A Study of Cr2 by Negative-Ion Photoelectron Spectroscopy

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Multiple metal–metal bonding[2] can be examined in its clearest form in the unligated transition-metal dimers. Chromium dimer,[3] in particular, has been the subject of numerous experimental[3-8] and theoretical[9-14] studies. Since the ground state of the Cr atom has a high-spin $3d^5 4s^1$ configuration, a closed-shell configuration for Cr_2 would lead to a formal bond order of six. Consistent with this picture, Cr_2 is known[3,5,6] to have a $^1\Sigma_g^+$ ground state and a bond length of only 1.6788 Å, even shorter than the very short "quadruple" Cr–Cr bonds in $Cr_2(DMP)_4$ [1.847 (1) Å] and $Cr_2(2\text{-MeO-5-MeC}_6 H_3)_4$ [1.828 (2) Å].[15]

However, other results belie the simple picture of a hextuple bond in Cr_2. For example, the bond dissociation energy (D_o) of Cr_2 is only 1.44 ± 0.05 eV (33.2 ± 1.2 kcal/mol),[4] actually *lower* than the 2.01 ± 0.08 eV bond energy[3] of the singly 4s–4s bonded Cu_2 molecule! Theoretical studies have shown that the situation is further complicated by the 2.7-times greater size of the 4s than the 3d orbital in atomic chromium,[9a] which may cause the 4s–4s
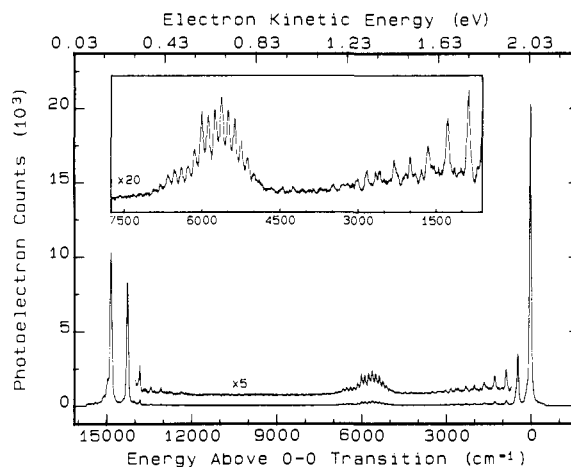
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Figure 1. 488-nm (2.540-eV) negative-ion photoelectron spectrum of Cr_2^-.

interaction in Cr_2 to be repulsive at the optimum distance for 3d–3d bonding. Modified GVB calculations by Goodgame and Goddard[11] predict that the ground state of Cr_2 has a double-minimum potential energy curve, dominated by five covalent 3d–3d bonds at short internuclear distance, and by a single 4s–4s bond (with the d electrons antiferromagnetically coupled) at long distance. The "long-bond form" of Cr_2 is predicted to have a 110-cm^{-1} vibrational frequency, a 3.06-Å bond length, and a binding energy of only 0.3 eV.[10,11] Results of elegant two-color resonance Raman experiments by Moskovits and co-workers on matrix-isolated Cr_2 have been interpreted as possible evidence for this double-minimum ground-state potential.[7b]

We report here a gas-phase study of Cr_2 by photoelectron spectroscopy of the Cr_2^- anion. Results reveal low-lying vibrational and electronic states of the neutral molecule and provide a test of theoretical calculations of its ground-state potential curve.

Spectra were obtained at an instrumental resolution of 5 meV (40 cm^{-1}) by use of a new negative-ion photoelectron spectrometer to be described in the full report on this study.[16] Our instrument is similar to the Lineberger apparatus,[17] but incorporates a 90° sector magnet for improved mass resolution and has an increased pumping capacity to enable mild supersonic cooling of the anions. The Cr_2^- sample was prepared in a flowing afterglow ion–molecule reactor operated at a helium pressure of 0.8 Torr, by injecting $Cr(CO)_6$ vapor[18] just downstream of a 2.45-GHz microwave discharge. Negative ions sampled from the flow tube were mass selected and then photodetached by the intracavity radiation of a CW argon ion laser.

The 488-nm (2.540-eV) photoelectron spectrum of Cr_2^- is shown in Figure 1. The strong feature at 2.035-eV electron kinetic energy corresponds to the "0–0" transition between the zero-point vibrational levels of the ground electronic states of the anion and the neutral molecule. The position of this peak yields a Cr_2 electron affinity of 0.505 ± 0.005 eV. The 455 ± 15 cm^{-1} separation between the 0–0 transition and the neighboring ($v_{neutral}$ = 1) ← (v_{ion} = 0) transition agrees with the known $\Delta G_{1/2}$ value[6] of 452.34 cm^{-1} for Cr_2, confirming that we are indeed observing the $^1\Sigma_g^+$ ground state of the neutral molecule. With the very reasonable assumption that the Cr_2^- bond length exceeds that of Cr_2, a Franck–Condon analysis of the relative intensities of these two peaks yields a bond length of 1.705 ± 0.010 Å for Cr_2^-.

The two intense features at lowest electron kinetic energy reveal an excited electronic state of Cr_2 14 240 ± 30 cm^{-1} above its ground state, with a vibrational frequency of 580 ± 20 cm^{-1}. The left-most peak is suppressed by a factor of ~2 by the reduced sensitivity of our instrument at very low electron kinetic energies.

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A weak absorption in this region has been reported by Andrews and Ozin for matrix-isolated Cr_2.[8c] Hot bands arising from ($v_{neutral}$ = 0) ← (v_{ion} = n, n = 1–3) transitions to this excited state, shown at ×5 magnification in Figure 1, yield ω_e = 470 ± 25 cm^{-1} and $\omega_e x_e$ = 20 ± 10 cm^{-1} for the Cr_2^- anion.

The ×20 inset to Figure 1 displays an expansion of the spectrum near the ground-state transition. As shown on the right side of the inset, vibrational states of neutral Cr_2 from v = 2 to v = 6 are observed 875, 1275, 1650, 1995, and 2305 cm^{-1} (±15 cm^{-1}) above the 0–0 transition. These features are far more intense than would be expected on the basis of Franck-Condon factors for a direct photodetachment process. With the v = 1 level constrained to its literature value,[6] the observed energies can be fit to within our experimental uncertainty to a Morse potential with ω_e = 479 ± 2 cm^{-1} and $\omega_e x_e$ = 13.5 ± 1.0 cm^{-1}. This anharmonicity constant is unusually large: $\omega_e x_e$ values for all other neutral homonuclear first-row transition-metal dimers measured to date[3] fall in the range 1–4 cm^{-1}. Interestingly, the excellent Morse potential fit to vibrational levels up to v = 6 (0.3 eV above the zero-point level) extrapolates to a dissociation asymptote of only 0.5 eV, far below the true[4] Cr_2 bond energy (D_o) of 1.44 ± 0.05 eV. Thus, it is clear that the Cr_2 ground-state potential energy curve strongly diverges from a Morse potential at higher energies.

A weak vibrational progression of the neutral molecule comprising more than a dozen peaks is observed from 5100 to 6700 cm^{-1} above the 0–0 transition, as shown on the left side of the ×20 inset to Figure 1. Surprisingly, the peak spacings are only 130 ± 10 cm^{-1}, and they exhibit no detectable anharmonicity. This low-frequency, harmonic vibrational progression displays an intensity profile noticeably more irregular than that expected for the photoelectron spectrum of a diatomic species. Furthermore, the intensity profile changes dramatically when the argon ion laser is tuned from 488 nm to any of the other lines (476, 496, or 514 nm) strong enough to be used in this experiment. The relative intensities of the v = 2 to v = 6 features discussed above also exhibit a pronounced wavelength dependence. In all cases, however, the separation between each peak and the 0–0 transition does not vary with laser wavelength. These observations suggest a one-photon process involving a resonance of the laser with one or more metastable states of the negative ion. The analogous formation of intermediate autoionizing resonances is well-documented in the literature of neutral molecule photoelectron spectroscopy.[19,20] This propitious resonance allows us to probe regions of the neutral molecule potential curve that would normally be inaccessible in this experiment due to negligible Franck–Condon overlap with the anion ground state.

The 130-cm^{-1} vibrational interval observed here is close to the 110-cm^{-1} value predicted by Goodgame and Goddard[10] for the singly 4s–4s bonded, "long-bond form" of the Cr_2 ground state. However, the 130-cm^{-1} progression appears only 0.6 eV above the 0–0 transition and displays no detectable anharmonicity over a 0.2-eV range. In contrast, the MGVB calculation[11] predicts the 4s–4s well to be bound by only 0.3 eV and to lie 1.6 eV above the 3d–3d well. No long-bond excited electronic states are predicted at lower energies. In addition, we measure an unusually large anharmonicity ($\omega_e x_e$ = 13.5 ± 1.0 cm^{-1}) for the "short-bond" region of the potential. These results suggest the need for improved calculations of the ground-state potential energy curve of Cr_2.

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Synthesis of Indoles via Palladium-Catalyzed Heteroannulation of Internal Alkynes

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The indole nucleus is prevalent in a wide variety of biologically active, naturally occurring compounds, and numerous approaches to its synthesis have been reported, including many employing transition metals,[1] particularly palladium.[2] Our interest in the palladium-catalyzed annulation of 1,2-dienes,[3] 1,3-dienes,[4] and unsaturated cyclopropanes and cyclobutanes[5] encouraged us to examine analogous alkyne chemistry for the synthesis of indoles.

There has been considerable interest of late in transition-metal-mediated cycloaddition reactions of alkynes in organic synthesis,[6] especially those involving palladium.[7] With a few exceptions, intermolecular attempts to annulate onto alkynes using palladium have generally resulted in multiple alkyne insertions or in insertion and subsequent cyclization back on to a preexisting aromatic ring (eq 1).[8]

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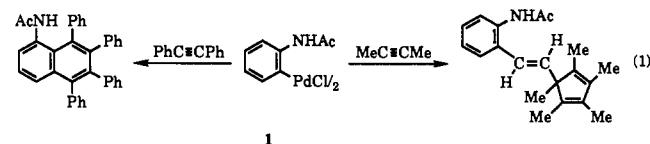
We now report a conceptually and experimentally simple, new approach to indoles involving the palladium-catalyzed heteroannulation of internal alkynes using *o*-iodoaniline and its derivatives (eq 2).[9] Our results are summarized in Table I.
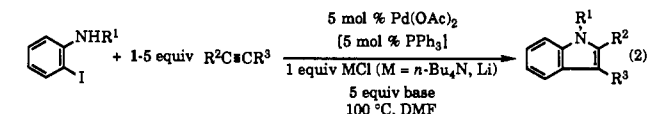
In general, we have used a procedure similar to those used by us for earlier annulation processes. Carbonate or acetate bases, in the presence or absence of catalytic amounts of triphenylphosphine, have afforded the best results. All of our early work was carried out by using 1 equiv of *n*-Bu$_4$NCl (Lancaster, pro-

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