LETTER TO THE EDITOR

Integral cross sections for electron impact excitation of the Herzberg pseudocontinuum of molecular oxygen

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Abstract
We report integral cross sections (ICSs) for electron impact excitation of the sum (c $^1\Sigma_u^-$ + A$'$ $^3\Delta_u$ + A $^3\Sigma_u^+$) of the three states that constitute the Herzberg pseudocontinuum in O_2. These ICSs were measured at seven incident electron energies in the range 9–20 eV in order to investigate for the existence of the strong resonance feature predicted by earlier R-matrix calculations. No such structure was observed in this letter.

Over the last decade we have undertaken an extensive series of experiments that studied the excitation of fundamental processes in molecular oxygen (O_2) by electron impact. These investigations included elastic scattering [1, 2], vibrational excitation ($v' = 0 \rightarrow 1, 2, 3, 4$) [3, 4] and excitation of the lowest-lying a $^1\Delta_g$ and b $^1\Sigma_g^+$ electronic states [5, 6]. Our motivation for these studies was twofold. Firstly, we aimed to provide reliable and accurate cross sections which would both add to the existing (limited) data base for these processes [7] and act as a stringent test for the accuracy of electron–molecule scattering theory computations. Secondly, we have specifically set out to test whether the resonance structures predicted by a detailed series of R-matrix calculations [3, 8, 9] are physical. For both vibrational excitation [3] and excitation of the a $^1\Delta_g$ and b $^1\Sigma_g^+$ electronic states [5] we were able to verify the existence of these calculated resonances, although for the electronic states we found they occurred at a somewhat higher energy than was predicted by the theory [5]. Consequently, in conjunction with the R-matrix calculations, we were able to ascertain that up to about 15 eV energy, elastic scattering, vibrational excitation and excitation of the a $^1\Delta_g$ and b $^1\Sigma_g^+$ states could be quantitatively understood in terms of four resonances with $^2\Pi_g$, $^2\Pi_u$, $^4\Sigma_u^-$ and $^2\Sigma_u^-$ symmetries.

This letter on electron impact excitation of the Herzberg pseudocontinuum c $^1\Sigma_u^-$, A$'$ $^3\Delta_u$ and A $^3\Sigma_u^+$ electronic states represents both a continuation of and conclusion to our work in O_2. In principle it could be argued that electron impact cross sections for both the excitation of the Schumann–Runge continuum and Tanaka's progression I [10] are still required by the atmospheric physics and modelling communities [7]. However, Lewis *et al* [11] recently demonstrated that application of current, standard, electron energy loss spectral decomposition

techniques [12] to them would invariably result in error. Available R-matrix theories [8, 9] both indicate that there should be a strong resonance feature in the sum of the integral cross section (ICS) (c $^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+$) for the Herzberg states. Given our previous experience with vibrational excitation [3] and excitation of the a $^1\Delta_g$ and b $^1\Sigma_g^+$ electronic states [5], we might expect to *a priori* hold a prejudice towards verifying the existence of this resonance. However, in this case there is one crucial difference. That is, the Herzberg pseudocontinuum states largely lie above the dissociation energy for the O_2 molecule, while the vibrational levels of the ground molecular state and a $^1\Delta_g$ and b $^1\Sigma_g^+$ electronic states lie below the dissociation limit. A previous R-matrix study into water (H_2O) by Morgan [13] found significant structure in the ICSs for the $^3B_1$, $^1B_1$, $^3A_1$ and $^1A_1$ dissociative states. This structure, or the strength of the calculated resonances, was not, however, typically found in a corresponding complex Kohn level calculation from Gil *et al* [14] and so the question must be asked, is it physical? Consequently the issue of whether the structure in the ICS for the Herzberg states is real or simply a pseudoresonance remains open and more than justifies the present investigation.

Previous experimental studies into the electron impact excitation of the c $^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+$ electronic states have been quite limited [7]. Konishi *et al* [15] reported an excitation function measurement at the electron scattering angle (θ_e) of 90° for energies in the 20–70 eV range, while Trajmar *et al* [16] published ICSs at 20 and 45 eV incident electron energies. Little work was then undertaken until the comprehensive investigation of Wakiya [17], who measured differential cross sections (DCSs) and ICSs at ten energies in the range 20–500 eV. The angular range of the DCS data was 10°–130°. Note that none of these early studies attempted measurements below 20 eV. The first experiment for excitation of the Herzberg pseudocontinuum states below 20 eV was reported by Teillet-Billy *et al* [18]. This was an excitation function measurement at $\theta_e = 90°$ and for energies in the range 10–20 eV. Also included in this paper was a theoretical calculation, based on effective range theory, that looked at the effect of the $^2\Pi_g$ resonance on the c $^1\Sigma_u^-$, A$'\,^3\Delta_u$ and A $^3\Sigma_u^+$ ICS from threshold to 20 eV [18]. Other scattering symmetries were not considered in this work. Allan [19] also reported an excitation function at $\theta_e = 90°$, although in this case the measurement was from threshold to 20 eV. He observed a broad featureless cross section over that energy range whose absolute values were reasonably consistent with those of Teillet-Billy *et al* [18] for energies $\geqslant 12$ eV. Campbell *et al* [12], in their discussion of their spectral deconvolution code and the spectroscopy of O_2, reported an ICS and a DCS at 15 eV. This was the first angular distribution reported for the sum (c $^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+$) of the Herzberg states below 20 eV and also the first experimental ICS below 20 eV. The most recent investigation, however, is the work of Shyn and Sweeney [20]. In this paper DCSs and ICSs for the individual c $^1\Sigma_u^-$, A$'\,^3\Delta_u$ and A $^3\Sigma_u^+$ electronic states are reported. The energies were 10, 15, 20 and 30 eV and the angular range was 24°–156°. Whilst we have strong reservations as to the uniqueness of their individual state DCSs and ICSs, given the spectral deconvolution they employed [20], and their error estimates [20] are overly optimistic for the uncertainty in the spectral deconvolution process, the DCS and ICS for the sum c $^1\Sigma_u^- + A'\,^3\Delta_u + $A $^3\Sigma_u^+$ of the three states should be valid. Indeed, when the 15 eV DCS of Campbell *et al* [12] and the corresponding DCS of Shyn and Sweeney [20] are compared, the agreement between them is good across the entire common angular range. As expected a similar level of agreement between them at the ICS level, and at 15 eV, is also found.

The present experimental cross sections are measured by crossing a beam of O_2, 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 θ_e are energy analysed and detected. The overall energy resolution is $\sim$55 meV (FWHM) and typical beam currents $\sim$1 nA are obtained in the interaction region for the energy range ($E_0 = 9$–20 eV) of this letter. The true zero-

scattering angle is determined as that about which the elastic scattering intensity is symmetric. The estimated error in this determination is $\pm 1°$. 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 of approximately -0.2 to 9.0 eV by ramping the analyser 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 this letter is described in Brunger and Teubner [21] 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 sum of the Herzberg pseudocontinuum states to that for the elastic scattering process. The known elastic differential scattering cross sections [3, 22], at each E_0 and θ_e, are then used to derive the required inelastic DCS for the $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ states. A full description of the present spectral deconvolution program and the necessary spectroscopic information for its application was given in Campbell *et al* [12] and so these details are not repeated here. The measured DCSs, at each energy, are then extrapolated to $0°$ and $180°$, integrated and the required $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ ICS determined from the standard formula [23]. The extrapolation of the DCS to $0°$ and $180°$ was accomplished using a slightly modified version of the molecular phase shift analysis (MPSA) procedure of Boesten and Tanaka [24] (and references therein). Full details of our technique can be found in Campbell *et al* [25], although we note that in the present application of the MPSA usually around seven partial waves were allowed to vary in the fit to our measured DCS. Higher-order partial waves were accounted for using the Born series result [23–25].

In table 1 we list our ICS for electron impact excitation of the $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ Herzberg states. These data are also plotted in figure 1 along with the results from previous experiments [15–17, 20] and theoretical calculations [8, 9, 18]. It is clear from figure 1 that at both 10 and 15 eV the present ICSs are in reasonable accord with the data of Shyn and Sweeney [20], while at 20 eV our ICS neatly bisects those of Trajmar *et al* [16] and Wakiya [17], on the one hand, and those of Konishi *et al* [15] and Shyn and Sweeney [20], on the other. The trend in the present ICS suggests that the higher-energy ICS of Trajmar *et al* [16] and Wakiya [17] may be more realistic than those of Shyn and Sweeney [20] and Konishi *et al* [15]. The errors in the present ICS reflect the small magnitude of these $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ excitation cross sections, the fact the Herzberg-state intensity is diffusely spread over a broad region in the energy-loss spectra, an uncertainty in our analyser transmission calibration and, finally, an error associated with the spectral deconvolution process [12]. This last error is quite significant and arises from application of the $\Delta\chi^2 = 1$ criterion of Bevington and Robinson [26], to which the reader is referred for more details.

The most significant point to emerge from figure 1 is the complete absence of any strong resonance structure in the present $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ ICS measurements. This result would appear to be contrary to those from the *R*-matrix computations of Noble and Burke [8] and Higgins *et al* [9], who both calculate a very strong peak in the ICS close to threshold. The observed discrepancy between theory and experiment is intriguing and invites some conjecture. Note that we have folded the ICS of both Noble and Burke and Higgins *et al* with our experimental energy resolution and in both cases the strong peaks in the ICS remain. Thus the discrepancy between theory and experiment is not due to the finite energy spread in the electron beam associated with the measurements. Hence, the first possible rationale between theory and experiment is that the resonance does not exist or, if it does, its energy width is much narrower than that predicted by Noble and Burke and Higgins *et al*.

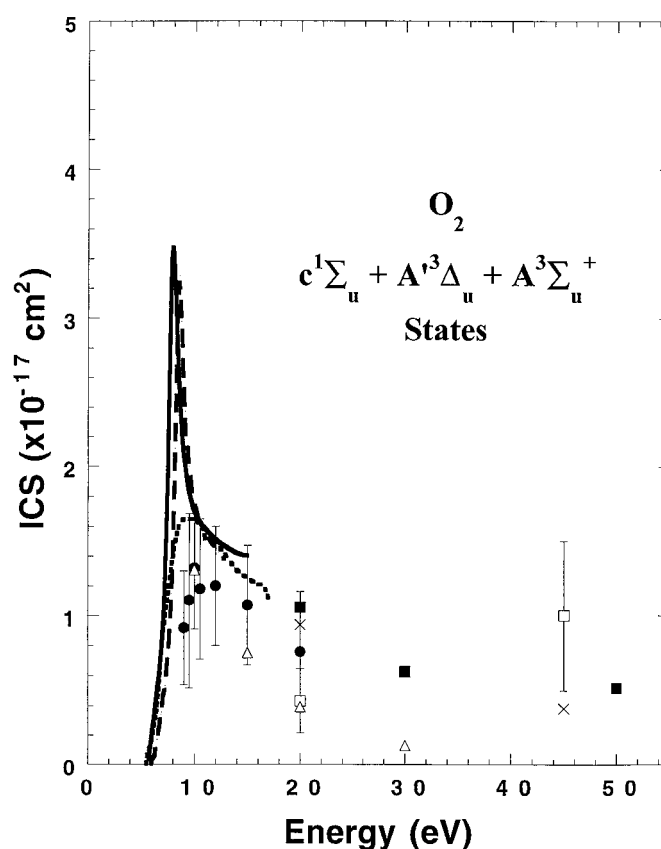A second possible rationale to explain this discrepancy can be gleaned from the *R*-

Figure 1. ICSs ($\times 10^{-17}$ cm^2) for the electron impact excitation of the (c $^1\Sigma_u^- +$ A$'$ $^3\Delta_u +$ A $^3\Sigma_u^+$) Herzberg pseudocontinuum states of O$_2$. The present data (•) are compared against the earlier results of Konishi *et al* (□), Trajmar *et al* (×), Wakiya (■) and Shyn and Sweeney (△) and the theoretical calculations of Teillet-Billy *et al* ($\cdots\cdots$), Noble and Burke (——) and Higgins *et al* (– – –).

Table 1. ICSs ($\times 10^{-17}$ cm^2) for the electron impact excitation of the (c $^1\Sigma_u^- +$ A$'$ $^3\Delta_u +$ A $^3\Sigma_u^+$) Herzberg pseudocontinuum states of O$_2$. Numbers in parentheses represent the percentage uncertainty on the data.

E_0 (eV)	ICS ($\times 10^{-17}$ cm^2)
9	0.920 (41%)
9.5	1.103 (43%)
10	1.320 (31%)
10.5	1.180 (40%)
12	1.200 (33%)
15	1.070 (33%)
20	0.760 (52%)

matrix [13] and complex Kohn [14] studies on four dissociative electronic states in H$_2$O. In this comparison the *R*-matrix calculation predicts significantly more structure and stronger structure than what was found by the corresponding complex Kohn calculation. The basis set used by Gil *et al* [14] was superior to that of Morgan [13], and it is our hypothesis that if the basis

set of Morgan provided an inadequate physical description of these dissociative H_2O states then this may have led to pseudoresonances appearing in her calculation. Supporting evidence for this proposition comes from McLaughlin [27], in his calculations on electron impact excitation of electronic states in N_2, where he was restricted to energies below 18 eV. This was because above 18 eV pseudoresonances formed in the scattering cross sections when the basis set began to break down. The relevance of this to the present letter is transparent. Namely, if the basis set [28] employed by both Noble and Burke and Higgins *et al* was inadequate for O_2 electronic states above oxygen's molecular dissociation energy, then this might lead to the formation of pseudoresonances in the ICSs for those states and, consequently, in the ICS for the sum of the three states. Whilst not wishing to minimize the difficulties of performing scattering calculations with open-shell molecules, it would be very interesting if the *R*-matrix groups at either Queens or UCL were to revisit this scattering system using a more sophisticated basis set.

A third possible rationale for the apparent discrepancy between measurement and calculation, as to the existence of resonant structure in the $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ ICS, might be due to the actual (physical) energy of the resonance peak being closer to threshold than the *R*-matrix calculations [8, 9] predict and therefore outside the energy range of our measurements. Both the *R*-matrix ICSs in figure 1 were calculated at the equilibrium geometry of O_2 with internuclear separation $R = 2.3a_0$. However, Higgins *et al* found that for larger internuclear separations (e.g. $R = 2.6a_0$) the resonance can indeed shift to energies closer to threshold. If the calculation at the larger internuclear separations was more realistic physically for the Herzberg states then this perhaps might explain the apparent discrepancy embodied in figure 1. Experimental measurements below 9 eV, to test this possibility, would be very difficult because the scattered electron analyser optics could become very nonlinear in behaviour, making the transmission of the analyser difficult to characterize quantitatively. In any event, our previous experience with excitation of the $a\,^1\Delta_g$ and $b\,^1\Sigma_g^+$ electronic states of O_2 [5] indicated that the energy of the experimental resonance was at a higher energy (by ~ 2 eV) than was calculated by the theory [8, 9]. Consequently, we believe this third possible explanation is unlikely to be correct, although we cannot definitively rule it out.

A final possible rationale for the apparent discrepancy between measurement and calculation could be that the fixed-nuclei approximation, as used at various internuclear separations in [8] and [9], may itself be inadequate. Considering the $e^- + N_2\,^2\Pi_g$ resonance as a model, then it is well known that the single resonance at ~ 2.5 eV, in the fixed-nuclei approximation [29], is considerably diminished in height and broadened when nuclear motion is dynamically taken into account [30]. Whilst in that case one also obtains substructure in the ICS, in the present situation the finite energy resolution of the measurements and the fact one is considering a superposition of final electronic states, might conspire to average any such substructure out.

In summary, we have presented new experimental ICSs for the $(c\,^1\Sigma_u^- + A'\,^3\Delta_u + A\,^3\Sigma_u^+)$ Herzberg pseudocontinuum states of O_2 at seven energies in the range 9–20 eV. This letter represents the first comprehensive study for the electron impact excitation of these states in that energy range. In contrast to the *R*-matrix calculation results [8, 9] we find no resonant-related structure in the measured ICS. We believe this unexpected discrepancy may be due to either inadequacies in the O_2 basis states [28] used by both Noble and Burke and Higgins *et al*, leading to pseudoresonance structure in their ICS results, or to a breakdown in the fixed-nuclei approximation.

We also thank the referee for drawing to our attention the possibility of the fixed-nuclei approximation being inadequate.

References

[1] Woeste G, Noble C J, Higgins K, Burke P G, Brunger M J, Teubner P J O and Middleton A G 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4141
[2] Green M A, Teubner P J O, Mojarrabi B and Brunger M J 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 1813
[3] Noble C J, Higgins K, Woeste G, Duddy P, Burke P G, Teubner P J O, Middleton A G and Brunger M J 1996 *Phys. Rev. Lett.* **76** 3534
[4] Brunger M J, Middleton A G and Teubner P J O 1998 *Phys. Rev.* A **57** 208
[5] Middleton A G, Teubner P J O and Brunger M J 1992 *Phys. Rev. Lett.* **69** 2495
[6] Middleton A G, Brunger M J, Teubner P J O, Anderson M W B, Noble C J, Woeste G, Blum K, Burke P G and Fullerton C 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 4057
[7] Brunger M J and Buckman S J 2001 *Phys. Rep.* submitted
[8] Noble C J and Burke P G 1992 *Phys. Rev. Lett.* **68** 2011
[9] Higgins K, Noble C J and Burke P G 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 3203
[10] Tanaka Y 1952 *J. Chem. Phys.* **20** 1728
[11] Lewis B R, England J P, Gibson S T, Brunger M J and Allan M 2001 *Phys. Rev.* A **63** 022707
[12] Campbell L, Green M A, Brunger M J, Teubner P J O and Cartwright D C 2000 *Phys. Rev.* A **61** 022706
[13] Morgan L A 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 5003
[14] Gil T J, Rescigno T N, McCurdy C W and Lengsfield B H 1994 *Phys. Rev.* A **49** 2642
[15] Konishi A, Wakiya K, Yamamoto M and Suzuki H 1970 *J. Phys. Soc. Japan* **29** 526
[16] Trajmar S, Williams W and Kuppermann A 1972 *J. Chem. Phys.* **56** 3759
[17] Wakiya K 1978 *J. Phys. B: At. Mol. Phys.* **11** 3931
[18] Teillet-Billy D, Malegat L, Gauyacq J P, Abouaf R and Benoit C 1989 *J. Phys. B: At. Mol. Opt. Phys.* **22** 1095
[19] Allan M 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 5163
[20] Shyn T W and Sweeney C J 2000 *Phys. Rev.* A **62** 022711
[21] Brunger M J and Teubner P J O 1990 *Phys. Rev.* A **41** 1413
[22] Sullivan J P, Gibson J C, Gulley R J and Buckman S J 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 4319
[23] Bransden B H and Joachain C J 1983 *Physics of Atoms and Molecules* (New York: Longman)
[24] Boesten L and Tanaka H 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 821
[25] Campbell L, Brunger M J, Nolan A M, Kelly L J, Wedding A B, Harrison J, Teubner P J O, Cartwright D C and McLaughlin B 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** at press
[26] Bevington P R and Robinson D K 1992 *Data Reduction and Error Analysis for the Physical Sciences* (New York: McGraw-Hill)
[27] McLaughlin B M 2000 Private communication
[28] Saxon R P and Liu B 1977 *J. Chem. Phys.* **67** 5432
[29] Burke P G and Chandra N 1970 *J. Phys. B: At. Mol. Phys.* **5** 1696
[30] Chandra N and Temkin A 1976 *Phys. Rev.* A **13** 188