

Resonant Mechanisms in the Vibrational Excitation of Ground State O₂

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We present new experimental and theoretical results for e^- -O₂ collisions which demonstrate the dominant contribution of the $^4\Sigma_u^-$ resonance and the significant contribution of the $^2\Sigma_u^-$ resonance to the $X^3\Sigma_g^-$ ground state vibrational excitation cross sections in the energy range 4–15 eV. This work, combined with earlier studies by the present and other workers, shows that low-energy vibrationally and electronically inelastic cross sections can be quantitatively understood in terms of four resonances with $^2\Pi_g$, $^2\Pi_u$, $^4\Sigma_u^-$, and $^2\Sigma_u^-$ symmetries. [S0031-9007(96)00114-7]

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Collisions between low-energy electrons and oxygen molecules are involved in a wide range of processes occurring in the upper atmosphere, electrical discharges, and plasma chemistry. A great deal of experimental and theoretical effort has therefore been invested over the years to measure the vibrational cross sections for these collisions and to identify the resonant processes involved. However, the particular resonances which dominate the process for impact energies in the range between 4 and 15 eV have remained ambiguous and controversial. In the present work we report the results of a combined experimental and theoretical investigation which resolves this question.

Previous studies of vibrational excitation in the $X^3\Sigma_g^-$ ground electronic state of O₂ have been carried out by Linder and Schmidt [1] who presented relative data for vibrational excitation of the $v = 0 \rightarrow 1, 2, 3, 4$ levels by electrons with energies in the range from threshold to 4 eV where the $^2\Pi_g$ resonance dominates. In addition, Wong, Boness, and Schulz [2] carried out the first experimental measurement of the absolute differential cross sections (DCS) for excitation to these vibrational levels at a scattering angle of $\theta_e = 25^\circ$ for electrons with energies in the range 4–15 eV. The broad maximum in these cross sections at about 10 eV indicated resonance enhancement. Wong, Boness, and Schulz [2] suggested that the $^4\Sigma_u^-$ resonance was responsible, on the basis of O₂⁻ potential energy curves of Krauss *et al.* [3] and qualitative Franck-Condon overlap arguments, although a contribution from the $^2\Sigma_u^-$ resonance could not be ruled out.

The most comprehensive experimental investigation prior to the present study was carried out by Shyn and Sweeney [4] who measured the absolute DCS for $v = 0 \rightarrow 1, 2, 3, 4$ excitation for scattering angles in the range 12° – 156° . These DCS were then extrapolated to yield the first absolute integral cross sections (ICS) at the scattering energies $E_0 = 5, 7, 10,$ and 15 eV. They noted the existence of a broad structure in the ICS around 10 eV, but did not discuss the possible resonance mechanisms involved in the scattering process. Finally,

in a recent absolute differential cross section measurement of vibrational excitation in the $^3\Sigma_g^-$ ground state, Allan [5] also found a broad structure near 10 eV in addition to the well-known sharp peaks below about 2.5 eV arising from the $^2\Pi_g$ resonance.

In addition to the investigation of electron scattering by gas-phase molecular oxygen, there is also considerable interest in scattering by molecular oxygen adsorbed on surfaces. For example, Jensen, Palmer, and Rous [6] measured the excitation function for the $v = 0 \rightarrow 1$ vibrational transition of O₂ physisorbed on graphite and interpreted the results as due to resonance enhancement by either the $^4\Sigma_u^-$ or $^2\Pi_u$ resonance depending on the orientation of the O₂ molecule. Full details are given in a review article by Palmer and Rous [7]. We simply note that the results of the present study impact significantly on the above interpretation.

It follows from the above discussion that there are still outstanding questions concerning the role of resonant mechanisms in the vibrational excitation of O₂ that need to be resolved and that their resolution impacts on a wide range of applications. In this Letter we first discuss our experimental measurements before going on to describe our calculations using the *R*-matrix method. Finally, we present our experimental and theoretical results and draw conclusions from our work.

The experimental cross sections are measured by crossing a beam of O₂ effusing from a molybdenum tube of internal diameter 0.6 mm with a beam of electrons with the desired energy, E_0 , where E_0 is selected using a high-resolution electron monochromator. Elastically and inelastically scattered electrons at a particular scattering angle (θ) are energy analyzed and detected. The overall energy resolution is ~ 65 meV (FWHM) and typical electron beam currents ~ 1 nA are obtained in the interaction region for the energy range of the present study. The true zero scattering angle is determined as that about which the elastic scattering intensity is symmetric. The estimated error in this determination is $\pm 1^\circ$. The electron energy scale is calibrated against the well-known helium

2^2S resonance at 19.367 eV and has an estimated accuracy of better than 50 meV.

The energy-loss spectra are obtained at each scattering angle over the energy loss range -0.2 to 0.86 eV by ramping the analyzer in an energy-loss mode in conjunction with a multichannel scaler. In making the present measurements it is essential that the transmission of the scattered electron spectrometer is known. The procedure adopted in the present work is described in Brunger and Teubner [8] and so is not repeated here.

Least-squares fitting techniques are then used to fit each energy-loss spectrum in order to obtain the ratio of the DCS for the rovibrational transition of interest, $\sigma_{v'}(E_0, \theta)$, and the elastic DCS, $\sigma_0(E_0, \theta)$. By measuring the elastic angular distributions for each E_0 in a separate series of experiments, the required rovibrational DCS are obtained for ten electron energies in the range 5–20 eV. At this point we note that our elastic DCS are in good agreement with the earlier data of Shyn and Sharp [9] and in fair agreement with the recent results of Sullivan *et al.* [10]. The respective vibrational DCS are then extrapolated using a method that has been employed successfully by Alle *et al.* [11] to yield the corresponding ICS.

We note that the good agreement in shape between the extrapolated vibrational DCS and the corresponding R -matrix results [12] confirms the validity of this extrapolation technique. As a further confirmation, we also derive the ICS from our DCS data using the results from a recent Schwinger multichannel calculation [13]. At worst the difference in the values of our derived ICS, using the two theoretical approaches, is of the order of 8% which is added in quadrature to the experimental uncertainties on our measured DCS to give us the overall error on the ICS. Further details of the experiment, including the normalization, will be given in a later paper [12].

We now turn to a description of the R -matrix calculations carried out in the present work. We have used this approach over the last ten years as the basis of a systematic and continuing program of research to develop a detailed theoretical understanding of all aspects of low-energy electron collisions with molecular oxygen. In our early work [14] only the three lowest electronic states of the target were included in the usual close coupling plus correlation terms expansion of the total wave function. However, in more recent work [15–17] including that presented in the present Letter, 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 $1\Sigma_u^+$ states, corresponding to the configurations $[\text{core}]1\pi_u^4 1\pi_g^2$ and $[\text{core}]1\pi_u^3 1\pi_g^3$, were included in the expansion. Each of these states is represented by a configuration interaction expansion wave function including up to 20 basis functions, where these functions are calculated using the self-consistent-field orbitals given by Saxon and Liu [18]. In this way we find that the relative excitation energies of the three lowest electronic states are accurate to about 0.2 eV, while the relative excitation energies of the three states

which lie approximately 6 eV above the ground state are accurate to about 0.1 eV. We show in Fig. 1(a) a potential energy diagram of O_2 which illustrates the nine target states which have been included in our calculations.

Adopting this target basis, T -matrix elements are then calculated in the fixed-nuclei approximation for all symmetries that yield a significant contribution to the cross

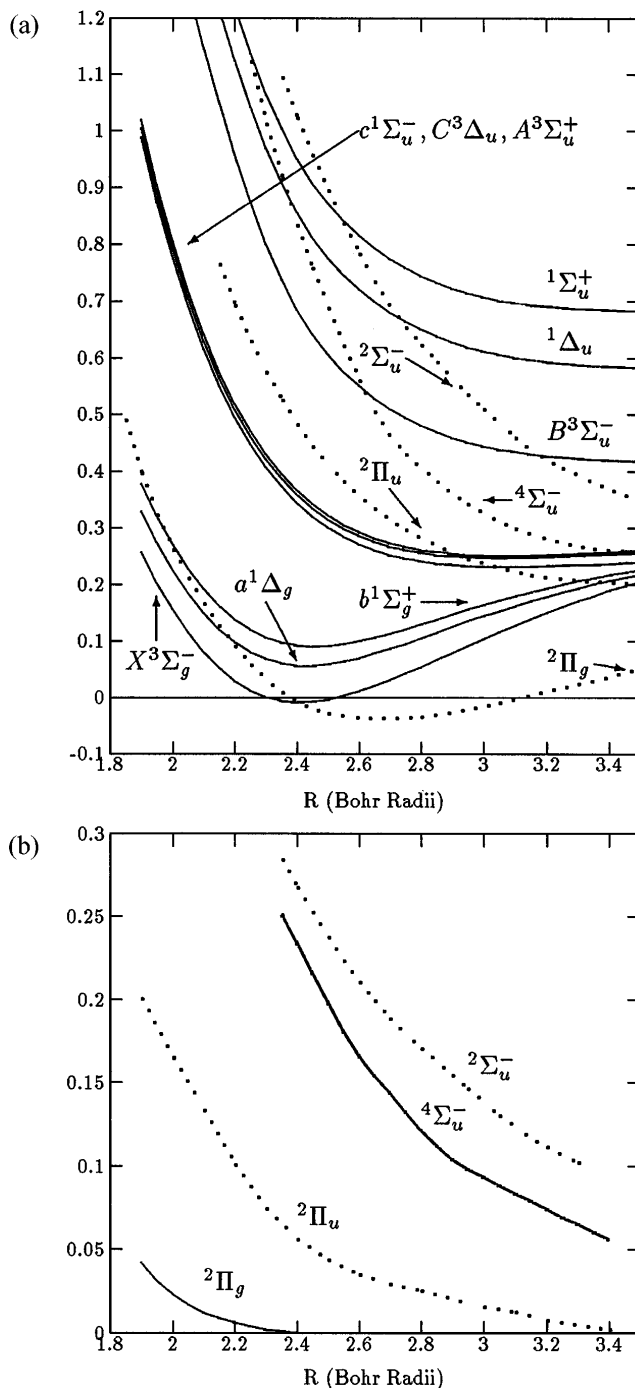


FIG. 1. (a) Calculated potential energy curves (in Ry) of the target states (—) and resonances (···). (b) Calculated widths (in Ry) of the resonances.

sections, for internuclear separations R in the range $1.85a_0 \leq R \leq 3.5a_0$ and for a grid of energies from threshold to 15 eV. We find that four of these symmetries are resonant in this energy range, corresponding to the ${}^2\Pi_g$, ${}^2\Pi_u$, ${}^4\Sigma_u^-$, and ${}^2\Sigma_u^-$ resonant states of O_2^- . By fitting the corresponding eigenphase sums in each case to a Breit-Wigner resonance formula, we are able to extract the resonance position E_r and the resonance width Γ as a function of R for each of these resonance states. The resonance positions are plotted in Fig. 1(a) while the corresponding widths are given in Fig. 1(b).

The reason that these four resonances can be expected to control inelastic collisions in the low-energy region can be understood by considering the dominant configurations that contribute to the resonant states in each case. These are $[\text{core}]1\pi_u^4 1\pi_g^3 ({}^2\Pi_g)$, $[\text{core}]1\pi_u^3 1\pi_g^4 ({}^2\Pi_u)$, $[\text{core}]1\pi_u^4 1\pi_g^2 ({}^3\Sigma_g^-) 3\sigma_u ({}^4\Sigma_u^-)$, and $[\text{core}]1\pi_u^4 1\pi_g^2 ({}^3\Sigma_g^-) 3\sigma_u ({}^2\Sigma_u^-)$. We see that the ${}^2\Pi_g$ and ${}^2\Pi_u$ resonances are formed when the colliding electron is temporarily captured into one of the open shells $1\pi_u$ or $1\pi_g$ of the target states included in the expansion, while the ${}^4\Sigma_u^-$ and ${}^2\Sigma_u^-$ resonances are formed when the colliding electron is temporarily captured into the first unoccupied $3\sigma_u$ orbital.

In our earlier work [14–17], it was shown that the ${}^2\Pi_g$ resonance dominates the vibrationally inelastic cross sections in the $X^3\Sigma_g^-$ ground state at very low energies (≤ 1 –2 eV) while the ${}^2\Pi_g$ and ${}^2\Pi_u$ resonances give the major contribution to the $X^3\Sigma_g^- \rightarrow a^1\Delta_g$ and $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ electronic transitions from threshold to about 15 eV [15,19]. We now consider the role that the ${}^4\Sigma_u^-$ and ${}^2\Sigma_u^-$ resonances play in vibrational excitation in the electronic ground state.

In order to obtain the vibrationally inelastic T matrices and cross sections from our ${}^4\Sigma_u^-$ and ${}^2\Sigma_u^-$ fixed-nuclei T matrices, we note from Fig. 1(b) that the width of these resonances in the neighborhood of the equilibrium internuclear separation $R_e \approx 2.35a_0$ is approximately 3–4 eV, which gives resonance lifetimes which are short compared to the vibrational period of the molecule. We can thus use the adiabatic approximation of Chase [20] to yield vibrationally resolved T -matrix elements.

Our experimental and theoretical integral cross sections for excitation from the $v = 0$ to the $v' = 1, 2, 3, 4$ vibrational levels of the ground state of O_2 are compared in Fig. 2 over an energy range 4–15 eV. We also include in this figure the experimental results obtained by Shyn and Sweeney [4]. The theoretical results also include contributions from the ${}^2\Pi_u$ symmetry but these are small and play only a significant role at the lowest energies considered. The peak in the cross section near 11 eV arises mainly from the ${}^4\Sigma_u^-$ resonance although there is a significant contribution to these cross sections above about 10 eV from the ${}^2\Sigma_u^-$ resonance. We notice from this figure that the peak in the experimental cross sections occurs at a slightly

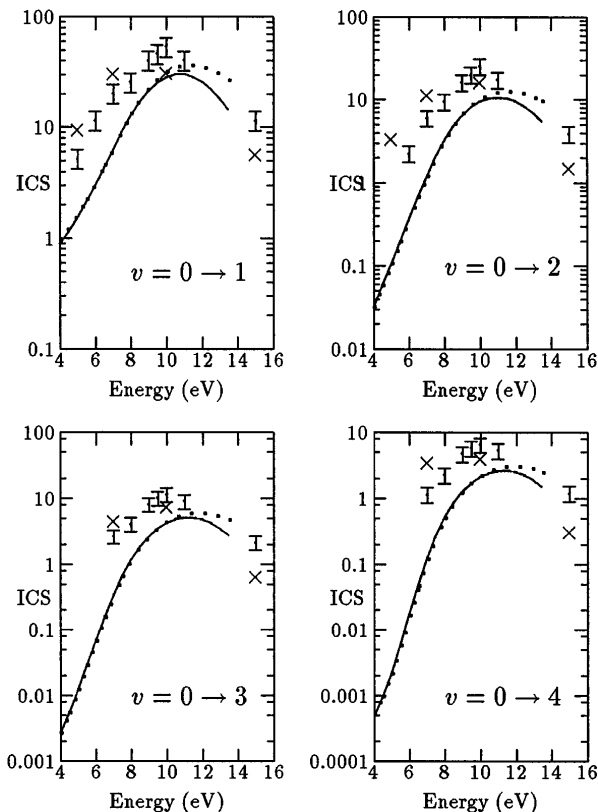


FIG. 2. Integral cross sections in 10^{-18} cm² for the transitions $X^3\Sigma_g^-(v=0) \rightarrow X^3\Sigma_g^-(v=1, 2, 3, 4)$. The solid line denotes the theoretical results including only the ${}^4\Sigma_u^-$ symmetry. The dotted line includes in addition the ${}^2\Sigma_u^-$ symmetry. The new experimental results (\square) include errors of 20% ($v=0 \rightarrow 1$), 22% ($v=0 \rightarrow 2$), 24% ($v=0 \rightarrow 3$), and 26% ($v=0 \rightarrow 4$). The (\times) denotes experimental results from Shyn and Sweeney [4].

lower energy and is larger than the theoretical predictions by a factor of about 1.7. A likely cause of this discrepancy is the inadequate representation of the ground state polarizability in our nine-state model. In fact we find that only about 30% of the parallel component of the ground state polarizability is accounted for by the inclusion of the $B^3\Sigma_u^-$ state in our expansion. Inclusion of the full polarizability would lower the positions of the resonances, bringing the peak in the cross section into closer agreement with experiment. However, we believe that our experimental and theoretical results are in good overall agreement bearing in mind the complexity of the collision process under consideration. In particular, the theoretical results clearly reproduce the observed decrease in the $v \rightarrow v'$ cross section as v' increases from 1 to 4. They also show the expected dominant role of the ${}^4\Sigma_u^-$ shape resonance in electronically elastic transitions where, as discussed above, the colliding electron is temporarily captured into the $3\sigma_u$ orbital leaving the target electrons unexcited in the $X^3\Sigma_g^-$ ground state. Similar arguments also explain why there is a significant contribution from the ${}^2\Sigma_u^-$ resonance. This is in contrast

to the ${}^2\Pi_u$ resonance, which is a core excited resonance and hence, as we have seen in our earlier work [15,19], contributes much more effectively to electronic excitation processes.

In conclusion, we have shown in this Letter that the ${}^4\Sigma_u^-$ and ${}^2\Sigma_u^-$ resonances control the process of vibrational excitation in the electronic ground state in e^- -O₂ collisions in the energy range from 4 to 15 eV. The relevance of this result to the interpretation by Jensen, Palmer, and Rous [6] of their data is manifest. The present study extends earlier work by ourselves and other workers which demonstrated that the ${}^2\Pi_g$ and ${}^2\Pi_u$ resonances give the major contribution to the $X^3\Sigma_g^- \rightarrow a^1\Delta_g$ and $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$ electronic excitation cross sections at low energies and that the ${}^2\Pi_g$ resonance dominates vibrational excitation at energies below 1–2 eV. Hence we have shown that vibrationally and electronically inelastic e^- -O₂ collision cross sections in the energy range up to 15 eV can be quantitatively understood in terms of four resonances with ${}^2\Pi_g$, ${}^2\Pi_u$, ${}^4\Sigma_u^-$, and ${}^2\Sigma_u^-$ symmetries. We are now extending our experiments and our theory to explore other aspects of these low-energy collisions including electron spin polarization, angular distributions, and dissociative attachment cross sections. We also hope in the future to be able to include considerably more configurations in our representation of the target and collision wave functions in order to remove the remaining small discrepancies between experiment and theory.

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