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A study of the valence shell electronic structure and photoionisation dynamics of para-dichlorobenzene and para-bromochlorobenzene

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ABSTRACT

The valence shell electronic structure and photoionisation dynamics of para-dichlorobenzene and para-bromochlorobenzene have been investigated both experimentally and theoretically. High resolution photoelectron spectra of the outer valence orbitals have been recorded with HeI radiation and the observed structure has been interpreted using calculated ionisation energies and spectral intensities. The theoretical predictions for the single-hole ionic states due to outer valence ionisation agree satisfactorily with the experimental results. Ionisation from the inner valence orbitals is strongly influenced by many-body effects and the with a particular orbital is spread amongst numerous satellites. Some of the photoelectron bands exhibit vibrational progressions and tentative assignments have been proposed. The photoionisation dynamics of the outer valence orbitals of para-dichlorobenzene have been investigated theoretically by using the continuum multiple scattering approach to calculate photoionisation partial cross-sections and photoelectron anisotropy parameters. The results show that ionisation from some of the orbitals is affected by the Cooper minimum associated with the chlorine atom. Synchrotron radiation has been used to record angle resolved photoelectron spectra of the entire valence shell, for photon energies between threshold and ~100 eV, and these have allowed the corresponding experimental data to be derived. A comparison between the predicted and measured anisotropy parameters confirms the influence of the Cooper minimum in those orbitals related to the chlorine lone-pairs.

1. Introduction

The influence of substituents on various physical properties of benzene has been studied extensively and has often been interpreted in terms of resonance and inductive effects [1,2]. One such property which has received considerable attention is the ionisation energy of the highest occupied molecular orbital (HOMO) [3,4]. Recently, DiLabio et al. [5] have calculated the ionisation energies of a wide range of para- and meta-disubstituted benzenes and have attempted to correlate the difference between the ionisation energy of the substituted molecule and that of the parent benzene molecule with the electron-withdrawing or electron-donating character of the substituent. The present experimental and theoretical investigation of the valence electronic structure and photoionisation dynamics of para-dichlorobenzene (pDCB) and para-bromochlorobenzene (pBCB) encompasses the entire valence shell and therefore provides much additional information, together with an improved understanding of substituent effects.

The dichlorobenzenes, where the two chlorine atoms may be placed in the parent benzene ring in the ortho (1,2), meta (1,3) or para (1,4) positions, constitute ideal candidates in which to study the influence of the substituent site on the valence electronic structure. Moreover, the influence of the substituent electronegativity and ionisation energy can be examined by replacing one of the chlorine atoms by a bromine atom. This article reports results for pDCB and pBCB, and describes the experimental and theoretical approaches. The corresponding data for the ortho and meta compounds will be given in a future publication.

In the present study, the electronic structure and photoionisation dynamics of pDCB have been investigated experimentally by using synchrotron radiation to record angle resolved photoelectron spectra of the entire valence shell. High resolution photoelectron spectra of the outer valence orbitals of pDCB and pBCB have been measured with HeI radiation. The observed structure has been interpreted with the aid of vertical ionisation energies and spectral intensities calculated with the third-order algebraic diagrammatic construction (ADC(3)) approximation for the one-particle Green's function [6–8]. This theoretical method can be applied even when the molecular orbital model of ionisation [9] becomes invalid, as is

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indeed found for the inner valence orbitals of pDCB, and spectral intensity is redistributed from main-lines to satellite states. Outer valence Green's function (OVGF) calculations [8,10–12] have also been performed. The photoionisation dynamics of the outer valence orbitals of pDCB have been investigated theoretically by employing the continuum multiple scattering (CMS-Xα) approach [13,14] to calculate photoionisation partial cross-sections and photoelectron anisotropy parameters. The results show that ionisation from some of the orbitals is affected by the Cooper minimum [15,16] associated with the chlorine atom and by shape resonances [17]. These predictions have been confirmed through comparison with the corresponding experimental data.

The photoionisation dynamics of halogen-containing molecules have proved particularly interesting because experimental studies have shown that the photoionisation partial cross-sections and the photoelectron anisotropy parameters associated with molecular orbitals possessing a strong halogen character exhibit atomic-like behaviour. For example, measurements on the hydrogen halides [18–20] showed that the anisotropy parameter for the outermost npπ orbital (n = 3,4,5 for Cl, Br, I, respectively), of essentially lone-pair character, displayed a minimum which resembled that observed in studies on the closely related rare gas atoms [21]. In HCl, the experimentally determined minimum in the X $^2\Pi$ state anisotrophy parameter at a photon energy of ~42 eV was interpreted as being due to a Cooper minimum in the $l = 2$ channel [18,22]. Similar effects have been observed in larger halogen-containing molecules. In chlorobenzene [23], chlorothiophene [24], bromobenzene [25] and bromothiophene [26] the photoelectron angular distributions and branching ratios associated with the nominally halogen atom lone-pair orbitals display energy dependent variations which appear atomic-like. However, the extent to which these orbitals replicate the atomic-like behaviour depends upon the mixing between the lone-pair and the ring orbitals. The experimental results showed that the in-plane lone-pair orbital exhibited an atomic-like behaviour to a higher degree than did the out-of-plane orbital because the latter orbital bonds more efficiently with the ring orbitals. In iodobenzene [27] and iodothiophene [28] the dynamics become more complicated due to core-valence shell coupling at energies above the I 4d threshold [29,30].

According to our calculations, the ground state Hartree–Fock valence shell electronic configuration of pDCB (D_{2h} point group) may be given as

Inner valence: [core] $1a_g^{\,2}\,1b_{1u}^{\,2}\,2a_g^{\,2}\,1b_{2u}^{\,2}\,2b_{1u}^{\,2}\,1b_{3g}^{\,2}\,3a_g^{\,2}$
Outer valence: $4a_g^{\,2}\,2b_{2u}^{\,2}\,3b_{1u}^{\,2}\,3b_{2u}^{\,2}\,4b_{1u}^{\,2}\,1b_{3u}^{\,2}\,2b_{3g}^{\,2}\,5a_g^{\,2}\,1b_{2g}^{\,2}\,3b_{3g}^{\,2}\,4b_{2u}^{\,2}\,2b_{3u}^{\,2}\,1b_{1g}^{\,2}\,2b_{2g}^{\,2}$

where the carbon K-shell orbitals and the chlorine K- and L-shell orbitals are not taken into account in the numbering scheme.

Similarly, the ground state Hartree–Fock outer valence shell electronic configuration of pBCB (C_{2v} point group) may be given as

$6a_1^{\,2}\,3b_2^{\,2}\,7a_1^{\,2}\,4b_2^{\,2}\,8a_1^{\,2}\,1b_1^{\,2}\,5b_2^{\,2}\,9a_1^{\,2}\,2b_1^{\,2}\,6b_2^{\,2}\,3b_1^{\,2}\,7b_2^{\,2}\,1a_2^{\,2}\,4b_1^{\,2}$

where the orbital numbering scheme, in addition to omitting the carbon and chlorine K- and L-shell orbitals, as described above, also does not take into account the bromine K-, L- and M-shell orbitals.

The axis orientation in both cases has been chosen such that z is the principal in-plane symmetry axis (here the Cl–C–C–Cl (Br) axis), the y axis is the short in-plane symmetry axis, and x is the perpendicular, out-of-plane axis (Fig. 1).

The correlation between the valence orbitals of pDCB and pBCB, and those of the parent benzene molecule and the chlorine (bromine) atomic levels is shown in Fig. 2, and their localisation can be assessed from the Mulliken population analyses (Table 1).

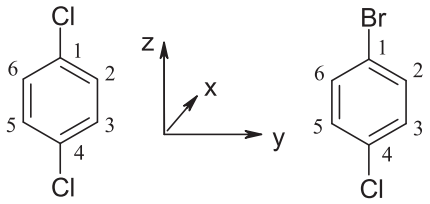

Fig. 1. Schematic representation of pDCB and pBCB, showing the atomic labelling and the adopted axis orientation.

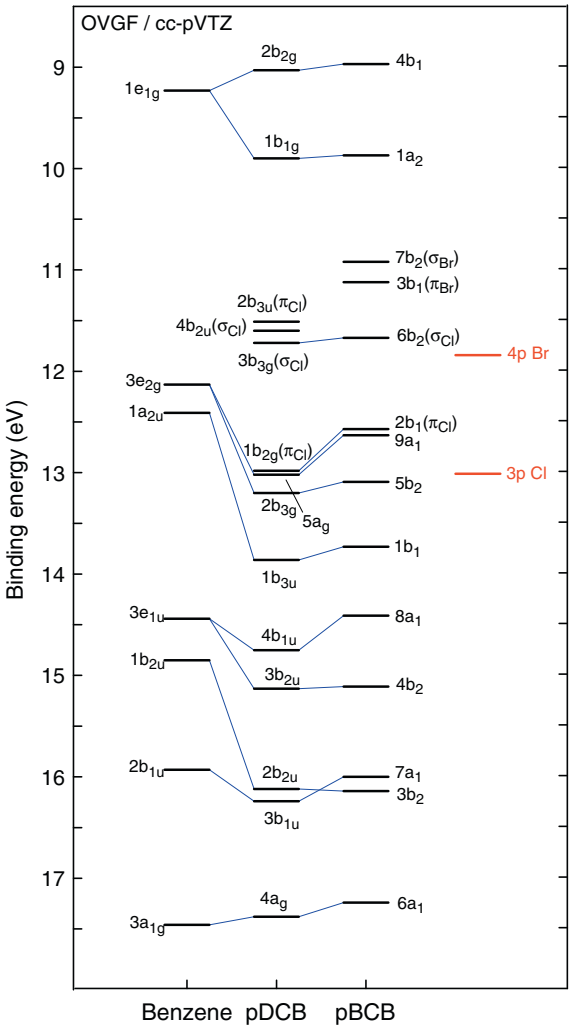

Fig. 2. A diagram correlating the outer valence molecular orbitals of benzene, pDCB, pBCB and the atomic Br 4p and Cl 3p levels.

The valence electronic structure of pDCB has been investigated previously using photoabsorption [31–34], photoelectron [3,35–41], photodissociation [42,43], fluorescence [36,44,45], REMPI [46] and MATI [47,48] techniques. Ionisation energies have also been calculated [49,50]. Previous work on pBCB is limited to a photoelectron spectroscopy study performed by Novak and Kovač [51].

2. Experimental apparatus and procedure

2.1. Synchrotron radiation excited angle resolved photoelectron spectra

Photoelectron spectra of pDCB were recorded using a rotatable hemispherical electron energy analyser and synchrotron radiation