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Absolute measurements of chlorine Cl^+ cation single photoionization cross section

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ABSTRACT

The photoionization of Cl^+ leading to Cl^{2+} was measured in the photon energy range of 19.5–28.0 eV. A spectrum with a photon energy resolution of 15 meV normalized to absolute cross-section measurements is presented. The measurements were carried out by merging a Cl^+ ion beam with a photon beam of highly monochromatic synchrotron radiation at the Advanced Light Source at Lawrence Berkeley National Laboratory. The measured photoionization of Cl^+ consists of several autoionization resonances superimposed on the direct photoionization signal. Most of the prominent resonances are assigned to members of Rydberg series originating from the singlet ground state and from metastable triplet levels within the ground-state configuration of Cl^+ . The direct ionization cross section is no larger than 12 Mb.

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1. Introduction

The photoionization of atoms and ions is a process of great interest in fundamental science and in many applications. Absolute cross-section measurements with high-energy-resolution provide an additional source of information for oscillator strengths and line positions, and offer an opportunity to test state-of-the-art calculations. The Cl^+ cation, with two electrons missing from the

outermost 3p subshell, has a sulfur-like electronic structure and is an excellent test case to complement the understanding of the behavior of open-shell systems. Moreover, this data is of chief importance to benchmark the calculations from the Opacity [1,2] and Iron [3,4] projects. The principal objective of these projects is to expand our understanding of astrophysical observations [5]. However, most of the data currently available on photoionization (PI) for neutrals and ions is obtained from theoretical calculations [6].

To our knowledge, measurements of Cl^+ photoionization cross sections are not available and high-resolution spectroscopic data on chlorine ions is scarce. This paucity of data may be due in part to the difficulty in producing

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intense chlorine ion beams. A recent experimental effort provided lifetimes and oscillator strengths for specific transitions observed with the Far Ultraviolet Spectroscopic Explorer (FUSE) [7] using the beam foil technique by colliding Cl^+ ions on carbon thin foils at energies on the order of 200 keV. Good agreement with the LS coupling scheme for the particular transitions studied was found. In addition, a multiconfiguration Hartree–Fock approach [8] showed strong correlation between Rydberg series and perturber states for the case of single-ionized chlorine.

There exists high-resolution data on the isoelectronic series of atomic chlorine-like ions such as Ca^{3+} [9] and Ar^+ [10]. For the case of atomic chlorine, the available data is reported by Rušćić and Berkowitz [11] and by Jimenez-Mier et al. [12] who studied the PI of atomic chlorine with synchrotron radiation in combination with a rf discharge. In astrophysics, element abundances are often derived from spectroscopic data that are measured with unique satellite-mounted spectrometers. Therefore, earth-based theoretical and experimental confirmation of spectroscopic properties is critical. For instance, Cl^+ and Cl^{2+} ions were detected in the Jupiter-Io plasma torus using the FUSE space spectrograph [13,14] and also by the Galileo probe [15]. Schneider et al. [15] noted that the only feature of their spectra was a $^2\text{D}-^2\text{D}^0$ transition of S^{3+} that was not clearly identified in spectroscopic databases [13]. Another example is the CORONAS-F spacecraft that recently detected high charge states of chlorine in coronal solar flares [16].

Chlorine is thought to exist in trace abundances in the interstellar medium, but Cl is highly reactive and readily forms molecules with H_2 . Hence, observed Cl molecular abundances appear to be comparable to those of CH and H_2O [17] and show correspondence with H_2 abundances and total hydrogen column densities [18]. Furthermore, the apparently large abundance of chlorine remains an unresolved question which emphasizes the need for measured absolute photoionization cross sections and high-resolution spectroscopic data needed to accurately model astrophysical environments.

In this paper, we study the ionization of a charge-to-mass analyzed ion beam interacting with a monochromatic VUV photon beam providing detailed, energy dependent single photoionization spectra for Cl^+ .

2. Experiment

The experiment was performed using the Ion–Photon Beam end-station on undulator beamline 10.0.1.2. of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The method is based on the merged-beams technique [19] and has been described in detail in previous measurements of photoionization cross sections for Se^+ [20] and Ne^+ [21]. A general description of the experiment with details related to the present measurement will be given here.

The fundamental idea of this technique consists in merging two beams, a photon beam and a parent ion beam travelling in opposite directions over a common collinear path of tens of centimeters. As a result of their interaction, ions from the parent ion beam may be further

ionized into product ions of higher charge state than those of the parent ion beam. The resulting ions are separated from the parent ion beam and counted while all relevant parameters of both beams and their overlap are measured.

The Cl^+ ion beam was generated with an all-permanent-magnet electron cyclotron resonance (ECR) ion source. This ion source is equipped with an insertion oven in which a small amount of ferric chloride (FeCl_3) was evaporated. The evaporated compound was ionized inside the ion source chamber by repeated collisions with electrons excited into cyclotron motion by a 10 GHz RF signal. Ions extracted from the ion source were accelerated to an energy of 6 keV. A 60° sector magnet was used to accurately mass-to-charge select the Cl^+ ions. A cylindrical einzel lens located before the sector magnet focused the ion beam in the center of a mesh cylinder that hereafter will be called the *interaction region*. The typical Cl^+ ion beam intensity was 200 nA.

The ion beam was directed toward a set of 90° electrostatic spherical-sector bending plates that merged the ion beam with the counter-propagating photon beam over the length of the interaction region. The overlap between the ion and photon beams is measured at the entrance, center and exit of the interaction region with mechanically controlled, two-dimensional slit scanners.

Light was generated with a 10-cm period undulator positioned in the 0.5 A, constant current, 1.9 GeV synchrotron storage ring of the ALS. This produced a highly collimated photon beam of spatial width less than 1 mm and divergence less than 0.05° , which was then filtered using a grazing-incidence spherical-grating monochromator. The photon energy was scanned by rotating the grating and translating the exit slit of the monochromator while simultaneously adjusting the undulator gap to maximize the photon beam intensity.

The photon flux was measured with a maximum uncertainty of 5% by a silicon photodiode that was calibrated in situ with the method described by Esteves et al. [20]. The analog output from a precision current meter was fed to a voltage-to-frequency converter, providing a normalization signal to the beamline data acquisition system. The photon beam was mechanically pulsed using a chopper wheel attached to a controlled stepper-motor to separate the photoionization product ions from those produced in collisions with the residual gas in the ultra-high vacuum system.

The photon energy was calibrated with a side-branch gas cell using photon ionization energies of He [22] and Kr [23] in an energy range from 21.218 eV to 63.355 eV. With this energy calibration, a conservative maximum photon energy uncertainty of ± 10 meV was estimated.

To differentiate the ions that are formed inside the interaction region from those produced along the rest of the ion beam trajectory, a voltage was applied to the interaction region to energy tag the Cl^{2+} ions produced therein. A 45° dipole analyzing magnet demerged the beams and separated the Cl^{2+} product ions from the parent Cl^+ beam, which was then collected in an extended Faraday cup. The magnetic field was set such that the Cl^{2+} product ions generated in the interaction region passed through an aperture located in the back of the Faraday cup.

A spherical 90° electrostatic deflector directed them onto a biased stainless steel plate from which secondary electrons were accelerated and detected by a channeltron electron multiplier.

At the photon energies given in Table 1, absolute measurements of the Cl^+ single photoionization cross section σ were determined from

$$\sigma = \frac{Rq e^2 v_i \epsilon}{I^+ I' \int F(z) dz} \quad (1)$$

where R is the photoion count rate, q is the charge state of the parent ion (in this case $q=1$), $e = 1.6 \times 10^{-19}$ C, v_i is the ion beam velocity in cm s^{-1} , ϵ is the responsivity of the photodiode (electrons per photon), I^+ is the ion beam current (A), I' is the photodiode current (A) and z is assigned to the propagation direction of the ion beam.

The integral $\int F(z) dz$ is the form factor $F(z)$ integrated over the interaction region length. $F(z)$ is sampled in the center, in the entrance and in the output of the interaction region. These three values of $F(z)$ are determined from

$$F(z) = \frac{\int \int I^+(x, y) I'(x, y) dx dy}{\int \int I^+(x, y) dx dy \int \int I'(x, y) dx dy} \quad (2)$$

where $I^+(x, y)$ and $I'(x, y)$ are respectively the ion and photon beam profiles that define the spatial overlap of the photon and ion beams along the common interaction region path. To obtain the integral of Eq. (1), $F(z)$ is interpolated within the interaction region length and

Table 1
Absolute cross section measurements for the photoionization of Cl^+ .

E (eV)	σ (Mb)	Total error (Mb)
20.61	0.26	0.1
21.92	0.23	0.1
23.02	0.33	0.3
24.35	88.60	18.2
24.49	8.03	2.0
26.03	9.48	2.2
26.24	18.10	3.8

integrated over z . Additional information on this integral is given in Ref. [21].

The main sources of systematic uncertainty in the absolute cross section measurements originate from the beams overlap integral, the beams profile measurements and the photodiode responsivity. Other contributions to the total systematic uncertainty are listed in Covington et al. [21] and account for a total error budget of 20%.

3. Results

The absolute photoionization cross section of Cl^+ measured with a resolution of 15 meV is shown in Fig. 1. This spectrum can be compared with an optical absorption spectrum for which final states correspond to those that lead to the single ionization of the Cl^+ cation. Then, the spectrum consists of the Cl^{2+} ion yield as a function of the photon beam (γ) energy for the process:

The spectrum shown in Fig. 1 was measured in energy scans of 1 eV intervals at a spectral resolution of 15 meV. All the individual scans of spectrum were combined after normalization. Each individual spectrum was overlapped by 0.5 eV. This method reduced effects of a slight mechanical backlash from the monochromator. The process of joining the spectra was conducted by grouping individual pieces of spectra when variations among them were very small so that their normalization factor was close to one. This procedure generated two spectra that were later merged with an average factor to avoid, as much as possible, the creation of artifacts. We estimate that the overall photon energy error caused by this procedure was not greater than ± 8 meV. Hence, taking into account the ± 10 meV uncertainty from the gas cell energy calibration, we quote a total photon energy uncertainty for this particular spectrum of ± 13 meV.

The resulting spectrum of Fig. 1 was the result of the normalization to the absolute cross section measurements of Table 1. To normalize the relative photo-ion yield spectrum, the absolute cross section values measured at

Fig. 1. Photoionization cross section of Cl^+ leading to Cl^{2+} measured with a photon energy resolution of 15 meV. Measured data are black dots joined by a straight line. The vertical lines indicate the position of the identified resonances E_n , and are grouped with horizontal or inclined lines according to the Rydberg series they were assigned to. The last vertical line of each group corresponds to its limit E_∞ . Series are identified with Roman numbers in Tables 3–5 where Gaussian fit centers E_n , principal quantum numbers n and quantum defects μ for the identified series are given. Absolute cross section measurements are indicated by the large dots and are tabulated in Table 1. Solid vertical lines in the top of this figure indicate the energy thresholds of the identified initial states of Cl^+ together with their state terms (see Table 2). For clarity, a shorter range of this same spectrum is given in Fig. 2.

discrete energies were used to derive a polynomial normalization function that was applied to the entire relative photo-ion spectrum. In this process, the relative spectrum was normalized to the absolute cross sections and a spectrum with an absolute cross-section scale was produced. The energies at which absolute cross-section measurements were performed had been selected in regions of the spectrum where there was no apparent resonant structure and also on one resonance. For the large regions of the spectra where no absolute values were available, the normalization function was extrapolated from a third-order spline interpolation to the absolute cross-section values. For this reason, the resulting cross section spectrum is most reliable around the intervals where absolute cross section measurements were available.

To check for reproducibility, an energy spectrum in the range of 23.0–24.0 eV was measured during an unrelated experimental program under different conditions. The spectrum was well reproduced within the energy uncertainty reported here.

The spectrum so normalized presents several resonant peaks (see Figs. 1 and 2). It was possible to assign most of the resonant structure to various Rydberg series. The resonance energies E_n and the calculated quantum defects μ are tabulated in Tables 3–5. Resonance energies E_n listed in the tables correspond to Gaussian fits to centers of the peaks. The quantum defects μ were calculated from the

modified Rydberg energy equation

$$E_n = E_\infty - \frac{Ry(Z - N_c)^2}{(n - \mu)^2}, \tag{4}$$

where Ry is the Rydberg constant, Z is the atomic number of the chlorine atom, N_c is the number of electrons of the resulting ion core and n is the principal quantum number. E_∞ is defined as the series limit of a given Rydberg resonance series corresponding to the energy where the electron being excited is promoted to the continuum thus producing direct, non-resonant ionization. This value is calculated by taking the ionization potential of Cl^+ (23.814 eV [24]) then subtracting the excitation energy of the initial Cl^+ state and adding the excitation energy of the final state of Cl^{2+} .

The identified series in Fig. 1 are indicated with vertical lines grouped with horizontal or inclined lines. The last vertical line of each group corresponds to the series limit E_∞ . The first principal quantum number n is shown close to its corresponding group of lines.

Table 3
Principal quantum numbers n , resonant energies E_n and quantum defects μ for the identified Rydberg series below the ground-state ionization threshold. The Cl^+ initial states and Cl^{2+} final states are indicated in the table headings. Series are identified in Fig. 1. Entries in parenthesis are uncertain.

n	$\text{Cl}^+ (^1S_0) \rightarrow \text{Cl}^{2+} (^2P_{1/2})$ I		$\text{Cl}^+ (^1D_2) \rightarrow \text{Cl}^{2+} (^2D_{5/2})$ II	
	E_n (eV)	μ	E_n (eV)	μ
4	20.426	0.13	–	–
5	21.742	0.15	–	–
6	22.463	0.15	22.979	0.27
7	22.900	0.13	–	–
8	23.178	0.12	23.718	0.21
9	–	–	23.907	0.23
10	–	–	24.040	0.27
11	–	–	(24.152)	(0.27)
⋮	–	–	–	–
∞	24.054 ^a	–	24.615 ^a	–

^a Energy limits were taken from NIST [24] database. For example, first limit of 24.054 eV was derived from subtracting the excitation energy of $\text{Cl}^+ (^1S_0)$ of 3.456 eV from Cl^+ ionization energy of 23.814 eV plus the excitation energy of $\text{Cl}^{2+} (^2P_{1/2})$ of 3.696 eV.

Table 2
Excitation and ionization threshold energies for the identified initial states of Cl^+ . They are tabulated in the order of appearance as a function on the photon energy in Fig. 1. Their positions are indicated with solid vertical lines with the corresponding state terms of Cl^+ . Energies were taken from NIST database [24].

Cl^+ initial state term.	J	Excitation energy (eV)	Ionization threshold (eV)
1S	0	3.456	20.357
1D	2	1.444	22.369
3P	0	0.124	23.690
	1	0.086	23.727
	2	0.000	23.814

Fig. 2. Smaller energy range zoom of Fig. 1. The position of NIST reference [24] value for Cl^+ ionization energy is indicated by a L label in the horizontal axis. Unidentified resonances are numbered. Their Gaussian fit centers are the following: 1, 22.740 eV; 2, 22.928 eV; 3, 22.949 eV; 4, 23.391 eV and 5, 23.458 eV.

In the low energy range of the spectrum, two series are identified. They originate from electronic excited initial Cl^+ in metastable states $^1\text{S}_0$ and $^1\text{D}_2$ that converge to final Cl^{2+} in states $^2\text{P}_{1/2}$ and $^2\text{D}_{5/2}$ respectively. A series of prominent resonances are assigned to Rydberg series: $\text{Cl}^+(^1\text{D}_2) \rightarrow \text{Cl}^{2+}(^2\text{D}_{5/2})$ (marked with number II in Fig. 1 and in Table 3). It starts with $n=6$. The corresponding resonance to $n=7$ is apparently obscured by the presence of two very close resonances marked with numbers 4 and 5 in Fig. 2. The rest of the series can be followed up to $n=11$.

A Rydberg series originating from the ground state configuration of $\text{Cl}^+(^3\text{P}_{J=2,1,0})$ and converging to the $^2\text{D}_{5/2}$ final state of Cl^{2+} is clearly identified with $n=6$ initial resonances for all three J states. The fine structure splitting for this state was also identified by Schectman et al. [7]. The most intense series in this energy range corresponds to $\text{Cl}^+(^3\text{P}_2) \rightarrow \text{Cl}^{2+}(^2\text{D}_{5/2})$ series (marked with number III in Fig. 1 and in Table 4). Resonance members of this particular series can be distinguish up to $n=11$.

Table 4

Principal quantum numbers n , resonant energies E_n and quantum defects μ for Rydberg series converging to $^2\text{D}_{5/2}$. The Cl^+ initial states correspond to $^3\text{P}_{J=2,1,0}$ manifold. Series are identified with Roman numbers in Fig. 1. Entries in parenthesis are uncertain.

n	$\text{Cl}^+(^3\text{P}_J) \rightarrow \text{Cl}^{2+}(^2\text{D}_{5/2})$					
	III $J=2$		IV $J=1$		V $J=0$	
	E_n (eV)	μ	E_n (eV)	μ	E_n (eV)	μ
6	24.348	0.36	24.259	0.37	24.219	0.37
7	24.829	0.35	24.750	0.33	–	–
8	25.128	0.36	25.036	0.38	(25.000)	(0.38)
9	25.335	0.34	25.238	0.40	–	–
10	25.479	0.32	25.384	0.40	–	–
11	25.583	0.32	(25.492)	(0.37)	–	–
∞	26.060 ^a	–	25.974 ^a	–	25.936 ^a	–

^a Energy limits were taken from NIST [24] database.

Table 5

Principal quantum numbers n , resonant energies E_n and quantum defects μ for Rydberg series converging to $^2\text{P}_{3/2}$. The Cl^+ initial states correspond to $^3\text{P}_{J=2,1,0}$ manifold. Series are identified with Roman numbers in Fig. 1. Entries in parenthesis are uncertain.

n	$\text{Cl}^+(^3\text{P}_J) \rightarrow \text{Cl}^{2+}(^2\text{P}_{3/2})$					
	VI $J=2$		VII $J=1$		VIII $J=0$	
	E_n (eV)	μ	E_n (eV)	μ	E_n (eV)	μ
5	(24.869)	(0.47)	(24.783)	(0.47)	(24.714)	(0.50)
6	(25.745)	(0.47)	(25.660)	(0.46)	–	–
7	26.246	0.47	26.157	0.47	26.108	0.51
8	26.564	0.46	26.475	0.47	26.430	0.50
9	26.778	0.45	26.687	0.47	26.648	0.48
10	26.928	0.43	26.833	0.49	–	–
11	27.031	0.47	–	–	–	–
12	(27.114)	(0.45)	–	–	–	–
13	27.175	0.48	–	–	–	–
∞	27.522 ^a	–	27.435 ^a	–	27.398 ^a	–

^a Energy limits were taken from NIST [24] database.

For the $\text{Cl}^+(^3\text{P}_0) \rightarrow \text{Cl}^{2+}(^2\text{D}_{5/2})$ series (marked with V in Fig. 1), it was possible to assign only two weak resonances. They are tabulated in Table 4.

In the higher energy range of the spectrum of Fig. 1, Rydberg series from ground state configuration $\text{Cl}^+(^3\text{P}_{J=2,1,0})$ converging in $\text{Cl}^{2+}(^2\text{P}_{3/2})$ is identified. The most intense feature in this energy range corresponds to $\text{Cl}^+(^3\text{P}_2) \rightarrow \text{Cl}^{2+}(^2\text{P}_{3/2})$ which is marked with number VI in Fig. 1 and in Table 5. Its two first resonances $n=5$ and $n=6$ are not well resolved possibly due to interference with other resonances but it can be clearly followed up to E_{13} .

To provide a more general test for self consistency of the quantum defects [25], we offer the next check: assuming a pure hydrogen-like ion behavior, the resonant energies E_n^H would be given by

$$E_n^H = E_\infty - \frac{Ry(Z - N_c)^2}{n^2}, \quad (5)$$

Fig. 3. Semilog plot of ΔE_n as a function of the same energy difference but calculated from quantum defects μ taken from Tables 3–5 according to Eq. (6). The dotted line corresponds to the identity function.

and a relationship between quantum defects μ and the energy difference $\Delta E_n = E_n^H - E_n$ is, according to Eqs. (4) and (5),

$$\Delta E_n = Ry(Z - N_c) \left[\frac{1}{(n - \mu)^2} - \frac{1}{n^2} \right] \quad (6)$$

The energy difference ΔE_n was calculated using the resonance energies E_n from Tables 3–5 and plotted as a function of the same difference but given by Eq. (6). The result is shown in Fig. 3. Except for two points from series marked with number II (see Figs. 1 and 2), all series show the same behavior. The points that do not follow the general trend from series II correspond to its first ($n=6$) and last ($n=11$) identified resonances. In the case of the first resonance, interference with close resonant structures in this particular section of the spectrum (see Fig. 2) may explain its deviation from the general trend. In the case of the last resonance, its low intensity did not allow a clear identification and may be the reason for the deviation of its behavior.

4. Summary and conclusions

We present results for the single photoionization of Cl^+ ion measured with photon energy resolution of 15 meV. The present results consist of a spectrum from below the ionization potential to 28 eV. Also, absolute measurements of the cross section are given. The resulting spectrum consisted of numerous resonances, most of which were identified as belonging to Rydberg series. These resonant structures were superimposed on a direct ionization background. The initial Cl^+ ion beam consisted of a mixture of ground-state ^3P and electronically excited states of terms $^1\text{S}^0$ and $^1\text{D}_2$. The large intensity of the resonant structure originated from $\text{Cl}^+(^1\text{D}_2)$ indicates that the population of this metastable component in the ion beam is important. The identified final states of the resulting Cl^{2+} correspond to the $^2\text{D}_{5/2}$ and $^2\text{P}_{3/2}$ state terms.

The present experimental verification of the photoionization of Cl^+ leading to Cl^{2+} provides supporting evidence for future theoretical efforts and the first absolute measurements of its cross section. These data are expected to assist future identifications of chlorine in the interstellar medium and in astrophysical atmospheres. In addition, the reported absolute Cl^+ photoionization cross section measurements will help future efforts to more accurately determine the interstellar abundance of chlorine.

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Appendix A. Supplementary data

Supplementary data associated with this paper can be found in the online version at <http://dx.doi.org/10.1016/j.jqsrt.2014.10.004>.

References

- [1] Seaton MJ. Atomic data for opacity calculations: I. General description. *J Phys B* 1987;20:6363.
- [2] Bizau JM, Champeaux JP, Cubaynes D, Willeumier FJ, Folkmann F, Jacobsen TS, et al. Absolute cross for l-shell photoionization of the ions n^{2+} , n^{3+} , o^{3+} , o^{4+} , f^{3+} , f^{4+} and ne^{4+} . *Astron Astrophys* 2005;439(1):387–99. <http://dx.doi.org/10.1051/0004-6361:20052641>.
- [3] Bautista M. Atomic data from the iron project. *Astron Astrophys Suppl Ser* 1999;137(3):529–35. <http://dx.doi.org/10.1051/aas:1999491>.
- [4] Bautista MA, Mendoza C, Kallman TR, Palmeri P. K-shell photoionization and electron impact excitation of fexvifexxi. *Astron Astrophys* 2004;418(3):1171–8. <http://dx.doi.org/10.1051/0004-6361:20034198>.
- [5] Cartledge E. What reionized the universe? *Science* 2012;336(6085):1095–6.
- [6] Berrington KA, Nakazaki S. Radiative data for chlorine and its ions. At Data Nucl Data Tables 2002;8(1):1–113. <http://dx.doi.org/10.1006/adnd.2002.0880> URL: (<http://www.sciencedirect.com/science/article/pii/S0092640X02908806>).
- [7] Schectman RM, Federman SR, Brown M, Cheng S, Fritts MC, Irving RE, et al. Oscillator strengths for ultraviolet transitions in cl ii and cl iii. *Astrophys J* 2005;621:1159–62.
- [8] Tayal SS. Strong term dependence of wavefunctions and series perturbations in singly ionized chlorine. *J Phys B: At Mol Opt Phys* 2003;36(15):3239 theory. URL: (<http://stacks.iop.org/0953-4075/36/i=15/a=306>).
- [9] Alnawashi GA, Lu M, Habibi M, Phaneuf RA, Kilcoyne ALD, Schlachter AS, et al. Valence-shell photoionization of the chlorinelike Ca^{3+} ion. *Phys Rev A* 2010;81:053416. <http://dx.doi.org/10.1103/PhysRevA.81.053416>.
- [10] Covington AM, Aguilar A, Covington IR, Hinojosa G, Shirley CA, Phaneuf RA, et al. Valence-shell photoionization of chlorinelike Ar^+ ions. *Phys Rev A* 2011;84(1):013413. <http://dx.doi.org/10.1103/PhysRevA.84.013413>.
- [11] Berkowitz J, Ruscic B. Photoionization of atomic Chlorine. *Phys Rev Lett* 1983;50:675.
- [12] Jiménez-Mier J, Schaphorst SJ, Caldwell CD, Krause MO. High-resolution photoelectron spectrometry of autoionizing resonances between the ^3p and ^1d thresholds in atomic chlorine. *Phys Rev A* 1997;56:3659–65. <http://dx.doi.org/10.1103/PhysRevA.56.3659> experimental.
- [13] Feldman P, Ake T, Berman AF, Moos H. Detection of chlorine ions in the far ultraviolet spectroscopic explorer spectrum of the Io plasma torus. *Astrophys J* 2001;554:L123–6. <http://dx.doi.org/10.1086/320920>.
- [14] Feldman PD. A spectroscopic tour of the solar system with FUSE. In: Sonneborn G, Moos HW, Andersson BG, editors. *Astrophysics in the far ultraviolet: five years of discovery with FUSE*, Astronomical society of the pacific conference series, vol. 348; 2006. p. 307.
- [15] Schneider NM, Park AH, Koppers ME. Spectroscopic studies of the Io Torus during Galileo encounters: remote plasma diagnostics and the detection of Cl^{2+} . In: AAS/division for planetary sciences meeting abstracts #32, Bulletin of the American Astronomical Society, vol. 32; 2000. p. 1057.
- [16] Sylwester B, Phillips KJH, Sylwester J, Kuznetsov VD. The solar flare chlorine abundance from resik X-ray spectra. *Astrophys J* 2011;738(1):49 URL: (<http://stacks.iop.org/0004-637X/738/i=1/a=49>).
- [17] Neufeld DA, Roueff E, Snell RL, Lis D, Benz AO, Bruderer S, et al. Herschel observations of interstellar chloronium. *Astrophys J* 2012;748(1):37 URL: (<http://stacks.iop.org/0004-637X/748/i=1/a=37>).
- [18] Mooney D, Federman SR, Sheffer Y. Revisiting the chlorine abundance in diffuse interstellar clouds from measurements with the copernicus satellite. *Astrophys J* 2012;744(2):174 URL: (<http://stacks.iop.org/0004-637X/744/i=2/a=174>).
- [19] Phaneuf RA, Havener CC, Dunn GH, Muller A. Merged-beams experiments in atomic and molecular physics. *Rep Prog Phys* 1999;62(7):1143 URL: (<http://stacks.iop.org/0034-4885/62/i=7/a=202>).
- [20] Esteves DA, Bilodeau RC, Sterling NC, Phaneuf RA, Kilcoyne ALD, Red EC, et al. Absolute high-resolution Se^+ photoionization cross-section measurements with Rydberg-series analysis. *Phys Rev A* 2011;84:013406. <http://dx.doi.org/10.1103/PhysRevA.84.013406>.
- [21] Covington AM, Aguilar A, Covington IR, Gharibeh MF, Hinojosa G, Shirley CA, et al. Photoionization of Ne^+ using synchrotron radiation. *Phys Rev A* 2002;66(6):062710. <http://dx.doi.org/10.1103/PhysRevA.66.062710>.

- [22] Domke M, Schulz K, Remmers G, Kaindl G, Wintgen D. High-resolution study of $1p^0$ double-excitation states in helium. *Phys Rev A* 1996;53: 1424–38. <http://dx.doi.org/10.1103/PhysRevA.53.1424>.
- [23] King GC, Tronc M, Read FH, Bradford RC. An investigation of the structure near the $l_{2,3}$ edges of argon, the $m_{4,5}$ edges of krypton and the $n_{4,5}$ edges of xenon, using electron impact with high resolution. *J Phys B* 1977;10:2479–95.
- [24] Kramida A, Ralchenko Yu, Reader J, NIST ASD Team. NIST atomic spectra database (ver. 5.1), [Online]. Available: <http://physics.nist.gov/asd> (February 25, 2014). Gaithersburg, MD: National Institute of Standards and Technology; 2013.
- [25] Gallagher TF. *Rydberg atoms*, 1st ed. Cambridge: Cambridge University Press, Press Syndicate of the University of Cambridge; 1994.