

Final Technical Report
Generation, Detection and characterization of Gas-Phase Transition Metal containing Molecules
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Timothy C. Steimle
School of Molecular Science
Arizona State University
Tempe, Arizona

I. Scientific Motivation

The results from this study have been published¹⁻²⁷. The objective of this project was to generate, detect, and characterize small, gas-phase, metal containing molecules. The ground and excited electronic state properties we determine were: a) electronic state distributions and lifetimes, b) vibrational frequencies; c) bond lengths and angles, d) hyperfine interactions, e) permanent electric dipole moments, $\vec{\mu}_{el}$, and f) magnetic dipoles, $\vec{\mu}_m$. In general terms, $\vec{\mu}_{el}$ gives insight into the charge distribution and $\vec{\mu}_m$ into the number and nature of the unpaired electrons. In addition to being relevant to high-temperature chemical environments (e.g. plasmas and combustion), gas-phase experiments on metal containing molecules serve as the most direct link to a molecular-level theoretical model for catalysis. In principle, simple gas-phase reactions, such as $\text{Pt} + \text{CH}_4$, can be modeled to the same level of accuracy that is now being achieved for lighter systems such as $\text{Cl} + \text{CH}_4$ ²⁸, $\text{F} + \text{CH}_4$ ²⁹ or $\text{O}(^3\text{P}) + \text{CH}_4$ ³⁰ and the same molecular level insight garnered. The theoretical formalism for predicting cross sections for these simple reactions involves using quasi-classical trajectory methods in conjunction with an accurately calculated, multi-dimensional, potential energy surface (PES). The major limitation for extending the formalism used for the lighter systems to metal containing systems is the current inability to generate high quality PES. Careful evaluation of the performance of the various electronic structure methodologies being developed for PES predictions can be achieved via a comparison of predicted and experimentally measured properties. The small molecules that we studied are the species associated with the bound portions of the multi-dimensional PES. The conceptual framework developed by the experiential/theoretical synergism established for the simple gas-phase systems is applicable to modeling the chemistry of the more extended systems.

Gas-phase reaction studies of metal containing ions³¹⁻³⁷, and the associated theoretical modeling of those systems, are more extensive than those of neutrals studied here due in a large part to the relative ease of ion manipulation and mass-spectroscopic detection. The neutral

molecules of this project are more relevant to the recent reaction studies of neutral metal and metal oxide molecules carried out primarily by Bernstein's group³⁸⁻⁴¹ and by Mafune's group³⁵. Inevitably, experimental studies of the reaction of either neutrals or ions are augmented by electronic structure calculations to predict relative energies of the products, reactants, and plausible transition states (i.e. fixed points on the PES) as a means of achieving a qualitative, mechanistic, understanding of the experimental observations (i.e. the generation of products or depletion of reactants). Although high-level, fully relativistic, wave function theory (WFT) predictions of PES for some simple reactions have been performed; density function theory (DFT) is more often applied⁴²⁻⁴⁶. In addition to being less computationally demanding, it is expected that DFT methods honed for the small systems can be applied to larger, more realistic, catalytic processes.

Electronic structure predictions, whether they are DFT or WFT, need to correctly account for electron-correlation and relativistic effects. The comparison of predicted hyperfine parameters, permanent electric dipole moment, $\vec{\mu}_{el}$, and magnetic dipole moments, $\vec{\mu}_m$ with our measured values is the most direct method of assessing various molecular relativistic Hamiltonians. As is well known, the hyperfine structure is a very sensitive probe of its electronic wavefunction, which allows its molecular orbital character to be modeled. Consider for example, the axial nuclear quadrupole hyperfine parameter for a linear molecule, eq_0Q :

$$eq_0Q(\text{MHz}) = Q \left[\frac{e \times 10^{-6}}{4\pi\epsilon_0 h} \right] \langle \Lambda | \sum_i \frac{(3\cos\theta_i - 1)}{r_i^3} | \Lambda \rangle, \quad (1)$$

where θ_i and r_i are the polar coordinates relative to the non-zero spin nuclei and the summation runs over all electrons. eq_0Q is the product of the nuclear quadrupole moment, Q , and the expectation value of the axial component of the electric field gradient (EFG) tensor, eq_0 . Since eq_0Q involves an operator proportional to r^{-3} , it is most sensitive to the electronic wave function in the immediate vicinity of the nucleus, which is precisely where relativistic effects are most pronounced. Similar to eq_0Q , magnetic hyperfine parameters (mhf) (i.e. the Fermi contact, b_F , parameter and electric dipole-nuclear dipole magnetic tensor) are sensitive to the nature of the wave function in the region of the nuclei. For a linear molecule there are four

magnetic hyperfine parameters (a , b_F , c and d) which are related to the electronic wave function by:

$$a/\text{Hz} = \left(\frac{\mu_0}{4\pi\hbar} \right) g_e g_N \mu_B \mu_N \frac{1}{\Lambda} \langle \Lambda \Sigma = S | \sum_i \frac{\hat{\mathbf{l}}_{zi}}{r_i^3} | \Lambda \Sigma = S \rangle_L \quad (2)$$

$$b_F/\text{Hz} = \left(\frac{\mu_0}{4\pi\hbar} \right) \left(\frac{8\pi}{3} \right) g_e g_N \mu_B \mu_N \frac{1}{S} \langle \Lambda \Sigma = S | \sum_i \hat{\mathbf{s}}_z \delta_i(r) | \Lambda \Sigma = S \rangle_S \quad (3)$$

$$c/\text{Hz} = \left(\frac{\mu_0}{4\pi\hbar} \right) \frac{3}{2} g_e g_N \mu_B \mu_N \frac{1}{S} \langle \Lambda \Sigma = S | \sum_i \hat{\mathbf{s}}_{iz} \frac{(3 \cos^2 \Theta_i - 1)}{r_i^3} | \Lambda \Sigma = S \rangle_S \quad (4)$$

$$d/\text{Hz} = \left(\frac{\mu_0}{4\pi\hbar} \right) \frac{3}{2} g_e g_N \mu_B \mu_N \frac{1}{S} \langle \Lambda = 1 \Sigma = S | \sum_i \hat{\mathbf{s}}_{i-} \frac{(\sin \Theta_i)}{r_i^3} | \Lambda = -1 \Sigma + 1 \rangle_S \quad (5)$$

In Eqs. 2 -5 $\delta_i(r)$ is the Dirac delta function, $\hat{\mathbf{s}}_{iz}$ the z-component of the spin angular momentum operator and, Θ_i and r_i are the polar coordinates of i^{th} unpaired electron. $\hat{\mathbf{s}}_{i-}$ is the spin lowering operator, Λ and Σ are total electronic orbital and spin molecule fixed projection quantum numbers. A major objective of this research was to determine a , b_F , c , d and $eq_0 Q$ and then use relationships given in Eqs. 1-5 to garner insight into the electronic wavefunctions $\Psi^{el} = |n, \Lambda, \Sigma\rangle$. Often only certain linear combinations of the a , b_F , c and d , defined as h_Ω , can be experimentally determined where :

$$h_\Omega \equiv a\Lambda + \left(b_F + \frac{2}{3}c \right) \Sigma. \quad (6)$$

The electric dipole moments were extracted from the analysis of the spectral shifts induced by a static electric field (i.e. the Stark effect). The Stark Hamiltonian was taken simply as

$$\hat{H}^{Stark} = -\vec{\mu}_e \cdot \vec{E} = -\mu_e E \cos(\theta) \quad (7)$$

where E is the electric field. The magnetic g-factors were extracted from the analysis of the spectral shifts induced by the application of a static magnetic field (i.e. the Zeeman effect). The electric dipole moments Zeeman Hamiltonian was taken to be

$$\hat{H}^{Zeeman} = -\vec{\mu}_m \cdot \vec{B} = \mu_0 T^l(B) \cdot \left[\sum_i g_l T^l(l_i) + g_s T^l(s_i) \right] \quad (8)$$

where μ_0 is the Bohr magneton, B the magnetic flux in Gauss and g_l and g_s are the electronic orbital and spin g-factors.

III. Experimental Approach

We developed, and implemented, a wide variety of spectroscopic methods for the detection and characterization of metal containing molecules during the course of this work. The bulk of the spectroscopic techniques exploit the sensitivity of laser induced fluorescence (LIF) detection. The spectroscopic schemes employed included: a) cw and pulsed laser field-free (FF) excitation and dispersed LIF (DLIF); b) optical Stark; c) optical Zeeman; d) pump/probe microwave double resonance (PPMODR); e) fluorescence lifetimes, and f) resonant and non-resonant two-photon ionization TOF mass spectrometry. Vibrational spacing, force constants and electronic states distributions were derived from the analysis of pulsed dye laser excitation and DLIF spectra. Geometric structure (bond lengths and angles) and hyperfine parameters were derived from the analysis of cw-laser LIF and PPMODR spectra. Permanent electric dipole moments, $\vec{\mu}_{el}$, and magnetic dipole moments, $\vec{\mu}_m$, were derived from the analysis of optical Stark and Zeeman spectra, respectively. Transition moments were derived from the analysis of radiative lifetimes. The spectral resolution of the pulsed, cw, and PPMODR techniques were approximately 300 MHz, 30 MHz, and 30 kHz, respectively. A supersonic molecular beam sample was generated by skimming the products of either a laser ablation/reaction source or a d.c. discharge source. TOF mass spectrometry was also used to aid in the molecular identification. In many cases this is the first detection of the molecule.

IV. Results

A. Electric dipole moments

Table 1 is a composite of the determined $\vec{\mu}_{el}$ values, which include 3d (TiO₂, VS, CuO, and CoO), 4d (RuF and MoC), 5d (RhO, RhN, RhS, IrF, PtF, IrSi, and AuF,) transition metal containing molecules, lanthanides (NdO, CeO, and PrO) and actinides (UO, ThS and UF). The observed wide variation in $\vec{\mu}_{el}$ values (e.g. IrSi (0.414 D) to ThS (6.72D)) is a result of numerous contributions to the change in bonding. A general observation is that $\vec{\mu}_{el}$ for excited electronic states tends to be smaller than those for the ground state due in part to the enhanced polarizability. It is also observed that theoretical predictions for excited state $\vec{\mu}_{el}$ values, when available, are in very poor agreement with

the observations. Although predicting both ground and excited state $\vec{\mu}_{el}$ values for the heavier metal containing molecules remains a major theoretical challenge, it was often possible to rationalize trends in the observed $\vec{\mu}_{el}$ values using simple molecular orbital correlation diagrams.

B. Magnetic g-factors

Table 2 is a composite of the determined effective magnetic g-values, which includes a $5d(\text{AuF}_3)$ transition metal containing molecule, lanthanides (NdO , HoO and PrO) and actinides (UO and UF). The late lanthanide oxide, HoO , has an extremely large g-value due to the dominate $\text{Ho}^{+2}(4f^{10}6s)$ configuration. The $4f^{10}$ electrons couple to give a $^5I_8$ term which then couples with the $6s$ electron to give a total electronic angular momentum, J_A , 8.5 and 7.5 for $\text{Ho}^{+2}(4f^{10}6s)$. The various coupling of $\text{Ho}^{+2}(4f^{10}6s)$ electrons produces a 65 possible low-lying electronic states. The very complex electronic state distribution of HoO , and other lanthanide monoxides, is caused by the insensitivity of the electronic energies to the numerous possible arrangements of the Ln^{2+} electrons in the $4f$ and $6s$ orbitals. The insensitivity of the electronic energies to the various occupations of the Ln^{2+} $4f$ and $6s$ orbitals also implies that disentangling the complex optical spectra may be aided by using simple ligand field theory (LFT) to establish the global electronic structure for the low-lying electronic states. We implemented this quasi-atomic picture based upon the highly insightful ligand-field theory (LFT) to develop a description of bonding and to rationalize the observed g-factors for the lanthanides.

C. Hyperfine interactions

Table 3 is a composite of the determined hyperfine parameters which include $3d$ (CoF and CoO), $4d$ (RuF and RuC), and $5d$ (RhO , RhN , RhS , IrF , IrSi , PtF , PtC , and PtN), transition metal containing molecules. Given that electronic structure calculations rarely predict hyperfine parameters, the results were interpreted using a semi-quantitative approach that used experimentally observed atomic hyperfine structure (an ‘atoms in molecule’ approach). In this approach a molecular orbital correlation diagram is constructed from which the molecular orbitals are written as linear combinations of atomic orbitals (LCAO). The spin-adapted wavefunctions for the molecular electronic states were then written as linear combinations of Slater determinants involving the predicted LCAO

molecular orbitals. The expectation values of the hyperfine operators were then derived from the rules for calculating the matrix elements of one-electron operators over Slater determinants. The experimentally derived atomic parameters were then used to estimate the expectation values such as $\langle 4s|\delta(r)|4s\rangle_s$, $\langle 3d|r^{-3}|3d\rangle_s$ and $\langle 3d|r^{-3}|3d\rangle_l$. The coefficients of the LCAO are then optimized by comparison of the predicted hyperfine parameters with the observed values. A very useful, and insightful, description of the electronic states results from this approach.

D. Detection and characterization of TiO₂ and ZrO₂

Among the more important of the numerous technological applications of TiO₂ and ZrO₂ clusters and nanoparticles are their uses as photocatalysts to degrade organic pollutants or to perform other useful chemical transformations. Studies of gas-phase clusters of TiO₂ and ZrO₂ provide a practical experimental and theoretical means of gaining a molecular level understanding of the properties that influence the activity of TiO₂ clusters and the isomeric dependence of absorption. Insight into the chemical activity of bulk TiO₂ and ZrO₂ may also be revealed from studies of clusters. A comparison of theoretically and experimentally derived properties for the monomer is the primary means of assessing methodologies being implemented for predicting the properties of clusters of TiO₂ and ZrO₂. The permanent electric dipole moments, vibrational frequencies and geometric structure for the ground and low-lying excited states of molecular TiO₂ using optical spectroscopy were determined^{11,13}. In addition to providing the most direct measure of the polarity of a Ti-O chemical bond, the permanent electric dipole moment is relevant to the description of numerous physical phenomena including the absorption and emission of light. Theoretical predictions for TiO₂ were shown to be in excellent agreement with the experimentally derived properties for the $\tilde{X}^1A_1$ state, but in poor agreement for those of the $\tilde{A}^1B_2$ state. Similarly the observed transition frequencies of forty five bands in the LIF, REMPI, and dispersed fluorescence spectra of ZrO₂ were analyzed to produce origin and harmonic vibrational parameters for the $\tilde{A}^1B_2$ and $\tilde{X}^1A_1$ states of this molecule¹⁶. The spectra both TiO₂ and ZrO₂ were modeled using a normal coordinate analysis and Franck-Condon factor predictions.

Table. 1 Experimentally determined permanent electric dipole moments.

Mol.	State	$\vec{\mu}_{el}$ (D)	Ref.	Mol.	State	$\vec{\mu}_{el}$ (D)	Ref.
UO	X(1)4	3.363(26)	1	CuO	$X^2\Pi_{3/2}$	4.57(3)	12
	[18403]5	2.684(31)	1		$A^3\Sigma^+$	1.12(71)	12
	[18404]5	3.110(24)	1	TiO ₂	$\tilde{A}^1B_2(100)$	5.00(5)	13
¹⁰⁴ RuF	$X^4\Phi_{9/2}$	5.34(7)	3		$\tilde{A}^1B_2(110)$	4.98(7)	13
	[18.2]5.5	1.97(8)	3	VS	$X^4\Sigma^-$	5.16(5)	14
¹⁰³ RhO	$X^4\Sigma^-$	3.81(2)	4		$C^4\Sigma^-$	2.38(13)	14
¹⁰³ Rh ¹⁴ N	$X^1\Sigma^+$	2.43(5)	5	IrF	$X^3\Phi_4$	2.82(6)	15
	[15.1](v=1)	1.75(1)	5		$A^3\Phi_4$	1.88(5)	15
¹⁰³ RhS	$X^4\Sigma^-$	3.40(2)	6	PtF	$X^2\Pi_{3/2}$	3.42(6)	19
MoC	$X^3\Sigma^-$	6.07(2)	7		[11.9]3/2	2.47(11)	19
	[18.6]1	2.68(1)	7	IrSi	$X^2\Delta_{5/2}$	-0.414(6)	21
NdO	X4	3.369(13)	8		[16.0]1.5	0.782(6)	21
	[16.7]3	3.742(16)	8	AuF	$X^1\Sigma^+$	4.13(2)	22
CeO	X ₁ 2	3.119(8)	9		[17.8]0 ⁺	2.03(5)	22
	X ₁ 3	3.115(7)	9	ThS	$X^1\Sigma^+$	4.58(10)	25
	[16.5]2	2.119(8)	9		[18.26]1	6.72(5)	25
PrO	X ₂ Ω=4.5	3.01(6)	10	UF	X(1)4.5	2.01(1)	26
	[18.1] Ω=5.5	4.72(5)	10		[18.6]3.5	1.88(1)	26
TiO ₂	$\tilde{X}^1A_1(000)$	6.33(7)	11	CoO	$X^4\Delta_{7/2}(v=0)$	4.18(5)	27
	$\tilde{A}^1B_2(000)$	2.55(8)	11		$E^4\Delta_{7/2}(v=0)$	3.28(5)	27

Table. 2 Experimentally determined magnetic g-factors.

Mol.	State	g_e	Ref.	Mol.	State	g_e	Ref.
UO	X(1)4	2.562(12)	1	HoO	X ₂ 8.5, J=8.5	11.04(2)	18
	[18403]5	3.508(14)	1		[17.6]7.5, J=7.5	10.04(2)	18
	[18404]5	4.837(13)	1		[17.6]7.5, J=8.5	9.86(2)	18
NdO	X4	2.116(6)	8	AuF	[17.8]0 ⁺	0.82(20)	22
	[16.7]3, J=3	2.084(6)	8	UF	X(1)4.5	3.28(1)	26
	[16.7]3, J=4	2.178(8)	8		[18.6]3.5	3.26(1)	26
PrO	X ₂ 4.5, J=4.5	4.48(8)	10				
	[18.1] 5.5, J=5.5	5.73(6)	10				

Table. 3 Experimentally determined hyperfine parameters.

Mol.	State	Par(cm ⁻¹)	Ref.	Mol.	State	Par(cm ⁻¹)	Ref.
CoF	$X^3\Phi_i$	h_4 (Co): 0.0324581(22) h_3 (Co):0.05239(39) eQq_d (Co):-0.002603(99) h_3 (F):0.007787(39)	2	PtF	$X^3\Pi_{3/2}$	$h_{3/2}$ (¹⁹⁵ Pt):0.02385(42) $h_{3/2}$ (F):0.01088(46)	19
	$[18.8]^3\Phi_i$	h_4 (Co): 0.09540(13) h_3 (Co):0.03790(87) h_3 (F):0.00946(78)	2		$[11.9]3/2(v=0)$	$h_{3/2}$ (¹⁹⁵ Pt):0.05900(57) $h_{3/2}$ (F):-0.00642(55)	
¹⁰⁴ RuF	$X^4\Phi_{9/2}$	$h_{9/2}$ (F):0.00931(6)	3		$[11.9]3/2(v=1)$	$h_{3/2}$ (¹⁹⁵ Pt):0.05881(56) $h_{3/2}$ (F):-0.00597(57)	19
	$[18.2]5.5$	$h_{11/2}$ (F):0.0484(20)	3	PtC	$X^1\Sigma^+$	C^{eff} (Pt):4.60(36)×10 ⁻⁶	20
¹⁰³ RhO	$X^4\Sigma^-$	b_F (Rh): -0.00698(32)	4	IrSi	$X^3\Delta_{5/2}$	$h_{5/2}$ (¹⁹¹ Ir):0.00501(13) $h_{5/2}$ (¹⁹³ Ir):0.00553(13) eQq_d (¹⁹¹ Ir):-0.00334(63) eQq_d (¹⁹³ Ir):-0.00403(64)	21
	$[15.8]^2\Pi_{1/2}$	d (Rh):0.00504(90)	4		$[16.0]1.5$	$h_{3/2}$ (¹⁹¹ Ir):0.00533(22) $h_{3/2}$ (¹⁹³ Ir):0.00622(21) eQq_d (¹⁹¹ Ir):-0.00518(79) eQq_d (¹⁹³ Ir):-0.00672(67)	
	$[16.0]^2\Pi_{1/2}$	d (Rh):0.0025	4		$[16.0]3.5$	$h_{7/2}$ (¹⁹¹ Ir):0.00261(14) $h_{7/2}$ (¹⁹³ Ir):0.00282(14) eQq_d (¹⁹¹ Ir):-0.00444(69) eQq_d (¹⁹³ Ir):-0.00389(67)	
¹⁰³ Rh ¹⁴ N	$[15.1](v=0)$	a (Rh):-0.018(4)	5	RuC	$X^1\Sigma^+$	eQq_d (¹⁰¹ Ru):0.01445(24) C^{eff} (¹⁰¹ Ru):-1.63(18)×10 ⁻⁶	23
	$[15.1](v=1)$	a (Rh):-0.014(4) a (N):-0.0011(3)	5	PtN	$X^3\Pi_{1/2}$	$h_{1/2}$ (¹⁹⁵ Pt):0.0639 d (¹⁹⁵ Pt):-0.0034 $h_{1/2}$ (N):0.00213(7) d (N):-0.00207(11)	24
¹⁰³ Rh ¹⁵ N	$[15.1](v=0)$	a (Rh):-0.019(4)	5		$A^2\Sigma^-$	b_F (¹⁹⁵ Pt):0.2307(14) c (¹⁹⁵ Pt):0.0777(56) b_F (N):0.00067(7) c (N):-0.0019(2)	24
¹⁰³ RhS	$X^4\Sigma^-$	b_F (Rh):-0.00574(14)	6	CoO	$E^4\Delta_{7/2}(v=0)$	$h_{7/2}$ (Co):0.057034(72) eQq_d (Co):-0.0032(16)	27
		c (Rh):-0.00213(42)	6		$E^4\Delta_{7/2}(v=1)$	$h_{7/2}$ (Co):0.05664(12)	27
	$[16.0]^2\Pi_{1/2}$	b_F (Rh):0.00603(49)	6				
		d (Rh):0.00931(14)	6				
IrF	$X^3\Phi_4(v=0)$	h_4 (¹⁹¹ Ir): 0.00787(18) h_4 (¹⁹³ Ir): 0.00882(13) h_4 (F): 0.00882(24) eQq_d (¹⁹¹ Ir):-0.01215(108) eQq_d (¹⁹³ Ir):-0.01003(64)	17				
	$A^3\Phi_4(v=0)$	h_4 (¹⁹¹ Ir): 0.01360(18) h_4 (¹⁹³ Ir): 0.01494(11) h_4 (F): 0.01410(24) eQq_d (¹⁹¹ Ir):-0.04324(77) eQq_d (¹⁹³ Ir):-0.03870(53)	17				

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