

Final Technical Report

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Title: Spectroscopy of Organometallic Radicals

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In this grant, we have been primarily concerned with characterization of the chemical bond between transition metals and carbon, although some work has also been directed toward understanding the bonding between transition metals and other main group elements. We have also undertaken some studies of the chemical bonding in the actinide metals.

I. Electronic structure and spectroscopy of the diatomic transition metal carbides, MC

When we began this project, there was rather little experimental knowledge of the diatomic transition metal carbides. These are important species that can be used to judge the capability of quantum chemical methods to accurately calculate the unsaturated reaction intermediates that are important in the catalytic processing of hydrocarbons into other products. By obtaining highly accurate information about these diatomic species, it has been our goal to assemble a database of precise knowledge that can be used to determine the level of theoretical treatment that is required for proper treatment of these species. At the same time, we seek to develop a qualitative understanding of the electronic structure of these species. Publications resulting from our work on the diatomic transition metal carbides are numbers 1-8 in the list at the end of this report.

Prior to our work on these molecules, the only transition metal monocarbides that were spectroscopically known in the gas phase were FeC, CoC, YC, NbC, RuC, RhC, IrC, and PtC. In our work we have added detailed spectroscopic knowledge of the new molecules VC, CrC, NiC, MoC, PdC, TaC, WC, and OsC. We have also added to the previously known data on FeC and RuC, and work is currently in progress that will provide a definitive identification of the ground electronic state and bond length of TiC. In all of the molecules that we have studied, we have determined the ground electronic state symmetry and bond length, and in some cases the electronic symmetry and bond length of excited states. For these molecules, the ground state bond lengths generally contract as one moves to the right in the periodic table, due to the overall orbital contraction as the nuclear charge is increased.

The ground state bond lengths (in Angstroms) that are now known for the metal carbides are listed below (bond lengths with an asterisk were determined in the Morse group):

Group	3d series	4d series	5d series
3 (Sc, Y, La)	unknown	2.05	unknown
4 (Ti, Zr, Hf)	1.695(2)	1.8066	unknown
5 (V, Nb, Ta)	1.6167*	1.7003	1.7490*
6 (Cr, Mo, W)	1.6188*	1.688*	1.7143*
7 (Mn, Tc, Re)	unknown	unknown	unknown
8 (Fe, Ru, Os)	1.5888	1.608*	1.6727*
9 (Co, Rh, Ir)	1.5612	1.6134	1.6858
10 (Ni, Pd, Pt)	1.627*	1.712*	1.6767
11 (Cu, Ag, Au)	unknown	unknown	unknown

More importantly, our work has elucidated the electronic structure of these molecules, and has demonstrated that across the bulk of the transition metal series, the added electrons are placed into the relatively nonbonding 3σ and 1δ orbitals. Further, the 1δ orbital is centered on the metal atom and is

essentially an unperturbed d orbital. The 3σ orbital is also centered on the metal atom, and is completely dominated by metal s character. Omitting the filled bonding orbitals, the transition metal monocarbides have the following ground electronic configurations (again, determinations made in the Morse group are indicated by an asterisk):

3d series	4d series	5d series
4 TiC $2\sigma^1 3\sigma^1$	ZrC $2\sigma^1 3\sigma^1$	HfC unknown
5 VC $1\delta^1*$	NbC $1\delta^1$	TaC $3\sigma^1*$
6 CrC $1\delta^2*$	MoC $1\delta^2*$	WC $1\delta^1 3\sigma^1*$
7 MnC unknown	TcC unknown	ReC unknown
8 FeC $1\delta^3 3\sigma^1$	RuC $1\delta^4*$	OsC $1\delta^3 3\sigma^1*$
9 CoC $1\delta^4 3\sigma^1$	RhC $1\delta^4 3\sigma^1$	IrC $1\delta^3 3\sigma^2$
10 NiC $1\delta^4 3\sigma^2*$	PdC $1\delta^4 3\sigma^2*$	PtC $1\delta^4 3\sigma^2$
11 CuC unknown	AgC unknown	AuC unknown

In reviewing these results, it is clear that there is a definite preference for placing electrons in the 6s-like 3σ orbital in the diatomic carbides of the 5d series. This is evident in comparing the electronic configurations of the isovalent molecules VC and NbC to TaC; CrC and MoC to WC; RuC to OsC; and CoC and RhC to IrC. This chemical behavior is a consequence of the relativistic stabilization of the 6s orbital in the isolated atom, and this stabilization is transferred in the molecule to the 3σ orbital. Our work has also shown that the 3σ orbital is dominated by metal (n+1)s character in the cases of RuC (~83% Ru 5s character), TaC (~75% Ta 6s character), and OsC (~90% Os 6s character). We have also noted that in the molecules (VC, NbC, CrC, MoC, and RuC) in which the 3σ orbital is unoccupied, a large dipole moment is expected. This prediction is experimentally verified in the cases of MoC and RuC by the Steimle group, who find values of 6.07(18) D and 4.09(14) D, respectively. Our work on WC has been of considerable interest for experimental attempts to measure the electron electric dipole moment, and has been the starting point for more detailed spectroscopic studies by the Steimle and Leanhardt groups.

II. Transition metal acetylides (MCCH) [Publications 9-12 listed below]

Although the spectroscopy of a large number of alkali, alkaline earth, and zinc-group monoacetylides (MCCH) are known, relatively little work has been done to unravel the spectroscopy of the transition metal acetylides, particularly for the molecules that have open d-subshells. Some pure rotational spectroscopy has been performed by the Ziurys group, but ours is the only group reporting electronic spectra of these species. In our first study, we found that laser ablation of chromium in the presence of methane generated a large number of different chromium compounds, many of which were found to have spectra in the red or near-infrared regions. We were able to obtain spectra of CrH, CrC, CrCH₃, CrCCH, and a few larger species using this method. The spectrum of CrCCH was complicated, but was shown to arise from a ${}^6\Sigma$ to ${}^6\Sigma$ transition, similar to known spectra in the CrH, CrF, and CrCl molecules. In the excited electronic state, a Cr-C vibrational frequency of 425.6 cm⁻¹ was measured, along with a C-C stretching frequency of 1944.3 cm⁻¹. Dispersed fluorescence measurements showed a Cr-C stretching frequency of 470(20) cm⁻¹ in the ground electronic state.

Optical spectroscopic studies of CuCCH were very enlightening. The molecule was found to have a closed shell ground state, with a pattern of excited electronic states that is quite similar to that of cuprous chloride (CuCl), cuprous bromide (CuBr), and cuprous iodide (CuI). These results show without any doubt that it is appropriate to think of the CuCCH molecule as an ionic system, cuprous acetylide. The electronic energies of the excited states of CuCCH, CuCl, CuBr, and CuI are close to those of the $3d^9 4s^1$ states of the copper(I) cation. This is perhaps not too unexpected, given the high

electron affinity of CCH (2.969 eV), which is similar to that of Cl (3.613 eV), Br (3.364 eV), and I (3.059 eV).

Work on NiCCH has shown that it has a $3d^9$ configuration on the nickel atom, with the $^2\Delta$ state emerging as the ground state. The observed excited electronic state is also of $^2\Delta$ symmetry, and falls at very nearly the same energy as the $^2\Delta$ excited states of NiH and NiCN. The excited state vibrational frequency for the C-C vibration in NiCCH is 2001.9 cm^{-1} , which is significantly larger than that found for CrCCH. This is evidence of considerably stronger metal $d\pi$ donation into the empty π^* antibonding orbital of CCH in the case of chromium, as compared to nickel. This result is expected given that the $d\pi$ orbitals of chromium lie at a higher energy than those of nickel. They are also larger than the highly compact $d\pi$ orbitals of nickel, making them much more accessible for chemical bonding.

III. Investigation of NiCO, Ni(CO)₃(¹³CO), and Ni(CO)₃(C¹⁸O) by infrared spectroscopy

In another investigation, we have used a lead-salt diode laser to record infrared spectra of NiCO, Ni(CO)₃(¹³CO), and Ni(CO)₃(C¹⁸O) in the C-O stretching region using a multipass IR absorption cell just downstream from a discharge slit nozzle. The result provided the first rotationally resolved spectra of these molecules. Attempts to extend these studies to other transition metal carbonyls, such as Ni(CO)₂ were unsuccessful. We believe this is due to severe spectral congestion, even at low temperatures, resulting from a bent molecular configuration that made the Ni(CO)₂ molecule an asymmetric top. We noted that when the Fe(CO)₅ molecule is substituted with a C-13 or O-18 isotope in the equatorial position, the resulting asymmetric top structure could not be rotationally resolved. This work is published in reference 13 below.

IV. Transition metal halides, hydrides, and nitrides [papers 14-17 listed below]

Although the focus of this project has been on the transition metal-carbon bond, we have also undertaken studies of the spectroscopy of YF, ZrF and ZrCl, OsN, and have measured the fluorescence lifetime of CrH in its $A\ ^6\Sigma$ state. The study of YF was initiated when we observed spectra of YF while scanning for YCH₃. The accidental source of fluorine was a piece of Teflon tape wrapped around a screw in the vaporization fixture. The interesting aspect of this study was that we observed both singlet to singlet transitions and singlet to triplet transitions. This allowed us to locate the singlet and triplet manifolds of states on the same energy scale. Measurements of the fluorescence lifetimes of the observed states were used to investigate the spin-orbit coupling between the two manifolds.

Following our study of YF, we discovered that the neighboring metal fluoride, ZrF, was poorly known. We employed a carrier gas containing a small percentage of CF₂Cl₂ and were able to simultaneously record spectra of ZrF and ZrCl. This allowed us to obtain the most accurate measurement of the ground state bond length and vibrational frequency for ZrF, and to identify four new electronic band systems in ZrCl. This has opened the path for other investigators to work out the electronic structure of these species in greater detail.

In the case of osmium, very little experimental data was known prior to our work on this metal. Chemical bonds between the transition metals and nitrogen are generally of high interest, so we pursued a study of the OsN molecule to complement our study of OsC. The ground state configuration of OsC, $1\delta^3\ 3\sigma^1$, changes to $1\delta^3\ 3\sigma^2$ in the related OsN molecule. Promotion of a 3σ or a 1δ electron to the antibonding 2π orbital leads to three $^2\Phi$ and four $^2\Pi$ states, all of which were identified in this study. Combining this study with a previous study, OsN is now among the best

characterized of the 5d transition metal nitrides. The ground state and 10 different excited electronic states are now well-known.

The A-X transition of CrH had been observed when we scanned the spectrum of CrCCH. At a conference, I learned that this transition is used to characterize brown dwarf stars, and that it would be very helpful to astronomers to have an experimental measurement of the absorption oscillator strength for this transition. While that is a difficult measurement for a highly reactive molecule, the related fluorescence lifetime is quite simple to directly measure. This measurement was quickly performed, resulting in a significant revision to the opacity function that is used to model the atmospheres of brown dwarf stars.

V. Actinide molecules: UN [paper 18 below]

The application of quantum chemical computational methods to the actinides is complicated by severe relativistic effects and highly correlated electronic motions. Accordingly, these are computationally extremely challenging systems. In order to provide a benchmark for theoretical studies, we have undertaken studies of the spectroscopy of UN and ThC. While the ThC study has not yet come to fruition, our work on UN has unambiguously provided information about the ground state of this molecule. In its ground state, UN has a bond length of 1.7650(12) Å, and has an angular momentum about the internuclear axis, Ω , of 3.5. We had expected to discover that UN has the same ground electronic state as the isoelectronic molecule, UO^+ , which has $\Omega = 4.5$. Hence, the discovery that UN has $\Omega = 3.5$ came as a surprise. While UO^+ is well-described as a U^{3+} ion with an electronic configuration of $5f^3$ adjacent to an oxide ion, O^{2-} , the Ω -value of 3.5 found in UN indicates a ground electronic configuration of $\text{U}^{3+} \text{N}^{3-}$, with the U^{3+} ion in a $7s^1 5f^2$ configuration. This initially surprising result may be understood by noting that such a highly charged ligand stabilizes the configuration in which the large, highly polarizable 7s orbital is occupied.

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