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THEORETICAL STUDIES OF ATOMIC AND MOLECULAR
PROCESSES IMPORTANT IN SPACE EXPERIMENTS

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FIELD	GROUP	SUB-GROUP	Photoionization of OII and NI S_{W} $F \subset N$ $\text{De} \cdots$,
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Calculations have been carried out on the photoionization of OII ($^4S^0$, $^2D^0$, and $^2P^0$) and on the photoionization of NI ($^4S^0$, $^2D^0$, and $^2P^0$). An explanation has been advanced for the enhanced abundance of heavy ozone in the stratosphere. A published proposal for resolving the apparent ozone deficiency in the region above the 95 km level has been examined and shown to be unsatisfactory. A method has been devised whereby the low density limit to the rate coefficient for the termolecular association of ions and polar molecules may be found from measurements on the rate coefficient even outside the region where third order kenitics prevail. The theory of radiative association when the stabilization is brought about by an electronic transition has been developed.

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Several papers mentioned as being in course of publication
in the last report have now been published.   They are:

D. R. Bates and W. L. Morgan, Adiabatic invariance treatment
of hitting collisions between ions and symmetrical top
dipolar molecules, J. Chem. Phys. 87, 2611 (1987).

D. R. Bates, Polyatomic ions: bond energies, most stable
isometric form and low excited states.   Int. J. Mass
Spectroscopy and Ion Processes 80, 1, (1987).

D. R. Bates, Recombination in the normal E and F layers of
the ionosphere, Planet. Space Sci. 36, 55 (1988).

The measured ozone abundance in the atmospheric region
above the 95 km level appears to be greater than can be
accounted for by the classical Chapman source

$$O + O_2 + M \rightarrow O_3 + M. \tag{1}$$

In an attempt to resolve the problem M. Allen suggested the
sequence

$$\left. \begin{array}{l} O + O + M \rightarrow O^*_2 + M \\[2em] O^*_2 + O_2 \rightarrow O_3 + O \end{array} \right\} \tag{2}$$
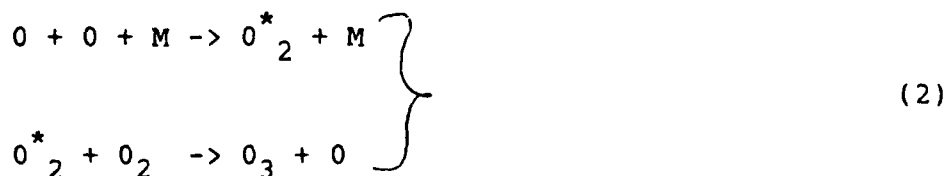
where O^*_2 is O_2 (c $^1\Sigma^-_u$, A' $^3\Delta_u$ or A $^3\Sigma^+_u$).   This
suggestion has been examined (D. R. Bates, Geophys. Res.
Lett. 14, 941, 1987).   Using rocket and other data on the
emission from these three states it has been shown that

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their contribution through sequence (2) is inappreciable but that the weakly bound $O_2(^5\Pi_g)$ may remove some of the discrepancy.

For some years the enhanced abundance of heavy ozone $^{50}O_3$ and $^{49}O_3$ relative to regular ozone $^{48}O_3$ discovered in the stratosphere by mass spectroscopic measurements has been an enigma. A suggested explanation has been put forward (D. R. Bates, Geophys. Res. Lett. 15, 13, 1988). On considering the formation of ozone from atomic and molecular oxygen by termolecular association taking the relevant symmetry numbers into account it has been inferred that an enhancement occurs that is dependent on the ratio $\tau(R)/\tau(D)$ where $\tau(R)$ is the energy randomization lifetime of the activated O_3 complex and $\tau(D)$ is the dissociation lifetime. In order to account for the observed enhancement the value of this ratio would have to be about one third which is within the range that the uncertainties in $\tau(R)$ and $\tau(D)$ allow. Several predictions were made (that the enhancement is an increasing function of the temperature and that there is no effect in the superficially similar case of the formation of carbon dioxide from atomic oxygen and carbon dioxide). The published abstracts (EOS, 69, 307, 1988) of the American geophysical Union April session on heavy ozone indicate that these predictions have since been verified in the laboratory.

The low density limit k_0 to the rate coefficient for the termolecular association of ions and polar molecules has been related through a double integral to an entity z_1 or z_2

that involved only the temperature, the reduced mass of the colliding pair, the polarizability and dipole moment of the neutral and k(exp) [M] where k(exp) is the measured rate coefficient at ambient gas density [M]. The results have been parameterized so that k_0 may easily be found from laboratory data (irrespective of whether or not third order kinetics prevail). A paper describing the work is in course of publication (D. R. Bates, J. Chem. Physics in press 1988).

In recent years a variety of rate coefficients have been calculated for radiative association reactions (A^+ + B -> A^+ B + hν) thought to be important in the chemistry of both dense and diffuse interstellar clouds. In the majority of these calculations radiative association has proceeded via an intermediate complex $A^+ B^*$ which exists in the vibrational quasi-continuum of the ground electronic state and radiates sufficient energy for stabilization in the infra-red via vibrational transitions. However recent experimental work on one important system (CH^+_3 + H_2 -> CH^+_5 + hν) indicates that in order to reconcile theory and experiment the required rate of radiative stabilization must be more than a power of ten greater than can be explained by vibrational transitions. Consequently stabilization via formation of a complex one electronic state followed by a rapid electronic transition to stable vibrational levels of another electronic state must be invoked. If such electronic relaxation is important in one system it may well

be important in a number of systems.   It has been shown (E.
Herbst and D. R. Bates, Astrophys. J. in press 1988) that
the existence of low-lying electronic states of species
produced in radiative association reactions can lead to
enhancements of rate coefficients previously calculated by
factors of 10 to 100.   However the lack of available
information on the positions and transition dipoles of such
excited states makes definite statements on the importance
of this mechanism premature.

A review article on radiative association (D. R. Bates
and E. Herbst in Rate Coefficients in Astrochemistry eds. T.
J. Millar and D. A. Williams, Dordrecht, Reidel 1988) and
another on dissociative recombination of polyatomic ions (D.
R. Bates and E. Herbst, ibid, 1988) have been written.

An investigation on the oxygen nightglow has been begun
(D. R. Bates in Progress in Atmospheric Physics eds. R.
Rodrigo, J. J. Lopez-Moreno, M. Lopez-Puertas and A. Molina:
Reidel 1988).   It has been shown inter alia that the
laboratory values for F(S) the fraction of associations that
enter directly into electronic state S

$$O + O + M \rightarrow O_2(S) + M$$
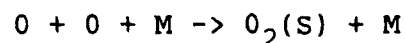
are generally seriously in error due to failute to take all
quenching processes properly into account.

Much of our work on the photoionization of atmospheric
atoms has been on the photoionization of atomic oxygen.
This is proving to be very difficult.   The main problem
being the description of the 2p electron as it is

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important to use different orbitals for the $(2s^2)$ $(2p^3)$ configuration and say the $(2s^2)$ $(2p^2)$ (3s) configuration.

While continuing our work on the photoionization of neutral oxygen we have started new calculations on the photoionisation of neutral nitrogen N I and O II.   On these we are having considerable success.

In both the N I and O II calculations we have used the following target states for the N II and O III $(2s^2)$ $(2p^2)$ ^3P, ^1D, ^1S, (2s) $(2p^3)$ ^5S, ^3D, ^3P, D^2, ^3S, ^1P, $(2p^4)$ ^3P, ^1D, ^1S.   The orbitals for the 1s, 2s, 2p electrons were taken from Clementi and Roetti and 3s, 3p, 3d correlation oribtals were used to obtain reliable energy splittings for the target states.   The target states plus about 20 continuum orbitals were used to generate wave function for N I and O II.   In the calculations presented in Figures 1 - 6 we give only the photoionization cross sections from the $(2p^3)$ $^4S^O$, $^2D^O$ and $^2P^O$ states for N I and O II.   These results were obtained using the dipole length approximation, they differed by less than 5% with the alternative dipole velocity approximation and this is an approximate estimate of the accuracy of the calculated data.
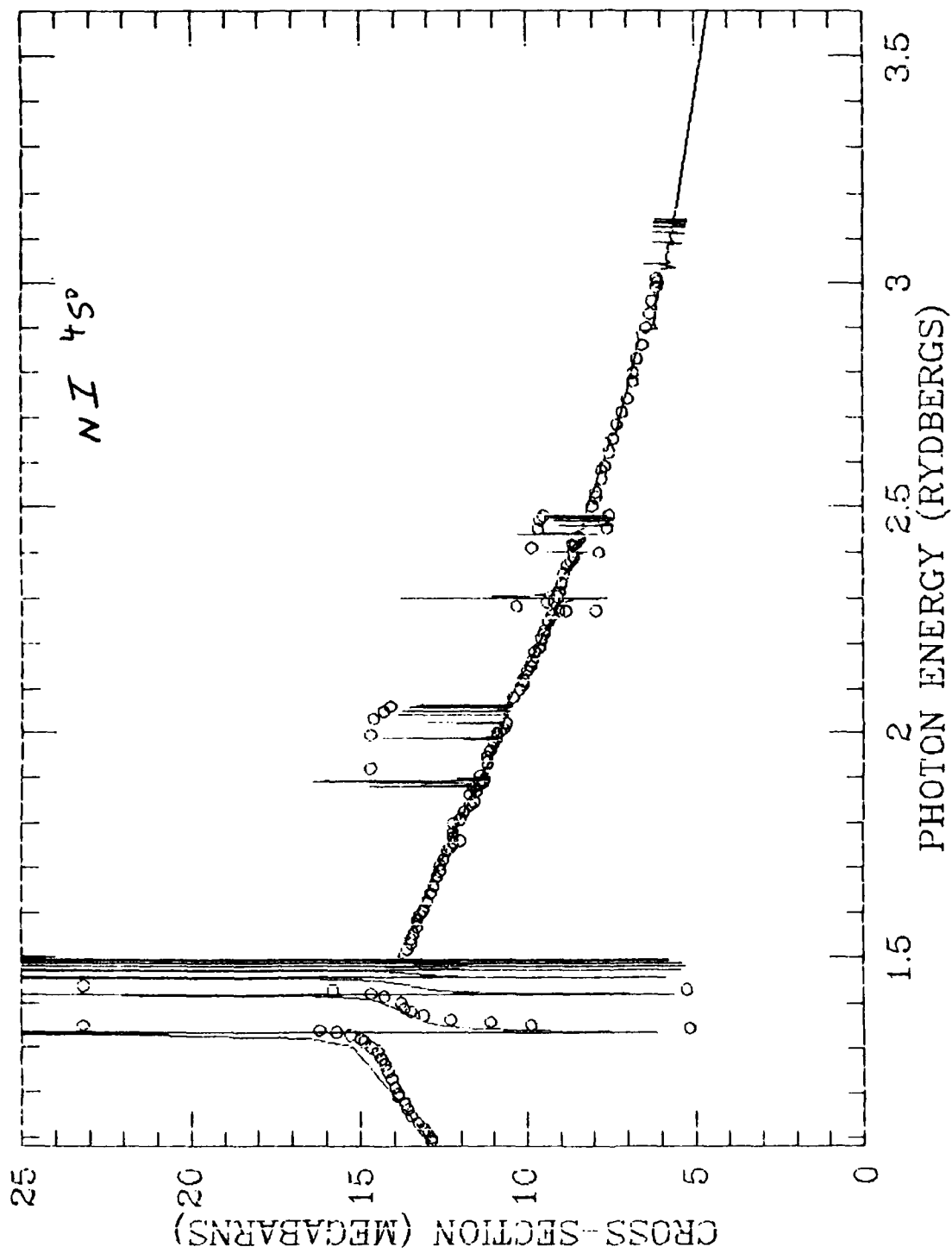
FIGURE 1. Photoionization cross section for the $^4S^0$ state of N I. The OO represent earlier calculations of Le Dourneuf et al.
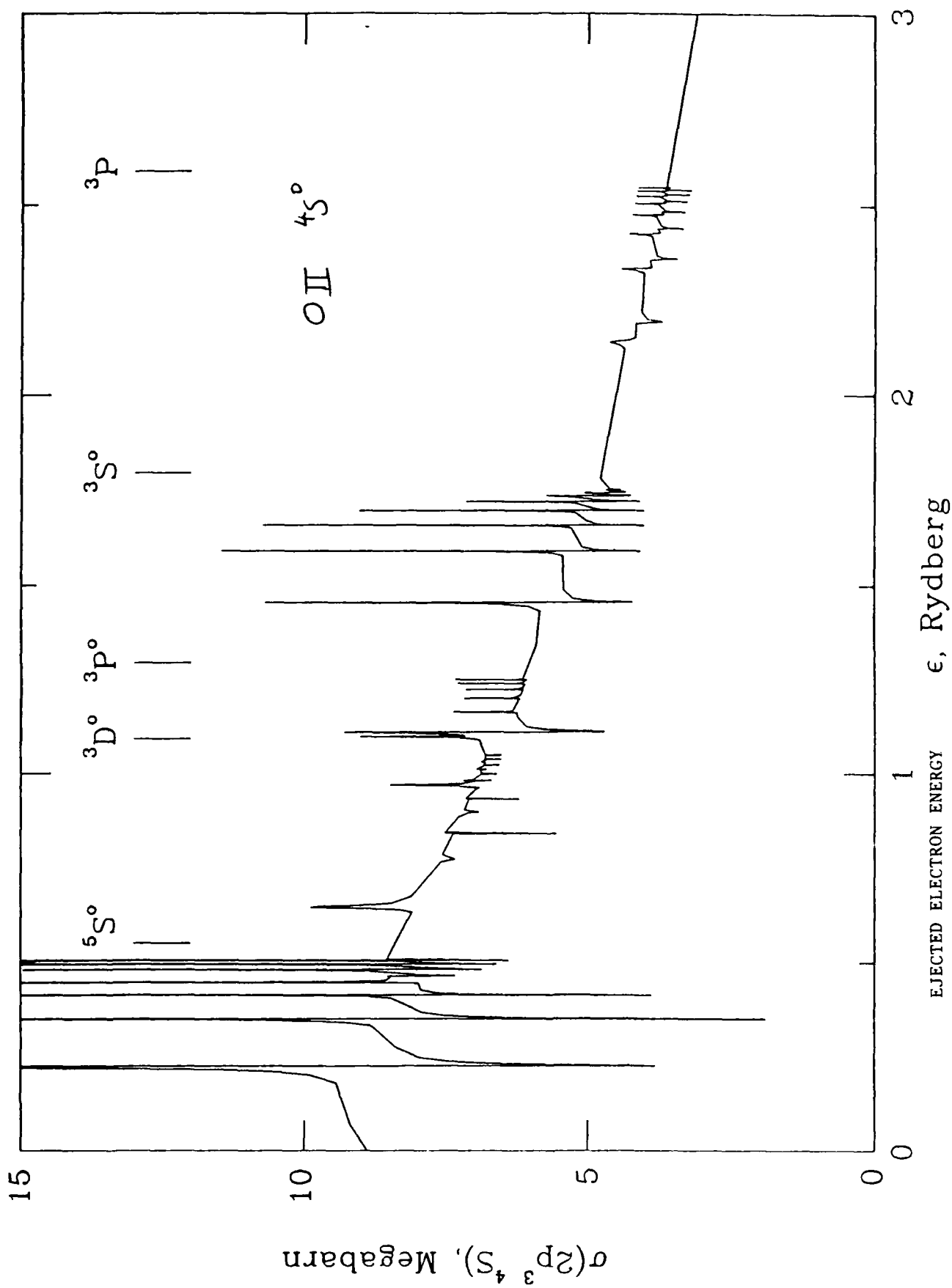
FIGURE 2. Photoionization cross sections for the $^4S^0$ state of O II. The energies of the final ^5S, ^3D, ^3P, ^3S and ^3P states are noted on this figure.
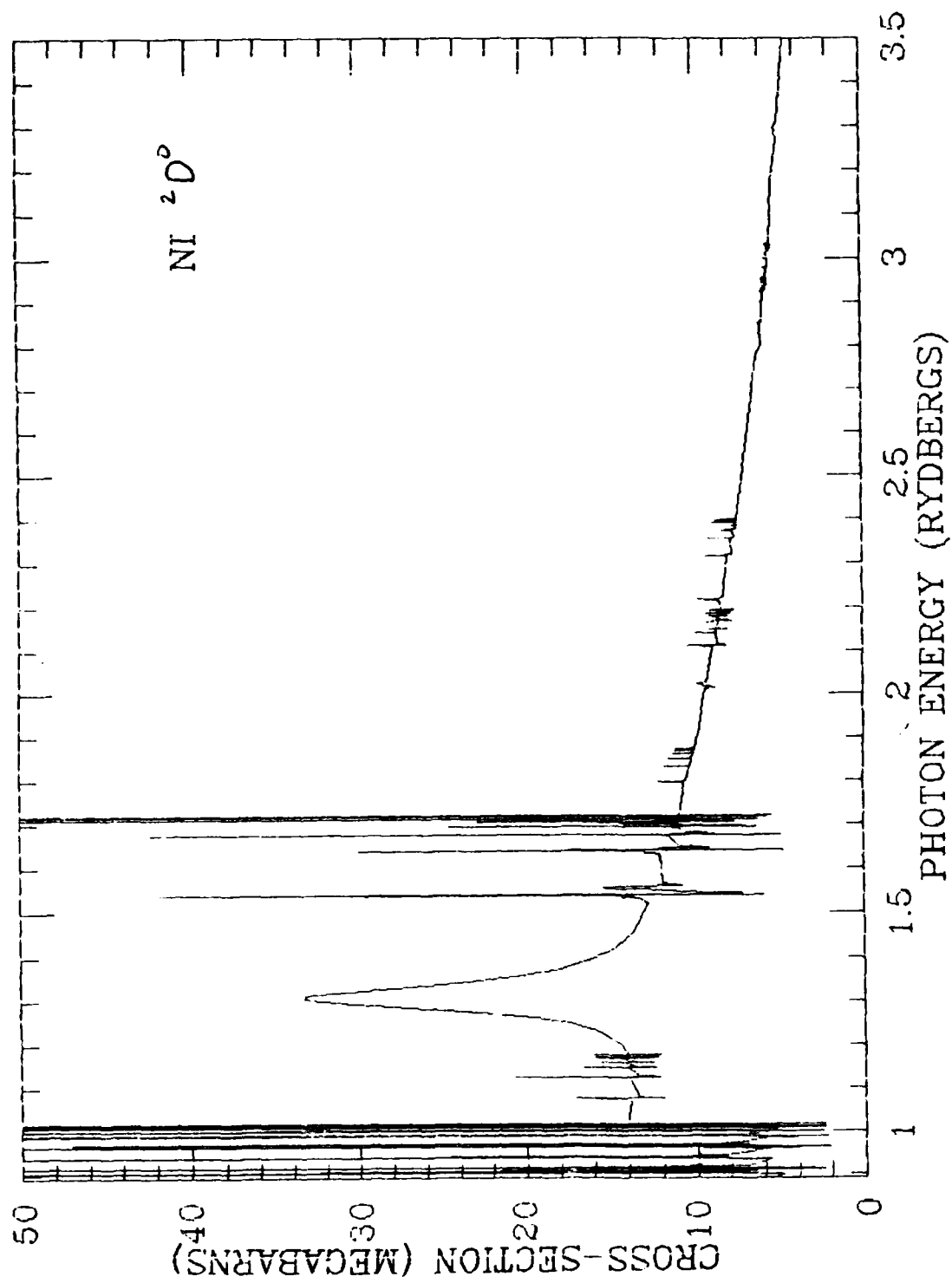
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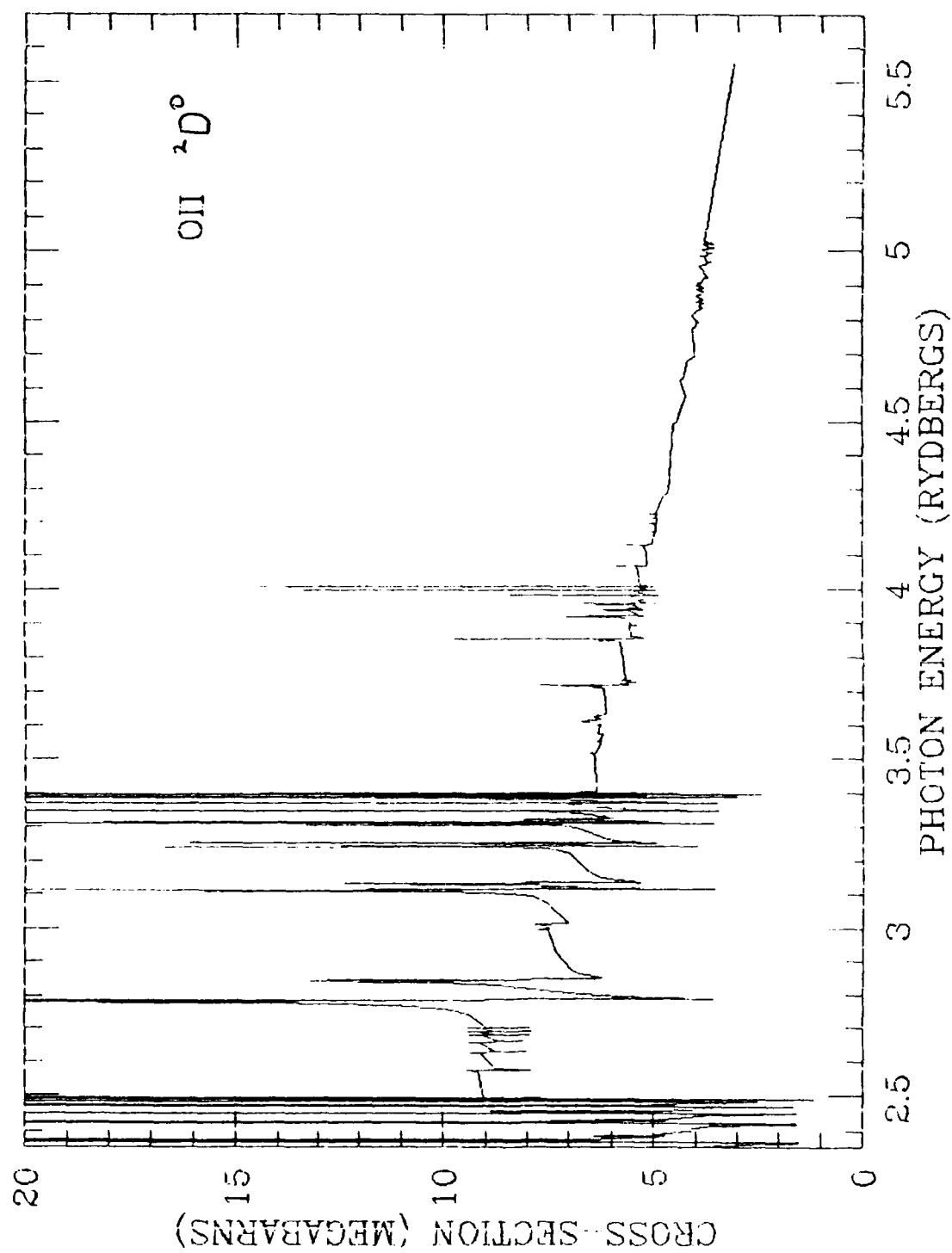FIGURE 3. Photoionization cross sections for the $^2D^0$ state of N I.

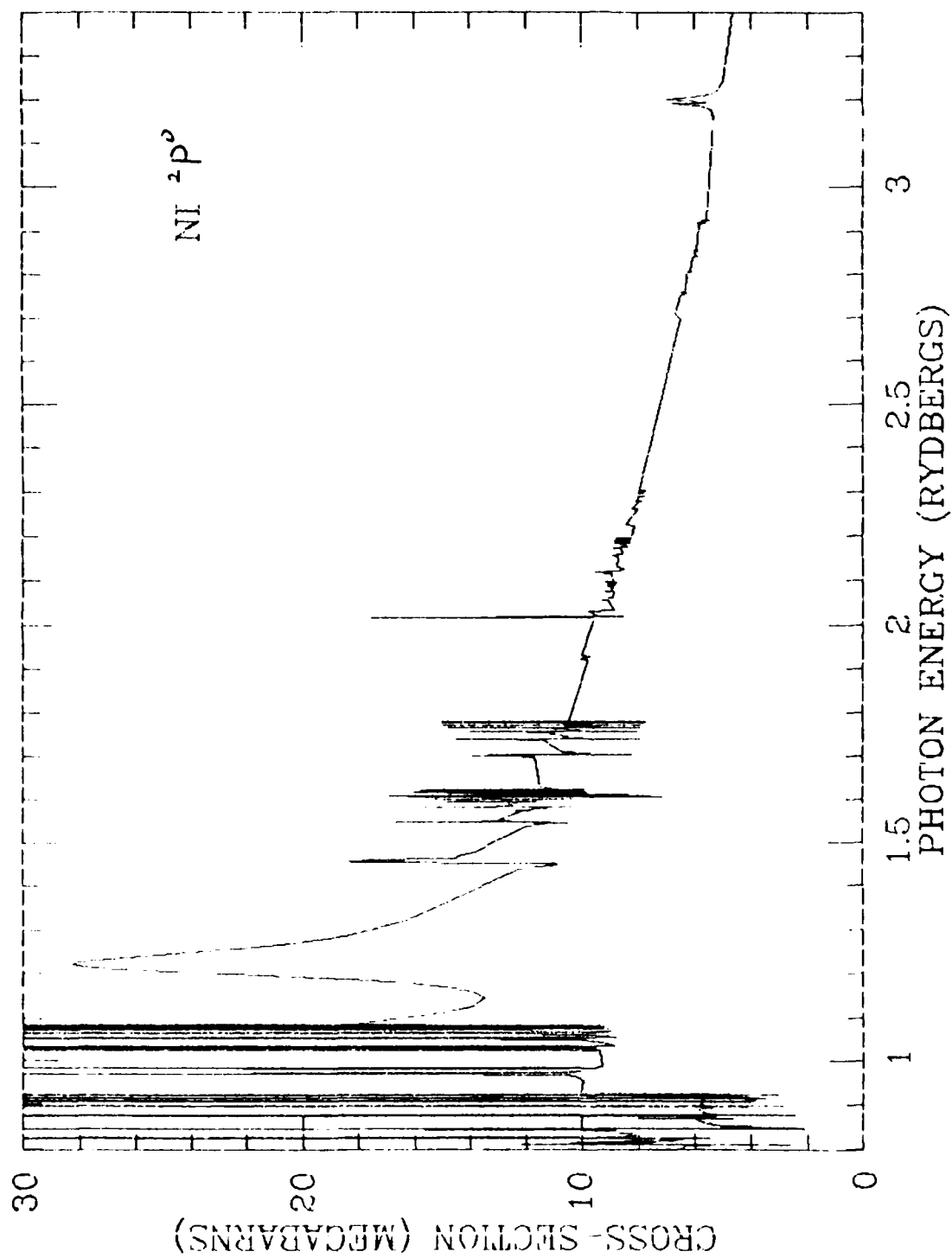FIGURE 4. Photoionization cross sections for the $^2D^0$ state of O II.

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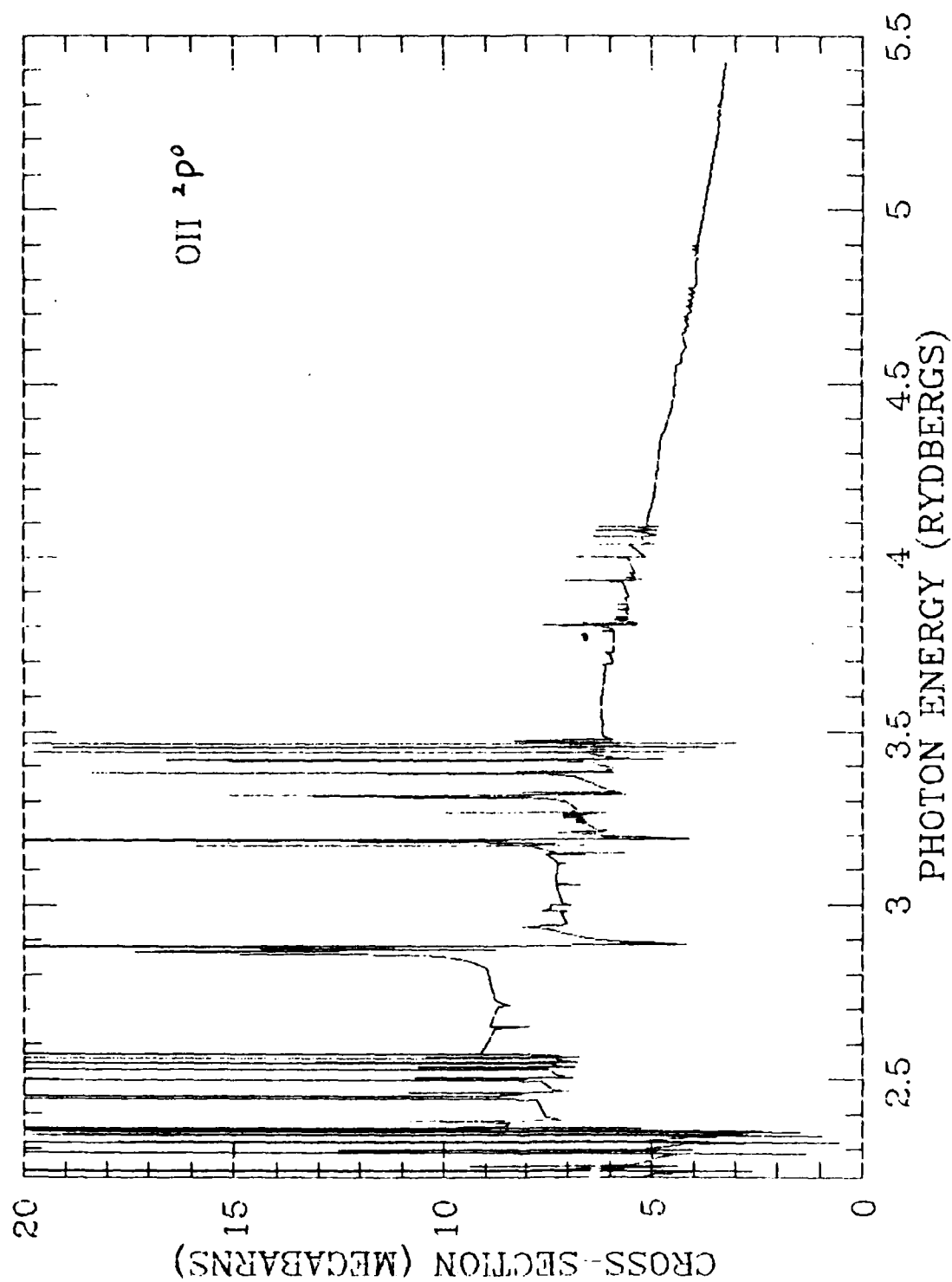FIGURE 5. Photoionization cross sections for the $^2P^0$ state of N I.

FIGURE 6. Photoionization cross sections for the $^2P^0$ state of O II.

List of Publications Generated under Grant

1. Hitting Collisions Between Ions and Linear Molecules Having a Quadrupole
   Moment
   Proceedings of the Royal Society (London), A402, 245-255 (1985)
   By D. R. Bates

2. Deduction of Low Density Limit to Rate of Ter-Molecular Ion-Molecule Association
   from Measurements
   Journal o f Chemical Physics, 84, 6233-6237 (1986)
   by D. R. Bates

3. Termolecular Ion-Molecule Association at Non-Vanishing Ambient Gas Density
   Chemical Physics Letters, 123, 187-190 (1986)
   by D. R. Bates

4. Product of Dissociative Recombination of Polyatomic Ions
   Astrophysical Journal, 306, L45-L47 (1986)
   by D. R. Bates

5. Minor Source of Ozone in the Lower Thermosphere
   Geophysical Research Letters, 14, 941-943 (1987)
   by D. R. Bates

6. Ion-Dipolar Molecule Rate Coefficients
   Astrophysical Journal, 314, 817-821 (1987)
   by W. L. Morgan and D. R. Bates

7. Adiabatic Invariance Treatment of Hitting Collisions Between Ions and Symmetrical Top Dipolar
   Molecules
   Journal of Chemical Physics, 87, 2611-2616 (1987)
   by D. R. Bates and W. M. Morgan

8. Interstellar Cloud Chemistry Revisited
   in *Recent Studies in Atomic and Molecular Processes*, A. E. Kingston, Editor
   Plenum Press, New York *(1987)*
   by D. R. Bates

9. Polyatomic Ions: Bond Energies, Most Stable Isomeric Form and Low Excited States
   International Journal of Mass Spectrometry & Ion Processes, 80, 1-16 (1987)
   by D. R. Bates

10. Suggested Explanation of Heavy Ozone
    Geophysical Research Letters, 15, 13-16 (1988)
    by D. R. Bates

11. Recombination in the Normal E and F Layers of the Ionosphere
    Planetary and Space Science, 36, 55-63 (1988)
    by D. R. Bates

12. Recombination
    in *Electronic and Atomic Collisions*, H. B. Gilbody, W. R. Newell, F. H. Read,
    and A. C. H. Smith, Editors, 3-12 **Elsevier, Amsterdam** *(1988)*
    by D. R. Bates

13. Radiative Association *via* Excited Electronic States: Model Calculations
    Astrophysical Journal, **329**, *410-417 (1988)*
    by E. Herbst and D. R. Bates

14. Radiative Association
    in *Rate Coefficients in Astrochemistry,* T. J. Millar and D. A. Williams, Editors.
    Reidel, Dordrecht *(1988)*
    by D. R. Bates and E. Herbst

15. Deduction of Low Density Limit to Rate Coefficient for Tertiary Association of Ions
    and Polar Molecules from Measurements
    Journal of Chemimcal Physics, **89**, *192-196 (1988)*
    by D. R. Bates

16. Oxygen Nightglow
    in *Progress in Atmospheric Physics,* R. Rodrigo, J. J. Lopez-Moreno, M. Lopez-Puertas,
    and A. Molina, Editors, **Reidel, Dordrecht** *(1988)*
    by D. R. Bates

17. Dissociative Recombination of Polyatomic Molecules
    in *Astrochemistry,* T. J. Millar and D. A. Williams, Editors. **Reidel, Dordrecht** *(1988)*
    by E. Herbst and D. R. Bates