Structural and spectroscopic study of the excited electronic states of silver dihalides by quantum chemical methods

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The structural and electronic properties of the excited electronic states of AgX_2 (X = F, Cl, Br, and I), have been calculated, taking electron correlation and spin–orbit coupling into account and employing improved relativistic-effective-core potentials for silver and the halogen atoms. The relative ordering of the excited states of these molecules has been discussed *via* molecular-orbital arguments. The spin–orbit splittings of three degenerate electronic states ($^2\Pi_g$, $^2\Pi_u$, and $^2\Delta_g$) have been calculated and the spin–orbit induced inter-state ($\Sigma - \Pi$) coupling has been discussed. The composition of the spin–orbit eigenstates is analyzed in terms of scalar-relativistic electronic states. Finally, a theoretical prediction of the photodetachment bands of the title molecules has been accomplished.

1. Introduction

The group XI metals, also known as coinage metals, have long held a special status in the periodic table due to their broad range of industrial applications in the field of medicine, catalysis, and material science. From a theoretical point of view, these metals serve as textbook examples of relativistic effects.[1] Among the complexes of these metals, the halides of silver have received much attention due to their practical applications. The chemistry of monovalent silver halide complexes are well studied by experimental[2–4] and theoretical[5,6] methods. Among dihalide silver complexes, $AgCl_2$ has been studied by Ramírez-Solís *et al.* by multireference perturbation theory and density functional theory.[7] They have calculated the adiabatic excitation energies and spin–orbit (SO) splittings of the excited states of $AgCl_2$. Silver dibromides, along with silver subbromides, have been studied by Rabilloud *et al.* focusing on the structural properties and stability of these complexes.[8] Recently, the structure and bonding of mono-, bi-, and tri-halides of silver have been studied by Müller-Rösing *et al. via* single-reference electronic structure methods.[9] For silver dihalides, their study is restricted to the lowest two electronic states. Among the pure silver dihalides, only AgF_2 is known experimentally and has been characterized structurally.[10,11] In addition to the neutral silver dihalides, their anionic counterparts have also received some attention. Waters and Basak have indicated the presence of linear, centrosymmetric silver dihalide anions in solution[12] and Cras *et al.* have structurally characterized $AgBr_2^-$.[13] Helgesson and Jagner have characterized $AgCl_2^-$ in the solid state.[14]

Schröder *et al.* have reported an experimental study of gaseous gold dihalides *via* photodetachment spectroscopy (PDS) of the corresponding anions and *via* sector-field mass spectrometry using charge-reversal and neutralization reioni-zation techniques in conjunction with the related neutral-and-ion decomposition difference method, see ref. 15. Recently, we assigned their photodetachment spectra by employing multi-reference quantum chemical methods and emphasized the importance of SO coupling in the spectroscopy of gold dihalides.[16,17] In the present work, we extend our previous study to silver dihalides by performing *ab initio* electronic structure calculations on AgX_2 and AgX_2^- (X = F, Cl, Br, and I), with explicit consideration of SO coupling. The present study leads to the prediction of the PDS of AgX_2^-.

2. Computational method

The AgX_2^-, X = F, Cl, Br, and I, are closed shell linear molecules in their ground electronic state, $X\,^1\Sigma_g^+$, with the following valence shell electronic configuration: $1\sigma_g^2\,1\sigma_u^2\,1\pi_u^4\,2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,1\pi_g^4\,1\delta_g^4\,3\sigma_u^2\,2\pi_u^4\,4\sigma_g^2\,2\pi_g^4$. Electron detachment from the latter eight molecular orbitals, of which three are electronically doubly degenerate, is the central focus of this work. In this section we will describe the strategy of the *ab initio* electronic-structure calculations of the title systems.

We describe silver atoms by the recently developed two-component relativistic-effective-core potentials (RECP) of the energy-consistent variety.[18] These pseudopotentials containing both scalar-relativistic and SO operators replace the 1s–3d core shells of the Ag atom, thereby reducing the burden of explicit treatment of 28 chemically inactive core electrons. In addition to this, the present pseudopotentials enable one to simulate a fully relativistic treatment including SO effects, since they are derived from a fitting procedure to reproduce four-component multi-configuration Dirac-Hartree–Fock (DHF) data.[18] The valence electrons of Ag are described *via* an energy optimized [12s12p9d3f2g]/[6s6p4d3f2g] basis set. For the halogen atoms, except fluorine, we have employed one-component (*i.e.*, SO averaged) semi-local energy-adjusted pseudopotentials to describe the core, *i.e.*, 1s–2p for Cl (10 electrons), 1s–3d for Br (28 electrons), and 1s–4d for I (46 electrons).[19] The valence electrons of Br and I are described by

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the basis sets of augmented quadruple-zeta quality, composed of optimized contracted s, p, d, f, and g functions,[19] while the valence shell of Cl is described by optimized contracted s and p functions of augmented quadruple-zeta quality.[20] The d, f, and g polarization functions are obtained from the augmented correlation-consistent polarized valence quadruple-zeta (aug-cc-pVQZ) basis set of Woon and Dunning.[21] For fluorine atoms all electron aug-cc-pVQZ basis set of Woon and Dunning are used. A core-polarization-potential (CPP)[22] calculation for the Cl, Br, and I centers is performed during every calculation, using the CPP parameters taken from ref. 19. All calculations are performed in the largest Abelian point group of the molecules, *i.e.*, D_{2h}.

The geometries of the AgX_2 anions have been optimized in their ground electronic state ($\tilde{X}\,^1\Sigma_g^+$) by a coupled-cluster calculation with singles and doubles and perturbative account of triple excitations (CCSD(T)).[23] In addition to this, the ground and first excited states of the neutral (open-shell) species are also optimized *via* a spin-restricted CCSD(T) method in which singles, doubles and perturbative triple corrections are obtained by excitation out of a high-spin restricted-Hartree–Fock (RHF) reference wave function. The lowest four valence orbitals (corresponding to the 4s and 4p atomic orbitals of Ag) were kept frozen in all the calculations. In case of AgF_2, the 1s atomic orbitals of F atoms are also kept frozen.

For an accurate electron correlation we have employed the multi-reference configuration interaction (MRCI) method,[24,25] which uses state-averaged (over the lowest $^2\Pi_{g/u}$, $^2\Sigma_{g/u}^+$, $^2\Delta_g$ states, with equal weight) complete-active-space self-consistent-field (SA-CASSCF)[26,27] orbitals as N-electron basis, for a scalar relativistic description of the lowest eight electronic states at the reference geometry of the anion. While CASSCF calculation captures the static electron correlation, the dynamic part of the electron correlation is extracted *via* MRCI calculation. To account for the size-consistency problem, the MRCI energy with Davidson correction[28] is used while calculating the vertical detachment energies. The active space involves all but eight (12 in case of AgF_2) valence electrons, correlated in 14 orbitals, *i.e.*, 25 electrons are correlated in 14 orbitals.

The MRCI wave functions obtained from the above mentioned scalar-relativistic electron correlation calculation are further used to calculate the Breit-Pauli SO matrix elements, where the most important two-electron contributions of the SO operator are incorporated by means of an effective one-electron Fock operator, as described in ref. 29 and as implemented in the Molpro package.[30] The diagonalization of the SO matrix in the space of all SO-free electronic states of interest finally provides information of the SO eigenstates. While the eigenvalues of the SO matrix reveal the SO splittings in the degenerate states, the eigenvectors are used to determine the composition of the SO eigenstates in terms of the SO-free states. It should be noted that the present way of treating SO effects, where electron correlation and SO coupling are calculated separately, is sufficiently accurate for the valence electronic states. For the low-lying orbitals, however, the electron correlation in the presence of SO coupling is important, part of which is reproduced by using the pseudopotentials fitted to four-component multi-configuration DHF data.[18] For a complete description of the electron correlation of the low-lying orbitals in the presence of SO coupling, one should employ computationally demanding relativistic four-component CASSCF/MRCI methods.[31]

All calculations reported in this work have been performed using the MOLPRO program suite.[30]

3. Results and discussion

The optimized geometries of the ground state ($\tilde{X}\,^1\Sigma_g^+$) of the closed-shell AgX_2^- are given in Table 1 along with the optimized geometries of the neutral species in their $^2\Pi_g$ and $^2\Sigma_g^+$ states. Our results are also compared with the geometries calculated by other authors, where available, see Table 1. As expected, the metal–halogen bond distances increase for heavier halides. The bond distances of the anions are calculated to be longer than the corresponding neutral species. The decrease in the Ag–X bond length in the $^2\Pi_g$ state of the neutral species, as compared to the Ag–X bond length in the $\tilde{X}\,^1\Sigma_g^+$ state, is due to the π-type antibonding overlap between the $4d_{xy}$ orbital of Ag atom and the np_x orbital of the halogen atoms in the $2\pi_g$ molecular orbital (MO), from which the $^2\Pi_g$ electronic state emanates. Here n is the valence principal quantum number, *i.e.*, 2, 3, 4, and 5 for F, Cl, Br, and I, respectively. This antibonding overlap, and hence the degree of bond-length reduction from anion to neutral species, decreases with increasing halogen size due to the poor overlap between Ag and the halogen orbitals. The same reason is again true for the reduced bond length of the neutral species in their $^2\Sigma_g^+$ state, which originates from the $4\sigma_g$ MO. In the $4\sigma_g$ MO, the $4d_{z^2}$ orbital of the Ag atom participates in a σ-type antibonding overlap with the np_z orbitals of the halogen atoms.

The vertical detachment energies of the lowest eight electronic states (the two nondegenerate and the three doubly degenerate states) with respect to the electronic ground state of the anion ($\tilde{X}\,^1\Sigma_g^+$), calculated *via* the SA-CASSCF/MRCI (with Davidson correction) method, are reported in Table 2. Since the energy spacing of the electronic states of the neutral AgX_2 matters, rather than the absolute values of the vertical detachment energies, we have also reported, in Table 2, the difference in vertical detachment energies of the excited states of the neutral AgX_2 with respect to its ground state. While going from AgF_2 to AgI_2, there occur several reorderings of the electronic states. While the $^2\Sigma_g^+$ state is the ground state

Table 1 Optimized bond distances (in Å) at the CCSD(T) level for the $\tilde{X}\,^1\Sigma_g^+$ state of AgX_2^-, and the $^2\Sigma_g^+$ and $^2\Pi_g$ states of AgX_2

	$^1\Sigma_g^+$	$^2\Pi_g$	$^2\Sigma_g^+$
AgF_2	2.017	1.886	1.888
		1.889^a	1.891^a
$AgCl_2$	2.291	2.171	2.209
		2.239^a	2.253^a
		2.282^b	2.286^b
$AgBr_2$	2.456	2.366	2.383
		2.351^a	2.375^a
AgI_2	2.626	2.554	2.600
		2.546^a	2.586^a

^{a} Ref. 7. ^{b} Ref. 9.

Table 2 Scalar-relativistic detachment energies (in eV) from the $\tilde{X}\,^1\Sigma_g^+$ state of AgX_2^- computed by the MRCI/SA-CASSCF method. The values in parentheses refer to the MRCI/SA-CASSCF results with the vertical detachment energy of the ground state adjusted to zero

State	AgF$_2$	State	AgCl$_2$	State	AgBr$_2$	State	AgI$_2$
$\tilde{X}\,^2\Sigma_g^+$	2.881	$\tilde{X}\,^2\Sigma_g^+$	5.245	$\tilde{X}\,^2\Pi_g$	6.349	$\tilde{X}\,^2\Pi_g$	6.739
$\tilde{A}\,^2\Pi_g$	3.678 (0.797)	$\tilde{A}\,^2\Pi_g$	5.369 (0.124)	$\tilde{A}\,^2\Pi_g^+$	6.612 (0.263)	$\tilde{A}\,^2\Pi_u$	7.225 (0.486)
$\tilde{B}\,^2\Delta_g$	5.156 (2.235)	$\tilde{B}\,^2\Pi_u$	6.386 (1.141)	$\tilde{C}\,^2\Pi_u$	7.003 (0.654)	$\tilde{B}\,^2\Sigma_g^+$	7.381 (0.642)
$\tilde{C}\,^2\Pi_u$	5.527 (2.646)	$\tilde{C}\,^2\Sigma_u^+$	6.614 (1.369)	$\tilde{C}\,^2\Sigma_u^+$	7.224 (0.875)	$\tilde{C}\,^2\Sigma_u^+$	7.436 (0.697)
$\tilde{D}\,^2\Sigma_u^+$	5.551 (2.670)	$\tilde{D}\,^2\Delta_g$	7.513 (2.268)	$\tilde{D}\,^2\Delta_g$	8.990 (2.641)	$\tilde{D}\,^2\Delta_g$	9.929 (3.190)

for the neutral AgF_2 and $AgCl_2$, this state is the first and the second excited state, respectively, for the neutral $AgBr_2$ and AgI_2, where the $^2\Pi_g$ state is the ground state. As mentioned above, while the $4\sigma_g$ MO exhibits an antibonding σ overlap between the metal and the ligand atoms, the $2\pi_g$ MO exhibits an antibonding π overlap between them. In case of the lighter dihalides, the antibonding σ (head-on) overlap destabilizes the $4\sigma_g$ MO as compared to the $2\pi_g$ MO, where a π-type (side-wise) overlap takes place. Therefore, the $^2\Sigma_g^+$ is the ground state in case of AgF_2 and $AgCl_2$. The overlap in the $4\sigma_g$ and the $2\pi_g$ orbitals, however, decreases with increasing halogen size. For heavier halides, the $4\sigma_g$ MO becomes increasingly more metal centric (i.e., develops a nonbonding character) whereas the $2\pi_g$ MO still exhibits an antibonding π overlap between the metal and the halogen atoms. This leads to the stabilization of the $4\sigma_g$ MO with respect to the $2\pi_g$ MO in case of heavier halides, thus making the $^2\Pi_g$ state the ground state in case of $AgBr_2$ and AgI_2.

The higher excited states: $^2\Delta_g$, $^2\Sigma_u^+$, and $^2\Pi_u$, of AgX_2 originate from the $1\delta_g$, $3\sigma_u$, and $2\pi_u$ MOs of AgX_2^-. The $2\pi_u$ and the $3\sigma_u$ orbitals are ligand centered with the former showing a bonding π orientation and the latter showing an antibonding σ orientation between the two side halogen atoms. The $1\delta_g$ state, on the other hand, is metal centric, consisting of nonbonding $4d_{x^2-y^2}$ orbital of the Ag atom. With increasing halogen size, the metal–halogen bond distance increases and thus increases the separation between the two side halogen atoms. This causes a destabilization of the $2\pi_u$ MO in heavier halides that results in having the $^2\Pi_u$ state as the first excited state in AgI_2, see Table 2.

The calculated SO splittings in the $^2\Pi_g$, the $^2\Pi_u$, and the $^2\Delta_g$ states of AgX_2 are given in Table 3. The SO splitting of both the $^2\Pi$ states increases, as expected, from AgF_2 to AgI_2, with the exception of the unexpectedly large SO splitting of the $^2\Pi_g$ state of AgF_2. The large SO splitting of the $^2\Pi_g$ state of AgF_2, as compared to that of $AgCl_2$, is due to the large metal character of the $2\pi_g$ MO of AgF_2. Unlike the $^2\Pi_{g/u}$ states, the SO splitting of the $^2\Delta_g$ state remains nearly the same (ca.

Table 3 SO splittings (in eV) of the $^2\Pi_g$, $^2\Pi_u$, and $^2\Delta_g$ states of AgX_2, computed in the basis of the $^2\Pi_g$, $^2\Pi_u$, $^2\Delta_g$, $^2\Sigma_g^+$, and $^2\Sigma_u^+$ SO-free states. Values in parentheses refer to the results obtained when the concerned state is assumed isolated

	$^2\Pi_g$	$^2\Pi_u$	$^2\Delta_g$
AgF$_2$	0.1869 (0.1420)	0.0012 (0.0036)	0.4069 (0.3910)
AgCl$_2$	0.1669 (0.1284)	0.0997 (0.0782)	0.3974 (0.3909)
AgBr$_2$	0.2705 (0.2887)	0.1215 (0.2918)	0.3928 (0.3901)
AgI$_2$	0.4475 (0.5632)	0.9569 (0.5744)	0.3907 (0.3894)

0.39 eV) for all the species reflecting the fact that the $^2\Delta_g$ state originates from the MO localized over the central Ag atom. The calculated SO splitting in the $^2\Delta_g$ state of AgX_2 is quite similar to the atomic SO splitting of the 4d orbital of Ag (0.55 eV).[32] In Table 3, the numbers in parentheses are the SO splitting of the corresponding degenerate states when their coupling with neighboring states are neglected, i.e., when they are assumed isolated. When compared with the true SO splitting, these numbers reveal the extent of interaction between different SO-free states via the SO coupling operator.

The true SO splittings in the $^2\Pi_g$ state of AgF_2 and $AgCl_2$ are larger than the SO splittings calculated under isolated $^2\Pi_g$ approximation, see the first column of Table 3. For $AgBr_2$ and AgI_2, however, this trend is opposite. This observation can be rationalized from the relative ordering of the scalar relativistic $^2\Pi_g$ and $^2\Sigma_g^+$ states. Since the $^2\Sigma_g^+$ state lies below the $^2\Pi_g$ state in the lighter halides, the interaction between the low-lying $^2\Sigma_{g,1/2}^+$ and the high lying $^2\Pi_{g,1/2}$ states, via the SO operator, pushes the latter state to a still higher energy, thus increasing the SO splitting of the $^2\Pi_g$ state. The opposite happens in the heavier halides, where the high-lying $^2\Sigma_{g,1/2}^+$ state pushes the low-lying $^2\Pi_{g,1/2}$ further down in energy, thereby decreasing the SO splitting in the $^2\Pi_g$ state of $AgBr_2$ and AgI_2, see Table 3.

Since the $^2\Pi_u$ state emanates from the MO centered on the halogen atoms, the SO splitting in this state increases, rather uniformly, from AgF_2 to AgI_2. The true SO splitting and the SO splitting under the isolated $^2\Pi_u$ state approximation are found to differ substantially in $AgBr_2$ and AgI_2. This difference in AgF_2 and $AgCl_2$ is rather minimal. This is due to the strong mixing of the $^2\Pi_u$ and the $^2\Sigma_u^+$ states in case of $AgBr_2$ and AgI_2, see Tables 3 and 4. While the SO splitting under an isolated state approximation is larger than the true SO splitting of the $^2\Pi_u$ state in $AgBr_2$, the reverse is true for AgI_2. In case of $AgBr_2$, the $^2\Sigma_u^+$ state lies above the $^2\Pi_u$ state, see Table 2, and hence via the SO operator the 1/2 component of the latter is pushed down in energy leading to a reduction of the SO splitting of the $^2\Pi_u$ state. In case of AgI_2, although the SO-free $^2\Sigma_u^+$ state lies higher in energy than the SO-free $^2\Pi_u$ state, the large SO splitting of the $^2\Pi_u$ state of AgI_2 leads to the positioning of the $^2\Sigma_{u,1/2}^+$ SO eigenstate in between the two SO components of the $^2\Pi_u$ state. The interaction between the 1/2 components of the $^2\Sigma_u^+$ and the $^2\Pi_u$ states leads to an increase of true SO splitting of the $^2\Pi_u$ state compared to its value when the SO-induced Σ–Π coupling is not included, see Table 3.

In case of the $^2\Delta_g$ state, the true SO splitting is negligibly different from the SO splitting obtained in the isolated-state

Table 4 Theoretical prediction of the photoelectron bands of silver dihalides (AgX_2) and composition of the SO eigenstates in terms of SO-free states

	SO state	Energy/eV	Composition (weight in %)
AgF_2	(1) $1/2_g$	0.000	$\tilde{X}\,^2\Sigma_g^+$ (97); $\tilde{A}\,^2\Pi_g$ (3)
	(1) $3/2_g$	0.740	$\tilde{A}\,^2\Pi_g$ (100)
	(2) $1/2_g$	0.926	$\tilde{X}\,^2\Sigma_g^+$ (3); $\tilde{A}\,^2\Pi_g$ (97)
	(1) $5/2_g$	2.109	$\tilde{B}\,^2\Delta_g$ (100)
	(2) $3/2_g$	2.516	$\tilde{B}\,^2\Delta_g$ (100)
	(1) $3/2_u$	2.673	$\tilde{C}\,^2\Pi_u$ (85); $\tilde{D}\,^2\Sigma_u^+$ (15)
	(1) $1/2_u$	2.674	$\tilde{C}\,^2\Pi_u$ (100)
	(2) $1/2_u$	2.704	$\tilde{C}\,^2\Pi_u$ (15); $\tilde{D}\,^2\Sigma_u^+$ (85)
$AgCl_2$	(1) $1/2_g$	0.000	$\tilde{X}\,^2\Sigma_g^+$ (88); $\tilde{A}\,^2\Pi_g$ (12)
	(1) $3/2_g$	0.085	$\tilde{A}\,^2\Pi_g$ (100)
	(2) $1/2_g$	0.252	$\tilde{X}\,^2\Sigma_g^+$ (12); $\tilde{A}\,^2\Pi_g$ (88)
	(1) $3/2_u$	1.134	$\tilde{B}\,^2\Pi_u$ (100)
	(1) $1/2_u$	1.204	$\tilde{B}\,^2\Pi_u$ (96); $\tilde{C}\,^2\Sigma_u^+$ (4)
	(2) $1/2_u$	1.409	$\tilde{B}\,^2\Pi_u$ (4); $\tilde{C}\,^2\Sigma_u^+$ (96)
	(1) $5/2_g$	2.105	$\tilde{D}\,^2\Delta_g$ (100)
	(2) $3/2_g$	2.502	$\tilde{D}\,^2\Delta_g$ (100)
$AgBr_2$	(1) $3/2_g$	0.000	$\tilde{X}\,^2\Pi_g$ (100)
	(1) $1/2_g$	0.271	$\tilde{X}\,^2\Pi_g$ (88); $\tilde{A}\,^2\Sigma_g^+$ (12)
	(2) $1/2_g$	0.432	$\tilde{X}\,^2\Pi_g$ (12); $\tilde{A}\,^2\Sigma_g^+$ (88)
	(1) $3/2_u$	0.655	$\tilde{B}\,^2\Pi_u$ (100)
	(1) $1/2_u$	0.777	$\tilde{B}\,^2\Pi_u$ (60); $\tilde{C}\,^2\Sigma_u^+$ (40)
	(2) $1/2_u$	1.193	$\tilde{B}\,^2\Pi_u$ (40); $\tilde{C}\,^2\Sigma_u^+$ (60)
	(1) $5/2_g$	2.593	$\tilde{D}\,^2\Delta_g$ (100)
	(2) $3/2_g$	2.985	$\tilde{D}\,^2\Delta_g$ (100)
AgI_2	(1) $3/2g$	0.000	$\tilde{X}\,^2\Pi_g$ (100)
	(1) $1/2g$	0.447	$\tilde{X}\,^2\Pi_g$ (80); $\tilde{A}\,^2\Sigma_g^+$ (20)
	(1) $3/2u$	0.482	$\tilde{B}\,^2\Pi_u$ (100)
	(1) $1/2u$	0.597	$\tilde{B}\,^2\Pi_u$ (45); $\tilde{C}\,^2\Sigma_u^+$ (55)
	(2) $1/2g$	1.042	$\tilde{X}\,^2\Pi_g$ (20); $\tilde{A}\,^2\Sigma_g^+$ (80)
	(2) $1/2u$	1.438	$\tilde{B}\,^2\Pi_u$ (55); $\tilde{C}\,^2\Sigma_u^+$ (45)
	(1) $5/2g$	3.278	$\tilde{D}\,^2\Delta_g$ (100)
	(2) $3/2g$	3.669	$\tilde{D}\,^2\Delta_g$ (100)

approximation. This is due to the fact that the $^2\Delta_g$ state hardly mixes with the neighboring states *via* the SO operator, see Table 4.

Using the SO splittings given in Table 3 and the scalar relativistic MRCI energies given in Table 2, we report the PDS of the AgX_2^- in Table 4. The calculated energies of the SO eigenstates are presented with respect to the energy of the lowest SO eigenstate which indicates the origin of the spectrum. The assignment of the spectra has been carried out by investigating the composition of the SO eigenstates in terms of the scalar relativistic electronic states.

In case of AgF_2, the lowest energy peak in the photodetachment spectra is found to be of $1/2_g$ symmetry which essentially belongs to the $\tilde{X}\,^2\Sigma_g^+$ state, followed by the 3/2 and 1/2 components of the $\tilde{A}\,^2\Pi_g$ state, see Table 4. The SO components of the $\tilde{B}\,^2\Delta_g$, the $\tilde{C}\,^2\Pi_u$, and the $\tilde{D}\,^2\Sigma_u^+$ states appear high in energy. While the $\tilde{X}\,^2\Sigma_g^+$ and the $\tilde{A}\,^2\Pi_g$ states exhibit negligible Σ–Π coupling (*via* SO operator), the $\tilde{D}\,^2\Sigma_u^+$ and the $\tilde{C}\,^2\Pi_u$ states show a moderate SO induced Σ–Π coupling in AgF_2. The relative ordering of the peaks in the calculated photodetachment spectra of $AgCl_2$ is quite similar to that of AgF_2, with the exception of the $^2\Delta_g$ state which, in case of the former, appears higher in energy than the $^2\Pi_u$ and the $^2\Sigma_u^+$ states. Unlike AgF_2 and $AgCl_2$, the $3/2_g$ SO eigenstate (corresponding to the 3/2 component of the $\tilde{X}\,^2\Pi_g$ state) represents

the origin of the photodetachment spectra of $AgBr_2$, see Table 4. The $1/2_g$ components of the $\tilde{X}\,^2\Pi_g$ and the $\tilde{A}\,^2\Sigma_g^+$ states appear next with moderate coupling (*via* SO operator) between them. The $1/2_u$ components of the $\tilde{B}\,^2\Pi_u$ and the $\tilde{C}\,^2\Sigma_u^+$ states, however, are strongly coupled *via* SO operator, see Table 4. Similar to $AgCl_2$, the two SO components of the $\tilde{D}\,^2\Delta_g$ state of $AgBr_2$, appearing at high photodetachment energy remain unmixed with other electronic states. The SO components of the $\tilde{X}\,^2\Pi_g$ state appear as the first two peaks in the photodetachment spectra of AgI_2, followed by the 3/2 component of the $\tilde{A}\,^2\Pi_u$ state. The very large SO splitting of the $\tilde{A}\,^2\Pi_u$ state puts the upper SO component of the $\tilde{A}\,^2\Pi_u$ state high in energy. This results in an interesting situation where the two nondegenerate states, namely, the $\tilde{B}\,^2\Sigma_u^+$ and the $\tilde{C}\,^2\Sigma_g^+$ states, appear in between the two SO components of the degenerate (in scalar-relativistic sense) $\tilde{A}\,^2\Pi_u$ state, see Table 4. This feature is also seen in case of AuI_2, see refs. 15, 16. In case of AgI_2, the 1/2 components of the $\tilde{A}\,^2\Pi_u$ and the $\tilde{C}\,^2\Sigma_u^+$ are strongly coupled *via* SO operator. In general, the SO-induced Σ–Π coupling is found to be stronger in the case of the heavier halides.

4. Conclusions

We have determined the geometries of anionic and neutral AgX_2 (X = F, Cl, Br, and I), at the CCSD(T) level, employing relativistic effective core potentials for Ag and the halogens. We have determined the SO-free vertical detachment energy of the ground as well as of the excited states of the neutral species using the MRCI method, where eight electronic states are averaged, *via* a SA-CASSCF calculation, to generate the *N*-electron basis. The relative ordering of the excited electronic states of the series of molecules have been described with molecular orbital arguments. Also determined are the SO splittings of the title molecules in three of their degenerate electronic states, namely, the $^2\Pi_g$, the $^2\Pi_u$, and the $^2\Delta_g$ states. It has been shown that the magnitude of the SO splitting in different electronic states of different species can be rationalized from qualitative molecular-orbital arguments. We have analyzed the SO eigenstates in terms of SO-free electronic states. The inter-state (Σ–Π) coupling *via* the SO operator and the effects of these couplings on the observed SO splitting have been discussed. With the aid of these high-level *ab initio* calculations, we have provided a theoretical prediction of the photodetachment spectra of AgX_2^-. It is hoped that this theoretical study will stimulate the recording of the photodetachment spectra of silver dihalide anions.

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