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**THEORETICAL STUDIES OF ATOMIC AND MOLECULAR
PROCESSES IMPORTANT IN SPACE EXPERIMENTS**

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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 (^{4.0} SO, ^{2.0} CDL, and ^{2.0} PL) and on the photoionization of NI (^{4.0} SO, ^{2.0} DO, and ^{2.0} PO). 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 kinetics 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).

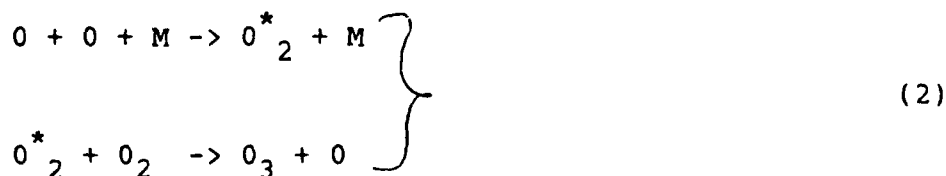
D. R. Bates, Polyatomic ions: bond energies, most stable isometric form and low excited states. Int. J. Mass Spectroscopy and Ion Processes 80, 1, (1987).

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



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



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

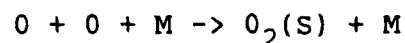
that involved only the temperature, the reduced mass of the colliding pair, the polarizability and dipole moment of the neutral and $k(\text{exp}) [M]$ where $k(\text{exp})$ is the measured rate coefficient at ambient gas density $[M]$. The results have been parameterized so that k_0 may easily be found 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 ($A^+ + B \rightarrow A^+ B + h\nu$) 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 ($CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$) 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



are generally seriously in error due to failure 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

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 orbitals 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.

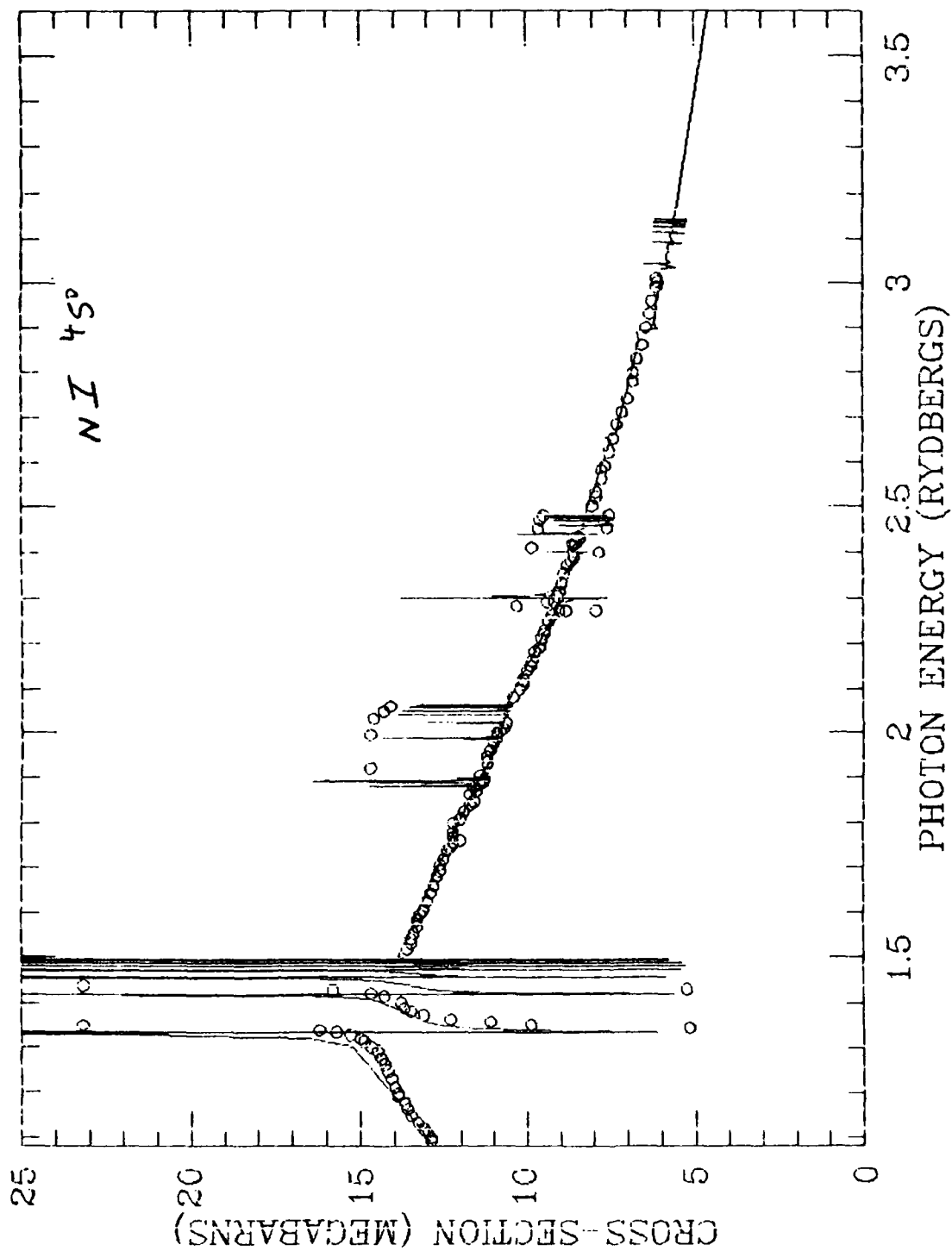


FIGURE 1. Photoionization cross section for the $4S^0$ state of N I. The 00 represent earlier calculations of Le Dourneuf et al.

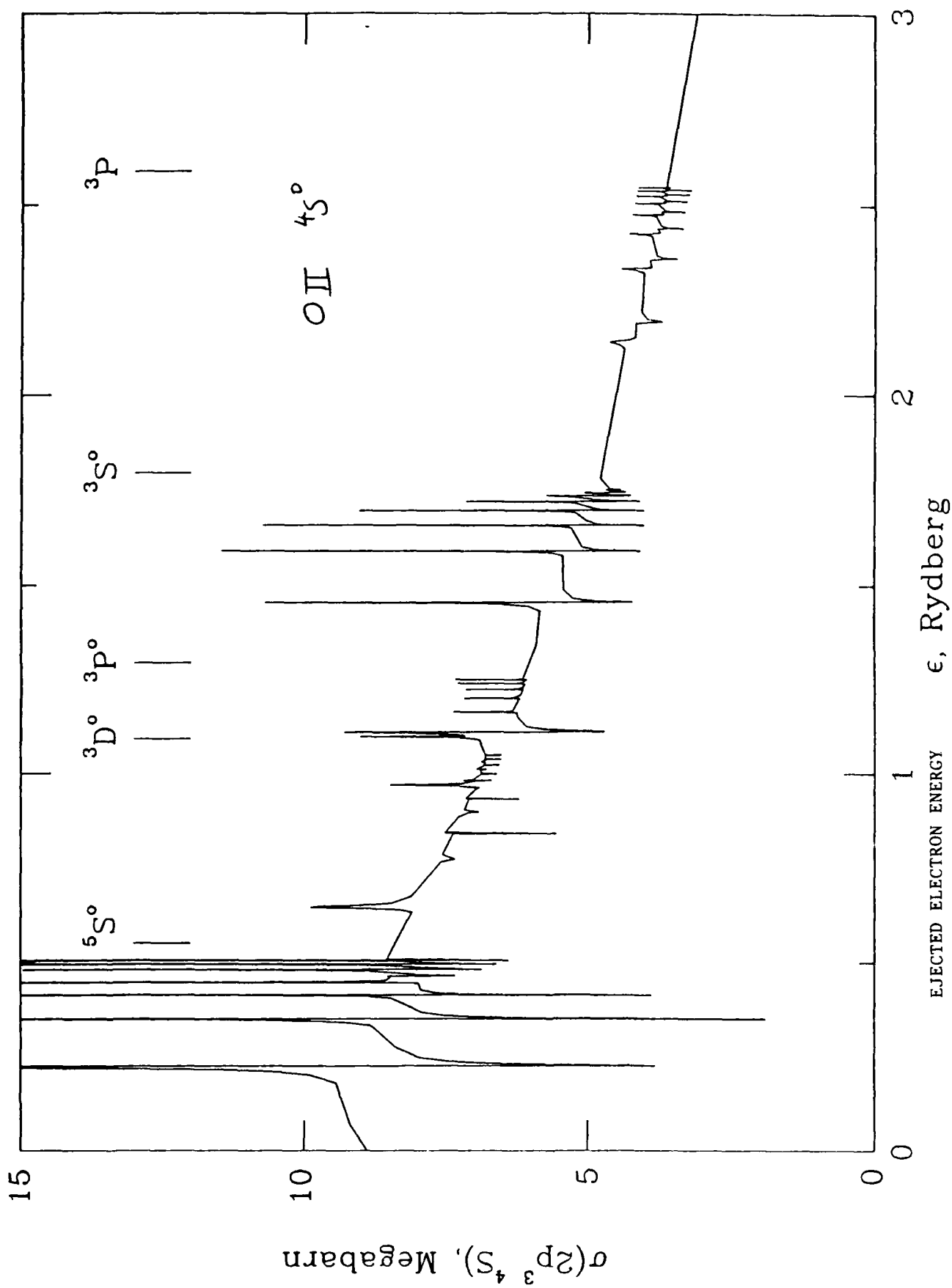


FIGURE 2. Photoionization cross sections for the $4S^0$ state of O II. The energies of the final $5S$, $3D$, $3P$, $3S$ and $3P$ states are noted on this figure.

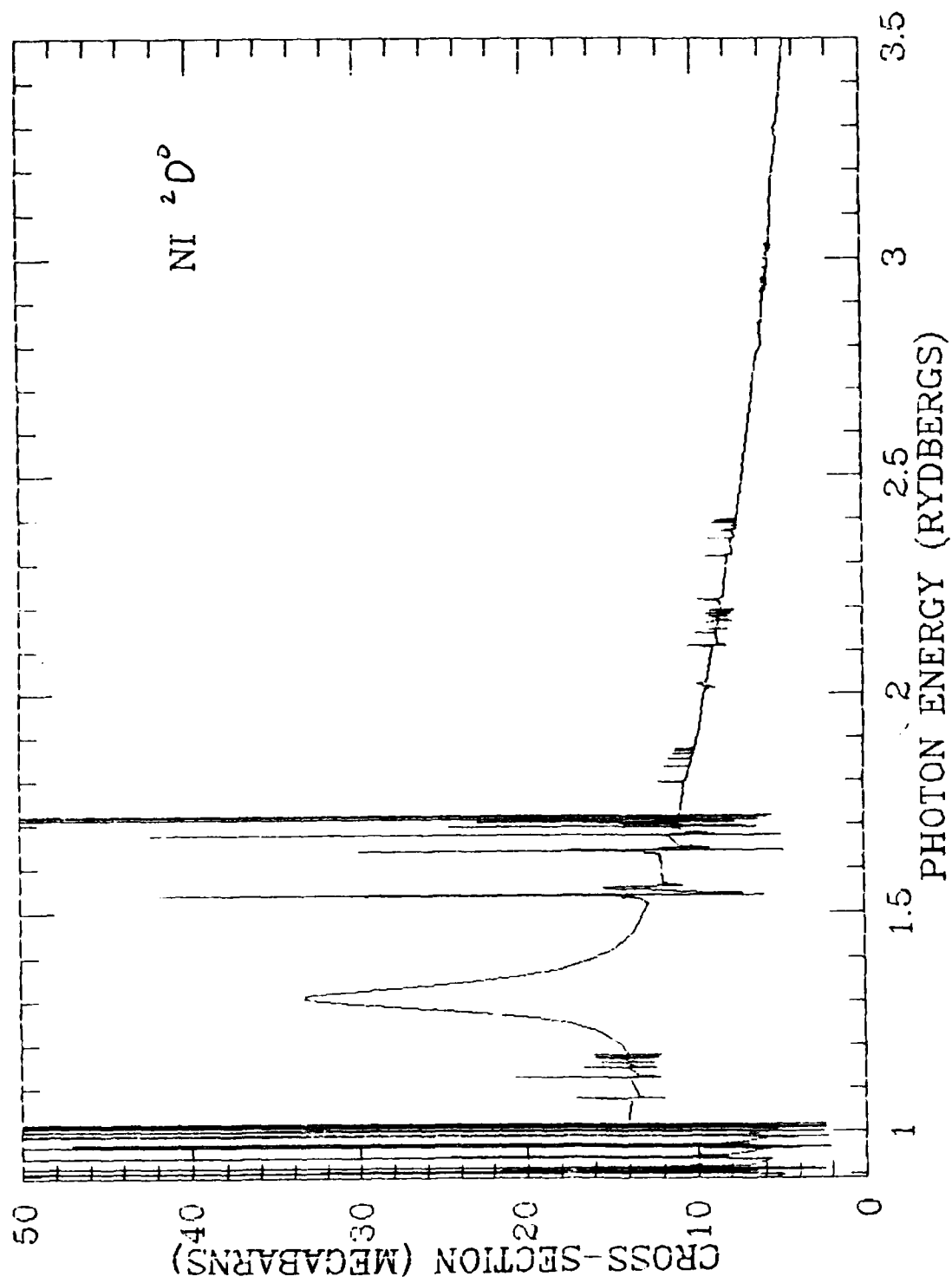


FIGURE 3. Photoionization cross sections for the $2D^0$ state of Ni.

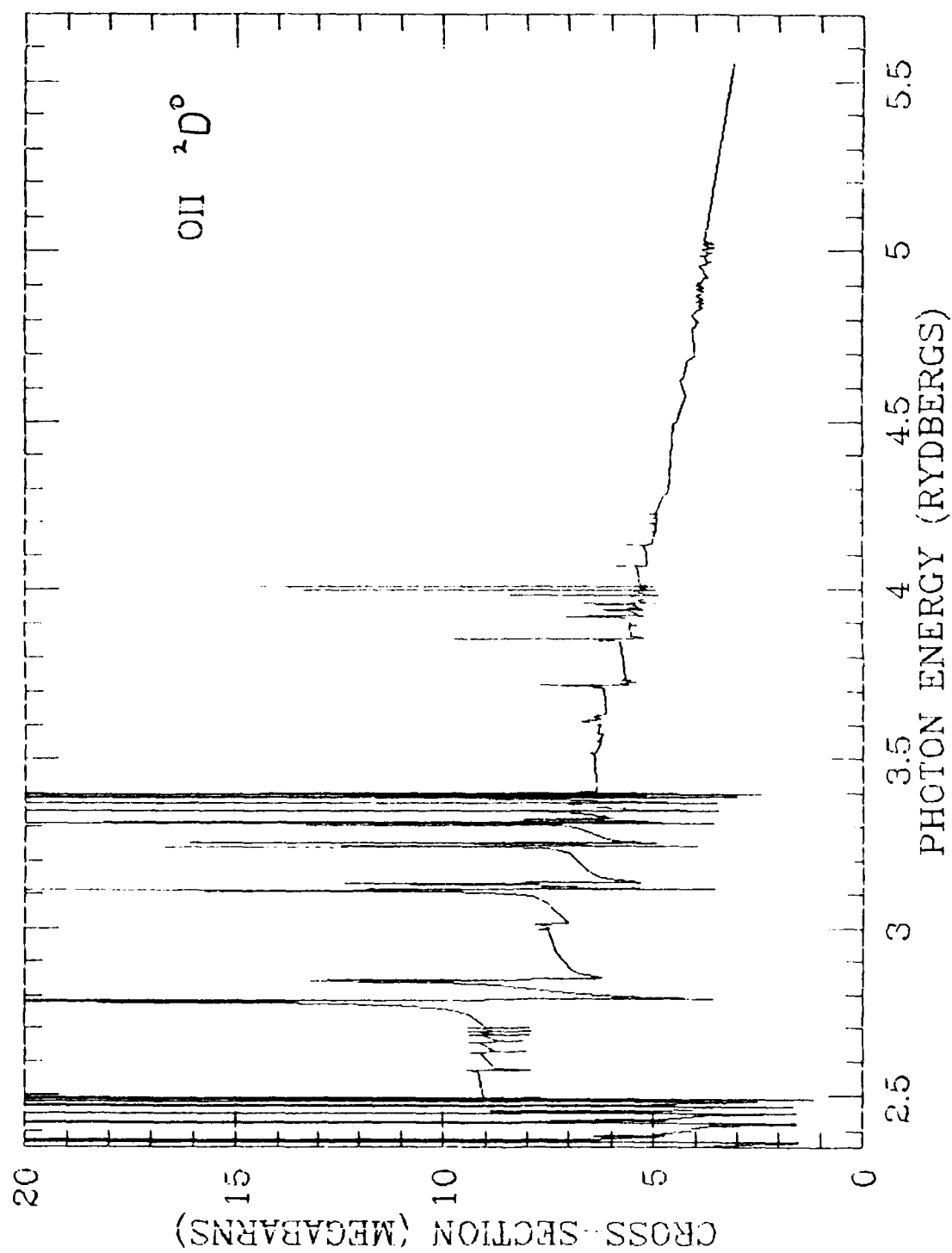


FIGURE 4. Photoionization cross sections for the $2D^0$ state of O II.

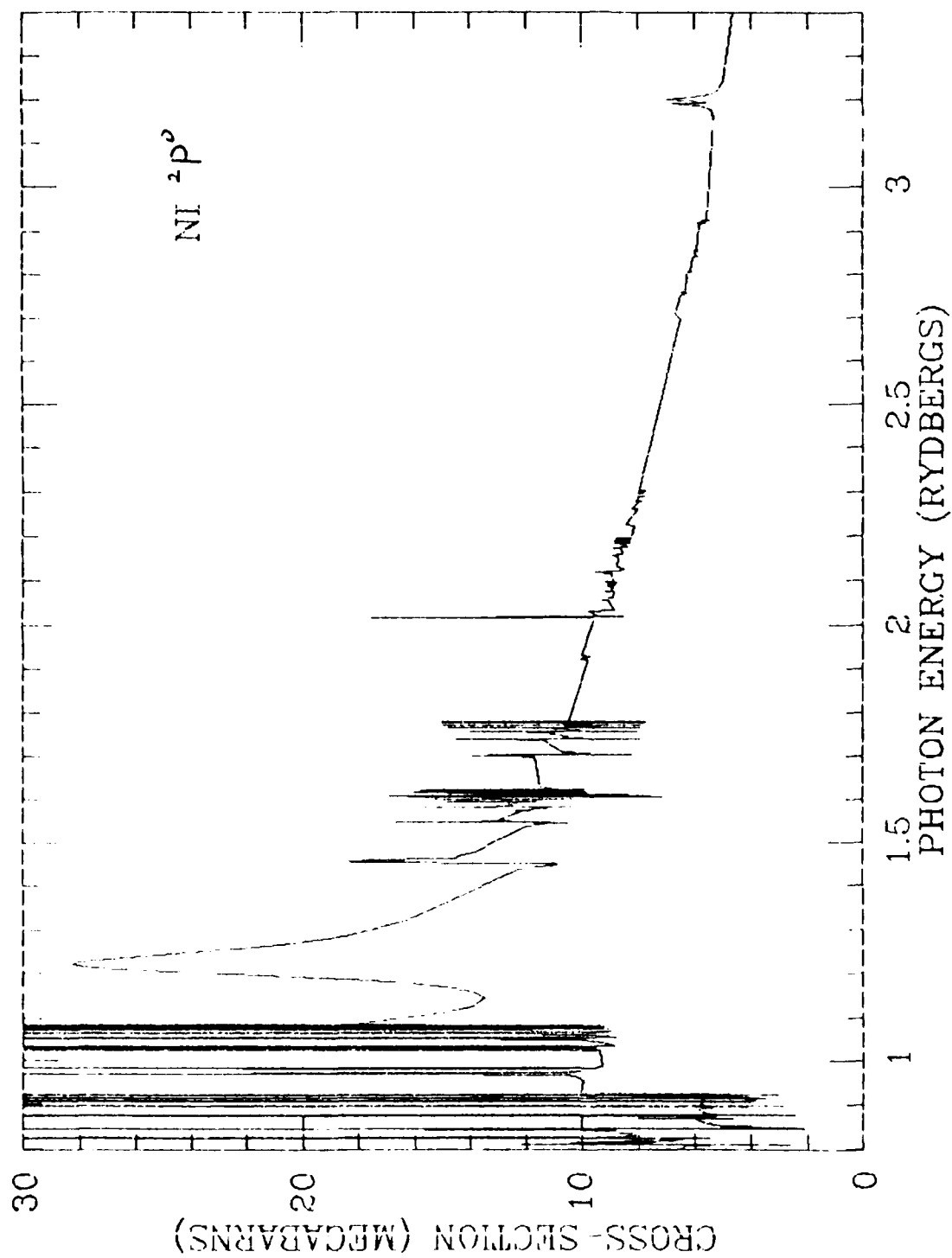


FIGURE 5. Photoionization cross sections for the $2p^0$ state of N I.

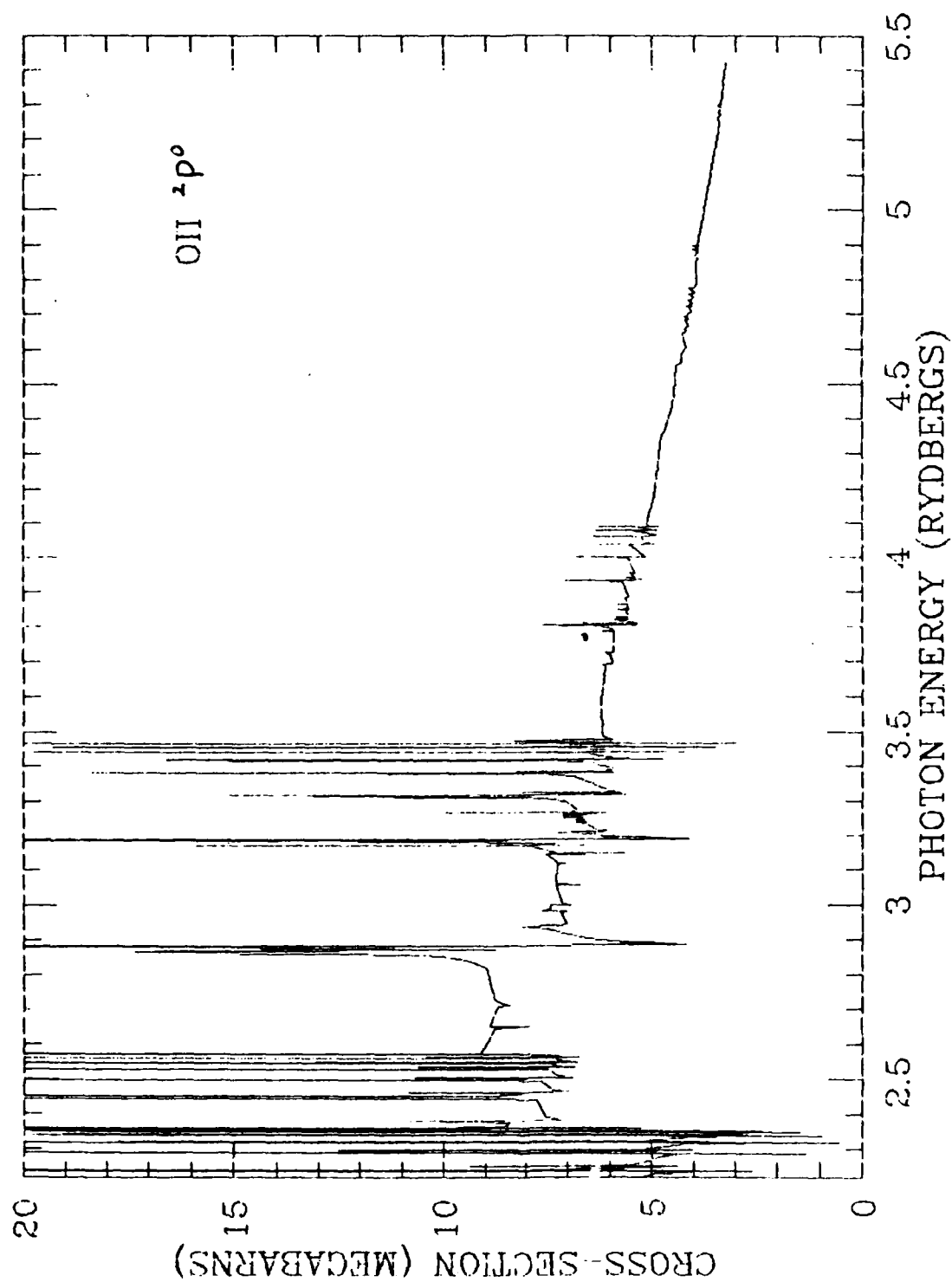


FIGURE 6. Photoionization cross sections for the $2p^0$ state of $O II$.

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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 of 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
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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)
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11. Recombination in the Normal E and F Layers of the Ionosphere
Planetary and Space Science, **36**, 55-63 (1988)
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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
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15. Deduction of Low Density Limit to Rate Coefficient for Tertiary Association of Ions
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in *Progress in Atmospheric Physics*, R. Rodrigo, J. J. Lopez-Moreno, M. Lopez-Puertas,
and A. Molina, Editors, **Reidel, Dordrecht (1988)**
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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