EXPERIMENT 32

NMR Determination of Paramagnetic Susceptibility

The energy levels of a nucleus with a magnetic moment are changed in the presence of a magnetic field. Transitions between these levels can be induced by electromagnetic radiation in the radio-frequency region, and this resonance is useful in characterizing the chemical environment of the nucleus. For this reason, nuclear magnetic resonance (NMR) spectroscopy has developed as one of the most powerful experimental methods used in chemistry; for other applications, see Exps. 21, 42, and 43. In a slightly different application, in this experiment we will examine the effect of paramagnetic "impurities" on NMR solvent resonances and will use the predicted resonance shifts to deduce the paramagnetic susceptibility and election spin of several transition-metal complexes.

THEORY

The magnetic moment of a nucleus with nuclear spin quantum number I is

$$\mu = g_N \mu_N \sqrt{I(I+1)} \tag{1}$$

where g_N is the nuclear g factor (5.5856 for a proton) and $\mu_N = eh/4\pi m_p$ is the nuclear magneton. Substitution of the charge e and mass m_p of a proton gives a value of 5.051×10^{-27} J T^{-1} for μ_N. The symbol μ_N is the unit of nuclear magnetic moment and is smaller than the electronic Bohr magneton μ_B (defined in Exp. 31) by the electron-to-proton mass ratio.

The nuclear moment will interact with a local *magnetic induction* (flux density)† B_{loc} to cause an energy change (Zeeman effect)

$$E_N = -g_N \mu_N M_I B_{\text{loc}} \tag{2}$$

Here M_I is the quantum number measuring the component of nuclear spin angular momentum (and magnetic moment) along the field direction, and it can have values $-I$, $-I+1, \ldots, +I$. The effect of the field is thus to break the $2I+1$ degeneracy and to produce energy levels whose spacing increases linearly with B_{loc} (or B) (Fig. 1). Transitions among these levels can be produced by electromagnetic radiation provided that the selection rule $\Delta M_I = \pm 1$ is satisfied. In this case, the resonant frequency is given by

$$\nu = \frac{\Delta E_N}{h} = \frac{g_N \mu_N}{h} B_{\text{loc}} \tag{3}$$

For protons ν (Hz) $= (4.26 \times 10^7) B_{\text{loc}}$ (tesla), so that, for typical fields of 1 to 5 T, ν falls in the radio-frequency region. In practice ν is usually fixed at some convenient value (e.g., 60, 100, or 220 MHz) and the induction B is varied until resonance is achieved.

†The vector quantity **B** is called either the *magnetic induction* or the *magnetic flux density*, although "magnetic field strength" would be a more appropriate name. Unfortunately, the name magnetic field strength was given to **H** at the time when **H** was considered to be the fundamental magnetic-field vector. It is now known that **B** is the fundamental vector (analogous to **E**, the fundamental electric-field vector). To add to the confusion, $\mathbf{B} = \mathbf{H}$ in a vacuum when gaussian units are used. This book uses SI units, for which $\mathbf{B} = \mu_0 \mathbf{H}$ in a vacuum and $\mu_0 \neq 1$. In SI units **B** is expressed in tesla (1 T = 1 weber $m^{-2} = 10^4$ gauss) and **H** is expressed in A m^{-1}. In many texts **B** is loosely called the *magnetic field*.

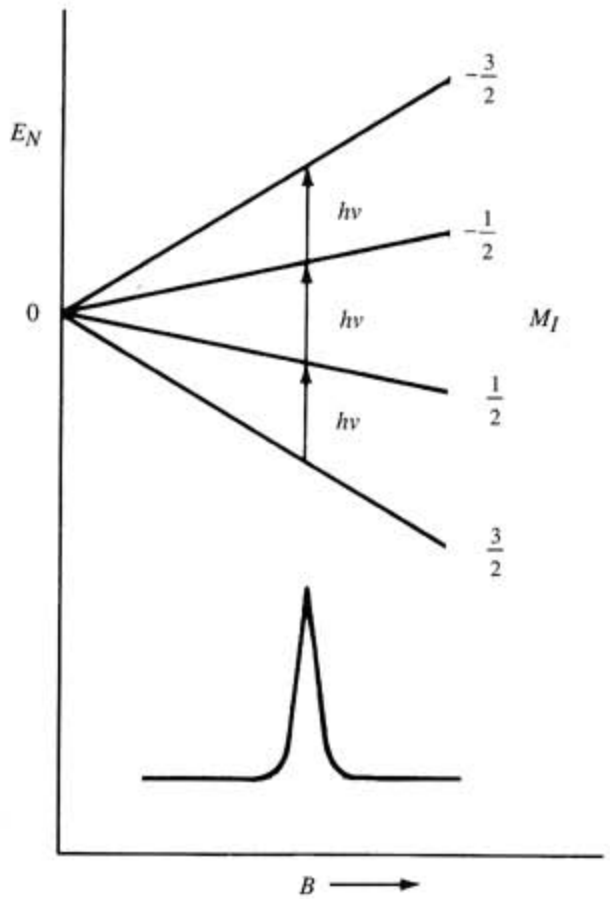


FIGURE 1
Energy levels, allowed transitions, and spectrum of a nucleus with $I = \frac{3}{2}$ in a magnetic induction of magnitude B.

In general, the local induction B_{loc} at the nucleus will differ from the externally applied induction B because of the magnetization M that is induced by B:

$$B_{\text{loc}} = B + \mu_0 M = (1 + \chi)B \tag{4}$$

where μ_0 is the vacuum permeability, defined as $4\pi \times 10^{-7}\ \text{N A}^{-2} = 1.2566 \times 10^{-6}\ \text{N A}^{-2}$ (N = newton; A = ampere). The volume susceptibility χ (a dimensionless quantity) is the magnetic analog of the dielectric polarizability (Exp. 29), and it can be converted to a mass susceptibility χ_{mass} by dividing by the density ρ. Multiplication by the molar mass M gives the molar susceptibility

$$\chi_M = M\chi_{\text{mass}} = \frac{M\chi}{\rho} = \tilde{V}\chi \tag{5}$$

where $\tilde{V}$ is the molar volume. See Exp. 31 for a discussion of units. As noted in Exp. 31, χ_M has the form

$$\chi_M = N_0\mu_0\xi + \frac{N_0\mu_0\mu^2}{3kT} = N_0\mu_0\xi + \chi_M^{\text{para}} \tag{6}$$

where N_0 is Avogadro's number. $N_0\mu_0\xi$ is a diamagnetic contribution while the second term is a temperature-dependent paramagnetic contribution that is dominant if the magnetic moment μ is not zero. This will be true only if the electron spin or electronic orbital angular momentum is not zero, a case that is fairly common for transition-metal compounds.

Most organic compounds are not paramagnetic, and so it is the diamagnetic susceptibility that is important in determining the resonance condition. The diamagnetic contribution arises because the orbital motion of the electrons is altered by the presence of B so that there is a net orbiting of electrons about the field lines. This circulating charge in turn generates a magnetic induction B_d, which is proportional to the applied field and *opposed* to B. Thus $B_{\text{loc}} = B + B_d$, with

$$B_d = \chi B = \frac{\rho}{M} N_0 \mu_0 \xi B \equiv -\sigma B \tag{7}$$

where M is the molar mass and σ is a positive constant. The resonant frequency is

$$\nu = \frac{g_N \mu_N}{h} B(1 - \sigma) = \nu_0(1 - \sigma) \tag{8}$$

where ν_0 is the resonance for a bare proton. The diamagnetic shielding constant σ is usually quite small ($\sim 10^{-5}$) and increases as the electron density about the nucleus is increased. Changes in the local induction $B_{\text{loc}} = B(1 - \sigma)$, and thus in ν, of a few parts per million (ppm) are typical when the chemical environment about a nucleus is changed. These chemical shifts relative to a convenient standard, such as tetramethylsilane, are easily measured with modern NMR instruments and hence serve to characterize the chemical bonding about a given nucleus. In addition, the relative intensities of for example proton resonances give a measure of the relative number of protons with different chemical environments (e.g., $-CH_3$ versus $-CH_2-$ groups). Finally, the coupling of magnetic moments of nearby nuclei can produce spin–spin splitting patterns that are quite useful in identifying the functional groups present in the molecule. Some further discussion of these applications is presented in Exp. 42.

If a proton of a diamagnetic molecule is present in a solution containing a paramagnetic solute, the induction ("local field") B at the nucleus will be increased because of the alignment of the solute magnetic moments in the applied field. Evans[1] has shown that this increase in the local field is given by

$$\Delta B = \frac{1}{6}(\chi_s - \chi_0)B \tag{9}$$

where χ_s and χ_0 are the susceptibilities of the solution with and without the paramagnetic solute, respectively. According to Eqs. (3) and (9), the proton resonance will shift by an amount

$$\frac{\Delta\nu}{\nu} = \frac{\Delta B}{B_{\text{loc}}} \approx \frac{\Delta B}{B} = \frac{1}{6}(\chi_s - \chi_0) \tag{10}$$

with the approximation $B_{\text{loc}} \approx B$ leading to negligible error.

To obtain the mass susceptibility χ_{mass} of the pure paramagnetic material, we assume that the volume susceptibility χ_s of the solution can be written as a sum of parts,

$$\chi_s = \chi_{\text{mass}\,s}\rho_s = \chi_{\text{mass}} m + \chi_{\text{mass}\,0}(\rho_s - m) \tag{11}$$

Here ρ_s is the density of the solution containing m kg of paramagnetic solute per cubic meter and $\chi_{\text{mass}\,0}$ is the mass susceptibility of the solution without the paramagnetic material. The density of the latter is ρ_0 so that $\chi_0 = \chi_{\text{mass}\,0}\rho_0$ and we obtain from Eqs. (10) and (11) the expression

$$\chi_{\text{mass}} = \frac{6}{m}\frac{\Delta\nu}{\nu} + \chi_{\text{mass}\,0} + \chi_{\text{mass}\,0}\frac{\rho_0 - \rho_s}{m} \tag{12}$$

The third term is a small correction that is unimportant for highly paramagnetic materials and is often neglected.[1] The value of χ_{mass} for a paramagnetic material can be determined therefore by measuring the difference in chemical shift of a proton in the solvent and in a solution containing a known weight of the paramagnetic solute. The value of $\chi_{\text{mass }0}$ can be obtained from tables such as those contained in Ref. 2 or by summing atomic susceptibilities χ_i according to Pascal's empirical relation:

$$\chi_{\text{mass }0} = \frac{\chi_{M_0}}{M_0} = \frac{1}{M_0}\left[\sum_i t_i\chi_i + \sum_j \lambda_j\right] \tag{13}$$

where M_0 is the solvent molar mass, t_i is the number of atoms of type i in the molecule, and the constitutive correction constants λ_j depend on the nature of the multiple bonds. See Table 1 for some typical values of χ_i and λ_j.

The molar susceptibility χ_M for the solute is obtained by multiplying χ_{mass} by the molar mass of the paramagnetic complex. As can be seen from Eq. (6), the paramagnetic contribution χ_M^{para}, and hence the paramagnetic moment μ, can be extracted by a temperature-dependence study (see also Exp. 31). For accurate results, a correction should be made to m to account for solvent-density changes with temperature.[3] Alternatively a measurement of χ_M at a single temperature can usually be combined with an adequate estimate of $N_0\mu_0\xi$ from Pascal's constants[2] to allow one to deduce the paramagnetic contribution. If χ_M^{para} is obtained in this manner, the paramagnetic moment is given by

$$\mu = \sqrt{\frac{3kT\chi_M^{\text{para}}}{N_0\mu_0}}$$

$$= 797.8\sqrt{T\chi_M^{\text{para}}} \text{ Bohr magneton} \tag{14}$$

where the Bohr magneton (μ_B) is 9.274×10^{-24} J T^{-1}. In the absence of any orbital contributions, the value of μ is related to the number n of unpaired electrons in the d shell of the transition metal by

$$\mu(\text{spin only}) = \sqrt{n(n+2)} \text{ Bohr magneton} \tag{15}$$

TABLE 1 Pascal's constants χ_i for diamagnetic susceptibility[a] (units of 10^{-11} m^3 mol^{-1})

Co^{2+}	−15	Br^-	−45	B	−8.8	N Open chain	−7.00
Co^{3+}	−13	CN^-	−23	Br	−38.5	Ring	−5.79
Cr^{2+}	−19	Cl^-	−33	C	−7.5	Monamides	−1.94
Cr^{3+}	−14	F^-	−14	Cl	−25.3	Diamides, imides	−2.65
Cu^{2+}	−14	NO_3^-	−25	F	−7.9	O Alcohol, ether	−5.79
Fe^{2+}	−16	OH^-	−15	H	−3.68	Aldehyde, ketone	+2.17
Fe^{3+}	−13	SO_4^{2-}	−50	I	−56.0	Carboxylic = O	−4.22
K^+	−16			P	−33.0		
Ni^{2+}	−15			S	−18.8		

λ_j Corrections for bonds

C=C	+6.9	C=N	+10.3
C≡C	+1.0	C≡N	+1.0
C=C—C=C	+13.3	C in aromatic ring	−0.30

[a] Adapted from Ref. 2.

As noted in Exp. 31, magnetic susceptibility measurements are thus quite useful in determining the electron configuration of a paramagnetic ion in a particular ligand field.

METHOD

The basic elements of an NMR spectrometer are outlined in Fig. 2. The principal magnetic field is provided by a permanent magnet (~1.5 T), an electromagnet (2.5 to 5.0 T), or a superconducting electromagnet (5.0 to 7.5 T). Since shifts of a few ppm are to be measured, the field must be quite stable and uniform. This is achieved by adding small adjustment coils to the magnet and by spinning the sample tube to average out residual inhomogeneities. An additional set of Helmholtz coils is wound around the pole faces to permit small linear variation in the field in recording spectra.

The sample tube is inserted into a probe region containing two radio-frequency (RF) coils wound at 90° to each other and to the magnetic-field coils. Radiation of some fixed frequency, usually 60 MHz or higher for protons, is sent through the sample by the transmitter coil. If the "local field" induction is such that Eq. (3) is satisfied, sample absorption and emission will occur. This reradiated signal is detected by the receiver coil, which, being oriented at right angles to the transmitter, senses no signal in the absence of sample coupling. The signal from the receiver coil is amplified and displayed on a chart recorder to yield the NMR spectrum as a function of field. Since the absolute value of the magnetic field is not easily determined with high precision, field shifts are measured relative to some reference compound such as tetramethylsilane and are expressed as chemical shifts in ppm,

$$\delta_i = \frac{B_r - B_i}{B_r} \times 10^6 \tag{16}$$

Here, B_r and B_i are induction values for resonance by the reference nucleus and by nucleus i, respectively, for a fixed spectrometer frequency ν. If B is fixed and ν is varied, δ_i is given by

$$\delta_i = \frac{\nu_i - \nu_r}{\nu_r} \times 10^6 \tag{17}$$

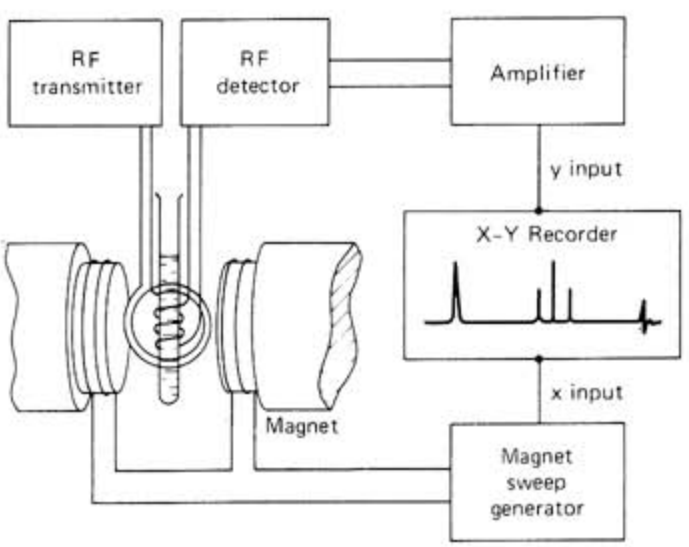


FIGURE 2
Schematic drawing of a nuclear magnetic resonance spectrometer.

The latter is the conventional definition of δ_i, but, to the accuracy of chemical shift measurements, Eq. (16) gives equivalent results. Many NMR chart displays are calibrated both in δ units and in frequency shift units appropriate to the fixed frequency source ν_r (60 MHz for most small proton NMR instruments).

EXPERIMENTAL

Operation of the NMR instrument will be described by the instructor. Particular care should be taken in inserting and removing the NMR sample tubes to prevent damage to the probe. All tubes should be wiped clean prior to insertion to avoid contamination of the probe.

To provide an internal reference, the solvent is sealed in a capillary, which is placed at the bottom of the NMR tube used for the sample solution. For this purpose, a melting-point capillary is closed at one end and a syringe is used to add the reference solution. For aqueous studies, a 2% solution of *t*-butyl alcohol in water can be used as reference and as solvent for the paramagnetic solute. The shift with respect to the methyl resonance of the *t*-butyl group is then monitored. With organic ligands such as acetylacetonate (acac) groups, complexes such as $Cr(acac)_3$, $Fe(acac)_3$, and $Co(acac)_2$ are soluble in benzene and the proton resonance of the solvent is a convenient reference. The capillary is filled one-third full, the lower end of the capillary is cooled in ice, and the upper part is sealed off with a small hot flame. Alternatively, the reference solution can be placed in one compartment of a coaxial pair of cylindrical NMR tubes, which are available commercially. In either case the spectral display should be expanded to permit an accurate measurement of the frequency shift.

The following complexes are suitable for study at room temperature. Either toluene or benzene can be used as the solvent, but it should be noted that toluene has *two* proton resonances.

d^3 $Cr(acac)_3$, chromium acetylacetonate ($M = 349.3$ g mol^{-1})

d^5 $Fe(acac)_3$, ferric acetylacetonate ($M = 353.2$ g mol^{-1})

d^8 $Co(acac)_2$, cobaltous acetylacetonate ($M = 257.2$ g mol^{-1})

The concentrations are not critical (0.02 to 0.05 molar), but they must be known precisely. These salts are available commercially, or they can be readily synthesized by methods described in Ref. 4.

If the NMR spectrometer is equipped with a variable-temperature probe, the $Fe(acac)_3$ shifts should be measured at four or five temperatures. A 0.025 molar solution in toluene can be employed over the liquid range from −95°C to +110°C. Care should be taken to seal and test the NMR tube if the high-temperature range is to be studied (i.e., heat the tube to ~135°C in a fume hood before mounting it in the spectrometer). Since the temperature variation of toluene density is appreciable,[3] the solute concentration m in kg per cubic meter should be corrected at each temperature T:

$$m_t \cong m_{rt}\left(\frac{\rho_t}{\rho_{rt}}\right) \tag{18}$$

where ρ_t is the density of *pure* solvent at temperature t and ρ_{rt} is that at room temperature. The density of toluene as a function of temperature is given to a fairly good approximation by $\rho_t = 0.8845 - 0.92 \times 10^{-3}\, t$, where t is in degrees Celsius; a more detailed temperature dependence from −95°C to +99°C is given in Ref. 5. Approximately 15 min should be allowed for equilibrium to be reached after changing the temperature. An accurate measurement of the probe temperature should be made in the manner described

in the spectrometer manual. This usually involves a measurement of the frequency separation between OH and CH resonances in methanol or ethylene glycol, since this separation changes by about 0.5 Hz K^{-1} for a 60-MHz instrument.

Appropriate salts for alternative aqueous measurements are

d^5 $Fe(NO_3)_3 \cdot 9H_2O$ (0.015 *M*), ferric nitrate† ($M = 404.0$ g mol^{-1})

d^5 $K_3Fe(CN)_6$ (0.06 *M*), potassium ferricyanide ($M = 329.3$ g mol^{-1})

d^6 $FeSO_4 \cdot 7H_2O$ (0.02 *M*), ferrous sulfate ($M = 278.0$ g mol^{-1})

d^8 $NiCl_2$ (0.08 *M*), nickel chloride ($M = 129.6$ g mol^{-1})

d^9 $CuSO_4$ (0.08 *M*), cupric sulfate ($M = 159.6$ g mol^{-1})

Three or more of these solutions should be made up in 10- or 25-mL volumetric flasks using as reference solvent ~2% (by volume) *t*-butyl alcohol in deoxygenated water. The Fe^{2+} and Fe^{3+} solutions illustrate the effect of oxidation state on the electron configuration of a single element. The Fe^{3+} and $K_3Fe(CN)_6$ solutions demonstrate the role of weak and strong ligand-field splitting on the electron configuration (see discussion in Exp. 31).

The $Fe(NO_3)_3$ or $NiCl_2$ solutions can be studied from 0 to 100°C in the same manner as described for the acetylacetonate complexes. In correcting for changes in m with temperature, the density variations of pure H_2O may be used.

CALCULATIONS

Neglecting the third term of Eq. (12), the mass susceptibility of a paramagnetic solute is readily determined from m and $\Delta\nu$. The diamagnetic mass susceptibilities $\chi_{\text{mass }0}$ of the solvents, in SI units of $m^3\ kg^{-1}$, are -8.8×10^{-9} (benzene), -9.0×10^{-9} (toluene), and -9.0×10^{-9} (*t*-butyl alcohol–water solvent). For temperature-dependence studies, correct m according to Eq. (18), calculate χ_M and plot χ_M versus $1/T$. The slope of the best straight line through these points is the Curie constant C (see Exp. 31), and the magnetic moment μ is given by

$$\mu = \left(\frac{3kC}{N_0\mu_0}\right)^{1/2} = 797.8\sqrt{C}\ \text{Bohr magneton} \tag{19}$$

The value of $N_0\mu_0\xi$ is obtained from the intercept of the plot. Compare this value of the diamagnetic susceptibility of the solute with that estimated from Pascal's constants in Table 1. For single-temperature measurements, estimates of the latter type should be used to obtain χ_M^{para} for use in Eq. (14).

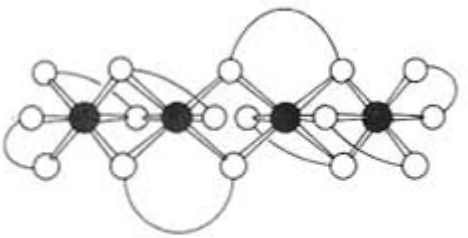
Report your values of μ in Bohr magneton and calculate the number of unpaired electrons using the spin-only formula, Eq. (15).

DISCUSSION

In an aqueous solvent, the ions Fe^{2+}, Fe^{3+}, Ni^{2+}, and Cu^{2+} are all complexed to six H_2O molecules in an octahedral arrangement. The magnetic moments can be understood in terms of the weak-field splitting of the five *d* orbitals as described in Exp. 31. In $Fe(CN)_6^{3-}$ the CN^- ligands are strongly bound to the Fe^{3+} ion and the ligand-field splitting is larger.

†This compound is hygroscopic, so the weighing should be done rapidly. It is also necessary to make the solution ~0.3 *M* in HNO_3 to prevent precipitation of $Fe(OH)_3$. The reference solvent used with this solution should have the same acid concentration.

The structures of $Cr(acac)_3$ and $Fe(acac)_3$ are also pseudo-octahedral, with the two oxygen atoms of each $acac^-$ ion occupying adjacent metal ligand positions. For $Co(acac)_2$ a square planar or tetrahedral arrangement of the ligands might be expected, but the energetics favoring octahedral coordination are such that there is intermolecular association to fill the two vacant ligand sites. The result is a tetramer in which a pseudo-octahedral arrangement is achieved by each cobalt atom.[6]



Discuss your observed magnetic moment values in terms of the number of unpaired electrons predicted for each transition-metal complex assuming octahedral structures. Comment on any differences from the predicted spin-only moments.

SAFETY ISSUES

Benzene or toluene is used as a solvent in this experiment. These potentially hazardous chemicals should be handled with care and disposed of properly. See p. 346 for further details about benzene.

APPARATUS

NMR spectrometer, with variable temperature capability if possible; several 10- or 25-mL volumetric flasks; NMR tubes; melting-point capillaries; syringe; torch for sealing capillaries; ethylene glycol and methanol in NMR tubes for temperature calibrations.

$Cr(acac)_3$, $Fe(acac)_3$, $Co(acac)_2$, where acac = acetylacetonate (~1 g each); benzene or toluene (250 mL); $Fe(NO_3)_3 \cdot 9H_2O$, $K_3Fe(CN)_6$, $FeSO_4 \cdot 7H_2O$, $NiCl_2$, $CuSO_4$ (~1 g each); 2% by volume *t*-butyl alcohol in deoxygenated water (250 mL); 3 *M* HNO_3 for acidifying $Fe(NO_3)_3$ and corresponding reference solution.

REFERENCES

1. D. F. Evans, *J. Chem. Soc.* 2003 (1959).

2. L. N. Mulay and E. A. Boudreaux, *Theory and Applications of Molecular Diamagnetism*, p. 303, Wiley-Interscience, New York (1976); R. L. Carlin, *Magnetochemistry*, p. 3, Springer-Verlag, New York (1986).

3. D. Ostfield and I. A. Cohen, *J. Chem. Educ.* **49,** 829 (1972).

4. T. H. Crawford and J. Swanson, *J. Chem. Educ.* **48,** 382 (1971).

5. E. W. Washburn (ed.), *International Critical Tables,* vol. III, p. 28, McGraw-Hill, New York (1929).

6. F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry,* 6th ed., Wiley, New York (1999).

GENERAL READING

F. A. Cotton et al., *Advanced Inorganic Chemistry,* 6th ed., Wiley, New York (1999).

R. S. Drago, *Physical Methods for Chemists,* 2d ed., chaps. 10–12, Saunders, New York (1992).

D. F. Shriver and P. W. Atkins, *Inorganic Chemistry,* 3d ed., Freeman, New York (1999).

EXPERIMENTS IN PHYSICAL CHEMISTRY

EIGHTH EDITION

CARL W. GARLAND
Massachusetts Institute of Technology

JOSEPH W. NIBLER
Oregon State University

DAVID P. SHOEMAKER
(*deceased*)
Oregon State University

McGraw-Hill Higher Education

Boston Burr Ridge, IL Dubuque, IA New York San Francisco St. Louis
Bangkok Bogotá Caracas Kuala Lumpur Lisbon London Madrid Mexico City
Milan Montreal New Delhi Santiago Seoul Singapore Sydney Taipei Toronto

The McGraw-Hill Companies

McGraw-Hill Higher Education

EXPERIMENTS IN PHYSICAL CHEMISTRY, EIGHTH EDITION

1 2 3 4 5 6 7 8 9 0 QPD/QPD 0 9 8

ISBN 978–0–07–282842–9
MHID 0–07–282842–0

Publisher: *Thomas Timp*
Senior Sponsoring Editor: *Tamara L. Hodge*
Director of Development: *Kristine Tibbetts*
Senior Developmental Editor: *Shirley R. Oberbroeckling*
Marketing Manager: *Todd L. Turner*
Senior Project Manager: *Kay J. Brimeyer*
Senior Production Supervisor: *Kara Kudronowicz*
Associate Design Coordinator: *Brenda A. Rolwes*
Cover Designer: *Studio Montage, St. Louis, Missouri*
Compositor: *Laserwords Private Limited*
Typeface: *10/12 Times Roman*
Printer: *Quebecor World Dubuque, IA*

Cover description: The figure depicts the absorption and emission spectra of CdSe nanocrystals, whose color is a sensitive function of size. The figure is based on spectral data provided by NN-Labs. The authors thank both NN-Labs and Evident Technologies for CdSe samples used in the development of the quantum dot experiment.

Library of Congress Cataloging-in-Publication Data

Garland, Carl W.
Experiments in physical chemistry.—8th ed. / Carl W. Garland, Joseph W. Nibler, David P. Shoemaker.
p. cm.
Includes index.
ISBN 978–0–07–282842–9—ISBN 0–07–282842–0 (hard copy : acid-free paper)
1. Chemistry, Physical and theoretical—Laboratory manuals. I. Nibler, Joseph W.
II. Shoemaker, David P. III. Title.
QD457 .S56 2009
541.078—dc22

2007043492

www.mhhe.com