Resonant Soft X-ray Spectroscopic Studies of C\textsubscript{60} and Related Materials

BY

TANEL KÄÄMBRE

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Abstract


This thesis addresses the electronic structure of molecular and correlated solids using resonant inelastic soft X-ray scattering (RIXS), non-resonant X-ray emission, photoemission and X-ray absorption spectroscopies. The use of monochromatised synchrotron radiation and improved energy resolution for X-ray emission have made it possible to study the normal state transport properties and to get further insight into the electron-vibration coupling in fullerenes and the related compounds. The latter is particularly important in order to understand the physical mechanism of superconductivity in fullerene materials. The characteristic intermolecular charge transfer times in K_{3}C_{60} are found to be longer than the X-ray scattering time-scale (a few femtoseconds). The slow intermolecular charge transport emphasizes that the reduced fullerene compounds can not be treated as simple metals, but rather as systems with strong electron correlation. The electron structure and the bonding character of the more covalent transition metal (V, Ti, Nb) fullerides have been addressed. Evidence indicating the existence of chemical bond between the metal atom(s) and C_{60} is presented, and the nature of the bond is discussed by comparing RIXS spectroscopic measurements and theoretical predictions. The (crystal) momentum conservation is discussed by comparing the spectroscopic data of a quasi-1D (carbon nanotubes) and quasi-2D (graphite) systems. Finally, the intra-atomic electron-electron correlation is discussed in the case of double core-hole state photo-excitation and de-excitation processes. RIXS including intermediate states with two core vacancies has been observed for the first time in the soft X-ray region.

Tanel Käämbre, Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden

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Printed in Sweden by Eklundshofs Grafiska, Uppsala 2002
Meie kohus on sundida saidisse stroofi
elementide pime raev.

Heiti Talvik (1904-1947)

To Eva Liina & my parents
List of papers

This thesis is based on a collection of articles listed below. Each paper will be referred to in the text by its Roman numeral.

I. A Soft X-ray Study of K$_3$C$_{60}$: Bulk Electronic Structure and Intermolecular Charge Transfer Rates
   In manuscript

II. Surface Electronic Structure of K$_3$C$_{60}$

III. Resonant inelastic X-ray scattering from solid C$_{60}$
   In manuscript

IV. Local Dephasing and Vibronic Character of Electron States in Solid C$_{60}$
   In manuscript

V. Study of oxygen-C$_{60}$ compound formation by NEXAFS and RIXS

VI. Single-Walled Carbon Nanotubes Studied By Resonant Inelastic X-ray Scattering Spectroscopy
   In manuscript

VII. Transition Metal-C$_{60}$ Compound Formation Studied by Resonant Inelastic X-Ray Scattering
   In manuscript
VIII. Bonding Mechanism in the Transition-Metal Fullerides Studied by Symmetry-Selective Resonant X-ray Inelastic Scattering

IX. Bond Formation in Titanium Fulleride Compounds Studied Through X-ray Emission Spectroscopy

X. Non-destructive chemical analysis of sandwich structures by means of soft X-ray emission

XI. Excitation Dynamics of the Beryllium Hypersatellite
T. Käämbre, M. Agåker, L. Gridneva, J.-E. Rubensson
*In manuscript*

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The following articles have been omitted from the thesis. They were omitted either due to the character of the material, or due to the limited extent of my contribution.

- **Magnetic circular dichroism in X-ray fluorescence of Heusler alloys at threshold excitation**  

- **Resonant Photoemission of CoCl₂**  
  A. Kikas, R. Ruus, A. Saar, E. Nõmmiste, T. Käämbre, and S. Sundin  

- **Mapping of Molecular C₁₇ Indandione-1,3 Pyridinium Betaine Adsorbates on Fused Silica by Surface Second Harmonic Generation**  
  D. Ding, T. Käämbre, S. Ljungström S, Y. Chen, K. Siegbahn, E. Wistus, P. Swensson, E. Mukhtar  

**Comments on my participation**

Experimental studies performed at synchrotron facilities, as is most of the work presented here, are always an effort of many people, which is also reflected by the lengthy author lists. My contribution to the papers has been on the experimental side, as well as in the analysis, discussions and writing of the papers. I have taken part in all the experiments, and in the preparations of most of them. I am responsible for the data analysis and writing of Papers I, III, V and XI. My contribution to the discussion and writing of the other papers is to some extent described by the position in the author list.
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Introduction

The main topic in this thesis is the physics and chemistry of $C_{60}$ and some of its compounds. A couple of experiment-related issues are discussed in order to characterise the central techniques used in these studies, the resonant inelastic soft X-ray scattering (RIXS) and the X-ray emission spectroscopy (XES).

Since the discovery of the soccerball fullerene $C_{60}$ by Kroto, Smalley and co-workers [1] in 1985 — followed shortly by the discovery of other fullerenes and the carbon nanotube structures — few substances or classes of materials have enjoyed such ardent scientific interest, probably only matched by the research activity on cuprate superconductors which started a few years earlier. In 1990, Krätschmer et al. [2] succeeded in producing gram quantities of $C_{60}$, which started the present publication rate of around 1000 articles per year on $C_{60}$ and related compounds.

The remarkably high symmetry of the molecule is intricately related to its superconductivity, first observed in 1991 by Haddon and co-workers [3]. Recently, superconducting transition temperatures as high as 117 K were obtained by doping lattice-expanded $C_{60}$ with holes (Schön et al. [4]). Superconductivity has even been detected in $C_{70}$ [5]. Apart from superconductivity, polymerised fullerides have provided the first permanent magnet that does not contain metal [6].

It is not straightforward to obtain a detailed theoretical understanding of the electron structure of $C_{60}$ and the derived compounds. On one hand, the high symmetry considerably reduces the number of independent variables and simplifies the theoretical calculations, but on the other hand, the choice of a model when taking into account, e.g., electron correlation and vibronic coupling has a critical effect on the ability to reproduce the experimental results. This underlines the significance of experimental studies which could provide criteria or at least hints for sorting out the relevant parameters for constructing adequate theoretical models.

This thesis contains a combined electron and X-ray emission study of $C_{60}$ and $K_3C_{60}$ (Papers I, II, III, IV), which attempts to provide some new information about the normal state (RT) transport properties, as well as the vibronic symmetry and coupling strength.

A useful aspect of resonant inelastic X-ray scattering (RIXS) when studying the electronic structure of $C_{60}$ and its compounds is the symmetry-selectivity of this spectroscopy. The interplay of the high symmetry of the molecules, the symmetry-selectivity of RIXS, and the “breaking” of the electronic symmetry by vibrations leads to some interesting phenomena which may contribute to the understanding of the physical nature of the resonant X-ray scattering process more generally. The symmetry properties are also strongly related to the observed spectral behaviour.
in the oxygen- and transition metal compounds with C$_{60}$ (Papers V, VII, VIII, IX).
Chapter 1

Methods and general background

This chapter gives an introduction into the basic mechanism of the interaction of soft X-ray radiation with an electronic system (i.e. an atom, a molecule or a solid), and the pathways and symmetry aspects of these processes.

1.1 Interaction of X-rays with matter

Figure 1.1 describes the interaction of an electronic system with X-rays with energies above the ionisation potential. There is a certain probability that the energy acquired by the system when it absorbs an X-ray photon will be released by emitting a photoelectron. The kinetic energy of the emitted electron, $E_{\text{kin}}$, is determined by the difference between the incident photon energy $h\nu$ and the binding energy $E_B$ of the electron combined with the work function $\phi$ of the system:

$$E_{\text{kin}} = h\nu - E_B - \phi.$$  

The kinetic energy distribution of the photoelectrons originating from different occupied levels carries information about the density of states in the system (e.g. a molecule or a solid), and is studied by X-ray photoemission spectroscopy (XPS).

By emitting a core electron, the system makes a transition to a state of finite lifetime $\tau_{\text{core}}$, typically a few femtoseconds. The minimal width $2\Gamma_{\text{core}}$ (i.e. full width at half maximum (FWHM) of the (Lorentzian) intensity distribution) of an XPS spectral line is then given by the Heisenberg uncertainty principle,

$$\Gamma_{\text{core}} \cdot \tau_{\text{core}} \geq \hbar.$$  

Consecutively, the core-ionised system decays by the transfer of a higher-level (i.e. less strongly bound) electron into the core hole, and the excess energy is carried away from the system either by another higher-level electron (the Auger effect) or, alternatively, the core hole can decay by emitting an X-ray photon. In the
ultra soft X-ray energy range ($\approx$50-1000 eV), the Auger electron emission is typically a factor of $10^2$-$10^3$ more probable than X-ray emission (XE). Despite the low yield, the X-ray emission spectroscopy (XES) has several advantages (as compared to photoelectron emission) when studying the valence electronic structure. For instance, it can provide information about the local partial density of states on different atomic species in a chemical compound, because the core levels of different chemical elements are generally well separated in energy, and because it follows dipole selection rules. Because of the short mean free path (a few tens of Ångströms) for electrons in a solid, the electron emission spectroscopies are extremely surface sensitive, as compared to the photon emission (with probe depths on the order of 1000 Å), which is dominated by the signal from the bulk of a material.

If the energy of the incoming X-ray photons is tuned to core-valence absorption resonances (see Figure 1.2), information can be obtained about both the unoccupied and the occupied parts of the valence band electronic structure. X-ray absorption spectroscopy (XAS, sometimes also called by the more precise term NEXAFS — “near-edge X-ray absorption fine structure” — to distinguish it from the techniques which study the X-ray absorption high above the ionisation threshold) provides information about the unoccupied valence band structure by studying the transition probabilities from core to the unoccupied valence region. Resonant X-ray inelastic scattering (RIXS) and resonant photoelectron emission spectroscopy (RPES) study the decay of the core-excited (not ionised) XAS final states. Depending on whether the electron filling the core vacancy is the electron excited to the empty states or an electron from the occupied part of the valence band, both techniques distinguish two contributions: participator and spectator decay in RPES, and the electronically elastic (REXS) and inelastic (RIXS) contributions in the resonant X-ray scattering (RXS). Additional information about the electronic structure, as well as of the dynamics, becomes available in these spectroscopic techniques, e.g. (in RIXS), the symmetries of the electron orbitals.

![Figure 1.1: X-ray interaction with the electrons in non-resonant processes: X-ray photoemission, Auger electron emission and X-ray emission.](image)

Due to the largely different escape depths, the comparison of the information obtained using electron and photon emission spectroscopies can be very useful in identifying bulk and surface states. The de-excitation cross-sections, however, can
1.2 Theoretical description of the X-ray processes

In classical theory, the interaction of radiation with an atomic system is described by the Hamiltonian [7]

\[ H = H_0 + H_{\text{int}} = \sum_i \left( \frac{1}{2m} (p_i + eA)^2 + V(r_i) \right), \]

where \( H_0 \) is the unperturbed Hamiltonian

\[ H_0 = \sum_i \left( \frac{1}{2m} p_i + V(r_i) \right) \]

and the sum is over all electrons. The interaction term can be expressed as a perturbation

\[ H_{\text{int}} = \frac{e}{m} \sum_i (A \cdot p_i + eA \cdot A), \]
where the field is described by its vector potential \( \mathbf{A} = \mathbf{A}(r_i, t) = A_0 \exp(i(k \cdot r_i - \omega t)) \) at electron \( i \).

In the soft X-ray region, the scalar product \( k \cdot r \) is much less than one and the series expansion of the respective term can be approximated by \( \exp(ik \cdot r)=1 \). The field is then given as a harmonic oscillator (an oscillating dipole) \( \mathbf{A} = A_0 \exp(\omega t) \).

For an electronic transition, this so-called dipole approximation imposes the selection rules \( \Delta l = \pm 1 \), \( \Delta s = \pm 0 \), \( \Delta j = 0, \pm 1 \), \( \Delta m_j = 0, \pm 1 \) (with the exception that \( m_j 0 \to 0 \) is not allowed when \( j = 0 \)).

Since the \( \mathbf{A} \cdot \mathbf{A} \) term changes the total number of photons by 0 or 2, it does not contribute to the first order interaction process, but it describes the elastic part of a scattering event in first order. For the inelastic scattering, one has to look at the interaction described in the formulae above in second order. The inelastic scattering is thus dependent on a \( \mathbf{A} \cdot \mathbf{p} + \mathbf{A} \cdot \mathbf{p} \) term in the second order perturbation theory. The differential cross-section of X-ray scattering is given by the Kramers-Heisenberg formula \[17\]

\[
\frac{d^2 \sigma}{d\omega' d\Omega} \propto \frac{\omega'}{\omega} \frac{e^2}{2mc^2} \left< |\mathbf{A}' \cdot \mathbf{A}| i > \right>
+ \frac{e}{mc} \sum_m \left( \left< |\mathbf{A}' \cdot \mathbf{p}| m > \right| m |\mathbf{p} \cdot \mathbf{A}| i > \right) \frac{E_m - E_i - \hbar \omega - i\Gamma_m/2}{E_m - E_i + \hbar \omega'} \left. \right|^2 \delta(\omega - \omega' - \omega_{fi}),
\]

where \( d\Omega \) is the solid angle element, \( \hbar \omega, \hbar \omega' \) and \( \hbar \omega_{fi} \) are the energies of the incident photon, the emitted photon and the of the transition from the initial \((i)\) to the final \((f)\) state, respectively; \( m \) denotes the intermediate state, and \( \Gamma \) is the core-hole lifetime width.

### 1.3 Selection rules and symmetry

Selection rules are useful when one has to separate the non-zero probability (the “allowed”) transitions from the “forbidden”, or zero-probability ones. In a simple, one-electron, one-dimensional picture the intensity \( I \) of a transition is given by the integral

\[
I \propto \left| \int_V \psi_f^*(x) g_f(x) \psi_i(x) dx \right|^2 ,
\]

over all space. Here \( \psi \) is the one-electron wave function, \( g \) is the transition operator and the indices \( f \) and \( i \) denote the final and initial states, respectively. For this integral to be non-zero, the integrand has to be a function of even (gerade) parity.

In case of an even parity operator \( g \), the wave functions should be of the same parity, and if the operator is represented by an odd (ungerade) function, the wave function parity should change upon transition between the states.

In a general case (where inversion symmetry, and parity, need not be present) the above requirement can be rephrased in group theory terms: the direct product of the symmetry representations of the initial state (\( \Gamma_{\text{initial}} \)), the operator
(\(\Gamma_{\text{operator}}\)) and the final state (\(\Gamma_{\text{final}}\)) must not vanish under the equivalence transformations of the group, i.e. the direct product must contain the totally symmetric irreducible representation \(\Gamma_0\) of the group:

\[
\Gamma_{\text{final}} \otimes \Gamma_{\text{operator}} \otimes \Gamma_{\text{initial}} \supset \Gamma_0.
\]

For that, of course, one has to know, besides the symmetries of the states, the symmetry of the interaction operator.

The wavelengths of the ultra soft X-rays (50-1000 eV) range approximately from 20 to 250 Å (\(\approx 10^2-10^3\) eV) and can therefore be considered large compared to the dimension of an atom they are interacting with. The field strength at each given moment of time \(t\) can be regarded as constant within the molecule, and the field experienced by the atom or molecule to vary as a function of time only. In the excited state, achieved by absorbing a light quantum with the frequency close to an atomic or molecular eigenfrequency, it can then be regarded as an oscillating dipole. This so-called long-wave or dipole approximation, where applicable, leads to some considerable simplification when calculating the transition probabilities.

For a transition to have non-zero probability and thus to be observable in a spectrum, the integral

\[
\int_V \psi_i^* H_{ij} \psi_j d\tau,
\]

where \(H_{ij}\) now is a transition operator, has to be different from zero. E.g. in a system with inversion symmetry, such an integral would vanish, if the integrand is an ungerade function with respect to the origin (viz. the nucleus), and can be non-zero, if it is gerade.

This can be exemplified in a simple picture, where a dipole field (of linearly polarised radiation) is impinging on an \(s\)-orbital (which is isotropic) and, if energetically allowed, induces a transition into a \(p\)-orbital, which has the symmetry of a Cartesian coordinate, which is the same as the symmetry of the field.

1.4 Vibrations and electronic “symmetry breaking”

XES and RIXS study firstly the transitions between different electron energy levels (orbitals or bands). If the excitation is localised to a single atom (as in an atomic gas or, e.g., if in solid state, as an Anderson impurity), the transitions between the atomic orbitals follow strictly the selection rules of the dipole interaction. In an absorption or emission event, the scalar sum of the orbital quantum numbers of all individual electrons is always changed by one unit, \(\Delta \sum l_i = \pm 1\). The atomic part can then neatly be described using the symmetry selection rules for the atomic orbitals.

Even in systems that contain several or a large number of nuclei, it is in many cases reasonable to assume that the electronic part of the wave function is independent of, e.g. the movements of the atomic nuclei (vibrations) due to its short time-scale. In this case the ungerade vibrations have to couple to the electron function and cause a parity change either in the intermediate or the final step.
With increasing amount of vibronic coupling, the symmetry- and, particularly, the parity-selection rules cease to apply strictly and become what is called propensity rules in the sense that the changes in relative intensities still to a certain extent express the symmetry properties of the electronic part of the wave-function.

However, when the interaction time can be made extremely short (on the time-scale of the vibrations), theory predicts the symmetry to become “purified” due to the decreased role of interaction with vibrations [8] — as observed experimentally in RIXS and RPES (see, e.g., Ref. [9]). In the energy-dependent picture, this corresponds to excitation not at a resonance, but rather displaced from the resonance peaks of any particular (vibrational) state, i.e. exciting on a manifold of Lorentzian tails. Far from the resonance, the tail excitations to different vibrational states can become comparable in magnitude and in the limit of large detuning, the excited state would be equally distributed over all the vibrational eigenstates of the vibrational manifold, i.e. the vibrational part of the excited state wave function becomes totally symmetric, and the symmetry character of the electronic state is regained [9–11].

1.4.1 The Jahn-Teller effect and distortions

A special case of vibronic coupling is made up by the coupling of the electron excitation to the electronic symmetry lowering Jahn-Teller (JT) active vibrational modes.

The principle of the Jahn-Teller effect and the distortions is that in systems with (viz. orbital) degeneracy, the degenerate subsystems start to interact with each other spontaneously in order minimise the energy by transforming the system symmetry into a sub-group of the original, in which the ground state of the many-electron system becomes less degenerate, favourably totally symmetric.

This effect can occur in almost all systems (with the exception of linear molecules) which have partially filled sub-shells. Depending on the energy gain, the distortions can be either static (e.g. lattice distortion) or dynamic (induced vibrations). The symmetries of the possible distortions are determined by the symmetry of the degenerate initial state: these have to be contained in the decomposition of the symmetric (or antisymmetric in the case of half-integer angular momentum quantum number values) part of the direct product of the initial representation with itself, as expressed by the direct product

$$\Gamma_i \otimes \Gamma_i \supset \Gamma_{JT}$$

where $\Gamma_i$ is the initial state symmetry representation and $\Gamma_{JT}$ is the JT-distorted symmetry. From this it is obvious that the allowed modes are always gerade, i.e. not changing the parity of the electron sub-system.

When a JT vibration is excited, the total symmetry of the electron-vibrational (the vibronic) system is preserved, but is split into subspaces of electronic and vibrational character. From the point of view of the electron subsystem, the JT vibration acts as a gerade operator $\hat{V}_{JT}$ on the initial system of wave function: $|i>: \n
$$<i|\hat{V}_{JT}|i>.$$
In the work presented in this thesis, the Jahn-Teller effect is most relevant to the studies of C\textsubscript{60} and K\textsubscript{3}C\textsubscript{60} (see Section 3.2 and 4.2).

1.4.2 Coupling to “infrared-active” vibrations

As stated above, the JT distortions can couple to the excited electron state, but they cannot change the parity of the system and in that way explain the observation of “violating” the selection rules for transitions of purely electronic character. On the other hand, if the electronic and the vibrational part of the total wave function are strongly coupled, as is the case for C\textsubscript{60}, then even the selection rules apply to the total vibronic (vibrational-electronic) wave function. For example, if a transition is forbidden electronically (adiabatically), it can become allowed in the diabatic regime when exciting the system both electronically and vibrationally by coupling to an ungerade vibration of suitable multiplicity. If the core orbitals have a small overlap, with the bandwidth less than the vibrational energy, then the vibrations will be able to annihilate the core overlap and thereby to localise the core-hole, so that the initial (electronic) symmetry is lowered or lost and the initially (electronically) forbidden transitions become allowed [12–14].

In infrared absorption and scattering spectroscopy, the vibrational modes that can be excited (in a first-order process) by absorbing a light quantum are termed infrared-active modes, and the modes that can be excited by scattering light are called Raman-active. The parallels to the spectator and participator components of RIXS spectra are quite straightforward and can be rationalised as follows: the participator decay has the same selection rules for the decay as for the excitation,

\[ < \Gamma^\text{el}_N | \Gamma^\text{EM}^- | \Gamma^\text{el}_m \Gamma^\text{vib}_m > < \Gamma^\text{el}_m \Gamma^\text{vib}_m | \Gamma^\text{EM}^+ | \Gamma^\text{el}_i \Gamma^\text{vib}_i > , \]

where \( N = i, f \) and \( i, m, f \) correspond to the initial, intermediate and the final states, respectively, and the \( \Gamma^\text{el}_N \) is the electronic state symmetry, \( \Gamma^\text{vib}_m \) is the vibrational mode symmetry, and \( \Gamma^\text{EM} \) stands for the symmetry of the dipole field, which in the \( I_h \) symmetry group of C\textsubscript{60} corresponds to three-fold degenerate ungerade \( T_{1u} \) irreducible representation. From this expression it can be seen that any vibrational energy loss in participator-RIXS has to be due to coupling to the gerade JT modes, with selection rules for the vibrational component of the spectra similar to Raman spectroscopy (parity unchanged, and the degeneracy corresponding to that of a Cartesian coordinate squared). The spectator RIXS (i.e. the part that includes scattering on electronic transitions; \( N = f \) in the expression above), on the other hand, can in principle involve the excitation of an ungerade vibration in either the excitation or the de-excitation “step”, and thus with no change of parity of the electronic part of the wave-function during this stage of the scattering process. If the other “half” of the process proceeds then without the (de-)excitation of an ungerade vibration, X-ray emission from the electronically forbidden transitions becomes allowed (hence the term “symmetry breaking”). To avoid confusion it should be emphasised that the words “step” and “half” do not reflect thinking in the “two-step” (excitation + de-excitation) framework of the scattering, but are used merely as schematic aids in order to explain scattering on a vibronic, instead of a purely electronic transition. It is also clear, that due to the degeneracy of
the excited electronic state as a starting point, the degeneracy of the *ungerade* vibrations is less defined than in the case of the usual infrared scattering. Still, this illustrative parallel should explain the character of vibrations that can couple to the participator and the spectator scattering paths. This conclusion is not limited to the systems studied here, but is of more general nature.

The experimental results relevant to these considerations are described in Papers III and IV.

### 1.5 Charge transfer vs. localisation

Although the overlap of the core orbitals can be small, it still is non-zero and the core levels of the atoms in, *e.g.*, C\(_{60}\) form molecular orbitals in a way similar to the valence electrons. The difference, of course, is the narrowness of the core ‘band’, which has to contain all the 120 C 1s-electrons ordered in symmetries available in the \(I_h\) group. As already described above, by exciting an electron from the core to the unoccupied part of the valence band, the hole left behind has to carry certain symmetry information, just as the extra electron in the LUMO-band does. The total symmetries are then represented by the decomposition of the direct product of these two particles (the hole and the electron), since the C\(_{60}\) many-electron ground state is totally symmetric.

For a solid state sample, the character of the RIXS spectra depends on the charge transfer rate or more explicitly, on the presence or absence of the symmetry information carried by the excited electron at the de-excitation event. In an atomic lattice like for example Si, the excited electron wave function can extend over a large volume, whereas the preserving of the symmetry information depends on the absence of inelastic scattering on the other particles. In a molecular solid like C\(_{60}\), preserving the information means firstly that the excited electron is not removed from the excited molecule, because due to the large number of intramolecular vibrations and their large coupling strength to the electronic part of the wave function, the probability that the (back-)scattering of the electron from another molecule could be elastic, can be considered negligible.

An alternative possibility for observing an apparent “symmetry-selectivity” in the spectra which can in principle be due to the polarisation of the incoming light which creates a preferred orientation for the excited molecular dipoles. However, due to the high symmetry of C\(_{60}\), and the observation that the spectral profiles characteristic of excitation to the different absorption resonances are not dependent on the orientation with respect to the polarisation [10], the effect of polarisation can probably not be expected to be dominant.

It is interesting from the viewpoint of the transport properties in the alkali-doped fullerenes that the symmetry information is preserved even in the case of the conductive, metallic K\(_3\)C\(_{60}\), as described in more detail in Section 4.7.1 and in Paper I.
1.6. ELECTRON CORRELATION

Electron correlation, i.e. many-body effects, determine the physics of a system or a process in a variety of cases. In the studies presented in this thesis, it is relevant in two different mechanisms: 1) the Coulomb interaction of electrons, determining to a large extent the transport properties of a system and 2) as an ultrafast interaction between a core electron, excited well above the continuum limit and another core electron, which also gets ejected due to this interaction, on time-scales of the photoelectron leaving the atom, thus elucidating the limits of the ‘sudden approximation’.

1.6.1 Hubbard interaction

If there is a small overlap of the wave functions centered at different lattice sites and the resulting narrow (valence) bands, the prerequisites (assumptions) of the conventional band theory — that the electron can move freely in the periodic potential and a mean field of the other electrons — may no longer be present. The on-site \((U)\) and nearest-neighbour \((V)\) Coulomb interaction strength may become comparable to the band width \(W\), and the electron-electron interaction has to be taken into account explicitly.

The classes of materials which require such theoretical treatment are, \textit{viz.}, many transition-metal oxides, including the superconducting copper ceramics and the giant magneto-resistance (GMR) compounds. The alkali salts of \(C_{60}\) have also shown properties which are hard to explain in the framework of band theory, and have in several cases been consistently described by taking into account correlation effects. Although the correlation phenomena lack a general analytical theory, a number of models exists, which in spite of quite severe approximations still give good account of the spectra observed.
The Hubbard Hamiltonian

\[ H_{\text{Hubbard}} = -t \sum_{(i,j),\sigma} (c_i^\dagger c_j + c_j^\dagger c_i) + U \sum_j n_{j\uparrow} n_{j\downarrow} \]

(where \( t \) is the transfer integral (assumed equal for all sites), \((i,j)\) marks summation over nearest neighbours, \( c_i^\dagger \sigma \) and \( c_i \sigma \) are the creation and annihilation operators with spin \( \sigma \) at site \( i \), and \( n_{i\sigma} = c_i^\dagger c_i \) is the number operator of electrons with spin \( \sigma \) at site \( i \)) provides an analytical solution for a simple case of one-dimensional system of \( s \)-states [15–21].

The ground state energy for an array of atoms or molecules in charge state \( n \) is seen to be \( M \cdot \frac{1}{2} n(n-1)U \), where \( M \) is the charge state. It is readily calculated that the creation of an electron-hole pair increases the energy of the system by \( U \).

Figure 1.3 shows schematically some transitions from the ground state of an \( n \)-charge state atom array, and the arrows with transition energies lead to different excited states. For instance, the top right system corresponds to a photoemission final state (neglecting here charge transfer screening that could neutralise the effect of the nearest-neighbour interaction \( V \); see also Paper I). The magnitude of \( U \) can in principle be measured directly as the difference of the PES (top right in Figure 1.3) and inverse PES (bottom right) energies (e.g. \( \approx 1.5 \) eV for \( C_{60} \)).

Although the basis seems quite limited, it has been generalised to systems of higher dimension and has been shown to give consistent explanation to a range of correlation-related deviations from the band theory prediction.

For instance, it also appears to provide a quite adequate description of some aspects of the spectroscopic data of the alkali-reduced fullerite solids of stoichiometry \( A_x C_{60} \), and in that way to be a theoretical link between the measured electron structure data and the (normal state) transport properties.

### 1.6.2 Double core-hole photoionisation

This phenomenon seems to go outside the limits of the dipole approximation. However, if an electron is excited to the continuum with kinetic energy sufficient to eject another electron, it has a small but finite probability to do so during the time while it still is within the spatial range where it effectively interacts with the rest of the electron system through Coulomb forces. Such shake-up and shake-off processes are commonly observed in PES (viz. for isolated molecules) as far as accompanying valence excitations are concerned. The electron-electron interaction triggering the creation of an empty core atom is similar, but the important difference lies in the high instability of a hollow-core system, and the much shortened lifetimes open a time-window for studying fast correlation effects in multi-electron systems.
Chapter 2

Experimental

2.1 Synchrotron sources

For most studies in this thesis, tunable high brilliance undulator radiation sources at synchrotrons are a prerequisite. The radiation in a synchrotron source is generated when the electrons, travelling at very close to the speed of light, are accelerated, i.e. forced to change the direction of their velocities. Magnetic fields are used for controlling the beam direction. Three types of radiation sources on the storage ring are distinguished (see Figure 2.1): the bending magnet, the wiggler and the undulator. The bending magnet is a dipole magnet placed at a vertex of the synchrotron “ring” (or more precisely: a polygon), generating forward-directed cone of light, and has a characteristic frequency, which is determined by the electron energy and the field strength. A wiggler is mounted on a straight section and consists of several “bending-magnet”-poles to gain intensity. The most selective and bright source is the undulator, which like a wiggler is a periodic magnetic structure, but the number of poles is considerably larger, and their distance and the field strength are chosen so that the light is generated coherently at different bending stages and interferes with itself. The interference of light from different periods concentrates the intensity from an undulator source into narrow spectral regions, the “undulator” peaks, which are the result of interference in different orders.

The synchrotron measurements presented in this thesis were carried out using undulator radiation sources. The measurements reported in Papers V, VI, VII, VIII, IX were carried out at Beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA, and the measurements for Papers I, II, III, IV, XI at beamline I511 at MAX-Lab in Lund. The experimental setups are described at the end of this chapter.

2.2 X-ray absorption (NEXAFS) measurements

The X-ray absorption spectra of gaseous materials can at least in principle be measured in transmission mode, recording the changes in the “transparency” as
a function of the incident photon energy. Due to the extremely short attenuation lengths of soft X-rays in solids, this is not possible in solids (except possibly in some cases for ultrathin films). Instead, the incident photon energy dependence of the yield of secondary particles (electrons or photons), which are produced during the decay of the core excitation, can then be used in order to get information on the energy-dependence of the absorption cross-section. Due to practical reasons, these techniques are favoured even when recording gas-phase NEXAFS, and due to the relatively longer escape depths of photons, the photon yield measurements can also be used on liquids.

To obtain an experimental spectrum which is more or less directly corresponding to the absorption cross-section, total or partial electron or photon yields can be recorded. These different options generally use different detectors, and have advantages and limitations, which are reviewed below.

First, total electron yield (TEY) can be obtained most simply by recording the sample drain current, as electrons are photoemitted from the sample upon interaction with incident light either directly or due to decaying of an autoionising state. The drain current setup essentially consists of a wire, which connects the sample holder, which is isolated from the ground, through a vacuum feedthrough to a picoamperemeter. An obvious advantage of this technique is the simplicity of the setup, while the results for metallic, or even semiconducting samples are nevertheless as good as for the more sophisticated setups. However, applicability to conducting samples only and the shallowness of the surface layer of the sample that is probed, can sometimes make it necessary to use a different setup. Other
2.2. X-RAY ABSORPTION (NEXAFS) MEASUREMENTS

Figure 2.2: Saturation effect in TFY (absorption) spectroscopy: due to the large photon escape depth, the photon yield recorded with near-normal exit angles may at different energies (for different energy-dependent absorption cross-sections) contain contribution from different depths in the sample, neutralising the effect of the absorption cross-section. At near-normal detection angles, the light at energies with smaller absorption coefficient can originate from deeper in the sample than at energies with large absorption cross-section. The total intensity observed can at the same time be almost constant.

possibilities for recording the TEY signal are to use a channeltron detector or an MCP detector.

Second, the total photon yield, alias total fluorescence yield (TFY) signal can be recorded by using a channeltron detector, an MCP detector or, as a less efficient option, by using the XE spectrometer in zero order diffraction. Being a photon-in-photon-out technique, this method can reach considerably larger probe depths (on the order of 1000Å) and is less sensitive to possible surface contamination. It can also be used to measure absorption in buried layers (e.g. in samples covered by a layer of material protecting the sample from oxidation during transfer, as in Paper VII).

When using this technique, however, one should be careful considering the effects of self-absorption, and the fact that the absorption cross-section need in many cases not be proportional to the photon yield signal. The effect of self-absorption

\[ I_f(E_{in}) \propto I_0(E_{in}) \frac{\mu(E_{in})}{\mu_{total}(E_{in}) + \mu_{total}(E_{out}) \cdot \tan \alpha}, \]

is illustrated in Figure 2.2. For a bulk sample or a thick film, all of the incoming light gets absorbed, although the effective absorption length depends on the energy-dependent cross-section. If the TFY signal is then recorded at a near-normal (exit) angle, the secondary photons come from different depths in the sample for different incident energies, but due to the long escape depth these photons are still capable of leaving the sample and the dependence of the total number of emitted photons can in the extreme case be constant (independent of energy and only dependent of the incident intensity). The best way to prevent this from happening is to use near-normal incidence angles and grazing exit angles, so that photons emitted only from a thin surface layer are detected. This signal should then be proportional to photons absorbed in the same layer of limited thickness, and the total number of the absorbed, and emitted, photons should be proportional to the absorption cross-section. The amount of self-absorption differs from
material to material between the extremes of wiping off all structure in the spectrum to negligible effects. The technique can still be very useful, especially in the cases when this is the only option, e.g. for buried layers or for liquids in a containing cell equipped with a window.

Third, partial electron yield (PEY) can be measured by using a photoelectron spectrometer and choosing an energy window (and integrating the total countrate within the window). This will give the decay rate via a certain transition. A less sophisticated alternative to this is to use a total yield detector in combination with one or several retarding grid(s) in order to set a low kinetic energy limit for the electrons which can reach the detector. Using the PEY instead of TEY enables to enhance the element-specificity to some extent (in case of a composite sample) and gives some flexibility to choose the probe depth by recording decay channels with quite different kinetic energies.

Fourth, partial fluorescence yield (PFY) measures the decay rates (of an energy-dependent magnitude of a core-excited population) via a specific fluorescent decay channel. Although this technique usually suffers from extremely low countrates, the capability to discriminate more strictly against (the approximately constant background) fluorescence from other elements in a composite sample make it in certain cases useful. The signal can be detected by choosing a suitable energy window in the spectrometer and integrating the countrate for each incoming photon energy step.

2.2.1 NEXAFS detectors

Several detector setups for measuring NEXAFS were introduced above, two of which (PFY, PEY) require the use of spectrometers, which are described in Sections 2.3 and 2.4, respectively. An option is to use the sample current which lacks any particular details to be elucidated. The following is a brief account details of the functioning mechanism of the MCP and channeltron detectors for total yield NEXAFS measurements.

The multichannel plate (MCP) consists of a multitude of parallel glass tubes of typically \( \leq 10\mu m \) in diameter. A high voltage is applied at the opposite ends of the tubes (i.e. at the opposite MCP surfaces). A primary particle (viz. an electron) impinging onto the tube wall will then initiate a chain reaction of releasing a stepwise growing number of secondary electrons. When reaching the opposite side of the MCP, the number of electrons is sufficient to be recorded as a current pulse (if the rate of arriving of the primary particles is not too large so that pulses from different primary hits start to overlap temporally). In order to avoid back-ringing and positive feedback, and to increase the sensitivity of an MCP detector, MCPs of opposite tube tilt angles (with respect to the plate surface normal) are often used in stacks (i.e. in series). A major advantage of an MCP-based NEXAFS detector is its large acceptance solid angle due to its diameter, which typically ranges up to 40 mm.

An MCP-detector can be switched between detecting electron and photon (plus ion) yield in principle simply by applying opposite voltages to the MCP-stack. For photon-detecting mode, however, it is advantageous to coat the incidence-surface of the MCP(-stack) with some material of low work-function (most typically CsI),
which would then generate a bunch of electrons upon a photon hit. The other aspect when measuring the photon yield, the attraction of ions when a negative high voltage has been applied to the front surface, can be overcome by placing a grid in front of the front MCP surface at a positive voltage somewhat higher than the incident photon energy.

The channeltron detector works on roughly the same principle as the MCP, with the exception that there is only one, large diameter “tube”. The voltages are applied in much the same way as for an MCP, the principle of using grids to block ions (when measuring photon yield) and/or low-energy electrons (“the secondaries’ tail”) is the same. The yields are somewhat lower than those obtained using an MCP-detector, but the ease of construction and the small size can make it easier to have it close to the sample in a vacuum chamber and in some cases it might be intensity-wise even more advantageous than using an MCP.

2.3 X-ray emission spectrometer

The X-ray emission and scattering spectra were measured using a grazing incidence soft X-ray spectrometer, developed in the group [22] (and commercialised through Gammapdata as XES300). The working principle of the spectrometer is explained in Figure 2.4. The principal elements of the spectrometer are the (entrance) slit, the grating selector, three spherical gratings (for different energy regions), and the detector (a stack of five 40 mm diameter multichannel plates (MCPs) combined with a resistive anode position-sensitive readout). Since there are three gratings mounted in the instrument, the grating selector is used to limit the illumination to one grating and to block the incoming light from reaching the other two gratings. The slit and the grating are (fix-)mounted in the Rowland circle (i.e. on a circle of diameter equal to the radius of curvature of the grating, see Figure 2.3) geometry. The detector can be positioned to contain/reach the energy window under study.

![Figure 2.3: Rowland mounting of a spectrometer with a concave diffraction grating and without exit slit. The light is coming from the right. Note that the radius of curvature of the grating is double that of the Rowland circle. Two detector positions at the foci for different wavelengths are shown.](image)
Many conventional optical spectrometers, which work by the principle of a monochromator, use spherical gratings in order to focus the wavelength-dispersed light on an exit slit. Such setup would then allow to record the signal of one wavelength at a time, and a spectrum can be obtained, e.g., by scanning the grating incidence angle. However, due to the often (very) low intensities, the acquisition time of a spectrum would quite often become impractically long in the soft X-ray energy region.

Instead, the image of the slit is focussed by the spherical concave mirror or grating onto a line on the Rowland circle. More generally, and within the region where the distance between the mirror (grating) surface and the Rowland circle can be considered negligible, different exit (diffraction) angles correspond to foci at different points on the Rowland circle. The detector is placed to be tangent to the Rowland circle, and the large radius of the Rowland circle (1.5 m or 2.5 m, depending on the grating used) makes the signal focussed at least over most part of the detector, so that all wavelengths within the contained energy window can be recorded simultaneously. The energy resolution is then of course limited by the number of channels per wavelength interval, in addition to being limited by the
2.4 PHOTOELECTRON SPECTROMETERS

sharpness of the focus, which is determined by the slit width and the quality of
the grating and the detector surfaces.

However, as also depicted in Figure 2.4, the image of the straight entrance
slit of the spectrometer is a curved line at the detector. In order to be able to
compensate for that, the width of the detector has been divided into 32 stripes
(“slices”) perpendicular to the dispersion direction. Considering the curvature of
the line negligible over the width of any such stripe allows then to align these
slices by shifting them in the energy direction and consecutively summing to give
one-dimensional spectrum.

Theoretically, the slit-width-limited resolution of the spectrometer is given by

$$\Delta \lambda = \frac{1.1 \cdot w}{mRn},$$

where $w$ is the slit width, $m$ is the order of diffraction, $R$ is the grating radius
of curvature and $n$ is the grating line density. The resolution obtainable by de-
creasing the slit width is, however, limited by other factors, such as the size of
a sensing element (“pixel”) of the detector and the deterioration of the grating
surface from the Rowland circle. These factors become dominant when the slit
width is decreased to less than $\approx 8 \mu m$.

The Rowland circle mounting of the optical elements has an additional ad-

vantage when aiming to improve the inherently low acceptance solid angle of a
grazing incidence spectrometer: namely, if the size of the source (viz. beam focus
of a synchrotron beamline, or the spot of a fine-focus electron gun) can be made
comparable to the slit widths, the same resolution of the emitted photon energies is
obtainable by removing the slit (which normally is considered as a source) and use
the beam-spot as the source. By doing this, the intensity seen in the spectrometer
can be increased up to an order of magnitude.

2.4 Photoelectron spectrometers

To obtain a kinetic (or binding) energy distribution of photoelectrons, created by
interaction with incident photons of well-defined (and constant) energy, one needs
an energy-dispersive detecting system.

The electron energy analysers mostly use electrostatic deflection to energy-
separate electrons. A quite popular exception (using magnetic deflection) to this
is the so-called “magnetic bottle”-type spectrometer, which is a cost-effective al-
ternative to more sophisticated apparati, and is very useful in the case of small
energies. A more detailed description of different electrostatic analysers can be
found, e.g., in [23]. The hemispherical electron energy analyser (Scienta SES-200)
was used in valence and core photoemission, resonant photoemission (C$_{60}$) and
partial (Auger, and multiply-scattered) electron yield NEXAFS measurements in
Papers I - IV.
2.5 Experimental stations

As mentioned above, almost all the experimental studies in this thesis have been conducted at two synchrotron beamlines (BL7.0.1 at ALS and I511 at MAX-Lab). The data for Paper X were collected in Uppsala using electron excitation.

Because the instrumental facilities and degrees of freedom determine to a certain extent the nature and quality of the data, I will give in the following some details of the experimental facilities used.

2.5.1 Beamline 7.0.1 at ALS

Beamline 7.0.1 at the Advanced Light Source uses an undulator source with 89 magnetic periods of 5 cm length, a minimum gap of 23 mm and $K_{\text{max}} = 2.2$. The undulator beamline employs a spherical grating monochromator with fixed en-

![Figure 2.5: The schematic overview of the Surface Endstation on beamline I511 at MAX-Lab (the view looking towards the storage ring). The photoelectron spectrometer (Scienta200 hemispherical analyser) is seen at the top and the XES300 X-ray emission spectrometer to the right. The spectrometers are mounted on the analysis chamber which is rotatable around the beam axis.](image)
trance slit and sliding exit slit. The maximum resolution of the beamline is 10000. The spectra recorded for work included in this thesis were typically measured at resolution $\frac{E}{\Delta E} \approx 1000$. A bendable mirror images the exit slit to the experiment, giving a small spot ($\approx 40-50 \mu m$ vertical FWHM) across the operational range. The undulator gap can be changed as the grating rotates so that the beamline performs at the peaks of the undulator spectrum.

### 2.5.2 Bulk and Surface Endstations at I511 at MAX-Lab

At this beamline, the light is provided by an undulator source, which has 49 periods of 52 mm length, and provides linearly polarised light (horizontal polarisation). The light is further monochromatised by a Zeiss SX700 plain grating monochromator [24,25]. The monochromator does not use an entrance slit, relying on the geometrical stability of the undulator source (i.e., the stored electron beam) instead. (In case of beam instability, this could cause some minor divergence in the energy resolution, but experience shows that the energy calibration is outstandingly stable, not least due to the relatively fast (0.5 Hz feedback) beam position control in the storage ring.)

The beamline is divided into two branches with their respective endstations, one mostly dedicated to surface studies (see Figure 2.5) and the other one to spectroscopy of bulk samples (Figure 2.6). A flip mirror just after the monochromator exit slit is used to direct the light into one of the endstations. Both stations
are equipped with refocussing optics, a XE spectrometer (see Section 2.3) and NEXAFS detectors, the surface station additionally has a Scienta hemispherical electron analyser. The measurements on C$_{60}$ and K$_3$C$_{60}$ were carried out on the Surface Endstation (see Figure 2.5). Bulk Endstation was used to perform the measurements of Be hypersatellite in Paper XI.

The minimum spot size (FWHM), provided by the (bendable) Kirkpatrick-Baez elliptical refocussing mirrors is 10 µm vertical (ca \(\approx\) 30 µm horizontal) according to the specifications, and the value that has been measured in the analysis chamber (while using monochromator slits less than \(\approx\) 100 µm) is very close to the specified. The small spot-size provides an opportunity to remove (i.e. completely open) the entrance slit of the X-ray spectrometer, which allows to gain up to an order of magnitude in intensity (see Section 2.3).

2.5.3 The experiment station in Uppsala

The “Uppsala station” is a twin of the I511 “Bulk” endstation. Instead of X-rays, electrons are used for excitation. As no polarised excitation is produced, the analysis chamber is not rotatable. The electron gun is usually mounted at the beam port, so that the angle between the electron beam and the spectrometer axis is 90 degrees. Highest X-ray emission yields are expected for electron energies 3-8 times the transition energy, so typical electron energies used are around 2-3 keV.
Chapter 3

Electron structure and geometry of the fullerenes

Before elaborating on the results of the experimental studies presented in the Papers (in Chapter 4), this short chapter aims to provide some more general information about C$_{60}$, in particular on the geometry and electron structure of the molecule, and the molecular solid compounds. Topologically, the C$_{60}$ molecule is a truncated icosahedron, consisting of 60 equivalent vertices (where the carbon atoms are located), 12 pentagonal and 20 hexagonal faces. There are 120 edges in total: 60 edges of the pentagons (obtained by cutting the corners of a regular...
Figure 3.2: The molecular orbital filling of C_{60}.

The C-C distances are by a few per cent larger at the pentagon edges (1.45 Å) than at the edges between two hexagons (1.40 Å; there are no adjacent pentagons). The diameter of the molecule, measured through the nuclei is 7.1 Å. The pentagons consist of single σ bonds; the edges between two hexagonal faces have some additional, π-like, charge density, and are usually referred to as the “double bonds”. The upper part of the occupied valence band and the lower part of the unoccupied valence band are mainly π-character. The chemical and transport properties are thus mainly determined by the π-electrons.

It might be interesting to observe that despite the high symmetry of the molecule, there are no axes of rotation through the atoms at the vertices. To give a single example of the effect of the high symmetry to the accessibility to basic and simple physics, one could note that the lack of such symmetry axes as mentioned above means that in RIXS, if the core hole were be localised on a single atom, the inherent symmetry information would be lost in the spectra. The fact that symmetry information indeed is readily accessed in RIXS therefore brings us directly into a more general discussion of core-hole localisation.

3.1 The electronic structure of C_{60}

Of the 4×60=240 carbon 2 sp valence electrons, 180 are contained in the more strongly bound (tangential) σ-bonds. The remaining 60 electrons are strongly delocalised and occupy the π-like molecular orbitals, which are centered at the carbon atoms and point nearly radially outwards.

If the C_{60} molecule is considered to be spherical in the first approximation, the molecular orbitals \( \psi(r) \) can to a good approximation be represented in terms of
3.2 VIBRATIONAL MODES

their projections onto spherical harmonics,

\[ f_L(r) = \sum_m |\int_S Y_{Lm}^*(r)\psi(r)d\Omega|^2. \]

Integration over a spherical surface of radius \( r \) with the origin at the center of the \( C_{60} \) molecule typically yields parameters \( f_L \) which are approximately an order of magnitude larger for a particular spherical harmonic than all the others. While performing this procedure, notice has to be taken of the fact that the highest degeneracy of a single orbital is limited to five, resulting in the lifting of higher degeneracies present in full spherical symmetry.

The resulting molecular orbitals are classified in terms of the orbital quantum number \( L \), with the three lowest orbitals having the symmetry which is basically similar to that of the \( s, p \) and \( d \) orbitals of free atoms (i.e. non-degenerate, three-fold and five-fold degenerate, respectively, as shown in Figure 3.2). The higher molecular levels are split into sub-levels with five-fold degeneracy as highest.

In this picture, it is easy to see that the levels with \( L=1..4 \) are filled completely by 50 electrons, whereas the remaining 10 \( \pi \) electrons fill the five-fold degenerate \( h_u \) sub-level of \( L=5 \), which in total can accommodate 22 electrons. The partially filled \( L=5 \) level is the source of the very high, almost halogenic, electronegativity of \( C_{60} \).

Because no sub-levels are partially filled, the \( C_{60} \) ground-state symmetry of the many-electron state is totally symmetric. In the case of compounds (viz. the alkali salts \( A_3C_{60} \)) this no longer holds, and the degeneracy of the electronic state makes the charged \( C_{60} \) prone to coupling to the Jahn-Teller vibrations (described in Section 1.4.1), important for their superconducting properties.

Apart from the valence electronic structure, which gives structure to an energy “band” covering more than 10 eV, even the \( C 1s \) core orbitals have a non-zero overlap and, consequently, have to be ordered in a manner similar to the valence electrons. The width of this band is approximately 10 meV, so that in the case of core spectroscopies they have to be treated as energetically degenerate. Nevertheless, the existence of a large number of degenerate core-electron orbital symmetries (the 120 \( 1s \) electrons populate levels up to a partial filling of \( L=7 \)) has a certain bearing on the spectroscopic information. E.g., the RIXS many-electron intermediate state symmetry is defined by the symmetries of the excited electron and that of the core hole, and the preserving of the symmetry information in the RIXS spectra indicates that the symmetry has, to a good extent, to be preserved, i.e. even the core hole state appears not to be localised on a single atom.

3.2 Vibrational modes

Containing 60 carbon atoms, the \( C_{60} \) has in total 3·60=180 degrees of freedom. Six of these correspond to 3 translations and 3 rotations of the molecule as a whole. The remaining 174 degrees of freedom form the manifold of intramolecular vibrations, which can be classified, according to the symmetries available, to a number of generally degenerate modes. The decomposition of the group
representation of the vibrations along the normal coordinates gives the following
vibrational structure (the number in front of the mode gives the number of modes
of a given symmetry): $2a_g + 3t_1g + 4t_2g + 6g_g + 8h_g + a_u + 4t_1u + 5t_2u + 6g_u + 7h_u$. The
modes frequencies range approximately from 30 to 200 meV (see, viz., [26, 27]).

An electronic excitation, e.g. to the $t_{1u}$ LUMO state induces a degeneracy in
the electron wave-function, which readily couples to (i.e. excites) the Jahn-Teller
active vibrational modes (see Section 1.4.1; an excellent account of JT effects is
also given in Ref. [28]). Let us consider the core level as being shared (because of
the narrow core bandwidth) by an almost complete set of basis functions resulting
effectively in a totally symmetric core hole state. In that case the symmetry
of the Jahn-Teller modes involved is determined solely by the intermediate state
occupied by the excited electron. The Jahn-Teller modes that are allowed to couple
to a given degenerate state are contained in the symmetric part of the Kronecker
product (i.e. the direct product with itself) of the state symmetry. In the case of
LUMO, this product yields

$$t_{1u} \otimes t_{1u} = [A_g + H_g]_{symmetric} + \{T_{1g}\}_{antisymmetric},$$

and therefore in the case of an extra electron in the LUMO only the $A_g$ and $H_g$
mode are allowed to couple to the JT distortions. In solid state, the intramolecular
modes appear to be only weakly perturbed by intermolecular interaction. This
can be rationalised by the interatomic distances and bonding nature of $C_{60}$: the
intramolecular nearest-neighbour interatomic distances are $\approx 1.5 \, \AA$, compared to
the intermolecular distances between the van der Waals bound molecules, which
are at least twice as long. The intermolecular, i.e. lattice vibrations have therefore
at least an order of magnitude lower energies, and can in many cases be regarded
as of negligible influence to the electronic and vibrational structure of the
molecules. Within the experimental resolution of the X-ray spectroscopies used
here, an influence of the intermolecular modes could hardly be detectable.

In the studies presented in this thesis, the relevance of the Jahn-Teller effect is
most obvious in the case of $K_3C_{60}$ (Papers III and I), which has a half-filled triply
degenerate ground state (cf. the totally-symmetric ground state of $C_{60}$. Therefore,
the possibility of static JT distortions already in the ground state, stabilised to
some extent by the weak crystal field, can not a priori be excluded [27, 29].

If the ground state degeneracy is not completely removed in $K_3C_{60}$, and the
JT distortion correspondingly fully statically stabilised (considering the weakness
of the crystal field, the potential barrier can hardly be considered as of infinite
height though), the pattern of the allowed JT vibrations gets even somewhat more
intricate.

The allowed JT vibrations should be fully capable of introducing spectral shifts
or splits even for the resolution of RIXS, if coupled at least moderately to the
electron excitation, since the frequencies of the highest JT vibrations are around
0.2 eV. (Of course here one has to account also for the intra- and intermolecular
Coulomb interactions.)

In the case of symmetry selectivity in $C_{60}$, the Jahn-Teller effect, however, can
not be held responsible for observing the electronically parity-forbidden transition,
since as already pointed out, the JT modes have always even parity.
Chapter 4

Results

4.1 Electron-vibration coupling in $C_{60}$ viewed using RIXS and RPES

The main results of Paper III (Figure 4.1) depended critically on the enhanced energy resolution in both excitation and the spectrometer. First, it became possible to observe a purely vibrational energy loss peak in participant-RIXS (see Figure 4.2). Additionally, significant effects of quenched symmetry breaking, expressed in the changes in relative intensities of the peaks, were observed even with sub-electronvolt detuning of the excitation energy to either side of the $C_{60} C_{1s} \rightarrow$ LUMO absorption resonance in RIXS. The closely related results are found also in Paper IV: the energy loss to vibrations in RPE was huge, being close to the limit of linking different electronic states. This was interpreted in terms of loss to the Jahn-Teller modes which are readily accessible in the core-excited state of $C_{60}$.

The role of vibronic coupling in $C_{60}$ is interesting from at least two viewpoints: it is generally agreed to play an important role in the superconducting properties of (positively or negatively) charged $C_{60}$, and, on the other hand, the large number and the high symmetry of the vibrations can make it a test case for more general physical principles (see *viz.* Refs. [26,29,30]).

The role of the vibrations in the studies included in this thesis is reflected in the spectra in two ways: as energy loss to the vibrations, which causes shifts and changes in the profiles of single electronic states, but also as the source of “symmetry breaking” of the electronic part of the total wave function. The latter phenomenon has to be caused by the odd parity vibrations, since these can reverse the parity selection rules and possibly cause core hole localisation.

4.1.1 Jahn-Teller effect

The instability of a high symmetry system with respect to a degenerate atomic configuration, the Jahn-Teller effect, accounts for the lowering of the total energy through effective lowering of the symmetry and producing a totally-symmetric
(non-degenerate) configuration in the lower symmetry. This symmetry-“breaking”
can be either static (if the energy gain is large enough to stabilise a new electron
configuration) or dynamic, in which case vibrations around the equilibrium point
are involved.

For instance, adding an electron into the C\textsubscript{60} LUMO, which is of \(T_{1u}\) symmetry,
produces a system where the added electron can with equal probability populate
each of the three degenerate molecular orbitals. Given the Coulomb repulsion,
however, the energy of this system can be decreased by allowing the electron to
spend unproportionately more time in one of these orbitals, with accompanying
modifications in charge distribution in the rest of the orbitals. Effectively, the or-
bital starts to interact with itself. The effect of this is the creation of a disturbance
of a lower (viz. a \(D_{5d}\) elongation) symmetry as the electron becomes effectively

\begin{figure}[h]
    \centering
    \includegraphics[width=\textwidth]{figure4.png}
    \caption{Scattering spectra recorded at excitation energies (see inset) in the
    LUMO absorption resonance range. Inset: the 1s–\(\pi^*\) (LUMO) absorption profile of
    C\textsubscript{60} showing the excitation energies of the RIXS spectra.}
\end{figure}
Figure 4.2: The part of the previous spectrum near the excitation energy. The purely vibrational energy loss feature is resolved and shows a non-dispersing peak at energy which corresponds to emission from vibrational ground state.

localised in a “belt” around an axis connecting two opposite pentagons. In the case of large stabilising energy gain the electron would remain localised in one of these new multiple orbitals.

In the case of C_{60}, however, where the interaction is moderate, this means that the electron is not completely free to hop from one sub-level to another, but has to overcome (pro: tunnel through) an energy barrier in order to do that. The dwell time in one of the equivalent is inversely proportional to the tunneling frequency through the barrier. The excess energy gained by the partial localisation is transformed into a molecular vibration. The dynamic energy flow between the electronic and the vibrational part of the symmetry allows the electron to
hop between the equivalent sub-levels. This vibration is required to have the symmetry determined by the self-interaction, \textit{i.e.} it must be a component of the symmetric part of the Kronecker product (\textit{i.e.} the direct product of the irreducible representation with itself) of the initial electronic state symmetry.

An obvious consequence of this is that if the initial system has inversion symmetry, the Jahn-Teller active vibrational modes have to transform as even \textit{(gerade)} functions upon inversion. Generally, the vibration can produce a coupling not only within the same electron symmetry, but can also couple different electronic levels. However, the choice of these levels is subject to certain symmetry (selection) rules. As the vibration has to maintain its symmetry properties, it can neither relax the inversion symmetry of the system nor couple modes (or electronic levels) of opposite parity.

For interpreting the scattering spectra, especially the parity restriction of the Jahn-Teller interaction is important, since it states that the transitions, forbidden in the purely electronic transitions (and often observed in the RXS spectra) do \textit{not} become allowed through the (static or dynamic) Jahn-Teller effect. (However, energy loss to the Jahn-Teller modes is, of course, allowed, as long as a degenerate electron state is involved in the initial, intermediate, or the final state, or in any combinations of those.)

4.1.2 The effects of the core-hole state symmetries

As explained in the previous section, the Jahn-Teller distortions can not be held responsible for the observation of the electronically forbidden transitions in the RIXS spectra. Another effect which could distort the symmetry and possibly cause localisation of the excited state and, consequently, relaxation of the selection rules is the symmetry and (de-)localisation parameters of the core-hole state.

In a system with symmetry as high as that of $C_{60}$, the 1s core orbitals of the carbon atoms have a small, but non-zero overlap, \textit{i.e.} even the core electrons are not completely localised on individual atoms. Therefore, in order to follow the Pauli exclusion principle, the core electrons also have to be ordered in configurations of different symmetries, so that their wave functions are orthogonal within the molecule. In short, this means that despite the huge difference in bandwidth, the \textit{structure} of the core electron levels contains at least a similar multitude of all symmetries that are available in the symmetry group.

The 120 core electrons fill completely the shells corresponding to (molecular) angular quantum numbers $L=0...6$. A closed sub-shell configuration is then obtained by filling the $t_{1u}$, $t_{2u}$ and $h_u$ sub-levels of $L = 7$, and leaving the $g_u$ orbital unoccupied.

This multitude of symmetries means that there are virtually no symmetry-restrictions for the energetically allowed core excitations (\textit{i.e.} XAS). To contrast, for RIXS this obviously still means strong symmetry selection rules, since the core-hole has a symmetry and consequently restricts the (intermediate) states from where the electron filling the core hole can come from.
4.2 Effect of Jahn-Teller distortions on the spectra

The effect of the Jahn-Teller distortion is expected to cause broadening and shifts due to vibrational energy loss, rather than big changes in the relative intensities of, *viz.*, transitions from different parities and symmetries. It is also possible that the vibrations in the narrow electronic band act as a dynamic charge transfer barrier, which scatters the electrons and smears out the band.

In K$_3$C$_{60}$ the JT modes are even active in the electronic ground state. The spectral broadening, as seen in RIXS, is larger than for C$_{60}$, although this is probably not caused only by the JT modes, but is also in part a result of the charge density fluctuations and the Hubbard interaction.

The Papers III and I aim to elaborate more on this topic.

4.3 Effect of coupling to ungerade vibrations

C$_{60}$ has a multitude of near-degenerate molecular core-levels, with both parities and all possible symmetries of the truncated icosahedron. These core-levels form a narrow (FWHM $\approx$10meV) band. For a vibrationless, purely electronic C 1$s$ $\rightarrow$ $t_{1u}$(LUMO) photoexcitation then, of course, the core hole has to originate from an *even* parity core orbital. If the core-hole then decays by emitting an X-ray photon, this means that the electron filling the core hole has to originate from a valence state of suitable symmetry of *odd* parity. In case of non-zero vibronic coupling to *even* parity vibrations, the symmetry selection rules can generally be modified, with the exception of parity selection criteria, which remain exactly the same as in the purely electronic case.

What is observed in the experimental RIXS spectra (see Figure 4.1), however, is an excitation-energy dependent “symmetry breaking”, *i.e.* emission from the valence levels with the parity opposite to that of the orbital that was occupied by the excited electron.

The amount of this “symmetry breaking”, *i.e.* the ratio of the intensity of the electronically allowed transitions, in this case emission from *ungerade* valence states, to the emission intensity from the *gerade* valence states depends on the excitation energy. Figure 4.3 shows the energy dependence of this intensity ratio for excitation energies around the C 1$s$ $\rightarrow$ LUMO absorption resonance. The solid curve is the fit to the theoretical model proposed for dynamical symmetry breaking in CO$_2$ [9]. This model is appropriate if the vibrational envelope is considerably broader than the core-hole lifetime width. In the case of C$_{60}$, the core-hole lifetime width is 0.115 eV, and the width of the absorption resonance is more than twice that, so the model is not exact, but could still give an idea of the nature of the dynamics of the “symmetry breaking”. It should be noted that the absorption profile is actually not symmetric to begin with, and part of the deviation on the high energy side is probably a result of that. At least two things are important to note in Figure 4.3: 1) the effective vibronic coupling strength (0.18 eV) agrees well with the estimate from the photoemission data (0.147 eV) [27], 2) this is less
4.4 Relevance to superconductivity

It is generally accepted as plausible that the mechanism of superconductivity in C$_{60}$ is a result of coupling of the electronic wave function to the Jahn-Teller active intramolecular vibrations (see, e.g. the comments on that in Review [29]). However, it is hard to obtain conclusive evidence on that matter. The vibrational energy loss observed in (resonant) photoemission is usually assumed to be taken up by the JT modes. On the other hand, the RIXS symmetry selectivity provides some additional means to gain information on whether other effects also need to be considered or not.

E.g. for DC-superconductivity, the coupling of a Cooper pair has to proceed via vibrations which are symmetry-wise allowed for a process which does not include an oscillating dipole field. This implies that the symmetry of the vibrations has to originate from the interaction of the LUMO-band with itself, i.e. it makes possible the excitation of the relevant JT vibrations.

The experimental RIXS spectra, on the other hand indicate violating of the purely electronic parity selection rules, which with highest probability proceeds via the excitation of ungerade vibrations which are coupled to the electronic part of the wave function. The amount of the “wrong parity” levels in the resonant scattering spectra thus gives a measure of coupling of the electronic part of the wave function to vibrational modes which do not initiate the superconducting state. If this can be compared to the total coupling (which is easier to obtain in electron spectroscopies than directly the coupling to JT-vibrations), a high-limit of the critical temperature obtainable in a given class of metals can be assessed.

The data of Paper III indicate an effective vibronic coupling strength (of the
4.5 \textit{C}_60 intercalation compounds

\textit{C}_60 chemical compounds can be characterised by the location of the bound atom or molecule (inside or outside the cage), as well as by the bond character (ionic or covalent). In the work included in this thesis, only exohedral (lattice intercalated) compounds have been studied. Considering the bond character, K$_3$C$_{60}$ can be described as ionic, whereas the bonds in the oxygen and transition metal C$_{60}$ compounds appear to have a certain degree of covalency.

At room temperature, C$_{60}$ forms a van der Waals-bound crystal solid of face centered cubic (\textit{fcc}) crystal structure. The \textit{fcc} lattice constant is 14.01 Å, and the smallest distance between carbon atoms of neighbouring fullerene molecules \(\approx\) 3 Å. There are two types of lattice voids (octahedral and tetrahedral) in the C$_{60}$ \textit{fcc} crystal. The large size of the C$_{60}$ molecules makes the intermolecular voids in the \textit{fcc} fullerite lattice large enough to accommodate smaller atoms or molecules. The octahedral voids have a larger effective diameter (4.15 Å) than the tetrahedral (1.12 Å) voids.

The alkali metals: ionic crystal

In alkali intercalation compounds, the outermost \(s\)-electrons of the metal atoms are almost completely donated to the C$_{60}$ molecules, and the valence band structure is almost purely determined by the molecular properties of the (charged) C$_{60}$ molecules. The effect of this on e.g. transport properties is very similar to the case of electrostatically doped fullerenes (see, \textit{viz.}, Ref. [32]).

It is seen from the XE spectra that the bulk electronic structure of K$_3$C$_{60}$ is only slightly modified compared to C$_{60}$ (see Figure 4.4; more details in Papers II and I.

Oxygen in the C$_{60}$ lattice

Simple geometric considerations — the radii of the intermolecular voids in the C$_{60}$ crystal and the radii of the oxygen molecules — suggest that oxygen would preferably occupy the larger octahedral sites. Even the presence of oxygen appears to have a minor influence on the C$_{60}$ electronic structure, as seen by RIXS (in Paper
Figure 4.4: Valence band PES, carbon Kα XES and RIXS data of C_{60} and K_{3}C_{60}, measured with the excitation energies 110 eV (PES), 306 eV (XES) and at the C 1s—LUMO absorption resonance: 284.45 eV (C_{60} RIXS) and 284.1 eV (K_{3}C_{60} RIXS). All data are plotted on a binding energy scale. The non-resonant excitation for XES leads to broader spectra and extra intensity due to shake-up (see, e.g., shaded peak at 0 eV for pure C_{60}). The position of bulk and surface contributions to the PES spectrum are marked with two separate line sets.

V). This, and the other experimental observations suggest that the oxygen stays in the lattice mostly in molecular form.

Transition metal fullerides
For several transition metals, the cohesive energy has been considered too large to make bonds to C_{60} rather than to form metal aggregates, or to form carbides
4.6 Carbon Nanotubes

Carbon nanotubes are interesting as a link between the 2-dimensional structure of graphite and the 0-dimensional structure of the ball. Nanotubes are usually produced in the form of “buckypaper” using an electric arc, producing single- and multiwall nanotube bundles of a wide variety of tube diameters and chiralities. The use of suitable catalysts enables to enhance the yield of single-wall nanotubes (SWNT-s) significantly (see, e.g. [33]).

In an earlier study of the electronic structure of the single-wall nanotubes by Eisebitt et al. [34], it was observed that the spectra looked very similar to graphite. In our relatively similar study, but by using better spectral resolution, but also lower excitation energies around the C 1s absorption threshold (see Paper VI) it was observed that for excitations far above the threshold the spectra of a SWNT sample are indeed similar to graphite 4.5.

Figure 4.5: Vibrational losses originating in the de-excitation of the core exciton for the core exciton for the nanotube samples A (—) and B (····) are considerably decreased, compared to graphite (circles). Inset: the nanotube (A, B) and graphite RIXS spectra, excited at 291.7 eV photon energy. On the right, the part of the spectra near the elastic peak is plotted blown up.

which are significantly more strongly bound. As described in paper VII, we provide evidence of the existence of non-carbidic nature of electron structure modifications in C₆₀ aggregates with low concentrations (below 3-5%, depending on the material) of Ti, V, and Nb in C₆₀ by using RIXS, and particularly the symmetry-selectivity of this technique, as a probe.
RESULTS

However, at lower excitation energies there are indeed distinct differences between the graphite and the nanotube spectra (e.g., the exciton intensity as shown in Figure 4.5). This is taken as an indication of less strict crystal momentum conservation in the curved graphene sheets of the SWNTs as compared to graphite, where the effect of crystal momentum is large and well known.

4.7 Electron correlations

Correlation of electron motion is important at different levels. The results in Paper I, the effect of valence electron correlation on the transport properties in the superconducting fulleride $K_3C_{60}$ is discussed. To contrast, in Section 4.7.2, the results of Paper XI describe the observation of XES from doubly core-photoionised Be atoms, where the excitation mechanism probably has to involve strong intraatomic electron correlation, resulting in significant core-core shake-off probability.

4.7.1 Transport properties

The valence electron correlation via Coulomb interaction has been described in Section 1.6.1 for $K_3C_{60}$. In the case of a core excitation on a molecule, the Hubbard interaction creates a shallow potential minimum for the excited electron at the excitation site, and the intermolecular charge transfer becomes inhibited even though the substance appeared to be metallic. For $K_3C_{60}$, this is an indication that the metallicity is not of the same character as for simple, broad band metals, but has to be limited by correlation effects. This thought is elaborated in Paper I, not least through the RIXS observation that the resonant behaviour of the RIXS is preserved even for the higher excitations near the ionisation threshold.

4.7.2 Creating “hollow atoms”

Paper XI presents the results of a first preliminary study of the excitation-energy dependence of soft X-ray hypersatellites (shown in Figure 4.6), emission from photoionised double core hole states in beryllium metal.

In order to compare the hypersatellite to the main emission band, the energy scale of the latter is displaced by the 1s vacancy spectator shift, 40 eV (Figure 4.7). We believe that the screening reduces the shift in the final state so that the top of the band can be referred to a Fermi level in the presence of a core hole. The spectator shift can then be directly associated with the correlation between the two 1s electrons. We see, however, that the shape of the hypersatellite emission is substantially broader than the main band, and has the intensity redistributed towards lower energies. This is in general agreement with the change in the local partial density of states, upon the creation of a core hole [35].

Within our experimental accuracy the shape of the hypersatellite is independent of the excitation energy. In contrast, the overall intensity is critically dependent on excitation energy, and we plot the satellite-to-main line intensity ratio
4.8. X-RAY REFRACTION

Figure 4.6: X-ray emission spectrum of Be metal excited at 275 eV. The Be K\textsubscript{α} main line is peaked at 110 eV and the hypersatellite at 147 eV.

in Figure 4.8. The threshold for double ionization is situated at 262 eV, and the intensity raises monotonically towards higher energies.

We compare the excitation-energy dependence to the predictions of a time-dependent parameter model introduced by Thomas [36]. This model is based on shake theory and is aimed at bridging the gap between the adiabatic and sudden limits. It assumes that the shake process occurs during the short time when sufficient energy is available as the initial electron travels a relevant distance where it can interact. The model fits the data for a relevant distance of 0.13 Å.

After correction for self-absorption we find that the single-to-double-hole fluorescence cross section ratio at higher energies is around 0.15. This number does not directly reflect the ionization cross sections. We expect that the single-to-double ionization ratio should be close to the asymptotic value for the helium atom, 0.04. We believe that the remaining factor is due to an increased fluorescence yield for the double holes relative to the single holes. Such an increase has been predicted for low-Z elements [37].

4.8 X-ray refraction

X-ray emission has been treated so far in this thesis in the “usual” way as a technique which has a large and invariable probe depth, particularly when comparing it to photoelectron spectroscopies. Using near-normal exit (and incidence) angles, this is of course true. The X-ray probe depth can, however, be varied largely and
Figure 4.7: Hypersatellite (bottom energy scale) spectral profile compared to that of the Beryllium Kα emission main line (top energy scale).

Figure 4.8: Growth curve of the hypersatellite intensity vs. excitation energy. Experimental data (markers) are fitted with the Thomas function (line; see text for details).
reduced to a few monolayers of atoms or molecules of a material when using grazing incidence and/or exit angles. In this way the contribution to the signal from the surface and the bulk (or even from an interface) can be selectively enhanced and separated, giving additional information on the electronic structure of the material. In a multilayer structure, the amplitudes of the waves, reflected from different (smooth) surfaces and interfaces in the sample can add up constructively or destructively, giving rise to an interference pattern, which can be used to obtain information of the layer thicknesses, in addition to the spectroscopic information of the electronic structure within the layers. An example of the latter kind of experiment is given in paper X and will be briefly described below.

![Figure 4.9: Two examples of raw spectra where the angular dependence information was obtained from. Inset shows experimental geometry.](image)

### 4.8.1 Probe depth and film thickness from refraction studies

Paper X presents measurements and simulations on layered samples of Fe|$V$|$MgO$ and shows that the thickness estimation can be done with an error considerably smaller than 25 Å. (It has to be mentioned that after publication of this article, a mistake was found by the authors in the use of coefficients included in the simulation. As a result, the measured data agree better to the simulation. The figures displayed in the introduction part of this thesis use the correct coefficients.)

Furthermore, one can use grazing exit geometry for enhancing the signal, not only from the top layer, but also from deeper lying layers. Since SXES as a method
gives both elemental and chemical information this can be of great interest when studying e.g. thin film growth processes and multilayer samples in general. Based on the results of the paper, shown in Figures 4.9 and 4.10, one may conclude that it is possible to use the angular dependence of soft x-ray emission spectroscopy with electron excitation to estimate the thickness of the top layer of a layered sample when employing grazing exit geometry.
Summary

Vibronic coupling (i.e. the excitation of vibrations in the course of an electron transition or, more generally, the non-separability of the electron and vibrational partial wave functions) has been addressed in Papers III and IV. Almost complete vibrational relaxation is observed in both the RIXS and the RPES data. Additionally, the observation in RIXS of breaking of the parity selection rules characteristic of the purely electronic (adiabatic) transitions has to involve the excitation of odd parity vibrations, and the relative amount of electron-forbidden transitions in the spectra has to be indicative of coupling to these modes. This goes beyond the picture of coupling merely to Jahn-Teller vibrations in case of electron excitation, and probably has to be taken into account when estimating the superconducting transport properties from electronic and vibrational structure measurements, where coupling to the intramolecular $H_g$ Jahn-Teller vibrations has been considered as the driving mechanism of superconductivity and of the vibrational loss measured in, e.g. the PES.

The main result of Paper I is providing a measure of intermolecular charge transfer times in the superconducting compound $K_3C_{60}$. The results presented show that the charge transfer is slow on the core-hole lifetime timescale, i.e. $\tau_{CT} \geq 6 fs$ (where $\tau_{CT}$ is a typical charge transfer time).

The data presented in Papers I and II enabled us to discriminate the surface vs. the bulk electronic structure of $K_3C_{60}$. This was done both by comparing the XES and RIXS data to the valence and core PES data (I) and by studying the polarisation dependence of the photoelectron spectra (II). The electronic structure in the surface layer is seen to be electron-deficient as compared to the bulk, and insulating (or at best semiconducting), rather than metallic as the bulk. The origin of the PES broadening, and an interpretation in terms of the effect of electron correlation and Jahn-Teller distortions is discussed in these Papers.

The results of Paper VII show that transition metals do bond to $C_{60}$, and this happens without damaging the carbon cage, as seen from the preserved symmetry fingerprints in the spectra. These symmetry characteristics are also utilised in Papers VIII and IX in order to identify the bonding site(s) of the metal atom on the cage. The study of transition metal bonding (in Paper VII) additionally shows that despite the large, halogen-like electronegativity of $C_{60}$, the metal in such systems preferably still reacts with oxygen. The latter result is probably more important, as it gives information about the reactivity of $C_{60}$.

The reactivity of $C_{60}$ with oxygen is further studied in Paper V. Only small
net changes can be noticed in the carbon occupied and unoccupied valence band. The oxygen spectra, however, are seen \textit{not} to be of molecular character, although the \textit{fcc} lattice voids of $\text{C}_{60}$ are large enough to accommodate intact $\text{O}_2$ molecules. The spectral shape interpretation in terms of bonding and analogy to the carbon bonds in smaller molecules is discussed in the paper.

Paper VI investigates the relation of the curvature of a 2-dimensional carbon sheet and the electronic structure, momentum conservation and the localisation of an exciton in single-walled carbon nanotubes.

The two last Papers aim to characterise and explain the limits of the selectivity criteria that are generally assumed to be valid for the X-ray emission process (\textit{viz.} the bulk-sensitivity). Paper X treats the angular dependence of the information depth (and the length-scale of the bulk-sensitivity, used \textit{e.g.} in Paper I) obtained in X-ray emission. Paper XI presents the first observation of XES from doubly core-photoionised atoms in the soft X-ray region, and discusses how the electron correlation influences the cross-section for double photoionisation.
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