Infrared and Raman Spectroscopy of Polymers

H. W. SIESLER K. HOLLAND-MORITZ

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PREFACE

The aim of this book is to help scientists in universities and in industry to make effective use of vibrational spectroscopy in solving problems in polymer physics and polymer analysis. Although some excellent early monographs on the infrared (IR) spectroscopy of polymers are available, the publication of this book would appear justified, and indeed necessary, in view of both the introduction of new techniques, such as Fourier transform IR (FTIR) spectroscopy, and the resulting widening of the field of application for vibrational spectroscopy and also to deal at the same time with both IR and Raman spectroscopy of polymers.

Given the amount of material involved, the presentation of theoretical principles, experimental techniques, and application examples in a single volume must inevitably result in the individual reader's regretting the absence of certain items while feeling others to be superfluous. A detailed discussion of the results of vibrational spectroscopy for individual classes of polymers has deliberately been omitted.

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H. W. Siesler
K. Holland-Moritz

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Chapter 1

INTRODUCTION

Infrared (IR) and Raman spectroscopy have become most important tools for the characterization of the chemical and physical nature of polymers. Until the late 1960s, almost all investigations were based on information derived from IR spectra alone, but since the introduction of laser sources, Raman spectroscopy has increasingly contributed to the elucidation of polymeric structure.

In principle, IR and Raman spectra provide qualitative and quantitative information about the following structural details of the polymer under examination:

1. Chemical nature: structural units, type and degree of branching, end groups, additives, impurities
2. Steric order: *cis-trans* isomerism, stereoregularity
3. Conformational order: physical arrangement of the polymer chain, e.g., planar zigzag or helix conformation
4. State of order: crystalline, mesomorphous, and amorphous phases; number of chains per unit cell; intermolecular forces; lamellar thickness
5. Orientation: type and degree of preferential polymer chain and side group alignment in anisotropic materials

As a consequence of the sensitivity of IR and Raman spectroscopy to changes in the dipole moment and polarizability, respectively, of the vibrating group under consideration, IR spectroscopy generally yields more useful information for the identification of polar groups, whereas Raman spectroscopy is especially helpful in the characterization of the homonuclear polymer backbone. Furthermore, the complementary nature of IR and Raman analysis is of particular importance in connection with symmetry considerations of the investigated structure. Thus, generally speaking, asymmetric vibrations give rise to strong IR absorptions, while symmetric modes yield prominent Raman bands.

There exist two basic approaches to the study of polymers by vibrational spectroscopy. The empirical interpretation of IR and Raman spectra is based on the concept of nearly independently vibrating atomic groups in the macromolecule and collects information mainly on the single structural features of the polymer, e.g., chemical composition, configuration, conformation, crystallinity. The theoretical treatment, frequently supported by spectral data obtained from isotope-substituted polymer analogues and polarization measurements on specimens showing directional properties, focuses on the complete assignment of IR and Raman spectra in terms of the vibrational behavior of the polymeric system. Both treatments have their drawbacks and limitations which have to be kept in mind; while the empirical method is less comprehensive (e.g., the phase relations between the motions of individual groups are neglected), the idealized model of polymer structure and the associated inter- and intramolecular forces assumed in the theoretical treatment cannot be materialized in real polymers.

Despite the uncontested importance of IR and Raman spectroscopy for the characterization of macromolecular structure, it should be emphasized that only a limited number of problems may be solved by the exclusive application of these spectroscopic techniques. Thus, in the majority of analytical investigations of polymer constitution and any additives, chemical separation of the components is inevitable; a more complete picture of the sequence distribution and stereoregularity of structural units in polymers is obtained by a combination of vibrational and nuclear magnetic resonance (NMR) spectroscopy; the results of IR and Raman spectroscopic investigations at elevated temperature are advantageously correlated with differential thermal analysis (DTA) or differential scanning calorimetry (DSC) measurements; and last but not least, a thorough knowledge of the structure of crystalline polymers cannot be attained without application of x-ray diffraction. These few, far from comprehensive, examples demonstrate that maximum information on the structural details in question can be obtained only by an appropriate choice and combination of chemical and physical methods.

Chapter 2

THEORETICAL AND EMPIRICAL ASPECTS OF INFRARED AND RAMAN SPECTROSCOPY

In a first approximation the energy E of a molecule can be separated into four additive terms belonging to various motions of this molecule:

1. Translation of the molecule (This motion, however, does not lead to any interaction with electromagnetic radiation and will be neglected in this discussion.)
2. Motions of the electrons in the molecule (E_{el})
3. Vibrations of the atoms or atomic groups in the molecule (E_{vib})
4. Rotations of the entire molecule (E_{rot})

$$E = E_{el} + E_{vib} + E_{rot} \tag{2.1}$$

This simplification is justified because energies of the electronic, vibrational, and rotational motions differ considerably ($E_{el} >> E_{vib} >> E_{rot}$). Only in the case of gases do the absorption bands due to vibrations of the atoms show a fine structure caused by rotational transitions. In solids (crystals, polymers) free rotation of the molecule is restricted, and the rotational energy term in Eq. (2.1) can be neglected. Thus, the energy of such a molecule is determined by electronic and vibrational contributions only.

A molecule can interact with electromagnetic radiation when Bohr's frequency relation

$$\Delta E = h\nu \qquad \text{with } \Delta E = E_k - E_m \tag{2.2}$$

is fulfilled. In this equation, ΔE represents the energy difference between two allowed energy levels k and m, h Planck's constant, and ν the frequency of the absorbed or emitted electromagnetic radiation. Although IR and Raman spectroscopies are based on the same physical origin - the vibrations of the atoms of a molecule which in quantum mechanics correspond to allowed transitions between different vibrational energy levels - the interaction between electromagnetic radiation and the sample differs considerably in both spectroscopic methods. In IR spectroscopy specific frequencies of polychromatic radiation are absorbed by the sample, whereas in Raman spectroscopy the monochromatic, generally visible radiation can be scattered elastically with the same frequency (Rayleigh scattering) or inelastically with higher or lower frequencies (Raman scattering). Energies, wavenumbers, and wavelengths of the radiation used in IR and Raman spectroscopy are listed in Table 2-1.

TABLE 2-1 Energies, Wavenumbers, and Wavelengths of the Radiation Used in IR and Raman Spectroscopy

	Excitation source (nm)	Absolute wavenumber range (cm^{-1})	Relative wavenumber range (Δcm^{-1})	Wavelength range (nm)	Vibrational energy (kJ/mol)
IR	Hg, Globar		10-10000		$1.3 \cdot 10^{-1}$ - 120
Raman	Ar^+, 488	20486-10486	3-10000	488 - 953	$4 \cdot 10^{-2}$-120
	Ar^+, 514.5	19430- 9430	3-10000	514.5-1060	
	Ar^+, 568.2	17595- 7595	3-10000	568.2-1316	
	He-Ne, 632.8	15798- 5798	3-10000	632.8-1724	
	Kr^+, 530.8	18839- 8839	3-10000	530.8-1131	
	Kr^+, 647.1	15449- 5449	3-10000	647.1-1834	

2.1 INTERACTION OF MOLECULES WITH ELECTROMAGNETIC RADIATION[†]

Before discussing the theory of molecular interaction with electromagnetic radiation, we give an example from electronics to illustrate the effect of absorption. The electromagnetic radiation of a defined frequency irradiated by a broadcasting station can be received in a radio by means of a simple oscillatory circuit with antenna, capacitor, and coil. This circuit selectively "absorbs" only that frequency which corresponds to its *eigen-* or *resonance* frequency. From this example a very simplified model for the interaction of IR radiation with matter can be derived. Let us assume in a first approximation that the sample consists of vibrating dipoles which interact with the incident radiation. Each dipole can interact with that frequency which corresponds to its eigenfrequency. Thus, the molecule absorbs only those frequencies from the incident radiation which coincide with the frequencies of the atomic oscillators. The residual nonabsorbed radiation is reflected or transmitted.

In a more theoretical consideration we have to examine how the electromagnetic radiation can perturb the potential energy of a molecule and induce a transition from an initial stationary state. In quantum mechanics this problem is solved by introduction of an additive term, the *interaction operator* H_{int}, to the Hamiltonian H_o of the unperturbed system. Thus, the Schrödinger equation of the stationary system can be written as follows:

$$(H_o + H_{int})\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} \qquad (2.3)$$

Since the perturbation alters the state of the system, a superposition of the solutions $\Psi_k(r,t)$ of the unperturbed system can be used to provide a solution of Eq. (2.3):

$$\Psi(r,t) = \sum_k a_k(t)\Psi_k(r,t) \qquad (2.4)$$

The coefficients $a_k(t)$ are time-dependent weighting factors, where $a_k^*(t)a_k(t)$ gives the importance of the state k. From Eqs. (2.3) and (2.4) it follows that

---

[†] For further comprehensive studies see Refs. 1 to 10.

$$(H_o + H_{int})\sum_k a_k(t)\Psi_k(r,t) = -\frac{\hbar}{i}\sum_k \dot{a}_k(t)\Psi_k(r,t) \tag{2.5}$$
$$-\frac{\hbar}{i}\sum_k a_k(t)\dot{\Psi}_k(r,t)$$

Since $\Psi_k(r,t)$ are solutions of the Schrödinger equation for the conservative system, Eq. (2.5) simplifies to

$$H_{int}\sum_k a_k(t)\Psi_k(r,t) = -\frac{\hbar}{i}\sum_k \dot{a}_k(t)\Psi_k(r,t) \tag{2.6}$$

Because of the orthogonality of the wavefunctions Ψ_k, left multiplication with Ψ_m^* and integration over all space gives

$$\dot{a}_m(t) = -\frac{i}{\hbar}\sum_k a_k(t)\int\Psi_m^*(r,t)H_{int}\Psi_k(r,t)\,d\tau \tag{2.7}$$

The residual terms in the sum $\sum \dot{a}_k(t)\Psi_k(r,t)$ cancel because the initial state of the system is characterized by $a_m(0) = 1$ and $a_k(0) = 0$ for $k \neq m$. Thus, upon separation of $\Psi_k(r,t)$ into $\Psi_k(r)\exp(\frac{i}{\hbar}E_k t)$, it follows with Eq. (2.3) for the rate at which a system can change from one stationary state to another under the influence of a perturbing electromagnetic field:

$$\dot{a}_m(t) = -\frac{i}{\hbar}\sum_k a_k(t)\exp\{\frac{i}{\hbar}(E_m - E_k)t\}\int\Psi_m^*(r)H_{int}\Psi_k(r)d\tau \tag{2.8a}$$

The expression

$$\int\Psi_m^*(r)H_{int}\Psi_k(r)\,d\tau = \langle m|H_{int}|k\rangle \tag{2.9}$$

is called the *transition moment*. With this notation we can rewrite Eq. (2.8a) as follows:

$$\dot{a}_m(t) = -\frac{i}{\hbar}\sum_k a_k(t)\exp\{\frac{i}{\hbar}(E_m - E_k)t\}\langle m|H_{int}|k\rangle \tag{2.8b}$$

Putting

$$a_k(t) = b_k(t)\exp(\frac{i}{\hbar}E_k t) \tag{2.10}$$

we obtain a set of homogeneous differential equations

$$\dot{b}_m(t) = -\frac{i}{\hbar}\{E_m b_m(t) + \sum_k b_k(t)\langle m|H_{int}|k\rangle\} \quad (m = 1,\ 2, .., n) \qquad (2.11a)$$

Assuming that the time-dependent factor of H_{int} is either constant within the interval $0 \le t \le \theta$ or proportional to $\exp(i\omega t) + \exp(-i\omega t)$, this system can be resolved by any standard method [11, 12], since $\exp[\frac{i}{\hbar}(E_m - E_k)t]$ in Eq. (2.9b) can be replaced by the following expression $\exp[\frac{i}{\hbar}(E_m - E_k - \hbar\omega)t] + \exp[\frac{i}{\hbar}(E_m + E_k - \hbar\omega)t]$. Introduction of $b_k(t) = c_k \exp(\alpha t)$ leads to:

$$-(\frac{\hbar}{i}\alpha + E_m)c_m = \sum_k c_k\langle m|H_{int}|k\rangle \qquad (m = 1,\ 2,\ ..,\ n) \qquad (2.11b)$$

This system can be solved only if the determinant of the coefficients vanishes:

$$\begin{vmatrix} -E_1 - \frac{\hbar}{i}\alpha & \cdots & \langle n|H_{int}|1\rangle \\ \langle 1|H_{int}|2\rangle & \ddots & \\ \cdots\cdots & -E_k - \frac{\hbar}{i}\alpha \ \ddots & \cdots\cdots \\ \langle 1|H_{int}|n\rangle & \cdots & -E_n - \frac{\hbar}{i}\alpha \end{vmatrix} = 0 \qquad (2.12)$$

Since the perturbation caused by the interaction of the molecule with electromagnetic radiation can be adopted to be small, we have to expand Eq. (2.12) only up to second-order terms. Thus, we obtain

$$\frac{h}{i}\alpha_t = -E_l + \sum_{k\neq l}^{n} \frac{\langle m|H_{int}|l\rangle\ \langle l|H_{int}|k\rangle}{E_k - E_l} \qquad (l = 1,\ 2, ..,\ n) \qquad (2.13)$$

With these eigenvalues of Eq. (2.12) we can finally derive, after determination of c_k and $b_k(t)$, the expression for $a_k(t)$:

$$a_k(t) = \frac{\langle m|H_{int}|k\rangle}{E_m - E_k}\left\{1 - \exp[\frac{i}{\hbar}(E_k - E_m)t]\right\} \qquad (2.14)$$

$$+ \frac{1}{E_m - E_k}\sum_{l>m}^{k} \frac{\langle m|H_{int}|l\rangle\ \langle l|H_{int}|k\rangle}{E_m - E_l.}\left\{1 - \exp[\frac{i}{\hbar}(E_k - E_m)t]\right\}$$

$$+ \sum_{l>m}^{k} \frac{\langle m|H_{int}|l\rangle\ \langle l|H_{int}|k\rangle}{(E_m - E_l)\ (E_l - E_k)}\left\{1 - \exp[\frac{i}{\hbar}(E_k - E_m)t]\right\}$$