Interplay of Intra-atomic and Interatomic Effects: An Investigation of the $2p$ Core Level Spectra of Atomic Fe and Molecular $FeCl_2$

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The $2p$ photoabsorption and photoelectron spectra of atomic Fe and molecular $FeCl_2$ were studied by photoion and photoelectron spectroscopy using monochromatized synchrotron radiation and atomic or molecular beam technique. The atomic spectra were analyzed with configuration interaction calculations yielding excellent agreement between experiment and theory. For the analysis of the molecular photoelectron spectrum which shows pronounced interatomic effects, a charge transfer model was used, introducing an additional $3d^7$ configuration. The resulting good agreement between the experimental and theoretical spectrum and the remarkable similarity of the molecular with the corresponding spectrum in the solid phase opens a way to a better understanding of the interplay of the interatomic and intra-atomic interactions in the $2p$ core level spectra of the $3d$ metal compounds.

The $2p$ core level photoemission of the $3d$ transition metal compounds has been studied extensively in the solid phase to obtain information on their electronic structure [1–10]. As a $2p$ core hole strongly perturbs the electronic states of the outer electrons, it can be used as a test charge to investigate the response of the valence electrons. The interpretation of the experimental spectra for the evaluation of electrical properties or local magnetic moments due to the unpaired $3d$ electron spins relies on the interplay of intra-atomic and interatomic interactions. The well investigated satellite structure of the $2p$ photoelectron spectra of the $3d$ transition metal oxides, sulfides, or halides, for example, is controversially discussed by either the intra-atomic effects of multiplet splitting and $2p$ hole interaction or the interatomic charge transfer from the neighboring ligand valence orbitals to the $3d$ states of the transition metal [11–13].

In cluster model calculations the $2p$ photoelectron spectra are described in terms of a few parameters, such as the charge transfer energy, the ligand p, and metal d hybridization, and the on-site d-d Coulomb repulsion energy. These parameters are generally adjusted to reproduce the experimental spectra. To obtain these parameters by *ab initio* methods would therefore be a substantial progress [8]. One step for such a program is the careful study of corresponding spectra both for metals and metal compounds in the gas phase.

The study of the $2p$ photoelectron spectra of the $3d$ transition metal atoms and $3d$ transition metal compounds in the gas phase is hampered by experimental difficulties in the production of atomic or molecular beams and due to the small cross sections for the direct $2p$ photoionization of these elements. Because of the increased photon flux of undulator beam lines at third generation synchrotron radiation facilities, these experiments are now feasible [14–17]. This Letter presents the first results of an experimental and theoretical study of the $2p$ photoionization of atomic Fe and molecular $FeCl_2$.

The experiments were performed at BESSY, beam line U49/1-SGM in Berlin, Germany. The atomic and molecular beams were produced by thermal evaporation of the metal or the metal compound using temperatures of about 1750 K for Fe and 700 K for $FeCl_2$. For the absorption experiments, photoions were produced in the excitation energy range from 700 to 730 eV and were detected by a time-of-flight spectrometer which was operated in pulsed voltage mode. The photoelectrons were produced by photons of about 800 eV and analyzed using a Scienta SES 2002 spectrometer.

Figure 1 shows the total ion yield from Fe and $FeCl_2$ in the energy range of 700 to 730 eV. The total ion yield corresponds to the main decay channels of Fe and $FeCl_2$
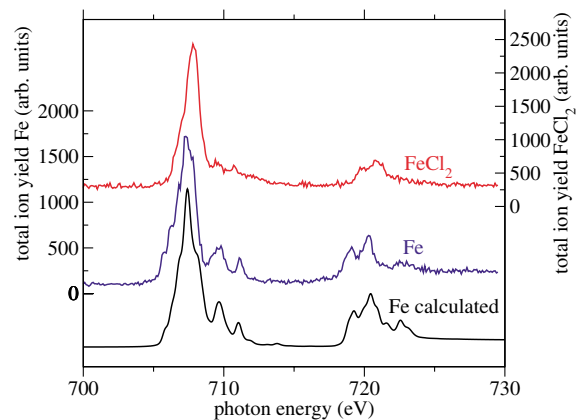

FIG. 1 (color online). Total ion yield spectra from Fe and $FeCl_2$ in the energy region of 700 to 730 eV. Calculated spectrum for Fe.

and can therefore be assumed to be equivalent to the absorption signal. The absorption spectrum of atomic Fe is dominated by two groups of resonances at about 707 and 720 eV, which correspond to the discrete $2p$-$3d$ transitions of the spin-orbit doublet $2p_{3/2}$ (707 eV) and $2p_{1/2}$ (720 eV). This one-electron picture, however, cannot explain the additional features within each group, which are due to the Coulomb interaction within the $3d^7$ subshell and the Coulomb interaction of the $2p$ hole with the $3d^7$ subshell. Therefore intermediate coupling must be used to incorporate these many-body interactions.

For the analysis of the absorption spectrum, we performed configuration interaction (CI) calculations using Hartree-Fock (HF) wave functions as a zero order approximation. The calculations have been carried out using the Cowan code [18] including relativistic extensions. The initial state consisted of the sum of the thermally populated fine structure levels ^5D_J with $J = 4, 3, 2, 1$ of the ground state configuration Fe $3d^6 4s^2$, weighted according to the Boltzmann distribution at the evaporation temperature of 1750 K. To take into account the intra-atomic CI with a large number of weakly perturbing states, the Coulomb integrals have been scaled down to 80% of their *ab initio* value. This slightly reduces the multiplet splitting, which is overestimated otherwise. The reduction of the Coulomb integrals was found to improve the agreement between experiment and calculation in all previous photoionization studies on $3d$ metal atoms [14–16,19,20] (the improvement only holds for the angular integrated cross section; see [20] for details). This scaling is the only empirical parameter in our calculation. The resulting theoretical spectrum is also depicted in Fig. 1. For better comparison with the experimental spectrum, it was convoluted with Gaussian profiles of 0.6 eV width; the spectrum also had to be shifted by 2.7 eV towards lower photon energies. The agreement with the experimental spectrum is excellent.

Comparing the absorption spectrum of atomic Fe with that of molecular FeCl$_2$ in Fig. 1, one observes that the many-body multiplet effects are reduced in favor of the remaining spin-orbit doublet. This already indicates the influence of the molecular binding on the valence electrons. Nevertheless, the differences between the atomic and molecular $2p$ photoelectron spectra, which are shown in Fig. 2, are more pronounced. A more detailed examination of the $2p$ photoelectron spectra should therefore be rewarding.

The atomic photoelectron spectrum in Fig. 2 mirrors the main structure of the atomic $2p$ photoabsorption in Fig. 1, which is characterized by a spin-orbit doublet in combination with a distinctive multiplet splitting. The molecular $2p$ photoelectron spectrum in Fig. 2, however, shows a broadened doublet and a second doublet structure which is shifted by several eV towards lower binding energies.

For the evaluation of the atomic photoelectron spectrum, we performed CI calculations using the Cowan
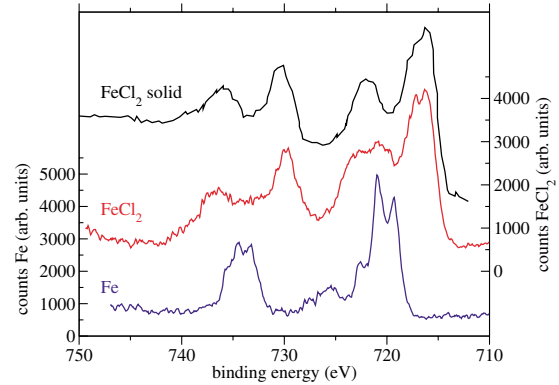

FIG. 2 (color online). $2p$ photoelectron spectra of Fe and FeCl$_2$ taken at a photon energy of 800 eV. Also shown is an FeCl$_2$ electron spectrum from the solid state, taken from [21].

code. A detailed description of our calculation method and of the influences of CI effects has been published recently [20]. The result of these calculations is shown in Fig. 3. As in the case of the absorption spectra, the thermal population of the fine structure levels Fe $3d^6 4s^2$ ^5D_J with $J = 4, 3, 2, 1$ was taken into account using the
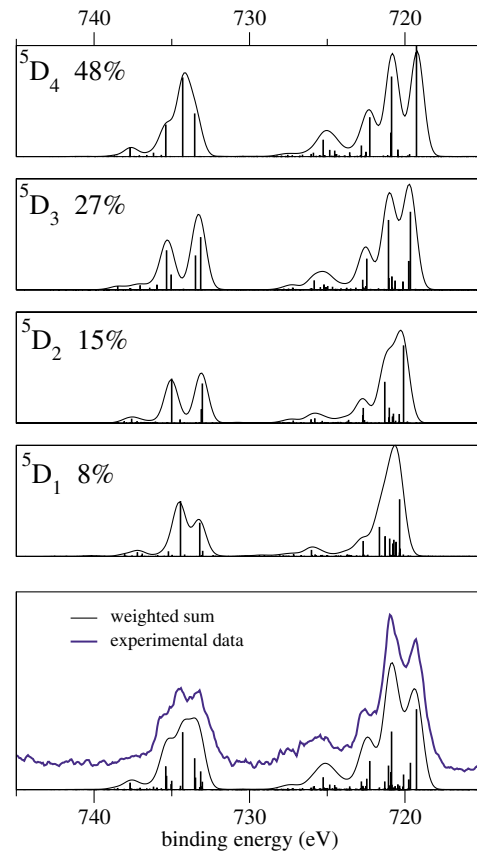

FIG. 3 (color online). Experimental and calculated $2p$ Fe electron spectrum. Contributions of the different fine structure components $J = 4, 3, 2, 1$ of the initial states Fe $3d^6 4s^2$ ^5D_J. The components are weighted according to the Boltzmann distribution at the evaporation temperature of 1750 K.

Boltzmann distribution. For a better comparison with the experimental spectrum, the calculated line spectrum was convoluted with Gaussian profiles of 1.0 eV width. The calculated photoelectron spectra have been shifted by 1.5 eV towards lower binding energies in order to match the measured ones. The multiplet structure seen in the photoelectron spectrum can be divided into two main groups, which in first order approximation can be assigned to $2p_{3/2}$ (at about 720 eV) and $2p_{1/2}$ (about 734 eV) core hole states. The $2p$-$3d$ Coulomb interaction leads to a further splitting of this spin-orbit doublet. The recoupling of the $3d$ valence electrons is another important element which determines the Fe $2p$ spectrum. This recoupling, which can be described as a spin flip of one or more $3d$ electrons, gives rise to the satellite lines seen between 721–728 eV and at about 737 eV. For atomic Mn and Cr this satellite structure has been discussed before in great detail [14,15]. Since the general considerations for the mechanism giving rise to these satellites are analogous, we refer to these references for a more in-depth analysis of the multiplet structure. Note that the multiplet structure for atomic Fe is well described using only the $3d$ shell configuration $3d^6$ and that evidently the whole satellite structure of atomic Fe is solely caused by intra-atomic effects. The excellent agreement of the atomic experimental spectrum and the *ab initio* calculations is a strong confirmation for the accuracy of the theoretical treatment above.

From this solid understanding of the atomic spectrum we now proceed with the discussion of the molecular data. First we compare the molecular $2p$ FeCl$_2$ spectrum with the solid phase in Fig. 2. The solid state spectrum taken from [21] had only a relative energy scale, so it was positioned to comply with the molecular spectrum. The comparison shows that the main structures of both spectra are nearly identical. It is therefore very convincing to use the same charge transfer model, which is very successful for the analysis of the $2p$ FeCl$_2$ spectrum in the solid state [4], also for the interpretation of the corresponding gas phase spectrum. The charge transfer from Cl valence orbitals to Fe $3d$ states is manifested by the appearance of the additional configuration $3d^7$. The energetic ordering of the $3d^6$ and $3d^7$ configurations is reversed by the $2p$ hole; this is responsible for the appearance of the second doublet shifted towards lower binding energies. In the absorption process the energetic ordering of the $3d^6$ and $3d^7$ configurations is conserved by interactions with the additional valence electron [8], so no additional doublet structure could be seen in Fig. 1.

To model the charge transfer, we performed CI calculations for the photoelectron spectra of both configurations $3d^64s^2$ and $3d^74s$. As a first approximation, the fine structure states of both configurations were all equally included in the calculation, as the charge transfer cannot be assumed to use the population distribution for, e.g., thermal excitation. The calculated line spectra were convoluted with Gaussian profiles of 3.9 eV width for

the configuration $3d^64s^2$ and 1.5 eV width for the configuration $3d^74s$. This difference in the linewidths should account for the more localized character of the $3d$ electrons compared to the $4s$ in FeCl$_2$ [22]. The sum of the spectra with a d^6/d^7 ratio of 0.93 is shown in the lower panel of Fig. 4 together with the experimental spectrum. These parameters (individual widths and mixing ratio) were chosen to fit the experimental data and were not obtained by *ab initio* methods. The energy shift between both configurations, however, is directly computed by the configuration interaction HF code. The derived mixing ratio of 0.93 corresponds to a $3d$ shell population number of 6.52, which is in good agreement with previous studies [22].

The structure of the spectrum for molecular FeCl$_2$ as well as for its solid phase resembles two spin-orbit split lines each with additional satellites on their high binding energy side. Neglecting the different relative intensities of the satellites, one could be tempted to use an intra-atomic multiplet model. This, however, is not supported by the above charge transfer modeling of the spectra. Here the prominent features arise from different configurations populated by interatomic effects. While there still is an underlying multiplet structure with the spin-flip satellites known from atomic Fe, as can be seen in the top two panels of Fig. 4, it is strongly superposed by the charge transfer influences. So the overall appearance of the spectra can only be explained by the charge transfer.
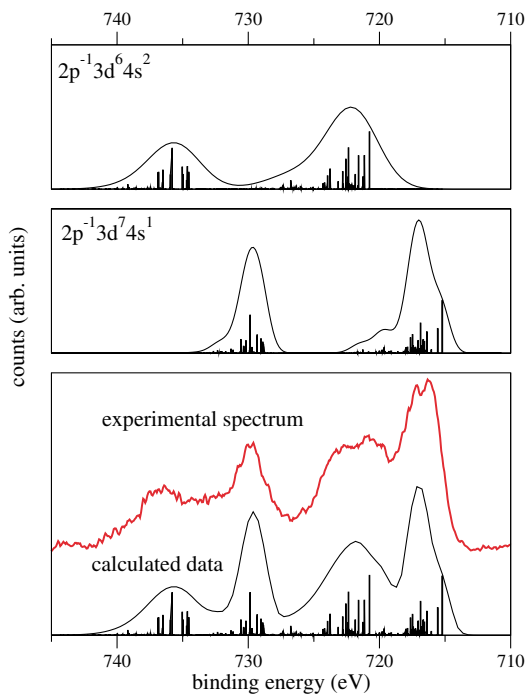

FIG. 4 (color online). Experimental and calculated molecular FeCl$_2$ $2p$ spectrum (lower panel; see text) with the different contributions of the configurations $3d^64s^2$ and $3d^74s$ in the upper panels.

Note that the above calculation used states of the neutral atom, although metal halides are often referred to as ionic compounds. A complete removal of the $4s$ electrons in the calculation would yield spectra heavily shifted towards higher binding energies. We only see a 1.5 eV offset in the $3d^6$ configuration between the molecular and the atomic case, so the presence of the completely atomic $4s$ electrons in our modeled molecular spectrum accounts just for a partial charge back donation of the chlorine ligands.

Despite the same main structure of molecular and solid $FeCl_2$, there is one noteworthy difference. Whereas all the $3d^7$ peaks have a similar shape and width, the $3d^6$ peaks differ. In solid $FeCl_2$ the peaks have a width comparable to the $3d^7$ peaks; however, in molecular $FeCl_2$, the peaks have more than twice the width. Most likely this can be attributed to the different symmetries in the solid and the molecule. The solid can be described by a $(FeCl_6)^{4-}$ cluster [22]. All d orbitals will be affected by their environment in quite the same way. However, for the free molecule, a linear Cl-Fe-Cl symmetry can be assumed [23]. This modified symmetry will result in a different molecular field. For orbitals in the plane of the molecular axis, it will be similar to the solid. Whereas orbitals in the plane perpendicular to the molecular axis will see a different molecular field. These will thus be shifted relative to the in-plane orbitals, resulting in the broader structure. The $3d^7$ states should encounter the same effect; however, for the $3d^7$, only one charge is transferred to the Cl ligands, resulting in a smaller molecular field and therefore a smaller broadening of the $3d^7$ peaks.

It is obvious that our "atomic" approach to analyze the molecular spectrum cannot replace a more refined molecular orbital calculation. A proper treatment of the charge transfer in our calculations would consist of the usage of CI wave functions according to the symmetry group of the whole molecule. This is hampered to date by the state-of-the-art computing power, which is barely sufficient to calculate the $2p$ multiplet effects of a single $3d$ metal atom alone (see, e.g., [20]). Alternatively density functional theory (DFT) calculations (see, e.g., [24]) are able to calculate the intramolecular charge transfer. With future inclusion of the intra-atomic multiplet effects of open-shell $3d$ metal atoms, DFT would be a promising approach towards a more complete description.

In conclusion this study of the $2p$ photoionization spectra of atomic Fe and molecular $FeCl_2$ both experimentally and theoretically can be regarded as an exemplary step towards a better understanding of the $2p$ core spectra of the $3d$ transition metal compounds. Starting from the thorough understanding reached for the atomic spectrum, we succeeded to analyze the molecular $FeCl_2$ spectrum by incorporating the basic idea of a charge transfer model into calculations using both configurations $3d^6$ and $3d^7$. This should also bring new insight into the important and sometimes controversial de-bate on the nature of the structure of solid transition metal compounds.

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