

DISSOCIATIVE RECOMBINATION OF O_2^+ , NO^+ AND N_2^+

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This is the fourth Semi-Annual Progress Report describing research on the dissociative recombination (DR) of diatomic ions with electrons.

Introduction

I have developed a new L^2 approach for the calculation of the threshold molecular capture width needed for the determination of DR cross sections. The widths are calculated with Fermi's golden rule by substituting Rydberg orbitals for the free electron continuum coulomb orbital. It is shown, using the $1\Sigma_u^+$ state of O_2 as an example, that the calculated width converges exponentially as the effective principal quantum number, n^* , of the Rydberg orbital increases. The threshold capture width, determined in the limit $n^* \rightarrow \infty$ is then easily obtained. Since atmospheric recombination involves very low energy electrons ($T_e < 3000K$), the threshold capture widths are essential to the calculation of DR cross sections for the atmospheric species studied here. The approach described below makes use of bound state computer codes already in use. The only new program required is one that collects width matrix elements over CI wavefunctions for the initial and final states (see below).

Method

The "golden rule" formula^{1,2} for the capture width is given by,

$$\Gamma = 2 \rho |\langle \psi_f | H | \psi_i^c \rangle|^2 \quad (1)$$

where we take ψ_i^c to be the initial continuum state consisting of a molecular ion and an unbound free electron, ψ_f is the post capture final neutral state and ρ is the density of states in the continuum. ψ_i^c can be constructed from an appropriately antisymmetrized product of bound ion orbitals and a coulomb orbital, i.e. $\psi_i^c = a \phi_{ion} \phi_c$. However, to solve for the appropriate coulomb orbital, the molecular potential must be expanded about a single center (e.g., the midpoint for diatomic molecules). As a result, for diatomic molecules, an axially symmetric potential must be approximated by a spherically symmetric potential. Furthermore, in order to calculate the Hamiltonian matrix element shown in (1) a slowly convergent single center expansion of the tight valence orbitals of the ion must be used. In order to avoid these difficulties we replace ψ_i^c in (1) with a Rydberg wavefunction, ψ_i^R of the neutral molecule,

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i.e. $\psi_i^R = a \phi_{ion} \phi_{Ryd}^{n^*, \ell}$. We will show below that relatively low lying Rydberg states allow for the determination of threshold widths from (1). In order to gain further insight into the use of Rydberg orbitals in (1), we must first examine the dependence of the Rydberg orbital on the principal quantum number, n^* .

For diatomic molecules of the first row of the periodic table, molecular Rydberg orbitals have most of their amplitude outside of the region occupied by the valence orbitals, and it is a good approximation to center the Rydberg orbital at the molecular midpoint. If we approximate the Rydberg orbital by a hydrogenic function we can write the energy of the Rydberg orbital in atomic units as

$$E = - \frac{1}{2(n^*)^2} \quad (2)$$

where $n^* = n - \delta$, and n is the principal quantum number and δ is the quantum defect. For atoms and for high Rydberg states of molecules, δ is nearly constant with n for a fixed angular momentum quantum number, ℓ . If we take $n^* \gg \ell$ we can write for the radial part of the bound molecular hydrogenic Rydberg orbital³

$$(\phi_{Ryd}^{n^*, \ell} = R_{n^*, \ell}(r) \chi(\theta, \psi)),$$

$$R_{n^*, \ell}(r) = 2 \left(\frac{z}{n^*} \right)^{3/2} \frac{(2zr)^\ell}{(2\ell+2)!} e^{-\frac{zr}{n^*}} F \quad (3)$$

where F is the confluent hypergeometric function which is dependent upon r but independent of n^* for $n^* \gg \ell$. Also we take the nuclear charge, z , to be unity for high Rydberg orbitals. For large n^* the radial portion of the Rydberg orbital is independent of n^* aside from the $(n^*)^{-3/2}$ normalization factor and the exponential factor which will be close to unity for small r . The question that needs to be asked here is how important is the exponential factor in determining the magnitude of the matrix element in (1) when the continuum orbital is replaced by a Rydberg orbital? Since the remaining orbitals in the integral are valence orbitals it is to be expected that the integral in (1) will cover a region of r very close to the nuclei. The importance of the exponential factor will be explored further below. Taking r to be small and replacing ϕ_c by a

bound Rydberg orbital where the radial part is given by (3) we see that the matrix element in (1) varies as $(n^*)^{-3}$. The density of states can be defined for the bound Rydberg orbitals as follows⁴:

$$\rho = \frac{1}{E(n^* - \frac{1}{2}) - E(n^* + \frac{1}{2})} .$$

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Inserting (2) we have,

$$\rho = 2 \left[\left(1/(n^* - \frac{1}{2}) \right)^2 - \left(1/(n^* + \frac{1}{2}) \right)^2 \right]^{-1} . \quad (4)$$

From (4) we see that ρ varies approximately as $(n^*)^3$. As a result the full expression for the width in (1) will be independent of n^* for high n^* if the portion of coordinate space sampled by the matrix element in (1) is close to the nuclei. Therefore if we calculate Γ using orbitals having successively higher n^* we would expect a constant Γ as n^* increases and a flat approach to $n^* \rightarrow \infty$. These ideas are explored below in a calculation on the $1\Sigma_u^+$ repulsive autoionizing state of O_2 .

Calculation of a Capture Width for O_2

The lowest $1\Sigma_u^+$ valence state of O_2 arises from $1D + 1S$ atoms. If Rydberg character is excluded from this state it provides a diabatic route for direct dissociative recombination (DR) of O_2^+ . Previous calculations⁶ have shown that the $1\Sigma_u^+$ potential curve crosses the O_2^+ ground state potential curve between the large R turning points of the $v=1$ and $v=2$ vibrational levels. The $1\Sigma_u^+$ state provides the lowest energy route for generation of $O(1S)$ from DR of O_2^+ . DR of O_2^+ is the major source of $O(1S)$ at high altitudes in the earth's upper atmosphere.

For the calculation of the width matrix element given in (1) we use the valence gaussian basis set reported previously^{5,6} supplemented with 18 diffuse $2p\pi$ gaussians centered on the internuclear axis at the midpoint. Exponents of .0532, .0210, .0103 and .0041 were taken from Dunning and Hay⁷. To these were added two additional basis functions with exponents of .037 and .0072. The remaining exponents were determined by using a multiplicative factor of 0.6 starting with the exponent .0041. The midpoint functions were only allowed to

enter the Rydberg $n\pi_u$ orbitals of the $1\Sigma_u^+$ Rydberg states. The Rydberg orbitals were also expanded over the valence basis set described above.

The $1\Sigma_u^+$ state was expanded over orbitals determined in MCSCF calculations on the ground $X^3\Sigma_g^-$ state of $O_2^{5,6}$. The $1\Sigma_u^+$ state was represented by the 12 configurations shown in Table I. These are all the $1\Sigma_u^+$ configurations which can be formed in the valence space while keeping the 1σ and 2σ orbitals fully occupied. The first 8 configurations listed are needed for proper dissociation of $1\Sigma_u^+$ to $O(1S) + O(1D)$. A $1\Sigma_u^+$ Rydberg state described by the two degenerate configurations shown below was used,

$$\dots 3\sigma_g^2 \pi_{ux}^2 \pi_{gx} \pi_{uy}^2 n\pi_{ux} + \dots (x \leftrightarrow y) \quad (5)$$

where \dots denotes $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2$ and $(x \leftrightarrow y)$ denotes the orbital occupancy obtained by replacing π_x with π_y . Note that a negative sign in (5) would give rise to a $1\Delta_u$ state. The valence orbitals used in (5) were the same as those used in the dissociative state described above. The Rydberg orbitals were determined in Improved Virtual Orbital (IVO) calculations⁸ appropriate to the orbital occupancies shown in (5), i.e. the Rydberg orbitals see a potential due to both the $2\Pi_{gx}$ and $2\Pi_{gy}$ O_2^+ cores. As a result the Rydberg orbitals for $1\Sigma_u^+$ Rydberg states^s are not the same as those for $1\Delta_u$ states. The Rydberg $n\pi_{ux}$ orbitals for $1\Sigma_u^+$ are eigenfunctions of the Hamiltonian

$$H = h + \sum_i 2J_i - K_i + 3/2 J_{\pi_{gx}} + 3/2 K_{\pi_{gx}} - \frac{1}{2} J_{\pi_{gy}} - 1/2 K_{\pi_{gy}}$$

where h is the one electron operator, i runs over all the closed shell orbitals and J and K are the two electron coulomb and exchange operators.

The results are shown in Table II. A total of 6 $1\Sigma_u^+$ states have been accurately determined in the IVO calculations. The calculated adiabatic excitation energies (obtained by subtracting the IVO ionization potential from the experimental adiabatic ionization potential, 12.052 eV)⁸ agree well with the energies for the two experimentally determined f and j $1\Sigma_u^+$ Rydberg states. The remaining experimentally derived energies in Table II are estimates obtained from Eq. (2) with the quantum defect obtained from the energy of j $1\Sigma_u^+$. The energies of the four higher calculated states agree quite well with the experimental estimates. In column four we list $\rho/(n^*)^3$ where it can be seen that the

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highest states differ by about 1% from an $(n^*)^3$ dependence. Indeed the density of states can be represented quite well with the expression $\rho = (n^*)^3 e^{-\frac{.5000}{(n^*)^2}}$ where for high n^* , the exponential factor represents a small correction to ρ . The fifth column of Table II lists the square of the Hartree-Fock (i.e. using only the first 2 terms in Table II for ψ_f) matrix element multiplied by $2\pi(n^*)^{-3}$

$\times 1.586 e^{-\frac{.2626}{n^*}}$ (eV). The fit represents the predissociation widths of the bound Rydberg states. The exponential part of the matrix element is a necessary

but small contributor to the fit and arises from the $e^{-\frac{r}{n^*}}$ term in the Rydberg radial orbital given in (3). For $n^* = 7.396$ it gives a correction factor of .9651 to the fit. The Hartree-Fock capture or autoionization width is given by the product of the above two factors,

$$\Gamma = 1.586 e^{-\frac{.2626}{n^*}} e^{-\frac{.5000}{(n^*)^2}}$$

Taking the limit $n^* \rightarrow \infty$, we have $\Gamma = 1.586$ eV at $R = 2.2819 a_0$. Note that the limiting value of the width is only .061 eV above the highest calculated width. Now let us consider the effect of configuration interaction in the dissociative state upon the calculated width. Column 7 of Table II is the same as Column 5 except that ψ_f is now represented by the 12 configuration wavefunction of Table I. It is seen that the results in Column 7 are again exponentially converging

with the high roots represented by $.5412(n^*)^3 e^{-\frac{.2698}{n^*}}$. Once again the latter expression represents the predissociation widths of bound Rydberg states. The

exponential dependence is due to the $e^{-\frac{r}{n^*}}$ term in the radial orbital. Multiplying by the exponential density of states fit given above we find $\Gamma = .5412$ eV for the 12 configuration representation of ψ_f at $R = 2.2819$. We see that the configuration interaction width is only 39% of the Hartree Fock width. Therefore one should exercise caution when calculating widths from Hartree Fock representations of the dissociative state, especially when other configurations having significant matrix elements with the Rydberg states have CI coefficients greater than 0.1.

At $R = 2.0 a_0$, the calculated Rydberg widths for the CI representation of the $1\Sigma_u^+$ dissociative state are given by $\Gamma(2.0) = .5207 e^{-\frac{.2248}{n^*} - \frac{.5000}{(n^*)^2}}$. Compared to the result for $R = 2.2819$, we note that the coefficient of $1/n^*$ in the exponent has decreased slightly due to the smaller region of coordinate space involved in the width matrix element. From these results we would expect that for polyatomic molecules, the coefficient of $1/n^*$ in the exponent will be greater than the coefficient for diatomic molecules. For an equivalent n^* , the calculated Rydberg width for a diatomic molecule will be closer to the capture width than that for a polyatomic. Nevertheless, once the exponential fit is determined for a polyatomic, the limit of $N^* \rightarrow \infty$, will give the capture width.

I am currently investigating the effects of further configuration interaction in both ψ_i and ψ_f on the magnitude of the calculated width. This approach allows for the rapid calculation of width matrix elements and the study of CI effects in entrance and exit channels while using programs designed for bound state calculations.

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Table I. CI Wavefunction for the $1\Sigma_u^+$ Dissociative State

| <u>CI Coefficient</u> | Orbital Occupancy ^a | | | | | |
|-----------------------|--------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| | <u>$3\sigma_g$</u> | <u>$3\sigma_u$</u> | <u>$1\pi_{ux}$</u> | <u>$1\pi_{gx}$</u> | <u>$1\pi_{uy}$</u> | <u>$1\pi_{gy}$</u> |
| .66402 | 2 | 0 | 2 | 2 | 1 | 1 |
| .66402 | 2 | 0 | 1 | 1 | 2 | 2 |
| -.21346 | 1 | 1 | 2 | 2 | 2 | 0 |
| -.21346 | 1 | 1 | 2 | 0 | 2 | 2 |
| -.11427 | 1 | 1 | 2 | 2 | 0 | 2 |
| -.11427 | 1 | 1 | 0 | 2 | 2 | 2 |
| -.01955 | 0 | 2 | 2 | 2 | 1 | 1 |
| -.01955 | 0 | 2 | 1 | 1 | 2 | 2 |
| -.00645 | 2 | 2 | 1 | 1 | 2 | 0 |
| -.00645 | 2 | 2 | 2 | 0 | 1 | 1 |
| -.00505 | 2 | 2 | 0 | 2 | 1 | 1 |
| -.00505 | 2 | 2 | 1 | 1 | 0 | 2 |

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a. All configurations include the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2$ orbital occupancy.

Table II. Calculated Excitation Energies and $1\Sigma_u^+$ Widths^a

| n^* | T_e | | $\rho/(n^*)^3$ | $2\pi \langle \psi_F^{HF} H \psi_I^R \rangle ^2 \cdot (n^*)^{3b}$ | Γ_{HF}^b | $2\pi \langle \psi_F^{CI} H \psi_I^R \rangle ^2 \cdot (n^*)^{3c}$ | Γ_{CI}^c |
|-------|------------|--------------|----------------|--|-----------------|--|-----------------|
| | Calculated | Experimental | | | | | |
| 2.363 | 9.615 | 9.434 | .9125 | 1.337 | 1.220 | .4571 | .4171 |
| 3.383 | 10.863 | 10.812 | .9564 | 1.450 | 1.387 | .4947 | .4731 |
| 4.389 | 11.346 | 11.320 | .9744 | 1.490 | 1.452 | .5081 | .4951 |
| 5.393 | 11.584 | 11.570 | .9826 | 1.510 | 1.484 | .5150 | .5061 |
| 6.394 | 11.719 | 11.711 | .9878 | 1.522 | 1.503 | .5189 | .5125 |
| 7.396 | 11.803 | 11.798 | .9909 | 1.530 | 1.516 | .5218 | .5171 |

- a. All energies are in electron volts.
- b. These results are for the 2 configuration wavefunction of the dissociative $1\Sigma_u^+$ state.
- c. These results are for the 12 configuration wavefunction of Table I.

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