PHYSICAL REVIEW LETTERS

Resonances in Electron-Impact Electron Detachment of $C_2{}^-$

Gabriela Halmová and Jonathan Tennyson

Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom

Molecular *R*-matrix with pseudostate calculations are reported for the electron-impact ionization cross section of the carbon dimer anion. A $^1\Sigma_g^+$ resonance is found near the detachment threshold and two further resonances, of $^3\Pi_g$ and $^1\Pi_g$ symmetry, are found near 10 eV close to the structures observed experimentally. These unusual shape resonances are a result of the competition between the repulsive Coulomb interaction and the large, attractive polarizability of $C_2{}^-$. Use of the Born approximation to allow for higher partial waves gives a total cross section close to that observed experimentally.

The temporary trapping of a continuum particle in a potential well behind a centrifugal barrier is a common physical phenomenon. The resulting long-lived states are generally described as shape resonances. However other shapes of interaction potential can also lead to resonance formation. In this Letter, we present evidence for the temporary trapping of a continuum electron undergoing a repulsive Coulomb interaction by polarization forces. The particular problem considered is the continuum states of the $C_2{}^{2-}$ molecular anion, but it is likely that similar resonances occur in other physical situations.

More than a decade ago, Andersen *et al.* [1] observed resonance structures in the electron-impact detachment cross section of $C_2{}^-$ caused by the temporary formation of $C_2{}^{2-}$ resonance states. Further studies on electron collisions with $C_2{}^-$ [2,3] and other diatomic anions [2–5] confirmed that these resonance states are indeed a common feature of diatomic anions. Similar features have since been found for larger molecular anions [6,7].

That small diatomic anions should be able to temporarily capture an extra electron well above their ionization threshold would appear counterintuitive [8]. However, this possibility has sparked a number of theoretical investigations. Absorbing potential calculations by Sommerfeld and co-workers [9,10] identified a closed shell $^1\Sigma_g^+$ resonance close to the ionization threshold. Bound state electronic structure calculations by Pedersen *et al.* [3] identified a number of possible resonance features. However, it is well documented that pure bound state methods are not a reliable way to characterize resonances [11]. Therefore, despite this work, and more qualitative theoretical models [1,5], there remains no proper theoretical interpretation of the resonance structures arising in the electron-impact detachment experiments cited above.

In this Letter, we present a complete treatment of the electron-impact detachment process in the $C_2{}^{2-}$ system which both reproduces the measured cross sections for the process and gives a resonances structure similar to the one observed.

Calculations on electron-impact ionization or electron detachment in the near-threshold region are very challenging because they, in principle, require the treatment of two continuum electrons. Recently, Gorfinkiel and Tennyson [12,13] developed a molecular *R*-matrix with pseudostates (RMPS) method for treating near-threshold electron-impact ionization. They showed that their method gave reasonable cross sections and, importantly for this study, provides a means for converging the long-range polarizability of the target, something that is hard to do in standard close-coupling scattering calculations.

The basic idea of the molecular RMPS procedure is the use of an additional set of even tempered basis Gaussian functions placed at the molecule center-of-mass which are used to represent the discretized target continuum within the *R*-matrix box, here a sphere of radius $10a_0$. These functions are characterized by Gaussian exponents of the form $\alpha_0\beta^n$ where $n = 0, 1, \ldots N$, where the stability of the calculation can be checked by varying α_0 and β.

Gorfinkiel and Tennyson [12,13] only used the molecular RMPS method to study ionization of two electron molecules; this work is first to consider a many-electron target. To extend this method to a many active electron problem required running a large number of different models for both the target plus pseudostates calculations and the scattering calculations. Some of these calculations were too large to be performed using the standard UK *R*-matrix polyatomic codes [14] and required the implementation of a partitioned *R*-matrix technique [15]. These calculations, which support the results presented below, are detailed in a fuller paper we will submit elsewhere [16]. In this Letter, we present results from a single model which had the advantage of being consistent and computationally tractable while retaining sufficient physics to give a good representation of the experiments.

Calculations were performed for a fixed $C_2{}^-$ bond length of $2.396a_0$. The starting point for the present calculations is our study of electron—C_2 collisions [17] which used a double zeta plus polarization basis and a complete active space configuration interaction (CAS-CI) representation of the target. This showed that this system supports three bound states of symmetry $X\ ^2\Sigma_g^+$, $A\ ^2\Pi_u$, and $B\ ^2\Sigma_u^+$. To the basis used previously, we added

213202-1

PHYSICAL REVIEW LETTERS

(10,10,6) pseudocontinuum orbitals (PCOs) of (s, p, d) symmetry, respectively. Within the model used here, the target configurations used can be written

$$(1\sigma_g 1\sigma_u)^4 (2\sigma_g 3\sigma_g 2\sigma_u 3\sigma_u 1\pi_u 1\pi_g)^9,$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^4 PCO^1,$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^3 (3\sigma_g 3\sigma_u 1\pi_g)^1 PCO^1.$$

The four physical target states and 110 pseudostates (counting degenerate states twice as we work in D_{2h} symmetry) were retained in the close-coupling expansion which are sufficient to span energies up to 19 eV.

This model, in common with other reliable models we tested, gives a large C_2^- isotropic polarizability of about $32a_0^3$ depending slightly on the precise values of (α_0, β) used. We could find no literature value for this property of the anion, but a large polarizability is to be expected for a system with a weakly bound and relatively diffuse outer electron. However, we note that the polarizability given by just considering the physical target states is only $9.5a_0^3$.

For the scattering calculations, the basis is augmented by Gaussian-type continuum orbitals (COs) [18] up to and including g orbitals from which the short-range functions which overlap the PCOs were removed. Unlike the other orbitals used in the calculation, the COs have amplitude on the R-matrix boundary which was taken as a sphere of radius $10a_0$. The scattering wave function was built from configurations of the form

$$(1\sigma_g 1\sigma_u)^4 (2\sigma_g 3\sigma_g 2\sigma_u 3\sigma_u 1\pi_u 1\pi_g)^9 CO^1,$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^4 (3\sigma_g 3\sigma_u 1\pi_g)^2 PCO^1 CO^1,$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^3 (3\sigma_g 3\sigma_u 1\pi_g)^3 PCO^1 CO^1.$$

$$(1\sigma_g 1\sigma_u)^4 (2\sigma_g 3\sigma_g 2\sigma_u 3\sigma_u 1\pi_u 1\pi_g)^{10},$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^4 PCO^2,$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^3 (3\sigma_g 3\sigma_u 1\pi_g)^2 PCO^1,$$

$$(1\sigma_g 2\sigma_g 1\sigma_u 2\sigma_u)^8 1\pi_u^3 (3\sigma_g 3\sigma_u 1\pi_g)^1 PCO^2,$$

which give a balanced representation between the 13 electron C_2^- target and the 14 electron C_2^{2-} system. Both singlet and triplet scattering symmetries were considered.

This model gives a resonance of $^1\Sigma_g^+$ symmetry near the electron detachment threshold for all the PCO basis sets we tested. This resonance is that identified by Sommerfeld *et al.* [10] but is too low-lying to be detected in the electron-impact electron detachment cross section. This resonance, and the others identified below, can be seen in both the elastic and electronic excitation cross sections.

At higher energies, our calculations give a series of resonances, as is characteristic of RMPS methods. Most of these are narrow and move significantly as the PCO basis is altered. However, as shown in Fig. 1, all our calculations also showed two much broader resonance
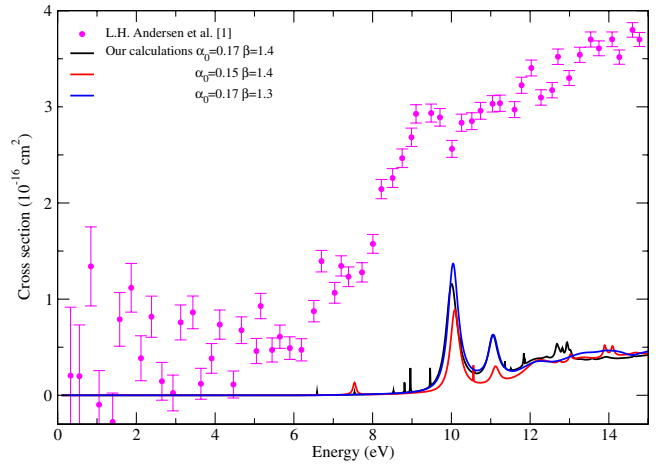

FIG. 1 (color online). Electron-impact ionization cross section for C_2^- calculated using different pseudostate basis sets.

features which are stable to changing the PCO basis. These resonances, which are of $^3\Pi_g$ and $^1\Pi_g$ symmetry, only occurred in models which reproduce the large long-range polarizability of C_2^-. Table I summarizes the resonance parameters obtained in this work by fitting the eigenphase sums to a Briet-Wigner form [19], and in previous calculations. It can be seen that while all these calculations give a $^1\Sigma_g^+$ resonance close to the ionization threshold of C_2^-, there are notable differences at higher energies. At higher energies, the Coupled-Clusters singles and doubles (CCSD) quantum chemistry calculations of Pedersen *et al.* [3] suggested nearly degenerate singlet and triplet resonances of "Σ_u" symmetry at about 6.8 eV. We find no evidence for either Σ_u^+ or Σ_u^- resonances in our calculation. Pedersen *et al.* [3] also found nearly degenerate singlet and triplet resonances of Π_g symmetry at 8.3 eV which they associated with the somewhat higher lying experimental features. Our calculation also find $^3\Pi_g$ and $^1\Pi_g$ resonances, albeit at somewhat higher energies and separated by over 1 eV.

Experimentally, the resonance features were observed in several channels. The structure visible in the electron-impact electron detachment cross section was placed at 10 eV with a width of 2.1 eV by Pedersen *et al.* [3]. These values are very close to the ones given by our calculation especially once allowance is made for the broadening effect of including nuclear motion. However, Pedersen

TABLE I. Calculated C_2^{2-} resonance energies, E_r, and widths, Γ, in eV.

Sommerfeld *et al.* [10]			Pedersen *et al.* [3]		This work		
	E_r	Γ		E_r		E_r	Γ
$^1\Sigma_g^+$	3.5	0.3	$^1\Sigma_g^+$	3.8	$^1\Sigma_g^+$	4.86	0.65
			$^{1,3}\Sigma_u$	6.3	$^3\Pi_g$	9.71	1.14
			$^{1,3}\Pi_g$	8.3	$^1\Pi_g$	10.92	0.52

et al. also observed a stronger resonance feature at the same energy in the dissociative channels they investigated. In this case, the resonance are broader with a width of 3 to 4 eV.

It is a standard and tested assumption of the RMPS method that electron-impact ionization cross sections can be obtained by summing the cross sections for exciting pseudostate which lie in the continuum [20]. This assumption is particularly appropriate in this work since we consider an anion and therefore are able to explicitly include all the actual electronic excited states of the target in our close-coupling expansion. Figure 2 compares our molecular RMPS electron-impact electron detachment cross sections with observed ones: while our resonances appear close to the observations, our cross sections are much too small. This is to be expected since the dominant, non-resonant detachment process will be via long-range collisions which are favored by the Coulomb interaction. To reproduce the experimental cross sections, it is necessary to account for such collisions which are almost entirely associated with higher partial waves ($\ell > 4$) not allowed for in our CO basis set.

Higher partial waves were introduced by applying a Born correction directly to all the cross sections arising from dipole allowed electronic excitation channels associated with pseudo states of $^2\Sigma_u^+$ and $^2\Pi_u$ symmetry. The result, shown in Fig. 2, is a significant increase in the calculated electron-impact electron detachment cross section. The calculated values are now close to those measured by Pedersen *et al.* [3]. In practice, our calculations do not discriminate between the electron-impact detachment process and the weaker but also observed [3] related processes involving dissociation. Figure 2 therefore also gives the sum of these experimental cross sections; in practice, the difference between these two measurements is less than the probable error in our calculation.

Given that a range of diatomic anions appear to temporarily attach an extra electron, a major aim of this study is to establish the binding mechanism for this. As has been suggested previously [5,6], our calculations show that these resonances can be classified as shape resonances in that the extra electron is temporarily bound by a potential given by the C_2^- ground state. Representing shape resonances in an *ab initio* scattering calculation is usually reasonably straightforward and is now done fairly routinely even for small biomolecules. However, the quasibound shape resonances of the C_2^{2-} system are significantly different as they also require a good representation of the long (and presumably short) range polarization potential in order to achieve the temporary binding of the extra electron. As demonstrated here, this can be achieved using pseudostates to give a discretized representation of the continuum in the geometric region close to the target.

The resonances detected here do not conform to the standard pattern of shape resonances. Here, the dominant term is the Coulomb repulsion between the anion and the incoming electron. The local minimum, deep enough to temporarily bind an electron, is caused not by an angular momentum barrier but by the attractive polarization interactions between the C_2^- anion and the incoming electron. This dip in the potential does not depend on the partial wave of the incoming electron and can therefore bind an *s*-wave, hence the $^1\Sigma_g^+$ resonance. It is likely that this mechanism is also responsible for the resonances observed in electron collisions with other diatomic anions. Indeed, it may well be a feature of other collision problems whose dominant background potential is repulsive.
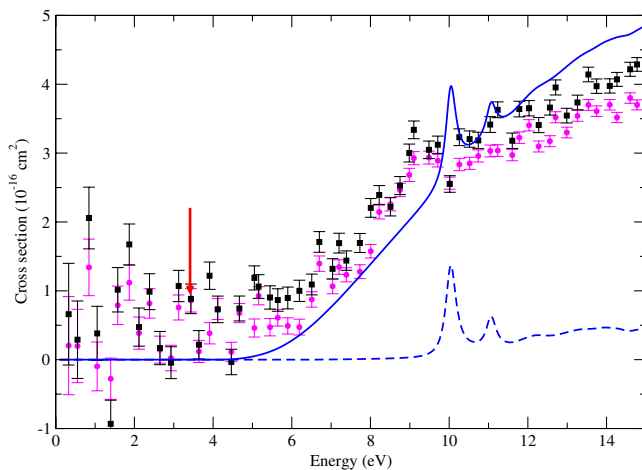
FIG. 2 (color online). Total ionization cross section. Electron-impact ionization cross section due to Pedersen *et al.* [3] with (squares) and without (circles) dissociative channels; dashed curve molecular RMPS calculation with $\alpha_0 = 0.17$, $\beta = 1.3$, solid curve molecular RMPS calculation with Born correction. The arrow indicates the ionization threshold, below which the cross sections should be zero.

[1] L. H. Andersen, P. Hvelplund, D. Kella, P. H. Mokler, H. B. Pedersen, H. T. Schmidt, and L. Vejby-Christensen, J. Phys. B **29**, L643 (1996).

[2] H. B. Pedersen, N. Djurić, M. J. Jensen, D. Kella, C. P. Safvan, L. Vejby-Christensen, and L. H. Andersen, Phys. Rev. Lett. **81**, 5302 (1998).

[3] H. B. Pedersen, N. Djurić, M. J. Jensen, D. Kella, C. P. Safvan, H. T. Schmidt, L. Vejby-Christensen, and L. H. Andersen, Phys. Rev. A **60**, 2882 (1999).

[4] L. H. Andersen, J. Bak, S. Boye, M. Clausen, M. H. M. J. Jensen, A. Lapierre, and K. Seiersen, J. Chem. Phys. **115**, 3566 (2001).

[5] G. F. Collins, D. J. Pegg, K. Fritioff, J. Sandström, D. Hanstorp, R. D. Thomas, F. Hellberg, A. Ehlerding, M. Larsson, and F. Österdahl *et al.*, Phys. Rev. A **72**, 042708 (2005).

[6] L. H. Andersen, R. Bilodeau, M. J. Jensen, C. P. Safvan, S. B. Nielsen, and K. Seiersen, J. Chem. Phys. **114**, 147 (2001).

[7] A. Svendsen, H. Bluhme, M. O. A. El Ghazaly, K. Seiersen, S. B. Nielsen, and L. H. Andersen, Phys. Rev. Lett. **94**, 223401 (2005).

[8] M. K. Scheller, R. N. Compton, and L. S. Cederbaum, Science **270**, 1160 (1995).

[9] T. Sommerfeld, U. V. Riss, H. D. Meyer, and L. S. Cederbaum, Phys. Rev. Lett. **79**, 1237 (1997).

[10] T. Sommerfeld, F. Tarantelli, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **112**, 6635 (2000).

[11] D. T. Stibbe and J. Tennyson, Chem. Phys. Lett. **308**, 532 (1999).

[12] J. D. Gorfinkiel and J. Tennyson, J. Phys. B **37**, L343 (2004).

[13] J. D. Gorfinkiel and J. Tennyson, J. Phys. B **38**, 1607 (2005).

[14] L. A. Morgan, J. Tennyson, and C. J. Gillan, Comput. Phys. Commun. **114**, 120 (1998).

[15] J. Tennyson, J. Phys. B **37**, 1061 (2004).

[16] G. Halmova, J. D. Gorfinkel, and J. Tennyson, arXiv:0802.1254v1.

[17] G. Halmova, J. D. Gorfinkel, and J. Tennyson, J. Phys. B **39**, 2849 (2006).

[18] A. Faure, J. D. Gorfinkiel, L. A. Morgan, and J. Tennyson, Comput. Phys. Commun. **144**, 224 (2002).

[19] J. Tennyson and C. J. Noble, Comput. Phys. Commun. **33**, 421 (1984).

[20] K. Bartschat and I. Bray, J. Phys. B **29**, L577 (1996).