UPPSALA UNIVERSITY
INSTITUTE OF PHYSICS

Correlation between core level
chemical shifts obtained by
ultrasoft X-ray emission and ESCA

by

L.O. Werme, B. Grennberg, J. Nordgren,
C. Nordling, and K. Siegbahn.
Uppsala University,
Institute of Physics, Uppsala,
Sweden

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Abstract:

High resolution C:K X-ray emission spectra have been
recorded from six molecules in the gas phase. The spectra
are interpreted by comparing the relative X-ray energies
with the vertical ionization energies of the valence orbi-
tals and comparing the intensities predicted by the $C2p$
populations from CNDO calculations with the measured inten-
sities. The obtained $C1s$ binding energy shifts are found
to be in excellent agreement with shifts measured with
ESCA.

In previous papers we have reported high resolution X-ray emission spectra from free molecules. [1,2,3] In these papers the interest was focussed on the valence electron orbitals which could be examined in rather great detail. Thus it was possible to resolve the individual molecular orbitals and molecular excitation states and to make a direct comparison with electron spectra. Due to the high resolution it was even possible in one of these experiments to go one step further and examine the fine structure imposed on an X-ray line by the vibration of the molecule in the final state of the X-ray transition.

X-ray spectra mediate information also on the initial states of the transitions, i.e. the core levels of the molecules. These inner levels can be derived from the X-ray emission spectra if one can make accurate assignments of the final states and if accurate data are available on the energies of these states. Both these requirements can be fulfilled since the resolution in our spectra is sufficiently high to permit the identification of the individual molecular orbitals and since the binding energies of these molecular orbitals can be obtained from electron spectroscopy (see e.g. refs. 4 and 5). As will be shown in the present paper this procedure for deriving molecular core level energies is now sufficiently accurate to allow the exact determination of chemical shifts in core levels and a direct comparison with the shifts obtained in ESCA. Some low resolution X-ray emission spectra from gases[6,7] have recently been analyzed with help of molecular orbital theory[8,9]. However, due to the low resolution it is difficult to determine the core level shifts accurately from data available up to now.

The ultrasoft X-ray spectra were recorded in a high resolution grating spectrograph, especially designed for gaseous samples[10,11]. Direct electron impact was used for the excitation; an electron beam of typically 50 mA and 10 kV was directed into the source, where a sample pressure of $\approx$ 1 torr was maintained. The analyzer was a 3 m grazing incidence (87°) grating spectrograph and the spectra were recorded photographically.

In order to educe the carbon 1s binding energies from the X-ray emission spectra, it was necessary to accurately identify the upper as well as the lower states taking part in the transitions. Simple molecules have therefore been chosen since the orbital binding energies and the ordering and symmetries of the valence orbitals of such molecules are well known. However, all the valence orbitals do not participate in the X-ray process because some of the transitions can be dipole forbidden. The intensities of the dipole allowed transitions to a carbon 1s hole can be estimated by considering the relative emission probability to depend mainly on the amount of carbon 2p character describing the vacancy in the final state[8].

The X-ray emission spectra of six carbon compounds (CO, CO_2, C_6H_6, $C_2H_4O^*$, CHF_3, CF_4) were recorded. The CO_2 spectrum was found to be very simple. Because of the gerade symmetry of the C1s level only transitions to ungerade levels are allowed. Two such orbitals are found in the valence shell at the vertical ionization potentials 17.6 eV (π_u) and 18.1 eV (σ_u), respectively[5]. In UV excited electron spectroscopy the π_u band, which consists of a rather long vibrational progression, overlaps the σ_u band where the intensity resides mainly in one single peak. The X-ray spectrum exhibited a line with a maximum corre-

*ethylene oxide.

sponding to the σ_u level with the π_u band appearing as an unresolved structure on the high energy slope. No other intense lines were present in the CO_2 spectrum. This X-ray line was therefore chosen as reference for the other spectra, which were recorded on double exposures together with the CO_2 on the same photographic plate. An example of this is shown in Fig. 1. The narrow CO_2 line ensured a minimum overlap with X-ray lines from the other molecules and it was therefore possible to measure the relative X-ray shifts with high precision. The photographic recordings of the spectra are shown in Fig. 2. The identification of the X-ray lines was based on intensity and energy considerations. Comparison was made between the measured relative intensities and the relative intensities as predicted by CNDO populations and also between relative X-ray energies and vertical ionization potentials of the valence orbitals as obtained from electron spectroscopy.

Low C1s binding energies are found for the hydrocarbons[4]. The simplest hydrocarbon molecule, CH_4, could be a good representative for these carbon atoms with low 1s binding energies since its X-ray spectrum should consist of one line only ($1a_1 \leftarrow 1t_2$); all other transitions being symmetry forbidden. However, a very broad line ($\approx$ 3 eV) was obtained due to the strong Jahn-Teller distorsion of the molecule upon ionization from the t_2 orbital. This is also to be expected from electron spectroscopy, where the t_2 band exhibits a broad structure. On basis of this CH_4 was excluded from the investigation and replaced by C_6H_6 where in spite of the rather complicated molecular orbital structure the outermost orbital is well separated in energy from the other ones and the corresponding X-ray line can be measured relative

to CO_2 with sufficient precision. The highest Cls binding
energy is found in CF_4[4]. As for CH_4 only transitions from
t_2 orbitals are symmetry allowed. In CF_4 only one t_2 orbital
has appreciable C2p population and the Cls X-ray spectrum
consists of one line. However, this line partly overlapped
the CO_2 line and CF_4 was therefore measured against CO. The
measured X-ray shifts and the Cls shifts deduced from this
experiment are presented in Table 1. Table 1 also shows the
corresponding Cls shifts from ESCA. The core level binding
energies were established by adding the X-ray energy of a
transition to the vertical ionization energy of the valence
orbital involved in the transition. In deducing the Cls shifts
from X-ray results it is therefore necessary to have an accu-
rate knowledge of the ionization energies of the valence orbi-
tals. Such information can for many molecules be obtained from
electron spectroscopy. The correlation between X-ray and ESCA
shifts presented in Fig. 3 shows excellent consistancy between
the two spectroscopies.

X-ray spectra are inherently more complicated to interpret
than electron spectra. X-ray spectra from molecules containing
several carbon atoms with different 1s binding energies can
be expected to exhibit a complicated structure. However, in
many cases X-ray emission spectroscopy applied to free mole-
cules offers an alternative method for measuring chemical shifts
in core levels and is therefore a useful complement to ESCA.

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Table 1.

The X-ray shifts and the studied transitions in the investigated molecules. The deduced carbon 1s shifts are compared with ESCA results.

Molecule	X-ray transition	vertical I.P. of the valence level (eV)	X-ray shifts relative CO_2 (eV)	C1s shifts (eV)	
				This work	ESCA
CF_4	C1s $\leftarrow$ $3t_2$	22.0^{12}	-2.1^a	4.5	4.3^4
CHF_3	C1s $\leftarrow$ $3a_1+2e$	20.5^{12}	-1.2	1.2	1.3^4
CO_2	C1s $\leftarrow$ $3\sigma_u$	18.1^5	—	—	—
CO	C1s $\leftarrow$ 3σ	14.0^5	2.7	-1.5	-1.6^4
C_2H_4O	C1s $\leftarrow$ $6a_1$	11.8^{13}	1.2	-5.2	-5.2^{14}
C_6H_6	C1s $\leftarrow$ $1e_{1g}$	9.3^5	1.6	-7.2	-7.3^{15}

^{a} X-ray shift relative CO.

Figure captions:

Fig. 1.   The X-ray emission spectra of CO and CO_2 on a double
exposure for calibration purpose. All spectra have
been recorded with an overlapping section in the
middle of the plate where the X-ray shifts can be
directly measured.

Fig. 2.   The C:K X-ray emission spectra from the investigated
molecules. The energies of the observed X-ray lines
are indicated under each spectrum. Broken lines in-
dicate the position of the CO_2 line, which was used
as a reference in the calibration of the spectra.
(Except for CF_4 where CO was used for calibration.)

Fig. 3.   Correlation between chemical shifts from X-ray emission
and ESCA. The scale on each axis has the CO_2 binding
energy established in ESCA as reference point. The line
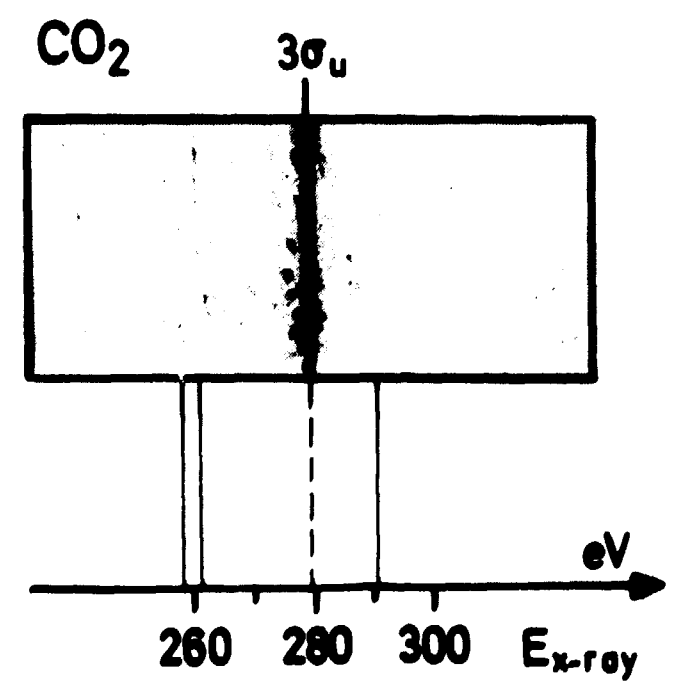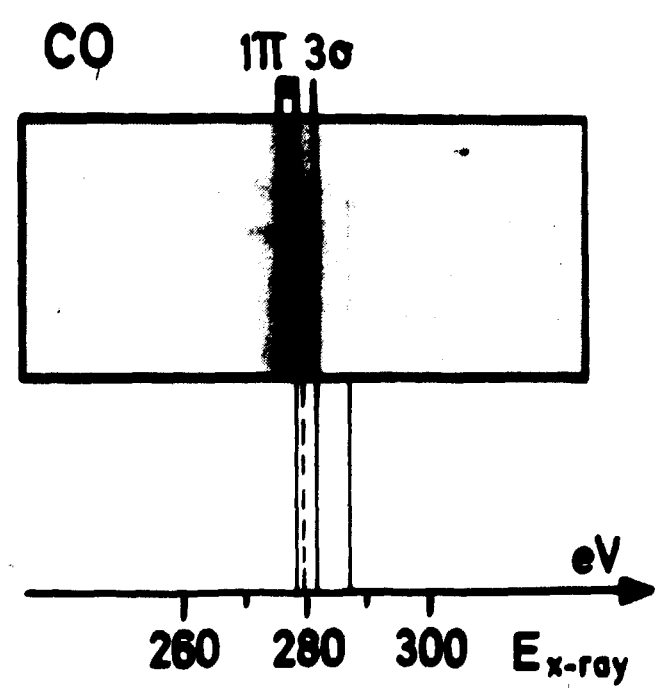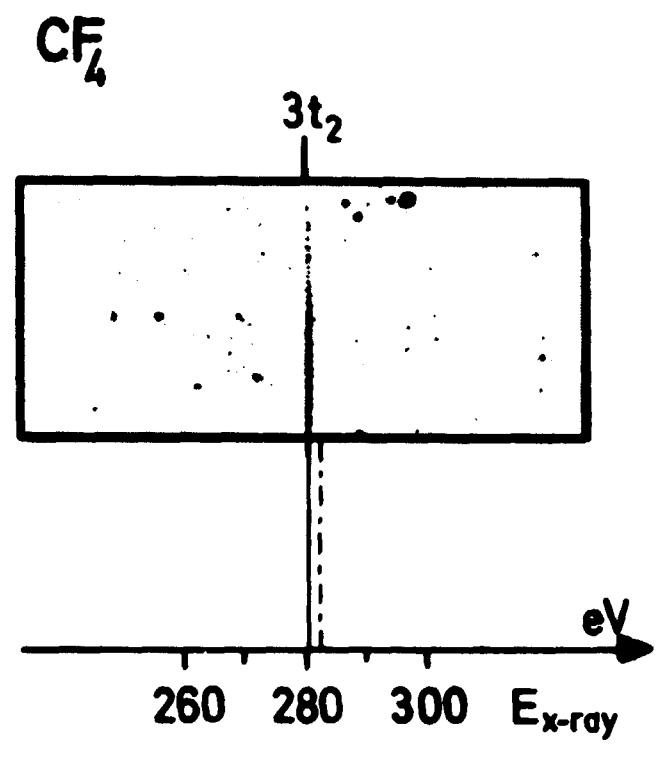is drawn with slope 1.0.

Fig. 1.

C₆H₆

C_6H_6

$1b_{2u}$
$3e_{1u}$
$1a_{2u}$
$3e_{2g}$
$1e_{1g}$

eV

260 280 300 E_{x-ray}

C_2H_4O

$5a_1$
$1b_2$
$1a_2$
$3b_1$
$6a_1$

eV

260 280 300 E_{x-ray}

CHF_3

$3a_1$
$2e$
$4e$
$4a_1$

eV

260 280 300 E_{x-ray}

CF_4

$3t_2$

eV

260 280 300 E_{x-ray}

CO

1π 3σ

eV

260 280 300 E_{x-ray}

CO_2

$3\sigma_u$

eV

260 280 300 E_{x-ray}

Fig. 3.