State-resolved valence shell photoionization of Be-like ions: experiment and theory

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Abstract
High-resolution photoionization experiments were carried out using beams of Be-like C2+, N3+ and O4+ ions with roughly equal populations of the 1S ground state and the 3Po manifold of metastable components. The energy scales of the experiments are calibrated with uncertainties of 1–10 meV depending on photon energy. Resolving powers beyond 20 000 were reached allowing for the separation of contributions from the individual metastable 3Po0, 3Po1 and 3Po2 states. The measured data compare favourably with semi-relativistic Breit–Pauli R-matrix calculations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The most abundant elements in the universe next to hydrogen and helium are oxygen and carbon with nitrogen not far off in abundance. On earth we experience neutral C, N and O as main constituents of organic matter. In most parts of the universe, however, baryonic matter is ionized and the charge states of atoms depend on the temperature of their local environment and on the degree of irradiation by energetic photons from external sources. Photoionization of ions is an important mechanism for the production of highly charged ions in cold astrophysical plasmas. Ionization in such plasmas is usually balanced by low-energy electron–ion recombination [1]. Photoabsorption by ions (and atoms) in the interstellar medium modifies the radiation spectrum of distant objects in the universe and thus complicates the interpretation of observations of such objects. On the other hand, the observation of absorption lines of neutral or ionized gas illuminated by a continuous background electromagnetic spectrum provides detailed knowledge about the atomic abundances in the gas as well as its density and temperature. Hence, photoionization and the inverse process, photorecombination, of ions are important phenomena in astrophysical plasmas. Beryllium-like ions in particular are among the most abundant species in ionized gases owing to their relative stability as four-electron closed-shell systems. They serve as sensitive probes for the diagnostics of astrophysical and technical plasmas. Detailed knowledge of their structure and behaviour in atomic interactions, particularly in photoionization processes, is thus essential for understanding astrophysical observations.

Besides their importance in plasma applications, Be-like ions with their two loosely bound electrons in the L-shell and two tightly bound K-shell electrons are almost perfect objects for investigating two-electron effects. Photoionization of ions and...
Theoretical work on photoionization of Be-like systems started with a calculation by Altick [5] of the near-threshold photoionization cross section of the Be atom using the configuration-interaction method. Since then photoionization of neutral Be has been treated in numerous theoretical studies. References are given in the most recent work by Hsiao et al [6, 7]. Also, ions in the Be sequence were addressed early on [8]. Quantum defect theory was applied to obtain photoionization of atoms, molecules and ions [9]. Photoionization cross-section calculations for C\textsuperscript{2+} were carried out employing a close-coupling method [10]. Results for the singlet ground level and, for the first time, also for the lowest lying, metastable triplet level were presented. A substantial extension of the early theoretical studies was accomplished by the work of Tully et al [11] using the non-relativistic R-matrix technique to calculate photoionization cross sections in LS coupling for the beryllium isoelectronic sequence starting with Be and reaching up to Fe\textsuperscript{22+}. The data obtained for different ions and especially for the beryllium sequence are available from the Opacity Project [12] and can be retrieved from the TOPBASE database (http://rxte.gsfc.nasa.gov/topbase/). By using more extended eigenfunction expansions, Nahar and Pradhan calculated photoionization cross sections for the beryllium-like C\textsuperscript{2+} and N\textsuperscript{3+} ions [13]. The calculations were still performed in LS coupling and therefore could not predict the possible additional resonance structure that may arise due to intermediate coupling. In a subsequent paper, Nahar provided the results of related similar calculations for O\textsuperscript{3+} ions [14].

A new step forward in the theoretical treatment of photoionization of Be-like ions was made by McCaughlin by including relativistic effects in the R-matrix calculations within the confines of the semi-relativistic Breit–Pauli approximation and performing them for intermediate coupling. That work and its results for the B\textsuperscript{+} and C\textsuperscript{2+} ions were described in experimentally motivated papers by Schippers et al [15] and Müller et al [16, 17], respectively. It included data not only for the 1\textsuperscript{S} ground state of the Be-like parent ions but also for their 3\textsuperscript{P}\textsuperscript{0} metastable states. Stimulated by the theoretical and experimental progress, Kim and Manson carried out calculations of both ground- and metastable-state photoionization of B\textsuperscript{+} and C\textsuperscript{2+} ions using a non-iterative eigenchannel R-matrix method [18–20]. Kim and Kim carried out an extensive nonrelativistic calculation for the photoionization cross sections of the first excited p-states of the C\textsuperscript{2+} ion [21]. The computations were carried out on a fine energy mesh across all the autoionizing Rydberg series of resonances converging to Li-like C\textsuperscript{3+} 2p, 3s, 3p and 3d thresholds.

More recently, Chu et al studied photoionization of the beryllium isoelectronic series from neutral Be to Fe\textsuperscript{22+} for ground 1\textsuperscript{S} and metastable 3\textsuperscript{P}\textsuperscript{0} initial states [22]. Both nonrelativistic LS-coupling R-matrix and relativistic Breit–Pauli R-matrix methods were used to calculate the cross sections in the photon-energy range between the first ionization threshold and the 1\textsuperscript{s}\textsuperscript{2} 4\textit{f}\textsubscript{2} 2\textsuperscript{P}\textsubscript{0} threshold for each series member. The total cross sections compare well with available experimental results. The importance of relativistic effects was demonstrated by the comparison between the LS and the Breit–Pauli results. The same group of authors has just published R-matrix results on photoionization of Be-like ions including processes of ionization plus excitation of the target ion [2]. Another approach to photoionization was also presented recently. Hsiao et al applied the multiconfiguration relativistic random-phase approximation theory to the valence-shell photoionization of ions along the Be isoelectronic sequence [7]. The most recent theoretical work addresses total and partial cross sections for photoionization of the Be-like O\textsuperscript{4+} ion [3]. The calculations were based on a non-iterative variational R-matrix method combined with multichannel quantum-defect theory for the ground 2\textsuperscript{S}\textsuperscript{0} 1\textit{S} and excited 2\textit{s}2\textit{p} 1,3\textit{P} states. The photon energy region from the first threshold up to the O\textsuperscript{4+} 3\textit{d} threshold was covered.

Experimental work on photoionization of Be-like systems started with the observation of far-ultraviolet absorption spectra of beryllium vapour produced in a vacuum spark arrangement backlit from a second Be vacuum spark [23]. Photoionization of neutral Be atoms was studied in detail by exposure of Be metal vapour to synchrotron radiation [24, 25]. The absorption spectrum of Be-like B\textsuperscript{+} was investigated by using two laser produced plasmas [26]: one generating the B\textsuperscript{+} absorbing medium and the other the background continuum radiation. Series of lines arising from the 1\textsuperscript{S} ground and the 3\textsuperscript{P}\textsuperscript{0} metastable levels were observed followed by absorption continua at higher energies. Photoionization cross sections were derived and autoionization resonances observed. The associated resonance profiles were fitted with a parametric formula for series of autoionized lines [26] developed on the basis of quantum defect theory [9].

With the development of photon–ion merged-beam experiments located at synchrotron radiation facilities, systematic measurements of photoionization cross sections along isoelectronic and isonuclear sequences became possible. The techniques and applications of merged beams have been reviewed by West [27] and more recently by Kjeldsen [28]. The beryllium-like sequence was addressed previously in a number of merged-beam experiments providing absolute cross sections up to the (2\textit{p}n\textit{l}) resonance-series limits for photoionization of B\textsuperscript{+} ions with an energy resolution of 25 meV at around 30 eV photon energy [15], for photoionization of C\textsuperscript{2+} with an energy resolution of 30 meV at around 50 eV photon energy [16], for photoionization of O\textsuperscript{4+} with a quoted energy resolution of 230 meV at around 70 eV photon energy [29], and for photoionization of O\textsuperscript{5+} with an underestimated energy resolution of 250 meV at around 110 eV photon energy [29, 30]. For selected resonances in the photoionization of C\textsuperscript{2+} ions, measurements with energy...
spreads as low as 7.5 meV have been reported [17]. An investigation of state-selective photoexcitation of autoionizing levels of C\textsuperscript{2+}, N\textsuperscript{3+} and O\textsuperscript{4+} ions [31] was launched a few years later to test theory at an unprecedented level of detail. Very recently, photoionization of highly charged ions trapped in later to test theory at an unprecedented level of detail. Very recent, photoionization of highly charged ions trapped in metastable N\textsuperscript{3+} ions \( \rightarrow \) Be-like ions \( N \) \( + 1 \)-electron initial states of the Be-like ions C\textsuperscript{2+}, N\textsuperscript{3+} and O\textsuperscript{4+}. Here, \( N \) is the number of electrons in the ‘core’ of the ion \( (N = 3 \) in the case of Be-like ions) while ‘the active electron’ is counted as number \( N + 1 \). For generating the \( (N + 1) \)-electron wavefunction of the Be-like ions, the present R-matrix method started from the construction of nine Li-like LS states, 1s\textsuperscript{2}2s\textsuperscript{2}3\textsuperscript{3}S, 1s\textsuperscript{2}2s\textsuperscript{2}3\textsuperscript{3}P, 1s\textsuperscript{3}3s\textsuperscript{3}S, 1s\textsuperscript{3}3p\textsuperscript{3}P, 1s\textsuperscript{3}3d\textsuperscript{3}D, 1s\textsuperscript{4}s\textsuperscript{3}S, 1s\textsuperscript{4}p\textsuperscript{3}P\textsuperscript{0}, 1s\textsuperscript{4}d\textsuperscript{3}D\textsuperscript{0} and 1s\textsuperscript{4}f\textsuperscript{3}P\textsuperscript{0}, to represent the possible final states of the photoionized ions C\textsuperscript{3+}, \( N \textsuperscript{4+} \), and O\textsuperscript{5+}, respectively. The final state of the investigated photoionization processes is an \( N \)-electron state (termed as the target state for historical reasons). The target ion core is retained in the close-coupling expansions for both the 1S ground and the 3P\textsuperscript{0} metastable initial states of the Be-like ions. In the structure calculations for the Li-like target ions, all physical orbitals were included up to \( n = 4 \) in the configuration interaction wavefunctions used to describe the states. The Hartree–Fock 1s and 2s orbitals of Clementi and Roetti [34] were used, with the additional \( n = 3 \) and \( n = 4 \) orbitals determined by energy optimization on the appropriate spectroscopic state with the structure code CIV3 of Hibbert [35]. All of the nine states of each Li-like core were represented by multi-configuration interaction wavefunctions. The Breit–Pauli R-matrix approach was utilized to calculate the 15 C\textsuperscript{3+}(LSJ) \( (N\textsuperscript{4+}(LSJ), O\textsuperscript{5+}(LSJ)) \) target ion state energies which arise from the nine LS states, and the photoionization cross sections were determined for both the 1S ground and the 3P\textsuperscript{0} metastable initial states.

PI cross-section calculations for Be-like ions were performed in intermediate coupling using the semi-relativistic Breit–Pauli approximation which allows for relativistic effects to be included within the confines of the R-matrix approach [36–38]. The scattering wavefunctions were generated by allowing all possible three electron promotions out of the base 1s\textsuperscript{2}2s\textsuperscript{2} configuration of each Be-like ion into the orbital set employed. All the scattering calculations were performed with 20 continuum functions and a boundary radius of 15.8 Bohr radii for the C\textsuperscript{2+} ion, 12.8 Bohr radii for the N\textsuperscript{3+} ion and 10.8 Bohr radii for the O\textsuperscript{4+} ion. For the 1S ground state, dipole selection rules require only the following transition: \( 0^e \rightarrow 1^o \), whereas for the 3P\textsuperscript{0} metastable state one needs all the dipole transitions: \( 2^0 \rightarrow 3^e, 2^e, 1^e, 1^0 \rightarrow 2^e, 1^e, 0^e, 0^0 \) and \( 0^0 \rightarrow 1^o \) to be calculated. The Hamiltonian matrices for the \( 2^e, 1^e, 0^e \), \( 3^e, 2^e, 1^e \) and \( 0^0 \) symmetries were calculated, where the entire range of LS matrices that contribute to these \( J\pi \) symmetries is used. Effects of radiation damping [38] were included.

For the 1S ground state and 3P\textsuperscript{0} metastable initial states, the outer region electron–ion collision problem was solved using a suitably chosen fine energy mesh of 13.6 \( \mu \text{eV} = 10^{-6} \) Rydbergs between the thresholds in order to fully resolve the fine structure in the respective photoionization cross sections. The energy mesh of the present calculations substantially differs from that of our previous theoretical treatment on photoionization of C\textsuperscript{2+} ions [16]. Due to the large calculational effort required when using a fine mesh, the
energy steps were chosen to be 1.36 meV in that previous investigation, i.e., the step width was a factor 100 more coarse than that in the present study. The effect of the size of the energy mesh is discussed in section 4 of this paper.

The present state-of-the-art calculations were augmented with calculations employing the online version of the Los Alamos National Laboratory (LANL) Atomic Physics Codes package [39]. This easy-to-use package is based on Cowan’s Hartree–Fock atomic structure theory [40] and makes use of the Cowan atomic structure code CATS. It can provide oscillator strengths for specific transitions from a state $i$ to a state $f$ of an atom in a given charge state. It also calculates the associated transition energies although in the online version not nearly with the accuracy of the Breit–Pauli R-matrix theory. In combination with the state-of-the-art theory and the high-resolution experiments reported here, the online CATS package can be used to identify individual contributions to the photoionization cross sections studied.

3. Experiment

The experiment was performed at the ion–photon-beam (IPB) end station of the undulator beamline 10.0.1 at the ALS. A detailed description of the experimental setup has been provided by Covington et al [41]. For the present study on Be-like C$^{2+}$, N$^{3+}$ and O$^{4+}$ ions, similar procedures were utilized as in our earlier photoionization cross section measurements for Be-like boron and carbon ions [15–17]. The beryllium-like ions were generated inside a compact all-permanent-magnet electron cyclotron-resonance (ECR) ion source [42]. Collimated ion-beam currents of typically 30–100 nA were extracted using the ion source on a positive potential fixed between +5 and +6.5 kV. The ions were then passed through a bending dipole magnet selecting the desired ratio of charge to mass. The mass- and charge-selected ion beams were centred onto the counterpropagating photon beam by applying appropriate voltages to several electrostatic ion beam steering and focusing devices. Downstream of the interaction region, the ion beam was deflected out of the photon beam direction by a second dipole magnet that also separated the ionized C$^{3+}$ (N$^{4+}$, O$^{5+}$) product ions from the respective C$^{2+}$ (N$^{3+}$, O$^{4+}$) parent ions. The product ions were counted with nearly 100% efficiency using suitable single-particle detection [43, 44], and the parent ion current was monitored for normalization. The measured product count rate $R$ was only partly due to photoionization events. It also contained identical ions produced by electron removal collisions of the parent ions with residual gas molecules and surfaces. This background was determined by mechanically chopping the photon beam.

In the present experiments, relative energy-scan measurements were carried out by stepping the photon energy through a preset range of values at different photon beam energy resolutions. The desired experimental energy spread was preselected by adjusting monochromator settings of the beamline accordingly. It is not possible, however, to choose a well-defined resolution by just setting the monochromator slits. The real resolution has to be determined from the measured results after the experiment. The reason for this is the slit geometry and the small size of the photon beam at the entrance slit of the monochromator in the beamline used. Measurements were pushed to the practical limits of resolution which were mainly determined by limitations in the signal-to-background ratios acceptable for experiments and by the photon beamtime available since finer energy steps are needed to resolve features at higher resolution. Resolving powers $E/\Delta E$ of more than 20000 were reached. The scan data were normalized to absolute measurements available from previous work [16, 29]. The total systematic uncertainty of the cross sections thus determined is about ±20%. Additional uncertainty arises from the presence of unknown fractions of metastable and ground-state ions in the parent beams.

The energy scales of the experiments are calibrated with uncertainties of 1–10 meV depending on photon energy. The calibration was accomplished by carrying out separate photoionization measurements with neutral He, Ar (L-shell resonances in second order) and Kr gas and by comparing the results with the well-known resonance features [45, 46] at energies between about 60 and 120 eV. Calibrated monochromator settings from these ranges were linearly interpolated to obtain the scaling factors for measured energies in the present range of interest. Since the parent ions are in motion, a Doppler correction has to be carried out transforming the nominal laboratory energies to the centre of mass frame of the ions before applying the calibration factor. With all this carefully included, we estimate an absolute uncertainty of at most ±10 meV for the energy scale of the present measurements, at some energies close to the calibration energies the absolute uncertainties are as small as ±1 meV. Since the precision of peak position determinations is of the order of only 0.1 meV, the possible calibration error almost exclusively determines the absolute uncertainties of the resonance energies. Relative uncertainties of resonance energies within the range of one scan measurement are much smaller than ±10 meV. Especially in scan ranges of only about 200–300 meV, the relative uncertainties of peak positions are only about 0.1 meV.

4. Results and discussion

The results of the present work are described in detail in the following subsections for each of the Be-like ions investigated. Theoretical cross sections were calculated separately for each of the initial $\left(1s^2 \, 2s^2 \, 2p^2 \, \Sigma^+_{0} \right)$, $\left(1s^2 \, 2s^2p \, \Pi^0 \right)$, $\left(1s^2 \, 2s2p \, \Pi^+ \right)$ and $\left(1s^2 \, 2s2p \, \Sigma^+ \right)$ states of the Be-like C$^{2+}$, N$^{3+}$ and O$^{4+}$ parent ions. The calculated unconvoluted cross sections show very rich details with numerous resonances of very different widths. In order to assess the strengths contained in these features, it is convenient to convolute the calculated cross sections with a Gaussian distribution of defined width. The convoluted spectra provide an immediate overview over the relative importance of the different resonance contributions. For comparison with experiments, such convolution has to be carried out anyway in order to simulate the limited experimental energy resolution.

In the experiments, all the above initial states were present in the parent ion beams used for the measurements. The ECR
ion source has to provide electron energies sufficiently high to produce the desired multiply charged ions. Hence, population of the metastable \(^3\)P\(_o\) states with excitation energies of 6.50 eV for C\(^{2+}\), 8.34 eV for N\(^{3+}\), and 10.19 eV for O\(^{4+}\) ions [47] was unavoidable. Moreover, the lifetimes of the \(^3\)P\(_o\) states of the investigated ions are at least about 470 \(\mu\)s (for O\(^{4+}\)(1s\(^2\)2s2p \(^3\)P\(_o\)) [32]), while the time of flight between the ion source and the photon–ion interaction region is at most 8 \(\mu\)s. Therefore, ions in these metastable states constituted part of the primary ion beam. Comparison of the theoretical cross sections with the measured (apparent) cross sections indicates a fractional content \(f_m\) of metastable \(^3\)P\(_o\) states in the parent ion beams with \(f_m = (0.50 \pm 0.10)\) while the fraction of ground state \(^1\)S\(_0\) ions is \(f_g = (1 - f_m)\). The individual numbers found in each experiment will be discussed in the appropriate subsections.

The energy spacings between the three individual fine-structure states within the \(^3\)P manifolds are very small as compared to the excitation energies. The splitting between the energetically lowest state, \(^3\)P\(_o\), and the highest, \(^3\)P\(_i\), is only 9.99 meV for C\(^{2+}\), 25.7 meV for N\(^{3+}\) and 54.9 meV for O\(^{4+}\). The ratio of energy splitting versus excitation energy is largest for the O\(^{4+}\) ions, where it amounts to not more than 0.0054. Statistical population of the fine structure states therefore appears to be a good assumption, i.e., \(1/9\) of \(f_m\) is in the \(^3\)P\(_0\) state, \(3/9\) are in the \(^3\)P\(_i\) state and \(5/9\) of \(f_m\) are in the \(^3\)P\(_f\) state. The present comparisons of theory and experiment fully support this assumption. In our previous work on photoionization of the B\(^+\) ion [15], the assumption of an overall population of metastable states was \(f_m = 0.29\) and all of that in the \(^3\)P\(_i\) state gave the best result for a fit of the experiment with theory using the metastable fractions as fit parameters. The present analysis casts some doubt on those fractions. Our first study on photoionization of Be-like ions was carried out with C\(^{2+}\) ions [16, 17]. The calculations performed in that work were similar in nature to the present theory, but were carried out with an energy mesh of 1.36 meV, compared to a mesh of 13.6 \(\mu\)eV for the present calculations. It was discovered that such a finer mesh for the theory was needed to properly characterize the narrower resonances in Be-like ions, as illustrated in subsection 4.1. Basically, the theoretical results with an energy step width of 13.6 \(\mu\)eV can be regarded as new results and the previously derived metastable fractions have to be revised on the basis of the present new findings.

### 4.1. Photoionization of C\(^{2+}\)

Figure 1 shows the results of the present Breit–Pauli R-matrix calculations for photoionization of C\(^{2+}\) ions in the four different (1s\(^2\)2s\(^2\)1S\(_0\)), (1s\(^2\)2s2p \(^3\)P\(_o\)), (1s\(^2\)2s2p \(^3\)P\(_i\)) and (1s\(^2\)2s2p \(^3\)P\(_f\)) states carried out at a step width of 13.6 \(\mu\)eV. The cross sections are on logarithmic scales. The first question to be addressed is whether the very fine small-width resonances that may have been missed in the previous 1.36 meV calculation [16, 17] add substantial resonance strength to the photoionization spectrum. It should be noted that the continuous part of the cross section describing the direct single-ionization process is not influenced by the step width of the calculations. Integrating the two sets of spectra, calculated at step widths 1.36 meV and 13.6 \(\mu\)eV, over the investigated energy range results in only a small difference. The integral over the (1s\(^2\)2s\(^2\)1S\(_0\)) photoionization spectrum in the energy range from threshold to the series limit of the (1s\(^2\)2p \(^3\)P\(_o\)) photoionization spectrum gives 11.987 Mb eV at 1.36 meV step width and 12.001 Mb eV at 13.6 \(\mu\)eV, i.e. the strengths contained in the two spectra are practically identical. The largest difference in strengths for the older and the present calculations is found for the (1s\(^2\)2s2p \(^3\)P\(_o\)) photoionization spectrum. Integrating from threshold to the series limit of the (1s\(^2\)2p \(^3\)P\(_o\)) photoionization spectrum gives 16.145 Mb eV at 1.36 meV step width and 16.724 Mb eV at 13.6 \(\mu\)eV, i.e. a difference of about 3.5%.

While the overall picture is not changed by calculations on a narrower energy grid, clear differences become obvious when zooming into the calculated spectra. An example is provided in figure 2 where the results of the two sets of calculations are shown in an energy range from 44.210 to 44.235 eV covering a span of only 15 meV. At the energies where the cross sections were calculated at 1.36 meV step width, the previous and the present results agree. Linear interpolation between the calculated points, however, chops off excursions of the cross-section function in narrow energy ranges. The present calculations show that some of the narrow resonances reach peak values of more than 10 000 Mb. Again, one has to ask whether these excursions make a significant difference in experimental measurements under realistic conditions. A good way to illustrate the relative strengths contained in resonance features is to convolute the data with a Gaussian function of a given width greater than the natural width of the broadest resonance in the spectrum as already discussed above. Such convolution can also be used to simulate an experiment with finite resolving power.

The lowest panel in figure 2 shows a simulated experimental result that would be obtained at infinite resolving...
Figure 2. Results of the R-matrix calculations from figure 1 in a narrow energy range where only the $3P^o$ states can contribute to photoionization. The present calculations with a 13.6 $\mu$eV spacing are represented by solid (red) dots connected by straight solid black lines. The previous calculations with 1.36 meV resolution [16] are shown by the open circles connected by straight dashed lines. The lowest panel simulates experiments with infinite resolving power using a primary $C^2+$ ion beam with a metastable fraction $f_m = 0.5$ and statistical population of the $3P^o$ fine structure components. The solid (red) line results from the present calculations while the dotted line represents the previous theoretical data. Note the logarithmic cross-section scale.

Figure 3. Simulated results of an experiment on photoionization of $C^2+$ ions with 3 meV resolution in a narrow energy range. The primary ion components are the same as those assumed for the lowest panel of figure 2. The dotted line results from the previous calculations [16] with 1.36 meV spacing; the solid (red) line results from the present theoretical data calculated at 13.6 $\mu$eV resolution.

The new calculations are shown in figure 4 along with the published experimental overview spectrum for photoionization of the $C^2+$ ion [16] measured at resolving power smaller than 2000. In the previous analysis, an experimental energy spread of 30 meV was inferred. In the present re-analysis on the basis of the new calculations the experimental energy spread was found to be slightly smaller, namely 28 meV. Thus, the new theoretical data for the $C^2+$ ion were convoluted with a 28 meV FWHM Gaussian to simulate the experimental energy resolution and are shown separately in the four upper panels of figure 4 for the different initial states relevant to the experiment. The lowest panel presents the measured data (solid line).

For quantitative comparison of the new calculations with the previous experimental data, figure 5 shows the photoionization cross section measured at 28 meV energy spread and a theoretical model spectrum obtained by assuming a metastable fraction $f_m = 0.5$ in the parent ion beam and statistical population of the $(1s^2 2s2p \, ^3P^o_0)$, $(1s^2 2s2p \, ^3P^o_1)$ and $(1s^2 2s2p \, ^3P^o_2)$ metastable states. Evidently, these assumptions lead to a very satisfying agreement between theory and experiment. Given the total systematic uncertainty of $\pm 20\%$ of the experimental cross sections, the metastable fraction $f_m$ has an uncertainty as well. In the previous work on photoionization of $C^2+$ [16], $f_m$ was assumed to be $f_m = 0.4$ with $3/4$ of that in the $^3P^o_0$ state and $1/8$ each in the $^3P^o_1$ and $^3P^o_2$ states. These numbers must be attributed to the previous R-matrix calculations on an insufficient 1.36 meV energy mesh and to the experiment with its limited energy resolution.

In the present study, new measurements were conducted with the goal to push the energy resolution to its practical limits. For that purpose, the energy range 44.035–44.265 eV was scrutinized, zooming in on the first two resonances seen in the overview spectrum in figure 5. These

\[ \text{Cross section (Mb)} \]

\[ \text{Photon energy (eV)} \]

\[ \text{Cross section (Mb)} \]

\[ \text{Photon energy (eV)} \]
Figure 5. Comparison of the experimental overview of C_{2+} photoionization [16] with a model spectrum obtained from the present Breit–Pauli R-matrix calculations. The theoretical spectrum was obtained by assuming a metastable fraction $f_m = 0.5$ in the parent ion beam and statistical population of the (1s$^2$ 2s2p $^3P_0$), (1s$^2$ 2s2p $^3P_1$) and (1s$^2$ 2s2p $^3P_2$) metastable states. The experimental cross section is displayed as a solid line with light gray shading. The theoretical model spectrum is represented by the dotted (red) curve. The series of vertical lines indicate the Rydberg sequences of different groups of resonances excited by the photons as the photon energy increases. The (coloured) numbers on the resonances mark the principal quantum numbers of the associated Rydberg series.

peaks are associated with 2s→np photoexcitations of the $^3P_o$ metastable levels of C_{2+} leading to states with configuration (1s$^2$ 2p5p). Calculations of transition energies and absorption oscillator strengths $g_f$ using the CATS code [39, 40] showed that the first peak is made up of contributions to $^3D_{1,2,3}$ states while the second peak is associated with the $^3P_{0,1,2}$ states. The detailed structure contained in the second resonance peak is already shown in figure 2. For the energy range selected in the high-resolution experiment of this study, the new calculations are shown in figure 6 for the $^3P_0$ initial states of the C_{2+} ion with total angular momenta $J = 0$, 1 and 2 (first three panels). The bottom panel shows the data for a high-resolution photoionization scan in that energy range. The peak structure near 44.075 eV is associated with excitations (2s2p $^3P_o$)→(2p5p $^3D$) while the peak at 44.21 eV is related to excitations (2s2p $^3P_0$)→(2p5p $^3P$). The solid (red) line is a fit to the data assuming the presence of only four contributing resonances in the experimental spectrum. This fit suggested an energy spread of 7 meV. Detailed comparison with the present theory results in an experimental energy resolution of 6.3 meV in this experiment. Note the logarithmic scale in the upper three panels.

Figure 6. Results of the present R-matrix calculations in the energy range 44.00–44.27 eV for the $^3P_0$ initial states of the C_{2+} ion with total angular momenta $J = 0$, 1 and 2 (first three panels). The bottom panel shows the data for a high-resolution photoionization scan in that energy range. The peak structure near 44.075 eV is associated with excitations (2s2p $^3P_o$)→(2p5p $^3D$) while the peak at 44.21 eV is related to excitations (2s2p $^3P_0$)→(2p5p $^3P$). The solid (red) line is a fit to the data assuming the presence of only four contributing resonances in the experimental spectrum. This fit suggested an energy spread of 7 meV. Detailed comparison with the present theory results in an experimental energy resolution of 6.3 meV in this experiment. Note the logarithmic scale in the upper three panels.

In order to find out which of the peak structures in figure 6 contribute significantly to the experimental observation, the theoretical data were convoluted with a 6.3 meV FWHM Gaussian. The results are shown in figure 7. The cross sections in the sequence of the upper three panels are for pure parent ion beams each consisting of ions in (1s$^2$ 2s2p $^1P_0$), (1s$^2$ 2s2p $^1P_1$) or (1s$^2$ 2s2p $^1P_2$) states, respectively. For direct comparison with the experimental data, a weighted sum of the individual contributions from the three metastable components of the parent ion beam has to be calculated. From the comparison shown in figure 4, one has to expect $f_m = 0.5$ for the total metastable fraction and statistical population, i.e., 1/9, 3/9 and 5/9 for the $J = 0$, 1 and 2 metastable components, respectively.

For the detailed comparison of the theoretically simulated cross section with the experiment, figure 8 shows simulated and measured photoionization cross sections of C_{2+} ions at an energy resolution of 6.3 meV in the energy range of figures 6.
and 7. The cross-section scale is logarithmic putting emphasis on the small contributions from direct photoionization and on the interference patterns of resonant and direct photoionization channels. The total fraction of metastable contributions was varied assuming $f_m = 0.5$ (solid line), $f_m = 0.6$ (dashed line) and $f_m = 0.4$ (dotted line). The energy scale of the theoretical results was subjected to a linear shift function correcting the energy at the low-energy side of the theoretical spectrum by $-2$ and $-12$ meV at the high-energy side. Error bars displayed are statistical only.

Although the resolving power of the new experimental scan measurement is already as high as 7000, it is not sufficient to really resolve individual contributions from the different $3^P_o$ fine structure states. Therefore, an effort was made to further reduce the experimental energy spread. Figure 10 shows a comparison of theory and a scan measurement at 3 meV resolution of the second peak from the last several figures. Now the resolving power is 14 700. For the theoretical simulation of the experiment, a total metastable fraction $f_m = 0.5$ was assumed in this case. The theoretical data were shifted in energy by $-11$ meV. The contributions of the individual fine structure states were calculated assuming statistical weights. In spite of the energy shift of the theoretical data, the simulated cross section and the measurement do not fully line up with one another. Beside the overall shift, there are additional small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states. In spite of the remaining small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states. In spite of the remaining small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states. In spite of the remaining small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states. In spite of the remaining small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states. In spite of the remaining small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states. In spite of the remaining small discrepancies, it is seen that the experiment at this level of resolving power starts to separate the individual $3^P_o$ fine structure states.
the calculated data, it is possible to get an impression of the individual contributions of specified excitation channels to the observed photoionization cross sections. The photoionization resonance strengths for excitations from the initial states \( i \) to the final states \( f \)

\[
\sigma_{i,f} = \int_{-\infty}^{\infty} \sigma_{i,f}(E) \, dE, \tag{3}
\]

with the photoionization cross section \( \sigma_{i,f}(E) \) can be calculated as the product of the oscillator strength for absorption \( gf \) and the branching ratio for autoionization, i.e.,

\[
\sigma_{i,f} = 4\pi^2 \alpha a_0^2 \mathcal{R} \frac{gf}{g_i} \omega_i, \tag{4}
\]

with the fine structure constant \( \alpha \), the Bohr radius \( a_0 \), the Rydberg constant \( \mathcal{R} \) and the statistical weight \( g_i \) of the initial state \( (4\pi^2 \alpha a_0^2 \mathcal{R} \approx 109.76 \text{ Mb eV}) \). The branching ratio \( \omega_i \) can be assumed to be unity. Not regarding the effects of finite natural line widths and neglecting the influence of interference between resonant and direct photoionization, the oscillator strengths found for individual transitions are directly related to the individual contributions of these transitions to the experimental cross sections. To be more precise, the oscillator strengths allow one to obtain resonance strengths by employing equation (4) and by using the appropriate weight factors for the initial states.

For the initial (2s2p) configuration, there are three metastable \( ^3\text{P}^0 \) fine structure states with total angular momentum quantum numbers \( J = 0, 1, 2 \) and a short-lived \( ^1\text{P} \) component which is not present in the parent ion beam. For the (2p5p) final configuration, there are ten different states. Oscillator strengths \( gf \) for the 14 dominant specified transitions from the initial \( ^3\text{P}^0 \) states to the \( (2p5p) \) configuration were calculated. One obtains three groups of resonances clearly separated in energy. Comparison with the experiment shows that the (online-version) CATS calculations [39, 40] predict resonance energies that are roughly 0.3 eV too high. The energy shifts are even different for the three different groups of resonances. The results are illustrated in table 1 where the experimental resonance energies of the four peaks fit (see figure 6) to the experimental data taken at 6.3 meV resolution are compared with the shifted energies of the associated transitions. The oscillator strengths \( gf \) are provided for the 14 dominant photoexcitation channels. The agreement of these calculations with the measured cross sections is remarkably good. This provides confidence in the designation of the peaks seen in figure 9. Apparently, the two dominant peak features are associated with \( ^3\text{D} \) excited states for the low-energy group and \( ^3\text{P} \) states for the high-energy group of resonances. In between there is oscillator strength from excitations resulting in the population of the \( ^3\text{S}_1 \) state. The broad feature seen in the experiment between the \( ^3\text{D} \) and \( ^3\text{P} \) peaks (see figure 8) does contain some considerable resonance strength (proportional to \( gf \), see equation (4)) which is distributed over a relatively wide energy range. Apparently, the natural width of the \( ^3\text{S}_1 \) state is much larger than the widths of the excited \( ^3\text{D} \) and \( ^3\text{P} \) states.

4.2. Photoionization of \( \text{N}^+ \)

Figure 11 shows the results of the present Breit–Pauli R-matrix calculations for photoionization of \( \text{N}^+ \) ions in the

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**Table 1. Assignments of the resonance features in the photoionization of \( \text{C}^{2+} \) ions displayed in figure 9 inferred from results of a calculation employing the CATS code [39, 40]. Note that the three groups of transitions had to be shifted by different amounts of energy to match the experiment. The ratios of oscillator strengths \( gf \) are a measure of the individual contributions (see equation (4)) by the indicated transitions.**

| Peak no. | Energy (exp., eV) | Transition (2s2p \( \rightarrow \) 2p5p) | Energy (CATS, eV) | \( gf \) (CATS) |
|----------|------------------|----------------------------------------|-------------------|----------------|
| 1        | 44.074           | \( 3\text{P}^0 \rightarrow 3\text{D}_2 \) | 44.068\(^a\)     | 0.00784       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{D}_1 \) | 44.070\(^c\)     | 0.00798       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{D}_3 \) | 44.074\(^c\)     | 0.04701       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{D}_1 \) | 44.074\(^c\)     | 0.01140       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{D}_2 \) | 44.074\(^c\)     | 0.02573       |
| 2        | 44.170           | \( 3\text{P}^2 \rightarrow 3\text{S}_1 \) | 44.169\(^b\)     | 0.01042       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{S}_1 \) | 44.176\(^b\)     | 0.00722       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{S}_0 \) | 44.180\(^b\)     | 0.00251       |
| 3        | 44.208           | \( 3\text{P}^2 \rightarrow 3\text{P}_1 \) | 44.206\(^a\)     | 0.00926       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{P}_0 \) | 44.209\(^b\)     | 0.00674       |
|          |                  | \( 3\text{P}^2 \rightarrow 3\text{P}_2 \) | 44.209\(^a\)     | 0.02583       |
| 4        | 44.215           | \( 3\text{P}^0 \rightarrow 3\text{P}_1 \) | 44.213\(^b\)     | 0.00478       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{P}_0 \) | 44.216\(^b\)     | 0.00619       |
|          |                  | \( 3\text{P}^0 \rightarrow 3\text{P}_1 \) | 44.216\(^b\)     | 0.00876       |

\(^a\) Shifted by \(-0.277\) eV.  
\(^b\) Shifted by \(-0.240\) eV.  
\(^c\) Shifted by \(-0.322\) eV.
Figure 11. Results of the present Breit–Pauli R-matrix calculations for photoionization of N\(^{3+}\) ions in the four different initial states: (1s\(^2\)2s2p 3P\(_o^0\)) (top panel), (1s\(^2\)2s2p 3P\(_o^1\)) (second panel from top), (1s\(^2\)2s2p 3P\(_o^2\)) (third panel from top) and (1s\(^2\)2s\(^2\)1 S\(_o^0\)) (bottom panel). Note the logarithmic scale in each panel.

Figure 12. The theoretical data from figure 11 convoluted with a 40 meV FWHM Gaussian and the experimental spectrum (lowest panel) measured for photoionization of N\(^{3+}\) ions. Note the linear scale in all five panels.

Figure 13. Comparison of the experimental overview of N\(^{3+}\) photoionization with a model spectrum obtained from the present Breit–Pauli R-matrix calculations. The theoretical spectrum was obtained by assuming a metastable fraction \(f_m = 0.5\) in the parent ion beam and statistical population of the (1s\(^2\)2s2p 3P\(_o^0\)), (1s\(^2\)2s2p 3P\(_o^1\)) and (1s\(^2\)2s2p 3P\(_o^2\)) metastable states. The experimental cross section is displayed as a solid line with light gray shading. The theoretical model spectrum is represented by the dotted (red) curve. The series of vertical lines indicate the Rydberg sequences of different groups of resonances excited by the photons as the photon energy increases. The (coloured) numbers on the resonances mark the principal quantum numbers of the associated Rydberg series.

Figure 13 provides a comparison of the 40 meV resolution experimental overview of photoionization of N\(^{3+}\) ions with a model spectrum obtained from the present Breit–Pauli R-matrix calculations. The theoretical spectrum was obtained by assuming a metastable fraction \(f_m = 0.5\) in the parent ion beam and statistical population of the (1s\(^2\)2s2p 3P\(_o^0\)), (1s\(^2\)2s2p 3P\(_o^1\)) and (1s\(^2\)2s2p 3P\(_o^2\)) metastable states. Theory and experiment are in very satisfactory agreement. At energies between approximately 84 and 86 eV, the measured cross sections are slightly below the theoretical data. This is assumed to be an artifact of the experimental data taking procedure. For obtaining the spectrum displayed in figure 13, the total energy range of interest was divided up into about 20 individual overlapping scan ranges for each of which constant beam overlap form factors and constant photon energy spreads were assumed. Entrance and exit slits of the monochromator were only set for a given resolution at the centre energy of each scan. They were not individually adjusted to each individual energy step. The total experimental spectrum was assembled by adjusting the relative measurements of adjacent scan ranges to the mutual overlap regions and thus combining the pieces step by step. This procedure may result in small excursions of the cross section over extended energy ranges.

The final states that can be reached by photo single excitation of the (2s2p 3P\(_o\)) metastable states via electric dipole transitions are members of the (2p\(^n\)3S, 3P, 3D) Rydberg series. The associated series limits are the (2p\(^n\)3P\(_o^1\), 2p\(^n\)3P\(_o^2\)) states of the Li-like product ion. For each of these two states, Rydberg series with their resonance energies can be constructed using quantum defects. From a fit to our experimental data, we find that the dominating series have quantum defects 0.110 and 0.165. The resonance energies can
be described approximately by $E^{(1)}_n = 79.0998 \text{ eV} - 4^2 \times 13.6057 \text{ eV}/(n - 0.11)^2$ and $E^{(2)}_n = 79.1318 \text{ eV} - 4^2 \times 13.6057 \text{ eV}/(n - 0.165)^2$, respectively. The associated energies are shown by the vertical (coloured) bars above the data, the principal quantum numbers $n$ are provided to characterize the observed resonance features associated with the initial metastable $3P^o$ states.

From the $1S$ ground state, autoionizing resonant states can only be reached by two-electron excitations in this photon energy range. The final states that can be reached from the $(2s^2 1S)$ ground state are $(2p 2P^o)$ and $(2p 2D^o)$ states. Again, two series of Rydberg states are involved converging towards the series limits $(2p 2P^o_{1/2/3/2})$, shifted approximately by 8.35 eV (the average excitation energy of the $3P^o$ metastable states) with respect to the identical $(2p 2P^o_{1/2/3/2})$ states when reached from the $3P^o$ metastable initial states. The two associated resonance energies of the dominating series can be described approximately by $E^{(1)}_n = 87.4495 \text{ eV} - 4^2 \times 13.6057 \text{ eV}/(n - 0.239)^2$ for the $2P_{1/2}$ series limit and $E^{(2)}_n = 87.4816 \text{ eV} - 4^2 \times 13.6057 \text{ eV}/(n + 0.03)^2$ for the $2P_{3/2}$ series limit. The associated energies are shown by vertical (coloured) bars above the data, and the principal quantum numbers $n$ are provided to characterize the observed resonance features associated with the initial $1S$ ground state. The $(2p 1S)$ states form window resonances in the photoionization spectrum. The $(2p 1P)$ states form strong resonances in the photoionization spectrum. They interfere with direct photoionization of the $(2s^2 1S)$ ground state, giving rise to strongly asymmetric Fano–Beutler peak features.

Figure 14 shows a threshold scan for photoionization of $N^+$. The relative scan cross sections are normalized to the absolute measurements of Bizau et al [29] and are represented by open circles with gray shading. Only statistical error bars are shown. The step function (solid black line) was constructed by using the ionization thresholds [47] of the individual $1P^o$ fine structure states and distributing the height of the threshold step (0.65 Mb) over contributions of the fine structure states assuming statistical population. The dotted (red) line is a fit to the experiment using the known ionization thresholds from reference [47] and fitting the individual step heights as well as the experimental energy spread to the measured spectrum. The dashed (blue) line is a convolution of the theoretical result with a 9.3 meV FWHM Gaussian. For the theoretical simulation, a metastable fraction $f_m = 0.54$ and statistical population of the fine structure states was assumed.

Figure 15 shows results of the present R-matrix calculations in the energy range 69.7–70.1 eV for the $3P^o$ initial states of the $N^+$ ion with total angular momenta $J = 0$, 1 and 2 (see the first three panels). The theoretical data are to be compared with the experimental cross section from the overview spectrum displayed in figure 13 at 40 meV resolution. The bottom panel presents a high-resolution photoionization scan in that energy range. The solid (red) line is a fit to the data assuming the presence of seven contributing resonances in the experimental spectrum. This fit suggested an energy spread of about 4 meV. Detailed comparison with the present theory reveals an experimental energy resolution of 3.3 meV in this experiment. Note the logarithmic scale in the upper three panels.
shown here in the fourth panel and the data from a high-resolution photoionization scan in that energy range displayed in the bottom panel. The solid (red) line is a fit to the data assuming the presence of seven contributing resonances in the experimental spectrum. This fit suggested an energy spread of about 4 meV. Detailed comparison with the present theory reveals an experimental energy resolution of 3.3 meV in this experiment. Note the logarithmic scale in the upper three panels.

For the detailed direct comparison with experiment, the theoretical contributions have to be convoluted with 3.3 meV FWHM Gaussians simulating the energy spread in the measurement. The results of such convolution are provided in figure 16 and compared with the experiment (bottom panel). The next step is the modelling of the experiment by calculating the observed apparent cross section as a weighted sum of individual contributions from the different parent ion beam components. As in the analysis of the threshold energy scan (figure 14), the metastable fraction $f_m = 0.54$ was assumed. The weights are 1/9 for the (1s$^2$2s2p $^3$P$^o_0$) contribution, 3/9 for the (1s$^2$2s2p $^3$P$^o_1$) contribution and 5/9 for the (1s$^2$2s2p $^3$P$^o_2$) as in all other cases shown in this paper. In figure 17, the experimental data are compared to the theoretical model spectrum obtained by this procedure. In order to provide optimum conditions for detailed comparison, the energy scale of the theoretical results was shifted by −5 meV for the whole lower energy group at around 69.8 eV and by −12 meV for the whole higher energy group at around 70 eV. The figure distinguishes between the contributions of individual initial metastable components. Seven distinct peak features can be seen. This is due to the resolving power of about 21 200 in this particular experiment. For all the other ions, a correspondingly low energy spread could not be achieved. It is worthwhile, therefore, to take an especially detailed look at the features observed here. For supporting the present analysis, calculations of excitation energies and oscillator strengths relevant to the present region of interest were carried out using the CATS code [39, 40]. As in the case of C$^{2+}$, the photoexcitation transitions from the initial metastable (2s2p $^1$P$^o$) levels to the excited states with a (2p5p) configuration were calculated. Oscillator strengths $gf$ for the 14 dominant transitions were obtained. Again three groups of resonances are clearly separated from one another.

The relative strengths within each of the three resonance groups match the experiment extremely well, given the simplicity of the approach. In contrast to that, the relative strengths of the three different resonance groups with respect to one another do not agree equally well with the measured data. Also, the resonance energies are above the experimental values by about 0.3 eV and discrepancies differ from one resonance group to the other. Since the experiment does not provide much evidence for the presence of (2p5p $^1$S) excited states and the possible resonance strengths of such contributions cannot be experimentally assessed, the $^1$S channels are not included in table 2. Considering the extremely high resolution of the N$^{3+}$ experiment at 3.3 meV energy spread, the CATS calculations are in remarkably good accord with the experiment, providing high confidence in the designation of the peaks numbered in figure 17.

Simon et al [4] have observed the resonance group shown in figure 17 at a resolving power of approximately 2000. With an energy spread of 35 meV, they could not resolve any of the fine details revealed by the present study with an energy spread as small as 3.3 meV. Their $^3$D and $^3$P peak assignments for...
Figure 18. Results of the present Breit–Pauli R-matrix calculations for photoionization of O\(^{4+}\) ions in the four different initial states \((1s^22s2p\ ^3P^o)\) (top panel), \((1s^22s2p\ ^1P^o)\) (second panel from top), \((1s^22p^2\ ^3P^o)\) (third panel from top) and \((1s^22s^2\ ^1S^o)\) (fourth panel from top) together with an overview experiment (bottom panel) by Bizau et al [29]. The experimental data are shown as open circles with statistical error bars. The solid (red) line in the bottom panel is a simulation of the experiment on the basis of the present calculations assuming an energy spread of 436 meV, a metastable fraction \(f_m = 0.5\) and statistical population of the \(^1P^o\) fine structure states. Note the logarithmic scale in the upper four panels.

Table 2. Assignments of the resonance features in N\(^{3+}\) ions displayed in figure 17 inferred from calculations employing the CATS code [39, 40]. The ratios of oscillator strengths \(g/f\) indicate the relative individual contributions of the specified transitions. Note the energy shifts of the theoretical data required to match the experiment.

| Peak no | Energy (exp., eV) | Transition (2s2p \(\rightarrow\) 2p5p) | Energy (CATS, eV) | \(g/f\) (CATS) |
|---------|------------------|-----------------------------------|------------------|----------------|
| 1       | 69.804           | \(^3P^o \rightarrow ^1D^o\)        | 69.808           | 0.009          |
| 2       | 69.813           | \(^3P^o \rightarrow ^3D^o\)        | 69.813           | 0.008          |
| 3       | 69.822           | \(^3P^o \rightarrow ^3D^o\)        | 69.821           | 0.057          |
|         | \(^3P^o \rightarrow ^3D^o\) | 69.821           | 0.014          |
| 4       | 69.986           | \(^1P^o \rightarrow ^2P^o\)        | 69.984           | 0.012          |
| 5       | 69.995           | \(^3P^o \rightarrow ^2P^o\)        | 69.996           | 0.032          |
| 6       | 70.004           | \(^3P^o \rightarrow ^2P^o\)        | 70.004           | 0.005          |
| 7       | 70.012           | \(^3P^o \rightarrow ^2P^o\)        | 70.012           | 0.006          |

\(^a\) Shifted by \(-0.286\) eV.

\(^b\) Shifted by \(-0.330\) eV.

the two resonance features observed agree with the present; however, the total angular momentum associated with the two peaks is not just \(J = 1\) as assumed by Simon et al but results from various combinations of \(^3P^o_{2J^o} \rightarrow ^3D^o_{J^o}\) and \(^3P^o_{2J^o} \rightarrow ^3P^o_{J^o}\) photoexcitations with \(J = 0, 1, 2, J' = 1, 2, 3\) and \(J'' = 0, 1, 2\), respectively, as the present investigation demonstrates.

4.3. Photoionization of O\(^{4+}\)

Figure 18 shows the results of the present Breit–Pauli R-matrix calculations for photoionization of O\(^{4+}\) ions in the four different \((1s^22s2p\ ^3P^o, 1s^22s2p\ ^1P^o)\) and \((1s^22p^2\ ^3P^o)\) initial states contributing to the experimental cross section. The theoretical features can be recognized in the experimental data displayed in the bottom panel of the figure. These data are from the measurements by Bizau et al [29] carried out at the Aarhus photon–ion merged-beam facility [28]. The energy spread of this experiment was strongly underestimated to be about 250 meV. Comparison of the present theoretical results with the Aarhus experiment indicates an energy spread of 436 meV. Apart from that the agreement of the present calculations and the absolute measurement by Bizau et al [29] is excellent. An overall scaling factor of 1.13 applied to the present theory, i.e. a 13\% difference, would further improve the agreement. Discrepancies of this size are within the error bars of ±15\% estimated by Bizau et al for their experiment.

To elucidate the strengths of the individual O\(^{4+}\) photoionization contributions from the many resonances calculated within the present Breit–Pauli R-matrix approach for the initial \(^1S^o\) and \(^3P^o\) states, figure 19 shows the theoretical data from the first four panels of figure 18, this time convoluted with a 50 meV FWHM Gaussian. As in the previous examples, the convolution greatly simplifies the photoionization spectra and clearly demonstrates where the dominant resonance strengths are located. The bottom panel simulates an experiment at 50 meV resolution. The spectrum was obtained by assuming a metastable fraction \(f_m = 0.5\) in the parent ion beam and statistical population of the \((1s^22s2p\ ^3P^o, 1s^22s2p\ ^1P^o)\) and \((1s^22p^2\ ^3P^o)\) metastable states.

The present experimental study was focused on the first 2.5 eV energy range covering the photoionization threshold of O\(^{4+}\) and the first group of resonances associated with
Figure 20. Threshold scan for photoionization of O$^{4+}$ ions. The relative cross sections were obtained by a high-resolution relative scan measurement and normalized to the absolute measurements of Bizau et al [29]. The experimental data are represented by open circles with gray shading. Only statistical error bars are shown. The step function (solid black line) was constructed by using the ionization thresholds [47] of the individual 3P$^o$ fine structure states and distributing the height of the threshold step (0.39 Mb) over contributions of the fine structure states assuming statistical population. The dotted (red) line is from a convolution of the theoretical result with a 21 meV FWHM Gaussian. For the theoretical simulation, a metastable fraction $f_m = 0.5$ and statistical population of the fine structure states was assumed. Finally, the theoretical cross sections have been scaled up by a factor 1.13.

As in the cases of the ions C$^{2+}$ and N$^{3+}$, the region of the first two groups of photoionization resonances were experimentally investigated for O$^{4+}$ at the highest possible resolution that could be achieved under the constraints of the measurements. The resulting normalized high-resolution data are shown in figure 20. The step function (solid black line) was constructed by using the ionization thresholds [47] of the individual 3P$^o$ fine structure states and distributing the height of the threshold step (0.39 Mb) over contributions of the fine structure states assuming statistical population. The dotted (red) line is from a convolution of the theoretical result with a 21 meV FWHM Gaussian which provides excellent agreement with the experiment. For the theoretical simulation, a metastable fraction $f_m = 0.5$ and statistical population of the fine structure states was assumed. Finally, the theoretical cross sections have been scaled up by a factor 1.13 as already discussed in the context of figure 18.

Figure 21. Results of the present R-matrix calculations in the energy range 105.7–106.1 eV for the $^3P^o$ initial states of the O$^{4+}$ ion with total angular momenta $J = 0, J = 1$ and $J = 2$ (first three panels from top). The bottom panel displays the data (open circles with statistical error bars) for a high-resolution photoionization scan in that energy range. The solid (red) line is a fit to the data assuming the presence of six contributing resonances in the experimental spectrum. This fit suggested an energy spread of about 11.4 meV. Detailed comparison with the present theory reveals an experimental energy resolution of 11.0 meV in this experiment. Note the logarithmic scale in the upper three panels.

Figure 22. Simulated results of experiments on photoionization of individual O$^{4+}(2s2p\,^3P^o)$ ions with 11 meV resolution in the energy range of figure 21. The cross sections in all four panels are on a linear scale. The bottom panel shows the same experimental data as in figure 21, this time as a solid line.
as formed in the present energy
in figure 21. Peak assignments are provided in table 3. Autoionizing
numbers refer to the six peaks assumed in the fit to the data as shown
theoretical simulation. The 5/9 contribution of the 3P
range.

On top of that is the 3/9 3P
state is shown by the dashed line (hatched area with red shading).

The total metastable fraction in the beam was set to
displayed as open (yellow) shaded circles with statistical error bars. The
energy scale of the theoretical
and (1s22s21S0) ground state
containing not only ions in their (1s22s21 S0) ground state
by scanning the photon energy and observing the ionization
by Bizau et al [16] and by Bizau et al [29]. For several prominent
features in the photoionization spectra, the experimental
energy resolution was pushed to the limit of feasibility in order to
scrutinize the details of individual transitions between initial

| Peak Energy Transition Energy | Energy (CATS, eV) | gf |
|-----------------------------|-------------------|---------|
| 1 105.782 3P1 −→ 3P1 | 105.776e | 0.003 21 |
| 2 105.820 3P2 −→ 3P3 | 105.813e | 0.001 88 |
| 3 105.829 3P0 −→ 3P1 | 105.831e | 0.008 19 |
| 4 105.905 3P1 −→ 3P1 | 105.921e | 0.010 62 |
| 5 105.929 3P2 −→ 3P3 | 105.930e | 0.004 92 |
| 6 105.967 3P0 −→ 3P1 | 105.957e | 0.001 94 |

α Shifted by −0.311 eV.
β Shifted by −0.330 eV.

As part of the present analysis, calculations of excitation
energies and oscillator strengths relevant to the present region of interest were carried out using the CATS code [39, 40]. From the calculated data shown in table 3, one can infer that transitions from metastable initial states (2s2p 1P1) to (2p6p 1D, 1P) excited states are mainly responsible for the features observed in the present energy region of interest. Again the lower-energy structures are mainly due to (2p6p 3D) excited states but now also 1P1 resonances are calculated to contribute in this energy range with non-negligible strengths. The higher energy features originate from (2p6p 3P) excited states. The 3S levels present in the calculated cross sections are not obvious in the experiment, probably because of the large widths and reduced resonance strengths of these states. Therefore, the three calculated 3S contributions are omitted from table 3. Assignments of the resonance features in O4+ ions displayed in figure 23 are inferred from the CATS calculations presented in table 3. The ratios of oscillator strengths g/f indicate the relative individual contributions of the specified transitions. Note the shifts of the theoretical data required to match the experiment.

5. Conclusion

In this study, photoionization experiments on four-electron Be-
like C5+, N5+ and O4+ ions were carried out with ion beams containing not only ions in their (1s22s2 1S0) ground state but also in the metastable (1s22s2p 3P0), (1s22s2p 3P1) and (1s22s2p 3P2) states. Relative cross sections were obtained by scanning the photon energy and observing the ionization signal, the ion beam current and the photon flux. The relative data were normalized to published absolute measurements by Müller et al [16] and by Bizau et al [29]. For several prominent features in the photoionization spectra, the experimental energy resolution was pushed to the limit of feasibility in order to scrutinize the details of individual transitions between initial
and final states and their contributions to the photoionization cross sections. Resolving powers of up to 21 200 were accomplished. The measurements were accompanied by state-of-the-art Breit–Pauli R-matrix calculations showing extremely good agreement with even the finest details revealed in the high-resolution experiments. Supporting calculations employing the online version of the CATS Los Alamos National Laboratory Atomic Physics Codes package \[39, 40\] facilitated assignments of observed structures and resonances supported in part by the US National Science Foundation. Oakland, CA, USA, and on the Tera-grid at the National Institute for Astrophysics. The computational work was carried out through a grant to ITAMP at the Harvard-Smithsonian Center for Astrophysics, under project number Mu 1068/1 and through NATO Scientifisch under project number Mu 1068/10 and through NATO Collaborative Linkage grant 976362 as well as by the US Department of Energy (DOE) under contract DE-AC03-76SF-00098 and grant DE-FG02-03ER15424. B M McLaughlin acknowledges support by the US National Science Foundation through a grant to ITAMP at the Harvard-Smithsonian Center for Astrophysics. The computational work was carried out at the National Energy Research Scientific Computing Center in Oakland, CA, USA, and on the Tera-grid at the National Institute for Computational Science (NICS) in TN, USA, which is supported in part by the US National Science Foundation.

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