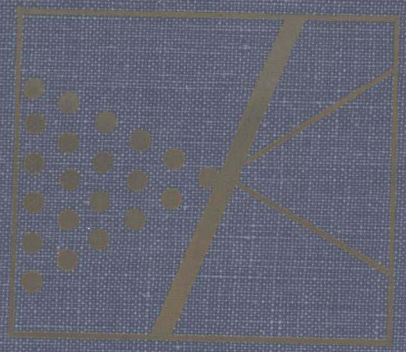

# Mössbauer Spectroscopy and Its Chemical Applications

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Based on a symposium jointly sponsored by the Divisions of Nuclear Chemistry and Technology and Inorganic Chemistry at the 179th Meeting of the American Chemical Society, Houston, Texas, March 24–26, 1980.

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# FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the ADVANCES IN CHEMISTRY SERIES maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

# PREFACE

Mössbauer spectroscopy has matured to the point that the experimental parameters can be obtained and fairly well understood, so the usefulness of the technique to study problems in a number of areas is being explored vigorously. The great diversity of applications is evident immediately upon scanning the main category headings in this volume. Valuable information is being obtained, much of which is contained herein. Mössbauer spectroscopy has been used in conjunction with other forms of spectroscopy to maximize understanding of particular systems. Several chapters, most of them using $^{57}Fe$, are demonstrations of ways in which very specific environments in materials such as catalysts, biological species, and surfaces can be investigated. The uses of the technique as an analytical tool for quantitative studies and in fast-time studies are also covered.

Specifically, the book is composed of seven extended papers and more than twenty short papers. These were selected from among those presented at the symposium upon which this book is based for expansion in order to give a good overview of the ways in which Mössbauer effect is being used in researching chemical problems. The seven longer papers contain reviews and/or useful detailed information on particular techniques. The topics include new uses, such as applications of resonance for isotopes other than $^{57}Fe$ and $^{119}Sn$ to important materials like coal, storage hydrides, steels, and catalysts, in modern technology, and to the studies of surfaces. Also included are use of internal conversion Mössbauer spectroscopy and the theoretical interpretation of Mössbauer spectroscopic measurements.

The short papers do not merely present new measurements or results, but provide, as well, introduction to the subject of the report, and generally give a critical evaluation of other relative studies. In many cases the experiments are quite novel. Collectively these papers show the breadth of new applications of the Mössbauer effect. Other isotopes reported in this volume besides $^{119}Sn$ and $^{57}Fe$ include $^{67}Zn$, $^{99}Ru$, $^{121}I$, $^{151}Eu$, $^{169}Tm$, $^{197}Au$, and $^{237}Np$. The applications of molecular orbital calculations are surveyed and evaluated and, by correlation with the Mössbauer data, give new insights into chemical bonding. Conversion electron Mössbauer spectroscopy is finding more and more widespread use in surface analysis. Several chapters deal with the applications of

Mössbauer spectroscopy to the characterization of coal and its utilization. Examples of the many kinds of materials that can be studied are given: soils, iron–sulfur biological clusters, catalysts, battery materials, and hydrogen storage materials, among others.

Serving with us on the organizing committee were L. H. Bowen (North Carolina State University), M. L. Good (Louisiana State University), R. H. Herber (The Rutgers University), C. H. W. Jones (Simon Fraser University), G. L. Long (University of Missouri—Rolla), L. May (The Catholic University), and J. J. Zuckerman (University of Oklahoma).

Industrial sponsors that made the symposium and thus this volume possible include New England Nuclear, Spire Corporation, Amersham Corporation and The Radiochemical Centre, Harwell, Elscint, Inc., Ranger Engineering Corp., and WissEl. During every stage of the symposium and the preparation of the book, assistance was received from the staff of the Mössbauer Effect Data Center of the University of North Carolina at Asheville. Special appreciation is due to Virginia Stevens, who was involved in the interminable details and decisions from the beginning to the end.

Finally, we would like to dedicate this book to the memory of Jan Trooster, a scientist and friend extraordinaire, who was to have contributed specifically but, because of illness, was unable to do so. However, his spirit of adventure, dedication to careful research, and abounding good humor provided those around him with the inspiration and energy necessary to do the kind of work this book represents.

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June 27, 1981

# INTRODUCTORY REMARKS

I am pleased to have the opportunity to review the breadth of applications of the Mössbauer effect which is represented by this book. My remarks reflect my two "hats" in that I represent the American Chemical Society through its Board of Directors and I am a member of that group of chemists who recognized early the potential utility of Mössbauer spectroscopy in solving chemical problems. First, I am pleased to see an interdisciplinary symposium such as this one attract such a diversified group of scientists for the extended exchange of basic science and technology in a specific area of interest. It illustrates the central place of chemistry in the discussion of major concepts in science and in the evaluation of current technological problems. The American Chemical Society, through its Divisions of Inorganic Chemistry and Nuclear Chemistry and Technology, is to be congratulated for providing a forum of this type.

A brief review of this volume reveals both the breadth and depth of the current state of the art of Mössbauer spectroscopy and its applications to current problems of interest. The chapters range from applications in theoretical chemistry to the analysis of the mineral content of coal. The overall symposium program, on which this book is based, proves that the early recognized potential of this technique for solving chemical problems has been realized. However, the obvious limitations are still with us. The overwhelming majority of the chapters focus on the Mössbauer effect in $^{57}Fe$; the extension to other isotopes is still not extensive. Perhaps what the symposium indicates best is our present ability to apply somewhat esoteric instrumental methods both to significant basic scientific questions and to applied research problems of technological interest. As our technological problems become more complex, this ability will become more and more important.

The organizers, particularly John Stevens, Virginia Stevens, and Gopal Shenoy, are to be congratulated for their efforts to bring this group together and for coaxing papers out of so many of the participants. Those who have helped organize meetings of this type know the work involved and can recognize the outstanding job that this small group has accomplished.

MARY L. GOOD

June 27, 1980

# CONTENTS

# CHEMICAL BONDING

# 1

# Application of Molecular Orbital Calculations to Mössbauer and NMR Spectroscopy of Halogen-Containing Compounds

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*Self-consistent field and charge molecular orbital (MO) calculations are applied to a series of fluorine-, chlorine-, bromine-, and iodine-containing molecules. Calculated orbital energies and dipole moments are used for testing and comparing the MO theories. The calculation procedures for deriving (1) electron charge densities $\rho(O)$, (2) electric field gradient tensors, and (3) internal magnetic fields are described in detail. In connection with calculated $\rho(O)$ values and measured isomer shifts $\delta$, the relative change of nuclear charge radius, $\delta R/R$, is derived for iodine. Together with the various contributions to the electric field gradient, the quadrupole polarization of electronic cores $\gamma(r)$ and the nuclear quadrupole moments Q for chlorine, bromine, and iodine are discussed. For one specific compound, $N(C_2H_5)_4$-$FeI_4$, the internal magnetic fields at the iron and iodine nuclei are evaluated simultaneously from the magnetic MO structure of this compound. All calculated data are compared with experimental results.*

Molecular orbital (MO) calculations provide us with electronic and magnetic structure properties of a molecule, from which suitable spectroscopic data can be derived for comparison with experimental Mössbauer and NMR work. Comparing experimental hyperfine data with

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computed electronic data yields nuclear properties such as $\delta R/R$ (relative change of nuclear charge radius) and $Q$ (nuclear quadrupole moments). Beyond this, the mutual feedback of theory and experiment helps the quantum chemist test the reliability of the various approximations involved in his calculations and helps the spectroscopist interpret his measured data.

In the present work, self-consistent field (SCF) and self-consistent charge (SCC) MO calculations are applied to a series of halogen-containing compounds. In the second section, some of the approximations inherent to these calculations are described, and experimental orbital energies and dipole moments are compared with calculated values derived from SCC–$X_\alpha$–MO, SCC–IEH–MO (iterative extended Hückel), SCF–MO (close to the Hartree–Fock limit), and Gaussian 76-MO versions. The following sections deal with isomer shift and electron charge density at the Mössbauer nucleus, with electric field gradients, and with the interpretation of measured magnetic hyperfine fields at the iron and iodine nuclei.

### *Molecular Orbital Calculations*

The one-electron equation that may describe the electronic structure of a many-particle system is (in a.u.)

$$(-\Delta + V(\vec{r}))\ \psi_k(\vec{r}) = \epsilon_k\ \psi_k(\vec{r}), \tag{1}$$

where $V(\vec{r})$ is a local pseudopotential, and $\psi_k(\vec{r})$ are molecular orbitals (MO)

$$\psi_k(\vec{r}) = \sum_{\nu j} \phi_j^{(\nu)}(\vec{r} - \vec{R}_\nu)\ c_{jk}{}^{\nu} \tag{2}$$

$\phi_j^{(\nu)}(\vec{r} - \vec{R}_\nu)$ is an atomic wave function characterizing the $(n_j, l_j, m_j)$-th atomic orbital of the $\nu$-th atom; for the present work, Slater-type orbitals (STO) are used. Multiplication of Equation 1 from the left by $\phi_i^{(\nu')*}(\vec{r} - \vec{R}_{\nu'})$ and integration over the electronic coordinates yields the secular equation

$$\sum_{\nu j} (H_{ij}^{\nu'\nu} - \epsilon_k\, S_{ij}^{\nu'\nu})\ c_{jk}{}^{\nu} = 0 \tag{3}$$

with the Hamiltonian matrix elements $H_{ij}^{\nu'\nu}$ and the overlap matrix elements $S_{ij}^{\nu'\nu}$

$$H_{ij}^{\nu'\nu} = \int \phi_i^{(\nu')*}(\vec{r} - \vec{R}_{\nu'})\,[-\Delta + V(\vec{r})]\,\phi_j^{(\nu)}(\vec{r} - \vec{R}_\nu)\, d^3r \tag{4}$$

$$S_{ij}^{\nu'\nu} = \int \phi_i^{(\nu')*}(\vec{r} - \vec{R}_{\nu'})\ \phi_j^{(\nu)}(\vec{r} - \vec{R}_{\nu})\, d^3r \tag{5}$$

With the short notations

$$H_{\text{at}}^{(\nu)}(\vec{r}) = -\Delta + V_{\text{at}}^{(\nu)}(\vec{r} - \vec{R}_{\nu}) \tag{6}$$

$$V_{\text{nb}}(\vec{r}) = V(\vec{r}) - \frac{1}{2}\left[V_{\text{at}}^{(\nu)}(\vec{r} - \vec{R}_{\nu}) + V_{\text{at}}^{(\nu')}(\vec{r} - \vec{R}_{\nu'})\right] \tag{7}$$

the Hamiltonian matrix elements can be written as

$$H_{ij}^{\nu'\nu} = \int \phi_i^{(\nu')*}(\vec{r} - \vec{R}_{\nu'}) \left[\frac{1}{2}\left(H_{\text{at}}^{(\nu)} + H_{\text{at}}^{(\nu')}\right) + V_{\text{nb}}\right] \phi_j^{(\nu)}(\vec{r} - \vec{R}_{\nu})\, d^3r$$

$$= \frac{1}{2}\left(\epsilon_i^{\nu'} + \epsilon_j^{\nu}\right) S_{ij}^{\nu'\nu} + \frac{1}{2}\left(V_{ij}^{\nu'\nu} + V_{ji}^{\nu\nu'}\right) \tag{8}$$

$$V_{ij}^{\nu'\nu} = \int \phi_i^{(\nu')*}(\vec{r} - \vec{R}_{\nu'})\left[V(\vec{r}) - V_{\text{at}}^{(\nu)}(\vec{r} - \vec{R}_{\nu})\right] \phi_j^{(\nu)}(\vec{r} - \vec{R}_{\nu})\, d^3r \tag{9}$$

where $\epsilon^{\nu}_{j}$ is the valence orbital ionization potential of the $\nu$-th atom or ion. From Equation 8 the extended Hückel type equations are obtained by the approximations

$$V_{ij}^{\nu'\nu} = \frac{1}{2}\left(V_{ii}^{\nu'\nu'} + V_{jj}^{\nu\nu}\right) S_{ij}^{\nu'\nu} \quad ; \quad \epsilon_i^{\nu'} + V_{ii}^{\nu'\nu'} = k\, H_{ii}^{\nu'\nu'} \tag{10}$$

yielding

$$H_{ij}^{\nu'\nu} = \frac{k}{2}\left(H_{ii}^{\nu'\nu'} + H_{jj}^{\nu\nu}\right) S_{ij}^{\nu'\nu}. \tag{11}$$

In the IEH calculations, the Cusachs approximation (*1*) is adapted for the proportionality constant $k$

$$k = 2 - |S_{ij}^{\nu'\nu}| \tag{12}$$

and the diagonal Hamiltonian matrix elements are described in terms of valence orbital ionization potentials which depend on the effective charge $Q_\nu$ of the $\nu$-th atom (*2*):

$$H_{ij}^{\nu\nu} = -\left(\epsilon_{j0}^{\nu} + \epsilon_{j1}^{\nu} Q_{\nu}\right) \tag{13}$$

So far we have successfully applied this method to the interpretation of electric and magnetic hyperfine parameters of $^{57}$Fe-containing compounds (*3*).

In addition to the IEH method, a method was used that explicitly includes neighbor contributions to the Hamiltonian. Recently we have described this method in detail (*4*), and have applied it to a series of small molecules including second-row elements (*5*). The main feature of this method is that $V(\vec{r})$ is described in terms of an $X_\alpha$-like model potential which depends on effective atomic charges, thus making the application of an SCC iteration procedure possible.

For one atom this potential is given by

$$V_{at}(r) = -\frac{2Z}{r} + 8\pi\left[\frac{1}{r}\int_0^r x^2\rho_{at}(x)\,dx + \int_r^\infty x\rho_{at}(x)\,dx\right] - 6\alpha\left[\frac{3}{8\pi}\rho_{at}(r)\right]^{1/3} \tag{14}$$

Assuming that the atomic charge density $\rho_{at}(r)$ depends exponentially on $r$

$$\rho_{at}(r) = \frac{N\eta^3}{8\pi}e^{-\eta r}, \quad \eta = \eta(Q) \tag{15}$$

where $N$ is the number of electrons, our atomic model potential has the form

$$V_{at}(r) = -\frac{2Q}{r} - N\left(\frac{2e^{-\eta r}}{r} + \eta e^{-\eta r}\right) - \alpha'\eta N^{1/3}e^{-\eta r/3};\ \alpha' = 1.5\,\alpha\left(\frac{3}{\pi^2}\right)^{1/3} \tag{16}$$

$V_{at}(r)$ is a function of the effective atomic charge via $Q$, $N$, and $\eta$.

We represent the molecular potential $V_{mol}(\vec{r})$ by the superposition of atomic potentials (Equation 16)

$$V_{mol}(\vec{r}) = \sum_{æ} V_{at}(|\vec{r} - \vec{R}_{æ}|) \tag{17}$$

Equation 17 implies

$$V_{ex,\,mol}(\vec{r}) \sim \sum_{æ} \rho_{æ}^{1/3}\,(|\vec{r} - \vec{R}_{æ}|) \tag{18}$$

which overestimates the exchange contribution because $V_{ex,mol}(r)$ should be replaced by