Evidence for Very Narrow Shape Resonances in Low-Energy Electron-Cs Scattering

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A relativistic scattering calculation based on the Dirac R-matrix method has been performed within a two-electron model-potential approach for negative-ion binding energies as well as elastic and inelastic scattering cross sections. We find multiplets of narrow shape resonances with $J=0$, 1, and 2, and widths of a few meV. Their J-averaged energies for even and odd parity are 119.0 meV below the $6p_{1/2}$ threshold and 9.1 meV above the $6s_{1/2}$ threshold.

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The Cs atom has long been an attractive subject for studies of low-energy electron-atom interactions, including scattering, binding to form negative ions, and photodetachment. A heavy atom can be used to probe relativistic effects deriving from its own structure and their effect on the electron-atom interaction. Being a rather simple one-electron-like system, Cs is conceptually uncomplicated. An element handled with relative ease in the laboratory, and historically of some technological interest, it has also been the subject of numerous experimental studies spanning more than fifty years.

Of particular interest are persistent suggestions that Cs may be the only atom known to have an excited negative-ion state bound relative to the ground state of its parent atom, and of a different parity than the ground state of the negative ion [1–4]. Fabrikant [1] used effective range theory (ERT) to show that earlier calculations predict a $6s6p\,^3P^o$ state bound by 27 meV. Krause and Berry [2] also predicted binding of these states of about 12 meV in a study of correlation in two-electron systems. Fabrikant, and Krause and Berry, expressed, however, pointed reservations about the credibility of this particular conclusion. An elaborate multiconfiguration Hartree-Fock calculation [3], in which relativistic effects were considered, subsequently yielded an estimated binding energy for these states between 1.2 and 11 meV. In a recent theoretical study [4] of alkali-metal negative-ion photodetachment spectra, the $6s6p\,^3P^o_J$ states of Cs^- were also found to be bound by an energy (J averaged) of 18 meV relative to the $6s\,^2S_{1/2}$ ground state of Cs. Fabrikant [1] and Greene [4] have also cited the absence of any resonance structure in the $^3P^o_J$ symmetries in prior [5,6] calculations (both of which included some relativistic effects) of very-low-energy electron-Cs scattering as evidence in support of the hypothesis that the $6s6p\,^3P^o_J$ states are bound.

The only evidence that the $6s6p\,^3P^o$ state of Cs^- is a resonance (at very low positive energies relative to the Cs ground state) is indirect [7], the result of ERT analysis of the perturbation of Cs Rydberg levels by ground-state Cs [7] and of the electron transport properties of weakly ionized Cs vapor.

Another bound state of Cs^-, labeled $6p^2\,^3P^e$, has also been predicted [8] above the ground state of Cs. Bound relative to the first excited state of Cs, it is strictly forbidden to autoionize in LS coupling. It has never been observed. Its existence has been confirmed in one theoretical study [2], but later calculations [6] suggested that it is unbound relative to the first excited state of Cs.

We revisited this problem as part of a larger effort to develop a new program for relativistic electron-atom/ion scattering calculations. Our immediate goal is one of the first fully relativistic multichannel close-coupling calculations for electron interactions with an open-shell neutral atom, based on a highly accurate and fully relativistic representation of the target. There have been no such calculations using the Dirac formalism explicitly since the pioneering efforts of Chang [9] and Walker [10]. From the detailed analysis of the eigenphase sums and partial cross sections within a given J^π symmetry we have obtained deeper insight into the scattering dynamics and identified several resonances. The results of this analysis will be published elsewhere in full. In this Letter we limit ourselves to the discussion of multiplets of narrow shape resonances in the $J=0$, 1, and 2 symmetries in the vicinity of the Cs ground state and just below the $6p_{1/2}$ threshold.

Our calculations are based on an earlier [11] solution to the relativistic structure problem for the Cs atom, in which a local potential was used to represent the interaction of the valence electron with the (polarized) Cs core. For each l,j angular momentum series, two parameters in the model potential were chosen so as to reproduce the observed spectra. We then used the same fully relativistic Dirac formalism, with the same effective one-electron interaction potential, to generate the basis set of bound and continuum orbitals necessary for the R-matrix scattering calculation. We also developed an entirely new relativistic R-matrix scattering program based on the theory described by Chang [9], modified to incorporate relativistic R-matrix boundary conditions that yield the known nonrelativistic limit and to incorporate all electrostatic multipole interactions in the asymptotic (beyond the R-matrix box) region [12].

The total two-electron Hamiltonian in the R-matrix region can be written as

$$H = H(r_1) + H(r_2) + 1/r_{12} + V_{\rm pol}(\mathbf{r}_1,\mathbf{r}_2)\,, \tag{1}$$

where the one-electron Dirac Hamiltonian is

$$H(r) = c\sum_{i=1}^{3}\alpha_i p_i + (\beta - 1)c^2 + V_{\rm core}(r) \tag{2}$$

and the dielectronic polarization correction to the electron-electron interaction is taken to be

$$V_{\rm pol}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\alpha_d}{r_1^2 r_2^2}[W_6(r_c,r_1)W_6(r_c,r_2)]^{1/2}P_1(\cos\theta_{12}) - \frac{\alpha_q}{r_1^3 r_2^3}[W_{10}(r_c,r_1)W_{10}(r_c,r_2)]^{1/2}P_2(\cos\theta_{12})\,. \tag{3}$$

The cutoff function is

$$W_n(r_c,r) = 1 - \exp[-(r/r_c)^n]\,, \tag{4}$$

α_i and β are the Dirac matrices, α_d and α_q are the static dipole and quadrupole polarizabilities of the core, θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, and r_c is the cutoff radius. The model potential in $H(r)$ is chosen as

$$V_{\rm core}(r) = V_{\rm TFDA}(\lambda,r) + V_{\rm pol}(r) \tag{5}$$

with the core-polarization potential

$$V_{\rm pol}(r) = -\frac{\alpha_d}{2r^4}W_6(\bar{r}_c,r) - \frac{\alpha_q}{2r^6}W_{10}(\bar{r}_c,r)\,. \tag{6}$$

The dielectronic polarization correction $V_{\rm pol}(\mathbf{r}_1,\mathbf{r}_2)$ represents the influence of the core polarization produced by one electron on the other electron [13]. For the scaling parameter λ in the Thomas-Fermi-Dirac-Amaldi potential $V_{\rm TFDA}$, as well as for α_d and α_q in $V_{\rm pol}(r)$ and $V_{\rm pol}(\mathbf{r}_1,\mathbf{r}_2)$, and for $\bar{r}_c$ in $V_{\rm pol}(r)$ we adopted the values ($\lambda \approx 1$, $\bar{r}_c \in [2.3,4.3]$ a.u., $\alpha_d = 15.644$ a.u., and $\alpha_q = 33.599$ a.u.) obtained by Zhou and Norcross [11] by fitting to experimental energies for the lowest energy levels of Cs.

TABLE I. Negative-ion energies and resonance positions $E_{\rm aff}$ and widths Γ in meV for Cs^- with respect to the $6s_{1/2}$ threshold (for $6s^2\,{}^1S_0^e$, $6s6p\,{}^3P_J^o$) or the $6p_{1/2}$ threshold (for $6p^2\,{}^3P_J^e$). $E_{\rm aff}^{(0)}$ is the approximate affinity obtained by diagonalizing H within the $R = 40$ a.u. R-matrix sphere. $E_{\rm aff}^{(-d)},\Gamma^{(-d)}$ are obtained after matching at R to solutions outside R. $E_{\rm aff},\Gamma$ are the final results including in addition the potential $V_{\rm pol}(\mathbf{r}_1,\mathbf{r}_2)$. Negative values indicate states not bound relative to the given threshold at the given level of approximation. The J-averaged affinities are given by $E = \sum(2J+1)E_{\rm aff}(J)/\sum(2J+1)$.

Dominant Configuration	J^π	Reference No.	$E_{Aff}^{(0)}$	$E_{Aff}^{(-d)}$	$\Gamma^{(-d)}$	E_{Aff}	Γ
$6s^2\,{}^1S_o^e$	0^e	this work	521.843	521.836		471.5	
		1		430.			
		2		513.			
		8		511.		470.	
		14 (exp.)				471.5	
$6s6p\,{}^3P_J^o$	0^o	this work	31.21	28.35		−1.78	0.42
		4		32.			
	1^o	this work	24.59	21.39		−5.56	2.43
		4		25.			
	2^o	this work	12.35	8.60		−12.76	9.32
		4		11.			
	J-av.	this work	18.53	15.06		−9.14	6.04
		4		18.			
		1[a]		27.			
		2[a]		10.97			
		3				1.2−11.	
		7 (exp.)				−12.6	9.1
$6p^2\,{}^3P_J^e$	0^e	this work		159.68	0.005	141.24	0.009
	1^e	this work		148.02	0.19	129.71	0.15
	2^e	this work		126.13	1.12	108.11	1.33
	J-av.	this work		137.15	0.69	118.99	0.79
		this work[b]		182.56		164.40	
		2[b]		315.5			
		8[b]		183.		166.	

[a]The authors do not expect this state to be bound were their calculations to be further refined.
[b]Relative to the center of gravity of the $6p_j$ states.

We carried out a five-state ($6s_{1/2}$, $6p_{1/2,3/2}$, $5d_{3/2,5/2}$) Dirac R-matrix calculation including 24 continuum orbitals per symmetry, the Buttle correction, and the dielectronic term. Table I shows our results in comparison with other theoretical predictions [1–4,8] and with the experimental values [7,14]. The approximate affinities $E_{\rm aff}^{(0)}$ are calculated as the difference of the eigenvalues we obtained by diagonalizing the full Hamiltonian within a finite volume given by the R-matrix radius of 40 a.u., and the energy of the neutral-atom ground state [11]. To satisfy physical boundary conditions, the negative-ion states must be matched to linear combinations of exponentially decaying states outside the R-matrix sphere. For this purpose we analytically removed the R-matrix pole closest to an expected negative-ion bound state from the matching matrix and subsequently looked for zeros of its determinant again without including the dielectronic term (3) in (1). The affinities thus obtained, $E_{\rm aff}^{(-d)}$, were found to be smaller than $E_{\rm aff}^{(0)}$. The difference between $E_{\rm aff}^{(0)}$ and $E_{\rm aff}^{(-d)}$ is negligible for the Cs^- ground state. The negative-ion ground state therefore fits into the R-matrix box of radius 40 a.u.

Next we included the dielectronic term, and found that it changes the negative-ion spectrum dramatically (Table I). We first adjusted r_c to fit the measured binding energy, 471.5 meV, of the Cs^- negative-ion ground state given by Slater *et al.* [14] which results in $r_c = 5.109$ a.u. for cutoff functions as given in (3) and (4). With the dielectronic term so specified, the $6s6p\ ^3P_J^o$ multiplets are shifted by 20–30 meV into the continuum, where they appear as shape resonances in the partial elastic cross section for the $J^\pi = 0^o, 1^o, 2^o$ symmetries. Within the multiplet, the energy and width of the resonances increase from $J=0$ to $J=2$. The J-averaged location of the resonances is 9.14 meV above the $6s_{1/2}$ ground state of Cs. For the $6p^2\ ^3P_J^e$ resonances, the dielectronic term shifts the resonance energies about 20 meV. Their widths amount to a few meV and increase with J.

Agreement between the present results for the parameters of the ^3P states and those of previous calculations [2–4,8] at a similar level of approximation is quite good (Table I). The J-averaged position and width of the $^3P^o$ resonances also agrees quite well with the prediction [7] based on ERT analysis of experimental data.

We investigated the influence of the choice of $W_n(r_c, r)$ and of the radius r_c on negative-ion bound states and shape resonances in a similar interval as the one given in Ref. [11] for $\bar{r}_c$. The affinities obtained for the same value of r_c but different cutoff functions differ by a few percent. If we modify the somewhat arbitrary analytical form of the cutoff functions by dropping the square root exponents in (3), we obtain $r_c = 4.467$ a.u. The sensitivity to the two cutoff functions and their corresponding cutoff radii for the odd-parity excited states of Cs^- is illustrated in Table II, demonstrating that the two-electron results are insensitive to the explicit form of the function (4). Attempts to match the odd-parity states to linear combinations of exponentially decaying solutions at R failed for all J values and both forms of the cutoff functions, i.e., all three states are unbound at this level of approximation.

TABLE II. Approximate negative-ion affinities of the $J^\pi = 0^o$, 1^o, and 2^o ($6s6p\ ^3P_J^o$) symmetries of Cs^- as obtained from the diagonalization of the total Hamiltonian within the R-matrix sphere including the dielectronic polarization correction for two cutoff functions with radii r_c obtained by fitting the experimental ground-state energy of Cs^-: (a) as in Eq. (3); (b) as in Eq. (3), but with $(W_n)^{1/2}$ replaced by W_n. Negative entries correspond to shape resonances above the $6s_{1/2}$ threshold.

	Electron affinity (meV)	
	(a)	(b)
J^π	$r_c = 5.109$	$r_c = 4.467$
0^0	1.2	1.1
1^0	−3.2	−3.3
2^0	−11.0	−11.2

Converged total scattering cross sections for incident electrons with energies up to 2.7 eV were obtained by summing over 20 symmetries ($J = 0, \ldots, 9$ and both parities) and including elastic and inelastic contributions for excitation to the final $6p_{1/2}$, $6p_{3/2}$, $5d_{3/2}$, and $5d_{5/2}$ states of Cs (Fig. 1). Our results, which include the dielectronic term (3), are in qualitative agreement with the two-state nonrelativistic calculations of Karule and Peterkop [15] and Burke and Mitchell [5]. Except near thresholds and resonances, the effect of the dielectronic term is to

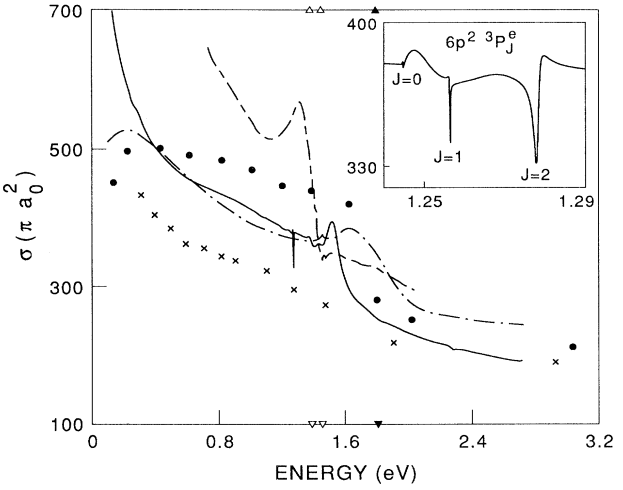

FIG. 1. Converged total cross section for low-energy e^--Cs scattering compared with published results. Theory: present work (——), Burke and Mitchell [5] (·-·-·), Scott *et al.* [6] (— — —), Karule and Peterkop [15] (●). Experiment: Visconti *et al.* [16] (×). The $6p_{1/2,3/2}$ and $5d_{3/2,5/2}$ thresholds are marked by the small triangles. Inset: The $6p^2\ ^3P_J^e$, $J = 0, 1, 2$ resonances (same units as main plot), which are not fully resolved in the main plot.

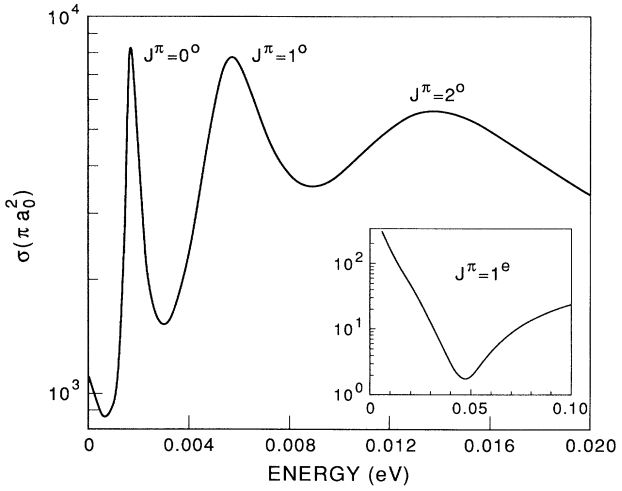

FIG. 2. Converged total elastic cross section for e^--Cs scattering. The peaks from left to right correspond to the $6s6p\,^3P_J^o$, $J=0,1,2$ shape resonances, respectively. Inset: The partial cross section associated with a Ramsauer-Townsend minimum in the $J^\pi=1^e$ symmetry (same units as main plot).

reduce the total cross section by (5–10)%. The discrepancy between the results of the five-state calculation by Scott *et al.* [6] and ours is puzzling and cannot be ascribed either to the dielectronic term or to additional relativistic interactions included in our calculation. Together with the results of Karule and Peterkop [15] and Burke and Mitchell [5] our results follow the trend of the measurement [16]. At energies below 20 meV the $6s6p\,^3P_J^o$, $J=0,1,2$ shape resonances and a structure associated with a Ramsauer-Townsend minimum in the $J^\pi=1^e$ symmetry can be identified in the elastic-scattering cross section (Fig. 2).

These features might be the explanation for the discrepancy between previous calculations and experiments as originally suggested [1]. The total cross section below 0.1 eV is in good qualitative agreement with the prediction [7] based on ERT analysis of experimental data, if one allows for the absence of fine-structure splitting of the $^3P^o$ resonances in the latter. The scattering lengths obtained for $J^\pi=0^e$ (-0.79) and 1^e (-19.0) are also in fair agreement with the ERT predictions of -2.40 and -22.7 for (in LS coupling) ^1S and ^3S scattering, respectively. The large value of the latter is responsible for the Ramsauer-Townsend minimum shown in Fig. 2.

We have shown that both core-polarization and relativistic effects are responsible for fascinating new resonance structures in electron-Cs scattering. The former converts $^3P_J^o$ negative-ion states from bound states to very narrow resonances. The latter gives fine-structure splitting and finite autoionization widths to $^3P_J^e$ states that in LS coupling are strictly uncoupled to the adjacent continuum. It might be possible to observe transitions between these ^3P multiplets by free-free absorption or emission. We plan further investigations of both electron-Cs scattering and photoprocesses involving Cs^-.

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[1] I. I. Fabrikant, Opt. Spektrosk. **53**, 223 (1982) [Opt. Spectrosc. (U.S.S.R.) **53**, 131 (1982)], and references therein.
[2] J. L. Krause and R. S. Berry, Comments At. Mol. Phys. **18**, 91 (1986).
[3] C. F. Fischer and D. Chen, J. Mol. Struct. **199**, 61 (1989).
[4] C. H. Greene, Phys. Rev. A **42**, 1405 (1990).
[5] P. G. Burke and J. F. B. Mitchell, J. Phys. B **6**, L161 (1973).
[6] N. S. Scott, K. Bartschat, P. G. Burke, O. Nagy, and W. B. Eissner, J. Phys. B **17**, 3775 (1984).
[7] I. I. Fabrikant, J. Phys. B **19**, 1527 (1986); High Temp. (U.S.A.) **27**, 183 (1989).
[8] D. W. Norcross, Phys. Rev. Lett. **32**, 192 (1974).
[9] J. J. Chang, J. Phys. B **8**, 2327 (1975); **10**, 3335 (1977).
[10] D. W. Walker, J. Phys. B **8**, L161 (1975).
[11] H. L. Zhou and D. W. Norcross, Phys. Rev. A **40**, 5048 (1989).
[12] T. Gorczyca and D. W. Norcross, Phys. Rev. A **42**, 5132 (1990).
[13] C. D. H. Chisholm and N. Öpik, Proc. Phys. Soc. London **83**, 541 (1964); G. A. Victor and C. Laughlin, Chem. Phys. Lett. **14**, 74 (1972).
[14] J. Slater *et al.*, Phys. Rev. A **17**, 201 (1978).
[15] E. M. Karule (unpublished); E. M. Karule and R. K. Peterkop (unpublished), as given in Ref. [5].
[16] P. J. Visconti *et al.*, Phys. Rev. A **3**, 1310 (1971).