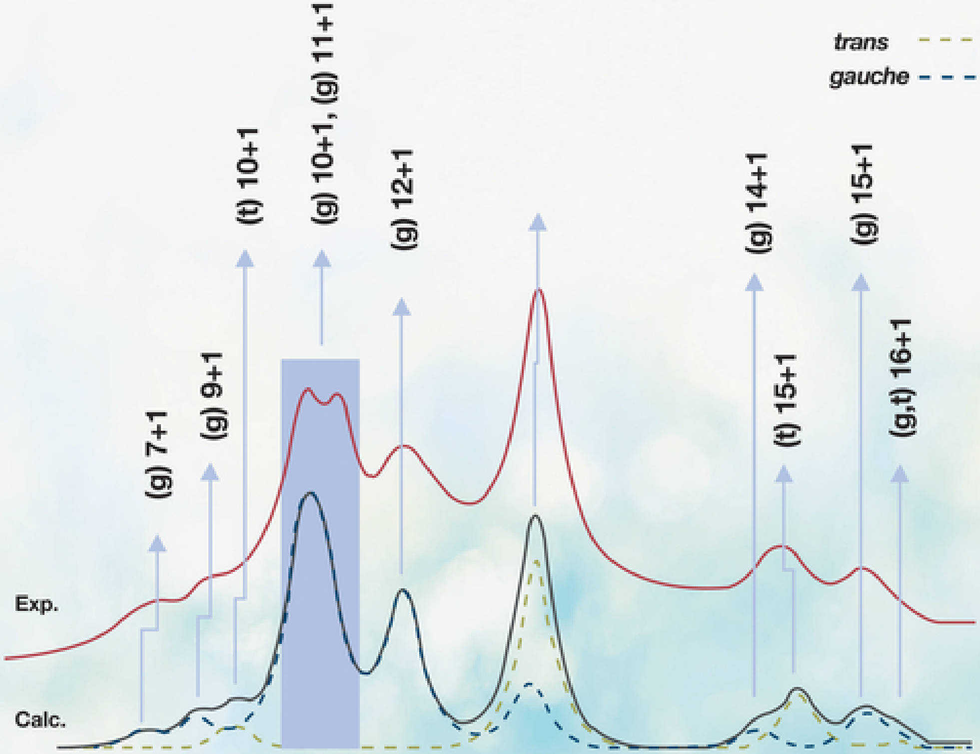
WILEY-VCH

Edited by Yukihiro Ozaki, Marek Janusz Wójcik,
and Jürgen Popp

Molecular Spectroscopy

A Quantum Chemistry Approach



Molecular Spectroscopy

Molecular Spectroscopy

A Quantum Chemistry Approach

Edited by
Yukihiro Ozaki
Marek Janusz Wójcik
Jürgen Popp

Volume 1

WILEY-VCH

Molecular Spectroscopy

A Quantum Chemistry Approach

Edited by
Yukihiro Ozaki
Marek Janusz Wójcik
Jürgen Popp

Volume 2

WILEY-VCH

Editors

Yukihiro Ozaki
Kwansei Gakuin University
Department of Chemistry
2-1 Gakuen
Kobe Sanda Campus
669-1337 Sanda, Hyogo
Japan

Marek Janusz Wójcik
Jagiellonian University
Faculty of Chemistry
Gronostajowa 2
30-387 Kraków
Poland

Jürgen Popp
Leibniz-Institut für Photonische Technol
Albert-Einstein-Str. 9
07745 Jena
Germany

Cover Image: Kindly provided by
Yukihiro Ozaki, Kwansei Gakuin
University, Japan; © Sirinarth
Mekvorawuth/EyeEm/Getty Images
(Background)

Library of Congress Card No.:
applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-34461-1
ePDF ISBN: 978-3-527-81462-6
ePub ISBN: 978-3-527-81460-2
oBook ISBN: 978-3-527-81459-6

Cover Design: Wiley
Typesetting SPi Global, Chennai, India
Printing and Binding

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

Contents to Volume 1

Contents to Volume 2

Contents to Volume 1

Contents to Volume 2

Preface

The purpose of this book is to outline the state-of-the-art quantum chemical approach to molecular spectroscopy. Over the last two decades or so, molecular spectroscopy has made remarkable progress; several novel spectroscopies such as terahertz spectroscopy, tip-enhanced Raman scattering (TERS), and far-ultraviolet (FUV) spectroscopy in condensed phase have emerged. Moreover, existing spectroscopies have shown prominent advances in this period. The advances in spectroscopies lie in the development of theory, instruments, spectral analysis, and applications. In spectral analysis quantum chemical approach is particularly important. It is useful not only for spectral analysis such as band assignments but also for studies of structure, reactions, and physical and chemical properties of molecules.

This book aims at making a strong bridge between molecular spectroscopy and quantum chemistry. For the last quarter of a century quantum chemistry has been extensively used for various spectroscopies such as vibrational spectroscopy, electronic spectroscopy, and nuclear magnetic resonance spectroscopy. However, one cannot find a good book that connects spectroscopy and quantum chemistry. This book may be the first one that explains comprehensively how quantum chemical approach can be applied to molecular spectroscopy. It covers FUV spectroscopy, UV–visible spectroscopy, near-infrared (NIR) spectroscopy, IR spectroscopy, far-IR spectroscopy/terahertz spectroscopy, Raman spectroscopy, and NMR spectroscopy. Almost all kinds of molecular spectroscopies are presented in this book. For quantum chemical approaches various new calculation methods are introduced. The recent rapid progress in supercomputers has made it possible to utilize these new methods. For example, anharmonic quantum chemical calculations are becoming popular due to advances in supercomputers. In applications many chapters deal with studies of hydrogen bonding and inter- and intramolecular interactions. In this book, we invited front runners from many countries who are currently very active in the molecular spectroscopy–quantum chemistry field.

This book is very useful not only for chemistry but also for applied physics, material sciences, biosciences, and industrial applications. It is suitable for molecular spectroscopists who are interested in quantum chemistry and quantum chemists who are interested in molecular spectroscopy. We hope this book will find many readers among students at graduate level as well as researchers and engineers in academia and industry.

Last but not the least, we would be most grateful if the book can inspire readers to use novel quantum chemistry approaches for molecular spectroscopy studies and/or to attempt to develop new approaches by themselves.

In closing, we would like to thank Dr. Lifen Yang, Ms. Shirly Samuel, and Mr. Jayakumar Ramprasad of Wiley for their continuous efforts in publishing this book.

April 2019

Yukihiro Ozaki, Sanda, Japan
Marek Janusz Wójcik, Krakow, Poland
Jürgen Popp, Jena, Germany

1

Interpretability Meets Accuracy in Computational Spectroscopy: The Virtual Multifrequency Spectrometer

Vincenzo Barone[1] *and Cristina Puzzarini*[2]

[1] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy*
[2] *Università di Bologna, Dipartimento di Chimica "Giacomo Ciamician", Via Selmi 2, 40126 Bologna, Italy*

The virtual multifrequency spectrometer (VMS), under active development in our laboratories over the last few years, is shortly described in this chapter by means of selected spectroscopic techniques and a few representative case studies. The VMS project aims to offer an answer to the following question: is it possible to turn strongly specialized research in the field of computational spectroscopy into robust and user-friendly aids to experiments and industrial applications? VMS contains a number of tools devised to increase the interaction between researchers with different background and to push toward new frontiers in computational chemistry. As a matter of fact, the terrific advancements in computational spectroscopy and the wide availability of computational and analytic tools are paving the route toward the study of problems that were previously too difficult or impossible to be solved and let imagine even more ambitious targets for fundamental and applied research. Under such circumstances, a robust, flexible, and user-friendly tool can allow for moving data analysis toward a proactive process of strategic decisions and actions. This chapter starts from these premises, and it proposes a perspective for a new virtual platform aimed at integrating past developments in theory, algorithms, and software with new workflow management and visualization tools. After a short review of the underlying theoretical framework, the features of the principal tools available in the current version of VMS for a selection of spectroscopic techniques are addressed in some details. Next, four case studies are presented, thus aiming to illustrate possible applications of VMS to systems of current interest for both fundamental and applied research. These applications convincingly show that even if several extensions of the software are planned or already under development, VMS represents a powerful and user-friendly tool for both computational and experimentally oriented spectroscopists.

Molecular Spectroscopy: A Quantum Chemistry Approach,
First Edition. Edited by Yukihiro Ozaki, Marek Janusz Wójcik, and Jürgen Popp.

1.1 Introduction

Spectroscopic techniques provide a wealth of qualitative and quantitative information on the chemical and physical–chemical properties of molecular systems in a variety of environments. Nowadays, sophisticated experimental techniques, mainly based on vibrational, electronic, and resonance spectroscopies, allow studies under various environmental conditions and in a noninvasive fashion [1, 2]. Particularly effective strategies are obtained when different spectroscopic techniques are combined together and further supported and/or integrated by computational approaches. Indeed, not only the spectral analysis is seldom straightforward, but also molecular spectra do not provide direct information on molecular structures, properties, and dynamics [3, 4]. The challenges can be posed by the intrinsic properties and complexity of the system and/or caused by thermal or environmental effects, whose specific roles are not easy to separate and evaluate. In such a context, computational spectroscopy is undoubtedly a powerful and reliable tool to unravel the different contributions to the spectroscopic signal and understand the underlying physical phenomena [5, 6]. However, direct vis-à-vis comparisons between experimental and computed spectroscopic data are still far from being standard. To fill this lack, a virtual multifrequency spectrometer (VMS) (http://dreamslab.sns.it/vms/) has been implemented with the aim of providing a user-friendly access to the latest developments of computational spectroscopy, also to nonspecialists [7–11]. As it will be better explained in the following section, VMS integrates state-of-the-art computational implementations of different spectroscopies with a powerful graphical user interface (GUI) [12], which offers an invaluable aid in preorganizing and displaying the computed spectroscopic information. For the sake of clarity, it should be noted that several codes incorporate implementation of spectroscopic properties at different levels of theory together with graphic engines. However, none of these tools offer the characteristics that should be considered mandatory for state-of-the-art computational spectroscopy (e.g. rigorous treatment of anharmonicity, vibronic contributions, etc.) and/or for flexible user-friendly graphical tools. In particular, it should emphasize the uniqueness of VMS in incorporating both general utilities needed by experimentally oriented scientists (e.g. conversion of theoretical quantities to experimental observables, manipulation of several spectra at the same time, etc.) and advanced tools for theoreticians and developers (e.g. resonance Raman [RR] spectra).

The aim of the present chapter is to provide an overview of the VMS software, thus focusing on its peculiarities and unique features. The chapter is organized as follows. In the following section, a brief summary of the general machinery of the VMS program and of the main technical aspects will be provided. This will be followed by a short introduction of the theoretical background for the selected spectroscopies (e.g. rotational, vibrational, vibronic, and magnetic) and of the corresponding quantum chemical (QC) requirements. Then, the current status of VMS will be presented in some detail with specific reference to rotational, vibrational, vibronic, and magnetic spectroscopy. Finally, applications will be illustrated with the help of four case studies, which will allow the capabilities of VMS to be demonstrated. Some general considerations will conclude the chapter.

1.2 The Virtual Multifrequency Spectrometer

VMS is a tool that integrates a wide range of computational and experimental spectroscopic techniques and aims at predicting and analyzing different types of molecular spectra as well as disclosing the static and dynamic physical–chemical information they contain [7]. VMS is mainly composed of two parts, namely, VMS-Comp, which provides access to the latest developments in the field of computational spectroscopy, and VMS-Draw, which provides a powerful GUI for an intuitive interpretation of theoretical outcomes and a direct prediction or comparison to experiment (http://dreamslab.sns.it/vms/) [7].

The spectroscopies supported by VMS are electron spin resonance (ESR), nuclear magnetic resonance (NMR), rotational (microwave [MW]), infrared (IR), vibrational circular dichroism (VCD), nonresonant Raman (nRR), resonance Raman, Raman optical activity (ROA), resonance Raman optical activity (RROA), electronic one-photon absorption (OPA) (i.e. UV–vis) and one-photon emission (OPE) (i.e. fluorescence), electronic circular dichroism (ECD), and circularly polarized luminescence (CPL).

1.2.1 The VMS Framework

The framework of the VMS program is graphically shown in Figure 1.1 [7]. The key feature of VMS is to provide a user-friendly access to computational spectroscopy tools also to nonspecialists. VMS integrates a powerful GUI, VMS-Draw, which offers an invaluable aid in the pre- and post-processing stages [12]. This permits a direct way to present the information produced by *in vitro* and *in silico* experiments, thus allowing the user to focus the attention on the underlying physical–chemical features without being concerned with technical details. VMS-Draw is interfaced with VMS-Comp [8, 9, 13], which

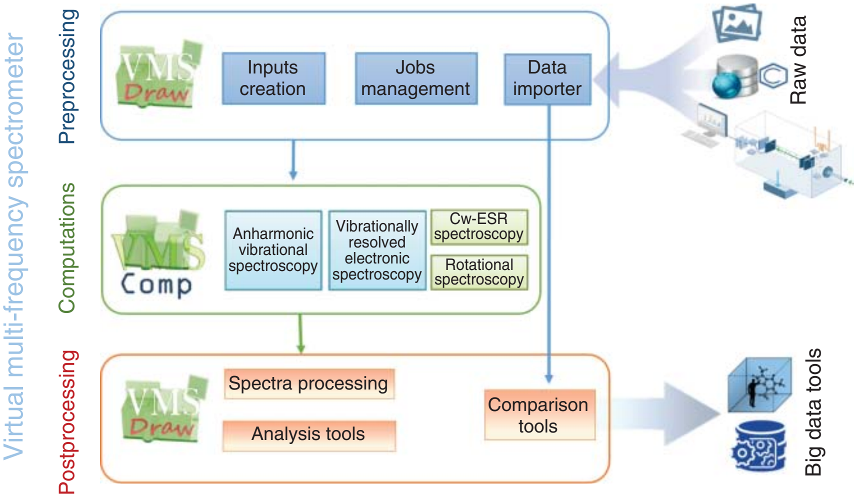


Figure 1.1 The framework of the virtual multifrequency spectrometer.

takes care of QC computations of the required spectroscopic parameters and all high-performance computing (HPC) aspects [7, 12]. Both VMS-Draw and VMS-Comp modules are either fully embedded with the Gaussian package [14] or loosely bound to other suites of QC programs, such as CFOUR [15]. In the last case, general input–output facilities as well as *ad hoc* scripts that permit effective interactions with other electronic structure codes than Gaussian have been developed or are still under development (see, for example, Ref. [10]). Overall, VMS has access to almost all computational models and to properties that are not yet available in the reference QC Gaussian suite. In addition to the large availability of QC methods and properties, VMS has the unique feature of allowing state-of-the-art computational spectroscopy studies driven by a flexible user-friendly graphical tool that furthermore includes those general utilities needed by experimentally oriented scientists (e.g. manipulations of several spectra at the same time, spectral normalization, etc.) and advanced tools for theoreticians and developers (e.g. resonance Raman spectroscopy). In the following sections, the theoretical background and the QC requirements for quantitative spectral prediction/analysis of selected spectroscopies are presented together with a description of the spectral simulation facilities and of the corresponding results.

1.2.2 The VMS Framework: Spectroscopies and Theoretical Background

The complete list of the spectroscopies available within the VMS software has been given above. In this chapter, we limit ourselves to the discussion of a selection of spectroscopies, namely, the rotational, vibrational, vibronic, and magnetic spectroscopies, for which we provide a short description of the theoretical background.

1.2.2.1 Rotational Spectroscopy

The terms of the effective rotational Hamiltonian are the pure rotational and centrifugal distortion contributions, which describe the rotational energy levels for a given vibrational state, with the ground state usually being the one of interest. While a complete treatment can be found in the literature (see, for example, Ref. [16]), here, we recall just the key aspects of interest.

The basic rotational Hamiltonian, within the semirigid rotor approximation, can be written as

$$H_{\mathrm{rot}} = H_{\mathrm{R}} + H_{\mathrm{qcd}} + H_{\mathrm{scd}} + \cdots \tag{1.1}$$

where H_{qcd} and H_{scd} are the quartic and sextic centrifugal terms, respectively. The dots refer to the possibility of including higher-order centrifugal contributions. H_{R} is the rigid rotor Hamiltonian:

$$H_{\mathrm{R}} = \sum_{\tau} \mathrm{B}_{\tau}^{\mathrm{eq}} \mathbf{J}_{\tau}^{2} \tag{1.2}$$

where $\mathrm{B}_{\tau}^{\mathrm{eq}}$ has been defined as follows:

$$\mathrm{B}_{\tau}^{\mathrm{eq}} = \frac{\hbar^{2}}{2hcI_{\tau\tau}^{\mathrm{eq}}} \tag{1.3}$$

where τ refers to the inertial axis. From a computational point of view, the equilibrium rotational constants are straightforwardly obtained from the geometry optimization.

Even if the equilibrium contribution to rotational constants is the most important, the effect of molecular vibrations cannot be neglected when aiming at a quantitative description of rotational spectra. Therefore, the term describing the dependence of the rotational constants on the vibrational quantum numbers should be incorporated in Eq. (1.3), and equilibrium rotational constants should be replaced by the effective rotational constants that contain the contributions beyond the rigid rotor harmonic oscillator (RRHO) approximation. Their effects on rotational motion can be conveniently described by means of vibrational perturbation theory (VPT), and we refer the reader to, for example, Refs. [16, 17] for a detailed treatment. While there are no corrections at the first order in VPT, at the second order (VPT2), the expression becomes [18]:

$$\mathrm{B}_{\tau}^{\mathrm{v}} = \mathrm{B}_{\tau}^{\mathrm{eq}} - \sum_{i=1}^{N} \alpha_{i,\tau} \left(v_i + \frac{d_i}{2} \right) \tag{1.4}$$

where the superscript v denotes a specific vibrational state and the sum runs on all fundamental vibrational modes i, with v_i being the corresponding quantum number and d_i its degeneracy order. The $\alpha_{i,\tau}$ values are the so-called vibration–rotation interaction constants and contain three contributions: the first one is a corrective term related to the moment of inertia, the second one is due to the Coriolis interactions, and the last is an anharmonic correction. Therefore, from a computational point of view, anharmonic force field (FF) calculations are required to correct the equilibrium rotational constants for vibrational effects.

The quartic centrifugal distortion Hamiltonian is defined as

$$H_{\mathrm{qcd}} = \frac{1}{4} \sum_{\tau\eta\varsigma\varrho} \tau_{\tau\eta\varsigma\varrho} \mathrm{J}_{\tau}\mathrm{J}_{\eta}\mathrm{J}_{\varsigma}\mathrm{J}_{\varrho} \tag{1.5}$$

where the tensor $\tau_{\tau\eta\varsigma\varrho}$ depends only on the harmonic part of the potential energy surface (PES). To obtain the quartic centrifugal distortion parameters actually employed, further contact transformations with purely rotational operators (thus diagonal in the vibrational quantum numbers) are then required. An analogous expression can be written for the sextic centrifugal distortion term H_{scd}, and the computation of the corresponding sextic centrifugal distortion constants involves harmonic, anharmonic, and Coriolis perturbation terms. Therefore, from a computational point of view, anharmonic force field computations are needed for their determination. To relate the experimental parameters to combinations of $\tau_{\tau\eta\varsigma\varrho}$ ($\tau_{\tau\eta\varsigma\varrho\epsilon\iota}$ in the case of sextics), it is necessary to further completely reduce the Hamiltonian. Different results are then obtained depending on the reduction chosen; see, for example, Refs. [16, 17, 19].

1.2.2.2 Vibrational Spectroscopy

For the simulation of vibrational spectra, a purely vibrational Hamiltonian (H_{vib}) is commonly used. In the framework of VPT2, which is based on Taylor expansions of the harmonic potential (V), vibrational (E_{v}) energies, and vibrational wavefunction, up to the second order [20], the vibrational Hamiltonian is defined as follows:

$$
\begin{aligned}
H_{\text{vib}} = {} & \frac{1}{2}\sum_{i=1}^{N}\omega_i(\mathbf{p}_i^{\,2}+\mathbf{q}_i^{\,2}) + \frac{1}{6}\sum_{i,j,k=1}^{N} k_{ijk}\mathbf{q}_i\mathbf{q}_j\mathbf{q}_k + \frac{1}{24}\sum_{i,j,k,l=1}^{N} k_{ijkl}\mathbf{q}_i\mathbf{q}_j\mathbf{q}_k\mathbf{q}_l \\
& + \sum_{\tau}\mathrm{B}_{\tau}^{\mathrm{eq}}\sum_{i,j,k,l=1}^{N}\zeta_{ij,\tau}\zeta_{kl,\tau}\sqrt{\frac{\omega_i\omega_k}{\omega_j\omega_l}}\,\mathbf{q}_i\mathbf{p}_j\mathbf{q}_k\mathbf{p}_l + U \qquad (1.6)
\end{aligned}
$$

For asymmetric tops, at the VPT2 level, the energy (E_m, in cm^{-1}) of a given vibrational state m is given by

$$
E_m = E_0 + \sum_{i=1}^{N} v_i^m\omega_i + \sum_{i,j=1}^{N}\chi_{ij}\left[v_i^m v_j^m + \frac{1}{2}(v_i^m + v_j^m)\right] \qquad (1.7)
$$

where v_i^m is the number of quanta associated with mode i in state m and ω_i the corresponding harmonic wavenumber. E_0 is the zero-point vibrational energy, which is defined as follows:

$$
\begin{aligned}
E_0 = {} & \sum_{i=1}^{N}\frac{\omega_i}{2} + \sum_{i,j=1}^{N}\frac{k_{iijj}}{32} - \sum_{i,j,k=1}^{N}\left[\frac{k_{iik}k_{jjk}}{32\omega_k} + \frac{k_{ijk}^{\;2}}{48(\omega_i+\omega_j+\omega_k)}\right] \\
& - \sum_{\tau}\frac{\mathrm{B}_{\tau}^{\mathrm{eq}}}{4}\left[1 - \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\{\zeta_{ij,\tau}\}^2\frac{(\omega_i-\omega_j)^2}{\omega_i\omega_j}\right] \qquad (1.8)
\end{aligned}
$$

In Eq. (1.7), χ is the anharmonicity contributions matrix, with its elements given by

$$
16\chi_{ii} = k_{iiii} - \frac{5k_{iii}^{\;2}}{3\omega_i} - \sum_{\substack{j=1\\ j\neq i}}^{N}\frac{(8\omega_i^{\,2}-3\omega_j^{\,2})k_{iij}^{\;2}}{\omega_j(4\omega_i^{\,2}-\omega_j^{\,2})} \qquad (1.9)
$$

$$
\begin{aligned}
4\chi_{ij} = {} & k_{iijj} - \frac{2\omega_i k_{iij}^{\;2}}{(4\omega_i^{\,2}-\omega_j^{\,2})} - \frac{2\omega_j k_{ijj}^{\;2}}{(4\omega_j^{\,2}-\omega_i^{\,2})} - \frac{k_{iii}k_{ijj}}{\omega_i} - \frac{k_{jjj}k_{iij}}{\omega_j} \\
& + \sum_{\substack{k=1\\ k\neq i,j}}^{N}\left[\frac{2\omega_k(\omega_i^{\,2}+\omega_j^{\,2}-\omega_k^{\,2})k_{ijk}^{\;2}}{\Delta_{ijk}} - \frac{k_{iik}k_{jjk}}{\omega_k}\right] \\
& + \frac{4(\omega_i^{\,2}+\omega_j^{\,2})}{\omega_i\omega_j}\sum_{\tau}\mathbf{B}_{\tau}^{\mathrm{eq}}\{\zeta_{ij,\tau}\}^2 \qquad (1.10)
\end{aligned}
$$

where

$$
\Delta_{ijk} = \omega_i^{\,4} + \omega_j^{\,4} + \omega_k^{\,4} - 2(\omega_i^{\,2}\omega_j^{\,2} + \omega_i^{\,2}\omega_k^{\,2} + \omega_j^{\,2}\omega_k^{\,2}) \qquad (1.11)
$$

Transition energies from the ground state v_m are therefore straightforwardly obtained from Eqs. (1.7) and (1.8) as $E_m - E_0$ difference.

The intensities for a broad range of spectroscopies at the VPT2 level can be obtained by referring to a generic property **P**, which can depend on either the normal coordinates (**q**) or their conjugate momenta (**p**):

$$
\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} + \mathbf{P}^{(2)} \qquad (1.12)
$$

where

$$\mathbf{P}^{(0)} = \mathbf{P}^{\mathrm{eq}} + s_0 \sum_{i=1}^{N} \mathbf{P}_i (a_i^\dagger + S a_i) \tag{1.13}$$

$$\mathbf{P}^{(1)} = s_1 \sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{P}_{ij} q_j (a_i^\dagger + S a_i) \tag{1.14}$$

$$\mathbf{P}^{(2)} = s_2 \sum_{i=1}^{N} \sum_{k=1}^{N} \sum_{j=1}^{N} \mathbf{P}_{ijk} q_j q_k (a_i^\dagger + S a_i) \tag{1.15}$$

In equations above, $a_i^\dagger$ and a_i are the creation and annihilation operators, respectively; s_0, s_1, and s_2 are constant factors; and S corresponds to a sign (i.e. it represents the multiplication by +1 or −1). The function of Eq. (1.12) is then used to obtain analytic formulas for the transition moments up to three quanta [21–25] and can be simply related to the property of interest by identifying the variables in Eqs. (1.12)–(1.15) with the actual quantities, as exemplified in Figure 1.2. The electric ($\boldsymbol{\mu}$) and magnetic ($\mathbf{m}$) dipoles and the polarizability ($\boldsymbol{\alpha}$) are used in IR, VCD, and Raman intensities, respectively, whereas the electric dipole–magnetic dipole optical activity ($\mathbf{G}'$) and the electric dipole–electric quadrupole ($\mathbf{A}$) tensors also enter the ROA intensities [13].

From a quick inspection of Eqs. (1.9) and (1.10), it is evident that for the VPT2 energies, the denominator might become exceedingly small. This situation leads to the so-called Fermi resonances (FRs), which can be distinguished in type I ($\omega_i \approx 2\omega_j$) and type II ($\omega_i \approx \omega_j + \omega_k$). Indeed, a near resonance can be sufficient to obtain unphysical results due to an excessive contribution from anharmonicity. This is a well-known issue of VPT2, which has been extensively studied in the literature [16, 26–39] and needs to be correctly addressed for a successful application of this method. A major difficulty lies in the definition of the resonance conditions. In the literature, several efficient identification processes have been

$\mathbf{P}$	$\mathbf{P}_0$	$\mathbf{P}_i$	$\mathbf{P}_{ji}$	$\mathbf{P}_{jki}$	s_0	s_1	s_2	S
$\boldsymbol{\mu}$	$\boldsymbol{\mu}^{\mathrm{eq}}$	$\frac{\partial \boldsymbol{\mu}}{\partial q_i}$	$\frac{\partial^2 \boldsymbol{\mu}}{\partial q_i q_j}$	$\frac{\partial^3 \boldsymbol{\mu}}{\partial q_i q_j q_k}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{6\sqrt{2}}$	+1
$\boldsymbol{m}$	0	$\mathbf{M}_i$	$\frac{\partial \mathbf{M}}{\partial q_i}$	$\frac{\partial^2 \mathbf{M}}{\partial q_i q_j}$	$\frac{i\hbar}{\sqrt{2}}$	$\frac{i\hbar}{\sqrt{2}}$	$\frac{i\hbar}{2\sqrt{2}}$	−1
$\boldsymbol{\alpha}$	$\boldsymbol{\alpha}^{\mathrm{eq}}$	$\frac{\partial \boldsymbol{\alpha}}{\partial q_i}$	$\frac{\partial^2 \boldsymbol{\alpha}}{\partial q_i q_j}$	$\frac{\partial^3 \boldsymbol{\alpha}}{\partial q_i q_j q_k}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{6\sqrt{2}}$	+1
$\mathbf{G}'$	$\mathbf{G}'^{\mathrm{eq}}$	$\frac{\partial \mathbf{G}'}{\partial q_i}$	$\frac{\partial^2 \mathbf{G}'}{\partial q_i q_j}$	$\frac{\partial^3 \mathbf{G}'}{\partial q_i q_j q_k}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{6\sqrt{2}}$	+1
$\mathbf{A}$	$\mathbf{A}^{\mathrm{eq}}$	$\frac{\partial \mathbf{A}}{\partial q_i}$	$\frac{\partial^2 \mathbf{A}}{\partial q_i q_j}$	$\frac{\partial^3 \mathbf{A}}{\partial q_i q_j q_k}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{6\sqrt{2}}$	+1

Figure 1.2 Equivalence relations between the model property **P** and actual properties.