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Comments

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Analysis of resonance structure in the photoionization of atomic chlorine

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We report a revised interpretation of the photoionization cross section of Cl I between the lowest ionization threshold ^3P and the ^1D threshold. The two series of narrow resonances which have been observed in the recent measurement by Ruščić and Berkowitz are interpreted as the $(^1D)ns\,^2D$ and $(^1D)nd\,^2S$ series, where the latter is allowed (and narrow) due to a (small) admixture of $(^1D)nd\,^2P$ into the ^2S wave function. The broad resonances are identified as a superposition of $(^1D)nd\,^2P$ and $(^1D)nd\,^2D$.

In a recent experiment Ruščić and Berkowitz[1] succeeded in obtaining a high-resolution ion-yield curve for photoionization of atomic chlorine from the ionization threshold at 956 down to 750 Å. They observed three autoionizing series converging to the $^1D_2$ ionic state, and made comparisons with two existing many-body calculations[2,3] that include part of the resonance structure in the region between the thresholds.

In an R-matrix calculation by Lamoureux and Combet-Farnoux[2] the resonances due to the $(^1D)nd\,^2P$ series were taken into account, while in a many-body theory (MBT) calculation by Brown, Carter, and Kelly[3] the $(^1D)ns\,^2D$ and $(^1D)nd\,^2D$ series were included as well. Both calculations[2,3] used LS coupling and did not include effects of spin-orbit coupling.

Of the three observed series,[1] two were very narrow (corresponding to long lifetimes for autoionization) while the third was very broad. Ruščić and Berkowitz used primarily regularities in the experimental quantum defects to interpret the observed spectra. The broad series and one of the narrow series could immediately be identified with the $(^1D)nd\,^2P$ and $(^1D)ns\,^2D$ series for $n \geqslant 4$ and $n \geqslant 6$, respectively. We will designate this narrow series (the longer wavelength one of the two) as the A series. Ruščić and Berkowitz identified the second narrow series (which we will call the B series) as $(^1D)nd\,^2D$. Ruščić and Berkowitz concluded that the major discrepancy between the MBT theory[3] and experiment is the prediction of one narrow series while the experimental spectrum shows two narrow series.

In this note we identify the broad series as a superposition of the $(^1D)nd\,^2P$ and ^2D series. In the paper by Brown *et al.*,[3] Fig. 11 presented "the sum of the ^1Dnd and ns resonances in the ^2D and ^2P channels of Cl I." The figure showed one broad series labeled nd and a narrow series labeled ns. Unfortunately, the paper did not stress that the single broad series was actually a superposition of two broad series $(^1D)nd\,^2P$ and ^2D although the calculations had shown this.[4] We also now identify the narrow series B as $(^1D)nd\,^2S$, which is not allowed as an autoionizing series in the strict LS coupling scheme used by Brown *et al.* [$A(^3P)\epsilon l\,^2S$ autoionization continuum requires $l=1$, which is the wrong parity.] However, the $(^1D)nd\,^2S$ series becomes allowed when departures from LS coupling are taken into account—a small amount of $(^1D)nd\,^2P_{1/2}$ then being mixed into $(^1D)nd\,^2S_{1/2}$. In Ref. 1, the ^2S series identification was discarded because the observed quantum defects did not agree with the quantum defect of a level at 99 534 cm^{-1}, identified as $(^1D)3d\,^2S_{1/2}$ by Radziemski and Kaufman.[5] However, we will show that this objection can be overcome, and that the new identification removes another difficulty encountered with the previous identification of the B series. The identification of the A series is unchanged.

QUANTUM DEFECTS

Estimates of the position of the $(^1D)nd\,^2S$ series are available from calculations by Cowan, Radziemski, Jr., and Kaufman[6] and by Smid and Hansen.[7] These calculations were carried out in order to study the perturbed $3s3p^6\,^2S$ term, which in Cl I is strongly mixed with both discrete and continuum members of the $(^1D)nd/\epsilon d\,^2S$ extended Rydberg series. Both calculations were configuration-interaction (CI) calculations including all these important interactions; Cowan *et al.*[6] employed a low-resolution discretized-continuum approach, whereas the Smid-Hansen calculation utilized a variation of Fano's theory[8] for the interaction

TABLE I. Predicted effective quantum numbers for the $(^1D)nd\,^2S$ series in Cl I compared to the values observed for the second (shorter wavelength) (^1D) series of narrow resonances.

Upper level	Observed[a]	Predicted Ref. 6[b]	Ref. 5[c]	Ref. 5[d]
$3p^4(^1D)3d\,^2S$	(2.586)[e]	3.06	2.97	
$4d\,^2S$	4.038	4.08	4.08	3.88
$5d\,^2S$	5.031	5.08	5.18	4.93
$6d\,^2S$	6.026	6.09	6.24	5.99

[a] Reference 1.

[b] The energies relative to the ionization limit given in Ref. 6 have been converted to n^* values.

[c] Based on computed energies relative to the computed ionization limit.

[d] Based on published n^* values for $(^1D)nd\,^2P$ (Ref. 1) and calculated $(^1D)nd\,^2P$-^2S energy difference.

[e] Based on the level at 99 534 cm^{-1} identified as $(^1D)3d\,^2S$ in Ref. 4. This identification is probably incorrect (see text).

between a perturber and a continuum.

In Table I we show the calculated positions of the $(^1D)nd\,^2S$ states for $n=3$–6 in terms of values of the effective quantum numbers n^* for easy comparison with the n^* values reported by Ruščić and Berkowitz for the B series. (In the case of the Cowan *et al.*[6] calculation, n^* values are given as obtained from the computed $nd\,^2S$ levels relative to the computed ^1D limit, and also as obtained from the computed ^2P-^2S energy difference combined with the observed[1] n^* values for ^2P. The latter set of numbers is probably the less reliable of the two.)

The theoretical values of n^* all agree that the quantum defect n-n^* is more or less independent of n and approximately equal to zero. The calculations also predict $(^1D)nd\,^2S$ to lie above $(^1D)nd\,^2P$ and $(^1D)nd\,^2D$ for all n, including $n=3$. Radziemski and Kaufman tentatively identify levels at 101 945 and 102 187 cm^{-1} as belonging to $(^1D)3d\,^2P$ and $(^1D)3d\,^2D$, respectively. It seems clear that their identification of the 99 534 cm^{-1} level as $(^1D)3d\,^2S_{1/2}$ [based on calculations that did not include the strong upward perturbation of $3s^23p^4(^1D)3d\,^2S$ by $3s3p^6\,^2S$] cannot be correct. The authors in fact indicated that Zeeman-effect data conflicted with assignment of $J=\frac{1}{2}$ to the 99 534 cm^{-1} level.

Identification of the B series as $(^1D)nd\,^2S$ can thus no longer be objected to on the basis of quantum defect considerations. Our identification also removes the difficulty encountered by Ruščić and Berkowitz in interpreting the B series as $(^1D)nd^2D$, namely, that the observed quantum defects disagree with that of the $(^1D)3d\,^2D_{5/2}$ level at 102 187 cm^{-1}.

We have retained the identification of the A series as $(^1D)ns\,^2D$, not only because of the good agreement between the observed quantum defects for this series and those for the bound members ($4s$ and $5s$) of the $(^1D)ns\,^2D$ series[5] but also because the observed separation between the maximum of the broad peaks and the A series is in good agreement with the separation between the maximum of the combined $(^1D)nd\,^2P$ and ^2D series and the $(^1D)ns\,^2D$ series calculated by Brown *et al.*[3]

AUTOIONIZATION RATES AND LINEWIDTHS

We have obtained further confirmation of our identifications through perturbation calculations of absorption oscillator strengths and autoionization linewidths[8,9] (using single-configuration Hartree-Fock functions for both bound and continuum electrons), with the results for $4d$ and $6s$ shown in Table II. The calculations are in semiquantitative agreement with the observations in that $(^1D)4d\,^2P$ and $(^1D)4d\,^2D$ contribute very strong and broad absorption (overlapping essentially completely), whereas $(^1D)4d\,^2S$ and $(^1D)6s\,^2D$ are weak, have autoionization widths within the experimental resolution (0.28 Å), and lie at a higher energy (shorter wavelength) than the strong lines. (Because of computational inaccuracies in energy level positions, it was necessary to empirically adjust the $6s\,^2D$ energy relative to $4d\,^2P$ and ^2D in order to obtain a realistic amount of mixing of the $4d$ basis states into the $6s$ eigenvectors for evaluation of the $6s$ widths and $3p$-$6s$ oscillator strengths. With this adjustment the $6s\,^2D$-$4d\,^2S$ separation is poor, but this does not affect the calculation of Γ and f, because of the difference in J values.)

The calculations predict that a third narrow series $(^1D)nd\,^2F_{5/2}$ should appear as a consequence of a spin-orbit-induced admixture of a small amount of $(^1D)nd\,^2D_{5/2}$ nature. This series may be difficult to observe because it is an order of magnitude weaker than the A and B series and somewhat wider than the experimental resolution, and also because of its position near the Fano minimum of the broad nd^2P and ^2D absorption. We note that Huffman, Larrabee, and Tanaka[10] have published a photograph of the autoionized absorption series of chlorine which shows the three series converging to $3s^23p^4\,^1D_2$. It would also be interesting to analyze this photograph for any evidence of the $(^1D)nd\,^2F_{5/2}$ series.

In support of the calculations we have included in Table II results for the $(^1S)3d$ and $5s$ features, which agree well with the observed spectrum.[1]

CONCLUSIONS

In conclusion, the major discrepancy noted by Ruščić and Berkowitz between MBT[3] and experiment[1] has been resolved. The second series of narrow resonances in the observed spectrum, which is absent in the MBT calculation, is due to breakdown of LS coupling, which was assumed in the calculation of Brown *et al.*[3]

A remaining discrepancy is the MBT prediction that the $(^1D)ns\,^2D$ series interacts with the $(^1D)nd\,^2D$ series in such a way as to produce a dip in the cross section, which is not

TABLE II. Computed energies (relative to the experimental values of the series limits ${}^1D = 116\,245$ and ${}^1S = 132\,469\ \mathrm{cm}^{-1}$), autoionization rates, full-width at half maximum (FWHM) widths, and oscillator strengths from the ground level $3p^5\,{}^2P_{3/2}$.

Upper level	E (cm^{-1})	$A\,(10^{13}\ \mathrm{s}^{-1})$	Γ(cm^{-1})	Γ(Å)	f
$3p^4({}^1D)4d\,{}^2F_{5/2}$	108 642	0.81	43	0.37	0.0003
${}^2P_{1/2}$	108 981	37.1	1970	17.0	0.016
${}^2P_{3/2}$	108 927	39.8	2110	18.3	0.085
${}^2D_{3/2}$	109 024	38.4	2040	17.6	0.009
${}^2D_{5/2}$	108 965	39.1	2080	18.0	0.111
${}^2S_{1/2}$	109 641	0.2	11	0.1	0.007
$3p^4({}^1D)6s\,{}^2D_{3/2}$	109 635[a]	0.43	23	0.20	0.0001
${}^2D_{5/2}$	109 635[a]	0.46	24	0.21	0.0023
$3p^4({}^1S)3d\,{}^2D_{3/2}$	118 524	11.3	600	5.2	0.0047
${}^2D_{5/2}$	118 500	9.8	520	4.5	0.047
$3p^4({}^1S)5s\,{}^2S_{1/2}$	119 203	2.4	130	1.1	0.011

[a] Energies empirically increased from the *ab initio* value 109 035 cm^{-1} in order to obtain a satisfactory $6s$-$4d\,{}^2D$ energy separation for the calculation of Γ and f (see text).

observed even at the high resolution attained by Ruščić and Berkowitz.[1]

After this paper was submitted for publication, we received a preprint[11] on the photoionization of atomic bromine which is similar to that of chlorine. In this work, Ruščić, Greene, and Berkowitz[11] attribute the "extra" narrow series to $({}^1D)nd\,{}^2S_{1/2}$.

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