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Localized high spin states in transition-metal dimers: X-ray absorption spectroscopy study

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X-ray absorption spectroscopy provides direct evidence for localized valence electrons in Cr_2^+, Mn_2^+, and $CrMn^+$ dimer cations. Bonding in these transition-metal molecules is predominantly mediated by 4*s* electrons. This behavior is markedly different from other 3*d* transition-metal dimers with open 3*d* subshells and can be ascribed to the highly stable $3d^5(^6S)$ configuration of the 3*d* subshell in chromium and manganese atoms and ions. In Cr_2^+, Mn_2^+, and $CrMn^+$, 3*d* electron localization indicates local high spin states.

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Electrons in atoms and solids are usually divided into two parts: core electrons, tightly bound to an atomic nucleus, and valence electrons, which are weakly bound and participate in chemical bonding. This division is not strict, a famous exception is 4*f* orbitals in lanthanoids, which are core electrons by their contracted radial wave function but which are filled in competition with 5*d* states and can thus be regarded as valence electrons.

In first row transition metals, the situation is similar, albeit less clear. Here, 3*d* electrons are usually considered as valence electrons which participate in chemical bonding and lead to a rich chemistry with a large variety of oxidation states. In terms of binding energy, 3*d* electrons are almost degenerate with 4*s* electrons. Regarding their radial distribution function, however, 3*d* electrons could also be considered core electrons because of the contracted 3*d* wave function which has no radial knots. The question of itinerant versus localized behavior is persistent in solids, where the peculiar properties of the 3*d* electrons lead to ferromagnetic ordering in iron, cobalt, and nickel and to antiferromagnetic order in chromium and manganese.

Among these 3*d* transition metals, chromium and manganese atoms are unique because of their half-filled 3*d* subshells with $3d^54s^1$ and $3d^54s^2$ configurations, respectively. The promotion energy required to break up this stable $3d^5(^6S)$ configuration is 1.48 eV in $Cr^+(3d^5 \rightarrow 3d^44s)$ and 1.78 eV in $Mn^+(3d^54s \rightarrow 3d^6)$.[1] The evolution of their atomic high spin ^7S and ^6S ground states to antiferromagnetically coupled bulk states has motivated intense research on chromium and manganese as well as many other transition-metal clusters.[2–7] In this context, already dimers as the simplest transition-metal aggregates show a large spread of binding mechanisms and bond energies. Even in these molecules the details of bonding are still unclear; especially, chromium and manganese with their half-filled 3*d* subshells pose problems to theory.

As neutral dimers, chromium and manganese are very different in their electronic structure and bonding. Cr_2 has a short bond length of 1.68 Å,[8] a formal sextuple bond with contributions from 3*d* electrons, and a bond energy of 1.53 ± 0.06 eV.[9] Mn_2 has a long equilibrium distance of 3.4 Å (Ref. 10) and is often termed as a van der Waals molecule with an experimental bond energy of 0.44 ± 0.30 eV,[11] while theory predicts even smaller values.[12] The differences between the neutral dimers can also be seen in bulk solids, where the exceptional stability of the atomic state with its half-filled 3*d* and filled 4*s* shells has implications for bonding in bulk manganese. While the crystal structure of antiferromagnetic bulk chromium is body-centered cubic, α-Mn, the stable allotrope at room temperature with its 58 atom cubic unit cell,[13] has complex structural and magnetic properties which are rooted in the highly stable atomic $3d^5(^6S)4s^2$ term. Together with a strongly contracted 3*d* orbital, this implies that 3*d* electrons can possibly retain their core character even in larger aggregates. For chromium with the same stable $3d^5(^6S)$ configuration, the open 4*s* subshell allows covalent bonding with an increased participation of 3*d* electrons. Based on stable Cr_2 units, a dimer growth model has been proposed for small chromium clusters.[2]

These different bonding characteristics of chromium and manganese dimers change dramatically upon ionization. For chromium, ionization of the neutral dimer removes an electron from a bonding $(4s\sigma)$ orbital which slightly reduces the binding energy. For atomic manganese, ionization opens up the 4*s* subshell which has a dramatic effect in the dimer. Here, a 4*s* electron is removed from an antibonding $(4s\sigma^*)$ orbital which leads to covalent bonding in Mn_2^+ with a strongly increased binding energy as compared to the neutral molecule. Therefore, cationic Cr_2^+ and Mn_2^+ are very similar in their experimental bond energies of 1.30 ± 0.06 eV (Ref. 14) and ≥ 1.39 eV,[15] respectively.

Experimentally, the electronic structure and bonding in transition-metal dimer cations have been investigated by collision-induced dissociation,[14,16] photodissociation,[4,15] and electron-spin resonance[10,17] spectroscopy. While these techniques have contributed significantly to the understanding of transition-metal dimers, especially with respect to their bond energies, they supply information on the electronic states rather indirectly. A direct probe for the electronic configuration would be highly desirable. We have investigated the extent to which 3*d* electrons participate in bonding and give direct evidence for strong localization of 3*d* electrons in Cr_2^+, Mn_2^+, and $CrMn^+$ dimer cations from local and element-specific x-ray absorption spectroscopy. According to the experimental results discussed below, 3*d* electrons in these

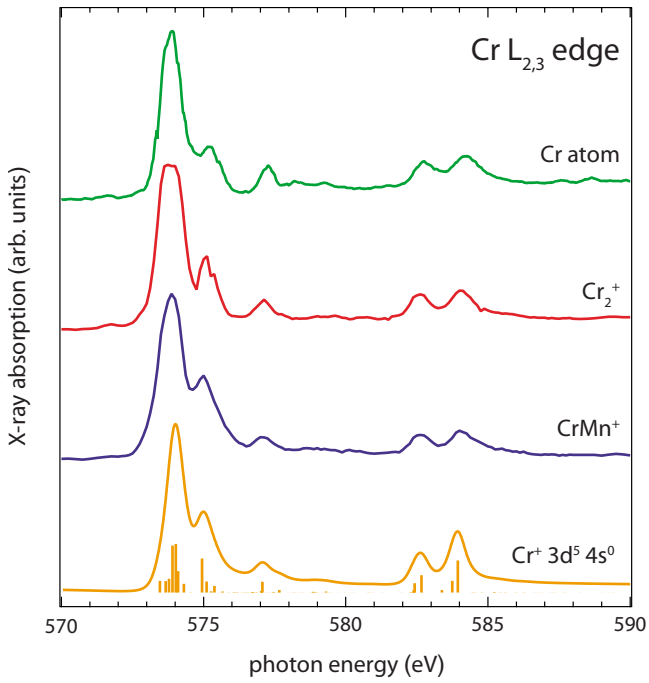

FIG. 1. (Color online) Surprisingly similar x-ray absorption spectra of atomic chromium (Ref. 18), Cr_2^+, and $CrMn^+$ taken at the chromium $2p$ edge. The spectra are dominated by $2p \rightarrow 3d$ transitions and can be reproduced by atomic multiplet calculations assuming a $3d^5$ initial-state configuration. This directly shows localization of $3d$ electrons. $2p \rightarrow 4s, 4d$ transitions do not contribute significantly to the spectra.

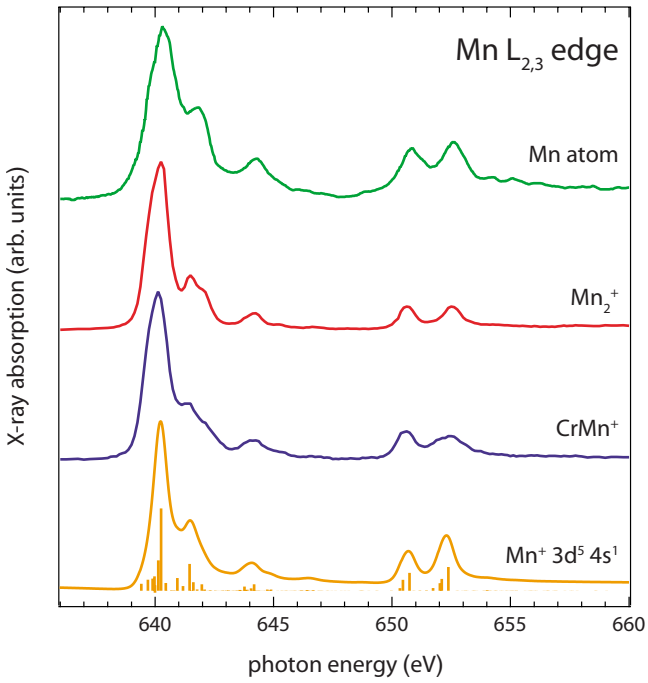

FIG. 2. (Color online) X-ray absorption spectra of atomic manganese (Ref. 21), Mn_2^+, and $CrMn^+$ taken at the manganese $2p$ edge. As for chromium, the spectra are dominated by $2p \rightarrow 3d$ transitions and can be reproduced by atomic multiplet calculations assuming a $3d^5 4s^1$ initial-state configuration, again indicating localization of $3d$ electrons. Differences in the spectra of atomic manganese and Mn_2^+ are due to different photon energy resolution.

transition-metal dimer cations could indeed be considered core electrons which hardly participate in chemical bonding.

The experimental setup is described in detail elsewhere.[19] Briefly, cationic transition-metal dimer molecules from a magnetron sputtering source are mass separated and stored in a buffer gas filled linear quadrupole ion trap kept at liquid-nitrogen temperature where they are irradiated by a soft x-ray beam along the trap axis. X-ray absorption spectra are taken in ion yield mode, monitoring the yield of photogenerated daughter ions as a function of incident photon energy.[20]

In general, $2p$ x-ray absorption spectra of $3d$ transition metals are dominated by transitions into local unoccupied $3d$ states. Transitions into $4s$ states, which are also accessible in a dipole transition, contribute very little to the spectra because of the much smaller overlap with $2p$ states. Core level spectra of molecules are usually very different from atomic spectra because they are highly sensitive to changes in the electronic configuration and the chemical surroundings. Therefore, $2p$ x-ray absorption spectroscopy can be used as a sensitive fingerprint method for the local electronic $3d$ configuration, which is applied here to Cr_2^+, Mn_2^+, and $CrMn^+$.

X-ray absorption spectra taken at the chromium $2p$ edge of chromium atoms,[18] Cr_2^+, and $CrMn^+$ are shown in Fig. 1. Very surprising, the experimental spectra are nearly identical in their transition energies and intensities. The same is true for experimental x-ray absorption spectra of manganese atoms,[21] Mn_2^+, and $CrMn^+$ at the manganese $2p$ edge, as shown in Fig. 2. In this respect, homonuclear chromium and manganese dimer cations are markedly different from other transition metals. Only Cr_2^+ and Mn_2^+ show spectra strikingly similar to the neutral atoms, while the spectra of other $3d$ transition-metal dimers with open $3d$ subshells differ from their atomic counterparts,[20] as would be expected for molecules where $3d$ electrons participate in bonding.

Theoretical x-ray absorption spectra of very small transition-metal molecules or clusters,[22] where atomic multiplets still have to be considered, are not available at present. However, x-ray absorption spectra of single atoms or ions can be calculated to high accuracy with atomic multiplet theory.[23] Although these calculations generally cannot address the electronic structure of molecules, in the special cases of Cr_2^+, Mn_2^+, and $CrMn^+$ they reproduce the experimental spectra very well. In the following we will therefore use experimental $2p$ x-ray absorption spectra together with the corresponding atomic multiplet calculations to identify localized $3d$ valence electrons.

Starting with Fig. 1 where the chromium $2p$ excitation is shown, we note again that the experimental spectra of chromium atoms,[18] Cr_2^+, and $CrMn^+$ are almost identical. Compared to the atomic chromium spectrum,[18] features in Cr_2^+ are better resolved because of a higher monochromator resolution of 150 meV as compared to 290 meV.[18] The nearly identical spectra of chromium atoms[18] and Cr_2^+ represent a local $3d^5$ initial-state configuration, as can be seen by comparison with an atomic multiplet calculation (stick spectrum in Fig. 1). In both cases, the experimental spectra can be well reproduced by calculating transitions from a cationic $[Ar]3d^5 4s^0$ initial-state configuration into a $2p^5 3d^6 4s^0$ final-

state configuration with atomic multiplet theory. Even more important, the experimental spectra of atomic chromium and Cr_2^+ are identical within the photon energy resolution. In all cases, final states with $3d^5 4s^1$ or $3d^5 4d^1$ configurations only contribute about 5% to the spectra. A lifetime broadening of 250 meV together with the experimental energy resolution of 150 meV were used in the calculations.

From the spectral fingerprint of Cr_2^+, we conclude that all $3d$ electrons are localized at their ionic cores and do hardly participate in bonding. This conclusion can be drawn even though x-ray absorption spectroscopy is not a direct probe of ground-state properties, and core hole relaxation can even rearrange the valence electronic structure such that electronic systems delocalized in their ground state become highly localized in the core excited state. Still, only a very similar structure of unoccupied d-symmetric states in the ground state would lead to the nearly identical spectra of the neutral atom and dimer cation observed experimentally.

Since $3d$ electrons are localized in Cr_2^+, bonding in Cr_2^+ is mediated predominately by the remaining $4s$ electron, shared between the two atoms in a bonding $(4s\sigma_g)^1$ configuration. This is consistent with an antiferromagnetic $^2\Sigma_g^+$ ground state predicted from theory[24] as well as proposed from collision-induced dissociation experiments.[14] Here, we give direct experimental evidence for the extreme case of $3d$ electron localization in Cr_2^+.

Very similar results are found for manganese, the second element in the $3d$ row with a half-filled $3d$ subshell. X-ray absorption spectra of manganese atoms,[21] Mn_2^+, and $CrMn^+$, excited at the manganese $2p$ edge, are shown in Fig. 2. Similar to chromium, the experimental spectra represent a local $3d^5$ configuration and can be reproduced with an atomic multiplet calculation taking $[Ar]3d^5 4s^1$ as the initial-state configuration and $2p^5 3d^6 4s^1$ as the final-state configuration, again only considering the dominant $2p \rightarrow 3d$ transitions. Within the monochromator resolution of 150 meV for Mn_2^+ and 500 meV for atomic manganese,[21] the experimental spectra are again identical. As in Cr_2^+, we conclude from the spectra given in Fig. 2 that $3d$ electrons in Mn_2^+ are practically nonbonding, fully localized at their ionic cores. The remaining three $4s$ electrons are situated in a fully occupied bonding $(4s\sigma)$ orbital and a singly occupied antibonding $(4s\sigma^*)$ orbital. The experimental result is consistent with a ferromagnetically coupled $^{12}\Sigma_g^+$ high spin state suggested by electron-spin resonance on matrix isolated Mn_2^+ (Refs. 10 and 17) and by photodissociation spectroscopy.[4] Theory predicts either a $^{12}\Sigma_g^+$ (Refs. 24–26) or a $^{10}\Pi_u$ (Ref. 24) ground state. This latter point illustrates the difficulty of predicting the electronic ground state of transition-metal dimers even at very high levels of theory. However, a $^{10}\Pi_u$ state would involve $4s$-$3d$ promotion and thus change the local $3d$ occupancy. This should clearly be visible in the spectrum and can therefore be ruled out based on the data given in Fig. 2.

Given the results on Cr_2^+ and Mn_2^+, the question arises of how $3d$ electrons behave in heteronuclear $CrMn^+$ dimer cations, isoelectronic to neutral Cr_2. Considering the number of $4s$ electrons, these heteronuclear dimer cations are halfway in between pure Cr_2^+ and Mn_2^+. Because of its element-specific nature, $2p$ x-ray absorption spectroscopy is well suited to investigate $3d$ electron localization at the chromium and manganese sites in $CrMn^+$. The spectra of the heteronuclear dimer cations are also shown in Fig. 1 for the chromium $2p$ excitation and in Fig. 2 for the manganese $2p$ excitation. Although these are also recorded with an energy resolution of 150 meV, the lines in the heteronuclear dimer cation are broadened but are still very similar to the neutral atoms and can well be reproduced by atomic multiplet calculation with $[Ar]3d^5 4s^n$ initial-state configurations where $n=0$ for chromium and $n=1$ for manganese, again indicating atomic localization of $3d$ electrons. In $CrMn^+$, two $4s$ electrons occupy a bonding $(4s\sigma)$ orbital, leading to a $^1\Sigma^+$ state[27] with a bond order of 1 compared to a bond order of 1/2 for Cr_2^+ and Mn_2^+. This is reflected in a predicted bond energy of 2.38 eV for $CrMn^+$ (Ref. 27) as compared to experimental values of 1.30 ± 0.06 eV for Cr_2^+ (Ref. 14) and ≥ 1.39 eV for Mn_2^+.[15] Broadening of the spectra can either be attributed to a slight participation in bonding of the $3d$ electrons or to the lowered symmetry in heteronuclear dimer cations. Future experimental studies on larger aggregates as well as theoretical investigations with explicit inclusion of all electrons at the optimized bond length will help clarify this point. Furthermore, it would be interesting to see how localization of $3d$ electrons evolves in larger manganese clusters, eventually reaching the peculiar crystallographic structure of α-Mn.

In summary, local and element-specific core-level spectroscopy has revealed strong $3d$ valence electron localization in Cr_2^+, Mn_2^+, and $CrMn^+$ due to their half-filled $3d$ subshells. Homonuclear as well as heteronuclear chromium and manganese dimer cations are predominantly bound by their $4s$ electrons. In all three cases, the local $3d^5$ configuration observed experimentally indicates local high spin $3d^5(^6S)$ states with a 5 μ_B spin moment of the $3d$ electrons at the ionic cores.

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