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PHOTOELECTRON EXCITATION
OF ATOMIC OXYGEN RESONANCE
RADIATION IN THE TERRESTRIAL AIRGLOW

BY

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Abstract

Recent laboratory measurements of the absolute cross sections for the excitation of the $OI(^3S)$ resonance state by electron impact on O and O_2 when combined with in situ measurements of the photoelectron energy distribution from 120 to 300 km show that photoelectron impact is the principal excitation mechanism for $\lambda 1304 \text{ \AA}$ resonance radiation in the dayglow; dissociative excitation of O_2 is found to play a minor role. The laboratory measurements indicate that the 3S state is strongly populated by cascade processes and imply that the $OI(3p^3P \rightarrow 3s^3S; \lambda 8446 \text{ \AA})$ transition should be a prominent dayglow emission feature. These experiments also show that the excitation of atomic oxygen by low-energy electron impact cannot account for the $\lambda 1304 \text{ \AA}$ or 1356 \AA emission observed in the tropical ultraviolet airglow.

INTRODUCTION

The resonance multiplet of atomic oxygen $O I(3s^3S - 2p^3P)$ consists of three lines at 1302, 1304 and 1306 Å and is a prominent emission feature in the vacuum ultraviolet spectrum of the terrestrial dayglow (Donahue and Fastie, 1963; Fastie and Crosswhite, 1964; Fastie et al., 1964; Kaplan et al., 1965; Katyushina, 1965; Fastie, 1968; Buckley and Moos, 1970; Barth and Schaffner, 1970), of the aurora (Crosswhite et al., 1962; Miller et al., 1968; Peek, 1970) and of the tropical ultraviolet airglow (Hicks and Chubb, 1970; Barth and Schaffner, 1970). In the dayglow it is generally believed that photoelectron impact augmented by resonance scattering of solar photons above 300 km is the dominant $O I(3S)$ excitation mechanism (Donahue and Fastie, 1963; Dalgarno, 1964; Tohmatsu, 1964; Kaplan and Kurt, 1965; Donahue, 1965; Tohmatsu, 1965; Strickland and Donahue, 1970).

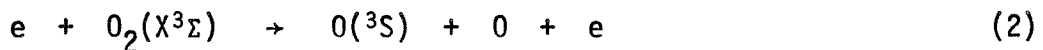
A definitive analysis of this problem, however, has been hampered by a lack of information on the absolute magnitude and shape of the total cross section for exciting the $3S$ resonance state by electron impact on O and on the actual photoelectron energy distribution in the day airglow. Although numerous attempts have been made to calculate the equilibrium electron energy distribution and the related excitation rates (Tohmatsu, 1964, Nagy and Fournier, 1965; Stewart, 1965; Tohmatsu et al., 1965; Green and Barth, 1967, Dalgarno et al., 1969; Prasad, 1969; Nagy and Banks, 1970), the results continue to differ widely from author to author reflecting in part the use of phenomenological cross sections that are in poor agreement with recent laboratory measurements. In general these calculations tend to overestimate the absolute excitation rate of various airglow features and place the altitude of peak

emission too low (Doering et al., 1970; Feldman et al., 1971).

The absolute cross section for the excitation of the $OI(^3S)$ state by electron impact on atomic oxygen



has now been measured by Stone and Zipf (1971a). Detailed information is also available on the absolute cross section for dissociative excitation



(Lawrence, 1970; Ajello, 1970; Mumma and Zipf, 1971), and Doering et al. (1970) have measured the photoelectron energy distribution from 120 to 300 km with the sun at a zenith angle of 60° . These experiments now permit (1) a quantitative assessment of the role played by photoelectrons in the excitation of $OI(^3S)$ atoms in the dayglow, (2) an evaluation of the relative importance of direct versus dissociative excitation, (3) a more accurate determination of the total inelastic cross section for electrons impacting on atomic oxygen in the important energy region from 9.5 to 200 eV, and (4) show that low-energy electron impact cannot be responsible for the $\lambda 1356 \text{ \AA}$ and $\lambda 1304 \text{ \AA}$ emission observed in the tropical ultraviolet airglow. In addition the laboratory measurements of Borst and Zipf (1971) show that dissociative excitation produces excited atoms with non-thermal velocity distributions. $OI(^3S)$ atoms formed by this process will emit broadened resonance lines with complex line shapes. This effect introduces additional complications into the analysis of airglow and auroral $\lambda 1304 \text{ \AA}$ data using radiative transport theory.

RESULTS AND DISCUSSION

In Figure 1 and Table 1 we summarize our present experimental knowledge of the absolute cross sections for the direct and dissociative excitation of the $OI(^3S)$ state. There is general agreement among laboratory workers on the magnitude and shape of the dissociative excitation cross section from threshold to 400 eV. The results are quoted with probable absolute errors of approximately $\pm 15\%$ making these vacuum ultraviolet measurements comparable in accuracy to the N_2^+ (0,0) first negative band cross section measurements (McConkey et al., 1967; Stanton and St. John, 1969, Borst and Zipf, 1970) that are widely used as laboratory standards in the visible spectral region. The absolute cross section for direct excitation of atomic oxygen is larger than the dissociative channel (process 2) by at least one order of magnitude throughout the important low energy range extending from threshold to 200 eV.

At low energies the $OI(^3S)$ excitation function exhibits a well-developed peak reaching a maximum absolute value of $1.2 \times 10^{-16} \text{cm}^2$ at 15 eV. The measured 3S excitation function does not have the characteristic shape of an allowed electric-dipole transition. This unexpected result has been discussed by Stone and Zipf (1971a) who have shown that the total cross section can be readily decomposed into a direct 3S channel with a maximum value of $\sim 2.3 \times 10^{-17} \text{cm}^2$ at 42 eV and a cascade component that dominates at low energies. This is shown in Figure 2. Although a multiplicity of atomic oxygen states may be excited initially, these states ultimately populate the 3S state through a series cascade transitions involving the $OI(3p^3P - 3s^3S; \lambda 8446 \text{ \AA})$ and $OI(4p^3P - 3s^3S; \lambda 4368 \text{ \AA})$ transitions as the principal intermediaries. Auroral

data (Dick, 1970) suggest that the $OI(3p^3P - 3s^3S)$ transitions is the preferred channel. A similar situation exists with respect to dissociative excitation. As Table 2 shows, nearly 66% of the total 3S population rate produced by dissociative excitation of O_2 is due to $\lambda 8446 \text{ \AA}$ cascade radiation while $\lambda 4368 \text{ \AA}$ emission contributes less than 2%. Similar results have been obtained in studies on CO. In both cases $(3p^3P)/(3s^3S)$ cascade ratio is nearly independent of the incident electron energy for $E > 50 \text{ eV}$; this behavior is consistent with the model of dissociative excitation proposed recently by Borst and Zipf (1971). For the direct excitation channel (process 1) the cascade ratio is a sensitive function of the electron energy as Table 2 shows. The laboratory measurements indicate that the cross section for exciting the $OI(3p^3P)$ state by electron impact on atomic oxygen is quite large at low electron energies ($\sim 1.1 \times 10^{-16} \text{ cm}^2$ at 15 eV) and that the $\lambda 8446 \text{ \AA}$ line should be an important emission feature in the dayglow.

In Figure 3 we compare the laboratory measurements of Stone and Zipf (1971a) with several theoretical electron excitation functions for the $OI(^3S)$ state that have been used extensively in recent airglow analyses. The excitation cross sections obtained by Stauffer and McDowell (1966) [curves A1 and A2] are based on a detailed quantum mechanical calculation which only considered direct excitation of the 3S state, cascade processes were not taken into account. The theoretical results overestimate the magnitude of the excitation cross section at electron energies greater than 21 eV [approximation A2] and at all electron energies above threshold in the case of A1. Inclusion of cascade contributions from more energetic 3P states will increase the disagreement so that airglow calculations based on the work of Stauffer and

McDowell tend to overestimate the $\lambda 1304 \text{ \AA}$ yield due to photoelectron impact and the importance of this inelastic process as an electron energy sink.

In addition to the detailed calculations of Stauffer and McDowell a number of semi-empirical cross sections for the 3S state have been developed by aeronomists. Green and Dutta (1967) and Jusick et al. (1967), for example, suggest that an adequate approximation to the total cross section is given by the formula

$$Q(E) = C f W^{-2} (1 - W/E)^{\nu} (W/E)^{\Omega} \quad (3)$$

where $Q(E)$ is the total excitation cross section [as a function of electron energy], f is the optical oscillator strength of the transition, E and W are the impact and excitation energies, and C , ν , and Ω are adjustable parameters. Curve B was obtained using parameter values recommended by these authors and the 3S oscillator strength obtained recently by Lawrence (1970) and Lin et al. (1970). The semi-empirical cross section obtained in this manner is not in good agreement with the experimental results.

Stewart (1965) has developed a similar set of phenomenological cross sections based on analogies with the few experimental results available. He assumes that optically allowed transitions have cross sections which have the same shape [as a function of E/W] as the hydrogen $1s - 2p$ transition, and have peak magnitudes, Q_{\max} , given by an expression due to Seaton (1962):

$$Q_{\max} W^2/f = 2.1 \times 10^{-14} \text{ cm}^2 \text{ eV}^2 \quad (4)$$

where W and f are as defined above. Spin-exchange or other optically forbidden transitions are assumed to follow the shapes of the helium $1^1s - 2^3s$ transition and the hydrogen $1s - 2s$ transition, respectively, and to have peak magnitudes determined by the formula

$$Q_{\max} W^2 = 1.5 \times 10^{-15} \text{cm}^2 \text{eV}^2 \quad (5)$$

Excitation cross sections $C1$ and $C2$, which account for the direct and total excitation of the $OI(^3S)$ state respectively, were constructed using these formulas. The total cross section obtained in this manner has a shape similar to the laboratory result, but is smaller in magnitude by nearly an order of magnitude.

OI 1304 Å AIRGLOW

The experimental cross sections presented in Figures 1 and 2 and the in situ photoelectron energy distribution measurements of Doering et al., (1970) were used to calculate the absolute population rates for the $OI(3s^3S)$ and $OI(3p^3P)$ states due to electron impact on O and O_2 with the sun at a solar zenith angle of 60° . These results are shown in Figure 4. The atomic oxygen densities used in the computation were taken from a CIRA summer model atmosphere with an exospheric temperature of 900°K . The calculation indicates that dissociative excitation is a minor source of $\lambda 1304 \text{ \AA}$ and $\lambda 8446 \text{ \AA}$ radiation in the dayglow ($\sim 1\%$). This is not surprising in view of the state of the excitation functions and the low-energy character of the photoelectron spectrum. Direct excitation of atomic oxygen by electron impact is found to contribute significantly to the population of the $OI(3s^3S)$ and $OI(3p^3P)$ states in the dayglow in agreement with the airglow models first discussed by Donahue and Fastie (1963) and by Dalgarno (1964). The calculated

population rate for the $OI(3p^3P)$ state implies that the zenith intensity of the $OI \lambda 8446 \text{ \AA}$ line would be approximately 1.7 kR with the sun at a zenith angle of 60° . The corresponding column production rate for the $\lambda 1304 \text{ \AA}$ triplet would be about 1.9 kR from electron impact plus an additional ~ 0.3 kR due to resonance scattering (Strickland and Donahue, 1970) at high altitudes. Bowen fluorescence (1934; 1947) will contribute approximately 0.2 kR (Donahue and Fastie, 1964) while O_2 absorption will decrease the overall column production rate by about 20 - 30% (Strickland, personal communication, 1971). Hence the effective $O(^3S)$ column production rate with the sun at a zenith angle of 60° would be approximately 2kR. If we invoke the resonance scattering model proposed by T. M. Donahue (c.f. Hicks and Chubb, 1970; Barth and Schaffner, 1970), the $O(^3S)$ column production rate implied by the laboratory and rocket experiments would correspond to a $\lambda 1304 \text{ \AA}$ intensity of ~ 4 kR as viewed by an overhead satellite. This value compares favorably with the average NRL satellite measurements of 5 - 8 kR for a 60° solar zenith angle (R. Meier, personal communication 1971). The results agree within the quoted experimental error, although the small difference may also be due to the use of a model atmosphere with insufficient atomic oxygen (von Zahn, 1971); in fact the recent increase in the O/O_2 density proposed by von Zahn (1970) and by Offermann and von Zahn et al., (1971) would bring our calculated $\lambda 1304 \text{ \AA}$ into nearly exact agreement with the NRL observations.

In Figure 5 we compare the $OI(^3S)$ population rate based on the laboratory and in situ measurements (curve B) with the results of two recent theoretical calculations. Curve C is based on the work of Stewart (1970) which involves an elaborate phenomenological calculation of the photo-electron energy distribution. The actual electron density profile obtained

during the rocket flight of Doering et al. (1970) was used to correct the 3S excitation efficiency curves presented by Stewart (cf. Figures 2 and 3; Stewart, 1970). Stewart's calculation places the altitude of peak emission at 160 km, predicts a peak population rate of $3.4 \times 10^2 \text{cm}^{-3} \text{sec}^{-1}$ and a column production rate for the $\lambda 1304 \text{ \AA}$ triplet of 3.5 kR. Curve A was obtained by Strickland and Donahue (1970) from a radiative transport analysis of $\lambda 1304 \text{ \AA}$ data obtained by Fastie et al. (1964) at a time when the level of solar activity was much lower. Their result implies a column production rate of 2.2 kR due to a source other than resonance scattering of solar photons. Both calculations are in good agreement with the NRL satellite data, although there are noticeable differences in detail.

TROPICAL ULTRAVIOLET AIRGLOW

The laboratory results of Stone and Zipf (1971a) suggest that the $OI(^3S)$ state is efficiently populated by cascade radiations at low electron energies and that from threshold to approximately 40 eV the cross section has a shape characteristic of a spin-change transition. Stone and Zipf (1971b) have also shown in a more recent experiment that the excitation function for the $OI(^5S)$ state due to electron impact on atomic oxygen



is very similar in shape to the cross section for the $OI(3p^3P)$ state (the difference component in Figure 2). Their results imply that, as far as low energy electrons ($E < 40 \text{ eV}$) are concerned, the 3S and 5S states have excitation functions that are nearly identical in shape. This possibility was not considered in previous discussions of the $1356 \text{ \AA} - 1304 \text{ \AA}$ airglow

problem. The laboratory measurements also show that at higher electron energies the 3S state is clearly favored over the 5S state.

The absolute magnitude of the $OI(^5S)$ cross section is not known with certainty at this moment. The laboratory results, however, place a lower limit on the magnitude of $Q_{\max}(^5S)$ of approximately $2 \times 10^{-17} \text{cm}^2$ assuming that the 5S radiative lifetime given by Garstang (1961) is correct. The dayglow experiments show convincingly that the $1356 \text{ \AA}/1304 \text{ \AA}$ ratio is quite small and are consistent with the lower limit established by the laboratory data (Stone and Zipf, 1971b). Barth and Schaffner (1970), for example, report a value of 0.06 for this ratio. When taken together, the laboratory and dayglow observations imply that the excitation of atomic oxygen by a flux of low energy electron invariably leads to a small $1356 \text{ \AA}/1304 \text{ \AA}$ ratio and therefore that this mechanism could not account for the large $1356/1304$ ratios observed in the tropical ultraviolet airglow (Chubb and Hicks, 1970; Barth and Schaffner, 1970).

Furthermore, the work of Stone and Zipf (1971a) implies that 10 - 20 eV electrons would also strongly excite the $OI \ 8446 \text{ \AA}$ line and that the $\lambda 8446 \text{ \AA}$ excitation rate would be comparable in magnitude to the $OI(^3S)$ population rate. This implies that in the tropical airglow the $\lambda 8446 \text{ \AA}$ zenith intensity would be approximately 500 R when the $\lambda 1304 \text{ \AA}$ intensity was approximately 1 kR as viewed from a satellite above the emission layer. The concomitant $\lambda 8446 \text{ \AA}$ emission would also be confined to the geographical regions of $O(^3S)$ enhancement. The work of Sparrow et al. (1970), however, appears to show clearly that this is not the case. They observe a maximum signal of only 50 R above the normal airglow signals in a spectral region ($6000 - 8500 \text{ \AA}$) which includes the

OI($3p^3P \rightarrow 3s^3S$) transitions. Furthermore, the weak red emission was not confined to the region of the tropical VUV anomaly. Hence the observational data place a stringent upper limit on the magnitude of $\lambda 8446$ emission in the enhanced equatorial airglow which is at least one order of magnitude smaller than the signal that would have resulted were electron impact on atomic oxygen the dominant source of the OI resonance radiation in the tropical ultraviolet airglow.

Although direct excitation of atomic oxygen alone cannot account for the observed $\lambda 1356 \text{ \AA} / \lambda 1304 \text{ \AA}$ in the tropical ultraviolet airglow, an alternative mechanism might involve excitation of the OI(3S) state by electron impact (accompanied by weak $\lambda 1356 \text{ \AA}$ emission) plus dissociative excitation of O_2 to produce the observed $\lambda 1356 \text{ \AA}$ signal. The possibility of this scheme is based on the conclusions of Wells et al. (1971) who have shown that the ratio of the dissociative excitation cross sections $Q(^5S)/Q(^3S) \approx 2$. To be effective dissociative excitation would require a sizeable flux of comparatively energetic electrons ($E > 30 \text{ eV}$) and they would have to be deposited low enough in the atmosphere to counteract the unfavorable O_2/O ratio at F region altitudes.

Although this mechanism can account for the $\lambda 1356 \text{ \AA} / \lambda 1304 \text{ \AA}$ ratio observed in the tropical ultraviolet, the relatively high energy electrons that would be required would also effectively excite various N_2 and N_2^+ band systems. None of these emission features are observed. The infrared atomic oxygen lines ($\lambda 8446 \text{ \AA}$ and $\lambda 7774 \text{ \AA}$) would also be strongly excited (Lawrence, 1970), but they have not been observed either (Sparrow et al., 1970). Hence, within the framework of existing laboratory and observational data there is

no process or self-consistent set of processes that would allow electron impact to be the dominant source of the $\lambda 1304 \text{ \AA}$ and 1356 \AA emission observed in the tropical ultraviolet airglow.

Because of the predominance of atomic oxygen in the F-region, the thermalization of energetic photoelectrons or secondary electrons formed in aurora at these altitudes is controlled almost entirely by a competition between elastic losses to ambient electrons and inelastic losses to atomic oxygen. In order to calculate the equilibrium photoelectron fluxes and the critical energy (Dalgarno et al., 1963) a complete set of inelastic cross sections for electrons impacting on O is needed; detailed experimental information of this kind is not yet available. However, useful guidelines do exist. Because the excitation of oxygen atoms to states lying between the ionization continuum and the threshold energies of the 3S and 5S states leads ultimately to the emission of $\lambda 1304 \text{ \AA}$ and $\lambda 1356 \text{ \AA}$ photons, the total excitation cross section for the 3S and 5S states can be used to estimate the mean electron energy loss rate in this important energy range. The laboratory measurements imply that inelastic losses to the manifold of quintet states is a minor energy sink, and that below 30 eV excitation of the high-lying 3P states is the preferred inelastic channel. In Figure 6 we show the principal inelastic cross sections for electrons impacting on atomic oxygen that have been identified so far on the basis of experiment or theory. The experimental details can be found in the work of Fite and Brackmann (1959), Rothe et al. (1962), and Stone and Zipf (1971a,b). No experimental data are currently available on the excitation of the 1S and 1D states of atomic oxygen by electron impact. For these processes we rely on the recent calculations of Henry et al. (1969).

Finally we note that dissociative excitation of the 3S state is particularly interesting because of the potential complications that this collision process introduces into a radiation entrapment calculation. The $OI(^3S)$ atoms produced by dissociative excitation are likely to have substantial kinetic energy (Borst and Zipf, 1971) and emit highly broadened resonance lines that may have unusual line shapes. The laboratory studies indicate that the average fragment atom may have an energy of 1 - 2 eV or more and that the velocity distribution of the dissociated atoms is a sensitive function of the incident electron energy. Much of the radiation emitted by these fast atoms will escape as though the atmosphere were optically thin. When this process is the dominant excitation mode, unusual limb-brightening effects may be observable. Dissociative excitation will be most important in auroral events where energetic electrons are abundant and are deposited at much lower altitudes where O_2 is a major atmospheric constituent.

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Table I
 Absolute Electron Excitation Cross Sections
 For The OI(³S) State.

| Target Gas | σ (max) (cm ²) | E(max) (eV) | Reference |
|----------------|--------------------------------------|----------------|-----------------------|
| O | [1.2 ± 0.4] (-16)* | 15 | Stone and Zipf (1971) |
| O ₂ | [3.18 ± 0.50] (-18) | 83 | Lawrence (1970) |
| O ₂ | 3.00 (-18) [†] | 100 | Ajello |
| O ₂ | [3.82 ± 0.50] (-18) ^{a,b} | 83 | Mumma and Zipf (1971) |
| O ₂ | [3.04 ± 0.50] (-18) ^c | 83 | Mumma and Zipf (1971) |

* Read (1.3 ± 0.4) × 10⁻¹⁶cm²

[†] Probable absolute error not stated.

Absolute calibration based on the branching ratio technique described by Mumma and Zipf (1970) and on the NI(²D - ²P⁰)/NI[²D → ²D⁰] branching ratio given by (a) Labuhn et al. (1966), (b) Stone and Zipf (1971c), and (c) Aarts and De Heer (personal communication, 1970).

Table II
Relative OI(³S) Population Rates

| Target gas | O ₂ | CO | O | O | O |
|------------------------------|----------------|-------|-------|-------|-------|
| Electron energy | 83 eV | 83 eV | 15 eV | 30 eV | 50 eV |
| Direct channel ^a | 0.350 | 0.282 | 0.10 | 0.50 | 0.83 |
| Cascade: 8446 Å ^b | 0.635 | 0.706 | 0.84 | 0.50 | 0.17 |
| 4368 Å ^c | 0.015 | 0.014 | 0.06 | --- | --- |

Collision Process:

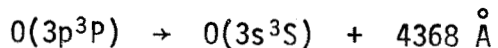
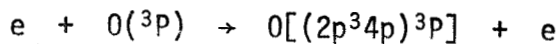
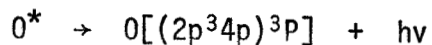
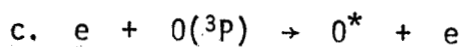
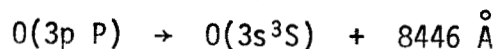
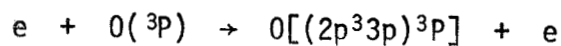
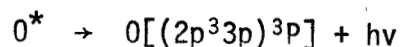
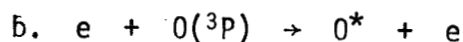


Figure Captions

- Figure 1. Absolute cross sections for the excitation of the $OI(^3S)$ by electron impact on O and O_2 based on the laboratory experiments of Stone and Zipf (1971) and Mumma and Zipf (1971) respectively.
- Figure 2. The total $O(^3S)$ excitation cross section for electron impact on atomic oxygen. The calculations of Stauffer and McDowell (1966) were normalized at 200 eV and used as a measure of the direct (3S) channel. The difference curve represents the total cascade contribution.
- Figure 3. Theoretical, semi-empirical and experimental cross sections for the excitation of the $OI(3s\ ^3S)$ state by electron impact on atomic oxygen:
- A1 and A2: Stauffer and McDowell (1966).
 - B: Jusick et al. (1967).
 - C1 and C2: Stewart (1965).
 - Experiment: Stone and Zipf (1971a).
- Figure 4. The absolute population rates for the $OI(3s\ ^3S)$ and $OI(3p\ ^3P)$ states due to photoelectron impact on O and O_2 with the sun at a zenith distance of 60° .
- Figure 5. A comparison of the $OI(^3S)$ population rate based on laboratory data and on in situ measurement of the photoelectron energy distribution (curve B) with recent theoretical treatments [curve A, Strickland and Donahue (1970); curve C, Stewart (1970)].
- Figure 6. Compilation of current laboratory and theoretical data on the principal inelastic cross sections for electrons impacting on atomic oxygen.

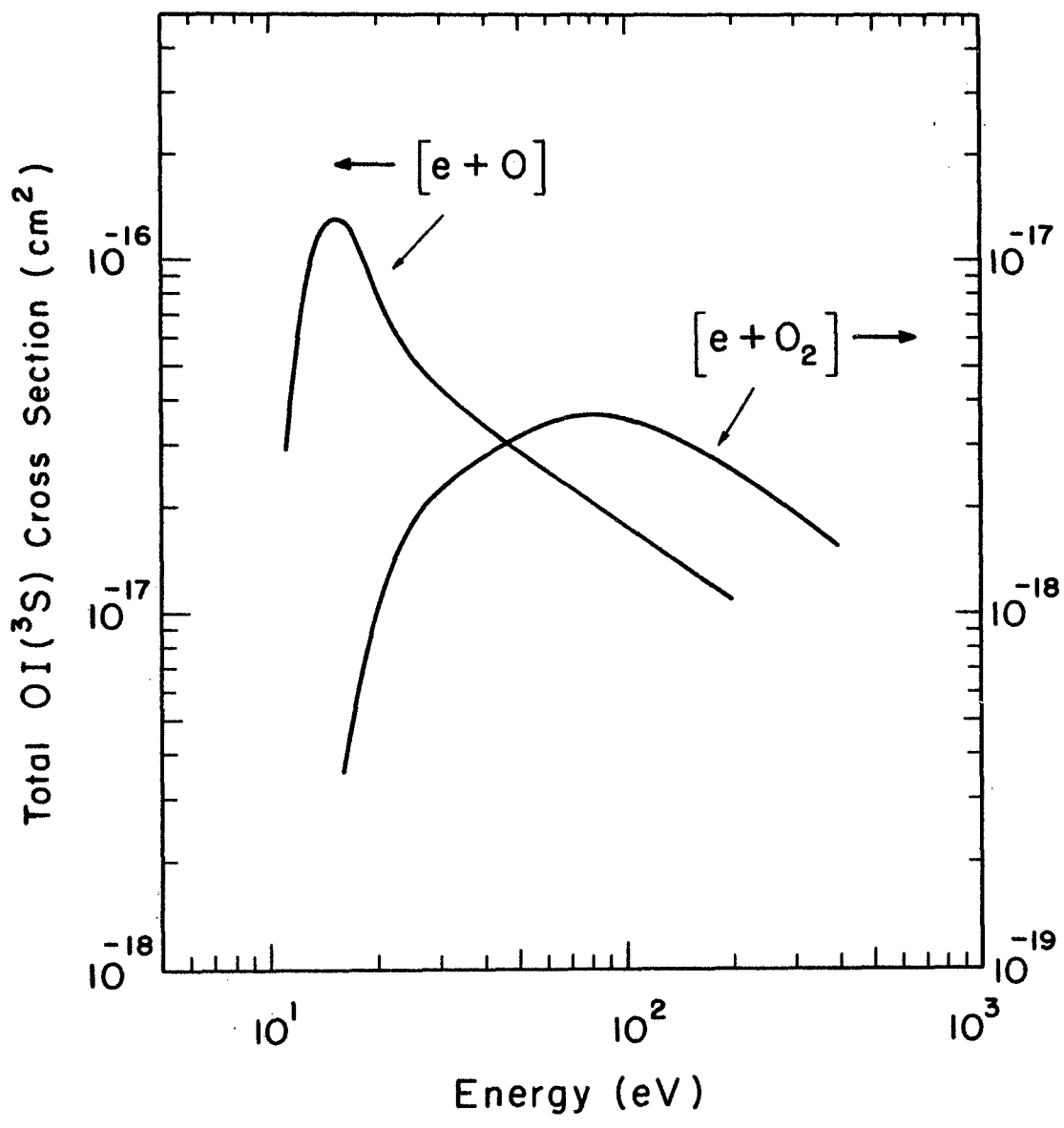


Figure 1

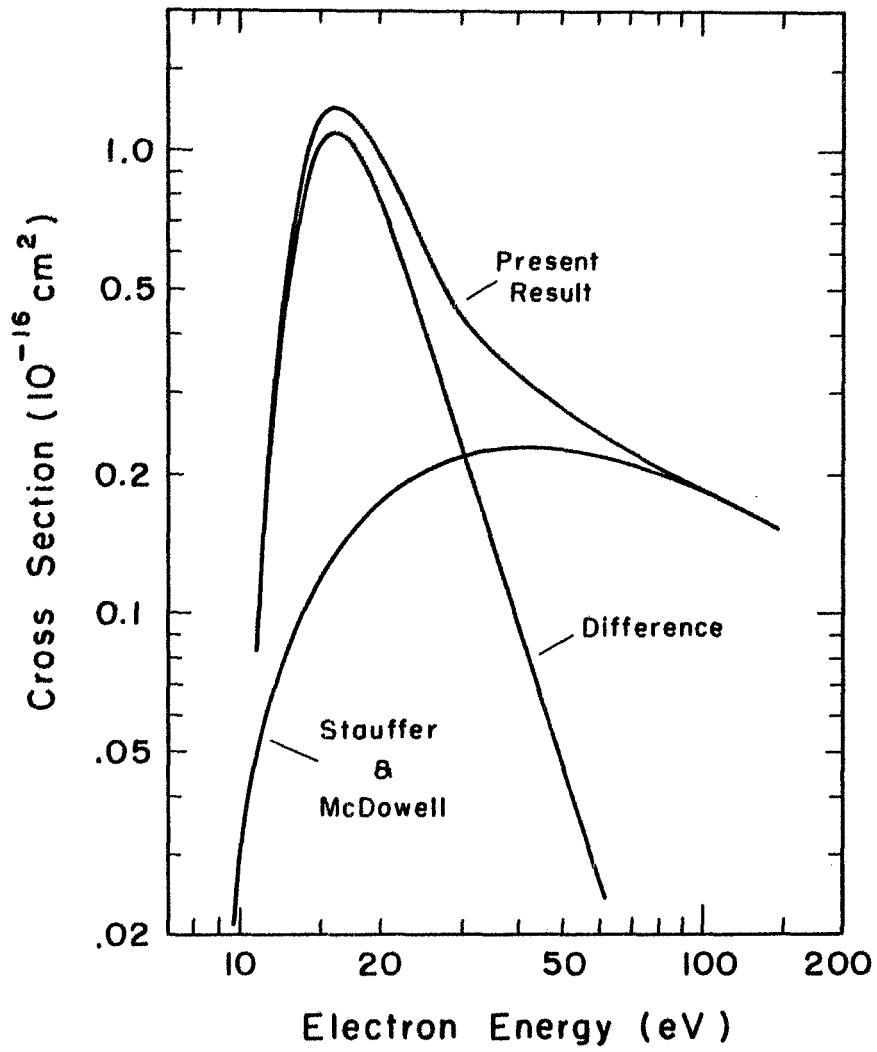


Figure 2

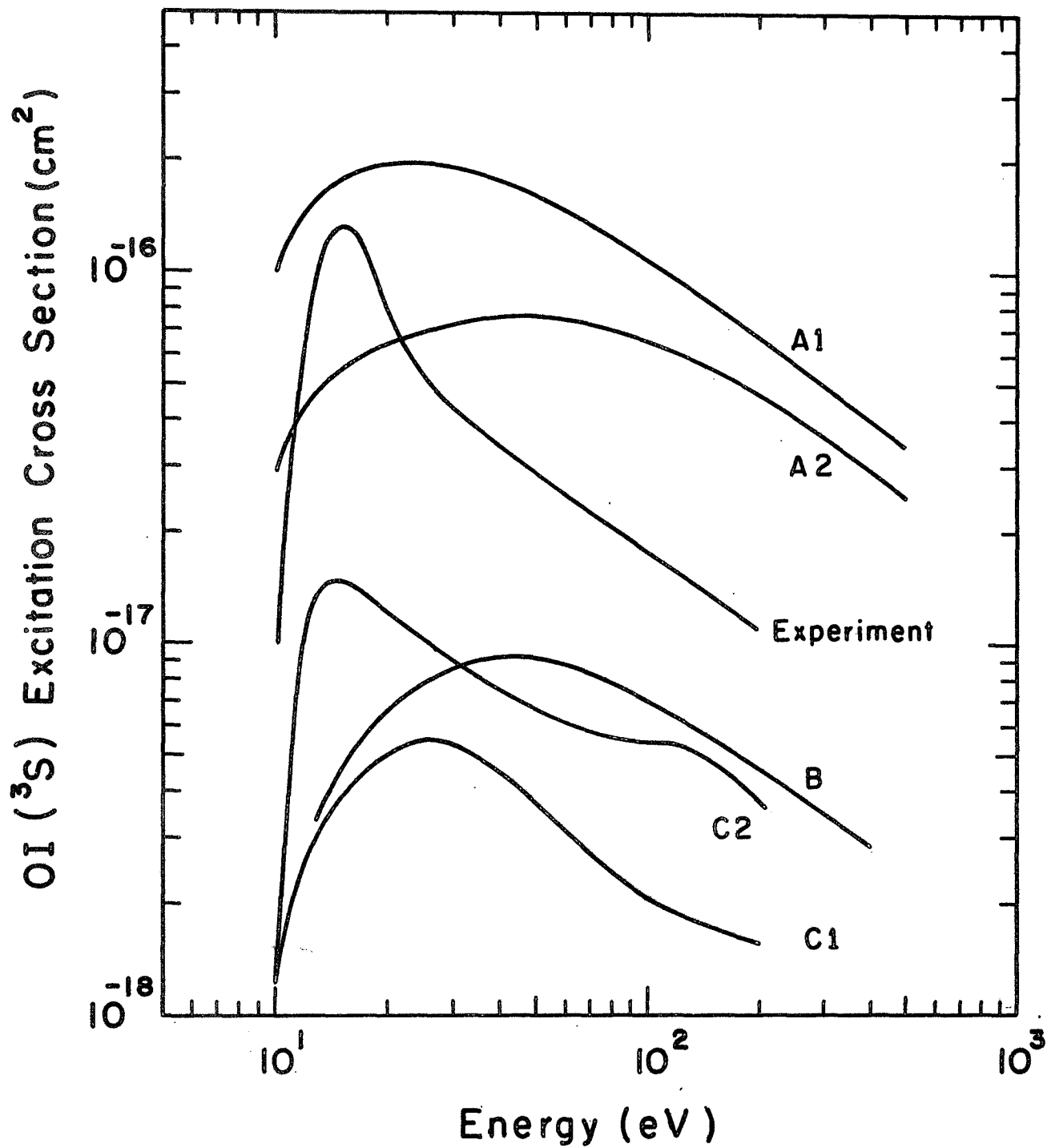


Figure 3

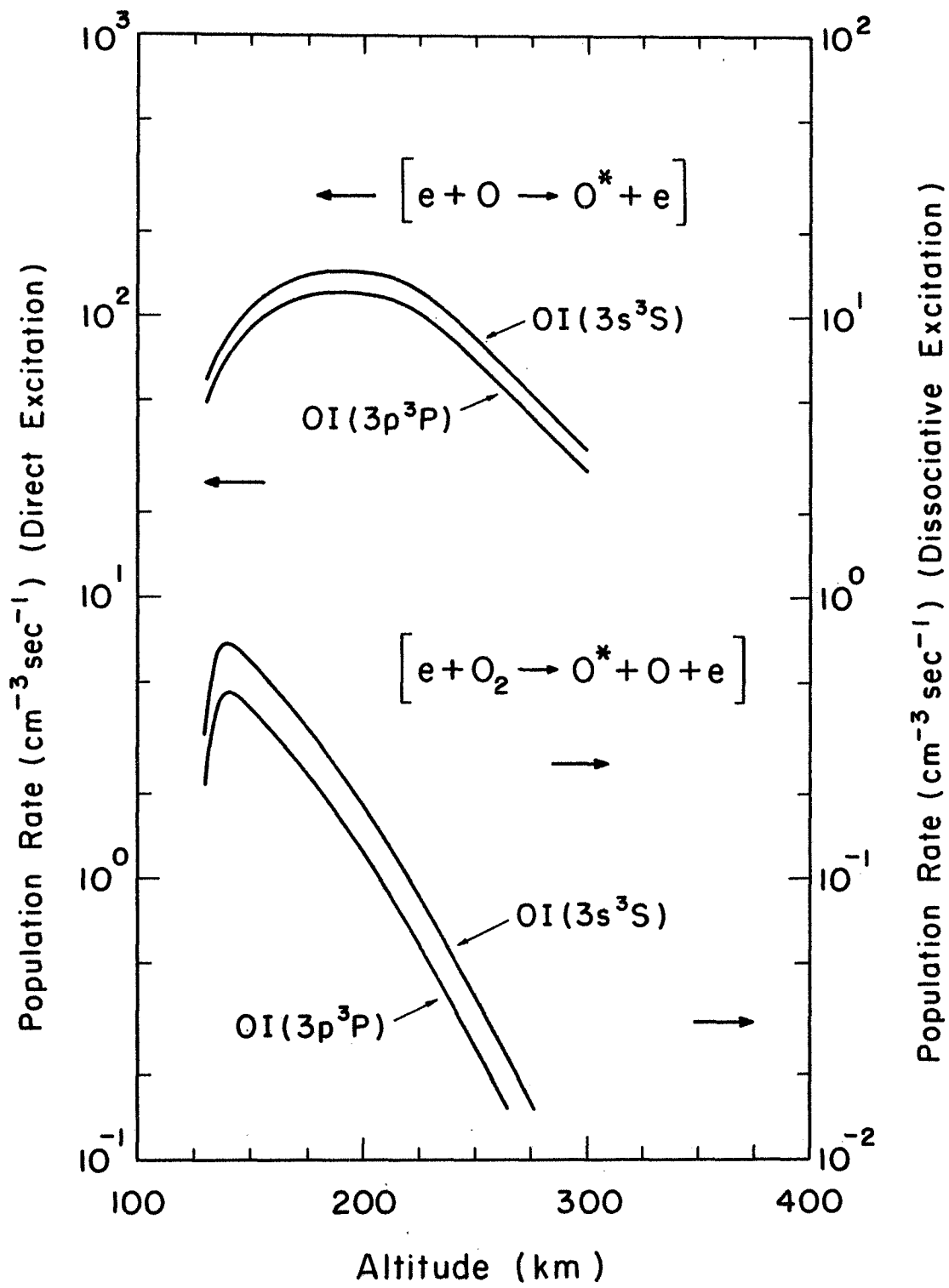


Figure 4

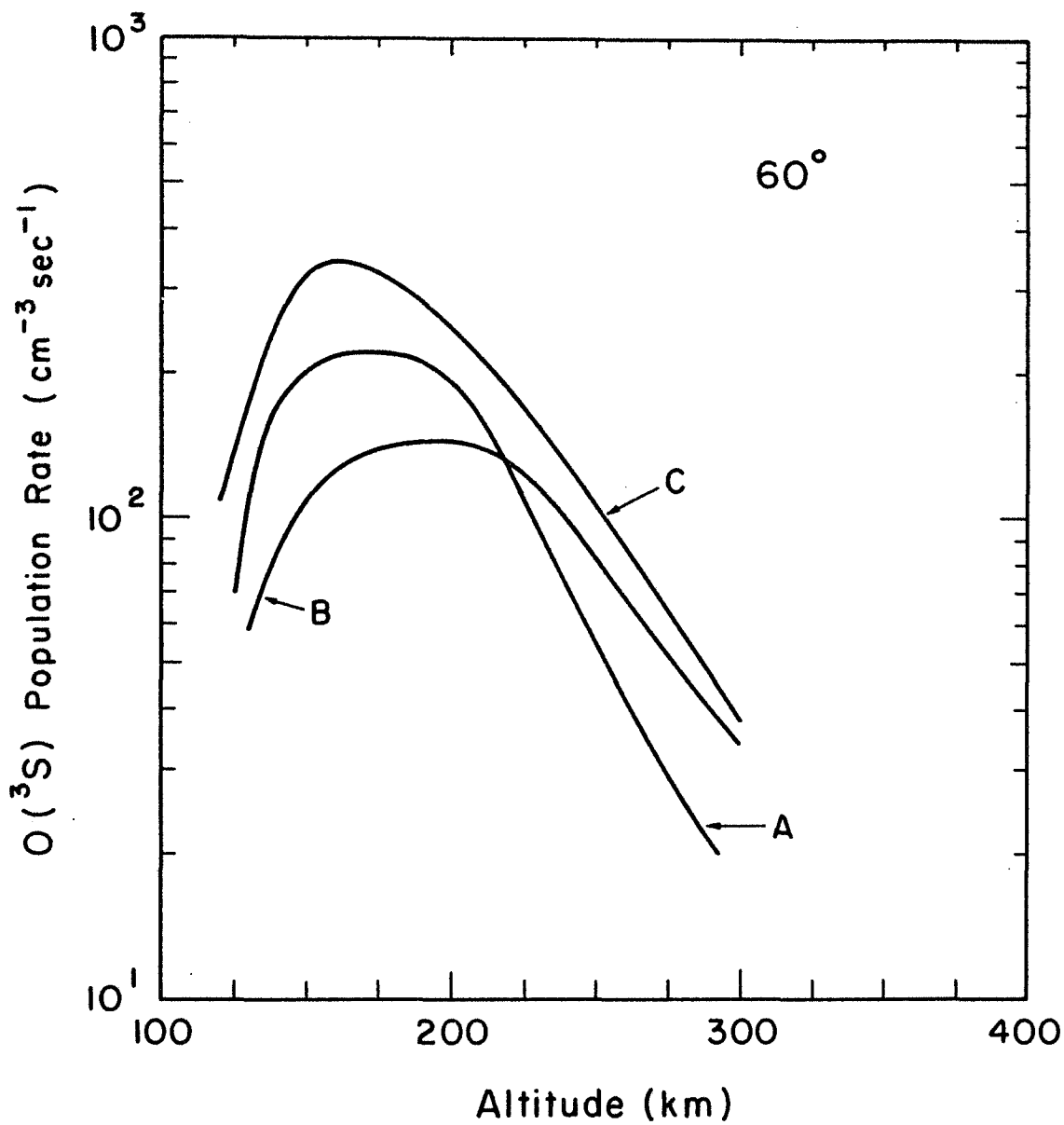


Figure 5

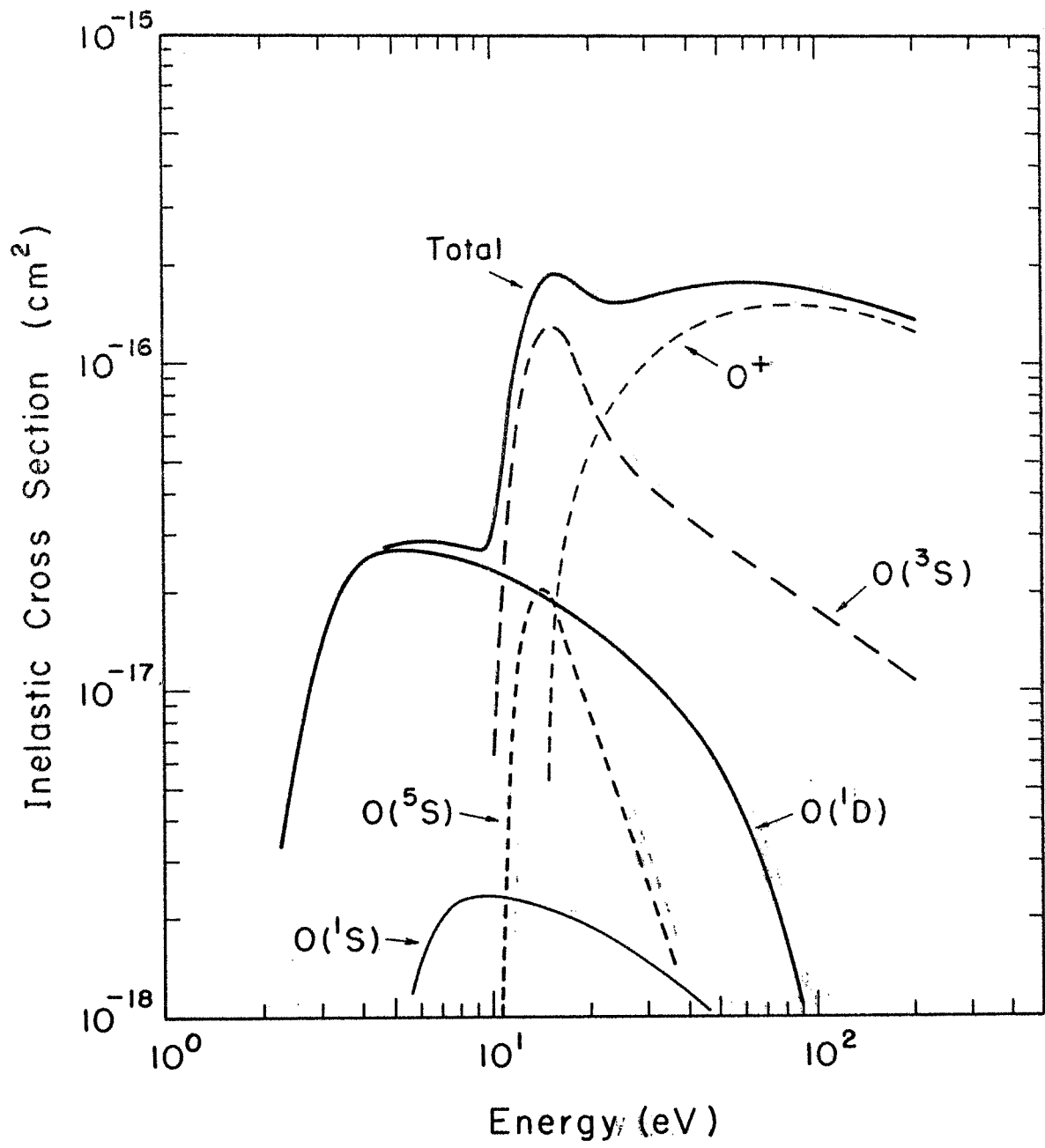


Figure 6