**Generation Detection and Characterization of Gas-Phase Transition Metal
Containing Molecules (DE-FG03-94ER14468)**

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Final Report

1. Introduction

New catalysts are increasingly necessary for greater utilization of a dwindling chemical feedstock and to reduce the anthropomorphic degradation of the environment. Efficacious synthesis of new catalysts will only be accomplished when there is a clear understanding of the associated microscopic molecular steps. The goal of this project was to generate, identify and characterize of transition metal containing molecules that can provide insight into these microscopic molecular steps. The molecular information we sought is both the geometric and electronic structure for metal carbides, carbenes, imides, nitrides, thiols, cyanides, halides, hydroxides, and hydrides from the reaction of CH₄, NH₃, H₂S, and CH₃CN, CH₃Cl, CH₃OH and H₂. All experiments depended upon recording and analyzing ultra-high resolution electronic spectra of gas-phase molecules. A laser ablation/supersonic expansion scheme for sample production was developed and utilized, which allowed variable control over the internal temperature of the molecules and chemistry. Skimming the supersonic expansion and using single frequency lasers resulted in spectral resolution of < 40 MHz linewidth, which is unprecedented for this class of molecules and was required for full exploitation of the information content of electronic spectra.

Geometric information (bond lengths and bond angles) were extracted from the analysis of the rotational fine structure that appears in the electronic spectra. Electronic structural information was derived primarily from the analysis of magnetic hyperfine structure and electric field induced (Stark) shifts in the optical spectra. The high density of levels, large nuclear magnetic moments and numerous unpaired electrons for the metal containing molecules, makes the spectra-to-property transformation non-trivial. Modeling of the quantum energy levels was achieved using an effective Hamiltonian operator, $\hat{H}^{\text{eff}}$, that includes a vibronic part, $\hat{H}^{\text{el,vib}}$, rotational part, $\hat{H}^{\text{rot}}$, fine structure interactions,

$\hat{H}^{\text{fs}}$, a hyperfine interactions $\hat{H}^{\text{hyf}}$, (unpaired electron interacting with the nuclear spin and quadrupole moment) and the application of an external electric field (Stark effect), $\hat{H}^{\text{Stark}}$. The adjustable parameters that enter into these operators are related to physically meaningful properties. Specifically for a diatomic molecule:

$$\hat{H}^{\text{rot}} \rightarrow B \text{ (rot. parameter)} \propto \left\langle \Psi^{\text{el,vib}} \left| \frac{1}{R} \right| \Psi^{\text{el,vib}} \right\rangle, \quad R = \text{bond distance} \quad 1)$$

$$\hat{H}^{\text{hyf}} \rightarrow b_F \text{ (Fermi contact parameter)} \propto |\Psi(0)|^2 = \text{spin density at nucleus}, \quad 2)$$

$$\rightarrow c \text{ (dipolar parameter)} \propto \left\langle \Psi^{\text{el,vib}} \left| \frac{3 \cos \theta - 1}{r^3} \right| \Psi^{\text{el,vib}} \right\rangle$$

where θ and r coordinate of electron, 3)

+ other terms

$$\hat{H}^{\text{Stark}} \rightarrow \mu^{\text{el}} \text{ (dipole moment parameter)} = \left\langle \Psi^{\text{el,vib}} \left| \sum_i e \vec{r}_i \right| \Psi^{\text{el,vib}} \right\rangle \quad 4)$$

Particular emphasis was placed on the determination of ground and excited state permanent electric dipole moments, μ , which are the most fundamental electrostatic property of a molecule and enter into the description of numerous phenomena. A comparison of experimentally derived and theoretically predicted values of μ is the most useful gauge of the quality of electronic wave function generated by modern computational methods. The extensive electron correlation and relativistic effects in transition metal containing molecules make *ab initio* generation of electronic wave functions with sufficient accuracy to predict even one-electron properties such as μ very challenging. A common method for predicting dipole moments is by simply calculating the expectation value of the electric dipole moment operator, as in Eq. 4, where the summation runs over all charged particles. In dealing with transition metal systems, the vibronic wavefunction, $\Psi^{\text{el,vib}}$, is often obtained from a large basis set multi-reference configuration interaction (MRCI) calculation. An alternative method for predicting μ is the finite field approach where:

$$\bar{\mu} = \left. \frac{\partial \text{Energy}}{\partial \vec{E}} \right|_{\vec{E} \rightarrow 0} \quad 5)$$

According to the Hellman-Feynman theorem, the two definitions for μ are identical when the approximate $\Psi^{\text{el,vib}}$ has been fully optimized in the variational sense. MRCI and many other methods for treating electron correlation produce a $\Psi^{\text{el,vib}}$ which is not fully optimized in the variational sense and the first order properties calculated as an expectation value will not be identical to those obtained as an energy derivative. The difference between the values obtained by the two methods becomes smaller as the quality of the approximate wave function increases. Thus a comparison of dipole moments predicted by the two methods, and more importantly with experimental values when available, is a major criterion for selection of a computational methodology

2. Measured Dipole Moments, μ , and equilibrium bond distances, R_e .

Dipole moments and bond lengths for numerous diatomic and polyatomic transition metal containing molecules were experimentally determined. The results are collected in Table I.

Table I. Measured Dipole Moments, μ , and equilibrium bond distances, R_e .

Molecule	State	$R_e(\text{\AA})$	μ (Debye)	μ / R_e	Configuration	Publ.
VN	$X^3\Delta_1$	1.566	3.07(7)	1.96	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^1 9\sigma^1$	8
	$D^3\Pi_{0e}$	1.587	6.1(4)	3.84	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^1 4\pi^1$	8
CrN	$X^4\Sigma^-$	1.565	2.31(4)	1.47	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^2 9\sigma^1$	8
	$A^4\Pi_{3/2}$	1.57	5.42(2)	3.45	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^2 4\pi^1$	8
FeC	$X^3\Delta_3$	1.588	2.36(3)	1.47	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^3 9\sigma^1$	14
	$[12.0] \Omega=2$	1.621	4.02(6)	2.48	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^2 9\sigma^1 4\pi^1$	14
	$[13.1]^3\Phi_4$	1.620	4.44(6)	2.74	$7\sigma^2 8\sigma^2 3\pi^4 1\delta^3 4\pi^1$	14
RuC	$X^1\Sigma^+$	1.610	4.09(14)	2.54	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^4$	15
	$[0.1]^3\Delta_3$	1.638	1.95(2)D	1.19	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1$	17
	$[0.9]^3\Delta_2$	1.631	1.86(2)D	1.14	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1$	17
	$[12.7]^3\Pi_2$	1.657	3.58(3)D	2.16	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi^1$	17
	$[13.9]^3\Pi_1$	1.661	3.44(3)D	2.07	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi^1$	17
	$[18.1]^1\Pi$	1.680	3.31(4)	1.97	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi$	15

Table I (cont.)

Molecule	State	$R_0(\text{\AA})$	μ (Debye)	μ / R_e	Configuration	Publ.
WN	$X^4\Sigma_{1/2}^-$	1.667	3.77(18)	2.26	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^2 12\sigma^1$	18
	$A^4\Pi_{3/2}$	1.682	2.45(3)D	1.45	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^2 12\pi^1$	18
ReN	X^0^+	1.633	1.96(8)	1.20	$10\sigma^2 11\sigma^2 5\pi^4 2\delta^2 12\sigma^2$	18
	$[26.0]0^+$	1.665	3.53(4)	2.12	$\dots 5\pi^4 2\delta^2 12\sigma^1 6\pi^1$	18
IrC ^a	$X^2\Delta_{5/2}$	1.686	1.60(7)	0.949	$1\sigma^2 2\sigma^2 3\pi^4 1\delta^3$	5
	$D^2\Phi_{7/2}$	1.722	2.61(6)	1.51	$1\sigma^2 2\sigma^2 3\pi^4 1\delta^2 4\pi^1$	5
IrN ^a	$X^1\Sigma^+$	1.6094	1.66(1)	1.03	$1\sigma^2 2\sigma^2 3\pi^4 1\delta^4$	5
	$A^1\Pi$	1.6885	2.78(2)	1.64	$1\sigma^2 2\sigma^2 3\pi^4 1\delta^3 4\pi^1$	5
PtC ^a	$X^1\Sigma^+$	1.679	1.08(4)	0.643	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\delta^4$	3
	$A''^1\Sigma^+$	1.713	1.94(2)	1.13	$1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi^4 1\delta^4$	9
	$A^1\Pi$	1.720	1.919(9)	1.11	$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4 2\pi^1 1\delta^4$	9
	$A^1\Pi$	1.766	2.455(2)	1.39	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1 1\delta^3$	3
PtN ^a	$X^2\Pi_{1/2}$	1.774	1.977(9)	1.11	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\delta^4 2\pi^1$	1
	$d^4\Pi_{1/2}$	1.923	1.05(11)	0.546	Strongly mixed	1
PtO ^a	$X^3\Sigma^-$	1.727	2.77(2)	1.603	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\delta^4 2\pi^2$	4
	$A^1\Sigma^+$	1.795	1.15(4)	0.638	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^4 1\delta^4 2\pi^2$	4
PtS ^a	$X(\Omega=0)$	2.042	1.78(2)	0.872	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 1\delta^4 2\pi^2$	4
	$B(\Omega=0)$	2.108	0.54(2)	0.267	$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^4 1\delta^4 2\pi^2$	4
YbO	$X^1\Sigma^+$	1.807	5.89(2)	3.26	$4f^{13} 1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	7
	$A(\Omega=0)$	1.770	5.93(4)	3.35	Strongly mixed	7
YC ₂	$\tilde{X}^2A_1$	2.102	6.49(3)D	3.02	$1a_1^2 1b_1^2 2a_1^2 3a_1^1$	12
	$\tilde{A}^2A_1$	2.155	7.03(7)D		$1a_1^2 1b_1^2 2a_1^2 4a_1^1$	12

a) Only the m.o. orbitals originating from the 6s, 5d metal centered atomic orbital and the 2s/3s and 2p/3p ligand centered orbital are considered in deriving the m.o. numbering scheme.

b) The numbers in parentheses represent a 2 σ error estimate.

The molecular orbital correlation diagrams for the first, second and third row transition metal diatomic molecules given, in Figure 1 for the representative FeC, RuC and PtC molecules, was developed in order to qualitatively reproduce the observed dipole moments.

Figure 1. The molecular orbital correlation diagram for the first and second row transition metal containing diatomic molecules derived from the analysis of trends in the measured permanent electric dipole moments.

Figure 2. A molecular orbital correlation diagram for the third row transition metal containing diatomic molecules developed from the analysis of the trends in observed dipole moments .

General observations:

- 1) Ab initio predictions for 2nd row metal containing molecules are more reliable than those for the first or third row.

- 2) The finite field predictions for dipole moments are more reliable than those from the expectation value approach. The large discrepancy given between the two theoretical approaches and with the observation shows that even the most sophisticated calculations are greatly under estimating the electron correlation effects.
- 3) All the dipole moments are much less than based on an ionic, point charge, model.
- 4) Configurations that have either the 12σ or 9σ (Figure 1) or 4σ (Figure 2) are greatly reduced from that that do not implying that simultaneous ns and $(n-1)d$ bonding is not favored.

3. Publications

1. "Experimental Determination of Dipole Moments, Hyperfine Interaction and *Ab Initio* Predictions for PtN," K.Y. Jung, T. C. Steimle, D. Dai and K. Balasubramanian, J.Chem. Phys. 102, 643-652 (1995).
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6. "Optical Detection of Yttrium Dicarbide, a "T-Shaped Molecule," T.C. Steimle, A.J. Marr, J. Xin, A. J. Merer, K. Athanassenas, and D. Gillett, J. Chem. Phys. 106, 2060-2066 (1997).
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11. "Permanent Electric Dipole Moments of Metal Containing Molecules", Timothy C. Steimle, Int. Reviews in Physical Chemistry, 19, No. 3, 455-477 (2000).
12. "Permanent Electric Dipole Moment of Yttrium Dicarbide, YC_2 " R. R. Bousquet and Timothy C. Steimle Bousquet, J. Chem. Phys. 114, 1306-1311 (2000).
13. "Rotational Analysis of the $A^2A_1-X^2A_1$ Band System of Yttrium Dicarbide: YC_2 " T.C. Steimle, R.R. Bousquet, K-I Namiki and A.J. Merer J. Mol. Spectroscopy 215, 10-28, (2002).
14. "The permanent electric dipole moments of iron monocarbide, FeC " T.C. Steimle, W. Virgo and David Hostutler, J. Chem. Phys. 117, 1511 (2002).
15. "The permanent electric dipole moments of ruthenium monocarbide, RuC " T.C. Steimle, W. Virgo and J. M. Brown, J. Chem. Phys. 118, 2620-2625 (2003)
16. "The permanent electric dipole moments and magnetic hyperfine interactions of ruthenium mononitride, RuN . Timothy C. Steimle and Wilton Virgo J. Chem. Phys. 118, 12965 (2003).
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18. "The permanent electric dipole moments of WN and ReN and nuclear quadrupole interaction in ReN " Timothy C. Steimle and Wilton Virgo J. Chem. Phys. **121** 12411 (2004).