On the electronic structure and conflicting d-orbital aromaticity in the Re$_3$O$_3^-$ cluster†

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Received 16th September 2011, Accepted 10th January 2012
DOI: 10.1039/c2ra00753c

The structure and chemical bonding in the Re$_3$O$_3^-$ cluster are investigated using photoelectron spectroscopy and density-functional theory calculations. Vibrationally-resolved photoelectron spectra were obtained, yielding an accurate electron affinity (2.54 ± 0.02 eV) and a ground-state Re=O stretching frequency (960 ± 30 cm$^{-1}$) for the Re$_2$O$_3$ neutral cluster. It is shown that the Re$_2$O$_3^-$ cluster possesses a $C_{2v}$ ($^4A_1$) ground-state structure consisting of a Re$_3$ triangle with one bridging and two terminal oxygens. Molecular orbital analysis reveals that the Re$_3$ core in Re$_2$O$_3^-$ possesses conflicting d-orbital aromaticity (π-antiaromatic and σ-aromatic), consistent with its $C_{2v}$ symmetry. Well-resolved photodetachment transitions from the Re 5d$^2$ δ orbitals allow the bond strength and resonance energy of a delocalized δ-bond to be estimated.

There has recently been increasing interest in free transition-metal oxide clusters, primarily aiming for a molecular-level understanding of oxide catalysts using well-defined and controllable model systems. Characterization of the structures and electronic properties of oxide clusters is a prerequisite to assess their suitability as models for catalytic active centers. Photoelectron spectroscopy (PES), among other gas-phase experimental techniques including infrared multiple photon dissociation (IR-MPD) spectroscopy, has emerged as a powerful tool to probe the intrinsic geometric and electronic properties of oxide clusters. Furthermore, the oxidation states of the metal centers in oxide clusters can be tuned by controlling the composition, providing opportunities to explore novel chemical bonding in transition-metal-containing systems. For example, d-orbital aromaticity and δ-aromaticity owing to multicenter d–d bonding have been discovered recently in transition metal oxide clusters. In the current communication, we report vibrationally resolved PES spectra for the Re$_2$O$_3^-$ cluster. Combined PES and density-functional theory (DFT) calculations show that the Re$_2$O$_3^-$ cluster adopts a $C_{2v}$ ($^4A_1$) global minimum with one bridging and two terminal oxygens. Molecular orbital analysis reveals conflicting d-orbital aromaticity (σ-aromatic and π-antiaromatic) for this cluster, consistent with the $C_{2v}$ structural distortion of the Re$_3$ core. The PES spectra also allow us to evaluate the strength and resonance energy of the delocalized Re 5d$^2$ δ-bond on the basis of well-resolved detachment transitions from the δ orbitals.

The Re$_2$O$_3^-$ clusters were produced in a laser vaporization supersonic cluster source and mass-selected for the photodetachment PES experiment (see the Experimental Section). The PES spectra at 193 nm (6.424 eV) and 355 nm (3.496 eV) photon energies are shown in Fig. 1. The ground-state band X is well-resolved at 355 nm with a short vibrational progression (960 ± 30 cm$^{-1}$). The 0–0 transition yields an accurate value for the electron affinity of the Re$_2$O$_3$ neutral.

Fig. 1 Photoelectron spectra of Re$_2$O$_3^-$ at (a) 355 nm (3.496 eV) and (b) 193 nm (6.424 eV). The vertical lines in (a) represent the resolved vibrational structures.
cluster as 2.54 ± 0.02 eV (Table 1), which also defines the first adiabatic (ADE) and vertical detachment energy (VDE) for the Re$_3$O$_5^-$ anion cluster. The 355 nm spectrum also reveals a relatively weak and sharp band A at 3.04 eV, which defines the first excited state of Re$_3$O$_5$. The sharp peak is followed by a broad weak feature, which will be shown below to be due to shake-up transitions. Band A displays a strong dependence on photon energies and its relative intensity is greatly enhanced at 193 nm (Fig. 1b). The weak band B at a VDE of 3.43 eV is better defined at 193 nm. Numerous broad bands are revealed at higher binding energies. Band C (VDE: 4.34 eV) has an estimated ADE of 3.95 eV. The spectrum is essentially continuous beyond 4.6 eV, and bands D (~4.8–5.2 eV) and E (~5.7 eV) are tentatively labeled for the sake of discussion.

Structural searches were conducted at the B3LYP level of theory (see the Computational Methods section). Candidate structures for Re$_3$O$_5^-$ and Re$_3$O$_3$ with a wide variety of initial geometries and different spin multiplicities are considered and all the optimized structures are summarized in the ESI (Figs. S1 and S2). The global minima of Re$_3$O$_5^-$ and Re$_3$O$_3$ and selected low-lying structures (within ~0.5 eV) are shown in Fig. 2. The global minimum of Re$_3$O$_5^-$ is a C$_3v$ ($^{1}A_1$) structure (Fig. 2a), in which the Re$_3$ trimer is coordinated with one bridging and two terminal O atoms. The bridging O exhibits typical single Re–O bond distances (1.920 Å), while the terminal O atoms give Re=O double bonds (1.728 Å). The Re atom that is not bonded with O gives two very short Re–Re distances (2.309 Å), the third Re–Re bond is elongated (2.808 Å). The low-lying anion structures (Fig. 2b and 2c) show similar atomic connectivities and bond distances, but possess lower symmetry relative to the global minimum. Alternative anion structures (Fig. S1, ESI†) are at least ~0.5 eV higher in energy. In particular, the highly symmetric tri-terminal $D_{3h}$ ($^{3}A_1$) and tri-bridged $D_{3h}$ ($^{1}A_1$) anion structures are 3.06 and 5.36 eV above the global minimum, respectively. The Re$_3$O$_3$ neutral cluster possesses a C$_9$ ($^{2}A_1$) global minimum (Fig. 2d), which closely resembles that of the anion (Fig. 2a). Three low-lying quartet C$_9$ or C$_{2v}$ neutral structures are within ~0.5 eV (Fig. 2e–2g). Additional neutral structures turn out to be at least ~0.8 eV above the global minimum (Fig. S2, ESI†). To ensure the reliability of the energetics of the B3LYP calculations, the relative energies for the low-lying structures of Re$_3$O$_5^-$ were further evaluated via coupled cluster [CCSD(T)] single-point calculations at the B3LYP geometries. As shown in Table 2 the B3LYP and CCSD(T) results are coherent, firmly showing that the C$_9$ ($^{2}A_1$) structure is the global minimum for the Re$_3$O$_5^-$ anion cluster.

To facilitate comparison with the experiment, we have simulated the PES spectra of Re$_3$O$_5^-$ on the basis of the C$_9$ global minimum (Fig. 2a), the low-lying C$_9$ structures (Fig. 2b and 2c), and selected $D_{3h}$ structures (Figs. S3 and S4, ESI†). The highly-symmetric and higher energy $D_{3h}$ structures are included because these are tempting candidates to account for the observed simple vibrational progression in the ground-state PES band (Fig. 1a). All simulated spectra are compared with the 193 nm experimental spectrum in Fig. 3. It is immediately clear that the two higher-energy $D_{3h}$ structures do not agree with the experiment (Fig. 3d and 3e) and they can be safely ruled out. The two low-lying C$_9$ ($^{2}A_1$) structures are both triplet states and they display slightly lower electron binding energies. The observed PES spectra of Re$_3$O$_5^-$ are very clean on the lower binding energy side, which suggests that there are no contributions from any low-lying isomers or even any vibrational hot bands, and a single isomer is responsible for the observed spectra.
The simulated spectrum of the $C_{2v}$ ($1A_1$) global minimum well reproduces the observed PES spectral features (Fig. 3a). The $C_{2v}$ ($1A_1$) global minimum is closed shell with the valence electron configuration $1a_1^21b_2^21b_1^22a_1^23a_1^22b_2^24a_1^2$. Detachment from the $4a_1$ highest occupied molecular orbital (HOMO) results in the neutral $C_{2v}$ ($2A_1$) ground state with a predicted VDE of 2.39 eV, which is in good agreement with the experimental value of 2.54 eV (Table 1). B3LYP appears to underestimate the ground-state electron binding energy by $\sim$0.15 eV. The VDE for detachment from HOMO−1 ($2b_2$) is predicted as 2.99 eV, in excellent agreement with the experimental band A (VDE: 3.04 eV). Both the $4a_1$ and $2b_2$ orbitals (Fig. 4) are primarily nonbonding Re 5d z lone pairs (or more strictly speaking, slightly antibonding orbitals), consistent with the observed sharp PES bands X and A, which suggest no or little geometry changes upon electron detachment. The next detachment channel is from HOMO−2 ($3a_1$) with a calculated VDE of 4.31 eV, which is in excellent agreement with band C (VDE: 4.34 eV). The $3a_1$ HOMO−2 is a Re−Re bonding orbital, consistent with the broad PES band observed. Detachment channels from HOMO−3 through HOMO−6 are predicted within the 4.6−5.6 eV binding energy range and all involve bonding or antibonding orbitals, consistent with the broad and nearly continuous spectral features (D and E). The above assignments leave band B unaccounted for. This relatively weak band is assigned to shake-up processes, due to the availability of low-lying unoccupied 5d orbitals. Indeed, B3LYP calculations predict a shake-up transition ($2B_1 \rightarrow 1A_1$) at 3.27 eV, which involves detaching an electron from the HOMO and simultaneously promoting another from the HOMO to the lowest unoccupied molecular orbital (LUMO). Another shake-up transition, $3A_2 \rightarrow 1A_1$, is predicted at 3.34 eV, where an electron is detached from the HOMO and another is promoted from the HOMO to LUMO+1. These shake-up transitions are in excellent agreement with band B (3.43 eV), demonstrating strong electron correlation effects in the Re$_3$O$_3$ cluster.

The well-resolved and simple vibrational progression in the ground-state transition (Fig. 1a) is remarkable, suggesting that both the Re$_2$O$_3^-$ anion and Re$_3$O$_3$ neutral cluster are of relatively high symmetry with little geometry change between them. The high frequency (960 ± 30 cm$^{-1}$) suggests that the vibrational mode should involve a totally symmetric Re−O stretching. Vibrational analysis for the neutral $C_{2v}$ ($1A_1$) global minimum reveals a totally symmetric Re−O stretching frequency of 1003.5 cm$^{-1}$ (unscaled) for the terminal oxygens, in good agreement with the experimental measurement. The HOMO ($4a_1$) of $C_{2v}$ ($1A_1$) anion is an antibonding $\delta^*$ orbital with minor contributions from the terminal O 2p atomic orbitals. Our calculations show that indeed very little anion-to-neutral structural changes take place regarding the Re−Re and Re−O−Re bond distances and the bond angles (Fig. 2a versus Fig. 3a).

Table 2: Relative energies (in eV) for the low-lying structures of Re$_3$O$_3^-$ cluster at the B3LYP level, as compared with those from the single-point CCSD(T) calculations at the B3LYP geometries

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>State</th>
<th>B3LYP$^a$</th>
<th>CCSD(T)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$</td>
<td>$1A_1$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$3A_2^*$</td>
<td>0.05</td>
<td>0.26</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$3A_2^+$</td>
<td>0.28</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$^a$ At the B3LYP/Re/Stuttgart+2fg/O/aug-cc-pVTZ level. $^b$ Single point energy at the CCSD(T)/Re/Stuttgart+2fg/O/aug-cc-pVTZ//B3LYP/Re/Stuttgart+2fg/O/aug-cc-pVTZ level.

The simulated photoelectron spectra (black curves) for the $C_{2v}$ ($1A_1$) global minimum (a), low-lying $C_{2v}$ structures (b and c), and selected $D_3h$ structures (d and e) of Re$_3$O$_3^-$, compared to the experimental 193 nm spectrum (red curve). Relative energies at the B3LYP level are shown. The simulations are done by fitting the distribution of calculated vertical detachment energies with unit-area Gaussian functions of 0.1 eV width. The simulated spectrum in (a) has been shifted to the blue by 0.15 eV to show its overall agreement with experiment.

Fig. 3: Simulated photoelectron spectra (black curves) for the $C_{2v}$ ($1A_1$) global minimum (a), low-lying $C_{2v}$ structures (b and c), and selected $D_3h$ structures (d and e) of Re$_3$O$_3^-$, compared to the experimental 193 nm spectrum (red curve). Relative energies at the B3LYP level are shown. The simulations are done by fitting the distribution of calculated vertical detachment energies with unit-area Gaussian functions of 0.1 eV width. The simulated spectrum in (a) has been shifted to the blue by 0.15 eV to show its overall agreement with experiment.
they do not contribute to net bonding in the Re$_3$O$_3$ structure. The Re atom possesses an electron configuration of 5d$_5$6s$_2$. The six delocalized orbitals from combinations of Re 5d$_s$ hybrid atomic orbitals, the four p$_s$ orbitals from each Re atom, and the 14e Re$_3$Cl$_9$ aromatic species after all. The conflicting d-orbital aromaticity observed in Re$_3$O$_3$ hints that there may potentially be a wide variety of transition-metal aromatic compounds with multiple aromaticity and/or antiaromaticity. It is noted that the well-known 12e Re$_3$Cl$_9$ compound possesses three localized Re=Re double bonds and the 14e Re$_3$Cl$_9$ dianion is a 2π aromatic system.

The δ-bond in transition metal compounds is known to be much weaker than either the σ- or π-bond. Delocalized multi-center δ-bond (δ-aromaticity) represents a new mode of chemical bonding, which should exert additional resonance stabilization. The unique electronic structure of the Re$_3$O$_3$ cluster offers an opportunity to experimentally quantify the resonance energy for a delocalized δ-bond. As shown in Fig. 4, the HOMO (δ*), HOMO−1 (δ*), and HOMO−2 (δ) of Re$_3$O$_3$− are the bonding and antibonding combinations composed of the Re d$_{z^2}$ atomic orbitals, which correspond to the observed PES bands X, A, and C, respectively (Fig. 1). These orbitals are fully occupied, resulting in negligible net bonding contribution, that is, three d$_{z^2}$ lone-pairs. If we take the centroid of the three observed PES bands as a reference (Fig. 5b), it is possible to estimate the stabilization energy of the bonding d$_{z^2}$ δ orbital and the destabilization energies of the d$_{z^2}$ δ* orbitals, using the differences of the measured ADEs as shown in Fig. 5a. The bonding δ orbital is stabilized by 0.77 eV, giving rise to an electronic stabilization energy for the delocalized δ-bond of 1.54 eV (~35 kcal mol$^{-1}$). This stabilization energy is substantially higher than that of a typical localized δ-bond as established for transition metal dimer complexes via electronic absorption spectroscopy (upper limit: 20 kcal mol$^{-1}$). The difference of ~15 kcal mol$^{-1}$ can be attributed to the resonance energy of the delocalized δ-bond, which is quite significant and nearly comparable to the strength of a localized δ-bond itself. It is stressed that the above values for bond strength and resonance energy of a delocalized δ-bond are based on the distorted C$_2v$ structure and should be considered qualitative estimates. For an ideally delocalized δ-bond, the resonance energy is expected to be even larger. Evaluation of the resonance energy of an aromatic molecule has been a notoriously difficult and complex task in general, relying largely on the choice of an appropriate reference system. Our PES study of Ta$_3$O$_9$− (ν = 1–5) clusters provides a hint that the delocalization indeed has an observable stabilization effect on the δ orbital, but quantification of this effect was not possible previously. It is instructive to compare the resonance energy of the delocalized δ-bond with those of the π-aromatic benzene (36 kcal mol$^{-1}$) and the d-orbital σ-aromatic W$_2$O$_9$− cluster (~24 kcal mol$^{-1}$), which suggests that the resonance energy correlates closely with the type of bond, as anticipated.

In conclusion, we have investigated the electronic properties and chemical bonding of the Re$_3$O$_3$− cluster via vibrationally-resolved

![Fig. 4 Molecular orbital pictures for the C$_2v$ (1A$_1$) global minimum of Re$_3$O$_3$−.](image-url)
photoelectron spectroscopy and density-functional theory calculations, showing that the Re$_3$O$_3^-$ anion cluster adopts a C$_{2v}$ ($A_g$) global minimum structure. Bonding analysis reveals a conflicting d-orbital aromaticity ($\pi$-aromaticity and $\pi$-antiaromaticity). The experimental data also facilitates the evaluation of the strength ($\sim 35$ kcal mol$^{-1}$) and resonance energy ($\sim 15$ kcal mol$^{-1}$) of a delocalized $\delta$-bond.

**Experimental and computational section**

**Photoelectron spectroscopy**

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization supersonic cluster source.$^{33}$ Briefly, Re$_m$O$_n^-$ cluster anions were produced by laser vaporization of a pure Re disk target in the presence of a helium carrier gas seeded with 0.01% O$_2$ and were analyzed using a time-of-flight mass spectrometer. Re$_3$O$_3^-$ clusters were mass-selected and decelerated before being photodetached. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectra of Rh$^-$ and Au$,^-$, and the resolution of the apparatus was $\Delta E/k_T \approx 2.5\%$, that is, $\sim 25$ meV for 1 eV electrons.

**Computational methods**

The DFT calculations were carried out using the hybrid B3LYP functional.$^{34-36}$ The global minimum searches were performed using analytical gradients with the Stuttgart relativistic small core basis set and effective core potential$^{37,38}$ augmented with two $f$-type and one $g$-type polarization function for Re $[(f) = 0.327, 0.955; (g) = 0.636]$ as recommended by Martin and Sundermann$^{39}$ and the aug-cc-pVTZ basis set for oxygen. Re$_3$O$_3^-$ clusters were used, where a restricted open-shell Hartree–Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the correlation treatment. The CCSD(T) calculations were performed using the MOLPRO 2010.1 package.$^{45}$

**Acknowledgements**

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U. S. Department of Energy under grant No. DE-FG02-03ER15481 (catalysis center program). X. H. gratefully acknowledges support from the Natural Science Foundation of China (21071031 and 90922022) and the Natural Science Foundation of Fujian Province of China (No. 2008J0151).

**References**

The two $C_1$ ($A'$) Re$_3$O$_3^-$ anion structures (Fig. 2b and 2c) can be ruled out from experimental observation for numerous reasons: (i) These isomers are consistently higher in energy at both the B3LYP and CCSD(T) levels of theory (Table 2); (ii) The observed PES pattern (Fig. 1) strongly suggests a closed-shell Re$_3$O$_3^-$ anion cluster, rather than an open shell; (iii) The simulated PES spectra for the $C_1$ ($A'$) anion structures disagree with experiment (Fig. 3b and 3c); (iv) Other arguments are based on the calculated first VDEs and the vibrational information, as described in the text.


28 The PES bands not only reflect the occupation of molecular orbitals in the anion, but also represent the ground state and excited states of the neutral species. In the PES spectra of the Re$_3$O$_3^-$ anion cluster, bands X, A, and C correspond to the ground state and excited states of the Re$_3$O$_3$ neutral cluster, whose electron configurations are $\ldots \delta(3a_1)^2 \delta^2(2b)^{2}\delta^4(4a_1)^2 \ldots \delta (3a_1)^2 \delta^2(2b)^{2}\delta^4(4a_1)^2 \ldots \delta(3a_1)^2 \delta^2(2b)^{2}\delta^4(4a_1)^2 \ldots$, respectively. The ADE differences for X-C and A-C, as shown in Fig. 5a, are thus equivalent to the $\delta$ to $\delta^*$ promotion energies. Two-thirds of the average of these $\delta$ to $\delta^*$ promotion energies represents the stabilization energy of the delocalized $\delta$ orbital (0.77 eV; Fig. 5b). The central idea here is to ensure that the net bonding for the $\delta^* \delta^* \delta^*$ framework in Re$_3$O$_3^-$ is negligible (that is, three $d_{\alpha\beta}$ lone-pairs), where the stabilization of the delocalized $\delta$ orbital is effectively compensated by the destabilization of the $\delta^*$ orbitals (0.64 and 0.14 eV; Fig. 5b). Consequently, the strength of a delocalized $\delta$ bond is estimated to be 1.54 eV ($\sim 35$ kcal mol$^{-1}$). The above procedure to evaluate the strength of delocalized $\delta$ bond is essentially the same as that used for a localized $\delta$ bond in the transition metal dimer complexes (ref. 29), which is associated with the electronic excitation from the $\delta$ to $\delta^*$ orbital.


30 It is appropriate to state explicitly here that the value of the resonance energy of the $\delta$-bond ($\sim 15$ kcal mol$^{-1}$) is qualitative due to the following approximations made. First, ideally the resonance energy of a delocalized $\delta$-bond in a triangular cluster should be evaluated at the difference in energy between the triangular cluster with a delocalized $\delta$-bond and the triangular cluster with a localized $\delta$-bond. It is chosen in our evaluation to replace the latter value with that of a localized $\delta$-bond in a non-triangular cluster (ref. 29), although the error thus introduced is expected to be small. A localized $\delta$-bond in a triangular cluster should not differ much from a localized $\delta$-bond in a non-triangular cluster. Second, in our evaluation the bond strength of the localized $\delta$-bond is taken from the upper limit estimated for the Tc–Tc or Mo–Mo $\delta$-bond (ref. 29), rather than from an appropriate localized Re–Re bond. It is believed that the Tc–Tc bond should be similar to the Re–Re bond, in particular for the weak $\delta$-bonding. We are not aware of any specific mention of the Re–Re $\delta$-bond strength in the literature. It may be stressed that the upper limit of the bond strength of 20 kcal mol$^{-1}$ for a localized $\delta$-bond is a general notion for the transition metal complexes, not specifically limited to Tc–Tc or Mo–Mo bonds. We think the upper limit value is good enough for the current discussion.


43 M. J. Frisch et al., Gaussian 03, revision D.01, Gaussian, Inc., Wallingford, CT, 2004.


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