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Autoionization in the uv Photoabsorption of Atomic Calcium[†]

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Detailed measurements of the absolute photoabsorption cross section of atomic calcium between 2028 and 1753 Å and 1589 and 1424 Å are presented. Structure is displayed in the absorption cross section below 1589 Å, confirming previous theoretical predictions of autoionization in this region. However, the observed peak magnitudes are an order of magnitude smaller than suggested by theory. A theoretical analysis has succeeded in achieving better agreement between experiment and the two-channel quantum-defect theory for the ${}^1S_0 \rightarrow {}^1P_1^0$ transitions in the 2028–1753-Å region, both in the magnitude and in the general shape of the absorption profile.

I. INTRODUCTION

Autoionization in the photoabsorption of atomic calcium has been observed by Garton and Codling,[1] Ditchburn and Hudson,[2] Newsom,[3] and more recently by Hudson and Carter.[4] Calcium and the processes which determine its state of ionization are of extreme importance in many astrophysical problems. For example, Burgess[5] has shown that calcium dielectronic recombination is orders of magnitude more probable than normal radiative recombination in the solar corona, and provides an estimate of the temperature in agreement with that derived from solar linewidth measurements. The existence of good experimental absorption spectra and the extensive interest given to the calcium atomic system in the past, make this atom ideal for continued study and for the development and testing of new theoretical techniques which can be extended with confidence to other lesser-understood systems.

This laboratory has developed techniques for obtaining absolute measurements of the absorption cross sections of the alkaline earths.[6,7] The apparent discrepancy between the relative calcium cross sections reported by Newsom,[3] the theoretical calculations of Moores,[8] and the earlier experimental work of Ditchburn and Hudson[2] in the interval 2028–1660 Å has motivated the theoretical study and experimental remeasurement of the absorption cross section in this region. At the same time the measurements were extended to wavelengths shorter than 1589 Å where Moores predicts strong autoionization features. Ditchburn and Hudson, using a hydrogen line-emission spectrum and photographic detection techniques below 1589 Å, found no evidence of structure. The photoelectric detection scheme and the emission continuum used in the present work result in a significantly improved system over that employed in the earlier work and justify a renewed search for structure at the very short wavelengths.

This paper presents absolute absorption cross sections for calcium between 2028 and 1753 Å and between 1589 and 1424 Å, and compares the former with new theoretical calculations performed using the two-channel quantum-defect method.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

Details regarding the basic theory and experimental arrangement employed in the determination of absolute cross sections of alkaline earths have been described previously.[6,7] The apparatus consists essentially of a 2.2-m normal-incidence monochromator using a 1200 lines/mm grating, behind the exit slit of which is a temperature-regulated furnace serving as an absorption chamber. For the absorption studies between 2028 and 1753 Å, the entrance and exit slits were set at 20 μm, giving an instrumental bandwidth of 0.075 Å; a molecular-hydrogen discharge lamp was used as the light source. For the region between 1600 and 1400 Å the entrance and exit slits were set at 100 μm and 50 μm, respectively; the light source was an argon lamp used in a repetitive-discharge mode. It proved to be relatively unstable unless the anode was placed at a positive potential, causing a gradual erosion of the entrance slit due to positive-ion bombardment. This resulted in a bandwidth which varied from 0.4 to 0.5 Å during the course of the experiment.

III. EXPERIMENTAL RESULTS

Hudson and Carter[4] have previously discussed the choice of a vapor-pressure formula for atomic calcium. For this paper we have reduced the data using the vapor-pressure data compiled by Hultgren, Orr, Anderson, and Kelley.[9] The atomic cross section $\sigma_a(\lambda)$ was then obtained from the measured ratio of the flux incident on the column of vapor, $A_0(\lambda)$, to the flux transmitted through the gas, $A(\lambda)$, by the relation

$$A_0(\lambda)/A(\lambda) = e^{C_a \sigma_a(\lambda) L} , \qquad (1)$$

where C_a is the concentration of the absorbing atoms, and L is the path length.

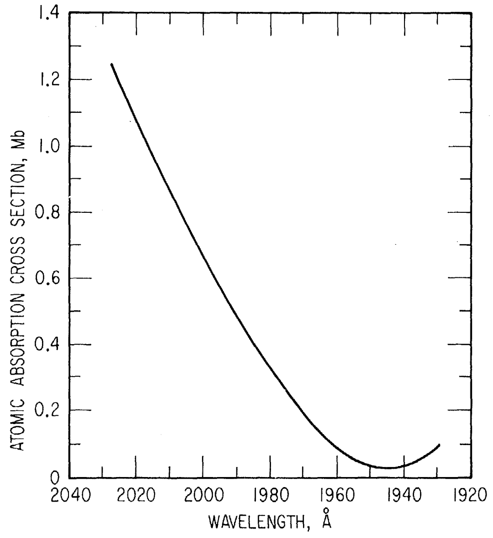

FIG. 1. Calcium continuous atomic-absorption cross section, 2028–1929 Å (1 Mb = 10^{-18} cm^2).

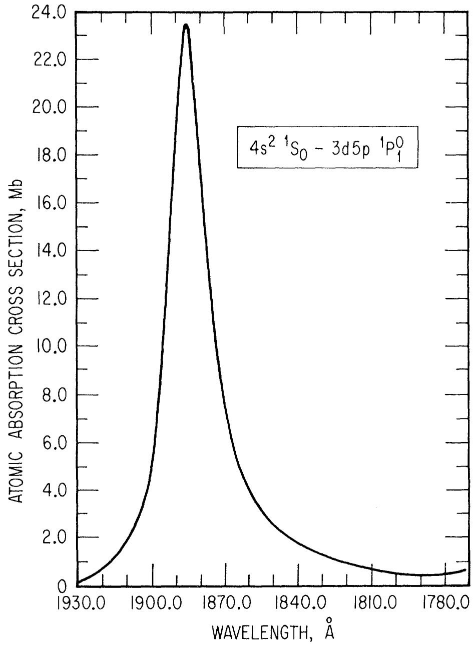

FIG. 2. Calcium atomic-absorption cross section in the vicinity of the 1885.90-Å line ($4s^2\,{}^1S_0 - 3d5p\,{}^1P_1^0$).

In Figs. 1–4 we display our best estimate of the atomic-absorption cross section of calcium vapor between 2028 and 1753 Å. Each point used to draw the smooth curves shown in Figs. 1–4 was obtained from a plot of $\ln(A_0/A)$ versus the product C_aL, and is estimated to have a statistical error of less than ±5%. The least detectable cross section for this experiment was 5.0×10^{-20} cm^2. In addition, we must assign to these measurements a total systematic error of ±15% arising from the temperature calibration, path-length determination, and vapor-pressure data.

In Fig. 5 we present our best estimate of the atomic-absorption cross section of calcium vapor

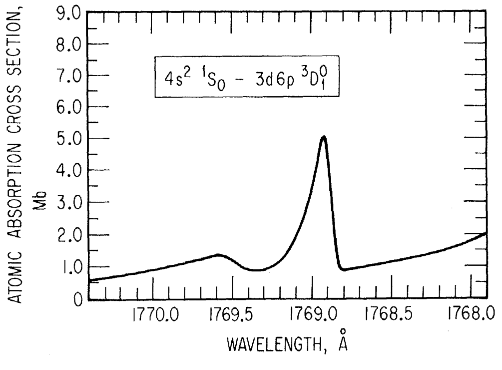

FIG. 3. Calcium atomic-absorption cross section in the vicinity of the 1768.92-Å line ($4s^2\,{}^1S_0 - 3d6p\,{}^3D_1^0$).

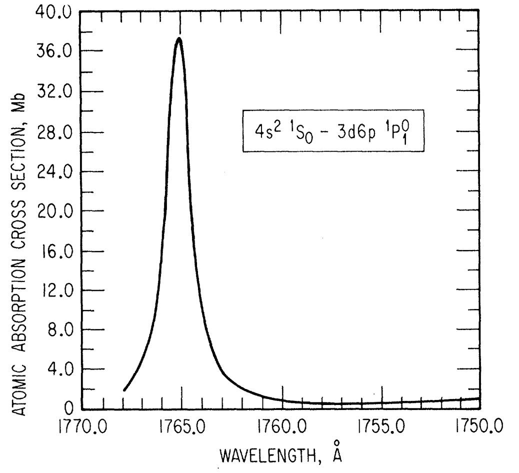

FIG. 4. Calcium atomic-absorption cross section in the vicinity of the 1765.10-Å line ($4s^2\,{}^1S_0 - 3d6p\,{}^1P_1^0$).

between 1600 and 1400 Å. As we have already mentioned, no exact bandwidth can be quoted for these data, but as the peaks are all much broader than our maximum bandwidth of 0.5 Å, we do not believe that errors will be introduced by this fact. Although we used a double-beam technique for recording the ratio A_0/A, the method does employ two photomultipliers.[10] Our data indicates a possible time-dependent variation in the ratio between the signals from these two detectors which could result in an uncertainty of ± 15% in addition to the errors discussed for the region 2028–1753 Å. Thus the results shown in Fig. 5 are subject to a possible systematic error of ± 30%.

IV. THEORETICAL ANALYSIS AND DISCUSSION OF RESULTS

The principal theoretical analysis of the autoionization peaks of calcium has been performed by Moores,[8] who utilized the recently developed multichannel quantum-defect theory to predict the photoabsorption profile for the allowed dipole transitions $4s^2\,{}^1S_0 \rightarrow 3dmp\,{}^1P_1^0 (m > 4)$ with parameters derived from bound-state spectral data. In view of the large disagreement between these two-channel calculations and the experimental results for energies immediately above the first ionization edge, a theoretical study was performed in an effort to determine the source of these differences.

The general procedures adopted for the theoretical calculation were the same as described by Moores[8] in his study of calcium. Following the suggestion of Seaton,[11] the elements of the two-channel Y matrix were expanded in terms of ϵ_α, the energy above the first $4snp\,{}^1P_1^0$ series limit, according to

$$Y_{ij} = [A_{ij} + B_{ij}\epsilon_\alpha + C_{ij}\epsilon_\alpha^{\,2}]^{-1} . \tag{2}$$

The experimental term values of Garton and Codling[8,12] for the bound states of the principal series of calcium were used to determine the different constants A_{ij}, B_{ij}, C_{ij}. This was accomplished with a general nonlinear least-squares curve-fitting numerical routine. Rapid convergence was achieved by giving special weighting to the interaction matrix elements in the region of, and the ($4snp$)-channel diagonal elements away from, the $3d4p$ perturbing level of the second series. The entries in Table I represent the results obtained, and suffice to reproduce the experimental term values to within 0.5 cm^{-1} near the perturbing level and to better than 0.1 cm^{-1} elsewhere.

These computed elements of the Y matrix were used to calculate the photoabsorption cross section for the ${}^1S_0 \rightarrow {}^1P_1^0$ transitions in the two-channel approximation for wavelengths near the first-series limit at 2028 Å, utilizing essentially the same formulas and computational procedures described by Moores. The configuration interaction wave function for the ground state (${}^1S_0$) of neutral calcium was chosen from the work of Chisholm and Öpik,[13] and final-state wave functions for the nonjumping electron of Ca$^+$ were taken from Hartree and Hartree.[14] The final state of the active electron in this region of one open and one closed channel was represented as a mixture of bound and free Coulomb functions, the amount of mixing being determined from the extrapolated Y matrix. These latter functions are defined by Burgess and Seaton[15] and can be calculated from expressions given by Burgess.[16] In particular, the bound Coulomb functions for the closed channel were represented in terms of the Whittaker function,[16] with the series expansion terminated at the minimum term to insure nondivergence near the origin.[15] In contrast, Moores[8] utilized a more complicated function to describe these latter states.

Figure 6 presents a comparison of the new calculations with the experimental results for the ${}^1P_1^0$ transitions (the $3d6p\,{}^3D_1^0$ structure at 1769 Å is

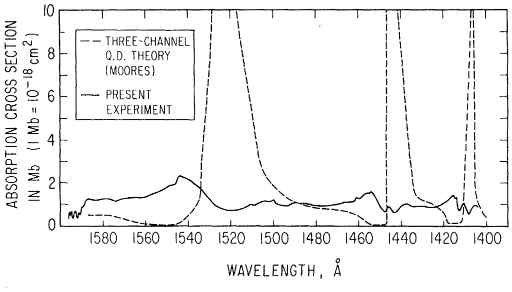

FIG. 5. Comparison of theoretical and experimental photoabsorption cross sections for calcium below 1589 Å.

TABLE I. Computed constants for [Y] matrix.

Matrix element	[A]	[B]	[C]
(1, 1)	− 0.5931	1.1391	− 3.3615
(1, 2) = (2, 1)	0.3951	− 0.3403	0.4634
(2, 2)	− 0.2397	0.2584	− 0.0748

omitted) and with the two-channel theoretical results of Moores.[8] Much better agreement has now been achieved between theory and experiment, especially with regard to the cross-section magnitudes at threshold and at the first absorption peak. The general shape of the absorption profile in the region near threshold is also in much better agreement with experiment.

The improved results with the two-channel quantum-defect theory are not attributed to the special form for the Y matrix expansion indicated by Eq. (2). Moores fitted the experimental term values to linear expressions of the form

$$Y_{ij} = A'_{ij} + B'_{ij}\epsilon_\alpha , \tag{3}$$

but converted to an associated η matrix for extrapolation and calculation of the photoabsorption cross section. A separate set of calculations was performed with the constants given by Moores for Eq. (3). The results in the wavelength region of interest have differed only insignificantly from those derived from the expansion of Eq. (2). Hence, the discrepancies which have existed between experiment and the previous theoretical calculation[8] must be a result either of the η-matrix formulation or of an error in the numerical procedures. They do not necessarily reflect inadequacies of the two-channel quantum-defect theory.

As discussed in detail by Moores,[8] disagreements between experiment and the two-channel quantum-defect theory are to be expected in the wavelength region below the first resonance peak due to perturbations from a member of a third ($4pks\ ^1P_1^0$) interacting series. The current form of the three-channel theory[8] utilizes these perturbations to compute the additional Y-matrix elements relevant to this third series. Extrapolations of this enlarged Y matrix can be made to yield information on the photoabsorption cross section for wavelengths beyond the second-series limit (~ 1589 Å).

Moores[8] has applied this technique to predict a second series of large resonance peaks in this latter region, in apparent disagreement with earlier experimental results of Ditchburn and Hudson.[2] These theoretical predictions are compared in Fig. 5 with the current measurements. Structure is observed in the vicinity of the predicted peaks. However, the magnitudes disagree by more than a factor of 10, an amount well beyond the combined experimental errors. This disagreement in magnitude is probably due to the difficulty in estimating the interaction matrix elements from the available data, and is not necessarily a fault of the three-channel theory. In addition, the measured line shapes are complex, suggesting that the isolated resonance description[17] may not be appropriate. These complex line shapes are similar to recent results presented for the $6pns$ transitions of barium by Hudson, Carter, and Young,[6] and to calculations for beryllium carried out by Altick[18] for the $2pns$ series.

V. CONCLUSIONS

Detailed curves of the absolute absorption cross section of calcium in the vicinity of the first ionization edge and of the first three elements of autoionization structure are presented. They confirm the relative measurements of Newsom.[3] We have also succeeded in achieving better agreement between these experimental results and theoretical predictions based upon the two-channel quantum-defect theory in this wavelength region, thus improving the usefulness of this theoretical technique for extension to other atomic systems.

Structure also has been observed beyond the second series limit at 1589 Å, confirming Moores,[8] prediction of auto-ionization in this region. However, the observed lines are broad and have peak values which have been overestimated by Moores's[8] by more than a factor of 10. Solar and astrophysical calculations and conclusions based upon the profiles and intensities of these absorption lines should be reexamined to determine their sensitivity to these factors.

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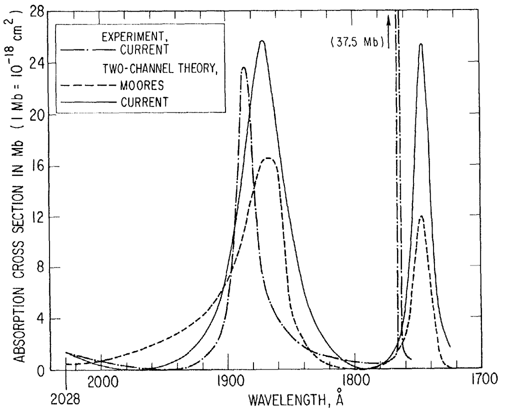

FIG. 6. Comparison of theoretical and experimental photoabsorption cross sections for calcium below 2028 Å.

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Theoretical Study of the van der Waals Forces in Alkali–Noble-Gas Systems

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The long-range interaction in alkali–noble-gas systems is studied in the multiconfiguration–self-consistent-field (MCSCF) formalism. Owing to the diffuse valence shell of the alkali, there are important contributions to the interaction potential from the higher-order multipole moments of the alkali (although the dipole moment states are by far the most important). The MCSCF formalism is shown to lead to a simple and effective way of handling the above effect, as well as evaluating intra-atomic correlation contributions and the coupling between interatomic and intra-atomic correlations when they are important. The nature of the intra-atomic–interatomic correlation coupling is analyzed and the relationship of the MCSCF results to perturbation-theory considerations clarified. Computed interaction potentials are presented for the systems HeH and LiHe. The results for HeH are in good agreement with the corresponding experimental results, while those for the system LiHe, agreeing with Dalgarno's recommended value of C_6, differ markedly from Baylis's semiempirical calculations.

I. INTRODUCTION

The long-range interaction between noble-gas atoms has been subject to a great deal of study by many authors. In particular, the system He_2 has been studied quite thoroughly, both in its ground and excited states. Until very recently,[1] however, a complete *ab initio* curve was not obtained that included both the attractive and repulsive interaction. The case of alklai–noble-gas systems is even less satisfactory. Apart from the semiempirical calculations of Baylis,[2] and the Hartree-Fock results,[3] there exists very little information, theoretical or experimental, on the nature of their long-range interaction. The long-range behavior of an alkali–noble-gas system differs in some important respects from a noble-gas–noble-gas system. First, while in the latter case the zeroth-order function can be assumed to a good degree of accuracy to consist of localized orbitals on each center, there exists in the former case appreciable overlap charge transfer. This complicates the treatment of the intra-atomic correlation. In addition, there is much more distortion in the alkali than in the noble-gas atom, necessitating the inclusion of the higher induced multipole moments on the alkali center.

Recently, the MCSCF method, which has been applied in the form of the method of optimized-valence configurations[4] to evaluate potential curves for chemically bound molecules, has also been employed with success in the study of the long-range interaction in He_2,[1] HeH,[5] and Li_2.[6] Moreover, the wave functions leading to these rather accurate potential curves are quite simple and compact, consisting of only a few configurations. This