Probing the Electronic Structure and Metal−Metal Bond of $Re_2Cl_8^{2-}$ in the Gas Phase

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Abstract: $Re_2Cl_8^{2-}$, the classical metal complex with a metal−metal multiple bond, was observed in the gas phase for the first time using electrospray. Photodetachment photoelectron spectroscopy (PES) was used to probe its electronic structure, metal−metal bonding, and gas-phase molecular properties. The PES spectra provide a unique and direct picture about the occupied molecular orbitals (MOs) of $Re_2Cl_8^{2-}$. Detachments from the metal−metal and metal−ligand bonding MOs were clearly observed and distinguished. We found that the metal−metal bonding MOs from the d orbitals (δ, π, and σ) have low electron binding energies and yielded three well-resolved detachment bands. The metal−ligand or pure ligand MOs all have higher binding energies and give congested PES features. The ground state of $Re_2Cl_8^{2-}$ with a configuration of $\cdots\sigma^2\pi^4\delta^2$ and a formal quadruple Re−Re bond is unequivocally confirmed. The PES spectra yielded a 1.00 eV adiabatic binding energy for the second excess electron in the doubly charged anion. The magnitude of the intramolecular Coulomb repulsion was estimated to be ~2.3 eV using photon-energy-dependent PES spectra. Despite its electronic stability, $Re_2Cl_8^{2-}$ was found to be metastable against the loss of a Cl^- in the gas phase, suggesting that the Re−Cl bond strength is less than 2.3 eV.

Introduction

The first discovery[1] of the quadruple metal−metal bond in $Re_2Cl_8^{2-}$ has stimulated intensive research activities, creating a major branch of modern inorganic chemistry.[2] The formation of metal−metal multiple bonds has become recognized as one of the most distinctive features in the chemistry of lower oxidation state transition metals.[2−4] Understanding the nature of the metal−metal multiple bond and metal−metal interactions is not only important for unraveling the new chemistry of these metal complexes but also important to other areas of research, such as catalysis, clusters, materials, and surface sciences. As a classical example of metal−metal multiple bonding, $Re_2Cl_8^{2-}$ has drawn particular interest and has been extensively investigated both experimentally[2,5−9] and theoretically.[10−13] The basic features of the quadruple bond in $Re_2Cl_8^{2-}$, $\sigma_d^2\pi_d^4\delta_d^2$, were qualitatively understood immediately after the initial discovery.[10] All further theoretical calculations and spectroscopic studies are consistent with this bonding picture, although their relative ordering is still not completely resolved.[10−13]

It is generally recognized that photoelectron spectroscopy (PES) is a powerful experimental technique to provide direct molecular electronic structure information. Unlike electronic absorption spectroscopy which involves electronic transitions between occupied and unoccupied molecular orbitals (MOs), PES involves only removing electrons from occupied MOs and provides a direct picture of the ground-state electronic configuration in the Koopmans' approximation. Indeed, PES has been applied to a number of neutral metal complexes containing metal−metal multiple bonds, and has proven to be particularly important in testing and verifying the ground-state electronic configurations of those complexes.[14−19] Surprisingly, there have

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been no PES data available for the classical metal complex, $Re_2Cl_8^{2-}$, largely due to experimental difficulties in producing this dianion or the relevant neutral molecules in the gas phase. Considering the importance of $Re_2Cl_8^{2-}$ in the development of the concept of the metal−metal multiple bond, it would be desirable to directly probe its electronic structure using PES. Such data would allow for a complete understanding and confirmation of its ground-state electronic configuration and the nature of its quadruple bond.

We have developed an experimental technique that allows PES experiments to be performed on gaseous multiply charged anions produced by an electrospray ion source.[20] This apparatus is ideal to investigate multiply charged metal complexes and provide molecular electronic structure information. Using this technique, we have recently obtained PES data on a series of gaseous octahedral and square-planar metal complexes.[21,22] In this paper, we report the first observation of gaseous $Re_2Cl_8^{2-}$ and its PES spectra at five different laser photon energies. We show that $Re_2Cl_8^{2-}$ is electronically stable as a free dianion with a 1.00 eV binding energy for the second excess electron. Numerous PES features are observed due to removing electrons from MOs responsible for the quadruple bond and those mainly of metal−ligand character. Three well separated bands at lower binding energies are clearly identified corresponding to the metal−metal bonding MOs, δ, π, σ, respectively. Stronger and higher binding energy features are observed which are due to ionization of predominantly metal−ligand MOs. Thus we have confirmed unequivocally the ground-state configuration of $Re_2Cl_8^{2-}$ as $\cdots\sigma^2\pi^4\delta^2$. We have also obtained information about the intramolecular Coulomb repulsion in $Re_2Cl_8^{2-}$, estimating that the net Coulomb repulsion within the doubly charged anion is ~2.3 eV. We find that $Re_2Cl_8^{2-}$ is thermodynamically unstable against loss of a Cl^-, despite its large electronic stability.

Experimental Section

The experimental apparatus, which is equipped with a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer, an electrospray ion source, and ion-trap mass spectrometer, has been described in detail elsewhere.[20] Only a brief description is given here. A 10^{-3} M tetrabutylammonium octachlorodirhenate(III) [$(Bu_4N)_2Re_2Cl_8$, Bu = $CH_3(CH_2)_3$, Aldrich] solution in a pure CH_3CN solvent was sprayed. The resulting ions after desolvation were guided by a radio frequency-only quadrupole device into a quadrupole ion-trap. The ions were accumulated for 0.1 s in the trap before being pulsed out for mass and charge analyses using a TOF mass spectrometer. The main anion signals were $Re_2Cl_8^{2-}$, which was then mass-gated and decelerated before being detached by a laser beam in the interaction zone of the magnetic-bottle PES spectrometer. The photoemitted electrons were collected with nearly 100% efficiency by the magnetic bottle and analyzed in a 4-m long electron flight tube. Photoelectron TOF spectra were collected and then converted to kinetic energy spectra, calibrated by the known spectra of I^- and O^-. The electron binding energy (BE) spectra presented were obtained by subtracting the kinetic energy spectra from the detachment photon energies. Both an excimer laser (157 and 193 nm) and a Nd:YAG laser (266, 355, 532 nm) were used for photodetachment in the current study. All experiments were done at 20 Hz with the ion beam off at alternating laser shots for background subtraction, which is essential for high detachment photon energies, namely, 266, 193, and 157 nm. The electron kinetic energy resolution was $\Delta E/E \approx 2\%$, i.e., 20 meV for 1 eV electrons.

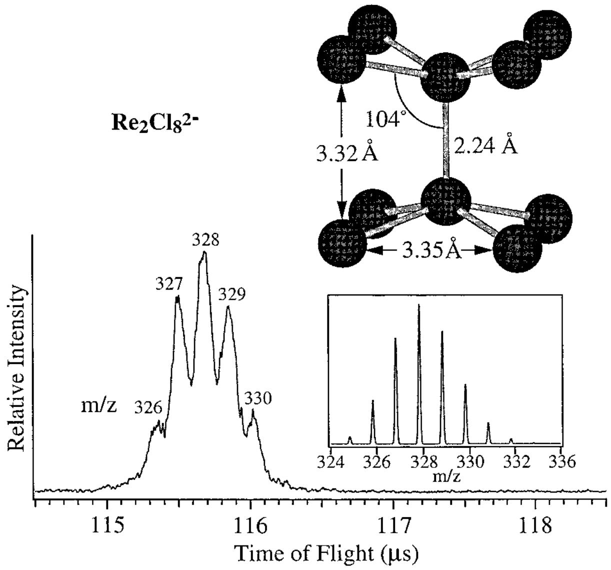

Figure 1. A time-of-flight mass spectrum of $Re_2Cl_8^{2-}$ produced using an electrospray ion source. The mass/charge ratios (m/z) for the different isotopic peaks are labeled. The inset shows a theoretical isotopic pattern for $Re_2Cl_8^{2-}$. The structure and structural parameters of $Re_2Cl_8^{2-}$ as determined from crystals are also shown.

Results

Figure 1 shows a TOF mass spectrum of $Re_2Cl_8^{2-}$ with its characteristic isotope pattern, compared to the theoretical isotopic distribution (inset). Because both Cl (76% ^{35}Cl, 24% ^{37}Cl) and Re (37% ^{185}Re, 63% ^{187}Re) have isotopes with two Dalton mass difference, one expects a difference of one in the mass-to-charge (m/z) isotopic distribution in the doubly charged anions, as observed in Figure 1. The structural parameters of $Re_2Cl_8^{2-}$ as determined in the crystal[2,3] are also shown in Figure 1. It has D_{4h} symmetry with a very short Re−Re bond (2.24 Å) indeed. The gas-phase structural parameters may alter slightly from the crystal structure due to the absence of the counterion and solvent and the anticipated intramolecular Coulomb repulsion.

Figure 2 shows the PES spectra of $Re_2Cl_8^{2-}$ taken at four different detachment photon energies. The 157-nm spectrum (Figure 2a) gives eight distinctly resolved features, as labeled by letters X and A−G. The first three bands (X, A, B), with similar and weaker intensities, are well separated, followed by two closely spaced groups of bands, (C, D, and E), and (F and G). There seem to be more features beyond band G, which are cut off due to the repulsive Coulomb barrier as will be discussed below. At 193 nm (Figure 2b), the F and G bands disappear completely and the intensities of the D and E bands decrease. There seem to be fine features discernible for the broader C band, but not well-resolved. At 266 nm (Figure 2c), the C, D, and E bands all disappear, and only a tail of the B band is observed. The A band is broader than the X and B bands, and there seem to be fine features resolved in the A band in the 266-nm spectrum. The two sharp peaks observed around 3.6 eV in the 266-nm spectrum are due to Cl^- as a result of photodissociation ($Re_2Cl_8^{2-} + h\upsilon \rightarrow Re_2Cl_7^- + Cl^-$) and subsequent photodetachment of Cl^- ($Cl^- + h\upsilon \rightarrow Cl + e^-$) at 266 nm. This two-photon process was also observed in our previous study of the octahedral metal complexes at 266 nm.[21] At 355 nm (Figure 2d), only the ground-state feature X was observed.

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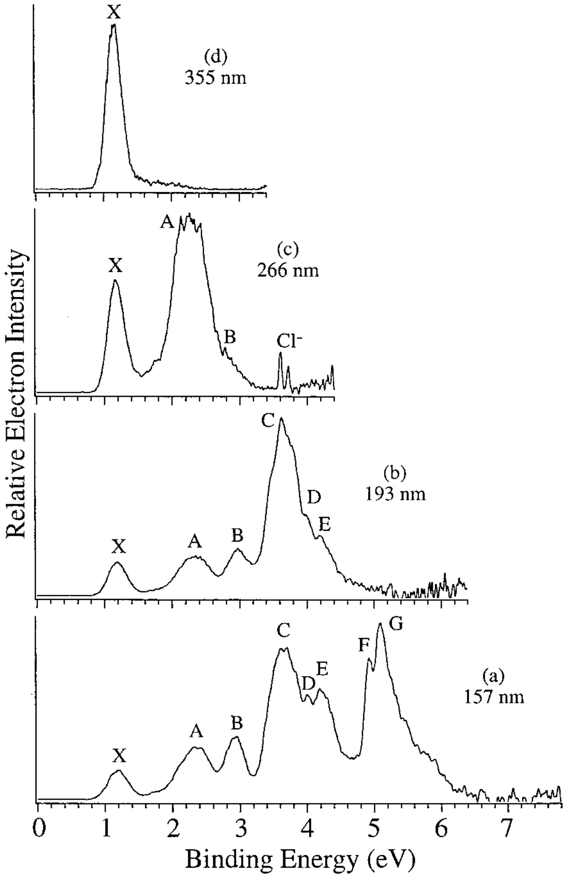

Figure 2. Photoelectron spectra of $Re_2Cl_8^{2-}$ at (a) 157 nm (7.866 eV), (b) 193 nm (6.424 eV), (c) 266 nm (4.661 eV), and (d) 355 nm (3.496 eV).

Table 1. Vertical Detachment Energies (eV)[a] Observed for $Re_2Cl_8^{2-}$

X	A	B	C	D	E	F	G
1.16(5)	2.32(10)	2.96(6)	3.63(6)	4.01(5)	4.20(5)	4.92(6)	5.09(6)

[a] See Figure 2 for the labels. Numbers in the parentheses are uncertainties for the last digit.

We also tried to measure the spectrum at 532 nm, but observed almost no photoelectron signals, despite the fact that the 532-nm photon energy is higher than the binding energy of the X band.

From the threshold of the X band, we obtained an adiabatic binding energy (ADE) for the second electron in $Re_2Cl_8^{2-}$ as 1.00 (0.05) eV, which is equivalent to the second electron affinity of Re_2Cl_8. The vertical binding energy (VDE) of the X band is measured to be 1.16 eV. The VDEs of all the observed features are given in Table 1. As we will discuss below, the photon-energy-dependent PES spectra of Figure 2 and the sequential disappearance of the high binding energy features at lower photon energies are characteristics of photodetachment of multiply charged anions and confirm the doubly charged nature of $Re_2Cl_8^{2-}$.

Discussions

A. Photon Energy Dependence of PES Features and the Repulsive Coulomb Barrier in $Re_2Cl_8^{2-}$. Unlike photodetachment of singly charged species, photodetachment of multiply charged anions produces an outgoing electron and another anion with one less charge than the parent anion. The superposition of the long-range Coulomb repulsion between the two negatively charged photoproducts and the short-range electron binding creates a repulsive Coulomb barrier (RCB) against electron detachment.[23] As we have shown previously,[21,22,24−27] the RCB prevents electron detachment even when the photon energy is higher than the electron binding energies, but lower than the RCB. In this case, photoelectron signals can only be observed through electron tunneling and are usually very weak and depend on how far the photon energy is from the RCB top. Figure 3 illustrates schematically the potential-energy curves and the RCBs for photodetachment of $Re_2Cl_8^{2-}$, leading to the different final states of the $Re_2Cl_8^{-}$ singly charged anion (VDEs are given in the parentheses). The positions of the five photon energies used are shown relative to the ground state of the dianion.

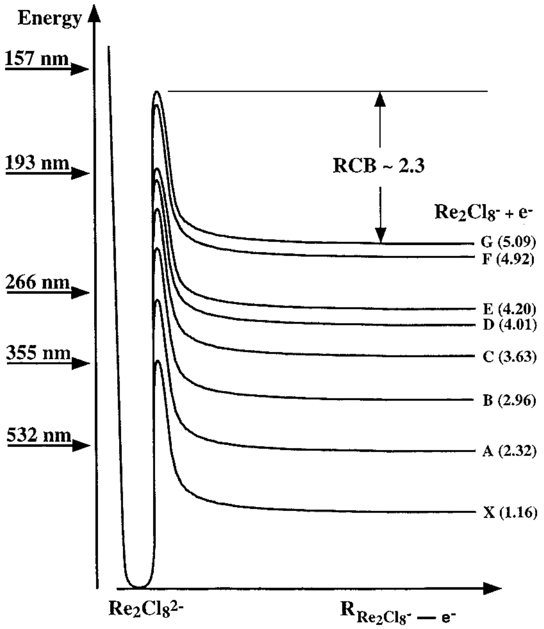

Figure 3. Schematic drawing of potential energy curves showing the repulsive Coulomb barriers (RCB) of the $Re_2Cl_8^{2-}$ dianion with respect to different final states of the singly charged anion $Re_2Cl_8^{-}$. The vertical binding energies (see Figure 2 and Table 1) and the estimated RCB are shown in eV. The relative positions of the five photon energies used are also indicated.

Each final state of the singly charged anion has its own RCB. If we assume that the RCB is similar for the different final states, the magnitude of the RCB can be estimated from the photon-energy-dependent PES spectral features, that is, based on the appearance or disappearance of the high binding energy features at different photon energies. The strong signal of the G band (VDE = 5.09 eV) at 157 nm suggests that the RCB for the G state must be smaller than ~2.77 eV (photon energy − VDE, i.e., 7.866 eV − 5.09 eV). The strong signals of feature C (VDE = 3.63 eV) in the 193-nm spectrum indicate that the RCB should be smaller than 2.79 eV (6.424 eV − 3.63 eV), consistent with the above estimate. On the other hand, the very weak signals of feature D (VDE = 4.01 eV) and feature E (VDE =

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4.20 eV) in the 193-nm spectrum show that the RCB should be around 2.4 eV (6.424 − 4.01 eV) and larger than 2.2 eV (6.424 − 4.20 eV). Therefore we estimate that the RCB should be ∼2.3 eV, assuming that the magnitude of the RCB is the same for the different states. This RCB is consistent with the cutoff of the 266-nm spectrum. The X band observed in the 355-nm spectrum is slightly shifted to the low binding energy side, that is, the high binding energy side was affected by the RCB, suggesting that the 355-nm photon energy (3.496 eV) is right near the top of the RCB for the X state.[26] This observation is also consistent with the derived RCB value of ∼2.3 eV. Thus, it is easy to understand that no direct detachment is expected to occur at 532 nm, even though this photon energy is higher than the binding energy of the X state. The very weak signals that we did observe at 532 nm (not shown in Figure 2) must be due to electron tunneling.[26] The tunneling probability is expected to be very small because the 532-nm photon is still quite far from the top of the RCB (in Figure 3), consistent with our observation.

We have shown previously[24] that the RCB is equal in magnitude to the intramolecular Coulomb repulsion among the excess charges in a multiply charged anion. For a dianion, the intramolecular Coulomb repulsion can be estimated simply according to Coulomb's law, $e^2/4\pi\epsilon_0 r$, or, $14.4/r$ in eV, where r is the effective distance between the two excess charges in Å. The structural parameters of $Re_2Cl_8^{2-}$ as determined in the crystal are shown in Figure 1. The two excess charges in $Re_2Cl_8^{2-}$ are presumably distributed over the eight symmetry-equivalent Cl atoms on average and their locations are difficult to pin down. However, if we use the maximum Cl−Cl separation (5.8 Å, the diagonal of the cube formed by the eight Cl), we obtain a Coulomb repulsion energy of ∼2.5 eV, which is quite close to our experimentally determined value of ∼2.3 eV. This observation suggests that the structure of $Re_2Cl_8^{2-}$ in the gas phase probably does not change very much from that in crystals.

B. Intramolecular Coulomb Repulsion and Stability of Gaseous $Re_2Cl_8^{2-}$. The strong intramolecular Coulomb repulsion makes multiply charged anions rather unstable in the gas phase. There are two types of stability for a multiply charged anion,[23,28,29] (1) electronic stability relative to electron detachment, and (2) thermodynamic stability relative to fragmentation. Similar to the RCB for electron detachment, there is also a potential barrier for fragmentation of a multiply charged anion. Both types of barriers provide dynamic stability for multiply charged anions. As we have seen above, $Re_2Cl_8^{2-}$ is electronically stable with an ADE of 1.00 eV. However, we found that $Re_2Cl_8^{2-}$ is still metastable. Using our ion-trap with different trapping times, we estimated that $Re_2Cl_8^{2-}$ has a half-life of ∼150 s. This result suggests that $Re_2Cl_8^{2-}$ must be thermodynamically unstable relative to fragmentation.

There are two possible decay channels for $Re_2Cl_8^{2-}$: (1) $Re_2Cl_8^{2-} \rightarrow ReCl_4^- + ReCl_4^-$, or (2) $Re_2Cl_8^{2-} \rightarrow Re_2Cl_7^- + Cl^-$. The Re−Re bond energy in the condensed phase has been estimated experimentally and theoretically. The most recent experiment[30] and calculation[31] indicate that the Re−Re bond energy is ∼100 kcal/mol (4.3 eV), which is much larger than the 2.3 eV intramolecular Coulomb repulsion. Thus, $Re_2Cl_8^{2-}$ is expected to be stable relative to fragmentation channel (1). Therefore, $Re_2Cl_8^{2-}$ must be unstable against loss of a Cl^-. The Re−Cl bond strength is not known. Our result suggests that the Re−Cl bond strength should be less than 2.3 eV, the intramolecular Coulomb repulsion. It would be interesting to directly measure the bond energies in the gas phase using either photodissociation or collision-induced dissociation.

C. The Re−Re Quadruple Bond and Assignments of the PES Spectra. The formal oxidation state of Re in $Re_2Cl_8^{2-}$ is III, with a d^4 configuration. A simple MO picture[10,12] can qualitatively explain the nature of the quadruple bond in $Re_2Cl_8^{2-}$. Taking the Re−Re bond as z axis and the Re−Cl bond axes as $\pm x$ and $\pm y$, one finds three different overlaps of the d orbitals of the two Re atoms, creating one σ bond ($d_{z^2} - d_{z^2}$), two π bonds ($d_{xz} - d_{xz}$, $d_{yz} - d_{yz}$) and two δ bonds ($d_{xy} - d_{xy}$, $d_{x^2-y^2} - d_{x^2-y^2}$). One of the δ bonds ($d_{x^2-y^2} - d_{x^2-y^2}$) will interact with the ligands to form metal−ligand σ bonding and no longer contributes to the metal−metal bonding. Therefore the Re−Re metal bonding can be simply written as $\sigma^2\pi^4\delta^2$, with a formal bond order of four. A simple extended Hückel MO calculation[10] indicated that all the three metal−metal MOs (σ, π, δ) lie above the metal−ligand MOs. Later, two SCF-Xα-SW calculations by Gray and co-workers[11] and by Cotton[12] (including relativistic effects) suggested that the Re−Re σ bond lies at a deeper energy than several metal−ligand MOs, although the first two highest occupied MOs were still the π and δ metal−metal bonds. At the same time, Hay[13] performed a comprehensive theoretical study of the electronic states of $Re_2Cl_8^{2-}$ using relativistic generalized valence-bond calculations. On the basis of the calculated transition energies from different occupied orbitals to the lowest unoccupied MO (δ^*), it was suggested that the first three highest occupied MOs were the metal−metal bonds (σ, π, δ). Both the calculations by Cotton and Hay gave an improved agreement between the observed and calculated electronic absorption transitions. However, no absorption transitions from the metal−metal σ bond to any empty MOs were available to compare to the calculated values. Thus, the position of the σ metal−metal MO level relative to the metal−ligand bond level has not been resolved.

Our observed PES features (Figure 2) can be viewed as removing electrons from the occupied MOs of $Re_2Cl_8^{2-}$ (Koopmans' theorem). The ground state of $Re_2Cl_8^{2-}$ is closed-shell and the final states of the singly charged anion should all be doublet states. If relaxation is not significant, the features revealed in the PES spectra provide a direct map of the occupied MO energy levels of $Re_2Cl_8^{2-}$. On the basis of the above discussion, the first two features (X and A) observed in our PES spectra should be assigned to detaching one electron from the δ and π MOs, respectively. The final states of X and A should be $^2B_{2g}$ (δ^{-1}) and ^2E_u (π^{-1}) in D_{4h} symmetry. The degenerate doublet state, ^2E_u, is expected to split further either due to Jahn−Teller or spin−orbit effects.[32] The much broader width of the A band is thus consistent with the removal of a π electron. The 266-nm spectrum (Figure 2c) even revealed some fine structures in the A band, probably due to Jahn−Teller or spin−orbit effects.

The feature B has a similar intensity and width as that of feature X, indicating that the feature B is due to removing a metal d-electron from a nondegenerate MO. Hence the B feature is assigned as a result of detaching one electron from the metal−metal σ MO, giving a $^2A_{1g}$ final state. Our previous PES study[21]

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of $ReCl_6^{2-}$ and PES studies of other complexes involving metal−metal bonds[14−19] showed that features due to removing d-electrons have similar intensities, which are usually weaker compared to features derived from ionizing electrons from ligand-based MOs. In particular, our assignments of the first three features to the metal−metal bonds are consistent with those for $W_2(O_2CCH_3)_4$,[15] which is isoelectronic with $Re_2Cl_8^{2-}$ in terms of the metal−metal bonds, thus lending considerable support to the current assignments.

The rest of the features C to G should be due to ionizations from deeper MOs mainly of metal−ligand or pure ligand character. These features are rather congested. In particular, the C band may contain several unresolved features. The F and G bands seem to be rather sharp, suggesting that they may be due to ionization of Cl lone-pairs. Detailed assignments of these higher energy features are not possible at the moment. We simply summarize our assignments and the MO energy levels for $Re_2Cl_8^{2-}$ in Figure 4, which also illustrates the relationship between PES features and the occupied MOs.

Conclusions

We have observed in the gas phase the isolated $Re_2Cl_8^{2-}$ doubly charged anion and obtained its photoelectron spectra at four detachment photon energies. We found $Re_2Cl_8^{2-}$ to be electronically stable with a 1.00 eV adiabatic electron detachment energy. The photon-energy-dependent photoelectron spectra clearly revealed the dianion nature of the species and allowed the repulsive Coulomb barrier (~2.3 eV) to be estimated. In addition, we found that $Re_2Cl_8^{2-}$ is unstable in the gas phase against loss of a Cl^-, suggesting that the Re−Cl bond strength is less than 2.3 eV. Well-resolved detachment features were obtained in the PES spectra of $Re_2Cl_8^{2-}$, yielding a wealth of electronic structure information about both the dianions and the singly charged species. Detachment from metal−metal MOs or ligand-derived MOs was observed and could be clearly distinguished. The first three features (X, A, and B) at low binding energies are due to removing one d-electron from the Re−Re multiple bond (δ, π, and σ), respectively, whereas those from the metal−ligand MOs or pure ligand MOs all take place at higher binding energies. The current work for the first time clearly shows that the three highest occupied MOs in $Re_2Cl_8^{2-}$ are all of metal−metal bonding nature and confirmed the ordering of the metal−metal MOs, $\delta > \pi > \sigma$, with a $\cdots\sigma^2\pi^4\delta^2$ ground-state configuration.

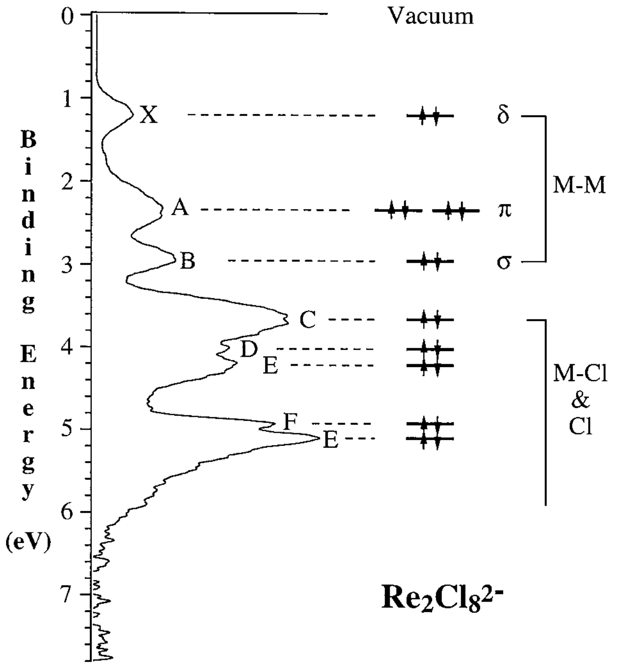

Figure 4. The 157-nm photoelectron spectrum of $Re_2Cl_8^{2-}$ with the corresponding molecular orbitals, showing the relationship between photoelectron features and the occupied molecular orbitals.

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