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K-shell photodetachment from C^-: Experiment and theory

N. D. Gibson,[1] C. W. Walter,[1] O. Zatsarinny,[2] T. W. Gorczyca,[2] G. D. Ackerman,[3] J. D. Bozek,[3] M. Martins,[4] B. M. McLaughlin,[5] and N. Berrah[2]

[1]*Department of Physics and Astronomy, Denison University, Granville, Ohio 43023*

[2]*Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008*

[3]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

[4]*Institut fuer Experimentalphysik, Universitaet Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany*

[5]*School of Mathematics and Physics, Queen's University of Belfast, Belfast BT7 1NN, United Kingdom*

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K-shell photodetachment from C^- has been investigated in the photon energy range between 280 and 285 eV using the merged ion-beam–photon-beam technique. C^- ions were produced using a Cs sputtering negative-ion source, while the photons were produced by the undulator beam line 10.0.1 of the Advanced Light Source. C^+ ions formed by double detachment were detected as a function of incident photon energy. Using this collinear arrangement, the relative cross sections were measured and compared with theoretical predictions. The measured spectrum shows the first experimental evidence of the $1s2s^22p^4(^4P)$ shape resonance near 281.7 eV, which is in excellent agreement with two independent *R*-matrix calculations for the 1*s* photodetachment cross section of C^- producing C^+.

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The study of negative ions continues to provide critical insights into the structure and dynamics of both atoms and ions. Negative ions are important in a wide range of physical processes, extending from radiation absorption in stellar atmospheres to plasmas and electrical discharges. Since the extra electron in a negative ion is bound predominantly by electron correlation effects, negative ions provide a fertile testing ground for state-of-the-art atomic physics calculations regarding these many-body interactions. Theoretical investigations of negative ions are some of the most stringent test cases for atomic theory, since both electron correlation and core-polarization effects need to be included.

Over the past two decades, theoretical and experimental negative-ion studies have provided many insights into correlation effects [1,2]. A number of studies have also investigated short-lived negative-ion resonances [3] or used electric-field effects to further understand the dynamics of the detaching electron [4–7]. Until recently, however, photodetachment experiments were confined to examining valence shell electrons. Therefore, most of the information concerned correlations only in the valence shell, but not in the strongly correlated core.

While scientific interest in these highly correlated systems has remained keen for some time, only recently, with the advent of third-generation synchrotron-radiation facilities, has sufficiently high energy photon flux become available to enable inner-shell photodetachment measurements. Studies involving inner-shell electrons reveal the more complex correlation of the core electrons that can give rise to significant differences in photodetachment cross sections between neutral atoms and negative ions [8].

To date, Li^- [8,9] and He^- [10] are the only nonhydrogenic systems to be studied experimentally for *K*-shell photodetachment. These two systems have generated significant theoretical interest [11–16]. C^- is one of the most complex negative ions from which K-shell detachment measurements can be made and for which comparisons between experimental data and theoretical predictions are likely in the near future.

The primary objective of this paper is to investigate the $1s \rightarrow 2p$ resonance structure in the photodetachment of C^-. This work was motivated by the theoretical prediction, using Cowan's atomic structure code [17], of a prominent shape resonance just above the *K*-edge threshold. Specifically, the process of interest is the following:

$$\begin{aligned} h\nu + C^-(1s^2 2s^2 2p^3\ ^4S^o) &\rightarrow C^-{}^*(1s2s^2 2p^4\ ^4P) \\ &\rightarrow C^*(1s2s^2 2p^3\ ^5S) + e^- \\ &\rightarrow C^+(1s^2 2l^3) + e^- + e^-. \end{aligned}$$

Here a core-excited state of neutral C is produced via resonant photodetachment, and it subsequently Auger decays, yielding a C^+ ion. This positive ion can then be detected experimentally, providing information on the initial $C^-(1s2s^2 2p^4\ ^4P)$ photodetachment shape resonance.

In general, negative ions have relatively low photoionization cross sections and, since they are charged particles, maximum sample densities are also rather low. For keV ion beams, collisional stripping cross sections are high enough that even at very good laboratory vacuums (5×10^{-10} Torr), neutrals and positive ions produced by stripping frequently overwhelm any photodetachment signal. Therefore, a high-brightness photon source is necessary in order to perform inner-shell photodetachment measurements. The present experiment was performed on the high-resolution atomic, molecular, and optical physics undulator beamline 10.0.1 at the Advanced Light Source at Lawrence Berkeley National Laboratory. A 7.5-keV negative-ion beam was created using a SNICS II cesium sputtering source [18] and mass analyzed to produce 50–140 nA of $^{12}C^-$ ions. The

collinear ion-photon beam line (10.0.1-IPB) has been described in detail elsewhere [19,20], but a few key features are discussed below.

The photon-ion interaction region in this apparatus consists of a 29.4-cm-long constant potential region where the incoming ions can be *energy tagged*. In our case, a potential of $V=+1.5$ kV accelerated the negative ions into the region, producing 9.0-keV $^{12}C^-$ ions for photodetachment. Neutral carbon atoms produced in this region have a kinetic-energy equal to 9.0 keV. Charged particles exiting this region undergo a kinetic energy shift equal to qV. The C^+ ions produced by double detachment in the interaction region have a kinetic energy of 10.5 keV and were steered out of the primary beam by a 45° bending magnet and collected as a function of photon energy. The photon energies were calibrated to the nearest 0.1 eV using known absorptions for neutral species and then modified by the Doppler shift of about $+360$ meV for 9.0-keV negative ions at a photon energy of 282 eV.

The interactions between a counterpropagating ion beam and a 300-eV incident photon beam are rather tenuous. Photodetachment signal levels are quite low, so the ion-beam–photon-beam overlap is optimized using a series of three beam profile monitors. At the front and the rear of the interaction region, spinning wire beam profile monitors (BPMs) track the position of the ion beam. The x-ray photons used in this experiment possess enough energy to eject electrons from the BPM and, therefore, register a signal as well. In the center of the interaction region, there is a vertically scannable slit arrangement that enables a check of the ion-beam–photon-beam overlap in the center of the region. This slit is scanned and the photons pass through in one direction to be collected by a photodiode. The counter-propagating ions pass through in the other direction and are collected in a Faraday cup. All three monitors are removed from the beam path during data collection.

Figure 1 shows the photodetachment cross section of C^- for the channel producing C^+ ions. These data were taken with a maximum photon energy bandwidth of about 0.35 eV [21] and a step size of 0.125 eV. The measured C^+ signal was normalized to the photon flux through the interaction region and to the C^- ion-beam current after the interaction region. Counting statistics were improved by summing multiple sweeps over the photon energies in each region. In order to reduce fluctuations in the background signal introduced by negative ion stripping caused by background gases and apertures, the photon beam was chopped at 6 Hz. A 2 s dwell time was spent at each data point with the photons incident on the ions, and another 2 s were spent acquiring background data. The relative cross section was then determined by subtracting the photons-off signal from the photons-on signal. The data shown are the result of averaging 11 1.5-hour-long scans. The error bars shown are 1σ statistical uncertainties in the data points.

In order to compare these measured cross sections to theoretical results, two independent nonrelativistic *R*-matrix calculations were performed (we assume that relativistic effects are negligible for this light system even in the $1s$ shell). The first (*R*-matrix I) calculation used a B-spline basis with non-

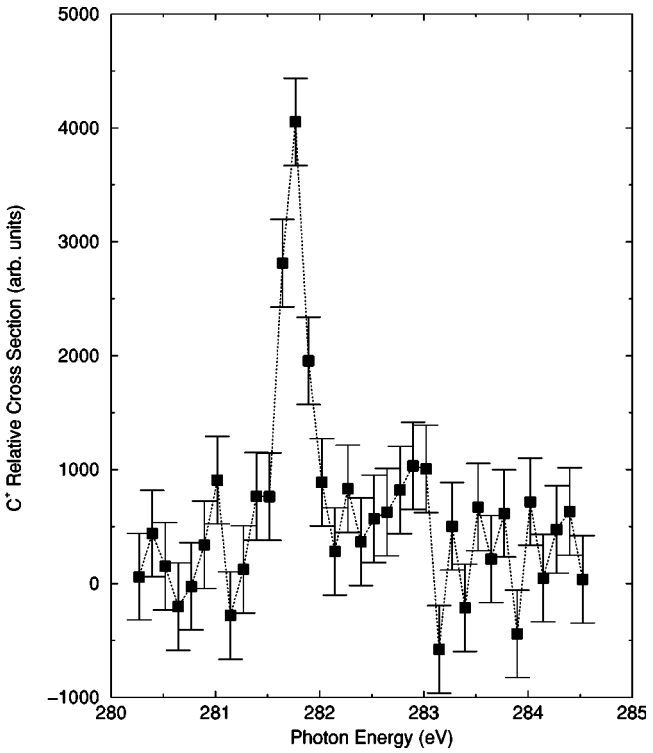

FIG. 1. Measurement of the C^- photodetachment cross section for the production of C^+.

orthogonal orbitals [12,22]. For this calculation, the close-coupling expansion included the 16 bound and autoionizing states of neutral carbon derived from the $1s^22s^22p^2$, $1s^22s2p^3$, $1s^22p^4$, $1s2s^22p^3$, $1s2s2p^4$, and $1s2p^5$ configurations. Each state was described by a different set of orbitals, which were separately determined from state-specific multiconfiguration Hartree-Fock (MCHF) [23] calculations including the $1s$, $2s$, and $2p$ physical orbitals as well as $3s$, $3p$, $3d$, and $4f$ pseudo-orbitals. The initial $1s^22s^22p^3(^4S)$ state of C^- was optimized separately, using additional $4l$ and $5l$ correlation orbitals. All single- and double-promotion configurations were used to describe the carbon states and the initial C^- state. It should be emphasized that the use of nonorthogonal orbitals easily accounts for relaxation effects in the carbon $1s$ vacancy states.

The second (*R*-matrix II) calculation relied on the standard orthogonal orbital *R*-matrix method [24] using the RmaX [25] suite of codes [26]. While this is equivalent to the first method, in principle, there are certain practical differences between the two approaches. Most important, the *R*-matrix II method is restricted to the use of a single set of orbitals for describing each carbon and/or C^- state. For the present case, the $1s$, $2s$, and $2p$ orbitals were determined from a Hartree-Fock calculation for the carbon $1s^22s^22p^2(^3P)$ state, and additional $3s$, $3p$, and $3d$ pseudo-orbitals were determined from a MCHF calculation optimized on the inner-shell excited $1s2s^22p^3(^3S)$ state. All single promotions from the $n=2$ configurations were then included in the configuration expansion for the same 16 states of carbon that were included in the first method.

Another major difference between the two is that the

R-matrix II method requires additional bound-type C^- configurations in the close-coupling expansion to compensate for the enforced orthogonality of orbitals. In the present study, it was crucial to include *only* those required configurations for the final ^4P symmetry, which was accomplished using a pseudoresonance elimination technique [27] to choose the correct expansion of C^- configurations. When this elimination was not performed, an imbalance between the correlation in the neutral and anion states occurred, and the C^- resonance state was more correlated, and therefore, closer to the exact energy value than the carbon states. This gave a $1s2s^22p^4(^4P)$ resonance in the *R*-matrix II cross section that was *below* the lowest $1s2s^22p^3(^5S)$ carbon threshold, i.e., it was a Feshbach, rather than a shape, resonance, with a much narrower width and a much smaller cross section, both background and resonant, to the C^+ channel. The pseudoresonance elimination technique, on the other hand, gave a (shape) resonance in the *R*-matrix II cross section *above* the $1s2s^22p^3(^5S)$ carbon threshold, in agreement with the *R*-matrix I and experimental results.

Whereas the *R*-matrix I results are fairly stable with respect to variations in atomic structure, the *R*-matrix II results, being restricted by the use of a single set of orbitals, are still extremely sensitive to slight changes in the orbital and/or configuration description. For example, when double promotions out of the $n=2$ configurations were also included in the expansion for the carbon states, a shape resonance was obtained that was closer in energy to the ^5S threshold, and, therefore, narrower and taller. On the other hand, when the orbitals were determined from a MCHF calculation on the ^5S term, rather than the ^3S term, the resultant shape resonance was farther away from threshold, giving a shorter, broader resonance profile.

The two *R*-matrix results and the scaled experimental data are shown in Fig. 2. For best comparison with experiment, the theoretical results were obtained by summing the partial cross sections only to the autoionizing states of C, since only C^+ ions were measured. Also, both theoretical results were shifted in photon energy so that the carbon $1s2s^22p^3(^5S)$ threshold was at 281.415 eV. This shift was only $+0.05$ eV for the *R*-matrix I cross section, indicating the excellent convergence of that calculation, but was -0.98 eV for the results from the *R*-matrix II calculation, which, limited by a single, smaller set of orthogonal orbitals, did not account for inner-shell relaxation as accurately, and consequently overestimated the carbon $1s2s^22p^3(^5S)$ energy. Nevertheless, the energy position of the shape resonance *relative* to threshold is the most important quantity determining the resonance profile, and it is seen that this value is about the same in both *R*-matrix results, giving resonance profiles of comparable width and height. The *R*-matrix I results show a somewhat larger oscillator strength, however. Given that a more flexible basis was used in that calculation, it is reasonable to assume that the *R*-matrix I results are more accurate; from that calculation, a width of 0.2 eV is found, with a branching ratio to the carbon $1s2s^22p^3(^5S)$ state of 76%, fully supporting the interpretation of this feature as a predominantly shape resonance, versus Feshbach resonance. (Note that this particular resonance has mixed character since it is above the $1s2s^22p^3\,^5S$ threshold but below the $1s2s^22p^3\,^3[D,P,S]$ ones.) Regardless of their differences, both theoretical results, once shifted, show a shape resonance that lines up remarkably well with the scaled experimental data.

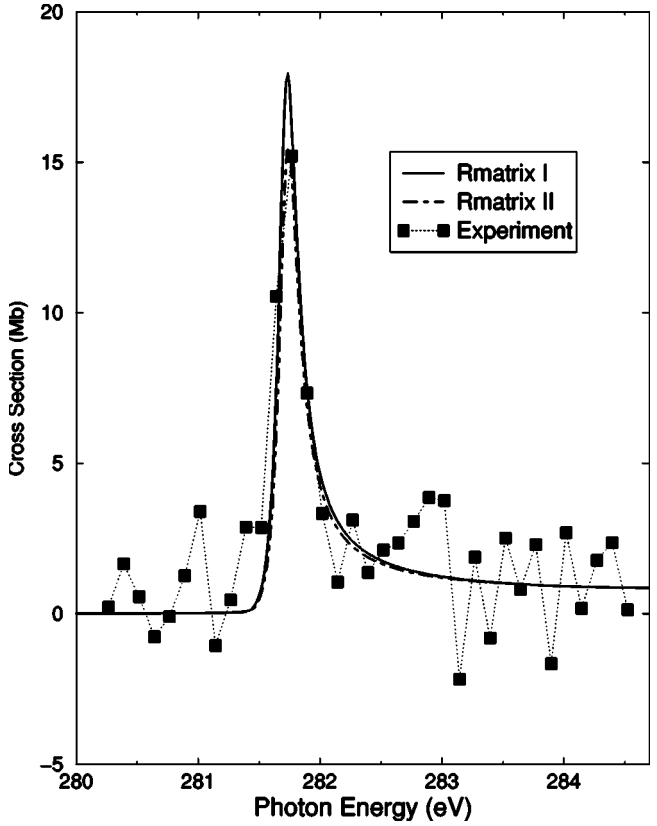

FIG. 2. Comparison between theoretical and experimental cross sections for photodetachment of C^- leading to C^+. The solid line (*R*-matrix I) corresponds to the nonorthogonal *B*-spline results, whereas the dash-dot line (*R*-matrix II) corresponds to the standard, single orthogonal basis set results.

It is interesting to compare these $1s$ photodetachment results with earlier $2s$ results [28–32]. Whereas the overall resonance and neutral structure would seem the same—$ns2p^4$ and $ns2p^3$ in either case, with $n=1$ or 2—the overlaps between the open ns shell and the $2p$ shell are radically different, and this can lead to different resonance behavior. Whereas a shape resonance is still predicted in most of those $2s$ photodetachment studies [28,30–32], the near-threshold results exhibited a much broader resonance feature, with a more pronounced background cross section, than is seen here for the $1s$ photodetachment. It is also interesting to note that a calculation similar to the present *R*-matrix II calculation found a Feshbach resonance *below* the $1s^22s2p^3(^5S)$ threshold [29], although a later experimental study disproved this possibility [30]; in that *R*-matrix calculation, the pseudoresonance elimination technique was not performed. The current photon energy range of the beam line prevents us from carrying out studies of $2s$ photodetachment from C^-. However, future anticipated experiments at the current resolution near the $2s2p^3$ threshold will be able to resolve the final outstanding discrepancies between various theoretical predic-

tions [28,29,31,32] in the energy range just above that accessible in the earlier experiment [30].

In conclusion, the present study provides both experimental and theoretical evidence for the C^- $1s2s^22p^4(^4P)$ shape resonance just above the carbon $1s2s^22p^3(^5S)$ threshold. Future studies will include investigations of the branching ratio between the decay channels that result in neutral carbon and the decay channels that produce C^+ ions. The partially filled p shell in C^- can therefore lead to a rich spectrum of short-lived negative ion states with a high degree of electron correlation.

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