A multireference configuration interaction study of photoelectron spectra of carbon tetrahalides

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Large scale multireference configuration interaction calculations of He(I) photoelectron spectra are presented for CCl₄, CBr₄, and CI₄. The spin-orbit coupling in CI₄ is also calculated using the relativistic configuration interaction approach. The theoretical results explain the salient features of the spectra. Calculated ionization energies are in good agreement with experimental data. The observed photoelectron peaks are reassigned based on the composition of the spin-orbit states in the relativistic configuration interaction.

1. Introduction

Although the first experimental He(I) photoelectron spectra of halomethanes have been reported long ago [1-4], the dispute over band assignments resulted in new high-resolution experiments [5-8]. Higher ionization potentials of chloromethanes have also been studied by an electron momentum spectroscopy technique [9].

Due to a large number of electrons and the complicated electronic structure of tetrahalomethanes, hitherto theoretical studies have been restricted to the SCF approach within semiempirical [10] or ab initio schemes [8,11-13]. Correlation effects are known to be important for these kinds of systems [14] and reliable calculations have to account for it. The molecular structure is additionally complicated by the relativistic effects which have to be taken into account at least in the case of the heaviest molecule namely, CI₄. The relativistic effects have been studied previously using a perturbational approach based on the SCF wavefunction [8]. Fortunately, the Jahn-Teller effect in the positive ions of halomethanes is too small to make substantial impact on the spectra.

This Letter presents large scale multiple reference singles and doubles configuration interaction (MRSDCI) study of photoelectron spectra of CCl₄, CBr₄ and CI₄. In the case of CI₄, molecular spectra are calculated with the inclusion of relativistic effects including the spin-orbit coupling. The computed results are in good agreement with available experimental data.

2. Method of calculations

2.1. Multiple reference single- and double-excitation configuration interaction method (MRDCI)

The configuration interaction treatment is of the standard multiple reference singlet and doublet configuration interaction methods (MRDCI) developed by Buenker et al. [15,16]. The computations are carried out employing the table CI algorithm.
The number of symmetry adapted functions (ASFs) generated by single and double excitations for a given electronic state was reduced by employing an energy selection criterion [18] with an assumed threshold \( T \). The eigenvalues of diagonalizing the matrix corresponding to \( T \) together with the summed perturbative energy lowerings of the non-selected configurations in the total MRDCI space have been employed [19] to determine an extrapolated zero-threshold value \( (E_{\text{EX,MRDCI}}) \). The energy corresponding to the full-CI treatment has been estimated via the relation

\[
E_{\text{FCI}} = E_{\text{EX,MRDCI}} + (E_{\text{EX,MRDCI}} - E_{\text{ref}})(1 - \Sigma c_i^2),
\]

which is a generalization [20] of the correction formula suggested by Langhoff and Davidson [21] where \( E_{\text{ref}} \) is the reference secular equation energy.

In a recent article, Buenker and co-workers [19] have shown that there is an excellent agreement of the MRDCI method with a large series of full-CI benchmark calculations. The present MRDCI calculations were performed using integral and SCF routines of the ATMOL 3 program [22] and transformation and CI routines of the MRDCI program [23]. One-electron integrals within the formalism of relativistic effective core potential were generated by the GAMESS program [24].

2.2. Relativistic CASSCF/MRSDCI/RCI

The spin–orbit coupling in the case of Cl\(_4\) and Cl\(_7\) was calculated using the relativistic configuration interaction RCI method. Spin–orbit integrals were obtained using the differences of 1+1/2 and 1−1/2 RECPs and included in the CI matrix. The MRSDCI natural orbitals were used for the RCI. This procedure used is described in refs. [25,26]. Further details pertinent to these calculations are in section 3.3.

All CASSCF/MRSDCI calculations were made using a modified version of ALCHEMY II codes \(^{#1}\) to include relativistic ECPs. The spin–orbit integrals over Gaussian basis sets were evaluated using ARGOS codes \(^{#2}\). The RCI was done using the method in ref. [26].

3. Computational Details

3.1. Geometry optimization

A full geometry optimization was performed for the ground state of CCl\(_4\) and CBr\(_4\). The formalism of the relativistic effective core potential (REP) [27] and \([nsnp]\) basis set for C, Cl [27] and Br [28] supplemental with one d polarization function [29] were used in the geometry optimization at the SCF level. Double zeta basis sets were prepared from single zeta collections by leaving s and p functions with the most diffuse exponent uncontracted. The predicted bond distances: 1.765 Å for C–Cl and 1.934 Å for C–Br are in good agreement with experimental data: C–Cl 1.76 Å [30] and C–Br 1.942 Å [31]. The MRSDCI optimized value 2.3051 Å for the C–I bond in Cl\(_4\) has been taken from ref. [32].

3.2. MRDCI calculations

MRDCI calculations were performed for the ground state of tetrahalomethanes and for a number of low-lying excited states of cations in the geometry of neutral molecules. The number of electrons was reduced by utilizing relativistic effective core potentials [27] for all atoms, leading to 2s22p\(^2\) for C and \(ns^2np^5\) valence configuration for halides. The basis set used for optimization of CCl\(_4\) and CBr\(_4\) was extended by the addition of a set of s and p diffuse functions [33]. In the case of Cl\(_4\) the basis set of C consists of [2s3p] decontracted basis of Pacios and Christiansen [27] with one d polarization function [29]. In the case of iodine the decontracted basis of La John et al. [34] has been adopted with polarization d function of 0.3 exponent. This choice leads to a total of 90 atomic basis functions for CCl\(_4\) and CBr\(_4\) to 89 for Cl\(_4\). Five lowest occupied molecular orbitals were kept doubly occupied in all configuration interaction calculations and 25 molecular orbitals (24 in case of Cl\(_4\)) with the highest orbital energies have been excluded. The remaining 60 mo-

\(^{#1}\) The major authors of ALCHEMY II are B. Liu, B. Lengsfield and M. Yoshimine.

\(^{#2}\) The author of ARGOS is R.M. Pitzer.
molecular orbitals were used for the generation of single and double excitations for a set of 11 reference configurations, about 700000 symmetry adapted functions (SAFs) in all. By applying the selection threshold of 22 μH approximately 9000 SAFs were included in the diagonalization. The estimate to the full-CI energy was obtained by applying the extrapolation procedure and adding the Davidson correction.

3.3. CASSCF/MRSDCI/RCI calculations for Cl₄

For the Cl₄ molecule and its positive ion the structural and spectroscopic properties were calculated by using the complete-active space self-consistent field (CASSCF) followed by the multireference single and double excited configuration interaction (MRSDCI) and relativistic configuration interaction (RCI) methods. The relativistic effective core potentials (RECPs) for C and I atoms with the outer 2s²2p² and 5s²5p² shells, respectively, were employed in the present calculations for Cl₄ and Cl⁺. All the calculations were performed with the C₂ᵥ point group, a subgroup of Td symmetry. The four outer s and p orbitals of each atom in Cl₄ combine to form eight a₁, five b₂, five b₁ and two a₂ orbitals in the C₂ᵥ point group. The orbitals generated by the CASSCF calculations constitute the starting point for the CI calculations. The two lowest a₁, one b₂ and one b₁ orbitals which are mostly of 5s character of iodine were treated as inactive orbitals. Thus, no excitations were allowed from these orbitals. The 8a₂ and 5b₁ antibonding orbitals with high energy were not included in the active space. Twenty-four active electrons (note that there are 8 inactive electrons) were distributed in all possible ways among the remaining five a₁, four b₂, three b₁ and two a₂ orbitals. The MRSDCI calculations were carried out for the low-lying states of Cl₄ following the CASSCF calculations. In the MRSDCI calculations, those configurations with coefficients larger than or equal to 0.1 in the CASSCF method were included as reference configurations.

We now discuss the method of calculation of spin-orbit splitting of energy levels of Cl₄ and Cl⁺. The relativistic configuration interaction (RCI) method was used for calculating the spin-orbit interaction. Following the MRSDCI calculations, the RCI calculations in which the low-lying electronic configurations of differential spatial and spin symmetries are allowed to mix in the presence of spin–orbit operator were carried out for Cl₄ and Cl⁺ species. The configurations corresponding to the low-lying states were used as reference configurations along with singly and doubly excited configurations from the reference configurations. All the calculations were performed with C₂ᵥ symmetry. In the RCI calculations for both Cl₄ and Cl⁺ species, four a₁, two from each b₂ and b₁ orbitals (1a₁ 2a₁ 1t₂ 2t₁ in Td symmetry) were treated as inactive orbitals and twenty-one a₁, thirteen from each b₂ and b₁, and six a₂ highest virtual orbitals were excluded from the calculations. The remaining sixteen electrons were distributed among the remaining nine a₁, seven b₂, seven b₁ and five a₂ orbitals. In the case of Cl₄ molecule seven reference configurations, one from the 1A₁ state with the 1a₁ 1t₂ 2a₁ 2t₁ 1e 3t₁ 1e configuration and six from the 3T₁ state with the 1a₁ 1t₂ 2a₁ 2t₁ 1e 3t₁ 1e 3t₂ 3a₁ configuration were included in the RCI calculations. In the case of Cl⁺ ion sixteen reference configurations, six from the 2T₁ state with the 1a₁ 1t₂ 2a₁ 2t₁ 1e 3t₁ 1e configuration, six from the 2T₂ state with the 1a₁ 1t₂ 2a₁ 2t₁ 1e 3t₁ 3a₁ configuration and four from the 2E state (1a₁ 1t₂ 2a₁ 2t₂ 3t₁ 1t₂ 1e²) were included in the spin-orbit calculations along the singly and doubly excited configurations.

4. Results and discussion

The valence electronic structure of tetrahedral tetrahalomethane molecules is 1a₁ 1t₂ 2a₁ 2t₁ 1e 3t₁ 1t₂. The SCF molecular orbitals (MOs) of parent molecules were used in multireference CI calculations. The electronic structure is dominated by electrons of halogens, since only four valence electrons come from the carbon atom. However, direct interactions between halogens are weak compared to carbon–halogen interactions. As a representative case in Cl₄ the Mulliken overlap population is 0.12 between the iodine atoms and 0.30 between the C and I atoms. The Mulliken population indicates that only the t₂ HOMO has slightly bonding character with electron distribution of 0.10 on C and 0.475 on I atoms. Two other HOMOs of t₁ and e symmetries are entirely localized on the iodine atoms with population of 0.5 on each
I atom. More information, regarding the nature of interactions between atoms in molecules can be extracted from the graphical representation of valence HOMOs, presented in figs. 1–3. The carbon atom at the center and two iodine atoms define the plane of cut. Dotted and solid lines correspond to negative and positive lobes of the molecular orbitals, respectively. The increment between successive contours is 0.05 bohr$^{-3/2}$. The highest occupied molecular orbital ($t_1$) is associated with the lone pairs on halogens. Very little interactions between halogens may be expected since the orbital has an antibonding character. The $t_2$ MO is responsible for the C–I bonds, as is clearly demonstrated in fig. 2, although the electron distribution is very diffuse in the area of C–I bonds. The HOMO of $e$ symmetry is again localized on lone pairs of iodines (fig. 3), however the interactions between atoms have bonding character. Molecular orbitals for CCl$_4$ and CBr$_4$ have qualitatively the same shape.

Calculated ionization energies for CCl$_4$ and CBr$_4$ are presented in tables 1 and 2. Results are in very good agreement with experimental data. Molecular states of the ionized molecule are associated primarily with a single determinant, constructed from the SCF configuration by removing an electron from the molecular orbital corresponding directly to the studied electronic state. The SCF results (within the Koopman’s approximation) differ by about 0.5 eV from correlated values emphasizing the importance of correlation effects.

The MRD-CI calculated energies for Cl$_4$ system (table 3) also agree with median experimental values. The remark concerning the wavefunction applies also here. The importance of the inclusion of correlation effects is clearly visible for higher ionization energies.

The available theoretical results in the literature come mostly from SCF Xα calculations. The relatively inexpensive Xα calculations give results comparable to large scale ab initio CI results. However, the examination of Xα results shows, that the proper reproduction of spectra within this approach depends upon the careful parametrization. Calculations performed for different parameters [12], reproduce better some electronic states at the expense of others. The results for a given set of parameters are final and cannot be improved by the inclusion of more subtle effects, like correlation effects. The sophistication of large scale calculations is needed for reliability of obtained data.

The approximate one determinant structure of the
Table 1
SCF and MRD-CI ionization energies, other theoretical and experimental results (in eV) for CCl₄ with percent of main configuration spin function (CSF) in the MRCI wavefunction

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>This work</th>
<th>Other theories</th>
<th>Exp.</th>
<th>Main CSF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCF ¹)</td>
<td>MRD-CI</td>
<td>Xα b)</td>
<td>Xα c)</td>
</tr>
<tr>
<td>²T₁</td>
<td>12.68</td>
<td>11.80</td>
<td>11.10</td>
<td>11.56-12.26</td>
</tr>
<tr>
<td>²T₂</td>
<td>13.51</td>
<td>12.65</td>
<td>11.92</td>
<td>12.11-12.83</td>
</tr>
<tr>
<td>²E</td>
<td>14.63</td>
<td>12.73</td>
<td>13.32</td>
<td>12.74-13.40</td>
</tr>
<tr>
<td>²T₂</td>
<td>18.25</td>
<td>17.23</td>
<td>14.96</td>
<td>16.28-16.68</td>
</tr>
</tbody>
</table>

¹) Koopman's theorem.

Table 2
SCF and MRD-CI ionization energies, other theoretical and experimental results (in eV) for CBr₄. Percent of main configuration in MRCI wavefunction. Vibrationally-averaged experimental quantities are quoted where vibrational structure is resolved

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>This work</th>
<th>Other theories</th>
<th>Exp.</th>
<th>Main CSF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCF ¹)</td>
<td>MRD-CI</td>
<td>Xα b)</td>
<td>Xα c)</td>
</tr>
<tr>
<td>²T₁</td>
<td>11.27</td>
<td>10.76</td>
<td>10.2</td>
<td>10.34-10.98</td>
</tr>
<tr>
<td>²T₂</td>
<td>12.01</td>
<td>11.61</td>
<td>11.1</td>
<td>10.88-11.51</td>
</tr>
<tr>
<td>²E</td>
<td>13.04</td>
<td>11.97</td>
<td>12.2</td>
<td>11.45-12.15</td>
</tr>
<tr>
<td>²T₂</td>
<td>16.46</td>
<td>15.79</td>
<td>13.3</td>
<td>14.74-15.06</td>
</tr>
</tbody>
</table>

¹) Koopman's theorem.

Table 3
SCF and MRD-CI ionization energies, other theoretical and experimental ionization energies (in eV) for the Cl₂ molecule

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>This work</th>
<th>Other theories</th>
<th>Exp.</th>
<th>Main CSF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCF ¹)</td>
<td>MRD-CI</td>
<td>Xα b)</td>
<td>Xα c)</td>
</tr>
<tr>
<td>²T₂</td>
<td>10.40</td>
<td>10.20</td>
<td>10.2</td>
<td>9.67</td>
</tr>
<tr>
<td>²E</td>
<td>11.35</td>
<td>10.82</td>
<td>10.9</td>
<td>10.25</td>
</tr>
<tr>
<td>²T₂</td>
<td>14.40</td>
<td>13.97</td>
<td>12.3</td>
<td>13.58</td>
</tr>
</tbody>
</table>

¹) Koopman's theorem.
²) Ref. [13].
³) Nonrelativistic results from ref. [8].
⁴) Ref. [8].
⁵) Photoelectron peaks are reassigned in text in accord with table 4.

wavefunction describing electronic states, allows us to draw qualitative conclusions from the picture of molecular orbitals. The first ionization potential, primarily associated with lone pairs of halogens, changes only 0.4 eV from CH₃Cl to CCl₄. The second ionization potential related to C–Cl bond, is much more sensitive to the Cl environment and the difference between CHCl₃ and CCl₄ rises to 1.98 eV. Although the ionization potentials of molecules are lowered compared to atoms[35] (Cl 13.01 eV, Br
11.84 eV, I 10.45 eV) the lowering is similar in all cases, mainly 1.32, 1.24, 1.25 eV, indicating similar influence from the rest of molecule.

We now discuss the spin–orbit coupling of the electronic states of CI⁺. The results of the RCI calculations are shown in table 4. In the presence of spin–orbit coupling, the RCI calculations show that the ground state becomes a mixture of 2T₁ and 2E states rather than the pure 2T₂ state predicted by the MRDCI results (without spin–orbit coupling). The first excited state E(I) with T₂ character is about 0.52 eV higher in energy compared to the ground state which is in excellent agreement with the value deduced from the photoelectron spectrum namely, 0.43 eV.

The photoelectron spectrum of CI⁺ contains several peaks. There are three spectral peaks at 9.10, 9.19 and 9.58 eV. These peaks were assigned previously to ionization from the orbital of t₁ symmetry by Jonkers et al. [8]. The first two peaks are attributed to the Jahn–Teller distortion since the ground state of CI⁺ is of 2T₁ symmetry. The third peak at 9.58 eV is attributed to the spin–orbit component of the 2T₁ state. Consequently, the splitting of the third peak from the center of the first two peaks is taken as the ground state spin–orbit coupling. While our computed E(I)–E(II) energy separation in table 4 (0.52 eV) agrees well with the value of 0.44 eV obtained in this way, we believe that the previous assignment of the peaks needs to be revised. As evidenced from table 4, the E(I) ground state of CI⁺ is 45% 2T₁ and 46% 2E and hence this state is strongly contaminated with spin–orbit coupling. The second root of the RCI (table 4) is actually composed of 86% 2T₂ and 8% 2T₁. That is, although the 2T₂–2T₁ splitting in the absence of spin–orbit coupling is 0.74 eV, the spin–orbit coupling stabilized 2T₂ so as to yield a net E(I)–E(II) separation of 0.52 eV. Consequently, the third peak in the photoelectron spectrum at 9.58 eV, which was previously thought to be due to the spin–orbit splitting of the t₁ orbital must be reassigned to the spin–orbit stabilized t₂ orbital. The near-proximity of the 2T₂ and 2E states combined with the fact that the spin–orbit coupling of iodine is quite large leads to an intermediately coupled electronic state for CI⁺.

The sixth peak at 10.76 eV corresponds to the third spin–orbit state E(III) in table 4. The separation of this peak from the center of the two lowest peaks at 9.10 and 9.19 eV is the spin–orbit splitting between the first and third spin–orbit state. The experimental value for this splitting is 1.61 eV compared to our computed value of 1.56 eV. This state is composed of 46% 2T₁ and 48% 2E is thus approximately reversed in composition compared to the ground state. We thus conclude that the electronic states of CI⁺ exhibit an intermediate coupling and one cannot assign the states based on the assumption that these states are pure and spin–orbit coupling is first-order in nature.

5. Conclusion

Large-scale relativistic configuration interaction calculations were performed to study the photoelectron spectra of carbon tetrachlorides (CCl₄, CBr₄, and Cl₄). The calculated ionization potentials are in good agreement with the experimental values. We found that the effect of spin–orbit coupling on the ionization potentials of CI⁺ is quite large. As a result, the electronic state of CI⁺ mix together and so the peaks of the spectra of CI⁺ are reassigned based on the spin–orbit states.

Table 4
Relativistic CI energies of electronic states with spin–orbit coupling for the CI⁺ ion

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Energy (eV)</th>
<th>Weights (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>theory</td>
<td>exp.</td>
</tr>
<tr>
<td>E(I)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E(II)</td>
<td>0.52</td>
<td>0.44</td>
</tr>
<tr>
<td>E(III)</td>
<td>1.56</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Acknowledgement

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