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Review

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Electrospray ionization photoelectron spectroscopy: Probing the electronic structure of inorganic metal complexes in the gas-phase

Tom Waters^{a,b}, Xue-Bin Wang^{a,b}, Lai-Sheng Wang^{a,b,*}

^a Department of Physics, Washington State University, 2710 University Drive, Richland, WA 99354, United States ^b W.R. Wiley Environmental Molecular Sciences Laboratory and Chemical Sciences Division,

Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352, United States

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Abstract

The coupling of electrospray to photoelectron spectroscopy has allowed a number of negatively charged solution phase transition-metal complexes to be transferred to the gas-phase and studied by photoelectron spectroscopy for the first time. Experiments have been performed on a range of species, including classic square-planar and octahedral transition-metal halide complexes, metal-metal bonded species, transition-metal bis(dithiolene) centers and a variety of mononuclear and polynuclear iron-sulfur clusters that are related to important bioinorganic centers. The studies have

Abbreviations: ADE, adiabatic detachment energy; BE, binding energy; CCSD(T), coupled cluster with single and double and noniterative inclusion of triple excitations; DFT, density functional theory; DMSO, dimethyl sulfoxide; ESI, electrospray ionization; HOMO, highest occupied molecular orbital; KE, kinetic energy; LUMO, lowest unoccupied molecular orbital; MO, molecular orbital; MS, mass spectrometry; PES, photoelectron spectroscopy; RCB, repulsive Coulomb barrier; TOF, time-of-flight; VDE, vertical detachment energy

Corresponding author. Tel.: +1 509 376 8709; fax: +1 509 376 6066.

E-mail address: ls.wang@pnl.gov (L.-S. Wang).

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provided detailed information about the electronic structure and molecular orbital energy levels of these species, allowing for direct comparison with theoretical calculations, and providing insight into their intrinsic redox properties in the absence of solvation. © 2006 Elsevier B.V. All rights reserved.

Keywords: Photoelectron spectroscopy; Electrospray; Electronic structure; Iron-sulfur; Metal halide; Dithiolene

1. Introduction

1.1. Valence photoelectron spectroscopy

Photoelectron spectroscopy (PES) is a direct method to probe the energies and ordering of molecular orbitals (MOs) in gaseous molecules or ions, providing direct insights into their electronic structure and bonding. The present account describes recent experiments carried out on an electrospray ionisationphotodetachment PES apparatus that has been developed in the author's laboratory [1], which has allowed a variety of anionic solution phase inorganic species to be studied by gas-phase PES for the first time. The application of other methods of solidstate and gas-phase photoelectron spectroscopy to inorganic, organometallic and coordination complexes are not described here, and detailed reviews are available elsewhere [2–11].

Gas-phase PES involves irradiation of a gaseous molecule (or ion) with a monochromatic light source of sufficient energy to cause electrons to be ejected, the so-called photoelectrons. The technique is based on Einstein's photoelectric equation, BE = hv - KE (where hv is the photon energy, KE the kinetic energy of the detached electron, and BE is the electron binding energy) and is conceptually very simple: the photon energy is known and photoelectron kinetic energies are measured experimentally, allowing for electron binding energies to be determined. The most straightforward quantities that can be measured are vertical and adiabatic detachment energies (VDE and ADE, respectively), which are determined from the peak maximum and peak onset, respectively, of the first detachment feature. These correspond to transitions from the ground state of the parent species to the ground state of the one-electron detached species with its geometry fixed at that of the parent (vertical) or at its relaxed geometry (adiabatic). In this respect, gas-phase ADEs are similar to solution phase redox potentials, and photodetachment can be viewed as an oxidation process, but in the absence of solvation. Therefore, PES can provide insights into the intrinsic redox properties of solution phase species, allowing for the effects of ligands and coordination environment to be examined in the absence of solvation, counterions and crystal packing.

Aside from these ground state transitions, PES can also provide information about the excited states of the ionized molecule, with detachment features in a photoelectron spectrum representing transitions from the ground state of the parent species to the electronic ground and excited states of the one-electron detached species. Accordingly, the energetic separation between detachment features corresponds to the difference in energy of different electronic states of the product species, and so PES can provide direct information about electronic excitation energies. Detachment features can alternatively be viewed within the single particle framework of Koopmans' theorem, which relates the energy of detachment features to the MO energy levels of the parent species. This *direct* information about MO energy levels contrasts with that obtained by other experimental techniques, which usually involve electronic transitions between occupied and partially occupied or vacant orbitals (e.g., electronic spectroscopy) and provide information about their *relative* energies. In addition, unlike optical absorption techniques, which are subject to stringent selection rules, the selection rules for photoelectron spectroscopy are significantly relaxed, and electronic states that are optically 'dark' and might not be accessible by other spectroscopic techniques can often be observed. The direct information about MO energy levels from PES experiments is also ideal for comparison with MO energy levels from theoretical calculations.

1.2. Electrospray ionisation-photodetachment photoelectron spectroscopy

The majority of gas-phase PES experiments on inorganic and coordination complexes have been carried out on species that require vaporization or sublimation for transfer to the gasphase [2–10]. As a consequence, these studies have been largely limited to neutral species of sufficient volatility and/or thermal stability such that they do not decompose prior to vaporization. However, electrospray ionization (ESI) is a soft ionization technique that allows for the direct transfer of charged species from solution into the gas-phase [12–16]. Although largely employed for the study of biomolecules [14,15], the technique is also ideally suited for inorganic and organometallic species, many of which exist as ions in solution and can be transferred directly to the gas-phase without the need for protonation/deprotonation [17-20]. The coupling of electrospray to PES has enabled the electronic structure of a number of inorganic solution phase species to be studied in the gas-phase by PES for the first time [21,22]. Examples of some recent work on inorganic complexes investigated using the ESI-PES technique in the author's laboratory are described in this review, including classic square-planar and octahedral transition-metal complexes, metal-metal bonded species, transition-metal bis(dithiolene) centers, and mononuclear and polynuclear iron-sulfur clusters that are models for important bioinorganic centers.

The electrospray process is also ideally suited for the transfer of multiply charged anions to the gas-phase, the majority of which had not been observed previously due to their inherent instability and/or difficulties associated with their formation or transfer to the gas-phase [21–24]. This has allowed a number of multiply charged anions to be studied experimentally in the absence of solvation for the first time, providing important insights into their fundamental and often unique properties [21,22]. Many of the inorganic complexes described in this review are multiply charged anions, and so some of the important properties of these species are described first.

1.3. Multiply charged anions

The properties of gaseous multiply charged anions are significantly different to those of their singly charged counterparts, in large part due to the presence of strong intramolecular Coulomb repulsion in the former [21,22,24]. Indeed, this Coulomb repulsion renders many multiply charged anions as unstable with respect to electron detachment, including common species such as CO_3^{2-} , SO_4^{2-} and PO_4^{3-} that are stabilized in the condensed phase by solvation or ion-pairing [24–27]. The energy of coulomb repulsion can also exceed that of chemical bonding, meaning that many multiply charged anions are also unstable with respect to charge separation fragmentation reactions [28].

Electron detachment from multiply charged anions also exhibits some important fundamental differences to that from their singly charged counterparts. The Coulomb repulsion in multiply charged anions induces a repulsive Coulomb barrier (RCB) for electron detachment, which is analogous to the potential barrier binding α -particles in a radioactive atomic nucleus [29], but with a different length and energy scale. The detached electron experiences nuclear attraction at short distances, while at larger distances it experiences Coulomb repulsion between the two negatively charged photoproducts (e.g., $A^{2-} \rightarrow A^- + e^-$), and superposition of these forces gives rise to the RCB [21,24,30,31]. This barrier means that photon energies higher than the RCB are required to detach electrons (neglecting electron tunneling), and is manifested in the experimental spectra by spectral cutoff at higher binding energies. The RCB can also result in multiply charged anions with negative electron binding energies being kinetically stable gas-phase species (metastable), with spontaneous detachment of the excess electron prevented by the RCB [32–37].

2. Experimental overview

The design and operation of the electrospray-photodetachment apparatus has been described in detail elsewhere [1], and only a brief overview is provided here. A schematic view of the instrument is given in Fig. 1, and important features are numbered and described below. Solutions containing the anions of interest (typically $\sim 0.1 \text{ mg mL}^{-1}$ in CH₃CN or 3:1 CH₃OH:H₂O) are sprayed through a syringe ($\sim 0.04 \text{ mL h}^{-1}$) whose tip is biased at high negative voltage (1). This generates highly charged negative droplets, which are fed into a desolvation capillary (2) that is heated to \sim 50–100 °C to aid with desolvation. Anions that emerge from the capillary are guided by an RF-only quadrupole ion guide (3) into a quadrupole ion-trap (4) where ions are accumulated for 0.1 s to generate sufficient quantities for the photodetachment experiment. The ions are ejected from the ion-trap (5) into a time-of-flight (TOF) mass spectrometer for mass/charge analysis (6–8). Once the m/zcomposition of the ion beam is known, the desired anions are mass selected by a mass gate and decelerated (9) before being detached by a laser beam in the interaction zone of the magnetic bottle photoelectron analyzer (10-12). Several photon energies are typically used, depending on the electron binding energy of



Fig. 1. Schematic view of the electrospray-photodetachment apparatus: 1, syringe; 2, heated desolvation capillary; 3, radio-frequency quadrupole ion guide; 4, quadrupole ion-trap; 5, TOF-MS extraction stack; 6, ion-beam deflector; 7, Einzel lens assembly; 8, 40 mm dual microchannel plate in-line ion detector; 9, three-grid mass gate and momentum decelerator assembly; 10, permanent magnet (NdFeB); 11, 4 m electron time-of-flight tube with a low-field solenoid and double layer μ -metal shielding; 12, 18 mm Z-stack microchannell plates photoelectron detector. Reprinted with permission from Ref. [1]. Copyright (1999) American Institute of Physics.

the anion of interest, and range from 532 nm (2.331 eV), 355 nm (3.496 eV) and 266 nm (4.661 eV) from an Nd:YAG laser to 193 nm (6.424 eV) and 157 nm (7.866 eV) from an excimer laser (ArF and F₂, respectively). Higher photon energies access more detachment features, while lower photon energy spectra exhibit better resolution due to the lower kinetic energy of the photoelectrons (KE = hv - BE). Photoelectrons are collected with high efficiency by the magnetic bottle (10) and analyzed by the 4 m long electron time-of-flight tube (11). The ion-trap and TOF mass spectrometer are operated at a 10 Hz repetition rate, while the laser and magnetic-bottle photoelectron analyzer are operated at 20 Hz, with the ion beam off at alternating laser shots to allow for background subtraction. Photoelectron kinetic energies are calibrated with the known spectra of anions such as I^- , O^- , ClO_2^- and $OsCl_6^{2-}$ [38,39], and the resolution of the magnetic-bottle photoelectron analyzer is estimated as about 2% $(\Delta KE/KE)$, i.e. ~20 meV for 1 eV electrons. Electron kinetic energies are then converted to binding energies using the known photon energy (BE = hv - KE).

3. Transition-metal halides

Octahedral and square-planar transition-metal halides MX_6^{2-} and MX_4^{2-} are classic transition-metal complexes that have been studied extensively both experimentally and theoretically, and are important complexes in the development of descriptions of inorganic electronic structure and bonding [40,41]. PES experiments have been performed on a range of species with a variety of different metal centers and halide ligands, allowing for changes in spectral features as a function of metal and ligand to be identified.

3.1. Square-planar MX_4^{2-}

The 4d and 5d square-planar dianions MX_4^{2-} (M = Pd and Pt; X=Cl and Br) are some of the smallest multiply charged anions that are stable in the gas-phase [33,42]. Spectra for each were recorded at three different photon energies (193, 266 and 355 nm), and those for $PtCl_4^{2-}$ and $PtBr_4^{2-}$ are presented in Fig. 2. The spectra were interpreted with the aid of MO energy levels from ligand field theory and previous theoretical calculations, as well as changes in the energy of detachment features as a function of metal (Pd, Pt) and ligand (Cl, Br). The most remarkable feature of the spectra for $PtCl_4^{2-}$ and $PtBr_4^{2-}$ were the observation of negative electron binding energies, with adiabatic detachment energies measured as -0.25 and -0.04 eV, respectively (Fig. 2). These negative ADEs demonstrate that gaseous $PtCl_4^{2-}$ and $PtBr_4^{2-}$ are both thermodynamically unstable with respect to electron detachment, but are kinetically stable on the timescale of the experiment due to the unbound electron being trapped behind the RCB (Section 1.3). The room-temperature half-lives for tunneling electron loss from PtCl₄²⁻ and PtBr₄²⁻ have been estimated in Fourier-transform ion-cyclotron resonance mass spectrometry experiments, with that for $PtCl_4^{2-}$ estimated as ~ 2.5 s, while PdCl₄²⁻ did not exhibit electron detachment and was stable for up to 10^3 s [34,35].



Fig. 2. Photoelectron spectra of: (a) $PtCl_4^{2-}$ and (b) $PtBr_4^{2-}$ recorded at 193 nm (6.424 eV, bottom), 266 nm (4.661 eV, middle) and 355 nm (3.496 eV, top). Note the negative electron binding energy for $PtCl_4^{2-}$, and the close correspondence between detachment features for both species.



Fig. 3. Schematic correlation diagram illustrating the relationship between electron binding energies for different molecular orbitals of $PtCl_4^{2-}$ and $PtBr_4^{2-}$.

The assignments for the photoelectron spectra of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ allowed a correlation diagram relating their frontier orbitals to be generated (Fig. 3). The first three low binding energy features for both of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ are very similar (X, A, B), occurring at slightly higher binding energy for the latter but with almost identical spacing for both species. Feature X was assigned to electron detachment from the metalbased HOMO (d_{xy}), while features A and B were assigned to the degenerate level (d_{xz}, d_{yz}) , which should give rise to two detachment channels due to spin-orbit and Jahn-Teller effects (Fig. 3). The very similar spacing between these features for both PtCl₄²⁻ and PtBr₄²⁻ were consistent with relatively small ligand contributions to these orbitals. Features C and D for PtCl₄²⁻ were assigned to the most stable metal-based orbital $(3a_{1g}, d_z 2)$ and the highest energy occupied ligand-based orbital $(1a_{2g})$, respectively, while the ordering of these orbitals was reversed for $PtBr_4^{2-}$ (Fig. 3). The remaining features for both species were assigned to ligand-based orbitals, and were shifted to slightly lower binding energy for $PtBr_4^{2-}$ due to the lower electron binding energy of bromide relative to chloride. In addition, the larger spin-orbit splitting observed for detachment from degenerate ligand-based levels for PtBr₄²⁻ (E&F) was consistent with the expected larger spin-orbit splitting for bromide relative to chloride.

3.2. Octahedral MX_6^{2-}

A range of six-coordinate dianions MX_6^{2-} (M = Re, Os, Ir and Pt; X = Cl and Br) have also been examined by PES [39]. The metal centers are formally M^{IV} with 5d-orbital occupations of d^3 , d^4 , d^5 and d^6 for M = Re, Os, Ir and Pt, respectively. Under ideal octahedral point symmetry the five d-orbitals are split into triply (t_{2g}) and doubly (e_g) degenerate sets, the latter of which are formally vacant for each of these low-spin MX_6^{2-} centers. This indicated ground state configurations of $(t_{2g})^3$, $(t_{2g})^4$, $(t_{2g})^5$ and $(t_{2g})^6$ for M = Re, Os, Ir and Pt, respectively, with ReX₆²⁻ (d^3) and PtX₆²⁻ (d^6) containing half-filled and filled t_{2g} levels. A comparison of photoelectron spectra recorded at 193 nm for ReX_6^{2-} and PtX_6^{2-} (X = Cl and Br) are presented in Fig. 4. Detachment features were qualitatively assigned by comparison of the spectra for each of ReX_6^{2-} and PtX_6^{2-} and from spectral changes as a function of metal (Pt and Re) and ligand (Cl and Br). The spectra for $PtCl_6^{2-}$ have recently been studied in more detail theoretically [43,44]. Features X, A and B were similar for both of ReCl₆²⁻ and ReBr₆²⁻, suggesting they should



Fig. 4. Photoelectron spectra recorded at 193 nm (6.424 eV) for MX_6^{2-} centers (M = Re and Pt; X = Cl and Br): (a) $ReCl_6^{2-}$, (b) $ReBr_6^{2-}$, (c) $PtCl_6^{2-}$, and (d) $PtBr_6^{2-}$.

arise from detachment from predominantly metal-based orbitals that are common to both species. In contrast, features C and D were different for these species, consistent with them arising from ligand-based orbitals. These assignments were supported by comparison with the spectra for PtX_6^{2-} (Fig. 4). Features C and D for $ReCl_6^{2-}$ appeared similar to features B and C for $PtCl_6^{2-}$, consistent with them being assigned to detachment from predominantly chloride-based orbitals that are common to both species. In contrast, features X, A and B for $ReCl_6^{2-}$ are significantly different to features X and A for $PtCl_6^{2-}$, consistent with them being assigned to detachment from metal-based orbitals.

The electron detachment and ionic fragmentation dissociation channels for a range of gaseous MX_6^{2-} species have since been investigated in more detail in both collision induced dissociation and photodissociation experiments [45–47]. Photodissociation and low-energy collisional excitation resulted in ionic fragmentation channels (e.g., $IrCl_6^{2-} \rightarrow IrCl_5^{-} + Cl^{-}$) while high-energy collisional excitation resulted in electron detachment ($IrCl_6^{2-} \rightarrow IrCl_6^{-} + e^{-}$) [45–47]. Gas-phase photodissociation spectra of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ have also been recorded, and were both very similar to their respective absorption spectra in aqueous solutions [47].

Electron detachment from MX_6^{2-} (M = Re, Os, Ir and Pt) is an oxidation event, and so gas-phase detachment energies should be inherently related to oxidation potentials measured in solution. Adiabatic detachment energies for MCl_6^{2-} from the PES experiments are compared with calculated values and solution phase redox potentials in Fig. 5 [48]. The close correlation between gas- and solution-phase results suggests similar effects of solvation for each of MCl_6^{2-} , consistent with their similar sizes. The calculated adiabatic detachment energies from a previous theoretical study show reasonable agreement with the experimental data, but appear to be underestimated in each case [48].



Fig. 5. Correlation between experimental and calculated gas-phase adiabatic detachment energies (ADE) for MCl_6^{2-} (M = Re, Os, Ir and Pt) and solution-phase redox potentials. Reprinted with permission from Ref. [5]. Copyright (1999) American Institute of Physics.

The formally d⁰ species ZrF_6^{2-} was also examined and compared with MCl_6^{2-} described above [49]. This exhibited a very high adiabatic detachment energy of ~2.9 eV, which was significantly higher than that observed for MCl_6^{2-} described above (between 0.5 and 1.6 eV). This was consistent with the first detachment feature in the formally d⁰ ZrF_6^{2-} arising from a ligand-based orbital that is delocalized across the electronegative fluoride ligands.

3.3. Ferric and ferrous halides FeX_3^- and FeX_4^-

High spin iron centers are important in many iron-sulfur proteins, and the electronic structures of such species have been the focus of a number of experimental and theoretical studies [11,50–53]. Theoretical calculations indicate that strong exchange interactions split the Fe 3d levels into a set of majority spin and minority spin levels [51-53]. The majority spin levels are stabilized relative to the frontier ligand-based levels, while the minority spin levels are destabilized and lie above these ligand-based levels. Simple ferrous and ferric iron-halide species such as Fe^{II}Cl₄²⁻, Fe^{II}Cl₃⁻, and Fe^{III}Cl₄⁻ have proven important models to test this scheme, and salts of FeCl₄²⁻ and FeCl₄¹⁻ have been examined previously by variable energy photoelectron spectroscopy using solid-state samples [11,54–58]. Equivalent singly charged anions such as $Fe^{II}Cl_3^-$, and $Fe^{III}Cl_4^-$ have also been examined by gas-phase PES, and are described below. However, the dianion $FeCl_4^{2-}$ has not been observed in the gas-phase, and is presumably unstable with respect to electron detachment, and so has not been studied experimentally.

The three-coordinate ferrous species Fe^{II}Cl₃⁻ was examined in comparison with a range of three-coordinate species MX₃⁻ (M = Mn - Ni; X = PCl and Br) [59]. The combined data provided insight into the relative energies of metal- and ligand-based orbitals and the stabilization of metal 3d-orbitals from Mn to Ni. The ferrous species FeCl₃⁻ exhibited a weak low intensity threshold feature (X) that was not observed for any of the other MX₃⁻ series (Fig. 6). Theoretical calculations indicated this should arise from detachment of the single minority spin electron that occupies a formally non-bonding d₇2 orbital in this $d^6 S = 2$ center [59,60]. This was supported by comparison with the related species MnX_3^- and FeX_4^- , both of which are high spin d^5 S = 5/2 centers. The absence of an equivalent low binding energy detachment feature for both of these centers was consistent with neither containing a minority-spin electron M 3d electron (Fig. 6). In contrast, the similarity between the second detachment feature for $FeCl_3^{-}$ (A) and the first feature for $MnCl_3^{-}(X)$ suggested this involved detachment from a ligandbased orbital that is common to both species, and is consistent with the occupied majority spin Fe 3d and Mn 3d levels occurring below the frontier ligand-based orbitals.

3.4. $CuCl_2^-$ and $CuBr_2^-$

The optical absorption spectrum and electronic structure of $CuCl_2$ has been the focus of a number of experimental and theoretical studies [61–63]. The anions $CuCl_2^-$ and $CuBr_2^-$ have also been examined by PES, providing insights into the



Fig. 6. Comparison between photoelectron spectra recorded at 157 nm (7.866 eV) for: (a) FeCl_4^- , (b) FeCl_3^- , and (c) MnCl_3^- . Note the weak low binding energy feature that is only present for FeCl_3^- .

MO energy levels of the parent species and ground and excited states of neutral CuCl₂ and CuBr₂ [64]. The related gold species AuX_2^- (X = Cl, Br and I) have also been studied [65], and their spectra interpreted in a later theoretical study [66].

Spectra for $CuCl_2^-$ and $CuBr_2^-$ were recorded at 157 and 193 nm photon energies and are presented in Fig. 7 [64]. The 193 nm spectrum of $CuCl_2^-$ exhibited five features (X, A–D), with two additional features (E, F) observed at higher binding energy in the 157 nm spectrum. The spectra were interpreted with that aid of theoretical calculations at the CCSD(T) level on the ground states of the parent anions and the ground and excited states of the product neutrals. Excitation energies for the neutral species were in good agreement with the experimental data, allowing for a detailed assignment of the experimental detachment features.

Detachment from the singlet ground states of CuX_2^- gives rise to doublet states of neutral CuX_2 . The first three detachment channels for CuX_2^- (${}^2\Pi_g$, ${}^2\Sigma_g^+$ and ${}^2\Delta_g$; Fig. 7) occurred at similar energies for both of $CuCl_2^-$ and $CuBr_2^-$, independent of the halide ligand, consistent with their assignment as arising from detachment from predominantly Cu 3d-based orbitals in both cases. In contrast, the next three detachment channels (${}^2\Pi_u$, ${}^2\Sigma_u^+$ and ${}^2\Pi_g$; Fig. 7) occurred at lower binding energy for $CuBr_2^-$, and were assigned as arising from halide-based orbitals. The lower binding energy and larger spin–orbit splitting observed for $CuBr_2^-$ relative to $CuCl_2^-$ was consistent with the lower ionization potential and the larger spin–orbit splitting expected for bromide relative to chloride.

3.5. Quadruple metal-metal bonded $Re_2Cl_8^{2-}$

The dianion $\text{Re}_2\text{Cl}_8^{2-}$ is the prototypical example of a binuclear transition-metal complex containing a metal-metal quadruple bond (σ^2 , π^4 and δ^2) [67,68], and its electronic structure has been examined by PES [69]. The spectra were consistent



Fig. 7. Photoelectron spectra recorded at 157 (7.866 eV, bottom) and 193 nm (6.424 eV, top) for (a) $CuCl_2^-$ and (b) $CuBr_2^-$. Assignments from the CCSD(T) calculations are included.



Fig. 8. A 157 nm photoelectron spectrum of $\text{Re}_2\text{Cl}_8^{2-}$ with the corresponding molecular orbital energy levels, showing the relationship between photoelectron detachment features and the occupied molecular orbitals. Reprinted with permission from Ref. [69]. Copyright (2000) American Chemical Society.

with the molecular orbital energy levels expected based on previous theoretical calculations [70–72]. The 157 nm spectrum is presented in Fig. 8 and labeled to indicate the expected origin of detachment features. Three well resolved features at lower binding energies were assigned to detachment from the three metal–metal bonding orbitals (σ , π and δ), while the features at higher binding energy were assigned to orbitals of metal–ligand or ligand-based character.

4. Iron-sulfur systems

Iron–sulfur centers are ubiquitous in living matter, and are important in such life sustaining processes as respiration, nitrogen fixation, and photosynthesis [73–75]. They are involved in a variety of functions, but their most special role is in electron transfer pathways. Numerous model systems have been designed to investigate the structure, reactivity, and spectroscopic properties of such clusters [76], and a variety of these have been examined by gas-phase PES. These studies have provided insights into their electronic structure and redox propoperties, as well as providing direct experimental data for comparison with modern theoretical treatments of their electronic structures.

4.1. [1Fe] mononuclear iron-sulfur complexes

The simplest biological iron–sulfur site is $[Fe(SR)_4]^{1-/2-}$ (–SR stands for thiolate sulfur ligand) which is found in the rubredoxin proteins, and is comprised of a single iron atom coordinated to four thiolate sulfurs of cysteine residues. The strong exchange interactions split the Fe 3d levels into a set of majority spin and minority spin levels, with the majority spin levels stabilized relative to the minority spin levels. The mainly sulfur-based Fe–S bonding, Fe–S antibonding and S 3p nonbonding levels lie between the spin polarized Fe 3d levels. Gas-phase PES of ferrous- and ferric-thiolate centers presents an ideal method to test the validity of these orbital energy level schemes, and a number of mononuclear ferrous species such as $Fe(SCH_3)_3^-$, $Na^+[Fe(SCN)_4^{2-}]$ and $Na^+[Fe(S_2-o-xyl)_2^{2-}]$ ($S_2-o-xyl = o-xylyl-\alpha, \alpha'$ -dithiolate) have been examined [77–79]. The bare dianions $Fe(SCN)_4^{2-}$ and $Fe(S_2-o-xyl)_2^{2-}$ were not observed experimentally, and are expected to be unstable in the gas-phase with respect to electron detachment, and so the equivalent ion-pairs $Na^+[Fe(SCN)_4^{2-}]$ and $Na^+[Fe(S_2-o-xyl)_2^{2-}]$ were examined instead.

Representative spectra for the ferric and the equivalent ferrous species are included in Fig. 9. The most striking feature for all the ferrous species was the observation of a weak low binding energy feature, regardless of the ligand number or type, which is similar to that observed for FeCl3⁻ and described above (Section 3.3, Fig. 6). In contrast, such a low binding energy feature was not observed for any of the ferric species. The spectra for Fe^{II}(SCH₃)₃⁻ and Fe^{III}(SCH₃)₄⁻ were interpreted with the aid of theoretical calculations at the DFT and CCSD(T) levels [79], which suggested the first detachment feature for ferrous Fe^{II}(SCH₃)₃⁻ was due to detachment of the single Fe 3d minority spin electron (Fe^{II}, $S = 2 \rightarrow Fe^{III}$, S = 5/2). The similar weak intensity of this feature for each of the ferrous species suggested it was also due to detachment of the single Fe 3d minority spin electron in each case. This assignment provides direct support for the orbital energy level schemes from theoretical calculations in which the single minority spin Fe 3d electron is the highest energy occupied orbital. In addition, the large energy gap between the first and second detachment feature for the two tetrahedral centers $Na^{+}[Fe(S_2-o-xyl)_2^{2-}]$ and $Na^{+}[Fe(SCN)_{4}]^{2-}$ (e.g., ~0.9–1.0 eV in both cases) corresponds to the difference in energy between the ground and first excited states of the Fe^{III} product species, and demonstrates the stability of the high spin d⁵ configuration in these tetrahedral ferric centers.

Electron detachment is an oxidation process, and so the photoelectron spectrum of a ferrous center should reflect the Franck–Condon factors between the species involved. The width of the first detachment feature for Fe(II) complexes was used to provide an estimate of the geometric relaxation energy (λ_{oxd}) associated with the Fe²⁺ \rightarrow Fe³⁺ oxidation process (Fig. 10) [77]. These ranged from 0.26 eV for the most ionic species FeCl₃⁻, to 0.44 eV for four coordinate Na⁺[Fe(SCN)₄]²⁻, with the larger value for the latter consistent with a larger number of vibrational modes in this system.

4.2. [4Fe–4S] cubane iron–sulfur clusters

[4Fe–4S] iron–sulfur clusters are present at the active sites of numerous enzymes, and adopt a cubane structure in which the four iron atoms are approximately tetrahedrally coordinated to three inorganic μ_3 -sulfide ions and one external cysteine



Fig. 9. Comparison of 193 or 266 nm photoelectron spectra for related ferrous (upper) and ferric (lower) centers: (a) $Fe(CH_3)_3^-$, (b) $Fe(CH_3)_4^-$, (c) $Na^+[Fe(SCN)_4]^{2-}$, (d) $Fe(SCN)_4^-$, (e) $Na^+[Fe(S_2-o-xyl)_2]^{2-}$ and (f) $Fe(S_2-o-xyl)_2^{1-}$. Note that the weak low binding energy feature is only observed for the ferrous center in each case.



Fig. 10. Schematic potential energy curves showing photodetachment of an hypothetical Fe(II) complex [FeL_n]⁻. The difference between the vertical (VDE) and adiabatic (ADE) detachment energies represents the potential energy of the Fe(III) complex at the geometry of the Fe(II) complex, and is called the oxidant intramolecular reorganization energy, λ_{oxd} .

residue (Fig. 11a) [73-75]. The clusters are commonly involved in electron transfer, and usually occur in three different oxidation states: $[Fe_4S_4]^{1+}$, $[Fe_4S_4]^{2+}$ and $[Fe_4S_4]^{3+}$. Reduction potentials have been observed to vary significantly, with these differences attributed to a range of environmental factors including interaction with the solvent and/or protein backbone [80]. Numerous synthetic analogues have been prepared with the aim of understanding the redox, spectroscopic, structural and reactivity properties of the [4Fe–4S] clusters [76], and their electronic structures have been the focus of numerous theoretical studies, in particular those based on broken-symmetry DFT calculations [51-53,81]. The $[Fe_4S_4]^{2+}$ core can be considered as a two-layer system, in which two high-spin Fe centers are coupled ferromagnetically to give a [2Fe–S2] sublayer (S = 9/2), and two of these [2Fe-2S] sublayers are coupled antiferromagnetically to give a low spin state (S=0, Fig. 11b). A range of [4Fe-4S] model complexes have been studied by PES, providing insight into their electronic structures and their intrinsic redox chemistry in the absence of solvation. The experimental results directly



Fig. 11. (a) Schematic structural model of the [4Fe-4S] cubane site in proteins, and (b) the $[Fe_4S_4]^{2+}$ cubane core showing the two antiferromagnetically coupled layers. The thick arrows represent majority spin electrons (d⁵, S = 5/2) and the small arrows represent a single minority spin electron (S = 1/2).

support the broken-symmetry description of their electronic structure, as well as provide insights into the effect of terminal and bridging ligands on their redox potentials. These studies have been comprehensively reviewed in a recent book chapter [82].

The doubly charged cubane complexes $[Fe_4S_4L_4]^{2-}$ (L = SEt, SH, Cl, Br and I) and $[Fe_4Se_4L_4]^{2-}$ (L = SEt and Cl)were examined to provide insight into the effect of terminal (L) or bridging (S and Se) ligands on the electronic structure of the cubane unit [83]. A comparison of the 193 nm spectra for $[Fe_4S_4L_4]^{2-}$ (L = SEt, SH, Cl, Br and I) with different terminal ligands is presented in Fig. 12. The weaker threshold feature (X) was observed for each species, while the second feature (A) was poorly resolved for $[Fe_4S_4(SEt)_4]^{2-}$ but more clearly resolved for the complexes with halide ligands. Electron binding energies were dependent on L, and increased in the order SEt < SH < Cl < Br < I, while the relative intensity of features X and A and their separation of $\sim 0.75 \text{ eV}$ was almost identical for each of $[Fe_4S_4L_4]^{2-}$. Comparison of $[Fe_4S_4L_4]^{2-}$ with $[Fe_4Se_4L_4]^{2-}$ revealed that substitution of Se for S had little effect on electron binding energies, and only minor effects on the overall spectra [83]. Overall, the experimental spectra were consistent with the electronic structure proposed for $[Fe_4S_4L_4]^{2-}$ centers on the basis of broken-symmetry DFT calculations (Fig. 11b) [51-53,81]. The two minority spin Fe 3d electrons (one on each redox sublayer) occupy the HOMO, which involves terminal Fe-S antibonding character and a bonding interaction between the two Fe on one sublayer, giving rise to a formal oxidation state of $Fe^{2.5+}$. Therefore, the weak threshold feature observed experimentally for each of $[Fe_4S_4L_4]^{2-}$ was consistent with detachment of an Fe 3d minority spin electron on a single 2Fe–2S sublayer (2Fe^{2.5+} S = $9/2 \rightarrow 2Fe^{3+}$ S = 10/2). This weak feature is directly analogous to that observed for detachment of the single minority spin electron in mononuclear ferrous centers such as Fe(SCH₃)₃⁻ and FeCl₃⁻ (Sections 3.3 and 4.1).

The effect of the terminal ligand on detachment energies was examined in more detail in a later study for a series of ligandsubstituted species $[Fe_4S_4Cl_{4-n}L_n]^{2-}$ (L = CN⁻, SCN⁻, AcO⁻ and EtS⁻; n = 0-4) containing a range of different terminal ligands [84]. The spectra of each species were qualitatively very similar, suggesting similar electronic structure. However, electron binding energies were observed to increase in the order EtS⁻ < Cl⁻ < AcO⁻ < CN⁻ < SCN⁻ and with the extent of substitution (e.g., Fig. 13a for $[Fe_4S_4Cl_{4-n}(CN)_n]^{2-}$). A linear relationship between electron binding energies and substitution number (*n*) was observed (e.g., Fig. 13b), consistent with that observed previously in solution for closely related species [85], and that expected based on a ligand additivity model [86].

Different oxidation states of the [4Fe–4S] core were accessed through a series of singly charged analogues $[Fe_4S_4I_n]^{1-}$ (n=1-4) containing varying numbers of terminal iodide ligands [87]. These were produced by collisional activation (fragmentation) of the parent dianions $[Fe_4S_4L_4]^{2-}$, which resulted in either symmetric fission to produce two equivalent $[Fe_2S_2L_2]^{1-}$ fragments (discussed in more detail below, Section 4.3) or electron detachment to yield singly charged



Fig. 12. Photoelectron spectra recorded at 193 nm (6.424 eV) for the series [Fe₄S₄L₄]²⁻ (L=SEt, SH, Cl, Br and I). Reprinted with permission from Ref. [83]. Copyright (2003) American Chemical Society.

 $[Fe_4S_4L_4]^{1-}$ [88]. The singly charged cluster with four iodide ligands $[Fe_4S_4I_4]^{1-}$ then underwent further fragmentation with sequential loss of up to four iodide atoms to give the series $[Fe_4S_4I_n]^-$ (n=0-4) [87]. These correspond to the [4Fe-4S] cubane core over five formal oxidation states, i.e. $[4Fe-4S]^{1-} \rightarrow [4Fe-4S]^0 \rightarrow [4Fe-4S]^{1+} \rightarrow [4Fe-4S]^{2+} \rightarrow$



Fig. 13. (a) Photoelectron spectra recorded at 157 nm (7.866 eV) for the series $[Fe_4S_4Cl_{4-x}(CN)_x]^{2-}$ (x = 0-4) showing the shift of features X and A to higher binding energies with increasing substitution number, n; (b) The linear relationship of detachment energies [ADE, VDE(X), VDE(A)] with substitution number, n.

 $[4\text{Fe}-4\text{S}]^{3+}$ (n = 0-4, respectively) with each extra iodide atom in $[Fe_4S_4I_n]^-$ corresponding to the removal of one Fe 3d electron. Photoelectron spectra for the five members of the series $[Fe_4S_4I_n]^-$ (n = 0-4) recorded at 193 nm are presented in Fig. 14 [87]. The systematic removal of iodide ligands from $[Fe_4S_4I_n]^{1-1}$ (n=0-4) resulted in significant changes in the spectra of these complexes, with the first detachment feature shifted to lower binding energy and the appearance of additional weaker detachment features near the threshold (Fig. 14). The spectrum for singly charged [Fe₄S₄I₄]⁻ was qualitatively similar to that of $[Fe_4S_4I_4]^{2-}$, except that the binding energies of the former were higher due to the absence of coulomb repulsion. The presence of the single weak onset detachment feature for $[Fe_4S_4I_4]^-$ was consistent with this feature arising from detachment of the single Fe 3d minority spin electron, and suggested that the inverted level scheme proposed for $[Fe_4S_4L_4]^{2-}$ was still appropriate for $[Fe_4S_4I_4]^{1-}$. Removal of a single iodine atom from $[Fe_4S_4I_4]^{-}$ to give $[Fe_4S_4I_3]^-$ should result in the presence of two minority spin electrons, however the presence of three iodide ligands renders the two Fe₂S₂ sublayers inequivalent, and should split the two minority spin levels. Indeed, two Fe 3d detachment features were observed for $[Fe_4S_4I_3]^{1-}$ (Fig. 14), and were even more clearly resolved for the related species $[Fe_4S_4Br_3]^{1-}$ (data not shown) [87]. The spectra for $[Fe_4S_4I_2]^{1-}$, $[Fe_4S_4I_1]^{1-}$ and $[Fe_4S_4]^{1-}$ show additional Fe 3d detachment features at lower binding energies, consistent with the presence of additional minority-spin electrons (Fig. 14). However, the spectra also appear more complex, presumably due to the possibility of different structural isomers and/or further splitting of the minority spin levels [87].

The diverse range of oxidation states and redox potentials observed for [4Fe–4S] clusters has been attributed to a range of environmental factors, including hydrogen bonding to the sulfide and terminal cysteine ligands [80]. The effect of hydrogen bonding on the redox potentials of [4Fe-4S] centers was examined by comparison of electron detachment energies for $[Fe_4S_4(SEt)_3(SC_nH_{2n+1})]^{2-}$ and $[Fe_4S_4(SEt)_3(SC_nH_{2n}OH)]^{2-}$ (n=4, 6 and 11), with the latter containing an hydroxyl functional group that is available for hydrogen bonding with the cubane core [89]. Spectra recorded at 355 nm for each case are presented in Fig. 15. The spectra were similar in each case, but detachment energies for $[Fe_4S_4(SEt)_3(SC_nH_{2n}OH)]^{2-}$ were shifted to $\sim 130 \,\text{meV}$ higher energy than those for $[Fe_4S_4(SEt)_3(SC_nH_{2n+1})]^{2-}$. This indicated stabilization of $[Fe_4S_4(SEt)_3(SC_nH_{2n}OH)]^{2-}$ due to the presence of an OH···S hydrogen bond that is absent in $[Fe_4S_4(SEt)_3(SC_nH_{2n+1})]^{2-}$. These conclusions were supported by Monte Carlo and DFT calculations, which suggested the presence of an hydrogen bond between the -OH group and a terminal -SEt ligand in $[Fe_4S_4(SEt)_3(SC_6H_{12}OH)]^-$ [89]. These experiments provided a direct and quantitative measure of the effect of a single Hbond in these clusters, in the absence of external factors such as solvation and the protein environment.

4.3. [2Fe-2S] dinuclear iron-sulfur clusters

Protein sites containing two iron atoms in a rhombic Fe_2S_2 core are found as $Fe_2S_2(S_{Cys})_4$ in Ferredoxins, and model complexes are based on the rhombic $[Fe_2S_2(SR)_4]^{2-}$ containing two distorted tetrahedral FeS₄ sites [76]. Three coordinate iron–sulfur sites might be expected to be more reactive, and may be relevant to the reactive sites and catalytic function of iron–sulfur centers, for example the XMoFe₇S₉ (X = C, N or O) cluster of the iron–molybdenum cofactor FeMoco [90,91].

A range of binuclear centers containing the Fe_2S_2 core were generated from the parent cubane complexes, with collisional



Fig. 14. Photoelectron spectra recorded at 193 nm (6.424 eV) for $[\text{Fe}_4\text{S}_4\text{I}_{\underline{n}}]^{1-}$ (n=0-4). The labels "d" indicate features assigned to detachment of Fe 3d electrons, and "S" denotes features assigned to S 3p-based molecular orbitals.



Fig. 15. Photoelectron spectra of $[Fe_4S_4(SEt)_3(SC_nH_{2n+1})]^{2-}$ (light curves) and $[Fe_4S_4(SEt)_3(SC_nH_{2n}OH)]^-$ (dark curves) (n = 4, 6 and 11) recorded at 355 nm (3.496 eV). Note the shift by \sim 130 meV to lower binding energies for the latter. Reprinted with permission from Ref. [89]. Copyright (2004) American Chemical Society.

activation of the parent dianions $[Fe_4S_4L_4]^{2-}$ [L = Cl, Br, I and SEt) resulting in either electron detachment or symmetric fission to yield two equivalent $[Fe_2S_2L_2]^{1-}$ fragments [88,92]. The electron detachment channel is not surprising given the low electron binding energies for $[Fe_4S_4L_4]^{2-}$ described above. However, the symmetric fission channel was unexpected, as it involves breaking four strong Fe-S bonds. Interestingly, similar conversions between Fe₂S₂ and Fe₄S₄ units have been observed in both model complexes and biological samples [76,93,94]. The fission process $[Fe_4S_4L_4]^{2-} \rightarrow 2 [Fe_2S_2L_2]^{1-}$ can conceivably proceed by two pathways (Fig. 16): (i) a high-spin pathway involving cleavage between the two antiferromagnetically coupled sublayers of $[Fe_4S_4L_4]^{2-}$ to generate two high-spin S = 9/2 $[Fe_2S_2L_2]^{1-}$ centers; or (ii) a low-spin pathway involving cleavage through the sublayers to generate two low-spin S = 1/2 $[Fe_2S_2L_2]^{1-}$ centers. The mechanism and energetics of these pathways were examined in detail in a later theoretical study [95]. This study indicated the low spin pathway was favored, and was exothermic by 0.5 eV with a barrier of 1.5 eV, while the high spin pathway was endothermic by 1.3 eV and with a higher barrier of 2.7 eV.

The fission channel provides direct access to dinuclear $[Fe_2S_2L_2]^{1-}$ clusters containing three coordinate iron sites, and whose electronic structures can be compared with that of the intact parent cubane $[Fe_4S_4L_4]^{2-}$. Photoelectron spectra



Fig. 16. Comparison of high-spin and low-spin symmetric fission pathways for $[Fe_4S_4L_4]^{2-}$ to generate high spin (S = 9/2) or low spin (S = 1/2) fission products $[Fe_2S_2L_2]^{1-}$, respectively.

recorded at 157 nm for the fission product $[Fe_2S_2Cl_2]^{1-}$ and parent $[Fe_2S_4Cl_4]^{2-}$ are presented in Fig. 17. The singly charged fission products have higher electron binding energies due to the absence of Coulomb repulsion, but the spectra were otherwise very similar, and suggested that $[Fe_4S_4X_4]^{2-}$ and $[Fe_2S_2X_2]^{1-}$ have similar electronic structures. In particular, the weak detachment feature X observed for the fission products $[Fe_2S_2L_2]^{1-}$ is characteristic of removal of a minority spin Fe 3d electron,



Fig. 17. Comparison between photoelectron spectra recorded at 157 nm (7.866 eV) for: (a) the intact cubane complex $[Fe_4S_4Cl_4]^{2-}$ and (b) the symmetric fission product $[Fe_2S_2Cl_2]^{1-}$.

and suggested that this is also the most weakly bound electron in $[Fe_2S_2X_2]^{1-}.$

The electronic structure and effect of terminal ligands of $[Fe_2S_2L_2]^{1-}$ were examined in more detail for a series of fission products $[Fe_2S_2Cl_{2-n}(CN)_n]^{1-}$, $[Fe_2S_2Cl_{2-n}(SEt)_n]^{1-}$ and $[Fe_2S_2(SEt)_{2-n}(CN)_n]^{1-}$ (n = 0-2) containing different terminal ligands [96]. A linear relationship with electron binding energy and substitution number (n) was observed for each of the three series, consistent with similar observations for the parent species [Fe₄S₄L₄]²⁻ [83,84]. In contrast, the binding energies for $[Fe_2S_2Cl(OAc)]^{1-}$ and $[Fe_2S_2(OAc)_2]^{1-}$ with one or two acetate ligands, respectively, were observed to decrease, in contrast with that observed for the parent cubane complexes $[Fe_4S_4Cl_{4-n}(OAc)_n]^{2-}$ [84]. These differences were attributed to the presence of reactive three-coordinate iron sites in dinuclear $[Fe_2S_2L_2]^{1-}$, which allowed the acetate ligands in $[Fe_2S_2Cl_{2-n}(OAc)_n]^{1-}$ to bind in a bidentate fashion. The presence of four coordinate iron centers in $[Fe_2S_2Cl(OAc)]^{1-}$ and $[Fe_2S_2(OAc)_2]^{1-}$ was proposed to destabilize the single Fe 3d minority spin electron relative to that in $[Fe_2S_2Cl_2]^{1-}$, thereby resulting in lower electron binding energies.

These effects were examined in more detail in a later study for the potentially bidentate ligand $L = SC_2H_4NH_2$ [97]. Sequential substitution of $L = SC_2H_4NH_2$ for -SEt in the parent cubane $[Fe_4S_4(SEt)_4]^{2-}$ resulted in a gradual increase in electron binding energies (Fig. 18a). In contrast, the binding energy of [Fe₂S₂(SEt)L]¹⁻ containing a single aminoethylthiol ligand was lower than that of $[Fe_2S_2(SEt)_2]^{1-}$, suggesting that the aminoethylthiol ligand was bound in a bindenate fashion (Fig. 18c). The binding energy for the disubstituted species $[Fe_2S_2L_2]^{1-}$ was lower still, and an additional detachment feature was observed (X', Fig. 18). These observations were rationalized by the presence of two isomers of $[Fe_2S_2L_2]^{1-}$, with the first involving two four-coordinate iron sites, and the second involving one three-coordinate and one four-coordinate site (Fig. 18c). These conclusions were also supported by DFT calculations.

4.4. Fe(I)-Fe(I) model complexes

All-iron hydrogenases catalyze the reversible activation of molecular hydrogen to protons $(H_2 \leftrightarrow 2H^+ + 2e^-)$, and involve a di-iron cluster that contains cyanide and carbon monoxide ligands, with the reduced state proposed to involve two Fe(I) centers [98–100]. The binuclear center $[(\mu-pdt)Fe_2(CO)_4(CN)_2]^{2-1}$ $(pdt^{2-} = propanedithiolate, SCH_2CH_2CH_2S)$ has been proposed as a model complex, and its electronic structure has been examined by PES (Fig. 19) [101]. The spectrum was interpreted based on valence photoelectron spectra and theoretical calculations reported previously for the neutral species $Fe_2(CO)_6(S_2)$, which is formally related to $[(\mu-pdt)Fe_2(CO)_4(CN)_2]^{2-}$ by substitution of two carbonyl ligands for cyanide and $(S_2)^{2-}$ for pdt^{2-} [102–105]. The data for $Fe_2(CO)_6(S_2)$ indicated the frontier orbitals for $[(\mu-pdt)Fe_2(CO)_4(CN)_2]^{2-}$ should occur in three major groups: the first group is comprised of the HOMO to HOMO-6 levels which are mainly Fe 3d in character; the second group is Fe-S bonding orbitals, while the



Fig. 18. Comparison of photoelectron spectra recorded at 266 nm (4.661 eV) for (a) $[Fe_4S_4(SEt)_{4-n}L_n]^{2-}$ (L = -SCH₂CH₂NH₂, n = 0–4) showing the increase in electron binding energy with increasing *n*, and (b) $[Fe_2S_2(SEt)_{2-n}L_n]^{1-}$ (L = -SCH₂CH₂NH₂, n = 0–2) showing the decrease in electron binding energy with increasing *n*, (c) structures proposed for $[Fe_2S_2(SEt)_2]^{1-}$, $[Fe_2S_2(SEt)_2]^{1-}$ and the two isomers of $[Fe_2S_2L_2]^{1-}$.

third broad group are primarily S lone-pairs and CO-based orbitals. Detachment features X, A and C were assigned to these three groups, respectively, and were also observed for Fe₂(CO)₆(S₂) previously [102]. In contrast, feature B was not observed for Fe₂(CO)₆(S₂), and was assigned to the cyanide ligands of $[(\mu$ -pdt)Fe₂(CO)₄(CN)₂]²⁻ that are not present in Fe₂(CO)₆(S₂). The spectra supported the normal level scheme in these Fe(I)–Fe(I) centers, in which all the Fe 3d orbitals lie at higher energy than the ligand-based orbitals.



Fig. 19. Structure and photoelectron spectrum of $[(\mu-pdt)Fe_2(CO)_4(CN)_2]^{2-1}$ recorded at 157 nm (7.866 eV).

5. Dithiolene centers

Transition-metal dithiolene centers have been extensively studied due to their interesting properties, complex electronic structures, and their relevance to the mononuclear molybdenum and tungsten containing enzymes [106]. A range of singly and doubly charged anions such as [MO(dithiolene)₂]^{*n*-} (M=Mo and W; *n*=1 and 2) and [M(dithiolene)₂]^{*n*-} (M=Ni, Pd and Pt; *n*=1 and 2) have been examined by PES. These studies have provided insight into the relative energies and ordering of metal-and ligand-based orbitals, of particular relevance given the well known redox "non-innocence" of dithiolene ligands [107].

5.1. Mono-oxo bis(dithiolene) centers of Mo and W

Metalloenzymes containing a single molybdenum or tungsten center at their active sites are important in the global metabolism of carbon, nitrogen and sulfur [108–110]. A common feature of these enzymes is the presence of one or two pyranopterin units coordinated to the metal center in a bidentate fashion through an ene-1,2-dithiolato moiety. The dimethyl sufoxide reductase family of enzymes contain two such units, and so models incorporate two dithiolene ligands as well as oxo and/or XR (X = O, S and Se) ligands [111].

A number of oxo-molybdenum complexes with dithiolene ligands have been investigated previously by gas-phase PES [112–115]. However, these previous studies were restricted to neutral species of sufficient volatility and thermal stability. The electrospray source on the present instrument has allowed a range of anionic $[M^VO(S_4)]^{1-}$ centers (S₄ = tetrathiolato,



Fig. 20. A variety of oxo-molybdenum anions that have been examined by PES.

bis(dithiolato), or bis(dithiolene)) to be examined [116,117], and examples are illustrated in Fig. 20. Photoelectron spectra for the singly charged anions $[MoOCl_4]^{1-}$, $[MoO(SPh)_4]^{1-}$, $[MoO(edt)_2]^{1-}$ and $[MoO(bdt)_2]^{1-}$ recorded at 157 nm are presented in Fig. 21 [116]. The first detachment feature (X) in these formally d¹ centers arises from detachment of the single Mo 4d electron in an Mo $4d_x^2$ non-bonding orbital. This was supported by comparison of $d^1 [MoO(bdt)_2]^{1-}$ with the related d^0 species $[VO(bdt)_2]^{1-}$, which exhibited a very similar spectrum, except for the absence of this first feature (Fig. 21e). The separation between features X and A for [MoOCl₄]¹⁻, [MoO(SPh)₄]¹⁻, $[MoO(edt)_2]^{1-}$ and $[MoO(bdt)_2]^{1-}$ corresponds to the energetic separation between the HOMO and HOMO-1 levels of the parent species, and was larger for the monodentate ligands (~1.3 eV for Cl and ~0.8 eV for SPh) than for the bidentate ligands ($\sim 0.5 \text{ eV}$ for edt and $\sim 0.4 \text{ eV}$ for bdt). These changes were attributed to changes in the O-Mo-S-C dihedral angle (e.g., $[MoO(SPh)_4]^{1-}$, ~60° cf. $[MoO(bdt)_2]^{1-}$, ~90°), with the larger dihedral angle resulting in destabilization of the frontier ligand-based orbitals relative to Mo $d_{x^2-y^2}$.

The doubly charged anions $[MO(mnt)_2]^{2-}$ (M = Mo and W; mnt = 1,2-dicyanoethenedithiolato) were examined in a later study, with the electron-withdrawing cyanide substituents chosen to ensure the parent species $[MO(mnt)_2]^{2-}$ were stable gas-phase dianions [117]. The first detachment feature occurred at ~0.2 eV lower binding energy for $[WO(mnt)_2]^{2-}$ relative to $[MoO(mnt)_2]^{2-}$, consistent with the HOMO being M d_{x²-y²} and tungsten being more easily oxidized than molybdenum. In contrast, the second detachment feature A occurred at very similar binding energy for both species, consistent with it arising from the highest energy ligand-based orbital with little metal contribution. The separation between features X and higher binding energy features provided estimates of the ligand–metal charge transfer energies in product $[MO(mnt)_2]^{1-}$ centers.

5.2. Bis(dithiolene) centers of Ni, Pd and Pt

Nickel bis(dithiolene) complexes have been extensively studied because of their unusual electronic structures and their interesting redox, magnetic, optical and conducting properties [106,118–120]. Early studies identified the existence



Fig. 21. Photoelectron spectra recorded at 157 nm (7.866 eV) of (a) $[MoOCl_4]^{1-}$, (b) $[MoO(SPh)_4]^{1-}$, (c) $[MoO(edt)_2]^{1-}$, (d) $[MoO(bdt)_2]^{1-}$, and (e) $[VO(bdt)_2]^{1-}$. Note the reduced separation between features X and A from (a) to (d), and the absence of feature X for $[VO(bdt)_2]^{1-}$.



Fig. 22. Schematic energy level diagrams indicating the relationship between the photodetachment transitions and excited states of $[Ni(mnt)_2]^{2-/1-/0}$. (a) The ground state of $[Ni(mnt)_2]^{2-}$ (X') and the ground (X) and excited (A–C) states of $[Ni(mnt)_2]^{1-}$. The intense ${}^2B_{2g} \rightarrow {}^2B_{1u}$ optical transition observed for $[Ni(mnt)_2]^{1-}$ in solution is shown; (b) the ground state of $[Ni(mnt)_2]^{1-}$ (X') and the lowest energy singlet (X) and triplet (A) states of $[Ni(mnt)_2]$. The singlet–triplet splitting of $[Ni(mnt)_2]$ is shown.

of the reversible three-member one-electron transfer series $[\operatorname{Ni}(S_2C_2R_2)_2]^{2-} \leftrightarrow [\operatorname{Ni}(S_2C_2R_2)_2]^{1-} \leftrightarrow [\operatorname{Ni}(S_2C_2R_2)_2]$ in which each member maintains a square-planar geometry. The anions $[M(mnt)_2]^{n-}$ (M = Ni, Pd and Pt; mnt = 1,2-S₂C₂(CN)₂; n = 1, 2) have been examined by PES, providing direct information about the MO energy levels and ground and excited states of each member of the electron transfer series $[M(mnt)_2]^{2-1/-1/0}$ (M = Ni, Pd and Pt) [121]. The first detachment feature for $[Ni(mnt)_2]^{2-}$ was assigned to a detachment from a ligand-based orbital, while the next two features were assigned to metalbased orbitals. Equivalent features were also identified for $[Pd(mnt)_2]^{2-}$ and $[Pt(mnt)_2]^{2-}$, and those arising from metalbased orbitals were shifted to higher binding energy (stabilized) for the heavier congeners, while those from ligand-based orbitals occurred at similar energy for each species, independent of the metal center. The separation between detachment features for [Ni(mnt)₂]²⁻ provided insights into the relative energies of excited states of $[Ni(mnt)_2]^{1-}$, and the energetics of ligand-ligand and metal-ligand charge transfer transitions for $[M(mnt)_2]^{1-}$ (Fig. 22). In particular, detachment transitions to ${}^{2}B_{2g}$ and ${}^{2}B_{1u}$ states of product $[M(mnt)_{2}]^{1-}$ were observed for each of $[M(mnt)_2]^{2-}$, and the energetic separation between these features was equivalent to the energy of the intense ${}^{2}B_{2g} \rightarrow {}^{2}B_{1u}$ optical transition observed in solution phase experiments (Fig. 22). The singly charged anions $[M(mnt)_2]^{1-}$ were also investigated, with detachment from these doublet anions giving rise to singlet and triplet states of neutral [M(mnt)₂]. The first two detachment features for each of $[M(mnt)_2]^{1-1}$ were assigned to the lowest energy singlet and triplet states of neutral $[M(mnt)_2]$, respectively, providing experimental estimates for the singlet-triplet splittings in neutral $[M(mnt)_2]$ (Fig. 22).

6. Overview and conclusions

The present account presents an overview of recent experiments from the author's laboratory on the application of electrospray ionisation-photodetachment photoelectron spectroscopy for the study of a range of negatively charged inorganic and coordination complexes. The experiments provide detailed information about the electronic structure of these species, and important experimental data for comparison with theoretical calculations.

A number of transition-metal halide complexes have been examined, including square-planar MX_4^{2-} , octahedral MX_6^{2-} , and metal-metal bonded $Re_2Cl_8^{2-}$. Experiments typically involved comparison between similar species, but with systematic variation of the halide ligands and the metal center, allowing for detachment features due to metal- or ligand-based orbitals to be identified. The experimental data provides direct insights into the MO energy levels of the parent species, and is ideal for direct comparison with energy level schemes from ligand field theory and theoretical calculations.

A variety of mononuclear and polynuclear iron–sulfur species related to important biological sites have been examined, ranging from mononuclear [1Fe] centers to the [4Fe–4S] cubane unit. The experiments provided direct support for the inverted level scheme proposed for these centers, in which the Fe 3d majority spin electrons are significantly stabilized relative to their minority spin counterparts. In particular, the observation of a very weak detachment feature for each of the ferrous centers was consistent with the HOMO in each case being an Fe 3d-based minority spin electron. Variation of the terminal ligands L in $[Fe_2S_2L_2]^{1-}$ and $[Fe_4S_4L_4]^{2-}$ provided direct insight into their effect on redox properties.

A range of transition-metal bis(dithiolene) centers have been examined. The studies provided insight into the relative energies and ordering of metal- and ligand-based orbitals, of particular relevance given the redox non-innocence of dithiolene ligands. Experiments have been carried out on oxomolybdenum bis(dithiolene) centers such as $[MoO(bdt)_2]^{1-}$ and $[MoO(mnt)_2]^{2-}$ that are model systems for the active sites of DMSO reductase, as well as the nickel-group bis(dithiolene) centers $[M(mnt)_2]^{2-}$ (M = Ni, Pd and Pt) that are of interest due to their complex electronic structures and redox chemistry. The coupling of an electrospray ionization source to a photoelectron spectrometer has allowed a number of negatively charged inorganic complexes to be studied by PES for the first time. The experimental data from PES experiments provides direct insight into the molecular orbital energy levels of the parent species, and is ideally suited for comparison with theoretical calculations. The ESI-PES technique shows great promise as a general tool to investigate in the gas-phase the electronic structures of anionic solution phase transition-metal complexes.

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