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Evidence for New Minima in Photoionization Cross Section Obtained by Spin-Polarization Measurements

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It has recently been predicted that Cooper-type minima of the photoionization cross section should also exist for $l \rightarrow l-1$ transitions. This theoretical conclusion is supported by measurements of the spin polarization of photoelectrons that have been ejected from thallium atoms by circularly polarized light.

Recently Msezane and Manson[1] predicted the existence of a new kind of minimum in the wavelength dependence of the photoionization cross section. Studying the example of the excited Cs 5d photoionization they found, apart from the well-known Cooper minimum,[2] a second minimum for the $l \rightarrow l+1$ photoionization channel and a minimum for the $l \rightarrow l-1$ channel. These minima arise when the matrix elements of the photoionization process vanish as a result of positive and negative contributions to their radial parts caused by details of the overlap between the discrete and continuum wave functions.

A zero of the matrix element for the $l \rightarrow l-1$ channel is a novel feature which has not been predicted before and which was thought not to exist. It is the purpose of the present Letter to report experimental evidence of such a zero which causes a zero minimum of the partial cross section for the $l \rightarrow l-1$ channel.

The measurements have been made with thallium atoms in their ground state $6s^2p\,(^2P_{1/2})$ which were photoionized by circularly polarized light. A measurement of the wavelength dependence of the photoionization cross section would have hardly revealed the new minimum, since the effect to be studied is masked by the influence of the $l \rightarrow l+1$ channel. Consequently, instead of measuring the photoionization cross section the polarization of the photoelectrons produced by the circularly polarized light has been observed.

The relation between the polarization P and the photoionization cross section has been discussed in an earlier paper[3] which also gives a brief account of the experimental procedure (a detailed description of the apparatus will be given elsewhere[4]). The following facts have been shown there: According to the selection rules $l \rightarrow l \pm 1$, the outer p electron of a thallium atom can make a transition into the S or the D continuum. If circularly polarized light is used for photoionization, the photoelectrons in the S continuum have a polarization $P=1$, whereas their polarization in the D continuum is $P=-0.5$. The resulting polarization of all the photoelectrons produced is therefore

$$P=(1\times Q_S-0.5\times Q_D)/(Q_S+Q_D), \qquad (1)$$

where the polarizations of the two final states have been superimposed after weighting them with the cross sections Q_S and Q_D for reaching the S and D continuum, respectively.

In a conventional photoionization experiment one measures the cross section

$$Q=Q_S+Q_D, \qquad (2)$$

since one cannot distinguish between transitions into different continua. A measurement of the polarization yields, however, information on the individual channels as one can immediately see from Eq. (1). If, for example, Q_S or Q_D dominates, the polarization tends to $+1$ or -0.5, respectively. If both P and Q are known, one has from Eqs. (1) and (2)

$$Q_S=Q\frac{P+0.5}{1.5}, \quad Q_D=Q\frac{1-P}{1.5}, \qquad (3)$$

so that one can study the $l \rightarrow l-1$ and the $l \rightarrow l+1$ channels separately.

In the case of thallium discussed here, the situation is complicated by the fact that the continuum cannot be reached solely by the direct transitions on which our interest in focused. There are also transitions via autoionizing states

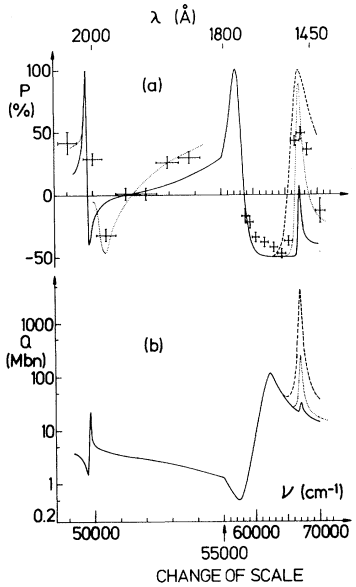

FIG. 1. (a) Spin polarization of photoelectrons from thallium. Experimental results are shown with error bars; full and broken curves are calculated with the use of the cross sections from (b); dotted line is mathematical fit yielding the polarization (without statistical error) that would have been obtained with a resolution as good as in the cross-section measurements. (b) Photoionization cross section of thallium. Experimental results from Refs. 5 and 6 (full curve) and Ref. 7 (broken curve). The dotted cross section is obtained with the parameters $q_1=4.45\pm0.05$, $\Gamma_1=2190\pm50$ cm^{-1} (from Ref. 5) and $q_0=15\pm5$, $\Gamma_0=360\pm100$ cm^{-1} ($\Gamma_0 q_0=5400\pm1000$ cm^{-1}) which result from the (dotted) experimental polarization curve.

which cause the resonances in the cross section shown in Fig. 1(b). These autoionizing resonances are described by Fano's resonance theory[8] which in our specific case yields[9]

$$Q_S=Q_S{}^0\frac{(1+q_0/\epsilon_0)^2}{1+\epsilon_0{}^{-2}},\qquad Q_D=Q_D{}^0\frac{(1+q_1/\epsilon_1+q_2/\epsilon_2)^2}{1+(\epsilon_1{}^{-1}+\epsilon_2{}^{-1})^2}, \tag{4}$$

where $i=0$, 1, and 2 denote the resonances $6^2P_{1/2}$, $6^2D_{3/2}$, and $6^4P_{3/2}$ at 67137, 62112, and 49826 cm^{-1}, respectively, and $\epsilon_i=(E-E_i)/\frac{1}{2}\Gamma_i$ are the energy parameters. E_i, Γ_i, and q_i determine position, width, and shape of the resonances; $Q^0(E)$ are the photoionization cross sections in the absence of autoionization.

Before the measurements were made, approximate values for the photoelectron polarization were calculated as follows[3]: The parameters in Eq. (4) were chosen so that the experimental values for $Q(E)=Q_S(E)+Q_D(E)$ were obtained. For this fit the energy dependence of $Q_S{}^0$ and $Q_D{}^0$ was assumed to be smooth. With the parameters thus obtained one has $Q_S(E)$ and $Q_D(E)$ so that the polarization $P(E)$ could be calculated from Eq. (1). The result is the full (broken) curve in Fig. 1(a), if the fit is based on the full (broken) cross section in Fig. 1(b).

Comparison of the polarization curve thus obtained with the experimental results between 1860 and 2030 Å shows a significant discrepancy: Whereas the minimum of the polarization curve that is based on the cross-section measurements is located at 49870 cm^{-1}, we find the experimental minimum at about 50500 cm^{-1}. (The results at larger wave numbers have been included for completeness; the differences between experimental and calculated results in this region have a trivial reason which has been discussed before[3]: uncertainties of the experimental cross sections on which the calculated polarization is based.)

Let us now discuss how experimental error sources which might produce such a shift have been excluded. Although in the polarization measurements a rather large bandwidth of the radiation (horizontal error bars) had to be chosen for intensity reasons, Fig. 1(a) shows clearly that this does not cause the discrepancy, the expected and the observed minimum being 630 cm^{-1} apart. The results (without statistical errors) which one would have obtained with a resolution as good as in the cross-section measurements are shown by the dotted line in Fig. 1(a). This line has been calculated by a deconvolution procedure. Another error source which might be suspected in our measurements is an error in the wavelength scale. It has been excluded by repeated calibration of the vacuum-ultraviolet monochromator.[4] The polarization curve which is represented by the full line would also be affected by uncertainties in the cross-section measurements on which it is based. Contrary to the situation near 67000 cm^{-1} these uncertainties are, however, very small around 50000 cm^{-1}. Careful remeasurements[6] have confirmed the position of the cross-section maximum which leads to a polarization minimum at 49870 cm^{-1}.

To be able to explain the apparent contradiction between cross-section and polarization measurements one is compelled to abandon the assumption made above that the wavelength dependence of the cross sections Q^0 is smooth: According to Eq. (1) the polarization yields directly Q_S/Q_D. From this and Eqs. (4) one obtains $Q_S{}^0/$

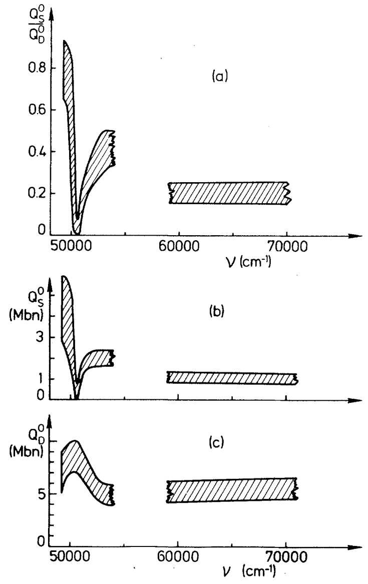

FIG. 2. Ratio of the cross sections for transitions into the S and the D continuum in the absence of autoionization. The curves have been calculated from the experimental polarization (dotted line). (b) Cross section for transitions into the S continuum in the absence of autoionization. The curves have been calculated from the experimental polarization and photoionization cross section. (c) Cross section for transitions into the D continuum in the absence of autoionization. The curves have been calculated from the experimental polarization and photoionization cross section.

Q_D^0, since the parameters ϵ_i and q_i are determined by the cross-section curve $Q_S + Q_D$. The result of this evaluation is shown in Fig. 2(a). The hatched areas illustrate the experimental uncertainty. At wave numbers where the curves are interrupted the polarization could not be measured because of the small photoionization cross section and low radiation intensity. If, in addition to the polarization values, the observed cross sections are utilized, one obtains from Eqs. (3) and (4) Q_S^0 and Q_D^0 separately. As illustrated by Figs. 2(a) and 2(b), the assumption of smooth wavelength dependence may be justified for Q_D^0 but not for Q_S^0. Q_S^0 has a minimum which must be of the type predicted by Msezane and Manson, since an autoionizing state of the S channel is not known in the region where the minimum occurs.

The calculations made so far by Manson do not yield the minimum of Fig. 2(b) for the ground state of thallium.[10] A possible reason for this could be that interchannel interaction due to many-body effects is not considered in these calculations. That interchannel interaction could probably play an important role near the ${}^4P_{3/2}$ resonance is indicated by the zero value of the resonance minimum, measured by two independent experiments[6,11] (in contradiction to Ref. 5). If the total cross section $Q_S + Q_D$ is zero, then both parts must separately vanish. This would occur if the resonance at 49 826 cm^{-1} (so far classified as ${}^4P_{3/2}$) could couple with both the D and the S continuum as a result of interchannel interaction. Up to now a quantitative explanation of the zero minimum of $Q_S + Q_D$ has not been given.

One might wonder why the minimum of Q_S^0 shown in Fig. 2(b) has not been observed in the total cross section Q measured by Ref. 5. As can be seen from the well-established value of Q at 57 300 cm^{-1}, where $Q_D = 0$, the partial cross section Q_S is usually of the order of 0.5 Mb and thus one order of magnitude smaller than Q_D in the wavelength range of interest. Therefore the minimum of Q_S (which results from the minimum of Q_S^0) is masked in $Q = Q_S + Q_D$ by Q_D. The most one could expect is a slight shoulder, which could not be detected in Ref. 5 because the shape of the cross-section curve is uncertain within the experimental error of ±16%. This high uncertainty of ± 0.7 Mb was caused by the difficulties of the measurement of the light intensity $I(E)$. [It is worth noting that the light intensity $I(E)$ does not have to be known for the measurement of the polarization $P(E)$, since the polarization is directly obtained from the ratio of the electron intensities in the two counters of the Mott analyzer.] It is interesting to see that newer results of the cross-section measurements[11] do show a shoulder in the wavelength range of interest, although this shoulder is not explained by the authors.

Even the nonexistence of a shoulder of $Q = Q_S + Q_D$ would still be compatible with a minimum in Q_S: Variations of Q_S can be compensated by Q_D so that the resulting $Q = Q_S + Q_D$ is smooth. Indeed, the values of Q_D^0 which are based on the results of Ref. 5 and are shown in Fig. 2(c) increase more rapidly with decreasing wave number than those one would obtain from the results of Ref. 11. These differences are, however, within the error limits given for Q_S^0 and Q_D^0.

Summarizing we can say that the polarization measurements give evidence of a minimum of the cross section Q_S^0 for phototransitions $6P \rightarrow \epsilon S$ of thallium in the absence of autoionization. This minimum is masked by the cross section Q_D so that a conventional cross-section measurement which yields $Q = Q_S + Q_D$ would be an unsuitable way of detecting it. A quantitative explanation of the minimum cannot be given at the moment. This example demonstrates, for a somewhat involved case, how spin-polarization measurements yield new information on the photoionization process that cannot be obtained from cross-section measurements alone.

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Detailed Study of Recombination: The Importance of the Rydberg State in Electron-H_2^+ Recombination*

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In the case of e-H_2^+ recombination the formation of Rydberg states of the molecule is an important channel through which recombination occurs. Through the energy interval 0.01 to ~4 eV, the direct H+H pair-production process is in direct competition with the indirect one which proceeds through an intermediate bound Rydberg state H_2^R. In the experiment one can see clear evidence of autoionization competing with predissociation and H^+-H^- pair production, particularly when vibrational levels $v > 2$ are suppressed in the H_2^+ beam.

In 1943 Sayers proposed to Bates[1] that inverse autoionization might explain the high rate of recombination of electrons and ions in the ionosphere. This process, now called dielectronic recombination, has been identified as the dominant mechanism for high-energy electrons to recombine with atomic ions, but it has generally been thought insignificant in the case of molecular ions. Although it has been suggested by Bardsley[2-4] and Chen and Mittleman[5] that the indirect process involving the temporary formation of bound H_2^R Rydberg states might be important, the model based upon the process which proceeds directly from e-H_2^+ to H+H originally proposed by Bates[6] and subsequently detailed by Bardsley[3,4] and Bottcher and Docken[7] has been accepted as the primary mechanism for recombination.

With the studies reported in this note, we have