

Relaxation and polarization effects in valence photodetachment of the negative fluoride and bromide ions

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The photodetachment cross sections, branching ratios, and angular-distribution asymmetry parameters have been calculated for F^- and Br^- in the relativistic random-phase approximation (RRPA) and modifications of the RRPA that allow for the inclusion of relaxation and core-polarization effects. Photodetachment cross sections are compared with experimental measurements to assess the effectiveness of the various approximations. The effects of core polarization are found to partially cancel relaxation effects.

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I. INTRODUCTION

The study of photodetachment of negative-ion systems provides an excellent probe of various electron correlation effects. In some cases the many-body interactions play a very important role since the core fields are neutral rather than Coulombic in nature as they would be for photoionization of neutral atoms or positive ions. Experimental data on photodetachment of negative ions is very limited in comparison with the corresponding photoionization data for neutral species. Such data is of practical importance in the study of opacities in the solar and stellar atmospheres as well as processes in the atmosphere of the Earth [1]. In the 1970's Mandl reported measured near-threshold photodetachment cross sections of the negative halide ions with an estimated accuracy of $\pm 20\%$. The measurements included total cross sections of Cl^- and Br^- [2] and F^- [3] and I^- [4].

Theoretical methods that have been successful in treating many-body effects in neutral atoms have also been applied to valence photodetachment of negative ions. These techniques include many-body perturbation theory (MBPT) [5], the method of Stieltjes imaging [6], close coupling [7], R matrix [8], multichannel quantum-defect theory [9], the random-phase approximation with exchange [10], and the relativistic random-phase approximation (RRPA) [11]. The effects of relaxation on inner-shell photodetachment have been considered for I^- [12] and Br^- [13] using the relativistic random-phase approximation modified to include relaxation effects. The theoretical progress in photodetachment studies has been documented in the excellent review by Ivanov [14].

Very recently, Kutzner, Robertson, and Pelley [15] reported results of a calculation of valence photodetachment of the negative chloride ion using the relativistic random-phase approximation modified to include relaxation and polarization effects (RRPARP). It was found that the inclusion of a polarization potential partially cancelled the effects of relaxation and improved agreement with experiment [2]. This pa-

per is a report on the application of the RRPARP to the negative halide ions F^- and Br^- . The methods used are described in Sec. II and the results are reported in Sec. III. Some of the implications of the paper are discussed in Sec. IV.

II. METHODS

The RRPA [16] has proven to be a very successful method for including the effects of interchannel coupling in calculations of photoionization parameters of closed-shell systems. Radojević, Kutzner, and Kelly [17] modified the RRPA to include relaxation effects (RRPAR) by calculating the continuum orbitals in the potential of the relaxed core. For a neutral atom, the relaxed core is a positive ion whereas for photodetachment of negative ions the relaxed core is the neutral atom. In the RRPARP, we add a polarization potential of the form [18],

$$V_{\text{pol}}(r) = -\frac{\alpha_d}{2(r^2 + h^2)^2}, \quad (1)$$

where α_d is the static dipole polarizability of the core and h is a cutoff radius (approximately the size of the valence electron cloud) which prevents the potential from becoming unmanageable for small radii.

Similar polarization potentials have been used previously for neutral atoms in the eigenchannel R -matrix approach [19] with the polarizability and cutoff radius treated as parameters determined semiempirically by optimizing the fitted agreement between the calculated and experimental energy levels. Such an approach is not possible when dealing with negative halide ions not possessing bound-excited states.

In the present paper, both α_d and h are determined from *ab initio* calculations. Polarizabilities for the neutral atoms F (3.76 a.u.) and Br (20.6 a.u.) are from coupled-electron-pair approximation (CEPA) calculations of Werner and Meyer [20,21]. These calculations contain most of the important valence-shell and intershell correlation and are considered to be accurate to within 2%. The cutoff radius h , was determined by requiring that $V_{\text{pol}}(0)$ be approximately equivalent to the energy correction of the valence orbitals. This condition may be expressed as

$$V_{\text{pol}}(0) \approx \Delta E_{\text{SCF}}(\text{valence}) - |\epsilon_{\text{valence}}|, \quad (2)$$

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TABLE I. Values of parameters used in calculation of polarization potentials for the negative halide ions F^- and Br^- in atomic units. Values used in a previous Cl^- calculation [15] are also shown to demonstrate the trend down the halide group. The second column is the experimental threshold energy Ref. [23]. The third column is the absolute value of the difference between the total ground-state self-consistent-field energies of the halide ion and the neutral halogen atom. Column four is the absolute value of the DHF eigenvalue. Column five is the difference between column three and column four. Column six is the CEPA dipole polarizability of the neutral halogen atoms, Refs. [20,21]. Column seven is the cutoff radius calculated from Eq. (3).

Ion	Expt	ΔE_{SCF}	$ \epsilon $	$V_{pol}(0)$	α_d	h
F^-	0.1249	0.04 897	0.17 965	-0.13 068	3.76	1.95
Cl^-	0.1329	0.09 274	0.14 799	-0.05 525	14.8	3.40
Br^-	0.1237	0.08 725	0.13 103	-0.04 378	20.6	3.92

where $\epsilon_{valence}$ is the Dirac-Hartree-Fock (DHF) eigenvalue and ΔE_{SCF} is the absolute value of the difference between the total ground-state self-consistent-field energies of the halide ion and the neutral halogen atom. Equations (1) and (2) may be combined to determine the value of the parameter h yielding

$$h = \sqrt[4]{-\alpha_d / \{2[\Delta E_{SCF}(valence) - |\epsilon_{valence}|]\}}. \quad (3)$$

The energy correction of Eq. (2) was determined using the Oxford multiconfiguration Dirac-Fock computer code of Grant *et al.* [22]. Table I lists the values of the energies, polarizabilities, and cutoff radii used in these calculations. The experimental photodetachment thresholds are from Ref. [23] with an estimated uncertainty of $\pm 7 \times 10^{-5}$ a.u.

Photodetachment transition matrix elements were calculated using the RRPA code of Johnson *et al.* [16], the RRPAP, which is a modified RRPA including relaxation effects [17], and the RRPARP, which includes relaxation effects as well as the polarization potential of Eq. (1) added to the single-particle potential for the calculation of RRPA excited-state orbitals. The F^- calculations included interchannel coupling between all nine dipole-allowed channels in jj coupling, namely,

$$1s_{1/2} \rightarrow \epsilon p_{3/2}, \epsilon p_{1/2},$$

$$2s_{1/2} \rightarrow \epsilon p_{3/2}, \epsilon p_{1/2},$$

$$2p_{1/2} \rightarrow \epsilon d_{3/2}, \epsilon s_{1/2},$$

$$2p_{3/2} \rightarrow \epsilon d_{5/2}, \epsilon d_{3/2}, \epsilon s_{1/2}.$$

For Br^- , we included coupling between 20 channels,

$$3s_{1/2} \rightarrow \epsilon p_{3/2}, \epsilon p_{1/2},$$

$$3p_{1/2} \rightarrow \epsilon d_{3/2}, \epsilon s_{1/2},$$

$$3p_{3/2} \rightarrow \epsilon d_{5/2}, \epsilon d_{3/2}, \epsilon s_{1/2},$$

$$3d_{3/2} \rightarrow \epsilon f_{5/2}, \epsilon p_{3/2}, \epsilon p_{1/2},$$

$$3d_{5/2} \rightarrow \epsilon f_{7/2}, \epsilon f_{5/2}, \epsilon p_{3/2},$$

$$4s_{1/2} \rightarrow \epsilon p_{3/2}, \epsilon p_{1/2},$$

$$4p_{1/2} \rightarrow \epsilon d_{3/2}, \epsilon s_{1/2},$$

$$4p_{3/2} \rightarrow \epsilon d_{5/2}, \epsilon d_{3/2}, \epsilon s_{1/2}.$$

Formally, Dirac-Hartree-Fock eigenvalues are used as threshold energies for the RRPA [16]. To facilitate comparisons with the experiments of Mandl [2,3], we used experimental thresholds [23] for the calculations. Although this undermines the gauge invariance of the strict RRPA results, the length and velocity discrepancy is largely removed when relaxation effects are included in the RRPAP and RRPARP. In the cross section results shown below are presented as the geometric mean of length and velocity since the geometric mean is less sensitive to the effects of ground-state correlation as demonstrated by Hansen [24].

III. RESULTS

The photodetachment cross sections in the RRPA, RRPAP, and RRPARP for F^- are shown in Fig. 1. The experimental measurements of Mandl [3] are also shown for comparison as are MBPT calculations [5] and Stieltjes imaging method [6]. The RRPA result is essentially that which was previously reported by Radojević, Kelly, and Johnson [11]. The effects of core relaxation are seen in the RRPAP result, which leads to a considerable reduction in the cross section that is in close agreement with the MBPT calculations [5] near threshold and with the method of Stieltjes imaging [6] at higher energies. Relaxation effects tend to displace oscillator strength from the near-threshold regions to higher energies. Experience has also shown [18] that the inclusion of only relaxation effects in valence photoionization without the partial cancellation contributed by polarization effects can unbalance the results. Indeed we find in this case, as in the recently reported case of Cl^- [15], that including the polarization potential effects in the RRPARP increases the photodetachment cross section near threshold, partially canceling the effects of the relaxed-core potential. The slope of the cross section is increased near threshold and the value is increased at all energies shown. This effect can also be understood in MBPT by considering the second-order diagrams corresponding to relaxation and polarization in the final state. These MBPT diagrams are similar in structure but opposite in sign [25].

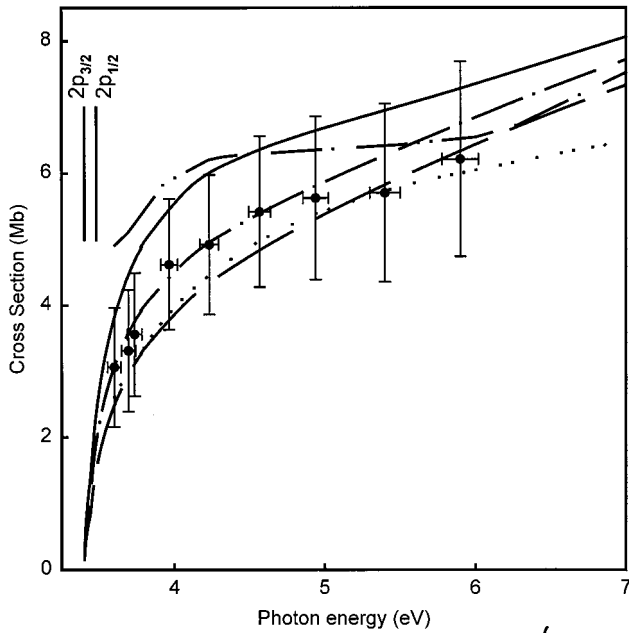


FIG. 1. Photodetachment cross sections for F^- . The solid line is RRPA, the dashed line is RRPAP, which includes relaxation effects. The dot-dashed line is RRPARP, which includes relaxation and polarization effects. The dotted line is the MBPT calculation of Ref. [5]. The dot-double-dashed line is the method of Stieltjes imaging calculation of Ref. [6]. The experimental data points are from Mandl [3].

The branching ratios, $\gamma = \sigma(2p_{3/2})/\sigma(2p_{1/2})$, for F^- are shown in Fig. 2. In all three models, the branching ratio deviates from the statistical value of 2 just above the $2p_{1/2}$ threshold because each partial cross section rises rapidly from zero at their respective thresholds, leading to the $2p_{3/2}$ partial cross section being disproportionately larger in this region. The angular-distribution asymmetry parameters, β , for F^- are shown in Fig. 3. The individual parameters for each subshell $2p_{3/2}$ and $2p_{1/2}$ have been averaged by weighting with their respective partial cross sections:

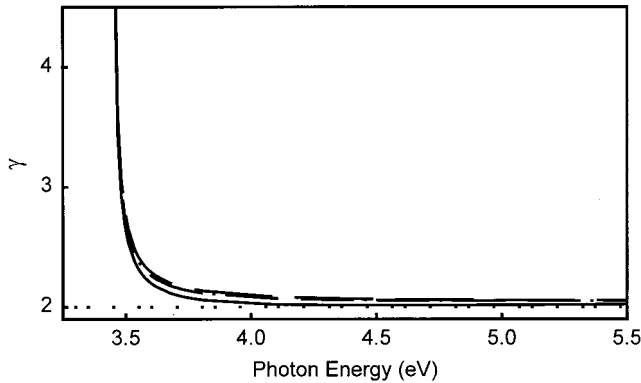


FIG. 2. The branching ratios, $\gamma = \sigma(2p_{3/2})/\sigma(2p_{1/2})$, of F^- . The solid line is RRPA. The long dashed line is RRPAP. The dot-dashed line is RRPARP. The statistical value of 2 is indicated by the dotted line.

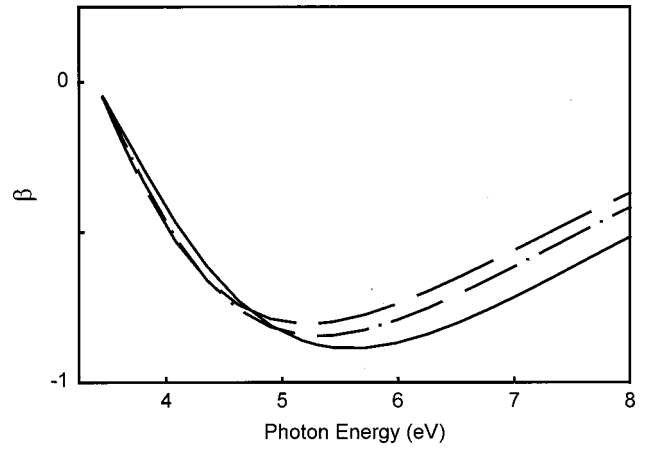


FIG. 3. Angular-distribution asymmetry parameters, β_{2p} , for threshold photodetachment of F^- . The solid line is RRPA. The dashed line is RRPAP. The dot-dashed line is RRPARP.

$$\beta_{\text{ave}} = \frac{\sigma_{3/2}\beta_{3/2} + \sigma_{1/2}\beta_{1/2}}{\sigma_{3/2} + \sigma_{1/2}}. \quad (4)$$

It is interesting that near threshold, where relaxation and polarization effects were pronounced in the cross sections, the effects are small on both the branching ratios and angular-distribution asymmetry parameters because these parameters depend on ratios of cross sections and matrix elements, respectively [26].

The total photodetachment cross sections for Br^- are shown in Fig. 4 in the RRPA, RRPAP, and RRPARP along with the experimental measurements of Mandl [2]. As was noted

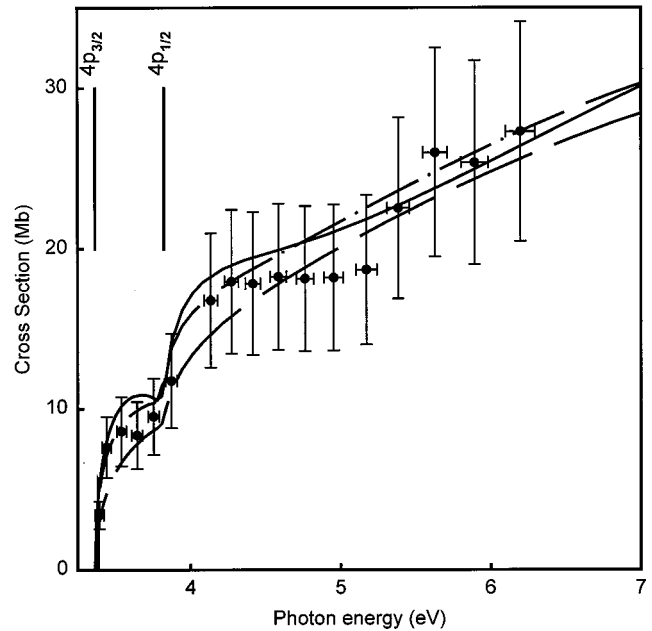


FIG. 4. Photodetachment cross sections for Br^- . The solid line is RRPA. The long dashed line is RRPAP, which includes relaxation effects. The dot-dashed line is RRPARP, which includes relaxation and polarization effects. The solid circles are the experimental cross sections of Ref. [2].

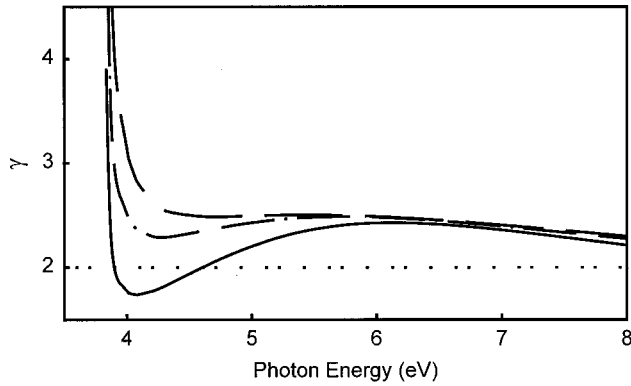


FIG. 5. The branching ratios, $\gamma = \sigma(4p_{3/2})/\sigma(4p_{1/2})$, of Br^- . The solid line is RRPA. The long dashed line is RRPAR. The dot-dashed line is RRPARP. The statistical value of 2 is indicated by the dotted line.

for both Cl^- [15] and F^- , the effect of core relaxation is to reduce the cross section near threshold. The inclusion of polarization effects in the RRPARP, almost completely cancels the relaxation effects for the bromide ion. From Table I, it is seen that moving down the group from F to Br to species with more electrons, larger Z, and larger atomic radii, the magnitude of the polarization potential is affected by two parameters, which partially offset each other, the polarizability and the cutoff radius. Although the polarizability increases down the group, so does the cutoff radius that prevents the polarization potential from becoming too large.

Interestingly, the branching ratios, $\gamma = \sigma(4p_{3/2})/\sigma(4p_{1/2})$, and angular-distribution asymmetry parameters for Br^- shown in Figs. 5 and 6, respectively, are much more sensitive to relaxation and polarization effects than was noted above for F^- . The larger magnitude of spin-orbit splitting between valence p orbitals with different j values for Br^- allows for larger variations in the branching ratios.

IV. CONCLUSIONS

The results of these photodetachment calculations on the negative halide ions F^- and Br^- along with the previously

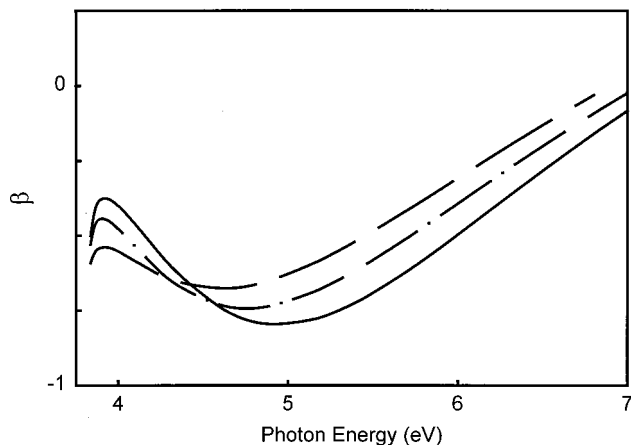


FIG. 6. Angular-distribution asymmetry parameters, β_{4p} , for threshold photodetachment of Br^- . The solid line is RRPA. The dashed line is RRPAR. The dot-dashed line is RRPARP.

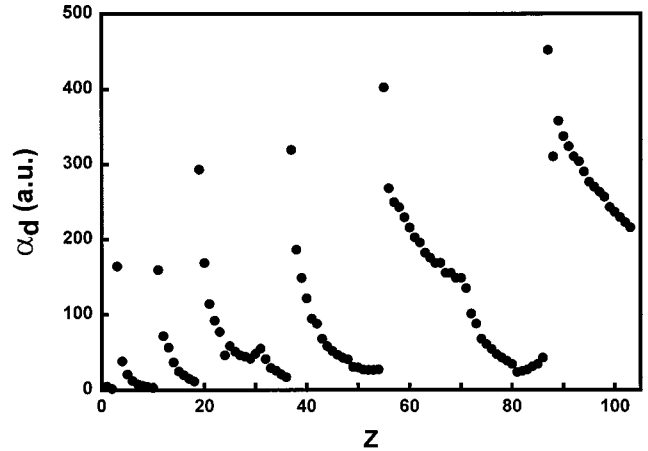


FIG. 7. Dipole polarizabilities for elements $Z=1$ through 103 from Ref. [21]. Accuracy varies from 2% or better for $Z = 1 - 19, 30 - 37, 54,$ and 55 to 50% for most other elements.

reported calculation for Cl^- [15], highlight the importance of including relaxation and polarization effects. It would appear that including core-relaxation effects in valence-shell calculations without also including polarization, leads to results that give a consistently low cross section relative to the experiments. Polarization effects are seen to partially cancel relaxation effects. A notable trend is the increasing effects of relaxation and polarization on the branching ratios and angular-distribution asymmetry parameter with increasing Z, because of the increasing relevance of spin-orbit effects. More accurate experimental measurements of the photodetachment cross sections would greatly enhance our ability to assess the theoretical models. Experimental determinations of the branching ratios and angular-distribution asymmetry parameters would also be welcomed. Future application of the RRPARP technique to even heavier systems such as I^- and At^- will enhance our understanding of such trends.

Figure 7 is a plot of dipole polarizabilities taken from data reported in Miller and Bederson [21] as a function of atomic number Z, for elements $Z=1$ to 103. This plot is of interest when considering which negative ions might exhibit large polarization effects in photodetachment cross sections. Clearly, the alkali-metal atoms and alkaline-earth-metal atoms have the largest polarizabilities, leading one to assume that polarization effects will be large for negative ions of these systems. However, as we have seen in this study of negative halogen ions, the magnitude of the polarizability of the neutral core is not the sole indicator of the importance of polarization effects in photodetachment. Indeed, the polarizability of Br is approximately 5.5 times larger than the polarizability of F, yet the effect of the polarization potential on the photodetachment cross section is not as large because the atomic radius (and therefore the cutoff radius h) is also larger. A more suitable indicator may be $V_{\text{pol}}(0)$, which may be estimated from Eq. (2).

It would also be of interest to apply the RRPARP to inner-shell photoionization. Radojević and Kelly [12] have already

determined that relaxation effects are important in photodetachment of $4d$ electrons in I^- . It is likely that polarization effects are also important. The technique is not limited to negative ions and should be applied to photoionization of the $4d$ subshell of barium where MBPT calculations [27] have already established the importance of both relaxation and polarization effects.

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