R-Matrix Calculations of Low-Energy Electron Scattering by Oxygen Molecules

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The R-matrix method has been used to study the scattering of electrons by oxygen molecules for impact energies in the range from threshold to 15 eV. Electronic excitation cross sections for transitions to the $a\,^1\Delta_g$, $b\,^1\Sigma_g^+$, and "6 eV" states of oxygen are presented. Important contributions from a $^2\Pi_u$ resonance, in addition to the well-known $^2\Pi_g$ resonance, are found to significantly modify previous theoretical predictions. Integral elastic scattering cross sections are also obtained for the first time for a complicated open-shell system using an *ab initio* method.

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Detailed information about collisions between low-energy electrons and oxygen molecules is required in studies of the physics of planetary atmospheres, gaseous discharges, and both astrophysical and laboratory plasmas. The collision has been extensively studied experimentally [1] but there have been few theoretical studies. The electronic excitation cross sections of the a and b excited states were first calculated by Noble and Burke [2] using the R-matrix method [3]. Only the three lowest electronic states of the target molecule were taken into account. The results confirmed the dominant role of the resonant $^2\Pi_g$ symmetry and were in reasonable agreement with experiment. More recently, Teillet-Billy, Malegat, and Gauyacq [4], using multichannel effective-range theory (ERT), have demonstrated the multichannel nature of the shape resonance in this symmetry and the necessity of including all electronic states of the target which are parents of the resonance in accurate collision calculations.

In this Letter we present new results for the electronic excitation from the ground state demonstrating that contributions from other scattering symmetries are important and significantly modify previous theoretical estimates of the cross sections. These results are obtained using the R-matrix method with a model including nine electronic states of the target molecule and configuration interaction (CI) representations of the target wave functions. We also obtain estimates of the elastic scattering cross section for impact energies up to 15 eV. This work represents one of the first *ab initio* calculations of electron scattering from an open-shell molecule.

The R-matrix method has now been successfully applied for more than a decade in studies of collisions between photons, electrons or positrons, and diatomic molecules. The essential techniques have already been described [5] and need not be repeated here. It is sufficient to note that the complete electrostatic interaction between the target and the incident electron is taken into account within a spherical region of configuration space defined by values of the radial coordinate of the incident electron being less than some predetermined value chosen to encompass the charge density of the target (10.0 a.u. in the present work). Within this region the entire Hamiltonian is diagonalized assuming the adiabatic nuclei (AN) approximation [6] in which the target nuclei are held fixed in space. The results depend parametrically on the internuclear separation R, which is held fixed in this work at 2.3 bohrs, and may be used in subsequent calculations to take full account of vibrational effects. An energy-independent basis of the form

$$\Psi_k = \mathcal{A}\sum_{ij}\Phi_i(1,\ldots,N;R)u_j(N+1;R)c_{ijk} + \sum_q \Phi_q(1,\ldots,N+1;R)c_{qk} \quad (1)$$

is used to determine the variational coefficients c_{ijk} and c_{qk}. The initial close-coupling summation in Eq. (1) involves products of target eigenstates Φ_i and functions u_j representing the scattering electron. The scattering electron must be antisymmetrized with respect to the target electrons and this is denoted by the operator $\mathcal{A}$. The summation is chosen to include the nine target states $X\,^3\Sigma_g^-$, $a\,^1\Delta_g$, $b\,^1\Sigma_g^+$, $c\,^1\Sigma_u^-$, $C\,^3\Delta_u$, $A\,^3\Sigma_u^+$, $B\,^3\Sigma_u^-$, $^1\Delta_u$, and $^1\Sigma_u^+$ corresponding to the configurations [core]$1\pi_u^4 1\pi_g^2$ and [core]$1\pi_u^3 1\pi_g^3$. Each of these states is represented by a configuration interaction wave function including up to twenty basis functions. These functions are calculated using σ and π self-consistent-field (SCF) orbitals given by Saxon and Liu [7]. In this way we find that the relative excitation energies of the lowest three states are accurate to about 0.2 eV, while the relative excitation energies of the three states which lie at about 6 eV above the ground state are accurate to 0.1 eV. We show in Fig. 1 a potential-energy diagram of O_2 which illustrates the nine states we have included.

The continuum orbitals u_j in Eq. (1) are obtained by numerically solving a single-channel model scattering problem and then Schmidt orthogonalizing with respect to the bound molecular orbitals. SCF $4\sigma_g$ and $3\sigma_u$ virtual orbitals are included in this set in addition to those occupied in the ground state. Continuum functions complete over an energy range up to 6.0 Ry and including

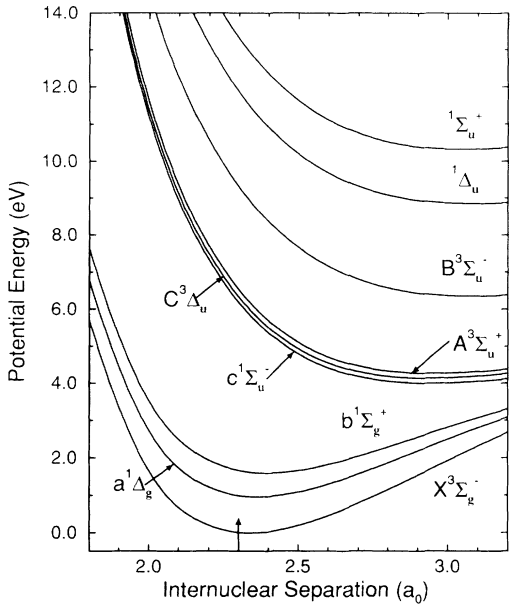

FIG. 1. Schematic potential-energy curves for the nine electronic states of oxygen included in the R-matrix calculations.

partial waves up to $l=5$ for Σ, Π, and Δ scattering symmetries are included in the calculations. The second summation in Eq. (1) involves $\mathcal{L}^2$-integrable $(N+1)$-electron terms and is constructed to relax orthogonality constraints and to account for short-range polarization effects. The R matrix is calculated from the internal region solution and provides the boundary conditions for the integration of the coupled Schrödinger equations in the external region.

In Fig. 2 electronic excitation cross sections for transitions from the ground $X^3\Sigma_g^-$ state to the metastable $a^1\Delta_g$ are shown as functions of the incident electron energy. The R-matrix results shown by the solid curve are seen to be slightly higher but in good overall agreement with the experimental results of Trajmar, Cartwright, and Williams [8] and of Linder and Schmidt [9]. Unfortunately the experimental uncertainties are large and preclude a definitive test of the theory. Also shown in the same figure are the ERT results of Teillet-Billy, Malegat, and Gauyacq [4] indicated by the long-dashed line. The ERT cross sections are in reasonable agreement with the $^2\Pi_g$ partial cross section calculated using R-matrix theory and shown by the dash-dotted line. This is expected since a fundamental assumption of the ERT approach is that the excitation is by one-electron processes via the shape resonance. However, the full R-matrix results demonstrate that there are significant contributions coming from other scattering symmetries. The most important of these is the resonant contribution in the $^2\Pi_u$ symmetry at around 8 eV. The partial cross section in this symmetry is illustrated by the dotted curve. Additional evidence for the existence of this contribution to the excitation process may be inferred from the measured dissociative attachment cross sections [10].

Our results for electronic excitation to the $b^1\Sigma_g^+$ state are illustrated in Fig. 3. Again the R-matrix results shown by the solid curve exhibit an important contribution around 8 eV arising from the $^2\Pi_u$ resonance. The

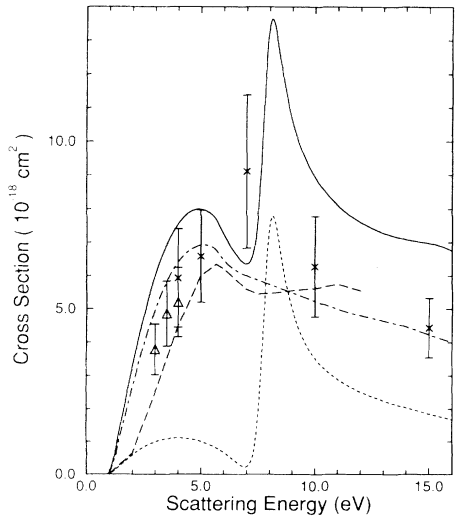

FIG. 2. Total cross sections for the excitation of the $a^1\Delta_g$ state. Present R-matrix results, solid line; ERT results [4], long-dashed line; R-matrix $^2\Pi_g$ partial cross section, dash-dotted line; R-matrix $^2\Pi_u$ partial cross section, dotted line. Experimental points of Linder and Schmidt [9], triangles; Trajmar, Cartwright, and Williams [8], crosses.

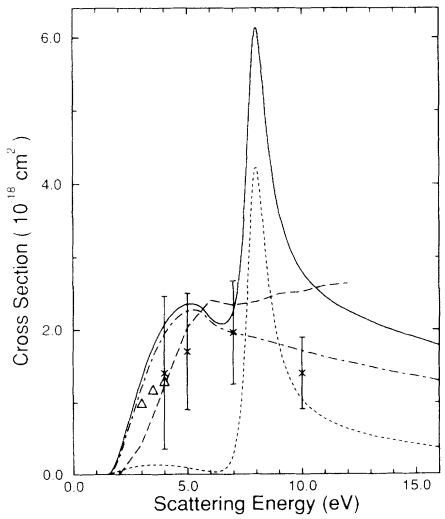

FIG. 3. Total cross sections for the excitation of the $b^1\Sigma_g^+$ state. Present R-matrix results, solid line; ERT results [4], long-dashed line; R-matrix $^2\Pi_g$ partial cross section, dash-dotted line; R-matrix $^2\Pi_u$ partial cross section, dotted line. Experimental points of Linder and Schmidt [9], triangles; Trajmar, Cartwright, and Williams [8], crosses.

corresponding partial cross section is shown by the dotted curve. For this transition there is a closer agreement between the ERT (long-dashed curve) and R-matrix $^2\Pi_g$ partial cross-section results (dash-dotted curve) at energies up to 5 eV than for the $X \rightarrow a$ transition. The behavior of the ERT cross section at energies around 10 eV suggests that the effective-range approximation itself is beginning to fail.

In Fig. 4 we present cross sections for transitions to the 6-eV group of states, $c\,^1\Sigma_u^-$, $C\,^3\Delta_u$, and $A\,^3\Sigma_u^+$. We compare the sum of these transitions with the experimental results of Teillet-Billy *et al.* [11]. The R-matrix results for the sum of these cross sections (solid curve) are only slightly above the upper limit of the error bars. The agreement with the ERT results shown by the long-dashed curve [12] must be regarded as fortuitous because the R-matrix results indicate that there are significant contributions from symmetries other than $^2\Pi_g$. It should also be noted that the experimental values of Teillet-Billy *et al.* [11] lie significantly below earlier measurements at 20 eV [13].

The calculation of elastic scattering cross sections provides a particular challenge as in this case there are important long-range polarization effects at low incident energies which are insignificant in the electronic cases discussed above. Our results are compared in Fig. 5 with experimental values obtained by Shyn and Sharp [14]. The agreement between theory and experiment is excellent over the energy range between 4 and 15 eV but the calculated cross section is up to a factor of 2 higher than

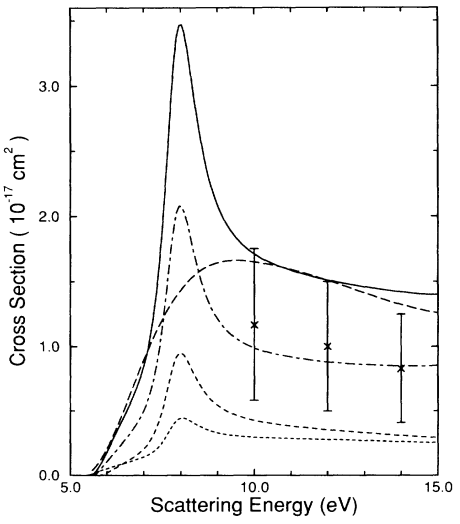

FIG. 4. Total cross sections for the electronic excitation of the 6-eV group of states. Present R-matrix results for the sum of cross sections to A, C, and c states, solid line; ERT results [12], long-dashed line; experimental results of Teillet-Billy *et al.* [11], crosses. R-matrix cross sections for transitions to the $c\,^1\Sigma_u^-$ state, dotted line; $C\,^3\Delta_u$ state, dash-dotted line; $A\,^3\Sigma_u^+$ state, dashed line.

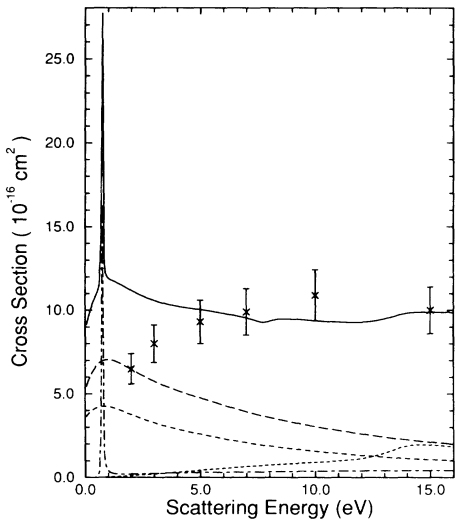

FIG. 5. Integral elastic cross sections in Å^2 vs the scattering energy. Present R-matrix calculations, solid line; experimental points of Shyn and Sharp [14], crosses. The calculated partial cross sections for symmetry $^4\Sigma_g^-$, long dashes; $^2\Sigma_g^-$, dashes; $^4\Sigma_u^-$, dots; $^2\Pi_g$, dash-dotted curve.

experiment at the lowest energies. Twelve scattering symmetries $^2\Sigma_g^-$, $^4\Sigma_g^-$, $^2\Sigma_u^-$, $^4\Sigma_u^-$, $^2\Pi_g$, $^4\Pi_g$, $^2\Pi_u$, $^4\Pi_u$, $^2\Delta_g$, $^4\Delta_g$, $^2\Delta_u$, and $^4\Delta_u$ have been summed to obtain the theoretical results and some of the partial cross sections are illustrated. In the low-energy region the dominant contributions to the cross section are from the $^4\Sigma_g^-$ and $^2\Sigma_g^-$ symmetries, both of which have $l=0$ components which are sensitive to polarization effects. Only about 30% of the expected ground-state polarizability is included in the present model. In the analogous case for the scattering of electrons by nitrogen molecules taking account of these long-range polarization effects reduces the calculated cross sections by 50% in the near threshold region [15]. The apparent discrepancy can therefore almost certainly be entirely accounted for by this omission. Also shown are the partial cross sections for the scattering symmetries $^4\Sigma_u^-$ and $^2\Pi_g$. Each of these symmetries is dominated by a shape resonance with positions and widths as shown in Table I. The position of the $^4\Sigma_u^-$ resonance may be shifted to slightly lower energies when polarization and nuclear motion effects are included. The

TABLE I. Resonance positions and widths obtained in the present calculation. Values in parentheses are three-state R-matrix results from Noble and Burke [2].

Resonance	Energy, E_r (eV)	Width, Γ_r (eV)
$^4\Sigma_u^-$	14.17	3.39
$^2\Pi_g$	0.700	0.026
	(0.757)	(0.035)
$^2\Pi_u$	7.845	1.027

remaining resonance occurs in the O_2^- $^2\Pi_g$ ground state and as we have already seen has important consequences for the low-energy electronic excitation cross sections. Experimental estimates of the width vary but recent work indicates a value of 2–3 meV [16]. The effect of including additional electronic states and target correlation is illustrated by comparing the position and width obtained here with the results of our previous calculations including only three electronic states and using SCF wave functions. The partial cross sections for the remaining O_2^- symmetries have not been illustrated but are smaller than those already discussed. The resonance in the $^2\Pi_u$ symmetry is a core-excited resonance and although important for electronic excitation makes a negligible contribution to the elastic scattering cross section.

It is clear that the R-matrix method provides both insight and physically accurate results despite the complications which arise from an open-shell target system and transitions which occur as a consequence of both direct and exchange interactions. The important role of the $^2\Pi_g$ resonance in the electronic excitation of O_2 is confirmed but we find that the $^2\Pi_u$ core-excited resonance and nonresonant contributions significantly modify the calculated cross sections. Improved theoretical results require both the inclusion of polarized pseudostates and an account of nuclear motion effects. We plan to investigate these and other questions in future work and will present more detailed results together with angular distributions in a longer publication. The results obtained here clearly point to the need for new accurate experimental measurements of these cross sections.

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