

COLLISIONAL QUENCHING OF O(¹D) BY O(³P)

J.-H. YEE

Space Physics Research Laboratory, University of Michigan, Ann Arbor, MI 48109, U.S.A.

STEVEN L. GUBERMAN

Institute for Scientific Research, 33 Bedford Street, Lexington, MA 02173, U.S.A.

and

A. DALGARNO

Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, U.S.A.

(Received 13 December 1989)

Abstract—Metastable O(¹D) atoms may be quenched in collisions with ground state O(³P) atoms by transitions in the avoided crossing regions of the three lowest ³Π_g states of O₂ of which the lowest separates to O(³P) + O(³P) and the two upper to O(³P) + O(¹D). Quantal calculations of the adiabatic potential energy curves of the ³Π_g states are carried out with particular attention to an avoided crossing region in the lowest two states around a nuclear separation of 3.2a₀. Diabatic potential matrix elements are constructed from the adiabatic curves by imposing the requirement that they be smooth everywhere. A multi-state diabatic formulation is used to describe the scattering and the cross-sections for the collision-induced quenching of O(¹D) atoms are calculated.

The rate coefficient for the quenching of O(¹D) atoms by O(³P) atoms is obtained as a function of temperature. At 1000 K, the value is 1.0 × 10⁻¹¹ cm³ s⁻¹, accurate probably to a factor of two. The theoretical rate coefficient is consistent with the empirical value inferred from upper atmosphere data.

1. INTRODUCTION

Analysis of the altitude profile of the emission at 630 nm of the red line of atomic oxygen suggested that the O(¹D) atoms are quenched by collisions with O(³P) atoms (Abreu *et al.*, 1986). The quenching occurs most probably by transitions between ³Π_g states of O₂. The adiabatic potential energy curves (Saxon and Liu, 1977; Guberman, 1983) indicate the existence of an avoided crossing between the two lowest ³Π_g states near 3.2a₀, at which transitions may be probable at low collision energies. By constructing diabatic representations of the potential energy curves, diabatic coupling matrix elements may be derived. A diabatic formulation of scattering theory (Heil *et al.*, 1981) may then be used to determine the quenching cross-sections.

To carry out a precise construction of the diabatic matrix elements, data points are needed at small intervals. We calculated them for the two lowest ³Π_g states, following the procedures of Guberman (1977, 1983). Additional calculations on the third ³Π_g state, which also separates to O(³P) + O(¹D) did not indicate the presence of any further avoided crossings and we omitted the third state from the scattering formulation. However, the adiabatic potential energy curves of Saxon and Liu (1977) indicate not only the avoided

crossing between the lower two ³Π_g states, but also a weak avoided crossing with the third state. Accordingly in the scattering calculations based on the curves of Saxon and Liu (1977), we employed a three-state formation.

2. ADIABATIC POTENTIAL ENERGY CURVES

The adiabatic wave functions and potential energy curves of the two lowest ³Π_g states of O₂ were obtained using a [3s, 2p, 1d] contracted Gaussian basis set and orbitals determined in earlier multiconfiguration self-consistent field (MCSCF) calculations on the ground state of O₂ (Heil *et al.*, 1981). The ground state MCSCF calculations employed the 14 molecular spin eigenfunctions that result from a full CI in the valence space with the restriction that the 1σ and 2σ orbitals remain fully occupied. With the ground state orbitals, first order configuration interaction (CI) wave functions were determined for the two ³Π_g states. The CI wave functions were generated from a reference set consisting of the 10 configurations which result from a full CI prescription in the valence space of ³Π_g symmetry with the restriction that the 1σ and 2σ orbitals remain fully occupied. In the CI calculation only the 1σ orbitals were so restricted and excitations were

taken from each of the reference configurations to the full virtual space of orbitals formed from the basis set. The 3σ combination formed from the 3d basis functions was excluded as were the 3d δ basis functions. All single and double excitations were taken with the restriction that at most a single electron was allowed to occupy a virtual orbital. This procedure generated a wave function with 784 different orbital occupancies and 2440 spin eigenfunctions.

The calculated CI energies are given in Table I and illustrated in Fig. 1. There occurs an avoided crossing in the region between $3.15a_0$ and $3.35a_0$. The lower ${}^3\Pi_g$ state, ${}^3\Pi_g(1)$, has a shallow well that is not deep enough to support bound vibrational levels. The upper, ${}^3\Pi_g(2)$, has a dissociation energy of 0.190 eV and an equilibrium separation of $3.3052a_0$. It may support several vibrational levels. Their locations may be severely perturbed by the interaction with the ${}^3\Pi_g(1)$ state. The calculations of Saxon and Liu (1977)

for the ${}^3\Pi_g(2)$ state yielded a dissociation energy of 0.327 eV and an equilibrium internuclear distance of $3.2522a_0$. The two sets of calculations are of comparable quality. In our scattering calculations we used both sets of potential energy curves; because we obtained curves on a grid of $0.05a_0$ in the avoided crossing region, the numerical procedures for constructing the diabatic representation can be carried through more reliably than with the curves of Saxon and Liu (1977), who presented data on a grid of $0.2a_0$.

3. DIABATIC REPRESENTATION

In a two-state representation $V_{11}(R)$ and $V_{22}(R)$ can be constructed by requiring that they vary smoothly everywhere, crossing each other at some nuclear separation in the avoided crossing region of the adiabatic curves. Outside the crossing region, they merge with the adiabatic curves. We determined them by using spline fits that match the potential points outside the crossing region. The crossing regions are narrow and this interpolation procedure should be reliable.

The matrix element $V_{12}(R)$ coupling the two diabatic states can then be determined by identifying the eigenvalues

$$E_{1,2} = \frac{(V_{11} + V_{22})}{2} + \left\{ \left(\frac{V_{11} - V_{22}}{2} \right)^2 + V_{12}^2 \right\}^{1/2} \quad (1)$$

of the diabatic potential matrix

$$\mathbf{V} = \begin{pmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{pmatrix} \quad (2)$$

with the adiabatic potential energy curves.

We reproduce in Fig. 2 the elements of the diabatic matrix for the two ${}^3\Pi_g$ states constructed in the crossing region from the adiabatic potential energy curves given in Table I. The values are relative to the asymptotic energy of the lower state taken as zero.

We have carried out a similar construction of the diabatic matrix for the three ${}^3\Pi_g$ states from the ${}^3\Pi_g(1)$, ${}^3\Pi_g(2)$ and ${}^3\Pi_g(3)$ diabatic potential energy curves of Saxon and Liu (1977). The crossing region of the first and second potential energy curves is distinct from that of the second and third and each of $V_{12}(R)$ and $V_{23}(R)$ may be determined independently of the other. The interaction matrix element $V_{13}(R)$ may be put equal to zero. We reproduce in Fig. 3 the derived diabatic potential matrix elements as functions of the nuclear separation. The lowest state separates to $\text{O}({}^3\text{P}) + \text{O}({}^3\text{P})$ and the upper two to $\text{O}({}^3\text{P}) + \text{O}({}^1\text{D})$.

For the scattering calculations at low energies, the potential energy curves are needed out to large

TABLE I. CALCULATED ENERGIES OF THE TWO LOWEST ${}^3\Pi_g$ VALENCE STATES OF O_2 IN HARTREES (1h = 27.2 eV)*

$R(a_0)$	Energy ${}^3\Pi_g(1)$	${}^3\Pi_g(2)$
1.80	-0.156232	+0.133332
1.85	-0.229708	+0.102353
1.90	-0.291992	+0.080531
1.95	-0.344707	+0.066241
2.0	-0.389242	+0.057841
2.1	-0.458363	-0.023266
2.2	-0.506966	-0.142078
2.2819	-0.535445	-0.225524
2.4	-0.563453	-0.323888
2.5	-0.578440	-0.389330
2.6	-0.587810	-0.441247
2.7	-0.593212	-0.482172
2.8	-0.595878	-0.514318
2.9	-0.596733	-0.539563
3.0	-0.596484	-0.559456
3.1	-0.595700	-0.575196
3.15	-0.595315	-0.581731
3.2	-0.595245	-0.587247
3.25	-0.596562	-0.590778
3.3	-0.600097	-0.591582
3.35	-0.604206	-0.591376
3.4	-0.608161	-0.590948
3.5	-0.615229	-0.589985
3.6	-0.621207	-0.589082
3.7	-0.626246	-0.588291
3.8	-0.630492	-0.587615
3.9	-0.634069	-0.587048
4.0	-0.637080	-0.586580
4.5	-0.646196	-0.585286
5.0	-0.649753	-0.584829
5.5	-0.651040	-0.584647
6.0	-0.651464	-0.584619
15.0	-0.651490	-0.584619

* To obtain the total energies, add -149 to all the entries.

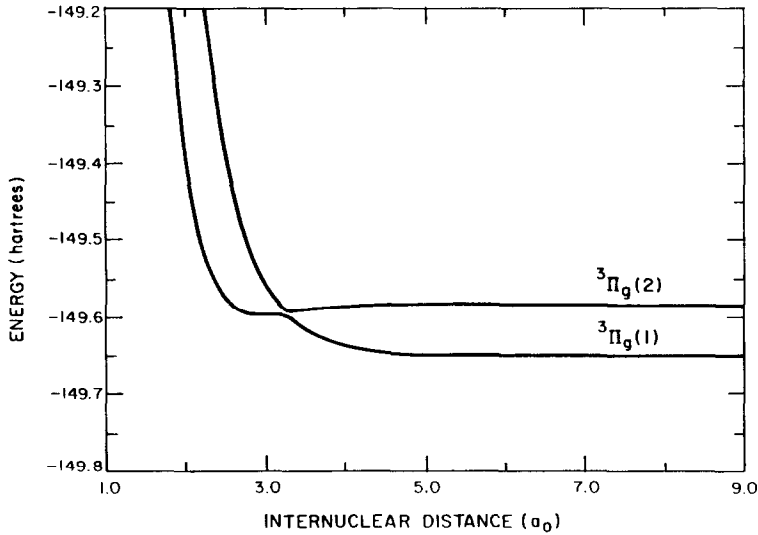
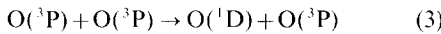


FIG. 1. CALCULATED ADIABATIC POTENTIAL ENERGY CURVES OF THE LOWEST TWO ³Π_g STATES OF O₂.

internuclear distances, where they have the form $V(R) \sim aR^{-5} - bR^{-6}$ (Knipp, 1939; Chang, 1967; Umanskij and Nikitin, 1969). The values of a and b that we adopted for the three states are given in Table 2.

4. SCATTERING THEORY

The excitation cross-section for the process



is given for an energy of relative motion E by

$$\sigma_{1j}(E) = \sum_{j=3,3} \sigma_{1j}(E), \quad (4)$$

where

$$\sigma_{1j}(E) = \frac{4\pi}{k^2} g_1 \sum_j (2J+1) |S'_{1j}|^2, \quad (5)$$

$g_1 = 6/81$ is the probability of approach along the lowest ³Π_g state, $k^2 = 2\mu E/h^2$ where μ is the reduced

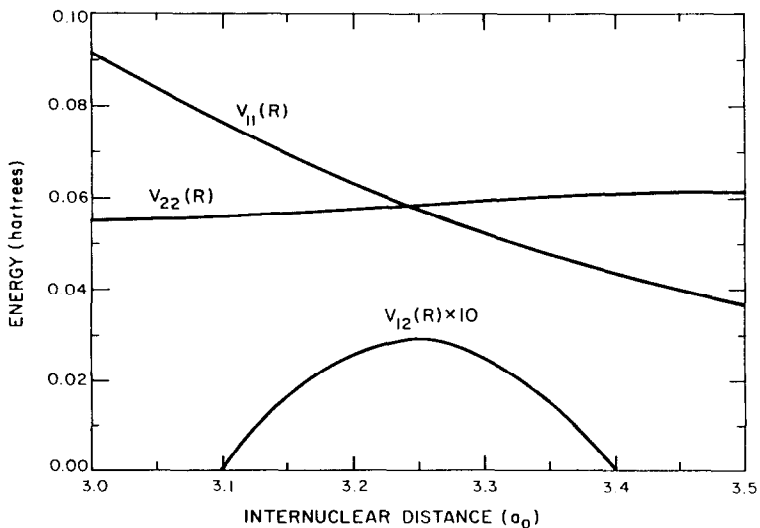


FIG. 2. THE DIABATIC POTENTIAL ENERGY MATRIX ELEMENTS CORRESPONDING TO THE ADIABATIC CURVES OF FIG. 1.

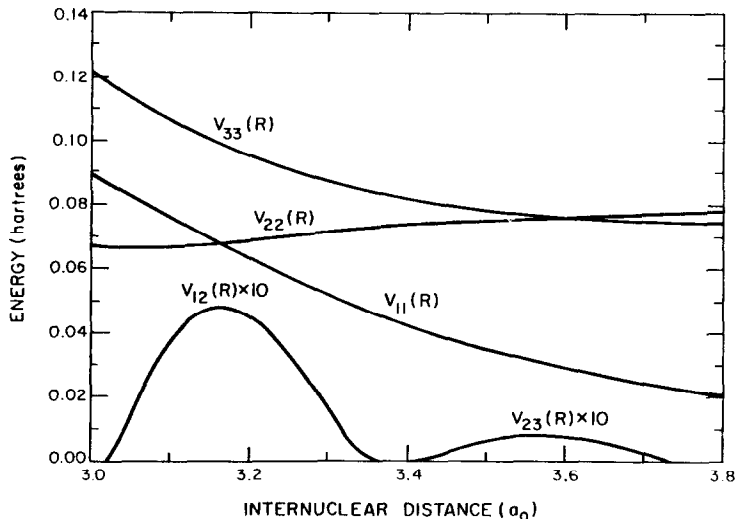


FIG. 3. THE DIABATIC POTENTIAL ENERGY MATRIX ELEMENTS CORRESPONDING TO THE ADIABATIC CURVES OF THE THREE LOWEST ${}^3\Pi_g$ STATES OF O_2 CALCULATED BY SAXON AND LIU (1977).

mass of the colliding system, J is the nuclear rotational angular momentum quantum number and S'_{1j} is the scattering matrix element connecting the initial state 1 to the final states $j = 2$ and 3, j labelling the two final ${}^3\Pi_g$ states that separate to $O({}^3P) + O({}^1D)$.

The cross-section for the reverse reaction, the quenching of $O({}^1D)$ by $O({}^3P)$, is given by

$$\sigma_{j1}(E') = \sum_{j=2,3} \sigma_{j1}(E'). \quad (6)$$

From detailed balance arguments,

$$g_j k'^2 \sigma_{j1}(E') = g_1 k^2 \sigma_{1j}(E), \quad (7)$$

where $E - E'$ is the internal energy change 1.94 eV, $k'^2 = 2\mu E'/\hbar^2$ and $g_j = 1/15$ is the probability of approach along either of the two ${}^3\Pi_g$ states formed by the approach of $O({}^3P)$ and $O({}^1D)$ atoms.

The scattering matrix elements S'_{1j} may be determined from the asymptotic behavior of the regular solutions of the coupled partial wave equations (Heil *et al.*, 1981)

$$\begin{aligned} \frac{d^2}{dR^2} F'_1(R) + \left\{ \frac{2\mu}{\hbar^2} (E - V_{11}(R)) - \frac{J(J+1)}{R^2} \right\} F'_1(R) \\ - \frac{2\mu}{\hbar^2} V_{12}(R) F'_2(R) - \frac{2\mu}{\hbar^2} V_{13}(R) F'_3(R) = 0 \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{d^2}{dR^2} F'_2(R) + \left\{ \frac{2\mu}{\hbar^2} (E - V_{22}(R)) - \frac{J(J+1)}{R^2} \right\} F'_2(R) \\ - \frac{2\mu}{\hbar^2} V_{21}(R) F'_1(R) - \frac{2\mu}{\hbar^2} V_{23}(R) F'_3(R) = 0 \end{aligned} \quad (9)$$

$$\begin{aligned} \frac{d^2}{dR^2} F'_3(R) + \left\{ \frac{2\mu}{\hbar^2} (E - V_{33}(R)) - \frac{J(J+1)}{R^2} \right\} F'_3(R) \\ - \frac{2\mu}{\hbar^2} V_{31}(R) F'_1(R) - \frac{2\mu}{\hbar^2} V_{32}(R) F'_2(R) = 0. \end{aligned} \quad (10)$$

For the two-state case, $F'_3(R) = 0$. The solutions of equations (8)–(10) are asymptotically

$$\begin{aligned} F'_j(R) \sim -k^{-1/2} \{ \exp[-i(kR - 1/2J\pi)] \\ - S'_{1j} \exp[i(kR - 1/2J\pi)] \} \end{aligned} \quad (11)$$

and

$$F'_j(R) \sim -k'^{-1/2} S'_{1j} \exp[i(k'R - 1/2J\pi)]. \quad (12)$$

We solved the partial wave equations using a modified version (Bienstock *et al.*, 1984) of Johnson's log-derivative method (Johnson, 1973).

TABLE 2. COEFFICIENTS a AND b ADOPTED FOR THE LONG-RANGE POTENTIALS $V(R) \sim aR^{-3} - bR^{-6}$

	${}^3\Pi_g(1)$	${}^3\Pi_g(2)$	${}^3\Pi_g(3)$
a	0.0	3.9265	-0.0764
b	17.57	16.2	16.2

5. RESULTS

The cross-sections obtained using the diabatic matrix elements illustrated in Figs 2 and 3 are presented in Fig. 4 for energies of relative motion up to 5 eV. They differ significantly very close to threshold, come into fair agreement at intermediate energies and appear to be slowly diverging from each other at higher energies. In the energy region near 0.1 eV, relevant to atmospheric quenching, the differences are not more than 25%.

The quenching rate coefficients corresponding to the two calculations of the cross-sections may be represented as functions of temperature T by

$$k(T) = (7.66 \cdot 10^{-12} + 2.13 \cdot 10^{-13} T^{1/2} - 1.84 \cdot 10^{-15} T) \text{ cm}^3 \text{ s}^{-1}, \quad (13)$$

calculated from the potential energy curves of Saxon and Liu (1977) and by

$$k(T) = (2.13 \cdot 10^{-12} + 2.60 \cdot 10^{-13} T^{1/2} - 2.24 \cdot 10^{-15} T) \text{ cm}^3 \text{ s}^{-1}, \quad (14)$$

calculated from the ³Π_g curves of Table 1.

At 1000 K, the values of $k(T)$ corresponding to expressions (13) and (14) are 1.3×10^{-11} and $8.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. The rate coefficients are sensitive to the potential energy curves and particularly to the separation of the diabatic curves in the

region of the avoided crossing of the ¹³Π_g and 2³Π_g valence states. The calculated separation is consistent with the results of a Landau-Zener analysis of the decay products of the ³Π_g Rydberg state of O₂ formed by charge transfer of O₂⁺ ions in Cs (van der Zande *et al.*, 1987) and it is unlikely that the predicted rate coefficients are in error by more than a factor of two.

The calculated rate coefficients are in harmony with the value $(8.0 \pm 7.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ inferred from one study of the emission of the red line of atomic oxygen in the upper atmosphere (Abreu *et al.*, 1986). The analysis contains several uncertain parameters and by suitable choices it is possible to reproduce the observational data without invoking quenching of O(¹D) atoms by collision with atomic oxygen (Link and Cogger, 1988, 1989; Solomon and Abreu, 1989). Thus, the atmospheric studies do not establish the importance of the quenching process. However our calculations suggest strongly that it should be included in theoretical models of the emission of the red line.

Acknowledgements—The research of A.D. was supported by the Aeronomy Program of the National Science Foundation under Grant ATM-87-13204, that of S.L.G. by the Aeronomy Program of the National Science Foundation under Grant ATM-8820643, by the National Aeronautics and Space Administration under Grant NAGW-1404 and by the National Center for Atmospheric Research which is sup-

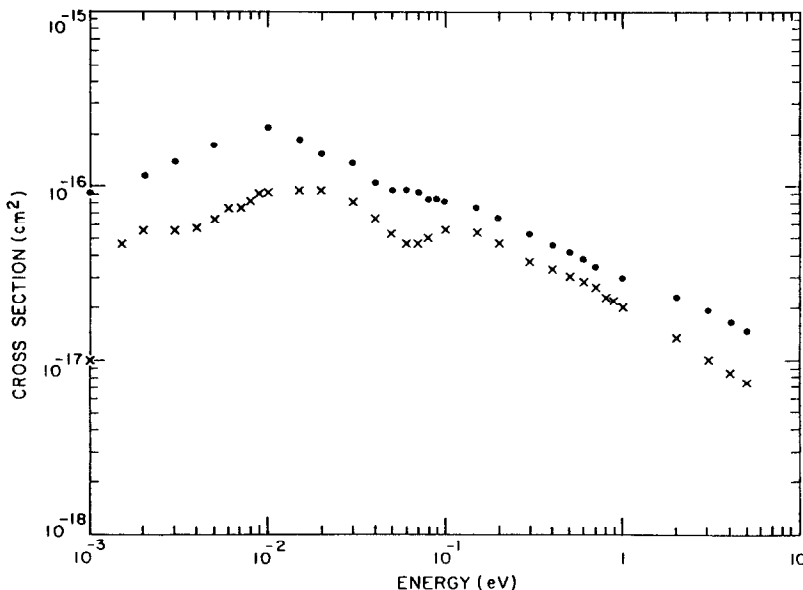


FIG. 4. THE CROSS-SECTIONS FOR THE QUENCHING OF O(¹D) BY COLLISIONS WITH O(³P) AS FUNCTIONS OF THE RELATIVE ENERGY: (x) REFER TO CROSS-SECTIONS CALCULATED FROM THE DATA OF FIG. 2 AND (●) REFER TO CROSS-SECTIONS CALCULATED FROM THE DATA OF FIG. 3.

ported by the National Science Foundation, and that of J.-H.Y. by NASA grant NAGW-496.

REFERENCES

- Abreu, V. J., Yee, J.-H., Solomon, S. C. and Dalgarno, A. (1986) *Planet. Space Sci.* **34**, 1143.
- Bienstock, S., Heil, T. G. and Dalgarno, A. (1984) *Phys. Rev. A* **29**, 503.
- Chang, T. Y. (1967) *Rev. mod. Phys.* **39**, 911 (1967).
- Guberman, S. L. (1977) *J. chem. Phys.* **67**, 1125 (1977).
- Guberman, S. L. (1983) *Potential Energy Curves for Dissociative Recombination in Physics of Ion-Ion and Electron-Ion Collisions* (Edited by Brouillard, F.), pp. 167-200. Plenum Press, New York.
- Heil, T. G., Butler, S. E. and Dalgarno, A. (1981) *Phys. Rev. A* **23**, 1100.
- Johnson, B. R. (1973) *J. comput. Phys.* **13**, 445 (1973).
- Knipp, J. K. (1939) *Phys. Rev.* **53**, 734.
- Link, R. and Cogger, L. L. (1988) *J. geophys. Res.* **93**, 9883; erratum *ibid.* **94**, 1556 (1989).
- Saxon, R. P. and Liu, B. J. (1977) *Chem. Phys.* **67**, 5432.
- Solomon, S. C. and Abreu, V. J. (1989) *J. geophys. Res.* **94**, 6817 (1989).
- Umanskij, S. Ja. and Nikitin, E. E. (1969) *Theor. Chim. Acta* **13**, 91.
- Zande, W. J. van der, Koot, W., Peterson, J. R. and Los, J. (1987) *Chem. Phys. Lett.* **140**, 175.