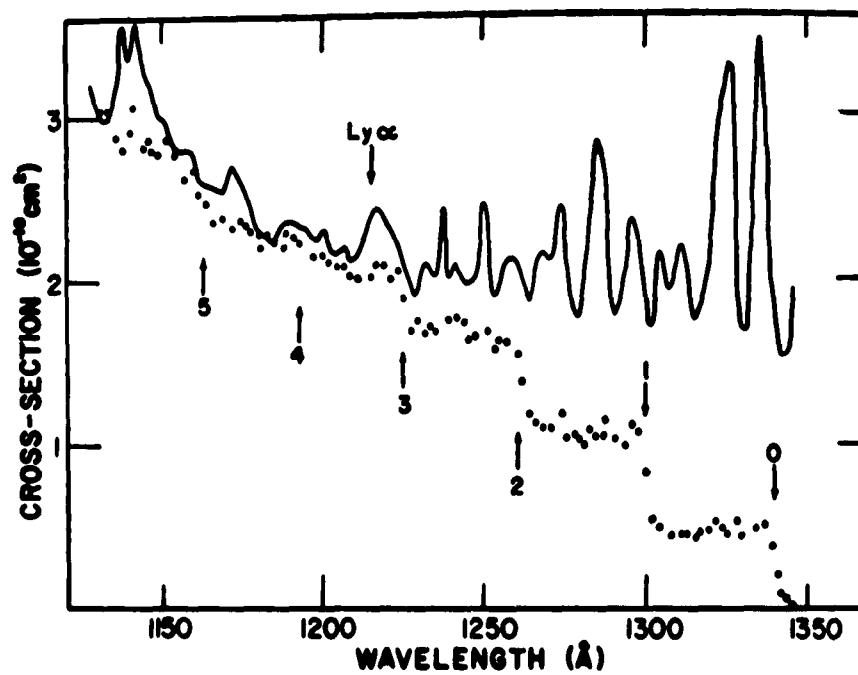


Figure 3. Total absorption cross section (solid curve) and photoionization cross section (dots) nitric oxide in the region 1100 to 1350 Å (reproduced, with permission, from Advances in Geophysics)

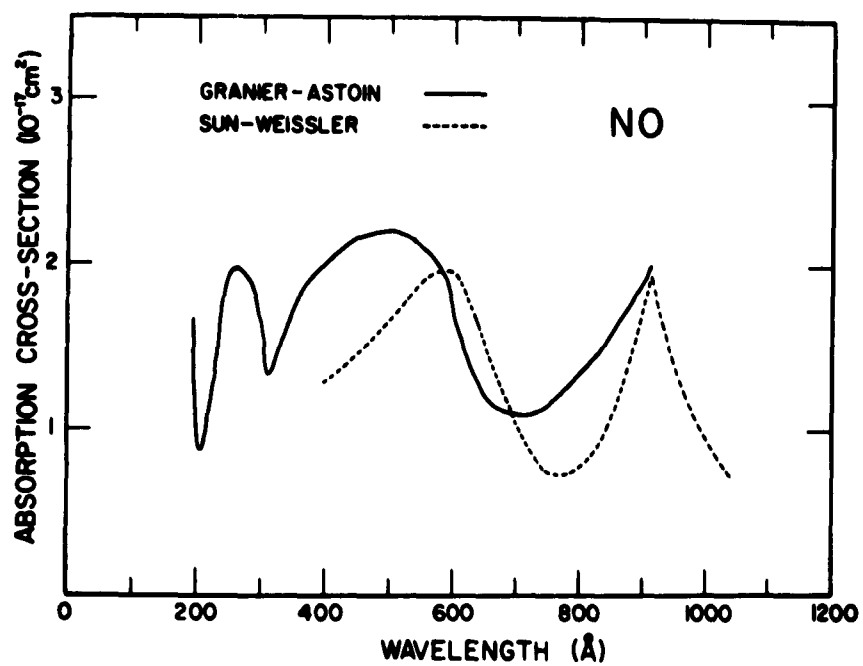


Figure 4. Absorption cross section of NO in the region 200 to 1000  $\text{\AA}$   
(reproduced, with permission, from Advances in Geophysics)

K. WATANABE

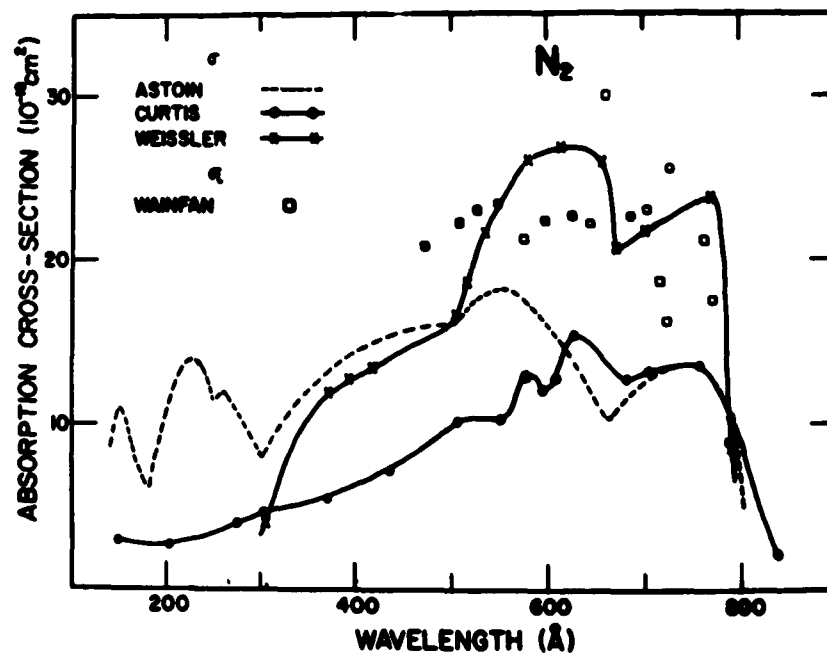


Figure 5. Absorption cross sections of  $N_2$  in the region 150 to 805  $\text{\AA}$   
(reproduced, with permission, from Advances in Geophysics)

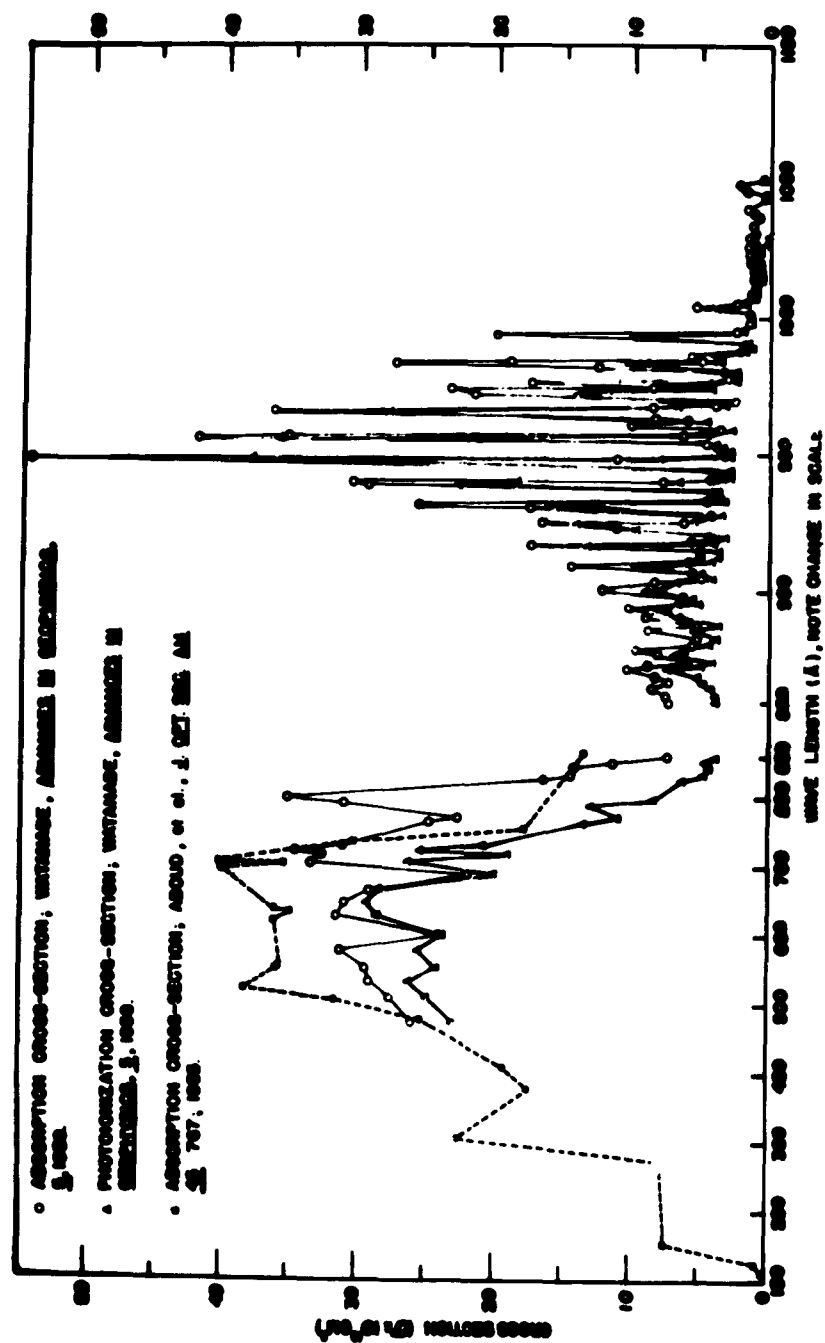


Figure 6. Oxygen total absorption and photoionization cross section from 100 to 1050 Å

largely of a mixture of atomic oxygen and molecular nitrogen. This is the result of dissociation of the oxygen molecule into oxygen atoms by absorption of solar vacuum ultraviolet radiation in the Schuman-Runge continuum centered near  $1450 \text{ \AA}$ . At higher altitudes, it is believed that there are appreciable amounts of atomic nitrogen as well.

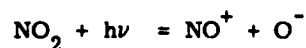
There have been several quantum mechanical calculations of the total absorption cross sections for these atoms. Figure 7 illustrates the results of Bates and Seaton<sup>3</sup> on atomic oxygen and atomic nitrogen. The atomic oxygen absorption cross section is initially much lower than the atomic nitrogen cross section, but the atomic oxygen curve eventually becomes larger when higher excited-state thresholds are crossed. Other calculations by Dalgarno and Packinson<sup>12</sup> cover a somewhat higher energy range. The calculations do not provide information on details of the absorption curve, such as pre-ionized absorption lines, which may be important in the upper atmosphere.

An experimental study of the atomic nitrogen absorption cross section by Ehler and Weissler<sup>14</sup>, using nitrogen atoms created in a Phillips ionization gauge, has given results close to the theoretical values.

To the best of our knowledge there have been no experimental measurements of absorption cross sections for oxygen atoms. Therefore, it would appear that additional experimental work in this area would be highly desirable, so that more reliable estimates of the importance of photoionization of atomic species in the atmosphere could be made.

Nitrogen dioxide ( $\text{NO}_2$ ) absorption and ionization cross sections recently determined by Watanabe and associates<sup>24</sup> are shown in Figure 8. The value of the ionization potential is much lower than previously thought. In this case no vibrational structure due to nitrogen dioxide ion can be observed, and the ionization and total cross sections are quite different at important wavelengths, such as the Lyman alpha hydrogen atomic line ( $1215.7 \text{ \AA}$ ). The break in the curve at  $10.83 \text{ eV}$  is thought to be due to the following ion-pair formation process:



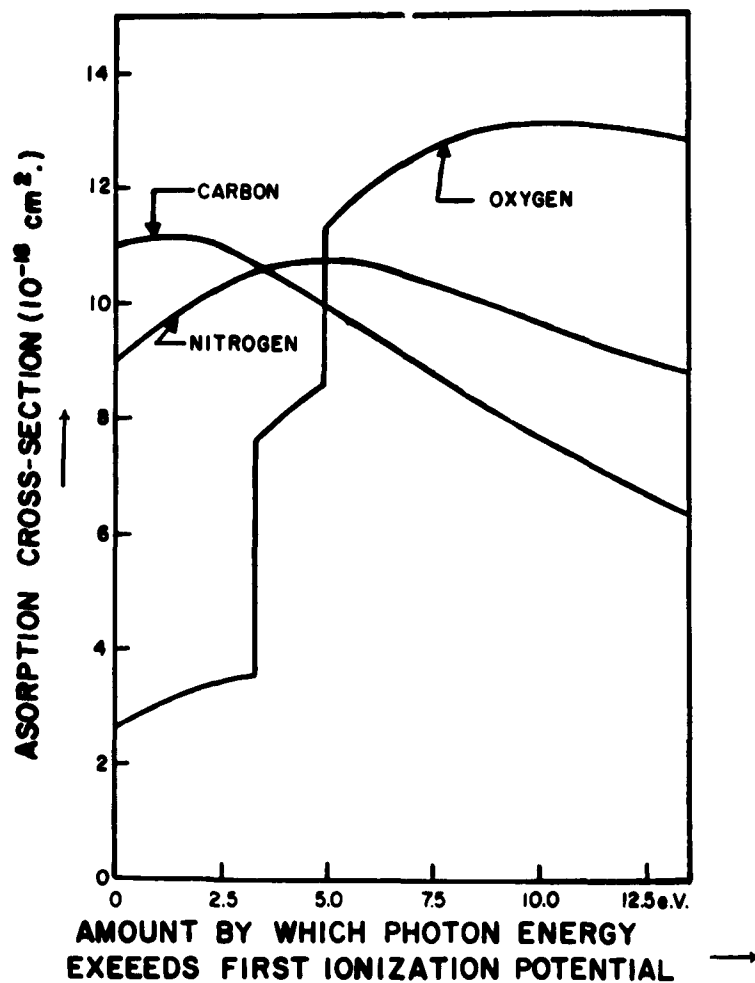


Dissociative ionization, as illustrated by (f.) in Table 3, may occur if the energy of the photon is sufficiently large. The molecule is split into a charged and an uncharged fragment which will affect its subsequent ionic reactions and eventual recombination as a neutral specie. In an experiment which does not discriminate between the products, these processes will be included in the ionization cross section. With mass spectrometric examination of the photoionization products, it is possible to separate these processes and to assess their importance. Available data on oxygen and nitrogen are shown in Figures 9 and 10, which are both due to the work of Weissler, Samson, Ogawa, and Cook<sup>35</sup>. The experiments indicate that these processes occur to a negligible extent in both oxygen and nitrogen, and are therefore not too important in the upper atmosphere.

In summary of the present data, it may be stated that the photoionization cross section for atmospheric gases reaches values of about  $1$  or  $2 \times 10^{-17}$   $\text{cm}^2$  in the principal ionization continuum just above the ionization potential, and that the cross section slowly decreases at lower wavelengths. Further work will be needed to obtain better data in the wavelength region below  $1000 \text{ \AA}$ , where most of the transitions which maintain the earth's ionosphere occur. Simple ionization, as in (c.) and (d.) of Table 3, appears to be the most important type of ionization process.

## ELECTRON ATTACHMENT

Negative ions may be formed in the ionosphere by attachment of electrons to electronegative atoms and molecules. This process leads to rapid removal of electrons after sunset, when photodetachment is no longer able to reverse the process and yield back a neutral specie and the electron. The attaching electrons are at low thermal energies. However, most experiments are done at somewhat higher energies because it is difficult to work at such low energies.



*Absorption cross-section curve for atomic oxygen, nitrogen and carbon.*

*(Note: The breaks in the oxygen curve are at the second and third ionization potentials.)*

Figure 7. Absorption cross-section curve for atomic oxygen, nitrogen, and carbon (reproduced, with permission, from Monthly Not. Roy. Astronom. Soc.)

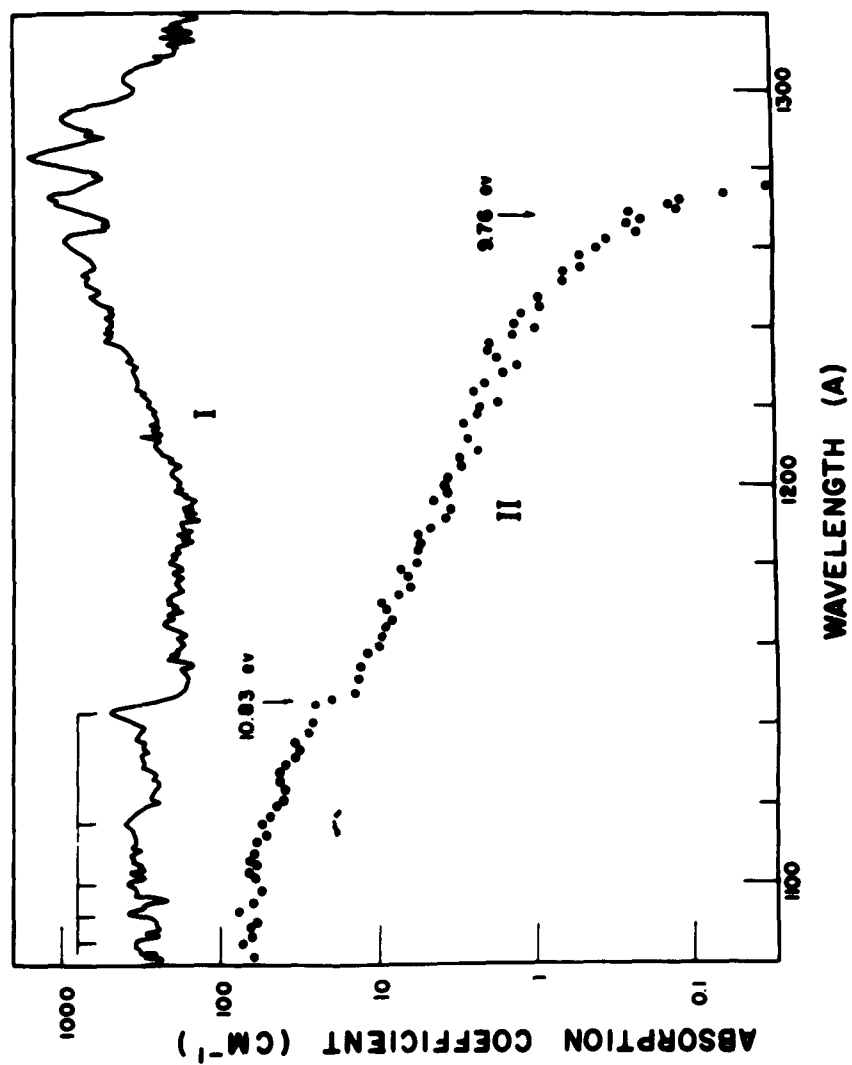


Figure 8. Absorption coefficient (curve I) and ionization coefficient (curve II) of NO<sub>2</sub> in the region 1080-1300 Å. Rydberg bands and ionization potentials are indicated.



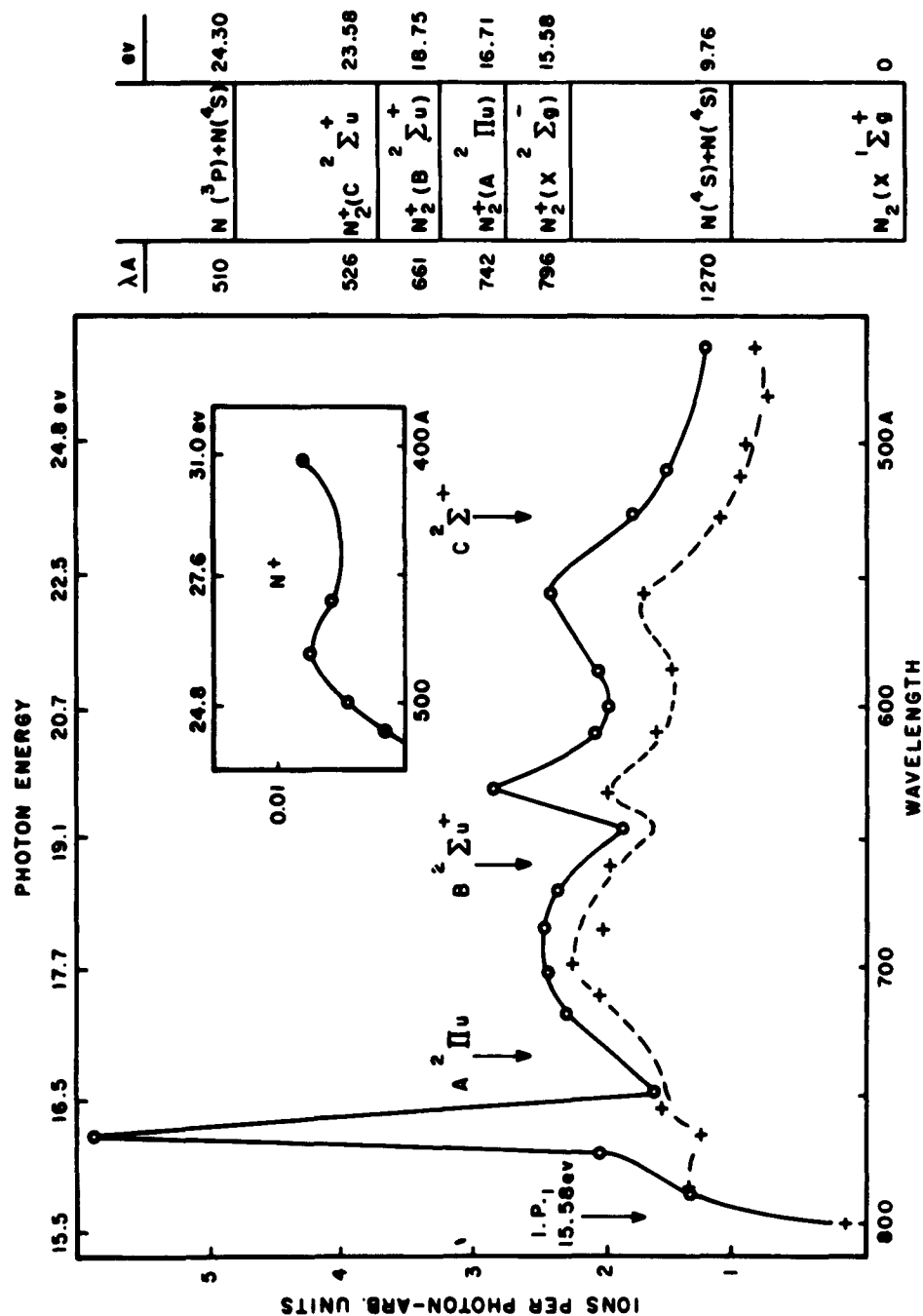


Figure 10.  $N_2^+$  and  $N^+$  yields per incident photon from the photoionization of  $N_2$ . Solid curve obtained with Air-He, dashed curve with argon in the light source.

The electron affinity is defined as the decrease in energy occurring when a neutral specie and an electron combine to form a negative ion; this must be positive for the negative ion to be stable. Values for atmospheric species are shown in Figure 11. The values are due to Branscomb, Burch, Smith, and Geltman<sup>7</sup>; Burch, Smith, and Branscomb<sup>8</sup>; Phelps and Pack<sup>25</sup>; and van Lint, Hammond, Perez, and Wikner<sup>27</sup>. The only species from which to obtain stable negative ions in the ionosphere are atomic oxygen, molecular oxygen, and nitrogen dioxide. For molecules, the electron affinity refers to the ground vibrational states of the lowest electronic states of the molecule and the molecular ion. However, applications of the Frank-Condon principle to transitions between potential curves for the molecule and the molecular ion lead to situations where the electron affinity differs from the vertical detachment threshold and the radiative attachment threshold as discussed especially by Branscomb<sup>6</sup> for  $O_2$  and  $O_2^-$ .

The types of electron attachment processes which may occur and the best available values for the rate coefficients are illustrated in Figure 12, which contains data from Chanin, Phelps, and Biondi<sup>9</sup>; van Lint, Wikner, and Trueblood<sup>27</sup>; Phelps and Pack<sup>25</sup>; and Haaland<sup>17</sup>. Electrons may attach to molecular species by a three-body process in which a third unspecified particle carries away the excess kinetic energy, by dissociative attachment where the excess energy is removed by rupturing a molecular bond, and by radiative attachment where the excess energy is removed by emission of a photon. For atomic species, three-body and radiative attachment can occur. Since the measurements indicate that dissociative attachment occurs only at electron energies above one electron volt, and since typical thermal energies are around 0.025 electron volt, the only processes to consider for attachment to molecular oxygen are three-body and radiative attachment. Since the rate of the three-body process varies as the square of the pressure while the radiative process rate varies as the first power, the amount of recombination occurring by the latter path will become larger at higher altitudes and will finally become the only attachment process. On the basis of the indicated measurements, the three-body process is more important below roughly 100 km and the radiative process is more important above this altitude. In addition, it is only above these altitudes that there is an appreciable concen-

|                 |                                     |                                                      |
|-----------------|-------------------------------------|------------------------------------------------------|
| O               | $1.465 \pm .005$                    | Branscomb, Smith                                     |
| O <sub>2</sub>  | $0.15 \pm 0.05$                     | Burch, Smith and Branscomb                           |
|                 | $0.46 \pm 0.02$                     | Phelps and Pack                                      |
| N               | very small or negative              |                                                      |
| N <sub>2</sub>  | very small or negative              |                                                      |
| NO <sub>2</sub> | Larger than O value<br>"very large" | Branscomb, Smith; van Lint<br>Hammond, Perez, Wikner |

Figure 11. Electron affinities of atmospheric constituents

|                           |                                                                                 |                                                           |
|---------------------------|---------------------------------------------------------------------------------|-----------------------------------------------------------|
| <u>Three-body:</u>        |                                                                                 |                                                           |
| $e + 2 O_2 = O_2^- + O_2$ | $2.8 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$<br>$T = 300^\circ \text{K}$ | Chanin, Phelps,<br>Biondi; van Lint,<br>Wikner, Trueblood |
| <u>Dissociative:</u>      |                                                                                 |                                                           |
| $e + O_2 = O^- + O$       | only above 1 volt<br>$10^{-12}$ - $10^{-11}$ at 1-4 volt                        | Chanin, Phelps,<br>Biondi                                 |
| <u>Radiative:</u>         |                                                                                 |                                                           |
| $e + O_2 = O_2^- + h\nu$  | $2 \times 10^{-18} \text{ cm}^3 \text{ sec}^{-1}$<br>$T = 230^\circ \text{K}$   | Phelps and Pack                                           |
| <u>Radiative:</u>         |                                                                                 |                                                           |
| $e + O = O^- + h\nu$      | $1.3 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$                             | Haaland from<br>data of Branscomb<br>and Smith            |

Figure 12. Electron attachment process

tration of oxygen atoms, which has been calculated to have a radiative attachment rate coefficient three orders of magnitude larger than the value for molecular oxygen. Useful future research in this area would be the development of new experimental techniques to study the attachment processes at low electron energies in atomic and molecular oxygen.

One of the most intriguing results of upper atmosphere mass spectrometric experiments is the discovery<sup>20</sup> that a negative ion of mass 46, assumed to be  $\text{NO}_2^-$ , is in much greater abundance than any other negative ion. Several other laboratory observations have indicated that  $\text{NO}_2^-$  may be a very stable molecular ion. For example, the photodetachment experiments of Branscomb<sup>5</sup> and associates found such an ion in discharges producing negative atomic oxygen ion, but the electron could not be photodetached by the visible radiation available. This seems to establish the ion as more stable than the negative ion of atomic oxygen, since the oxygen ion could undergo photodetachment in this apparatus.

It has been difficult to obtain more information about the negative ion of nitrogen dioxide and its mechanism of formation in the upper atmosphere. Experiments by Fox<sup>15</sup> have shown that it does not appear to form by direct attachment. The main process yields  $\text{O}^-$  at electron energies above 1.35 volt. The ion is also observed to be formed during the thermalization of 25 Mev electrons in experiments done by van Lint, Hammond, Perez, and Wikner<sup>27</sup>. These investigators find that the attachment cross section is large and that the attachment mechanism is complicated. Additional work in this area would be desirable in order to understand how this unusual triatomic molecular ion is formed in the upper atmosphere. It is possible, of course, that the ion is the most stable product of a series of charge transfer and other ion reactions, but available data do not yet allow detailed calculations.

## 2. Conclusions

It is apparent, after surveying the information presently available, that more laboratory research on these processes is vitally needed. This informa-



tion is necessary to properly utilize data from vehicles, and thereby better understand the earth's upper atmosphere. Applications of many kinds follow close behind fundamental knowledge in these areas.

In general, the research goals for ion formation cross section experiments should include several types of studies. The wavelength range should be extended and studied with continuum light sources down to the x-ray region below  $1 \text{ \AA}$ . This region begins at about  $1650 \text{ \AA}$ , the lowest wavelength of the well-known hydrogen continuum. High resolution studies of photoionization thresholds to allow a better theoretical understanding of photoionization processes, and accurate data on autoionization peaks to allow estimates of their lifetimes should also be studied with continuum sources. Methods for studying reactive atomic species must be developed. Pressure effects on absorption coefficients in molecular bands must be known. Research into experimental techniques may involve studies which are, of necessity, rather far removed from the immediate upper atmosphere applications, but which may incidently lead to valuable results in related scientific areas.

Problems concerned with electron attachment processes include investigations of all types on  $\text{O}_2^-$  and  $\text{NO}_2^-$ . This would finally involve the location of potential curves and surfaces which would, of course, provide the energy quantities such as the electron affinity. It seems desirable to develop new experimental techniques to measure these rate coefficients, so that more confidence may be placed in the results. The excited and metastable states of positive and negative ions must be considered. There are, of course, many related problems involving other processes, such as the mechanisms by which the observed atmospheric concentrations are produced.

Progress in the above areas must also involve periodic computations of theoretical atmospheric concentrations, so that the areas of highest priority may be studied. This, of course, again involves values of parameters for many other types of reactions among ions, photons, electrons, atoms, and molecules. Present GRD in-house and contractual programs, among others, plan to continue to yield cross sections and rate coefficients for these purposes.

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