

Comparison of
Ab Initio
Quantum Chemistry
with Experiment
for
Small Molecules

The State of the Art

edited by Rodney J. Bartlett

Comparison of *Ab Initio* Quantum Chemistry with Experiment for Small Molecules

The State of the Art

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edited by

Rodney J. Bartlett

*Quantum Theory Project,
University of Florida, U.S.A.*

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FOREWORD

At the American Chemical Society meeting in Philadelphia, Pennsylvania, U.S.A., a symposium was organized entitled, "Comparison of Ab Initio Quantum Chemistry with Experiment: State-of-the-Art." The intent of the symposium was to bring together forefront experimentalists, who perform the types of clean, penetrating experiments that are amenable to thorough theoretical analysis, with inventive theoreticians who have developed high accuracy ab initio methods that are capable of competing favorably with experiment, to assess the current applicability of theoretical methods in chemistry. Contributions from many of those speakers (see Appendix A) plus others selected for their expertise in the subject are contained in this volume.

Such a book is especially timely, since with the recent development of new, more accurate and powerful ab initio methods coupled with the exceptional progress achieved in computational equipment, ab initio quantum chemistry is now often able to offer a third voice to resolve experimental discrepancies, assist essentially in the interpretation of experiments, and frequently, provide quantitatively accurate results for molecular properties that are not available from experiment.

Recent successes of ab initio theory include the singlet-triplet energy separation in methylene, the prediction of a non Van der Waal's bound ground state for Be_2 , and the experimental identification via theoretical predictions of numerous cations like H_3O^+ and NH_4^+ , to name just a few well-known examples. But there are also apparent failures, as in many studies of Be_2 that missed the inner minimum, the equilibrium geometry and binding energy in the Cr_2 dimer, and questions surrounding the activation barrier in the $\text{F}+\text{H}_2$ chemical laser reaction, among others. The successes and failures of ab initio theory are a constant subject of contention among experimentalists and

theoreticians. This book attempts to provide a partial answer to what can be accomplished at the current state-of-the-art and identifies limitations where the theory still requires development.

Many research areas, sparked by the synergism among theorists and experimentalists, are addressed in this volume. These include such exciting topics as: the nature and bonding in small metal clusters and their catalytic activity; the spectroscopic identification and characterization of weakly bonded molecules like $\text{CO}_2 \cdot \text{NCH}$; many detailed studies of reaction paths and activation barriers in chemical reactions, including the characterization of reaction intermediates; the availability of very complete spectroscopic data for classes of small molecules like alkali hydrides, alkali dimers, and alkaline earth hydroxides, most of which would not be available from experiment alone; and careful predictions of energy transfer processes for molecular processes through the cooperative efforts of quantum chemists, who predict potential energy surfaces, and dynamicists, who use these surfaces to calculate the probabilities ("cross-sections") for different events to occur.

Although it is impossible for any one book to cover the wealth of contributions ab initio theory can now make to chemistry, or to assess its limitations, this volume provides a selection of topics by leaders in the field, both experimentalists and theoreticians, where theory has been instrumental in explaining, quantifying, and predicting properties of molecules. The book also identifies classes of problems for which detailed experimental data are forthcoming, and which will challenge future theoretical efforts. We hope the papers herein will serve as a reference point from which future progress may be measured.

Rodney J. Bartlett
Professor of Chemistry and Physics
University of Florida
and
Chairman of the Subdivision of
Theoretical Chemistry,
American Chemical Society

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The American Chemical Society symposium and this Proceedings on "Comparison of Ab Initio Quantum Chemistry: State-of-the-Art," was sponsored by Floating Point Systems of Portland, Oregon, U.S.A. Their help made it possible to prepare this volume and to present a symposium of very high quality. The participants, the authors, and I greatly appreciate their assistance.

This entire volume has been typed, supervised and organized by Ms. Jody-Kate Fisher. Considering the corrections and changes forced upon her in three or more levels of proofing, the innate difficulty with equations and scientific terminology, not to mention an often recalcitrant word processor, her effort was stupendous. Without Jody, we could not have undertaken this project. Thanks!

Also, I imposed upon members of my research group to help me in proofing this volume to attempt to ensure as much accuracy as possible. Hence, let me thank Dr. Sam Cole, Dr. George Fitzgerald, Dr. Robert Harrison, Dr. Bill Laidig, Mr. David Magers, Mr. Alan Salter and Mr. Gary Trucks for their help in preparing this volume.

Rodney J. Bartlett

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MOLECULAR INFORMATION FROM ESR SPECTRA: TRANSITION METAL MOLECULES

W. Weltner, Jr. and R.J. Van Zee
Department of Chemistry
University of Florida
Gainesville, Florida 32611

ABSTRACT. Electron spin resonance (ESR) spectroscopy at low temperatures can provide detailed electronic and magnetic properties of reactive molecules, such as their multiplicities, zero-field splittings, and hyperfine interaction constants. This has proved to be particularly valuable in the study of small transition metal molecules and clusters where ab initio theory is also being applied. A review of the experimental and theoretical knowledge of those molecules is brought up to date.

1. INTRODUCTION

Electron spin resonance (ESR) is a form of high resolution spectroscopy, and when it is applicable it can provide, directly, information that is usually obtained only by detailed analysis of optical spectra. ESR provides the most information when applied to gas-phase molecules, as done so successfully by Radford [1] and Carrington [2] and their coworkers, but the problems associated with maintaining a high enough concentration of reactive molecules in an ESR cavity have severely limited its application to gases. One can, however, trap most such recalcitrant species in rare gas matrices at low temperatures and measure their spectra by the conventional methods used for frozen glasses [3]. The spectra are then those of rigidly-held, randomly-oriented (not necessarily! [4]) molecules isolated from each other by a relatively nonperturbing medium. The loss in

rotational information in the gas phase must then be considered to be compensated by the wealth of magnetic and electronic information that can still be obtained from the solid state spectra. These matrix ESR spectra can establish the multiplicity and symmetry of the ground electronic state, g tensor components, zero-field splittings, hyperfine interaction constants and approximate spin densities, nuclear quadrupole coupling constants, and spin-rotation constants [3].

Figure 1 illustrates, in a very approximate way, the transitions observed and the significance of the Zeeman splittings occurring when a $^5\Sigma$ molecule (such as Sc_2 [5]) is placed in a magnetic field. Observation and analysis of fine structure transitions will yield g tensor components and zero-field splitting parameters (here b_2^0 and b_4^0) and further splittings within these levels due to magnetic nuclei produce hyperfine structure (hfs). Then all of the molecular parameters can be derived in the spin Hamiltonian, which is, for this $S = 2$ molecule:

$$\begin{aligned}
 H = & g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + b_2^0 [S_z^2 - \frac{1}{3} S(S+1)] + \\
 & + \frac{1}{60} b_4^0 (35S_z^4 - 155S_z^2 + 72) + \sum_i [A_{\parallel}^i S_z^i I_z^i + A_{\perp}^i (S_x^i I_x^i + \\
 & + S_y^i I_y^i)].
 \end{aligned}$$

Furthermore, the identity of the molecule being observed is established if hyperfine structure data from all nuclei can be obtained. For example, in the study of the $^2\Sigma$ TiCo molecule [23], the hfs due to each nucleus can be detected if the molecule is prepared from isotopically-enriched ^{47}Ti (see Fig. 2), thus identifying the molecule being observed as diatomic TiCo.

2. TRANSITION METAL MOLECULES

A review of the status of our knowledge of these molecules up to January, 1984, has recently appeared [7] in which all experimental and theoretical work on well characterized transition-metal molecules has been cited and discussed. As pointed out there, although many diato-

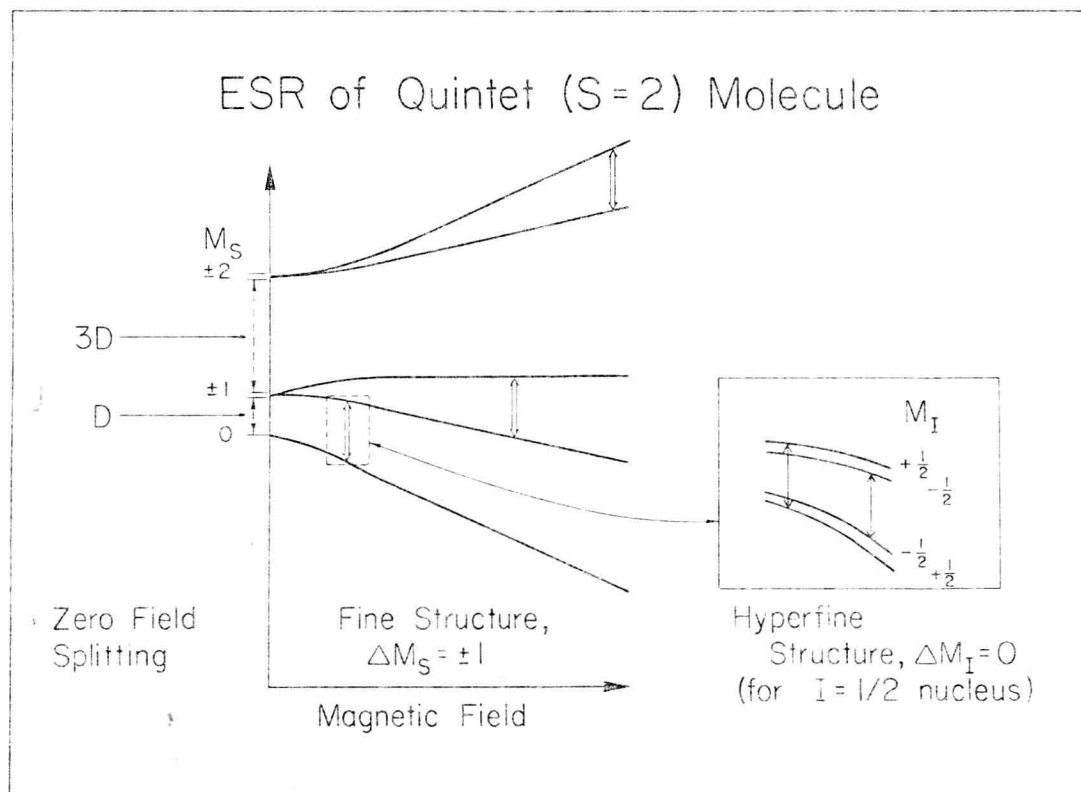


Figure 1. Depiction of Zeeman effect and the approximate transitions observed in the ESR spectrum of a $^5\Sigma$ molecule.

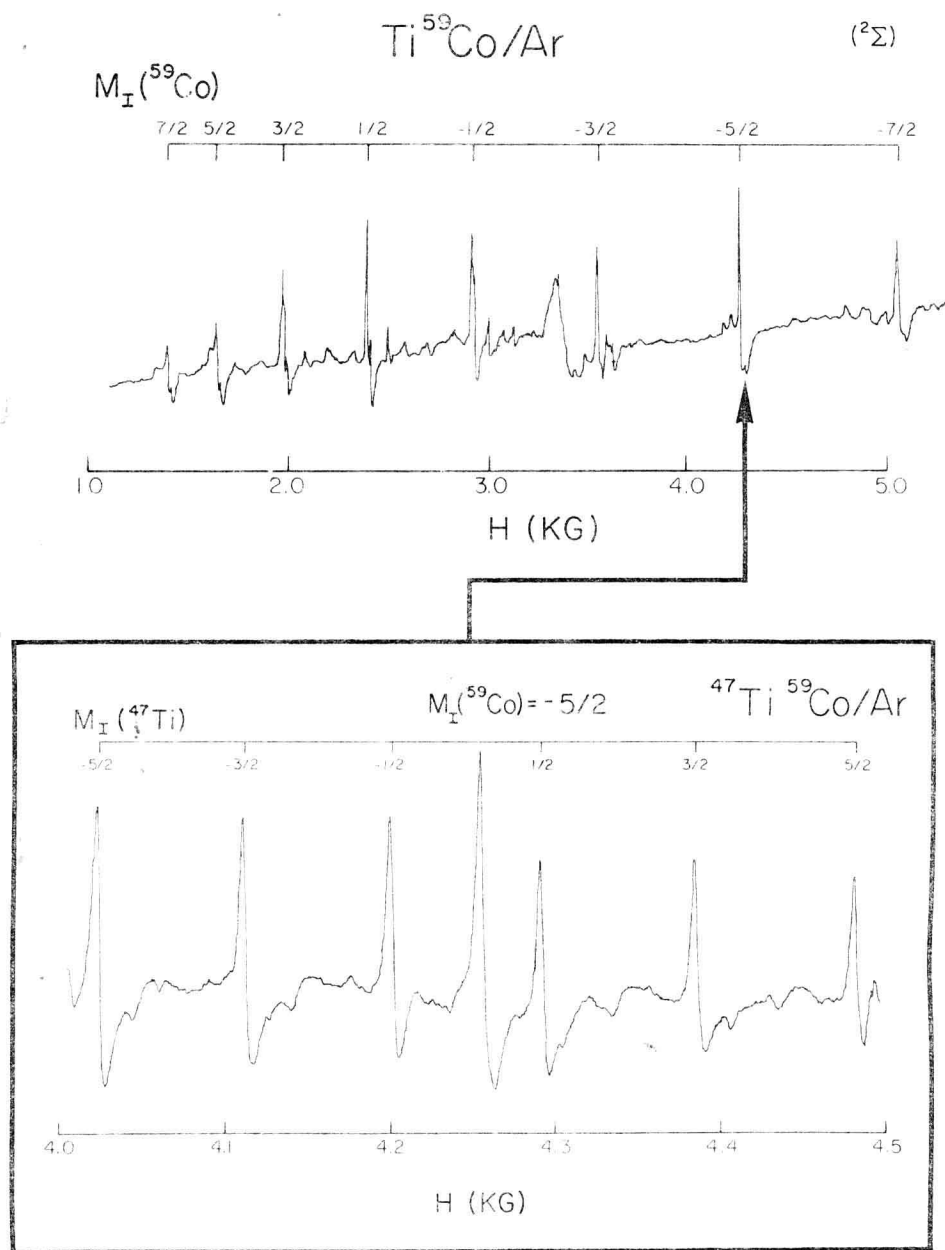


Figure 2. Top: ESR spectrum of the $\text{Ti}^{59}\text{Co} (^2\Sigma)$ molecule where $I(^{59}\text{Co}) = 7/2$. Bottom: additional splitting of each line when titanium metal enriched to 80% in ^{47}Ti ($I=5/2$) is vaporized along with cobalt metal [23].

mics fall in this category, detailed information about larger molecules is scarce. This is in spite of the detection of clusters of transition metals containing up to more than 20 atoms in supersonically-expanded [8] and thermally quenched [9] beams. All-electron theory has been applied, usually to diatomics, but even to clusters of 13 atoms.

Since that review many relevant publications have appeared. The Proceedings of a Bunsen-Kolloquium on "Experiments on Clusters" in October, 1983, has been published as a volume of the *Berichte der Bunsen-Gesellschaft für Physicalische Chemie* [10]. Among those papers is a review of their supersonic beam work on transition metal molecules by Morse and Smalley [11], and a preliminary report, later published in full [12], by Flad, Igel, Preuss and Stoll on Cu_n , Cu_n^+ , Ag_n , Ag_n^+ ($n \leq 4$) calculations. Here Table 1 cites that work and other recent experimental and theoretical papers published since January 1984 and/or omitted from the earlier review.

The role of ESR in the characterization of transition metal molecules is made more apparent by considering the diatomics formed from first-row elements. Figure 3 shows an array of all possible such diatomics, similar to one published earlier [7], but here also indicating the sources of information. Those molecules in bold frames are well characterized in that at least their ground electronic states have been established; one notes that seven have been determined via matrix ESR work. V_2 [25] and Cr_2 [26] have been observed in the gas-phase and their optical spectra analyzed. Ni_2 [15] has also been produced in a supersonically-cooled beam, but the complexity of its spectrum has made analysis difficult. A lowest $^1\Gamma_g$ or $^3\Gamma_u$ state, as suggested by theory [27], is consistent with the observations. The ground states given for diatomics containing Fe have been inferred from their Mössbauer spectra. In general, deduction of the ground state from such data is difficult, as shown by the calculations of Guenzburger and Saitovich [28] and Montano, et al [29]. TiFe and the three other molecules ScCo , TiNi , and VCo have been indicated as $^1\Sigma$ in this array. This state has been deduced from their adjacent $^2\Sigma$ molecules ScNi and

Table 1. Recent experimental and theoretical research on transition
metal molecules^a

Cr_2	Exptl:	optical spectra in matrices, absorption and emission	Pellin and Gruen [13]
	Theor:	comparison of HF-LCAO, GVB, $X\alpha$ -LCAO, and LDF-LCAO	Messmer [14]
		LCAO-LSD and $X\alpha$	Baykara et al. [14a]
Ni_2	Exptl:	spectroscopy in supersonic beam	Morse et al. [15]
Cu_2	Exptl:	optical spectra in solid neon, absorption and emission	Kolb et al. [16]
	Theor:	CAS SCF/SDCI or POLCI	Bauschlicher [17]
		ECP/UHF-SCF/LSD	Flad et al. [12]
		LCAO-MO-SCF	Cingi et al. [18]
Pd_2	Theor:	all electron HF-CI	Shim and Gingerich [19]
Ag_2	Theor:	ECP/UHF-SCF/LSD	Flad et al. [12]
		relativistic SCF- $X\alpha$ -Dirac-SW	Rabii and Yang [20]
		relativistic ECP/LSD	Martins and Andreoni [21]
		LCAO-MO-SCF	Cingi et al. [18]
Au_2	Theor:	relativistic ECP	Pitzer [22]
		relativistic SCF- $X\alpha$ -Dirac-SW	Rabii and Yang [20]
Mo_2	Theor:	comparison of HF-LCAO, GVB $X\alpha$ -LCAO, and LDF-LCAO	Messmer [14]

Table 1 (cont.)

	LCAO-LSD and $X\alpha$	Baykara et al. [14a]
ScNi, TiCo		
Exptl:	ESR in matrices	Van Zee and Weltner [23]
$\text{Cu}_{3,4}, \text{Ag}_{3,4}$		
Theor:	ECP/UHF-SCF/LSD	Flad et al. [12]
CuAg_4 and Cu_2Ag_3		
Exptl:	ESR in cyclohexane matrices	Howard et al. [24]
Cu_{13}		
Theor:	$X\alpha$ -SW and HF	Messmer [14]

^a This is an extension of the review in reference 7. See footnote 3 there for the meanings of the initialisms used here. Additional ones are LDF, local density functional and SDCI, single double configuration interaction.

TRANSITION METAL DIATOMICS

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
$^5\Sigma$						$^1\Sigma$	$^2\Sigma$		Sc
	$^1\Sigma$	$^4\Sigma$			$^1\Sigma$	$^2\Sigma$	$^1\Sigma$		Ti
		$^3\Sigma$				$^1\Sigma$	$^4\Sigma$		V
			$^1\Sigma$		$^7\Sigma$			$^4\Sigma$	Cr
				$^1\Sigma$	$^4\Pi$			$^5\Pi$	Mn
					$^7\Delta$	$^6\Sigma$	$^5\Pi$	$^2\Pi$	Fe
						$^5\Sigma$			Co
							$^1\Gamma$	$^2\Delta$	Ni
								$^1\Sigma$	Cu

GAS PHASE

ESR/MATRIX

MÖSSBAUER/MATRIX

INFERRED FROM EXPT.

THEORY

Figure 3. An array of all possible diatomic molecules formed from the first-row transition metals. The ground states of those in bold frames have been established experimentally. The source of information about each molecule is indicated.

TiCo by addition or subtraction of one electron in a half-filled σ orbital. ScCu would also fit into this category, but the stability of the d^{10} shell of Cu makes the validity of such an extrapolation less likely, so that it was not assigned a ground state in the array. Ab initio theory has been applied to all of the homonuclear molecules in this array and particularly to Cr_2 , Ni_2 and Cu_2 . We refer the reader to the earlier review [7] for discussion and references. Recently Walch, Bauschlicher et al. [30] have extended their calculations on Sc_2 , Ti_2 , V_2 and Cr_2 to TiV [6].

Sc_2 and Mn_2 exhibit quite different bonding and also illustrate a good interaction between theory and experiment. Sc_2 is the simplest transition-metal diatomic, but theory has predicted several possible ground states. The ESR spectrum was unambiguous, since natural Sc is 100% ^{45}Sc ($I = 7/2$), and it definitely established a $^5\Sigma$ ground state [5]. Following that, Walch and Bauschlicher showed that it was necessary to consider molecular states formed from the ground state 2D atom and an excited 4F atom in the calculation and then one obtained the strongly bound $X^5\Sigma$ state [31].

Mn_2 is an entirely different case because of the large promotion energy of the $3d^5 4s^2 \rightarrow 3d^6 4s$ excitation in the Mn atom [32]. This dictates against strong bond formation. The calculations made by Nesbet in 1964 suggested a very weak bond with $r = 2.88 \text{ \AA}$ and antiferromagnetic coupling of the ten d electrons to yield a $^1\Sigma$ lowest state but with an exchange coupling constant J of only 4 cm^{-1} [33]. This picture was essentially corroborated by the variations in the ESR spectra taken between 4 and $70^\circ K$ [34]. Again, because of the hfs, the identity of the molecule being observed was assured. As the temperature was raised, more and more fine-structure transitions were observed corresponding to successive population of the $S = 1, 2$, and 3 states. From the variation in intensity with temperature $J = -9(3) \text{ cm}^{-1}$ was derived, in excellent agreement with Nesbet's value. Furthermore, analysis of the spectral lines assigned to each spin state yielded anisotropic exchange contributions expected to vary as $\langle 1/r^3 \rangle$, where r is the interatomic distance in Mn_2 . r was found to 3.4 \AA , indicating