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Laser Spectroscopy of Solids

Edited by W. M. Yen and P. M. Selzer

With Contributions by
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With 117 Figures

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Preface

In this volume we have attempted to present a concise survey of the spectroscopic properties of insulators as derived from the application of tunable laser spectroscopic techniques. As has been the case in gaseous atomic spectroscopy, the use of tunable lasers has allowed the extension and the refinement of optical measurements in the condensed phases to unprecedented resolutions in the frequency and temporal domains. In turn, this firmer base of empirical findings has led to a more sophisticated theoretical understanding of the spectroscopy of optically excited states with major modifications being apparent in the area of their dynamic behavior. Yet the revivalistic nature of these advances implies that additional advances are to be expected as the techniques and developments outlined in this volume are put to widespread use. Regardless, it is our hope and that of our distinguished colleagues in this venture that the reviews presented here will be useful to neophytes and veterans to this field alike – to the former as a laissez-passer into solid-state spectroscopy, to the latter as a useful synopsis and reference of recent developments.

We have also attempted to expose the reader to the concept that optically active materials, be they organic or inorganic, as universality would require, behave in a like manner and, though terminology may vary in detail, the outline and general features of all insulators remain constant.

The book is organized as follows: Chapter 1 surveys in general terms the field of spectroscopy of insulators and establishes the basic features the other chapters refer to. Chapters 2 and 3, respectively, deal with the microscopic and macroscopic aspects of the theory of dynamics of optically excited states with emphasis on ion-ion interactions which are responsible for optical energy transfer and diffusion in condensed phases. Chapter 4 details experimental techniques which are used in laser spectroscopy in solids. Finally, the last three chapters present surveys of the empirical status of these studies in ionic or crystalline, glassine or amorphous, and organic solids, respectively.

The other areas in the study of optical properties of condensed matter where lasers have played crucial roles and where considerable advances have been made, such as semiconductors and the various types of light scattering experiments, are not the principal focus of this volume and, hence, will not be reviewed here.

Finally, we wish to acknowledge the many people who have encouraged us and collaborated with us in various phases of compilation. We specially wish to thank Dr. H.K.V. Lotsch and the editorial staff of Springer for their help and

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Contents

1. Optical Spectroscopy of Electronic Centers in Solids

G. F. Imbusch and R. Kopelman

With 20 Figures

1.1 Overview

In this chapter we present an outline of the optical spectroscopy of ions and mole-
cules in solids which will serve as a background for the later chapters. We adopt a
general approach which takes into account both organic and inorganic systems, and
we attempt to elucidate the similarities and differences between the two systems.
We start by considering the case of a low concentration of optically active centers
in an otherwise optically inert crystalline host. The centers are considered to be too
far apart from each other to interact. In this case, when all the centers are identical,
we need only analyze the properties of one representative center and apply appro-
priate statistical considerations. Afterwards we consider the case where the concen-
tration of optically active centers is large enough so that adjacent centers can inter-
act; this interaction then leads to the dynamical processes whose investigation by
laser techniques and subsequent theoretical analyses form the theme of this book.

1.2 Interaction of Electronic Center with Optical Radiation

Electromagnetic radiation interacts with an electronic center through the electric or
magnetic fields of the radiation, the operators describing the interaction being
$-\boldsymbol{p} \cdot \boldsymbol{E}$ or $-\boldsymbol{m} \cdot \boldsymbol{B}$ for these two fields respectively. The electric dipole moment is
$\boldsymbol{p} = \Sigma_i\, e\boldsymbol{r}_i$, where the summation is over all the optically active electrons. Similarly,
the magnetic dipole moment is $\boldsymbol{m} = \Sigma_i\, (e/2m)\, (\boldsymbol{l}_i + 2\boldsymbol{s}_i)$. The probability of a
radiative transition, emission or absorption, between an initial level a and a final
level b is proportional to the square of the matrix element between a and b of the
appropriate operator, and this quantity is called the strength, S, of the transition.

$$S(ab) = \sum_{a,b} |\langle b \,|\, D \,|\, a \rangle|^2 \tag{1.1}$$

where the general dipole operator, D, is replaced by $\boldsymbol{p}$ for an electric dipole transi-
tion and by $\boldsymbol{m}$ for a magnetic dipole transition. The summation in (1.1) is over the
two manifolds of states which make up levels a and b.

This matrix element is zero if states a and b differ in total spin, hence we find
the spin selection rule: $\Delta S = 0$. Because of spin-orbit coupling, some admixture of

difference spin states occurs and as a result spin is not a valid quantum parameter and the spin selection rule is not rigorous. Nevertheless, it is found that, in general, spin-allowed ($\Delta S = 0$) transitions are stronger than spin-forbidden ($\Delta S \neq 0$) transitions. When we have discussed the orbital nature of the states we will derive orbital selection rules.

It is useful to define a dimensionless quantity called the *oscillator strength, f* [1.1, 1.2]:

$$f(ab) = \frac{1}{g_a} \sum_{a,b} \frac{8\pi^2 m\nu}{3he^2} |\langle b | D | a \rangle|^2$$

$$= \frac{1}{g_a} \frac{8\pi^2 m\nu}{3he^2} S(ab) \tag{1.2}$$

where ν is the frequency of the transition and $h\nu = |E_b - E_a|$. D is the appropriate dipole operator, p or m, and g_a is the statistical weight of the initial state a. For an allowed electric dipole transition $f_{ED} \simeq 1$, while for an allowed magnetic dipole transition $f_{MD} \simeq 10^{-6}$, so the magnetic dipole process is very much the weaker. Higher multipole processes can also occur but they are negligibly small.

Macroscopically we measure the strength of an absorption transition by measuring the absorption coefficient $k(\nu)$ as the radiation passes through a material containing the optically active centers. $k(\nu)$ is defined by

$$I_\nu(d) = I_\nu(0) \exp\left[-k(\nu)d\right] \tag{1.3}$$

where $I_\nu(d)$ *is* the intensity of the radiation of frequency ν after traversing a thickness d of the material. We will assume that $k(\nu)$ is the absorption coefficient found after averaging over all polarizations relative to the crystal axes of the host material. We define a normalized absorption coefficient, $\sigma(\nu) = N^{-1}k(\nu)$ where N is the number of centers per unit volume. If the absorption occurs by an electric dipole process, then $\sigma(\nu)$ is related to f_{ED} and S_{ED} by [1.1, 2]

$$\int \sigma(\nu)d\nu = N^{-1} \int k(\nu)d\nu = \frac{1}{4\pi\epsilon_0} \frac{\pi e^2}{mc} \left[\left(\frac{n^2+2}{3}\right)^2 \cdot \frac{1}{n}\right] f_{ED}(ab)$$

$$= \frac{1}{4\pi\epsilon_0} \frac{8\pi^3\nu}{3hc} \left[\left(\frac{n^2+2}{3}\right)^2 \cdot \frac{1}{n}\right] \frac{1}{g_a} S_{ED}(ab) \tag{1.4}$$

The term in the square brackets takes into account the polarization of the material by the electric field. n is the refractive index. In these formulas SI units are employed. The formulas for cgs units are identical to the above except that the $1/4\pi\epsilon_0$ term is omitted.

The Einstein spontaneous transition probability for a radiative transition between a and b is $A(ab)$. If the radiative process is electric dipole, then we have

$$A_{ED}(\nu) = \frac{1}{4\pi\epsilon_0} \frac{8\pi^2 \nu^2 e^2}{mc^3} \left[\left(\frac{n^2+2}{3} \right)^2 \cdot n \right] f_{ED}(ab)$$

$$= \frac{1}{4\pi\epsilon_0} \frac{64\pi^4 \nu^3}{3hc^3} \left[\left(\frac{n^2+2}{3} \right)^2 \cdot n \right] \frac{1}{g_a} S_{ED}(ab). \tag{1.5}$$

If $A_{ED}(ab)$ is the only radiative process from level a, then $A_{ED}(ab) = \tau_R^{-1}$, where τ_R is the radiative decay time. Then by putting numerical values into (1.5) we can write (SI units)

$$f_{ED}(ab)\tau_R(ab) = 1.5 \cdot 10^4 \, \lambda_0^2 \left[\left(\frac{n^2+2}{3} \right)^2 \cdot n \right]^{-1} \tag{1.6}$$

where λ_0 is the wavelength in vacuum. For $\lambda_0 = 5000$ Å and $n = 1$ the quantity on the right has the approximate value $4 \cdot 10^{-9}$ s. This means that an allowed electric dipole transition ($f_{ED} = 1$) will have a radiative decay time of around $4 \cdot 10^{-9}$ s. For the trivalent rare-earth ions and the transition metal ions we usually find τ_R between 10^{-6} s and 10^{-2} s. These then are either weak electric dipole transitions or magnetic dipole transitions. For molecular centers one find the whole range of τ_R values, up to 10 s and longer.

The above formulas for absorption coefficient and radiative decay rate also hold for magnetic dipole processes, but f_{MD} and S_{MD} are used, and the $(n^2 + 2/3)^2$ term is replaced by n^2.

Lastly we mention the Einstein stimulated transition probability, B. If ρ_ω is the energy density of the radiation field per unit volume per unit frequency range ($\Delta\omega = 1$), then the probability per second that a transition between levels a and b will be stimulated by the resonant radiation field is $B\rho_\omega$. B is related to the Einstein spontaneous transition probability between the same levels, A, through

$$A/B = (\hbar\omega^3/\pi^2 c^3)n^3 = (4h\nu^3/c^3)n^3. \tag{1.7}$$

1.3 Eigenstates for the Electronic Center in a Solid

The Hamiltonian describing the optically active electronic center in an optically inert crystalline solid can be written

$$\mathcal{G} = \mathcal{G}_{\text{isolated center}} + \mathcal{G}_{\text{elec-static lattice}} \tag{1.8}$$
$$+ \mathcal{G}_{\text{elec-dynamic lattice}} + \mathcal{G}_{\text{dynamic lattice}}.$$

$\mathcal{G}_{\text{isolated center}}$ describes the electronic center as if it were isolated from the remainder of the solid. For dopant ions in an inorganic solid this is $\mathcal{G}_{\text{free ion}}$ with eigenstates $^{2S+1}L_J$. For molecular centers this can be written $\mathcal{G}_{\text{isolated molecule}}$, and we shall consider this term in more detail later in this section. For an F center, which is an electron trapped at a cation vacancy, $\mathcal{G}_{\text{isolated center}}$ and $\mathcal{G}_{\text{elec-static lattice}}$ cannot be separated from each other.

$\mathscr{G}_{\text{elec-static lattice}}$ describes how the center is affected by the average static environment. For dopant ions this is the crystal field or ligand field energy, and it is larger for transition metal ions than for rare earth ions. This is not an important term for molecular centers which interact only weakly with their environments.

$\mathscr{G}_{\text{dynamic lattice}}$ is the vibrational energy of the crystalline lattice, which is described in terms of lattice phonon modes.

$\mathscr{G}_{\text{elec-dynamic lattice}}$ describes how the electronic center is affected by the lattice modes. For ions in a crystalline solid this can be visualized as a dynamic crystal field energy, and it can modify the shape and strength of the optical transitions. In addition, it can give rise to nonradiative processes on the ions. For molecular solids this is not an important term as the interaction between the optically active molecular center and the adjacent molecules of the host material is weak. When the concentration of electronic centers is high so that adjacent centers can interact with each other, $\mathscr{G}_{\text{elec-dynamic lattice}}$ can affect the transfer of optical excitation energy between adjacent centers. This transfer will be discussed in a later section. Since the molecular center is a much more complicated entity than the ionic center, we need to consider $\mathscr{G}_{\text{isolated molecule}}$ in more detail. We write it as

$$\mathscr{G}_{\text{isolated molecule}} = \mathscr{G}_{\text{static molecule}} + \mathscr{G}_{\text{mol. vibrations}}$$
$$+ \mathscr{G}_{\text{elec-mol. vibrations}} \tag{1.9}$$

The first-term is the energy of the electrons in a rigid time-average molecular structure. The second term describes the allowed intra-molecular vibrations, while the third term describes how the electronic energy is affected by these intramolecular vibrations. This last term plays a similar role for molecular solids as $\mathscr{G}_{\text{elec-dynamic lattice}}$ plays for ionic solids. The three terms of (1.9) combined are often called $\mathscr{G}_{\text{vibronic}}$ but will be designated for simplicity as $\mathscr{G}_{\text{elec}}$.

In a spectroscopic treatment of ionic centers, one first works out the eigenstates of $\mathscr{G}_{\text{free ion}} + \mathscr{G}_{\text{elec-static lattice}}$. One gets a finite number of eigenstates with discrete energy levels, and one can calculate the strengths of the sharp optical transitions between these states. $\mathscr{G}_{\text{elec-dynamic lattice}}$ is then taken into account by perturbation theory. This treatment of ionic centers is described in Sect. 1.4.

In a spectroscopic treatment of molecular centers in solids, one first works out $\mathscr{G}_{\text{elec}}$ (actually $\mathscr{G}_{\text{vibronic}}$) from ab initio calculations or from *free molecule gas-phase spectroscopic data* (for which, if not available, liquid or solid solution data may be substituted). In the latter case one utilizes eigenvalues and optical transition strengths derived from spectroscopic analysis. The $\mathscr{G}_{\text{elec-static lattice}}$ term involves what is called the *site-shift* (energy shift) and *site-group splitting*. A group-theoretical consideration based on a correlation of the free molecule symmetry with that of the site gives the number of site-group components and predicts whether a transition, forbidden in the free molecule, becomes allowed in the solid. However, the magnitude of the shift and splitting are usually derived from spectroscopic measurements. The term $\mathscr{G}_{\text{elec-dynamic lattice}}$ is again treated in Sect. 1.4. The treatment of molecular centers is decribed in Sect. 1.5.

1.4 Energy Levels and Radiative Transitions in Ionic Centers

In this section we consider the optical spectroscopy of individual ionic centers in a solid when the concentration is so low that the centers do not interact with each other [1.3]. We treat rare earth ions and transition metal ions separately. Other centers, such as color centers, are not considered as these are not the systems of major interest in the later chapters.

1.4.1 Rare Earth Ions in a Static Environment

For the rare earth ions the crystal field energy, $\mathscr{G}_{\text{elec-static lattice}}$, is weak because of the shielding of the outer $5s$ and $5p$ shells of electrons. So we consider $\mathscr{G}_{\text{free ion}}$ first and take the other terms into account afterwards by perturbation theory.

We write the free ion Hamiltonian as

$$\mathscr{G}_{\text{free ion}} = \mathscr{G}_0 + \mathscr{G}_C + \mathscr{G}_{\text{s.o.}} \tag{1.10}$$

$\mathscr{G}_0$ describes the interaction of each optically active electron with the spherically symmetric ion core. This gives us the independent $4f$ atomic electron orbitals which form the $(4f)^N$ electron *configuration*. $\mathscr{G}_C$ takes into account the Coulomb interaction of the $4f$ electrons with each other. $\mathscr{G}_C$ splits the $(4f)^N$ configuration state into a number of states of different energy, each of which is characterized by values of L and S. We call these the *LS terms*. Configuration mixing by $\mathscr{G}_C$ is small and usually neglected. Particularly if the number (N) of $4f$ electrons is large, there can be more than one state with the same values of L and S, and so an additional label (γ) must be used. The states of different energy but with the same LS values are mixed together by $\mathscr{G}_C$.

Next spin-orbit coupling is taken into account. This interaction has the form

$$\mathscr{G}_{\text{s.o.}} = \sum_i \xi(r_i) l_i \cdot s_i \tag{1.11}$$

where the summation is over all the $4f$ electrons. Since $\mathscr{G}_{\text{s.o.}}$ commutes with J, the eigenstates of $\mathscr{G}_{\text{s.o.}}$ are labelled by J, M_J. If we assume that the matrix elements of $\mathscr{G}_{\text{s.o.}}$ are much smaller than the separation between terms, then we can neglect the mixing of different LS terms. In this approximation (the Russell-Saunders approximation), $\mathscr{G}_{\text{s.o.}}$ can be written as $\zeta L \cdot S$, and it splits up each term into a number of states each of which is characterized by the quantum numbers SLJ. These are the *J multiplets* and the separation between them should be in accordance with the Landé interval rule. Each of the LSJ levels is $(2J + 1)$-fold degenerate, these states being characterized by the M_J values.

In practice the different LS terms are too close together for the Russel-Saunders approximation to be valid and so $\mathscr{G}_{\text{s.o.}}$ mixes up states of the same J (and M_J)

but from different LS terms. The resultant *intermediate coupling* eigenstates, $|f^N\{\gamma SL\}J\rangle$, can be written in terms of the Russel-Saunders states ($|f^N\gamma SLJ\rangle$)

$$|f^N\{\gamma'S'L'\}J\rangle = \sum_{\gamma SL} c(\gamma SL)|f^N\gamma SLJ\rangle. \tag{1.12}$$

The c coefficients are generally obtained by computer diagonalization of the $\mathscr{G}_C + \mathscr{G}_{s.o.}$ matrix. The $\{\gamma'S'L'\}$ label for the intermediate coupling state in (1.12) is usually that which corresponds to the largest contributing Russell-Saunders state. Very elaborate and detailed methods have been worked out for obtaining fairly exact free ion states for the triply charged rare-earth ions. These methods are discussed in [1.4–7], in a recent review article by *Pappalardo* [1.8], and in some technical memoranda [1.9].

Figure 1.1 (the Dieke diagram) shows the energy levels of the trivalent rare earth ions in LaCl₃, and the states are labelled according to the $S'L'J$ values in the form $^{2S'+1}L'_J$. A measure of the deviation from Russell-Saunders coupling is the depature of the separation between different J levels in the same $^{2S+1}L_J$ group from the Lande interval rule.

The crystal field energy, $\mathscr{G}_{\text{elec-static lattice}}$, is now taken into account. This causes a splitting of the free ion levels, and the extent of the splitting in LaCl₃ is indicated by the width shown for the levels in the Dieke diagram. The crystal field for a particular site in a particular host crystal is parameterized by a number of parameters, B_q^k. Group theory tells us the number of parameters needed to characterize a given crystal field, and the values of these parameters are obtained by comparing calculated and observed splittings. The crystal field term can mix states with different J values (*J mixing*) which can affect radiative selection rules.

The positions of the levels shown in Fig. 1.1 were obtained by absorption studies. In addition, luminescence occurs from those levels in Fig. 1.1 which show a pendant semicircle. For a given rare-earth ion all these free ion levels are formed from the same $(4f)^N$ configuration and so transitions between them should occur only by a magnetic dipole process. Most transitions on rare earth ions, however, occur by an electric dipole process. Hence there must be some mixing of the opposite parity $(4f)^{N-1}5d$ configuration into the $(4f)^N$ configuration. This mixing can occur if the rare-earth ion experiences a crystal field which lacks inversion symmetry – which is the case in many crystals. But even when the rare earth ion appears to occupy a site with inversion symmetry, the transitions are often electric dipole. This may indicate a tendency for the substituting rare earth ion to distort its surroundings and remove the inversion symmetry.

We consider the transitions between free ion states, neglecting the splittings due to the crystal field but allowing for some admixture of opposite parity $(4f)^{N-1}5d$ states by the crystal field.

The strength of the transition $S_{ED}(ab)$ is given by

$$S_{ED}(ab) = \sum_{a,b} |\langle b|D|a\rangle|^2 \tag{1.1}$$

where a (or b) refers to the full set of states in the $f^N \{\gamma SL\} J$ multiplet. $S_{ED}(ab)$ is the sum of squares of a number of matrix elements. Now if an odd-parity crystal field term, $\mathscr{G}_{odd}$, mixes states of opposite parity and permits the electric dipole process, then the above matrix element has the form [1.10, 11]

$$\sum_{\beta} \frac{\langle b \,|\, \mathscr{G}_{odd} \,|\, \beta \rangle \langle \beta \,|\, D \,|\, a \rangle}{E_b - E_\beta} + \text{converse}$$

where β signifies all those opposite parity states mixed in by $\mathscr{G}_{odd}$. We do not have sufficient knowledge about the nature and positions of the β states to carry out an exact theoretical calculation of the above matrix element. *Judd* [1.11] and *Ofelt* [1.10], working on this problem independently, introduced a very helpful simplification by ascribing the same energy denominators to all β states. The constant energy denominator can now be removed from the summation and closure used. In this way one can regard

$$\sum_{\beta} \mathscr{G}_{odd} \,|\, \beta \rangle \langle \beta \,|\, D$$

as an even parity operator which operates between the free ion multiplets. S_{ED} can now be written

$$S_{ED}(ab) = e^2 \sum_{t=2,4,6} \Omega_t \,|\, \langle f^N \gamma_b S_b L_b J_b \,\|\, U^{(t)} \,\|\, f^N \gamma_a S_a L_a J_a \rangle \,|^2 \qquad (1.13)$$

Ω_t are the Judd-Ofelt intensity parameters and reflect the strength and nature of the odd-parity field. The reduced matrix elements of the tensor operator $U^{(t)}$ can be evaluated. Values have been tabulated for many ions in different hosts and the sources are listed by *Riseberg* and *Weber* [1.12]. *Carnall* et al. [1.9] have given a complete listing of values for transitions on trivalent rare earth ions in LaF_3.

The relationship between S_{ED} and f_{ED}, and how they are related to the absorption coefficient are given in (1.2, 4, 5). In this case the statistical weight factor g_a is $(2J_a + 1)$.

By measuring the absorption strengths for a number of transitions from the ground multiplet, one can determine the S_{ED} values and from these one can obtain values for the Judd-Ofelt parameters Ω_t. Once the Judd-Ofelt parameters have been obtained for a given rare earth-host combination, they can be used to calculate absorption strengths and radiative decay rates between any two of the f^N levels of the system. The radiative decay rate from a particular state a is given by

$$1/\tau_R = \sum_b A(ab). \qquad (1.14)$$

If the observed decay time, τ, is shorter than τ_R, the discrepancy is attributed to nonradiative processes. Hence one gets the nonradiative decay rate from state a:

$$W_{nr} = 1/\tau - \sum_b A(ab). \qquad (1.15)$$