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POTENTIAL ENERGY CURVES

FOR DISSOCIATIVE RECOMBINATION

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INTRODUCTION

The direct dissociative recombination (DR) of a diatomic molecular ion, AB^+ , with an electron is described by



where AB^* is a repulsive state of the neutral molecule which dissociates directly to A and B. The dissociation prevents the emission of an electron by AB^* and accounts for the high rate of electron recombination with molecular ions compared to atomic ions. This paper presents a discussion of ab initio calculations of potential energy curves for the AB^* and AB^+ states in (1). Results for recent large scale calculations for O_2 are presented along with additional results for H_2 and He_2 . These calculations provide answers to the following questions: What are the identities of the molecular states responsible for DR? What are the translational energies and states of the resulting atoms? How do the atomic state quantum yields vary with ion vibrational excitation and electron temperature?

DR is an important process in both atmospheric and laboratory plasmas. In the Earth's upper atmosphere DR of O_2^+ is an important electron sink and a major source of $O(^1S)$ (Frederick et al., 1976; Kopp et al., 1977) and $O(^1D)$ (Sharp et al., 1975; Cogger et al., 1977; Link et al., 1981; Torr et al., 1981). DR of O_2^+ may be the major contributor to a corona of hot O atoms surrounding the earth's thermosphere (Yee et al., 1980). DR is a source of hot O atoms on Venus (Nagy, et al., 1981) and may impart enough kinetic energy to

allow for the escape of hot O atoms from the atmosphere of Mars (McElroy, 1972; Nier et al., 1976). Numerous laboratory studies of DR of O_2^+ , H_2^+ and He_2^+ have been reported and the most recent of these will be compared to the calculated results. The AB^* states discussed here are also significant in indirect DR where the electron is initially captured into a vibrationally or rotationally excited Rydberg state followed by dissociation along AB^* . This process is thought to be important above 1000K (Mul et al., 1979) and will not be treated here. For reviews of much of the previous theoretical and experimental work on DR the reader is referred to the articles by Bardsley, Dalgarno, and Mitchell and McGowan in this volume and to previous reviews by Bardsley (1968a, 1968b), Bardsley and Biondi (1970), Bates (1974, 1979a), Dalgarno (1979), Dolder and Peart (1976) and Massey and Gilbody (1974).

ATOMIC AND MOLECULAR RECOMBINATION

In order to provide some perspective concerning the magnitude of molecular ion recombination rates a brief comparison to atomic ion recombination is presented here. At low electron densities where collision with a second electron is unlikely, atomic recombination can proceed by radiative or dielectronic recombination. In the former process the electron is captured into a vacant orbital of the ion and is stabilized by emission of a photon. About 10^{-8} seconds are needed for a dipole allowed transition compared to roughly 10^{-14} seconds needed for a 1 eV electron to traverse an atom. Radiative recombination is therefore expected to be slow. As an example, the rate constant for radiative recombination of O^+ is about 10^{-12} cm^3/sec at $1000^\circ K$ (Bates, 1974). For molecular ions we can expect the radiative recombination rate to be about the same magnitude as that found for atomic ions. However, for molecular ions the DR rate overwhelms the radiative rate. For O_2^+ at $1000^\circ K$ the DR rate is 10^{-7} cm^3/sec (Mul et al., 1979; Walls et al., 1974). In dielectronic recombination the electron is captured into an excited orbital and simultaneously a target electron is excited to a vacant orbital. The formation of the neutral doubly excited atom is similar to the formation of AB^* in (1). However for atoms the energy needed to reach the lowest accessible doubly excited state can be large. For He the energy needed is 35.2 eV while for O, about 0.5 eV is needed. For DR, as we will see below, electrons with near zero energy can often lead to the formation of "doubly excited" states of AB^* in (1). In order to prevent autoionization, the doubly excited atom can only stabilize by the relatively slow photon emission. Dielectronic recombination will only be important at very high electron temperatures. Calculations (Burgess, 1964) for

He⁺ show that at 10⁶°K dielectronic recombination is two orders of magnitude faster than the radiative rate but near 10⁵°K it is equal to the radiative rate. For O⁺, recent calculations (Beigman and Chichkov, 1980) show that near 5000°K the rate for dielectronic recombination is about 3×10⁻¹³ cm³/sec exceeding the rate for radiative recombination at this temperature.

DR MECHANISM

DR of O₂⁺ was first discussed by Kaplan (1931), Massey (1937) and Bates and Massey (1947) and for He₂⁺ by Bates (1950a). A mechanism for DR was first proposed by Bates (1950b).

DR of a diatomic ion with an electron will proceed with a high rate if there is a favorable crossing between the potential energy curves for AB* and AB⁺ in (1). Fig. 1 shows a favorable crossing for DR from the lowest vibrational state of AB⁺. For an electron energy of ϵ the cross section for DR is a maximum if the potential energy curves cross (as in Fig. 1) so as to give a maximum Franck Condon overlap for the vibrational wavefunctions of the bound ion and neutral continuum states. Once the dissociating atoms separate to distances greater than R_C, autoionization back to the molecular ion and a free electron is impossible and recombination is assured. As mentioned in the Introduction we see that near zero energy electrons can participate in DR if the potential curve crossings are favorable. A high DR cross section from v=0 of the molecular ion at low electron energies requires the intersection of AB* potential curves near the midpoint of the v=0 vibrational level. Molecular ions in the upper atmosphere and in laboratory plasmas can often be generated with substantial populations in excited vibrational levels. Vibrationally excited ground electronic state homonuclear diatomic ions generated under near collision free conditions will have long lifetimes (10⁵ sec) before radiative decay to the lowest vibrational level. Because of the importance of the Franck Condon factor between bound and continuum nuclear motion levels, vibrational excitation of the ion will have a large effect on DR cross sections. We expect maximal cross sections for DR at low electron energies for AB* curves which intersect excited ion vibrational levels near the turning points where vibrational wavefunctions have maximum amplitudes. For electron capture into AB* potential curves which intersect the small R turning points of the bound vibrational levels, autoionization can occur while the atoms are dissociating for separations less than the large R crossing point. As a result cross sections for DR will be highest for capture at large R turning point intersections.

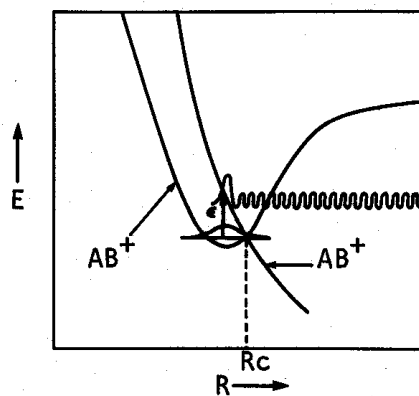


Fig. 1. Potential energy curves of a diatomic ion, AB^+ , and a neutral dissociative state, AB^* , leading to DR of the $v=0$ level by an electron of energy ϵ .

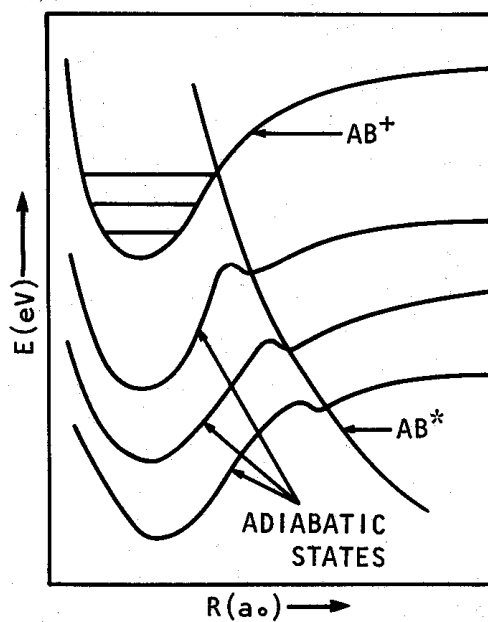


Fig. 2. Potential energy curves for adiabatic bound states showing perturbations due to the repulsive diabatic AB^* state.

NATURE OF THE DISSOCIATING STATES

At first glance the calculation of the Born-Oppenheimer states AB^* for DR appears to present a difficult problem. Any AB^* state arising from neutral atomic asymptotes must pass through an infinite number of states of the same symmetry before crossing above the ground state of the ion. According to the non-crossing rule, states of the same symmetry cannot cross. Therefore, it would appear impossible for a single molecular state arising from neutral separated atoms to cross the molecular ion curve. However there is ample experimental evidence for such states. AB^* states have been populated by photon and electron impact and dissociate to neutral atoms or autoionize to atomic ions or molecular ions. Indeed these states can be calculated by restricting the character of the wavefunction. For example if a repulsive AB^* state arises from valence states of the atoms, at intermediate internuclear distances this state can cross through the ion state if Rydberg character is not included in the wavefunction. Avoided crossings with Rydberg states that have the molecular ion as their series limit are eliminated by excluding Rydberg character from the wavefunction. However avoided crossings between tight valence molecular states will still be evident. The curves with only valence character are termed diabatic whereas the curves allowed to have the optimum mixture of Rydberg and valence character are termed adiabatic. A comparison of the adiabatic and diabatic states is shown schematically in Fig. 2. The diabatic AB^* states cross through the molecular ion and can account for DR and dissociative ionization by photon and electron impact. The wiggle in the adiabatic state is due to the character of the diabatic repulsive state mixing into the adiabatic state. The simplest example of such a state is the diabatic repulsive $1\Sigma_g^+$ state of H_2 which has primarily $(1\sigma_u)^2$ character at intermediate R . The state rises through a number of bound states of H_2 and is responsible for perturbations in the E, F and G, K and higher states (Wolniewicz and Dressler, 1977). The $1\Sigma_g^+$ diabatic state is the lowest accessible route for direct DR of H_2^+ . Once the dissociating atoms arising from DR pass the internuclear separation at which the ion and neutral curves intersect the dissociating probability will partition itself among the diabatic Rydberg states that cross the dissociating diabatic AB^* state. Thus it is possible to populate many atomic and molecular Rydberg states during dissociation.

In H_2 all the excited states of interest are Rydberg states. However it is easy to obtain an exact description of the one electron states of the molecular ion. In order to obtain the diabatic AB^* states of H_2 , we simply project out of the wavefunction the relevant one electron H_2^+ states (see discussion below). For O_2 , however, it is much more difficult to obtain the exact description of the ground state of the molecular ion. The diabatic

AB* states are valence states and they are obtained by eliminating Rydberg character from the O₂ wavefunction. For He₂ the example discussed below uses frozen atomic orbitals to obtain the diabatic AB* states. The construction of the wavefunction and the details of these techniques is discussed further in the following sections.

WAVEFUNCTIONS

A brief outline is presented here of some of the important features of large scale calculations. The purpose of this section is to convey some feeling for the current techniques used and the magnitude of the effort needed in calculations which yield quantitative accuracy for molecular spectroscopic properties. This section reviews the highlights of techniques used for the O₂ and H₂ DR calculations reported here.

Configurations and Orbitals

The many electron spatial wavefunction, Ψ_α , is expressed as a superposition of terms or configurations, Φ_i ,

$$\Psi_\alpha = \sum_{i=1}^M C_i^\alpha \Phi_i(\alpha) \quad (1)$$

The C_i^α are coefficients to be determined. The Φ_i consist of sums of products of one electron orbitals. Each Φ_i is restricted to one particular set of orbitals. The sum of products arises from the necessity to permute the electrons among the one electron spatial orbitals in order to satisfy Pauli's principle and in order to have a pure spin symmetry. For Φ_i we can write

$$\Phi_i = Op(\phi_1(1)\phi_1(2)\phi_2(3)\phi_3(4)\dots) \quad (2)$$

where Op is a general many electron operator which generates the required sum of orbital products. Each product has the electrons permuted in a different way among the orbitals in Φ_i . Also Op puts the correct coefficient in front of each permuted product so as to have the proper spin and spatial symmetry and satisfy Pauli's principle. For example, for the $^1\Sigma_g^+$ ground state of H₂ the most important term (largest C_i) is

$$\Phi_1(^1\Sigma_g^+) = 1\sigma_g(1) 1\sigma_g(2) \quad (3)$$

and the second most important term is

$$\phi_2(1^1\Sigma_g^+) = 1\sigma_u(1) 1\sigma_u(2) \quad (4)$$

For the first excited state of H₂ the most important term is

$$\phi_1(3^1\Sigma_u^+) = \frac{1}{\sqrt{2}} [1\sigma_g(1) 1\sigma_u(2) - 1\sigma_u(1) 1\sigma_g(2)] \quad (5)$$

where we have already operated with Op. For the ground state of O₂ the most important or Hartree-Fock (HF) configuration is given by

$$\phi_1(3^1\Sigma_g^-) = \text{Op} (1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2) \quad (6)$$

whereby $1\sigma_g^2$ we mean $1\sigma_g(1) 1\sigma_g(2)$.

Basis Functions

The orbitals shown above, ϕ_i , are in turn expanded over basis functions, χ_i , centered on the nuclei:

$$\phi_i = \sum_{j=1}^{M'} C_j^i \chi_j \quad (7)$$

Since we cannot take $M'=\infty$ in (7) we must be prudent in our choice of basis functions. A natural choice for basis functions could be the exact one electron solutions for the hydrogen atom. These solutions are linear combinations of the functions

$$\chi_{n\ell m\zeta} = N r^{n-1} e^{-\zeta r} Y_{\ell m} \quad (8)$$

where $Y_{\ell,m}$ is an angular factor, N is a normalization constant, and r is distance of the electron from the nuclear center. The functions in (8) are called Slater functions. A serious problem with Slater functions is that some of the integrals that must be calculated in order to solve for C_j^i in (7) and C_i^a in (1) cannot be done in closed form. An example is the two electron, two center integral,

$$\iint \chi_1^a(1) \chi_j^b(1) \frac{1}{r_{12}} \chi_k^a(2) \chi_\ell^b(2) d\tau_1 d\tau_2 \quad (9)$$

where the integration is over all space and a and b refer to the atomic centers. These integrals can be time consuming to compute. The problem becomes especially difficult for three and four center

integrals. In order to circumvent the integral evaluation problem Boys (1950) suggested the use of Gaussian functions which have the form

$$\chi_{stv\zeta} = N_{s,t,v,\zeta} x^s y^t z^v e^{-\zeta r^2} \quad (10)$$

where $x, y,$ and z are the cartesian coordinates and s, t and v are positive integers. $N_{s,t,v,\zeta}$ is a normalization constant. The advantage of Gaussian functions is that all the integrals can be done in closed form and evaluated quite rapidly by computer. However an advantage of Slater functions is that it can be shown that they have the proper limiting behavior at both small and large r . Nevertheless, by taking combinations of several Gaussians, each with a different exponent, we can correctly describe the electron distribution in the important regions of space. Because the computational time needed to solve for the C_j^{\pm} in (7) rises rapidly with the number of basis functions, it is most convenient to combine individual (primitive) Gaussian functions into groups with fixed coefficients. The coefficient before each group is optimized in molecular calculations while the coefficients within a group are often optimized in atomic calculations. Each group of Gaussians is referred to as a contracted set. Dunning (1970,1971,1977) has reported extensive studies of the construction of Gaussian basis sets in molecular and atomic calculations. Huzinaga (1965,1971,1977,1979) has reported optimized exponents for Gaussian basis sets for atoms extending in size to the fourth row of the periodic table. Raffanetti (1973) has devised an efficient method of contracting Gaussian functions and has written an efficient computer program BIGGMOLI (Raffanetti, 1976), for evaluating these integrals. A slightly revised version of this program has been used in the O_2 calculations reported here.

As an example of the effectiveness of Gaussian basis sets, consider first the lowest state of the H atom. A single Gaussian with an optimized exponent gives $E = -.42441$ hartrees (h) (Huzinaga, 1965) which is in error by 15% compared to the exact value given by a single Slater of $-0.5h$. Addition of a second Gaussian reduces the error to 2.8%. A four term Gaussian expansion gives $E = -.49927$ and is in error by only 0.15%. For H_2^+ (for which combinations of Slater functions are not the exact basis functions) a basis set on each center of nine 1s Gaussians contracted to five Gaussians and two $2p_z$ Gaussians ($s=t=0$ and $v=1$ in (10)) contracted to a single Gaussian gives an electronic energy of $E = -1.10184h$ at $R=2.0$ Bohr (a_0) (Guberman, 1982) compared to the exact energy of $E = -1.10263h$ (Bates et al., 1953) for an error of only .07%. For the ground state of the hydrogen molecule (Guberman, 1982) the basis set used for H_2^+ was supplemented on each atom with eight $2p_x$ and eight $2p_y$ Gaussians contracted to four $2p_x$ and four

$2p_y$ Gaussians plus four $3dx^2$ ($s=2, t=v=0$ in (10)), four $3dy^2$ and four $3dz^2$ functions contracted to four $3d\sigma$ functions. The C_j^i in (7) were optimized for the one electron states of H_2^+ and the final wavefunction took the form shown in (1) with 82 terms. The calculated total energy was $E = -1.168045h$ at $R = 1.4 a_0$ compared to the highly accurate energy of $E = -1.1744699h$ of Kolos and Wolniewicz (1964) for an error of only 0.54%. Using Gaussian basis sets similar in size to that for the ground state in a study of ten low lying excited states of H_2 gives energies which differ on the average by only .0029h from exact energies (Guberman, 1982). For the O_2 calculations reported here we have used a Gaussian basis set of nine $1s$ functions, five $2p$ functions and two $3d$ functions taken from Huzinaga (1965) and contracted to three $1s$, two $2p$ and one $3d$ function. The s and p contractions are from Dunning and Hay (1977) and the d contraction is from Dunning (1971). This basis set is shown in Table 1. The ground state O atom energy in this basis is $-74.798844h$ (Guberman, 1977) and is only .01054h above the HF limit energy (H. F. Schaefer III et al., 1969). The HF limit energy is the lowest energy obtainable with a one configuration wavefunction, i.e., it is the energy found in the limit of a very large basis set. For O_2 at $R = 2.2819 a_0$ the HF energy in this basis is $-149.63642h$ which is .0295h above the HF limit energy at $2.282 a_0$ (Cade and Wahl, 1974). The HF limit Slater basis set consisted of two $1s$, two $2s$, one $3s$, three $2p$, two $3d$ and one $4f$ function on each center (Cade and Wahl, 1974). If we assume that the error consists of twice the atomic error plus a molecular extra error, the molecular extra error is only .0084h. Indeed the Gaussian basis set used here accounts for 82% of the molecular HF limit binding energy. Thus the small Gaussian basis shown in Table 1 is able to account for most of the HF binding energy found in the much larger limiting basis set. It is energy differences such as binding energies and excitation energies rather than absolute energies that are of interest to chemists and are the real tests of basis set accuracy. Table 3 of Dunning and Hay (1977) shows excellent agreement between atomic excitation energies calculated in the Gaussian basis of Table 1 and HF limit energies. Further calculations by the author on the excited states of O_2 in a Gaussian basis show that general agreement is obtained for binding energies and excitation energies with similar wavefunctions calculated in a Slater basis (Saxon and Liu, 1977). Indeed the agreement is such that it is difficult to justify the use of Slater orbitals unless one has a highly efficient and rapid Slater integrals computer program.

Orbital Optimization

In this section a brief description is given of how we determined the optimum in C_j^i in (7). We can in theory skip this step and instead write the configurations in (2) in terms of basis functions instead of orbitals and go ahead to the next step of determining the

Table 1. Contracted Gaussian Basis Set for the O Atom^a.

Exponents	Type ^b	Contraction Coefficients
7817.	s	.001176
1176.	s	.008968
273.2	s	.042868
81.17	s	.143930
27.18	s	.355630
9.532	s	.461248
3.414	s	<u>.140206</u>
9.532	s	-.154153
.9398	s	<u>1.056914</u>
.2846	s	1.0
35.18	p	.019580
7.904	p	.124200
2.305	p	.394714
.7171	p	<u>.627376</u>
.2137	p	1.0
1.8847	d	.357851
.55826	d	.759563

^aThe exponents listed are from Huzinaga (1965) and the contraction coefficients are from Dunning and Hay (1977) and Dunning (1971).

^bThe Gaussian types are defined in Eq. (10) with $s+t+v=\omega$. For s, p and d type Gaussians $\omega=0,1$ and 2 respectively. For the p and d Gaussians all possibilities for the positive integers s, t and v are included except the combination $s=t=1, v=0$ for d.

C_i^{α} in Eq. (1). However M in Eq. (1) would then be extraordinarily large making the calculation of Ψ impossible in practice. The calculation of molecular orbitals represents, in a sense, a further contraction of the basis set. These molecular orbitals are often pseudoeigenfunctions of one electron Schroedinger equations. As a result we can interpret an orbital as containing an electron which sees an averaged field due to all the other electrons. This independent particle interpretation allows one to gain considerable qualitative understanding of molecular binding.

We consider here two approaches to solving for molecular orbitals: the single configuration HF method and the Multiconfiguration Self Consistent Field (MCSCF) method. In order to determine optimum orbitals we must consider the energy expression for the wavefunction in (1):

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (11)$$

where \mathcal{H} is the Hamiltonian operator for N electrons and N' nuclei,

$$\mathcal{H} = \sum_{i=1}^N h_i + \sum_{i>j}^N \frac{1}{r_{ij}} + \sum_{a>b}^{N'} \frac{z_a z_b}{R_{ab}} \quad (12)$$

where i is an electron index, h_i contains the one electron kinetic energy and electron-nuclear interaction terms, a and b are indices of the nuclei, and z_a is the nuclear charge. In order to determine the optimum orbitals, i.e., the orbitals that lead to the minimum energy in (11), the energy is required to be stationary ($\delta E=0$) for small changes in the C_i^{α} . Often it is also required that the orbitals be orthonormal, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. The orthogonality restriction leads to a considerable simplification in the resulting equations. This condition is relaxed in the calculations on He_2 described below. From these requirements pseudoeigenvalue equations arise for the orbitals. Applying the basis set expansion of the orbitals shown in (7) one then solves for the C_i^{α} by standard matrix techniques. The potential that an orbital "sees" is dependent upon all the other orbitals which are in turn dependent upon the first orbital. As a result an iterative procedure (which hopefully converges in a few iterations) is needed to determine all the orbitals. These orbitals are generally denoted HF orbitals if they are determined from a wavefunction which has the most important single configuration, i.e. $M=1$, in Eq. (1). If the orbitals are determined from a multiconfiguration wavefunction we refer to the procedure as MCSCF. The resulting pseudoeigenvalue equations are then more complicated since in MCSCF both C_i^{α} in (1) and C_j^{β} in (7) are optimized. The reader is referred to the articles by Wahl and Das (1977), Bobrowicz and Goddard (1977), and Hinze (1973) for the

details of these procedures. The O_2 MCSCF calculations reported here were done with a revised version of a program originally written by Das and Wahl (1972).

It has been recognized for several years that there are many problems with the HF description of molecules. A serious problem is the incorrect dissociation behavior of HF wavefunctions, i.e., as the intermolecular distance increases, single configuration HF wavefunctions often become a superposition of ionic and neutral atoms rather than dissociating to the proper states of the separated atoms. Closed shell molecules which dissociate to closed shell atoms can dissociate correctly in HF. However many chemically interesting systems do not involve closed shell species. A simple example of incorrect HF dissociation is the ground state of H_2 . The $1\sigma_g^2$ single configuration HF wavefunction with $1\sigma_g = 1/\sqrt{2} (1s_a + 1s_b)$ dissociates to ionic and neutral terms. However the $\frac{1}{\sqrt{2}} (1\sigma_g^2 - 1\sigma_u^2)$ two configuration wavefunction, where $1\sigma_u = \frac{1}{\sqrt{2}} (1s_a - 1s_b)$, dissociates correctly to two ground state H atoms. For larger systems MCSCF provides the solution to the incorrect dissociation problem. For example, for the ground state of O_2 six configurations are needed to properly dissociate to two ground state O atoms (Guberman, 1977). These configurations are referred to as the configurations for proper dissociation (CPD).

Configuration Interaction

The orbitals determined from the MCSCF procedure are determined in a static averaged potential due to all the other electrons. However this is only an approximation since each of the electrons in fact "sees" a dynamic instantaneous potential, i.e., for any arbitrary movement of one electron, all the other electrons will adjust. The additional energy is called correlation energy and is found by considering configuration interaction (CI). In CI we take the orbitals determined in the MCSCF procedure plus additional orbitals which can be formed from the basis set and construct a wavefunction as in (1). Now, however, the CI wavefunction in (1) extends over many more configurations and orbitals than the MCSCF wavefunction. If Ψ is constructed so that the configurations are orthonormal, the C_i^α in (1) can be determined by solving the matrix equation

$$HC = CE \tag{13}$$

where C is a matrix in which each column is the α^{th} linearly independent set of C_i^α coefficients in (1). Each element of the H matrix is an integral over the Hamiltonian operator between configurations shown in (1),

$$H_{ij} = \langle \phi_i | \mathcal{H} | \phi_j \rangle \quad (14)$$

The eigenvectors and the eigenvalues of H are then found by diagonalizing the H matrix. In general the CI H matrix can often have several thousand terms and standard techniques of matrix diagonalization are not very useful. A discussion of iterative techniques for diagonalizing large CI matrices and further details of CI calculations can be found in the article by Shavitt (1977). The program used in the CI calculations on O_2 and H_2 was written by the author and coworkers (R. C. Ladner, P. J. Hay, W. J. Hunt, F. W. Bobrowicz, N. W. Winter and T. H. Dunning) at the California Institute of Technology. The technique used to construct the H matrix is described in Bobrowicz (1974) while the diagonalization technique was devised by Shavitt (1977) and Shavitt et al (1973).

In the case of H_2 the determination of the types of configurations to include in (1) is quite straightforward. Namely, for two electrons and a particular total spatial symmetry one can generate all possible ways of distributing the electrons among all the orbitals formed from an adequate basis set and still have a relatively small wavefunction by modern standards. As discussed above, 82 configurations resulted when this full CI is generated for the ground state of H_2 . For systems with more electrons such as O_2 , a full CI in a basis set such as that shown in Table 1 is out of the realm of practical computations. However we can construct a good approximation to a full CI wavefunction from the following consideration. If we take ϕ_1 in Eq. (14) to be the HF configuration, H_{ij} will vanish for all ϕ_j which differ by more than two orbitals (a double excitation) from ϕ_1 if the orbitals are orthogonal. Because of the matrix elements of the electron-electron repulsion operator in the Hamiltonian, configurations differing by a triple excitation or higher from the HF configuration can be ignored to first order. Indeed it is now known that most (i.e. 90%) of the correlation energy can often be obtained with single and double excitations. However, because of the incorrect dissociation of the HF wavefunction it is often inadequate to generate the CI wavefunction from only the HF configuration. Since the HF wavefunction treats the equilibrium separation, R_e , much better than it treats larger internuclear distances (except in closed shell systems which dissociate correctly in HF) a CI generated only from the HF configuration will also be biased to give a better description at R_e . Such calculations can give dissociation energies and fundamental frequencies that are too large compared to experiment (Guberman, 1977). The situation is remedied if the configurations which dissociate the molecule correctly (CPD) are used as reference configurations. However all single and double excitations from the CPD can lead to too many configurations to be handled with current programs. As a result an approximation is used in which all double excitations are

generated from the CPD; however in each configuration only a single electron is allowed in the orbitals not occupied in the CPD. These orbitals make up the virtual space. This approximation is based on the first order wavefunction of Schaefer and Harris (1968) originally applied to a single reference configuration. Calculations on the excited states of O_2 using this approach give adiabatic excitation energies and dissociation energies that differ by about 0.15 eV from experiment. Calculated fundamental frequencies differ by only 50 cm^{-1} from experiment while equilibrium separations are about $.06 a_0$ larger than experiment (Guberman, 1982).

Practical Considerations

The calculations for O_2 and H_2 were performed on a CDC 6600 computer which has an available memory of about 97000 words. The programs and the matrix elements to be manipulated must be squeezed into this memory. The first step in the determination of molecular wavefunctions and potential energy curves is a calculation of integrals over the contracted Gaussian basis functions. These integrals are used to construct the MCSCF equations and the H matrix needed for determination of the CI wavefunction. There are overlap integrals and integrals over the one electron operator, h_i , in Eq. (12) consisting of kinetic energy and nuclear attraction integrals. For N total basis functions there are only $N(N+1)/2$ of each of the types of one electron integrals. As a result these integrals do not become large in number and their computer storage presents no problem. However for the two electron integrals there are $\frac{1}{8} (N^4 + 2N^3 + 3N^2 + 2N)$ integrals. This expression is arrived at if one considers the interchange symmetry of some of the indices in the two electron integrals. For example, for the integral shown in (9) switching index i with index j or index k with index l or indices k and l with indices i and j does not change the value of the integral so that we need only store in the computer a single representative value. For the basis set shown in Table 1 there are a total of 28 contracted Gaussians, 14 on each O atom. From the above formula one would expect a total of 82621 two electron integrals leaving very little room in the computer for the integral or MCSCF programs. In fact the situation is not quite so hopeless. If one considers the spatial symmetry of the orbitals it turns out that for O_2 most of the two electron integrals are zero by symmetry and calculation shows that there are at $R = 2.2819 a_0$ only 14706 non zero integrals which can easily fit in the machine memory. Usage of only the non-zero integrals requires efficient algorithms which indicate whether a required integral is zero or non-zero and, if non-zero, where its value can be found in memory. We can see from the above expression that the number of two electron integrals needed in a particular calculation can get rapidly out of

hand for molecules with more than three first row atoms or molecules with little symmetry.

In order to obtain the wavefunction for ${}^3\Sigma_g^-$ states of O_2 a first order wavefunction was generated from the CPD of each of the ${}^3\Sigma_g^-$ states giving a total of 2496 terms. Determination of the eigenvectors or eigenvalues requires diagonalization of a 2496×2496 H matrix. Obviously storage of the full matrix in memory is out of the question. It would not even fit into the fast memory of the largest supercomputers. Fortunately, however, these matrices are characteristically quite sparse. In the case of $X^3\Sigma_g^-$ only 7.5% of the matrix elements are non-zero. However this still leaves almost half a million matrix elements which must be considered. Iterative techniques have been developed which require that only a single row of the lower triangular H matrix need be in memory at any instant (Shavitt et al., 1973 and Shavitt, 1977). The remainder of the H matrix can be kept on disk or tape. Typically only a few of the lowest roots of the matrix are determined. For the case considered here the maximum number of non-zero elements in a lower triangular row of the H matrix is 280 and the diagonalization is quite manageable. For the $X^3\Sigma_g^-$ state of O_2 the integrals take about 80 seconds and the determination of the lowest six states of this symmetry from the 2496×2496 CI matrix took about 29 minutes on a CDC 6600 computer. About 65% of the 29 minutes was spent in the diagonalization while the remainder involved calculating the H matrix.

DISSOCIATIVE RECOMBINATION OF O_2^+

Calculations were performed on all 62 valence states of O_2 which arise from the $O({}^3P)$, $O({}^1S)$ and $O({}^1D)$ separated atom limits and the $X^2\Pi_g$ and a ${}^4\Pi_u$ states of O_2^+ (Guberman, 1982). DR of a ${}^4\Pi_u$ will be discussed separately (Guberman, 1982). The number of terms in the CI wavefunctions ranged from 672 for the ${}^5\Delta_g$ states to 3359 for $X^2\Pi_g$. In each case the CI wavefunction consisted of a first order wavefunction generated from each term of the CPD reference state to the full virtual space. Since we obtained all the valence states for each symmetry this was equivalent to generating a full CI in the space of the occupied valence orbitals (all the orbitals in (6) plus $3\sigma_u$) followed by a first order CI generated from each of the terms in the valence full CI. In all states the core $1\sigma_g$ and $1\sigma_u$ orbitals, which do not contribute much to molecular binding (corresponding mostly to atomic 1s orbitals), were kept fully occupied. The resulting valence state adiabatic excitation energies are shown in Table 2 where they are compared to the results of Saxon and Liu (1977) and experiment (Krupenie, 1972). The results differ on the average by about 0.16 eV from the experimentally known adiabatic excitation energies and are in excellent agreement with the results of Saxon and Liu (1977).

Table 2. O₂ Adiabatic Excitation Energies (eV)

	This Work	Saxon-Liu ^a	Experiment ^b
a $1\Delta_g$	1.1870	1.098	0.9817
b $1\Sigma_g^+$	1.6954	1.776	1.6360
c $1\Sigma_u^-$	3.9297	3.888	4.0987
A' $3\Delta_u$	4.1766	4.130	4.3066
A $3\Sigma_u^+$	4.2452	4.206	4.3889
B $3\Sigma_u^-$	5.9435	6.079	6.1737
ΔE^c	.1564	.153	
$5\Pi_g$	4.8817	4.746	
(1 $3\Pi_g$) ^d	6.5691	-	
2 $3\Sigma_g^-$	6.5977	6.699	
2 $3\Pi_g$	6.7055	6.884	
3 $3\Pi_g$	7.1782	7.072	
(1 $1\Pi_g$) ^d	8.1720	-	
2 $1\Pi_g$	8.2344	8.411	
1 $1\Delta_u$	8.6235	8.570	
$1\phi_g$	9.6050	9.282	
$1\Sigma_u^+$	10.058	10.430	
4 $1\Pi_g$	11.5336	11.667	

a. Saxon and Liu (1977).

b. Krupenie (1972).

c. ΔE is the average absolute value of the difference between the calculated and experimental energies.

d. These states have shallow wells and may not support a vibrational level.

In order to accurately describe DR it is necessary to accurately reproduce both the slopes of the dissociating states and the energy and internuclear distance of the intersection of the repulsive states with the molecular ion states. However it is very difficult to calculate an adiabatic ionization energy with the same accuracy as adiabatic excitation energies. Because O_2^+ has one less electron it has less correlation energy to account for than the neutral states. As a result comparable calculations performed on the neutral and ionic state will lead to ionization potentials that are too small compared to experiment. The calculated adiabatic electronic ionization potential of O_2 was 10.66 eV compared to the experimental value of 12.052 eV (Krupenie, 1972). This is mostly an atomic effect. In the figures presented below we have used the experimental (Krupenie, 1972) potential curve for $X^2\Pi_g$ for $R < 2.8 a_0$. For $R > 2.8 a_0$ the experimental $X^2\Pi_g$ curve has been joined to the calculated curve. $X^2\Pi_g$ is plotted so as to reproduce the experimental ionization potential relative to $X^3\Sigma_g^-$. However the curve has been shifted on the abscissa so that the R_e value for the ion state is the same as the calculated R_e value for this state. For $\chi^2\Pi_g$ this requires a shift to larger R by $.0518 a_0$. By plotting the ion curves at the calculated R_e we compensate for most of the error in the calculated R_e of the neutral states. For six low lying neutral states the average difference between experiment and theory for R_e is $.0650 a_0$. The results described here use in most cases a larger wavefunction than the previously reported results (Guberman, 1979) and are in good qualitative agreement with the earlier study.

About half of the 62 states arising from the valence asymptotes of O_2 can be eliminated as unimportant for DR of $X^2\Pi_g$ by examination of the configurational structure of the dissociating states. The cross section for DR is directly proportional to Γ , an electronic coupling matrix element,

$$\Gamma = 2\pi |\langle \Psi_\alpha(k) | \mathcal{V} | \Psi_{Res} \rangle|^2 \quad (15)$$

where Ψ_α is a multiconfiguration wavefunction of the ion plus a free electron with momentum $\hbar k_\alpha$. Because of the two electron operator, $\frac{1}{r_{ij}}$ in \mathcal{V} , states with important configurations which differ by more than two orbitals from the primary configuration of the ground state of the ion plus a free electron will have small width matrix elements. These considerations are similar to those discussed earlier in regard to the role of triple and higher excitations in CI wavefunctions. For example, the wavefunction of the ground state of O_2^+ plus a free electron is given by

$$\Psi(2\Pi_g, \phi_k) = \sum_{i=1}^{3359} C_i^{2\Pi_g} \phi_i(2\Pi_g, \phi_k) \quad (16)$$

where ϕ_k is the wavefunction of the free electron. The most important configuration has $C_1^Q = 0.95$ and is given by

$$\phi_1(2\Pi_g, \phi_k) = Op(\dots 3\sigma_g^2 \pi_{ux}^2 \pi_{gx}^2 \pi_{uy}^2) \phi_k \quad (17)$$

where ... denotes $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2$. For the $1\Sigma_u^+$ dissociating neutral state the wavefunction is given by

$$\Psi(1\Sigma_u^+) = \sum_{i=1}^{1618} C_i^{1\Sigma_u^+} \phi_i(1\Sigma_u^+) \quad (18)$$

The dominant terms in (18) are the equivalent configurations,

$$\phi_1(1\Sigma_u^+) = Op(\dots 3\sigma_g^2 \pi_{ux}^2 \pi_{gx}^2 \pi_{uy} \pi_{gy}) \quad (19)$$

and

$$\phi_2(1\Sigma_u^+) = Op(\dots 3\sigma_g^2 \pi_{ux} \pi_{gx} \pi_{uy}^2 \pi_{gy}^2) \quad (20)$$

The configurations in (19) and (20) each have coefficients of 0.6 in the CI wavefunction. Configuration (17) differs from (19) and (20) by two orbitals so that one contribution to the width matrix element will consist of

$$\langle \pi_{uy} \phi_{kx} | \frac{1}{r_{12}} | \pi_{gy} \pi_{gx} \rangle \quad (21)$$

multiplied by an overlap matrix element of the remaining orbitals. The overlap matrix element is equal to unity in this case since all orbitals are orthonormal.

On the other hand consider the seventh state of $1\Sigma_g^+$ symmetry which is dominated by the following two equivalent configurations:

$$\phi_1(7^1\Sigma_g^+) = 0p \left(\dots 3\sigma_g^2 \ 3\sigma_u^2 \ \pi_{ux}^2 \ \pi_{gx}^2 \right) \quad \text{and} \quad (22)$$

$$\phi_2(7^1\Sigma_g^+) = 0p \left(\dots 3\sigma_g^2 \ 3\sigma_u^2 \ \pi_{uy}^2 \ \pi_{gy}^2 \right) . \quad (23)$$

These configurations each have CI coefficients of .51 and differ by three orbitals from (17). These configurations will have zero matrix elements with the configuration in (17) and the width matrix element between the total wavefunctions will be small. A more quantitative statement concerning the relative importance of the dissociating states requires calculation of the width matrix element for states expected to have non-zero matrix elements between primary configurations. Nevertheless the above qualitative considerations allow for the identification of the states which are expected to be unimportant.

Dissociation to $O(^1S)$

There are 11 states which give rise to DR to $O(^1S)$. Of these states the width matrix elements with $X^2\Pi_g$ are expected to be small for 6 of the states leaving $1^1\Sigma_u^+$, $2^1\Delta_g$, $4^1\Pi_g$, $5^3\Pi_g$ and $3^3\Sigma_u^-$ as likely routes for DR to $O(^1S)$. These states are shown in Fig. 3 with the states of the dissociating atoms shown in parentheses after the molecular state symbol.

Fig. 3 shows that the lowest accessible state for production of $O(^1S)$ from $X^2\Pi_g$ is $1^1\Sigma_u^+$ which also dissociates to $O(^1D)$. The state crosses $X^2\Pi_g$ between $v=1$ and $v=2$. At low electron energies DR from $v=1$ will give atoms with 0.4 eV kinetic energy. The next accessible state, $5^3\Pi_g$, crosses the ion curve at $v=10$. Dissociation along this route will produce 2.5 eV atoms. Therefore we can expect that the rate constant for production of $O(^1S)$ by DR of $v=0$ will be very small.

Zipf (1979b;1980) has reported experimental evidence of the strong dependence of $O(^1S)$ production on the vibrational excitation of the ion. In order to bring measurements of an auroral rocket experiment (O'Neil et al., 1979) into agreement with laboratory experiments, Zipf proposed that the DR source of $O(^1S)$ has a quantum yield which is five times smaller than the previous laboratory measurements of O_2^+ DR (Zipf, 1970). The laboratory measurements (Zipf, 1970) which found an $O(^1S)$ quantum yield of 10% were believed to be vibrationally cold; however more recent experiments on N_2^+ (Zipf, 1979a) formed in similar conditions indicate that the ions are vibrationally excited. The earlier results (Guberman, 1979) calculated with a smaller wavefunction (in good agreement

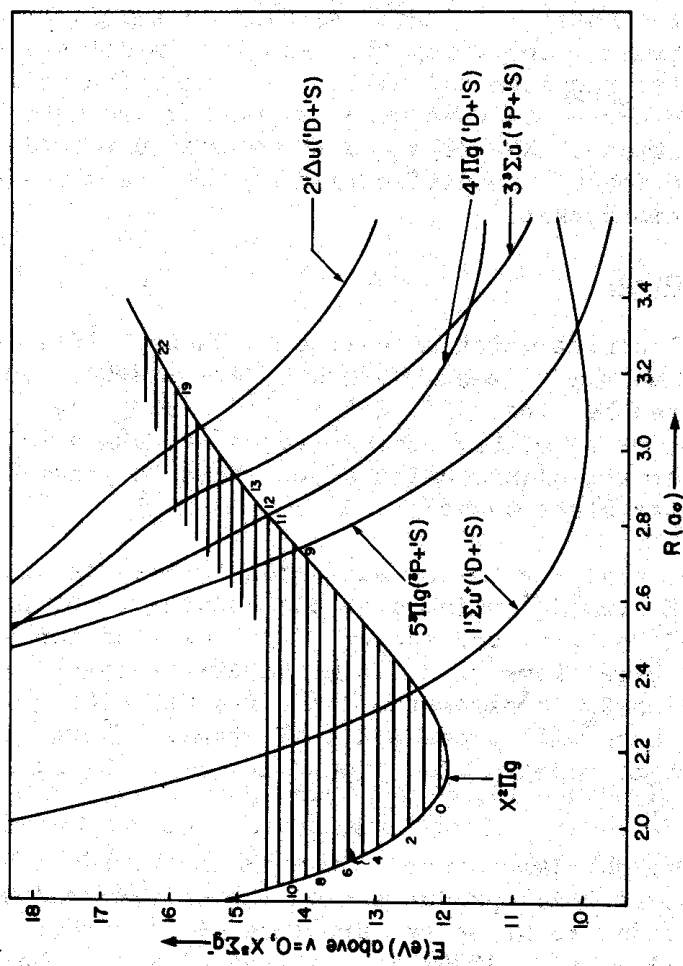


Fig. 3. Potential energy curves which are predicted to have non-negligible electronic matrix elements for DR of the ground state of O_2^+ leading to $O(1S)$.

with the results reported here) and the current results indicate that vibrationally excited O_2^+ will have a larger DR quantum yield for $O(^1S)$ than O_2^+ which is mostly in $v=0$. This led Zipf to conclude that the auroral rocket experiment encountered vibrationally cold O_2^+ at D region altitudes where quenching by O_2 was rapid. However other experiments at higher F region altitudes find $O(^1S)$ quantum yields of 9.4% (Kopp et al., 1977) in agreement with Zipf's earlier measurements. These results indicate that at F region altitudes quenching of excited O_2^+ may be less effective than at D region altitudes and that the F region $O(^1S)$ arises from DR of vibrationally excited O_2^+ (Zipf, 1979b) as in the earlier experiments (Zipf, 1970).

A plasma spectroscopy experiment has been reported by Zipf (1980) in which $X^2\Pi_g O_2^+$ ions were produced with $v \leq 12$ and $v \leq 3$ by charge exchange with Ar_2^+ and Kr_2^+ respectively. For O_2^+ with $v \leq 12$ an $O(^1S)$ quantum yield of about 10% was observed while for $v \leq 3$ ions, a 2% quantum yield was observed. These results appear to support the observations made above and may indicate that most of the $O(^1S)$ arises from $4 < v \leq 12$. From Fig. 3 and the above discussion of the electronic width matrix elements the results of Zipf (1980) indicate that the $5^3\Pi_g$ and $4^1\Pi_g$ states are important routes for DR of the excited levels with $v \leq 12$. The $5^3\Pi_g$ state may be dominant because of its statistical weight. Future calculation of the electronic widths and DR cross sections by the author are expected to identify the relative importance of these states.

A recent paper by Bates and Zipf (1980) presents a strong argument that vibrationally excited O_2^+ ($v \geq 2$) may be efficiently relaxed by collision with O at altitudes where $O(^1S)$ is thought to arise from vibrationally excited O_2^+ DR. It was proposed that $O(^1S)$ could be generated from a Rydberg $3^3\Pi_u$ state (Borst and Zipf, 1971) which is predissociated by $3^3\Pi_u (1S+3P)$. The former state appears to be the bound Rydberg $3s\sigma_g 3^3\Pi_u$ state (Katayama, 1981; Katayama et al., 1981) while the latter state is the $5^3\Pi_u (1S+3P)$ calculated here. The inner wall of the Rydberg state crosses the large R turning point of $v=2$ of $X^2\Pi_g$ while the $5^3\Pi_u$ state crosses the Rydberg state at the large R turning point of $v=3$ and the large R turning point of $v=12$ of $X^2\Pi_g$ (Guberman, 1982). Therefore these states do not appear to offer an important mechanism for DR of $v=0$ of O_2^+ , $X^2\Pi_g$.

Keto et al. (1981) have investigated the possibility of creating a laser based on an $O(^1S) - O(^1D)$ population inversion arising in electron beam excited mixtures of Ar doped with O_2 . With O_2^+ created by charge exchange of Ar_2^+ with O_2 an 11% quantum yield of $O(^1S)$ was found in agreement with the results of Zipf (1980). However, attempts to increase the $O(^1S)$ quantum yield by using Ne_2^+ charge exchange to access a higher dissociating state yielding

$O(^1S) + O(^1S)$ were not successful. As we have seen above, the pertinent state is the $7^1\Sigma_g^+$ state. The configurational character of this state allows for the prediction of a very small width matrix element and therefore a relatively small cross section for DR, consistent with the experimental results.

Dissociation to $O(^1D)$

There are 21 molecular singlet states and 18 triplet states that lead to $O(^1D)$ via DR. Ten singlet states are expected to have large electronic matrix elements for DR of $X^2\Pi_g$ and are shown in Fig. 4. The lowest accessible state is $1^1\Delta_u$ which intersects the large R turning point of $v=0$ and dissociates to two 1D atoms. Note that there are many routes giving rise to two 1D atoms as opposed to the case for two 1S atoms which from symmetry considerations can only arise from a single state, $7^1\Sigma_g^+$. $1^1\Sigma_u^+$ and $1^1\Delta_u$ are the only states accessible from the low vibrational levels. At higher energies $2^1\Pi_g$ becomes accessible near $v=4,5$. The well in the $2^1\Pi_g$ state near $R = 3.0 a_0$ is due to an avoided crossing with $1^1\Pi_g$ (see Fig. 6) which dissociates to 3P atoms. Therefore dissociation along $2^1\Pi_g$ can be expected to proceed partially in a diabatic manner through the curve crossing and will yield 3P as well as 1D atoms. The change in slope for $R < 2.6 a_0$ in $3^1\Sigma_g^+$ and for $R < 3.0 a_0$ in $2^1\Delta_u$ is due to a mixing with states of the same symmetry arising from $O^+ + O^-$ asymptotes.

Fig. 5 shows the important triplet states leading to $O(^1D)$. Each of these states dissociates to $O(^1D) + O(^3P)$ and because of spin are statistically more important than the singlets. The lowest state, $1^3\Sigma_u^-$, is the diabatic extension of the upper state of the well known Schmann-Runge system. From Fig. 5 we see that this state would be expected to have a large DR cross section from $v=1$ of $X^2\Pi_g$ and is the only accessible state for $v < 2$. The next accessible state, $2^3\Pi_g$, comes at the large R turning point of $v=3$. $2^3\Pi_g$ has a small well near $R = 3.3 a_0$ due to an avoided crossing with $1^3\Pi_g$ (see Fig. 6) which dissociates to two 3P atoms. As a result we can expect dissociation along $2^3\Pi_g$ to lead to additional 3P atoms by "jumping" the avoided crossing.

Dissociation to $O(^3P) + O(^3P)$

The most favorable route for DR of $v=0$ of $X^2\Pi_g O_2^+$, $1^3\Pi_u$, is shown in Fig. 6, which depicts the states expected to have large widths. Of all 62 possible dissociating states of O_2 the $1^3\Pi_u$ state is expected to have the largest cross section for DR of $v=0$ and is probably the most important route in the many experiments which have measured total recombination rates for O_2^+ . The total rate at room temperature is 2×10^{-7} cm³/sec (Mul et al., 1979). Clearly, vibrationally cold O_2^+ , mostly in $v=0$, will lead primarily

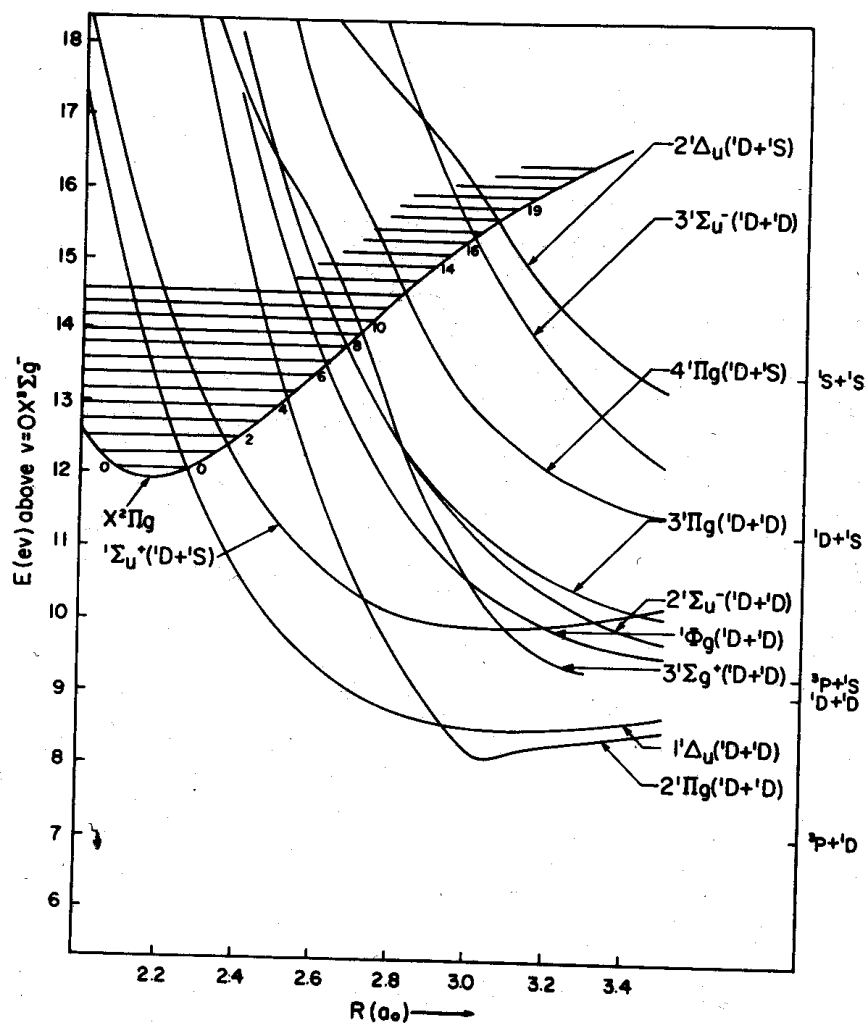


Fig. 4. Singlet states which are predicted to have non-negligible electronic matrix elements for DR of the ground state of O_2^+ leading to $O(^1D)$ atoms.

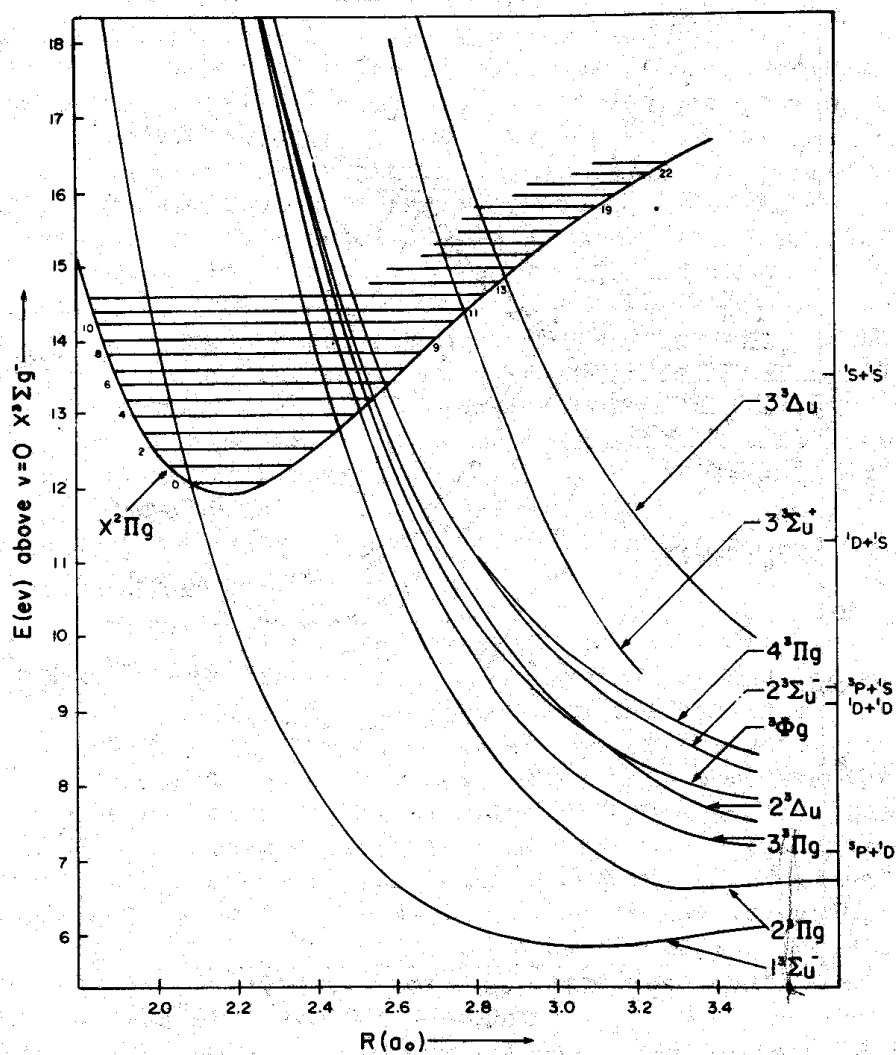


Fig. 5. Same as Fig. 4 except that triplet states dissociating to $O(^1D)$ atoms are shown.

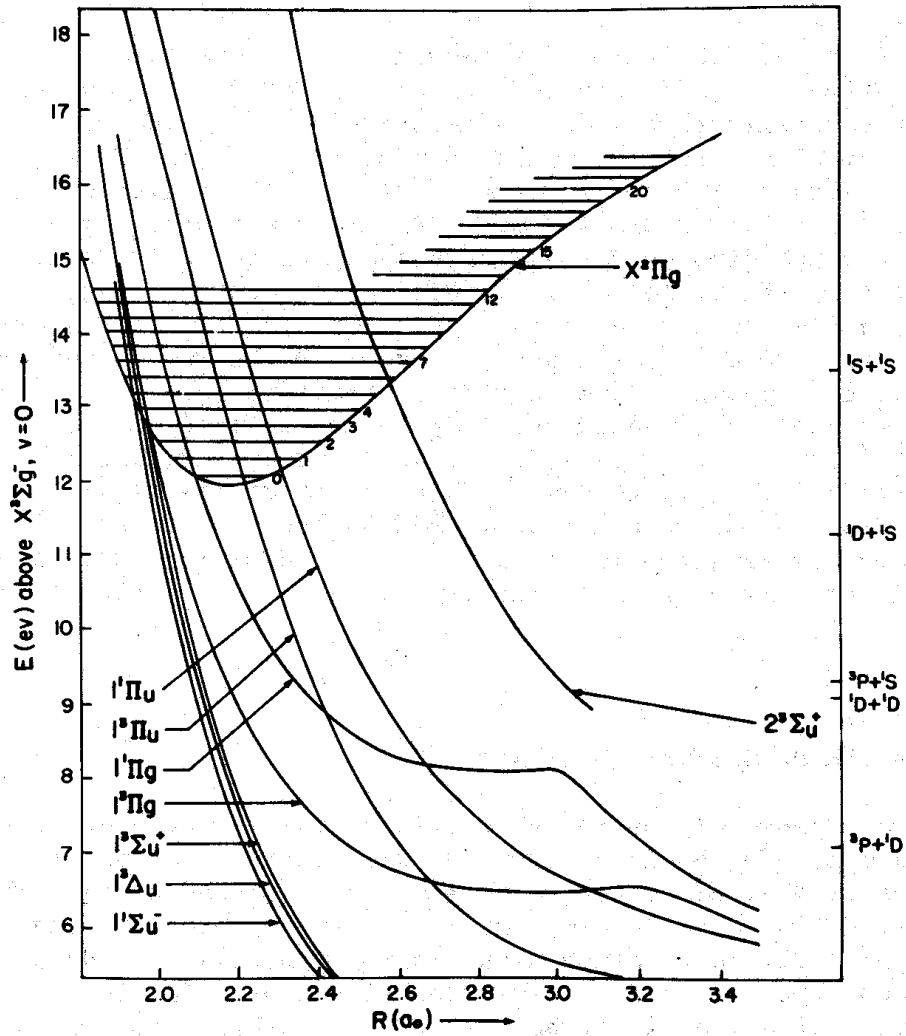


Fig. 6. Same as Fig. 4 except that states leading to $O(^3P) + O(^3P)$ are shown.

to $O(3P)$ with the $1^1\Delta_u$ state of Fig. 4 and the $1^3\Sigma_u^-$ state of Fig. 5 providing some $O(1D)$. Therefore these qualitative arguments lead to the prediction that the magnitude of atomic state quantum yields from $v=0$ will be in the order $3P > 1D > 1S$. This is in agreement with the result found by Zipf (1970), which appears to be appropriate for vibrationally excited O_2^+ (Zipf, 1979b, 1980). Dissociation on $1^3\Pi_u$ from $v=0$ will lead to hot $3P$ atoms each with 3.5 eV kinetic energy.

It is clear from the above results that vibrational excitation will be of major importance in determining the DR yield of ground and excited atomic states and in determining the magnitude of the total DR cross section. A comparison of trapped ion (Walls et al., 1974) and merged electron ion (Mul et al., 1979) measurements of the total DR cross section of O_2^+ indicates reasonable agreement between the two studies for electron energies below 1 eV, even though the degree of ion vibrational and possibly electronic excitation is probably different for these two experiments. However the extent of this difference is not known. Above 1 eV the merged ion experiment does not reproduce some dramatic structure seen in the ion trap experiment. This structure may be due to indirect DR through the $3\sigma_g$ $3\Pi_u$ state (Katayama, 1981; Katayama et al., 1981). Calculations currently underway of the width matrix elements, nuclear vibrational wavefunctions, and DR cross sections in this laboratory are expected to clarify the nature of the variation of the DR cross section with electron energy and ion vibrational excitation.

DISSOCIATIVE RECOMBINATION OF H_2^+

Some aspects of the H_2 calculations have already been discussed above. The basis set for the dissociative states is of the same size as that discussed above for the H_2 ground state. The calculations on the dissociating states were originally done (Guberman, 1982) to describe dissociative ionization of H_2 by photon and electron impact. The repulsive states involved in dissociative ionization of H_2 above 23 eV are the same states which provide routes for DR of H_2^+ at lower energies.

The H_2 CI wavefunctions were expanded over optimized H_2^+ orbitals. As opposed to the case for O_2 , all of the H_2 excited states of interest are Rydberg states. As a result, we cannot obtain the AB^* states by leaving out Rydberg character from the basis set. However, the Rydberg AB^* states of interest are the repulsive states having the repulsive $1\sigma_u$, $2\Sigma_u^+$ state of H_2^+ as the core orbital. These states are obtained by projecting out of the wavefunction all states having the $1\sigma_g$ orbital, i.e., the attractive state of the ion. Thus the problems with the non-crossing rule mentioned

earlier are avoided. The projection is carried out by simply not including any $1\sigma_g$ orbitals in the wavefunction in (1). The calculated state will be an upper bound to the exact autoionizing state in the space having $1\sigma_g$ projected out. Therefore the lower the energy given by the dissociating state wavefunction, the more accurate the description of the dissociating state. For further details the reader is referred to Guberman (1982).

The results for the potential curves relevant to DR are shown in Fig. 7. Clearly DR of the lower vibrational levels will be dominated by $1\Sigma_g^+$ which intersects the large R turning point of $v=1$. DR from H_2^+ mostly in $v=0$ is expected to have a low rate. Note that DR of $v=1$ at low electron energies can lead to $H(2\ell)$ atoms since the $1\Sigma_g^+$ state will cross through bound Rydberg states having the $H(1s) + H(2\ell)$ limit. DR from $v=1$ and $1\Sigma_g^+$ will require electron energies of about 0.8 eV to produce $H(3\ell)$ atoms. The next accessible state is $3\Pi_g$ which can lead to DR from $v>5$ and $3\Sigma_u^+$, $1\Sigma_u^+$ and $1\Pi_g$ which intersect near the $v=6$ large R turning point. At low electron energies direct DR from $v=5$ along $3\Pi_g$ and from $v=6$ along all the upper states can lead to $H(3\ell)$ and more highly excited atoms. In the region near the crossing with $2\Sigma_g^+$, the $1\Sigma_g^+$ state calculated here is about 0.23 eV below the result calculated by Bottcher and Docken (1974), 0.97 eV below that calculated by O'Malley (1969) and 0.30 eV below the result of Dastidar et al.

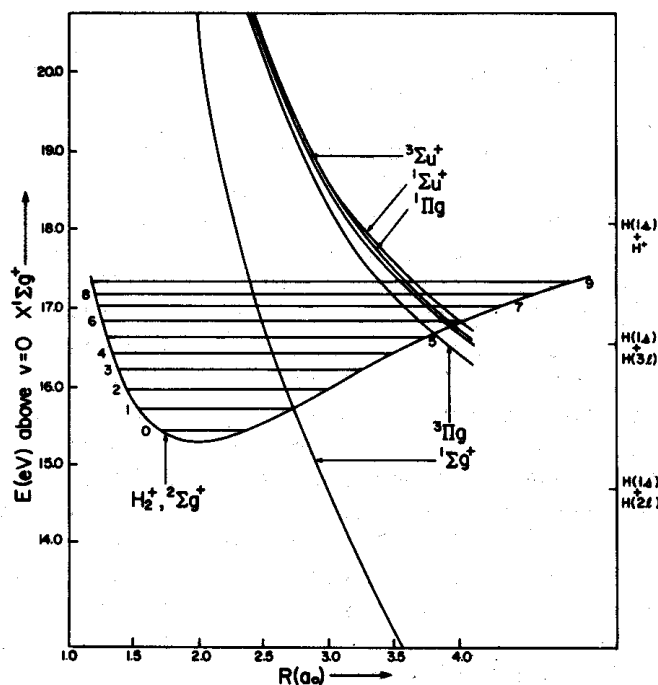


Fig. 7. States leading to DR of the lower vibrational levels of H_2^+ .

(1979). It should be pointed out that O'Malley and Dastidar et al. used considerably smaller wavefunctions than those reported here. The results are therefore in good agreement with the results of Bottcher and Docken and Dastidar, et al. There appears to be no previous reported calculation for the $3\Pi_g$ state. For $3\Sigma_u^+$ the current result is only .07 eV below the previous result (Bottcher et al., 1974) at $R = 4.0 a_0$ and .13 eV below results of Takagi and Nakamura (1980) at $R = 2.0 a_0$. For $1\Pi_g$ there are no previously reported results. For $1\Sigma_u^+$ the current result is only 0.22 eV below the previous result of O'Malley (1969) near $R = 4.0 a_0$ and 0.11 eV below the result of Takagi and Nakamura (1980) at $R = 2.0 a_0$.

A review of the experimental and earlier theoretical work on H_2^+ DR has been presented by Dolder and Peart (1976), Peart and Dolder (1974), Auerbach et al. (1977) and Phaneuf, Crandall and Dunn (1975). An important feature of these experiments is that they involve vibrationally excited H_2^+ with most ions in $v=1$ and $v=2$ in addition to considerable population in $v=5$ and 6. Therefore we can expect the dissociative $3\Pi_g$, $3\Sigma_u^+$, $1\Sigma_u^+$ and $1\Pi_g$ states to play an important role in these experiments. This appears to be confirmed by the merged beam results of McGowan et al. (1976) in which the removal of H_2^+ with $v>2$ from the beam led to a drop in the DR cross section by a factor of more than 2. Direct DR appears to dominate in these experiments. For energies greater than 0.07 eV structure is seen in the cross section curves which is attributed to indirect DR through bound H_2 Rydberg states (McGowan et al., 1979).

DISSOCIATIVE RECOMBINATION OF He_2^+

In Fig. 8, repulsive potential energy curves for DR of He_2^+ are shown. These curves were obtained (Guberman, 1972) from wavefunctions that are quite different from those used for O_2 and H_2 . The wavefunctions are constructed from orbitals that are not required to be orthogonal. Also the orbitals are not required to have gerade or ungerade symmetry, however, the total wavefunction has the proper g or u symmetry. This lack of restrictions on the orbitals provided for a highly interpretable wavefunction. Maxima in the excited states of He_2 which were not due to avoided crossings and which were considered to be anomalous at that time were explained in terms of the unfavorable overlap of a Rydberg orbital on one He with the doubly occupied 1s orbitals on the other He (Guberman and Goddard, 1972; Guberman and Goddard, 1975). Other features of the He_2^* potential curves could be explained in terms of the crossing of diabatic states which were constructed in the same manner as that for the fully optimized states except that the orbitals used were those which were optimum at $R=\infty$ only. These wavefunctions were referred to as frozen orbital (FO) wavefunctions.

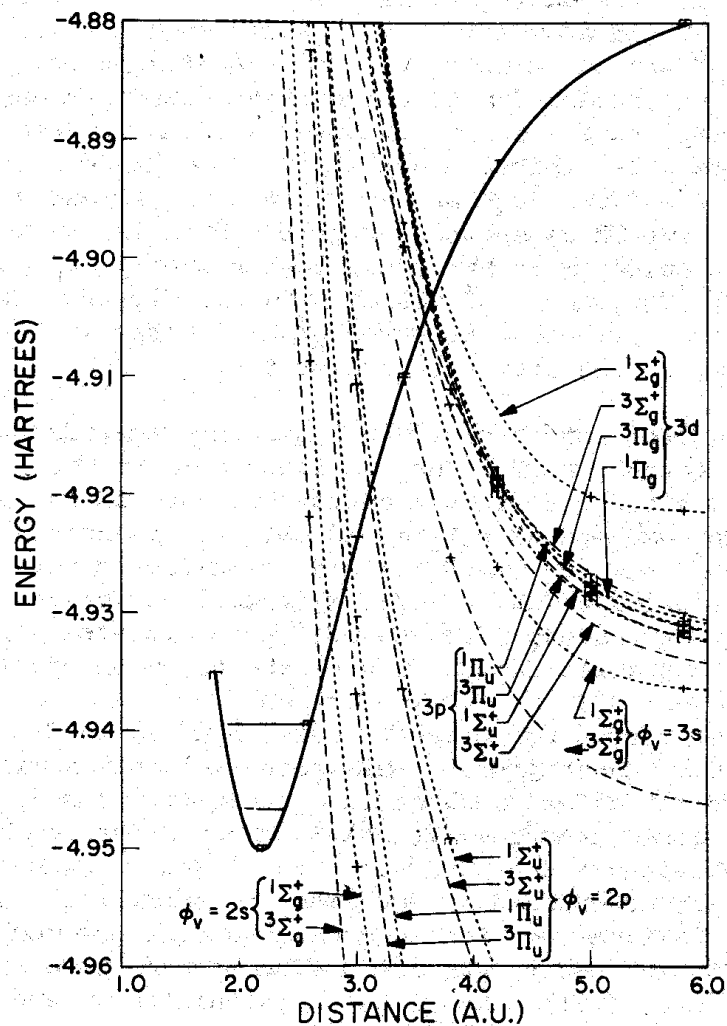


Fig. 8. Potential energy curves for DR of He₂⁺ (Guberman, 1972). The solid curve is the calculated ground state of He₂⁺. The dashed curves are the FO diabatic states of He₂.

It was shown that a change in character of a fully optimized state corresponds to a crossing of two diabatic FO potential energy curves.

The repulsive or attractive nature of the FO curves for $R < 5 a_0$ is dependent upon the nature of the three electron ion core of the excited neutral states. These excited states consist of a diffuse Rydberg orbital surrounding a tight He_2^+ core. The tight He_2^+ core is a mixture of the attractive $^2\Sigma_u^+$ ground state of He_2^+ and the repulsive $^2\Sigma_g^+$ state. Consider the states dissociating to $\text{He}(1s^2) + \text{He}(1s, 2l)$. At intermediate internuclear distances where the diffuse Rydberg orbital surrounds both He atoms, states having primarily a Rydberg 2s orbital and a $^2\Sigma_g^+$ core will be repulsive. These are the $^3\Sigma_g^+$ and $^1\Sigma_g^+$ states and are the lowest states providing routes for DR as shown in Fig. 8. For a 2p Rydberg orbital the repulsive states must be of ungerade symmetry and correspond to the $^3\Pi_u$, $^1\Pi_u$, $^3\Sigma_u^+$, and $^1\Sigma_u^+$ states shown in Fig. 8. The Π states shown in Fig. 8 correspond to the $^2\Sigma_g^+$ He_2^+ state shifted to have the same $R \rightarrow \infty$ limit as the four electron states.

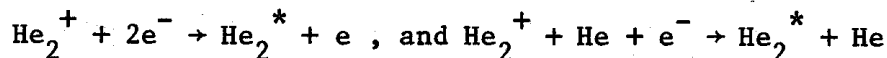
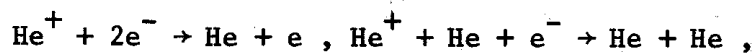
The potential curves shown in Fig. 8 are intended to provide a qualitative picture of DR of He_2^+ . Because the Σ states are obtained from frozen orbitals, these states can be expected to be more repulsive than the same states determined with the techniques used above for O_2 and H_2 . The He_2 DR curves are not expected to be more than 0.5 eV above optimized DR curves. Nevertheless because the DR curves in Fig. 8 are very steep near the He_2^+ ground state, a lowering of 0.5 eV would not qualitatively change the conclusions reached here.

Potential curves for triplet states leading to DR of He_2^+ have been reported by Cohen (1976). His potential curves are more repulsive relative to He_2^+ than those reported here. The $^3\Sigma_g^+$ curve arising from $\text{He}(1s, 2s) ^3S + \text{He}(1s^2) ^1S$ crosses the ion between $v=2$ and $v=3$ compared to a crossing between $v=1$ and $v=2$ shown in Fig. 8. Both results are therefore in agreement concerning the slow rate expected for DR from $v=0$ with low energy electrons. Cohen's calculated dissociation energy was 2.424 eV compared to the accurate value of 2.469 eV (Liu, 1971). Since these calculations tend to give too low a value for the $\text{He} + \text{He}^+$ asymptote compared to the $\text{He} + \text{He}$ asymptote the good result for D_e calculated by Cohen may have the effect of placing the He_2^+ ground state at energies that are too low compared to the neutral states. This can result in neutral states crossing too high on the ion potential curve. The calculated dissociation energy obtained here was 1.97 eV (Guberman, 1972) and effectively cancels much of the error (0.7 eV) in the He ionization potential leading to potential curve crossings that may be more reliable in the results reported here.

Mulliken (1964) reported qualitative potential curves for excited states of He_2 which also led to the conclusion that DR from $v=0$ of He_2^+ is slow. Mulliken's curves were mostly adiabatic in nature and required jumping from one adiabatic curve to another in order to generate $\text{He}(1s,2s) \ ^3S$ from DR. The FO diabatic curves described here provide a single route for dissociation to the separated atoms but cross other diabatic curves of the same symmetry.

From Fig. 8 it appears that DR of $v=0$ of He_2^+ will be very slow while DR of $v=1$ may be appreciably faster along the $^3\Sigma_g^+$ dissociative state leading directly to $\text{He}(1s,2s) \ ^3S$. Direct dissociation to $\text{He}(1s,2p)$ along the ungerade states shown in Fig. 8 will only be possible from higher vibrational levels ($v>3$). But it is possible to generate $\text{He}(1s,2p) \ ^3P$ from the crossing of the attractive $^3\Sigma_g^+$ state arising from $\text{He}(1s^2) + \text{He}(1s,2p) \ ^3P$ with the repulsive $^3\Sigma_g^+$ state arising from $\text{He}(1s^2) + \text{He}(1s,2s) \ ^3S$. An analogous situation applies to the production of $\text{He}(1s,2p) \ ^1P$ from dissociation along the $^1\Sigma_g^+$ state dissociating directly to $\text{He}(1s^2) + \text{He}(1s,2s) \ ^1S$ (Guberman, 1972).

Experimental measurements of DR of He_2^+ have taken a tortuous path since the first measurements over 30 years ago (Biondi and Brown, 1949). The experiments have been reviewed by Massey and Gilbody (1974), Deloche et al. (1976) and Bates (1979a;1979b). The measured rate constants differ by more than a factor of 100. The most recent results indicate that the rate constant is less than $5 \times 10^{-10} \text{ cm}^3/\text{sec}$ (Deloche et al., 1976) at room temperature. The experiments in microwave discharge afterglows are difficult because they involve He_2^+ which is mostly in $v=0$. Mulliken (1964) has remarked that the reported band spectra of He_2 taken from discharges at about 20 mm pressure involve almost entirely bands with $v=0$. Bates (1979b) argues that at 15 mm pressure He_2^+ is easily vibrationally relaxed by collision with He before recombination can occur. The potential curves shown in Fig. 8 in addition to those of Cohen (1976) and Mulliken (1964) indicate that DR from He_2^+ in $v=0$ will be very slow. Indeed the most recent experiments (Deloche et al., 1976; Boulmer et al., 1977) indicate that other recombination processes such as



are significant in He afterglows.

Note that a comparison of Figs. 7 and 8 indicates that the lack of favorable routes for DR of He_2^+ could lead to rates that are not

much larger than those for He_2^+ . However, in order to avoid the formation of H_3^+ and heavier ions the H_2^+ experiments are performed in beams generated from ion sources that produce vibrationally excited H_2^+ (see the previous section). If H_2^+ ions were mostly in $v=0$ the DR rate would be expected to be only slightly faster than that for He_2^+ .

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