

Inner-shell photoexcitation in an open-shell atom: The Cl $2p \rightarrow ns, md$ spectrum as a case study

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The $2p \rightarrow ns, md$ excitation spectrum has been measured and calculated for the open-shell Cl atom. A satisfactory accord between experiment and theory was found. Rydberg series cannot be discerned for transitions leading to a $2p, 3p, n\ell$ open-shell configuration. The $4s, 3d$ manifolds are dominant, and the $2p-3p$ coupling is seen to be much stronger than the $3p-n\ell$ coupling. Very narrow widths, 16 to 22 meV, for the $4s$ and $3d$ lines are observed. By contrast, only broad structures appear in the region of the highest excitations. [S1050-2947(99)50302-8]

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While studies of inner-shell excitations in solids, and even in free molecules and rare-gas atoms, have been extensive, similar studies in free open-shell atoms are practically nonexistent. However, apart from the trivial expectation of a multiline structure in the presence of open shells, fundamental properties such as the coupling strengths between the core and the excited electrons and the widths of the lines involving different initial and final states are of paramount interest. With this goal in mind we investigated, both experimentally and theoretically, the discrete part of the $2p$ photoabsorption spectrum of the multielectron chlorine atom with the fine resolution required to delineate the complex line spectrum arising from the transitions $2p^6 3s^2 3p^5 \rightarrow 2p^5 3s^2 3p^5 ns, md$. This represents an excellent case study for configurations with three open shells and, specifically, an $np, n'p, n''\ell$ configuration, which has never been fully explored.

In a wider context, related work concerns studies of $nd, n'p, n''\ell$ configurations in Br and I [1,2] and the inner-shell absorption spectra in some first-row elements involving the simpler $\ell=0$ states in Li [3], Be^+ [4], and O [5]. Closely related also are the absorption spectrum of the PF_3 molecule [6] and the photoelectron spectra of solid manganese compounds [7,8], where the open-shell character of the constituent P and Mn atoms was shown to play a critical role in the interpretation of the compound properties. However, in the absence of reference data for the free P atom, the conclusions had to remain somewhat uncertain for PF_3 .

Experimentally, the Cl $2p$ photoabsorption spectrum in the region of the $2p \rightarrow ns, md$ excitations was measured by way of the total ion yield as produced by the decay of the excited states. The undulator-plane-grating-monochromator (PGM) beamline [9] at the Synchrotron Radiation Center (SRC), University of Wisconsin, served as the photon source. As previously described, the atomic source was a microwave-driven discharge in Cl_2 or HCl [10]. The ion yield, normalized to the photon flux, was recorded in the

counting mode by a channeltron detector that viewed the ionization region through a 1.6-mm \times 6-mm slit along the photon beam [5]. Ions were extracted by a field of 100 V/cm and accelerated to a total energy of about 3.5 KeV per charge. For an auxiliary total electron yield measurement, extraction and detector potentials were suitably reversed. The pressure of the target gas was about 1×10^{-2} Pa and proved to be very stable. The bandpass for the PGM is nominally 16.5 meV at 205 eV for 17- μm entrance and 10- μm exit slits. The actual bandpass values were 10–25 % higher, as determined by reference to the narrow He $2snp, n=8$ to 16, resonance lines [11] and a bootstrap method on a very narrow Cl $4s$ line itself. Similarly, the He resonances served as the primary energy standard near 65 eV [11] and the Ar $2p_{3/2} \rightarrow 4s$ line at 244.39(1) eV [12] as a secondary calibrant. The target was roughly four parts atomic and six parts molecular, as extracted from Fig. 1. About 95% of the Cl atoms were in the $^2P_{3/2}$ ground state, as deduced from earlier data obtained under similar operating conditions [13].

The experimental result is presented in the three panels of Fig. 1, showing the composite $2p$ spectrum in which the atomic and molecular spectra are superimposed [panel (a)], the pure HCl spectrum recorded separately [panel (b)], and the pure Cl spectrum [panel (c)] obtained from the Cl/ HCl and HCl spectra by subtraction following matching in the region of the $\text{HCl } 4\sigma^*$ band near 201 eV. In addition, Cl atoms were generated from Cl_2 as the precursor molecule. The spectrum derived from Cl_2 was seen to be identical in all respects with the spectrum derived from HCl . Similarly, a total-electron-yield spectrum recorded over a smaller region agreed excellently with the ion measurement. While we were content with a bandpass of 32(2) meV (34×20 - μm slits) for recording this first spectrum of Cl, the lines 1 to 14 were also scanned with the best bandpass available, 21(1) meV, to delineate the finest detail as well as the linewidths.

Theoretically, energy levels and spectra were calculated using the standard Slater-Condon superposition-of-

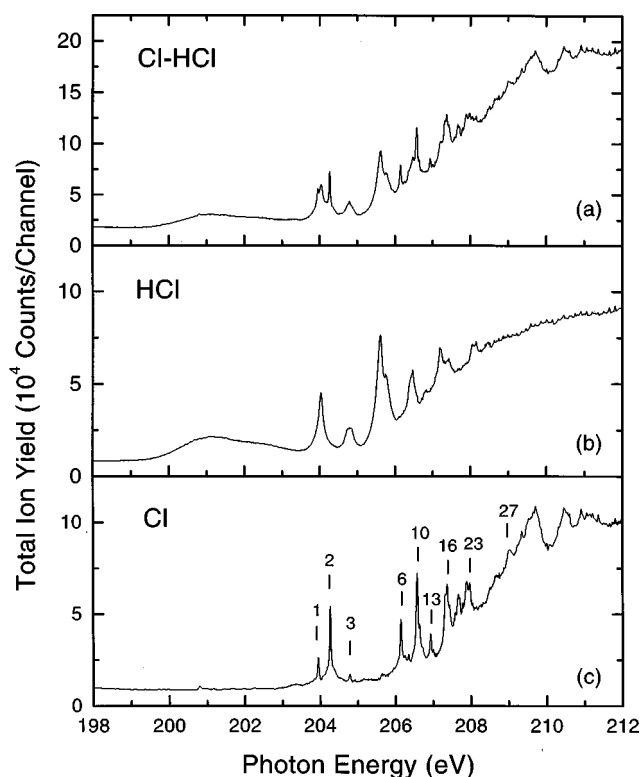


FIG. 1. Cl $2p$ photoabsorption spectrum recorded as total ion yield with a photon bandpass of 32 meV. The upper panel shows the Cl/HCl mixture with the discharge on, the center panel show the HCl spectrum with the discharge off, and the bottom panel shows the resulting Cl spectrum. The spectra contain 801 channels each.

configuration method [14]. We used Hartree-Fock wave functions, with the inclusion of approximate relativistic and correlation corrections to the center-of-gravity energy of each of the configurations considered, $2p^6 3p^5$, $2p^6 3p^4 4p$, $2p^5 3p^5 ns (n=4-9)$, and $2p^5 3p^5 md (m=3-8)$. In the calculation of level structure, the values of the open-subshell Coulomb integrals were scaled down by a factor of 0.8 to allow for effects of neglected weak configuration interaction; this is known empirically to be an appropriate value for neutral atoms of moderate Z .

The major contribution to level separations in the excited configurations is from the $2p^5 \ ^2P_{3/2-1/2}$ spin-orbit splitting. However, other spin-orbit effects are comparable with Coulomb splittings, even for $4s$ and $3d$, with the result that neither pure LS nor pure jj coupling provides a good approximation of the actual intermediate coupling, and eigenvectors consequently show very strong mixing in either pure-coupling representation. Configuration mixing has generally only a small effect on computed energy levels, but frequently quite a large effect on oscillator strengths for some members of the d series.

As examples, computed spectra are shown in Fig. 2 for transitions from the ground state to the $4s$ and the $3d$ configurations. Many of the lines, 17 lines for $4s$ and 47 lines for $3d$, are seen to have sizable strengths, and the individual spectra are seen to strongly overlap in energy.

Interpretation of the Cl $2p$ excitations relies heavily on the comparison of observation and calculation. This comparison is made visually in Fig. 3 and, for the major lines,

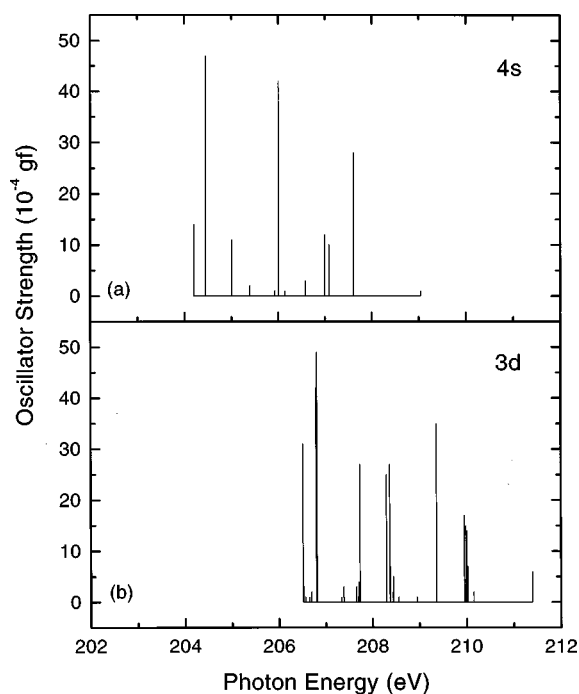


FIG. 2. Calculated spectral distributions for the transitions $2p \rightarrow 4s$ and $2p \rightarrow 3d$.

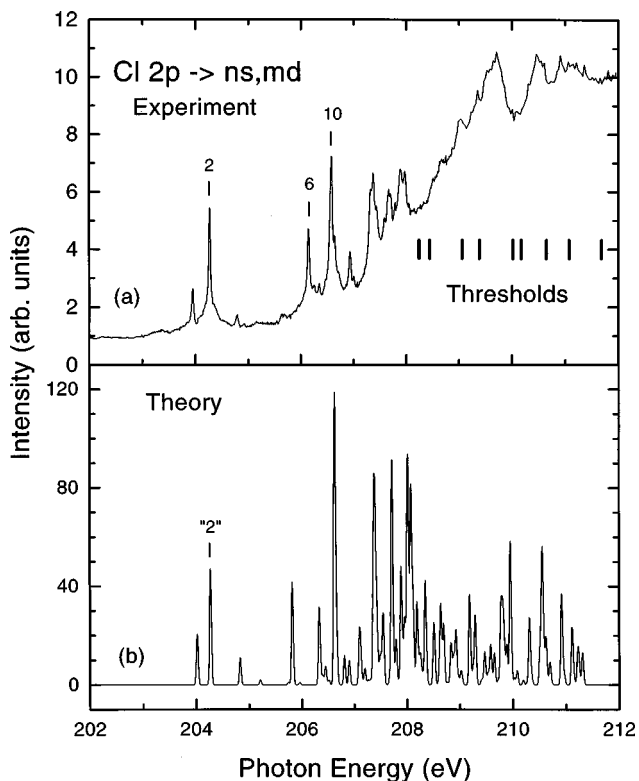


FIG. 3. Comparison of the experimental and the theoretical Cl $2p$ spectrum. The calculated spectrum comprises all transitions to $4s-9s$ and $3d-8d$ levels; it has been convoluted with a Gaussian of 40 meV width and has been shifted by -0.182 eV to match the experimental spectrum at line 2. The computed ionization thresholds are given in the upper panel, except for the highest threshold at 213.11 eV; these thresholds were not shifted.

TABLE I. Energies of major $2p \rightarrow ns, md$ transitions in Cl. Energy differences ΔE are referred to the energy of line 2. Upper-level identifications are given in terms of $n\ell$ and total J ; gf is the oscillator strength.

Line	Experiment			Theory				$E_{\text{theor}} - E_{\text{expt}}$ (eV)
	E (eV)	ΔE (eV) ^a	ΔE (eV)	E (eV)	$n\ell$	$2J$	gf^b	
1	203.949	-0.319(5)	-0.25	204.20 ^c	$4s$	1,3	21	0.25
2	204.268 ^d	0	0	204.450	$4s$	5	47	0.182
3	204.787	0.519(7)	0.560	205.010	$4s$	5	11	0.223
6	206.147	1.879(5)	2.063	206.513	$3d$	5	31	0.366
10	206.576	2.308(4)	2.36	206.81 ^c	$3d$	1-5	129	0.24
11	206.640	2.372(8)	2.394	206.844	$5s$	5	18	0.204
13	206.933	2.665(5)	2.83	207.28 ^c	$4d$	3,5	30	0.35
15	207.328	3.060(6)	3.10	207.55 ^c	$4d$	3,5	73	0.22
16	207.376	3.108(5)	3.14	207.59 ^c	$4d, 4s, 6s$	1,5	72	0.21
17	207.438	3.170(6)	3.279	207.729	$3d$	5	27	0.291
20	207.705	3.437(5)	3.45	207.90 ^c	$5d$	1-5	94	0.19
22	207.880	3.612(5)	3.75	208.20 ^c	$6s, 7d$	1-5	105	0.32
23	207.975	3.707(5)	3.80	208.26 ^c	$8d$	1-5	81	0.28

^aUncertainties of line energies are relative to position of line 2.

^bValues are multiplied by 10^4 .

^cWeighted average of several lines; the corresponding oscillator strengths listed are the sum of gf values for the lines in the blend.

^dUncertainty is ± 20 meV in absolute energy.

numerically in Table I. The theoretical spectrum, which contains all transitions to the $4s$ to $9s$ and $3d$ to $8d$ manifolds, has been convoluted with a Gaussian function of 40 meV full width at half maximum (FWHM) to approximate the experimental width [15]. In Table I we also give the oscillator strengths for the lines. We identify the lines only by $n\ell$ and the total J values of the upper levels because of the awkwardness of JJ -level notation, the low purity of levels, and the strong overlap of many lines once the natural widths and the instrumental resolution are included.

We find a quite satisfactory accord between experiment and theory up to about 208 eV. With a few exceptions, the calculated energies are within 0.3 eV of the measured values, and the line spacings display even smaller deviations. Although the agreement is not as good as for the energies, the general accord extends to the intensity patterns as well. This overall agreement indicates that energies and relative strengths for $2p \rightarrow ns, md$ ($n=4-9$, $m=3-8$) transitions are satisfactorily predicted within the approximations used. A major discrepancy occurs above 208 eV, starting with the first of the ten computed ionization thresholds. There the sharp structures measured and predicted below 208 eV no longer continue, but are replaced by broad, indistinct features in the observed spectrum. While we cannot pinpoint the cause for this behavior, which does not occur in the rare gases or for outer-shell excitations in the halogens, we believe a likely cause to be line broadening due to increased interactions with more and more continua. Such modes have not been considered in our calculation, and while they are evidently insignificant for the lower excitations, they appear to affect the higher members. The rise in the "background" toward the ionization edges is a general phenomenon not restricted to open-shell atoms. It has been studied and interpreted in the case of the Ar $2p$ absorption spectrum [16,17].

A comparison of the $2p$ spectrum of Cl with that of the Ar neighbor [18] demonstrates the strong influence of the open-shell structure for these inner-shell excitations. There is

only a faint resemblance between the spectra; the differences are more striking. The lifting of the degeneracy in the case of Cl has an obvious effect, the appearance of a multiline structure (a multiplet in LS notation). However, the loss of well-behaved ns and md Rydberg series that might be associated with $2p_{3/2}$ and $2p_{1/2}$ fine-structure states is not self-evident. This loss is mainly due to the strong $2p$ - $3p$ coupling, according to our calculation.

One of the most intriguing discoveries of this study is the narrow width of most lines. The width of line 2, which belongs to the $4s$ manifold, is 16(4) meV FWHM [19], as determined from a series of runs using different bandpasses, namely 21, 32, and 55 meV, and by reference to the He resonances [11]. This line is much narrower than the line-width of about 120 meV in Ar [17,20], the semiempirical level width given as 85 meV in Cl [20], or the width of 100 meV for an Auger satellite line in Ar with a $3p$ vacancy [21]. Other lines in the Cl spectrum are also narrow, 22(5) meV for lines 1 and 6 and 40(9) meV for line 10, which contains three lines of $3d$ character. A tentative explanation for this phenomenon would be to invoke hindered transitions from certain excited states to the final ionic states for the width-determining radiationless decay. This explanation receives support from a preliminary calculation we made for Cl and from an LS -based calculation [22] of radiationless processes in the analogous case of Ar⁺. The latter showed a substantial decrease of the Auger width from the $3p^6$ closed-shell case and a dependence of the partial widths on the multiplet configuration [22].

In conclusion, we have presented a detailed study of an inner-shell photoexcitation spectrum in a multielectron atom with an open shell. Many features of the measured spectrum Cl $2p \rightarrow ns, md$ can be correlated with the theoretical spectrum from an extensive intermediate coupling calculation of the transitions leading to the excited $np, n'p, n''\ell$ configurations. The $2p$ - $3p$ coupling is shown to be much stronger

than the $3p-n''\ell$ coupling, even for $n''\ell=4s$ or $3d$. A rich line structure with no Rydberg demarcations is observed. This stands in contrast to the occurrence of Rydberg series for $1s \rightarrow np$ excitations in the first-row oxygen atom [5]. Interestingly, among the more than 200 transitions given by our calculation, a limited number has significant strength to create a distinctive line spectrum. The results for Cl may be transferred to $2p$ excitation spectra in other second-row atoms, but not to $3p$ spectra of third-row atoms because of the influence of the $3d$ subshell. The resemblance of the Cl $2p$ spectrum to the Ar $2p$ spectrum is found to be tenuous; as a consequence, characteristics of closed-shell atoms should not be transferred to spectra of compounds containing an open-shell atom. Instead, the Cl case might serve as a basis for

including the effects of the open-shell character of constituent atoms. Several observations present further challenges to both theory and experiment. They include the smearing out of the higher excitation states in the spectrum and the narrow widths of many low-lying lines. In both instances, studies of the decay processes of the excited states hold the promise of providing further insights.

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- [1] L. Nahon, P. Morin, and F. Combet-Farnoux, *Phys. Scr.* **T41**, 104 (1992); L. Nahon and P. Morin, *Phys. Rev. A* **45**, 2887 (1992).
- [2] A. Cummings and G. O'Sullivan, *Phys. Rev. A* **54**, 323 (1996); G. O'Sullivan, C. McGuinness, J. T. Costello, E. T. Kennedy, and B. Weinmann, *ibid.* **53**, 3211 (1996).
- [3] D. L. Ederer, T. Lucatorto, and R. P. Madden, *Phys. Rev. Lett.* **25**, 1537 (1970).
- [4] E. Jannitti, P. Nicolosi, and G. Tondello, *Opt. Commun.* **63**, 37 (1987).
- [5] A. Menzel, S. Benzaid, M. O. Krause, C. D. Caldwell, U. Hergenbahn, and M. Bissen, *Phys. Rev. A* **54**, R991 (1996).
- [6] N. Kosugi, R. G. Cavell, and A. P. Hitchcock, *Chem. Phys. Lett.* **265**, 490 (1997).
- [7] B. Hermsmeier, C. S. Fadley, M. O. Krause, J. Jiménez-Mier, P. Gerard, and S. T. Manson, *Phys. Rev. Lett.* **61**, 2592 (1988).
- [8] B. Sonntag and P. Zimmermann, *Rep. Prog. Phys.* **55**, 911 (1992).
- [9] R. Reininger, S. L. Crossley, M. A. Lagergren, M. C. Severnson, and R. W. C. Hansen, *Nucl. Instrum. Methods Phys. Res. A* **347**, 304 (1994).
- [10] P. van der Meulen, M. O. Krause, C. D. Caldwell, S. B. Whitfield, and C. A. de Lange, *Phys. Rev. A* **46**, 2468 (1992).
- [11] Our own evaluation, which for the energies nearly coincides with the data of R. P. Madden and K. Codling, *Astrophys. J.* **144**, 364 (1965); the resonance widths are based on $\Gamma_n(n^*)^3 = 200(20)$ meV.
- [12] G. C. King, M. Tronc, F. H. Read, and R. C. Bradford, *J. Phys. B* **9**, L555 (1976).
- [13] J. Jiménez-Mier, S. J. Schaphorst, C. D. Caldwell, and M. O. Krause, *Phys. Rev. A* **56**, 3659 (1997).
- [14] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), Chaps. 8 and 16.
- [15] Actually a Voigt profile should be used, but such rigor need not be applied at this stage.
- [16] T. Hayaishi, E. Murakami, A. Yagishita, F. Koike, Y. Morioka, and J. E. Hansen, *J. Phys. B* **21**, 3203 (1988).
- [17] J. A. R. Samson, W. C. Stolte, Z. X. He, J. N. Cutler, and D. Hansen, *Phys. Rev. A* **54**, 2099 (1996).
- [18] See, for example, M. Domke, T. Mendel, A. Puschmann, C. Xue, D. A. Shirley, G. Kaindl, H. Petersen, and P. Kiske, *Rev. Sci. Instrum.* **63**, 80 (1992).
- [19] This line is suitable for bandpass calibrations of monochromators in the energy region around 200 eV, where no standards exist.
- [20] M. O. Krause and J. H. Oliver, *J. Phys. Chem. Ref. Data* **8**, 329 (1979).
- [21] D. Ridder, J. Dieringer, and N. Stolterfoht, *J. Phys. B* **9**, L307 (1976).
- [22] M. H. Chen and B. Crasemann, *Phys. Rev. A* **10**, 2232 (1974).