



A study of the valence shell electronic structure and photoionisation dynamics of ortho-dichlorobenzene, ortho-bromochlorobenzene and trichlorobenzene



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ABSTRACT

The valence shell electronic structure and photoionisation dynamics of ortho-dichlorobenzene, ortho-bromochlorobenzene and trichlorobenzene have been investigated both experimentally and theoretically. Angle resolved photoelectron spectra of ortho-dichlorobenzene have been recorded using synchrotron radiation in the photon energy range from close to threshold to 100 eV. The photoelectron anisotropy parameters derived from these spectra have been compared to predicted values obtained with the continuum multiple scattering approach. The comparison demonstrates that ionisation from some of the orbitals is influenced by the Cooper minimum associated with the chlorine atom. High resolution photoelectron spectra of the outer valence orbitals of ortho-dichlorobenzene and ortho-bromochlorobenzene have been recorded with HeI radiation and the observed structure has been interpreted using calculated ionisation energies and spectral intensities. Electron correlation affects ionisation of the inner valence orbitals and leads to satellite formation. Simulations of the \tilde{X}^2B_1 , \tilde{A}^2A_2 and \tilde{B}^2B_2 state photoelectron bands in ortho-dichlorobenzene have enabled most of the vibrational progressions appearing in the experimental spectrum to be assigned. Photoelectron spectra of trichlorobenzene have also been measured and the anisotropy parameters associated with some of the outer valence orbitals exhibit a photon energy dependence which resembles that predicted for atomic chlorine. This behaviour is consistent with the theoretically predicted character of these orbitals.

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1. Introduction

The substitution of one or more of the hydrogen atoms in the benzene aromatic ring, by an equivalent number of halogen atoms, changes the electron distribution within the molecule. This, in turn, alters the ionisation energies, the molecular geometry and, consequently, the vibrational modes. In the highly symmetric parent molecule, benzene (D_{6h} point group), the valence shell photoelectron spectrum [1] contains several relatively well separated bands, some of which exhibit extended vibrational progressions, and the resonant behaviour in the photoionisation dynamics can be attributed to shape resonances [1,2]. In chlorobenzene (D_{2h} point group) the photoelectron spectrum [3] is dominated by two prominent

bands associated with the nominally halogen lone-pair orbitals and the photoionisation dynamics are strongly influenced by the Cl 3p Cooper minimum [4] which affects the partial cross-sections and photoelectron angular distributions. An additional factor comes into play with the dichlorobenzenes where the dependence of the valence shell electronic structure and photoionisation dynamics on the substitution sites can be studied. In two recent articles [5,6] we have reported experimental and theoretical ionisation energies, and assignments for the vibrational structure observed in the photoelectron bands of meta-dichlorobenzene (mDCB) and para-dichlorobenzene (pDCB). Moreover, the measured and calculated photoelectron angular distributions for the essentially Cl 3p lone-pair orbitals showed atomic-like behaviour, whilst shape resonances played only a minor role. These two articles also reported on the valence shell photoelectron spectra of meta-bromochlorobenzene (mBCB) and para-bromochlorobenzene

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(pBCB), and revealed the way in which the electronic structure evolves as a result of the differing electronegativity of the Cl and Br atoms.

In this final article, our studies have been extended to ortho-dichlorobenzene (oDCB), ortho-bromochlorobenzene (oBCB) and 1,3,5-trichlorobenzene (TCB) (Fig. 1) to investigate both the effect of a severely reduced molecular geometry (C_s point group in oBCB) and an increased number of chlorine atom substitutions (in TCB). Very little information is currently available regarding the valence shell ionic states of TCB and photoelectron angular distributions have not been measured previously. This is particularly unfortunate because such measurements often provide the definitive evidence required to verify theoretically predicted molecular orbital sequences. An additional development in the present work concerns the assignment of the structure observed in the photoelectron bands. In the meta and para isomers these assignments were based upon calculated and/or measured vibrational energies, mostly in the neutral ground state. In this study, the photoelectron bands exhibiting vibrational structure have been simulated, thereby allowing more reliable assignments to be proposed.

One of the aims of our work is to assess which of the orbitals in the halogen substituted benzene molecules retain their benzene-like properties and which exhibit a strong Cl 3p or Br 4p character. For example, in the dichlorobenzenes, four of the orbitals correspond, nominally, to chlorine lone-pairs, and three of these orbitals have similar binding energies. Thus, the closely spaced ionic states may interact. This leads to photoelectron bands containing complex vibrational structure which contrasts markedly with the simple band normally associated with a non-bonding halogen localised orbital [7]. On the other hand, if the two hydrogen atoms in the aromatic ring are replaced by one chlorine atom and one bromine atom, then the larger difference in the binding energies of the Cl and Br lone-pairs results in weaker interactions and hence simpler photoelectron bands.

The photoelectron angular distributions of mDCB [5] and pDCB [6] were found to resemble those of either benzene [1] or the halogen atom [4], depending upon the character of the orbital from which the electron was ejected. Taking, again, the example of the nominally Cl lone-pairs, the photoelectron anisotropy parameter (β) associated with such an orbital exhibits an energy dependence expected for a chlorine 3p electron although the variations were somewhat diminished. In contrast, the β -parameter associated with an orbital retaining its benzene-like π -character increased rapidly with increasing photon energy to reach a high plateau

value for electron kinetic energies of ~ 25 eV. Such a behaviour is typical of π -orbitals in five- or six-membered ring type hydrocarbon molecules [8–10].

The present results for oDCB, oBCB and TCB were obtained by using the experimental and theoretical methods already described [5,6]. Hence, only a brief account will be given here, although the additional procedure for simulating the photoelectron bands will be discussed in greater detail. To date, the photoelectron spectrum of TCB [11–15] has only been recorded using resonance line radiation. As our studies cover the entire valence shell, the inner valence region where the molecular orbital model of ionisation [16] becomes invalid has also been examined.

2. Experimental apparatus and procedure

2.1. Synchrotron radiation excited angle resolved photoelectron spectra

Photoelectron spectra of oDCB and TCB were recorded using a rotatable hemispherical electron energy analyser and synchrotron radiation emitted by the Daresbury Laboratory storage ring [17]. Detailed descriptions of the monochromator [18] and the experimental procedure [19] have been reported.

The photoionisation differential cross-section in the electric dipole approximation, assuming randomly oriented targets and electron analysis in a plane perpendicular to the photon propagation direction, can be expressed in the form [20]

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[1 + \frac{\beta}{4}(3P \cos 2\theta + 1) \right]$$

where σ_{total} is the angle integrated cross-section, β is the photoelectron anisotropy parameter, θ is the photoelectron ejection angle relative to the major polarisation axis and P is the degree of linear polarisation of the incident radiation. At each photon energy, photoelectron spectra were recorded at $\theta = 0^\circ$ and $\theta = 90^\circ$, thus allowing the anisotropy parameter to be determined once the polarisation had been deduced. The degree of polarisation was determined by recording Ar 3p and He 1s photoelectron spectra as a function of photon energy, and using the well established β -parameters for these gases [19,20]. The spectra of oDCB were analysed by dividing the binding energy range into the regions specified in Table 1.

2.2. HeI excited photoelectron spectra

HeI excited spectra of the outer valence orbitals of oDCB and oBCB were recorded with a modified Perkin Elmer 127° cylindrical photoelectron spectrometer [21]. The spectrometer was operated with a pass energy of 1 eV which resulted in a resolution of ~ 12 meV (FWHM). The binding energy scale was calibrated by recording spectra of a mixture comprising oDCB (oBCB), Ar and

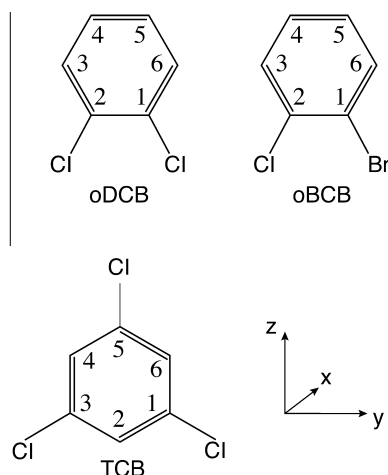


Fig. 1. Schematic representations of oDCB, oBCB and TCB, showing the atomic labelling and the adopted axis orientation.

Table 1

Energy regions used in the analysis of the photoelectron spectra of oDCB recorded with synchrotron radiation.

| Region | Binding energy range (eV) | Encompassed orbitals |
|--------|---------------------------|--|
| 1 | 8.6–9.4 | 3b ₁ ($\pi/(\pi_{\text{Cl LP}})$) |
| 2 | 9.4–10.45 | 2a ₂ ($\pi/(\pi_{\text{Cl LP}})$) |
| 3 | 10.7–11.45 | 7b ₂ ($\sigma_{\text{Cl LP}}$) |
| 4 | 11.45–12.15 | 9a ₁ ($\sigma_{\text{Cl LP}}/(\sigma)$), 2b ₁ ($\pi_{\text{Cl LP}}/\pi$) |
| 5 | 12.15–12.6 | 1a ₂ ($\pi_{\text{Cl LP}}$) |
| 6 | 12.6–13.35 | 6b ₂ (σ), 8a ₁ (σ) |
| 7 | 13.35–14.15 | 1b ₁ ($\pi_{\text{Cl LP}}/\pi$) |
| 8 | 14.15–15.35 | 7a ₁ (σ), 5b ₂ (σ) |
| 9 | 15.35–16.65 | 4b ₂ (σ), 6a ₁ (σ) |

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