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Electron Attachment to $Cr(CO)_6$ at Threshold Energies†

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Using electron transmission spectroscopy[1] (ETS), we have recently shown[2] resonance behavior in the electron scattering cross sections from threshold to about 4 eV for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. The resonances observed were assigned by using bound-state multiple-scattering (MS) Xα SCF MO calculations,[3] which predicted several anion states that were either bound or within 1 eV of threshold. Recently, an ab initio restricted Hartree–Fock (RHF) SCF MO calculation[4] on $Cr(CO)_6^-$ was reported that gave as the lowest energy anion a $^2T_{1u}$ state, 1.54 eV *above* threshold. A completely new assignment of the ETS features was suggested. No other properties were reported from the RHF calculation, and no interpretation was given for the several features below 1 eV in the electron transmission spectrum. A time-of-flight mass spectrometer has recently been appended to our ETS apparatus in order to monitor anions from dissociative attachment with the same high resolution (50 meV) that characterizes the ETS experiment. Using this instrument along with new computational capabilities, we are in a position to address the question of the nature of the interaction of low-energy electrons with $Cr(CO)_6$.

In Figure 1 we show the negative ion current from $Cr(CO)_6$ as a function of incident electron energy. The chief features of this spectrum—a large peak near 0.5 eV with shoulders between 1 and 2 eV and between 2 and 3 eV—correspond to the prominent features of the electron transmission spectrum. The vast majority of the ions observed are $Cr(CO)_5^-$ except near 1.6 eV where $Cr(CO)_4^-$ contributes about 15% to the total. The production of $Cr(CO)_4^-$ is clearly associated with features "B" in the electron transmission spectrum,[2] which we identified with processes involving the $3t_{2u}$ orbital. It is apparent that electron attachment readily occurs at energies below 1 eV, in sharp contrast to the RHF results.

In order to interpret our results we have performed continuum MS-Xα calculations on $Cr(CO)_6$ using the method described by Davenport et al.[5] We have generated self-consistent potentials

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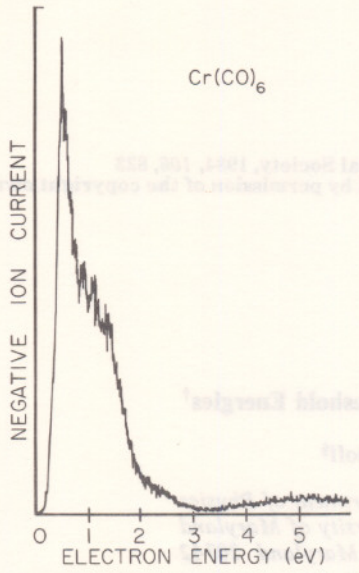

Figure 1. Ion current vs. electron impact energy on $Cr(CO)_6$. The ions are essentially all $Cr(CO)_5^-$.

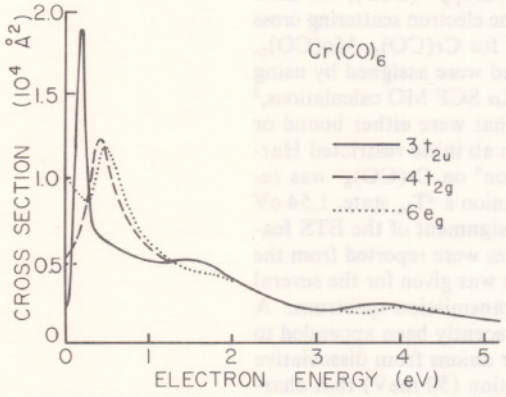

Figure 2. Calculated continuum MS-Xα elastic electron scattering cross section vs. electron energy for $Cr(CO)_6$ for three different potentials obtained by adding 0.5 electrons to the $3t_{2u}$, $4t_{2g}$, and $6e_g$ orbitals, respectively.

for use in the continuum calculation by adding 0.5 electrons to various empty orbitals, iterating to self-consistency, and subtracting out the effect of a stabilizing Watson sphere as described previously.[2] The cross sections shown in Figure 2 were determined from potentials corresponding to $3t_{2u}$, $4t_{2g}$, and $6e_g$ orbital occupations, which have calculated attachment energies of 1.7, 0.9, and 0.2 eV, respectively, within the bound-state stabilization approach.[2] A number of lower energy empty orbitals ($9t_{1u}$, $9a_{1g}$, $2t_{2u}$, $3t_{2g}$, and $2t_{1g}$) are predicted to generate stable anions. The calculated cross sections are similar to the experimental result, each showing maxima well below 1 eV and a shoulder between

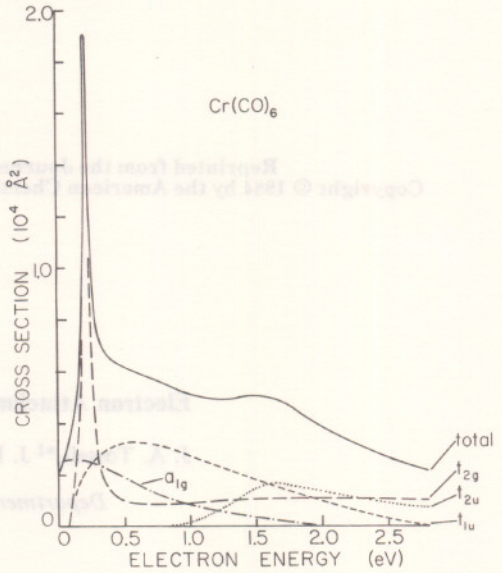

Figure 3. Decompoisition of calculated cross section by symmetry of continuum electron for the scattering potential given by occupation of the $3t_{2u}$ orbital (e_g and t_{1g} channels give $\sigma < 30$ Å^2 and are not shown).

1.2 and 2 eV. A decomposition of the cross section by the symmetry of the continuum electron for the $3t_{2u}$ potential shown in Figure 3 establishes that the low-energy maximum arises from the t_{2g} channel and the shoulder at 1.6 eV from the t_{2u} channel. The continuum MS-Xα results should be considered preliminary since we have used a small basis set more appropriate for bound-state calculations and have not explored the effect of adding higher partial waves.[6] Although the attachment energies from the bound-state calculation are in reasonable agreement with the calculated positions of the cross-section maxima, it is apparent that our previous analysis was somewhat oversimplified as evidenced by the substantial contributions in nonresonant channels and the unexpectedly low cross section in the e_g channel (also predicted by the RHF calculation[4]). It also appears that the RHF and MS-Xα calculations give the same order of anion states but that all the states lie higher by about 2 eV in the RHF calculation. A further comparison of RHF and MS-Xα results will be the subject of a later report.

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Registry No. $Cr(CO)_6$, 13007-92-6.

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(7) **Note Added in Proof**: We have recently learned of similar ion current results for $Cr(CO)_6$ obtained by Pignataro et al.: Pignataro, S.; Foffari, A.; Grasso, F.; Cantone, B. *Z. Phys. Chem.* (*Wiesbaden*) **1965**, *47*, 106.