MULTIPHOTON SPECTROSCOPY OF MOLECULES

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Preface

In the past decade there has been very rapid growth in multiphoton spectroscopy, one of the most interesting fields of research made possible by the development of powerful lasers. Multiphoton spectroscopy has been widely used in biology, chemistry, materials science, physics, and other disciplines. We realize that it is perhaps foolhardy to write a monograph about multiphoton spectroscopy at this time, when new results are still published at a high rate in scientific journals. Nevertheless, it is hoped that this volume may have lasting value. Since the field of multiphoton spectroscopy is still in a stage of rapid development, no effort has been made to give a complete bibliography or to achieve complete coverage of all experimental data. The fundamental theory and methods and the basic experimental results are stressed. This volume is intended for all who have an active interest in the field of multiphoton spectroscopy and those who want to enter this field. Thus the presentation is elementary and self-contained wherever possible.

After an introductory chapter giving a general survey of the progress of multiphoton spectroscopy and the features of the multiphoton processes, in Chapter 2 we present several theoretical methods (the time-dependent perturbation, Green's function, density matrix, and susceptibility methods) for treating the multiphoton transitions in a molecular system, starting from first principles. In Chapter 3 the development of two-photon

spectroscopy is reviewed, and then various experimental methods are given; multiphoton ionization mass spectroscopy is considered in some detail. Characteristics of molecular multiphoton spectroscopy are presented in Chapter 4, and intensity dependence, saturation phenomena, and polarization dependence are also discussed. In Chapter 5 spectroscopic properties of molecular multiphoton transitions in both nonresonant and resonant cases are presented. Mechanisms of vibronic coupling in forbidden two-photon transitions are discussed, and it is shown that some rovibronic bands appearing in the two-photon excitation spectra of benzene in vapor can be analyzed in terms of intramolecular vibrational relaxation. Visible/UV multiphoton spectroscopic results of the Rydberg and valence states of molecules of interest from a static or a dynamical point of view are discussed in Chapter 6. Interesting new applications of multiphoton spectroscopy, such as multiphoton ionization mass spectroscopy, multiphoton circular dichroism, and ion dip spectroscopy, are introduced in Chapter 7.

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CHAPTER 1

Introduction

1.1 GENERAL SURVEY OF THE PROGRESS OF VISIBLE/UV MULTIPHOTON SPECTROSCOPY

Visible/UV multiphoton spectroscopy has made a great contribution to molecular spectroscopy. This spectroscopy basically consists in the excitation of molecules by two or more photons of visible or UV frequency. New vibronic (vibration–electron) and electronically excited states, which were not found in ordinary single-photon spectroscopy because of their different selection rules, can be observed in a wide range from lower excited states to ionized continua.

Though the possibility of simultaneous two-photon absorption or emission (the lowest order multiphoton processes) in molecules was pointed out in 1931 by Goeppert-Mayer, who applied Dirac's dispersion theory, experimental observation of two-photon absorption in the optical region was made possible only after lasers were developed as an intense incident light source, especially after the late 1960s, when tunable dye lasers appeared (a detailed discussion of two-photon spectroscopy will be given in Chapter 3). In fact, compared with a one-photon cross section for a typical molecule ($\sim 10^{-17}$ cm^2), the cross sections of multiphoton transitions are extremely low at the intensity of conventional light sources: for example, $\sim 10^{-51}$ cm^4 s and $\sim 10^{-82}$ cm^6 s^2 for two- and three-photon transitions, respectively. Today we can measure multiphoton spectra associated with two or more photons in the visible/UV region with high-power pulsed lasers.

The development of visible/UV multiphoton spectroscopy since the late 1960s can be roughly divided into two stages. The first stage began with the advent of dye lasers, which opened up a new field in molecular spectroscopy. The tunability of dye lasers is particularly important for multiphoton processes because one can obtain an excitation source by using only a single-frequency beam rather than two or more lasers of different frequencies. During the first stage, two-photon absorption and excitation spectra of organic molecules in solid, liquid, and vapor phases were measured. *Gerade–gerade* (g–g) transitions of molecules with inversion symmetry, which are forbidden in one-photon spectroscopy, were observed. Low-lying excited ^1A_g states of linear polyenes were identified; we shall present these in Chapter 6. Mechanisms of vibronic coupling in nonresonant two-photon transitions were studied; we shall discuss these in detail in Chapter 5. Monson and McClain (1970) and McClain (1971) have reported polarization effects in the two-photon transition of randomly oriented nonrotating molecules, and polarization effects in the two-photon excitation of crystals have been theoretically investigated by Inoue and Toyozawa (1965). The polarization effects for freely rotating molecules in the gas phase have been theoretically described by Metz *et al.* (1978) and experimentally investigated by Hampf *et al.* (1977) and Wunsch *et al.* (1977). The two-photon transition probability, after averaging over the orientation, depends on the polarization of the incident laser beams (linear or circular, and so on). The one-photon transition probability in randomly oriented molecules, on the other hand, is independent of the polarization. Polarization measurements are a very convenient method for determining the symmetry of the excited states. The polarization effects of rotating and nonrotating molecules are presented in Chapter 4. Meanwhile, progress with dye lasers that generate tunable radiation of narrow bandwidth (less than 0.01 cm^{-1}) has made it possible to measure the rotational structure of the vibronic bands. Two-photon spectroscopy was somewhat restricted to the observation of low-lying excited states because the method of detecting signals from excited molecules was limited.

The second stage of development began in 1975, when a multiphoton ionization technique for detecting information from excited molecules was developed independently by Johnson and Dalby (see Johnson, 1975; Johnson *et al.*, 1975; Petty *et al.*, 1975). This method consists in collecting electrons released from the molecules after irradiation by a tunable laser pulse, amplifying the pulse, and recording the signal as a function of the laser frequency. The experimental method is presented in Chapter 3. The sensitivity of ion detection is high compared with that of absorption. The sensitivity even exceeds that of fluorescence detection if high-lying states close to the ionization threshold, which only weakly fluoresce, are investi-

gated. However, this method is more sophisticated in interpretation because resonances of different absorption steps may overlap, giving rise to overlapping spectra. It is possible to observe Rydberg states as well as valence states. Spectroscopic properties of the excited states of a large number of molecules in various conditions have thus been clarified, and this method has become an increasingly popular area of molecular spectroscopy.

A new branch of multiphoton ionization called multiphoton ionization mass spectroscopy (MPIMS), in which a mass spectrometer is used to identify the ionization products, is now being developed (Boesl *et al.*, 1978; Zandee *et al.*, 1978; for a review see Bernstein, 1982; Schlag and Neusser, 1983). MPIMS yields important information on the dynamic behavior involving both energy relaxations and fragmentation reactions that take place in the excited states of neutral and ionic molecules. The mechanisms of MPIMS are discussed in Chapter 7. This may be regarded as the third stage in the development of multiphoton molecular spectroscopy.

1.2 CHARACTERISTIC PROPERTIES OF MULTIPHOTON TRANSITIONS

Visible/UV multiphoton transitions have several characteristic features such as laser intensity dependence, resonance enhancement, and polarization dependence; we shall study these properties in this volume. As preliminaries, intensity dependence and the resonance effect on molecular multiphoton spectroscopy are briefly outlined in this section.

1.2.1 Intensity Dependence

The multiphoton transition probability is formulated according to time-dependent perturbation theory, as can be seen in Chapter 2. As an example, let us consider a two-photon absorption from states a to n, as shown in Fig. 1.1a. The transition probability $W^{(2)}$, taking into account only the lowest

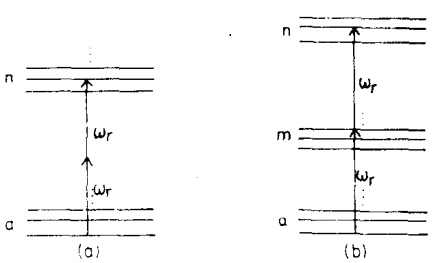

Fig. 1.1 The two-photon absorption processes of a molecule: (a) nonresonant, (b) resonant.

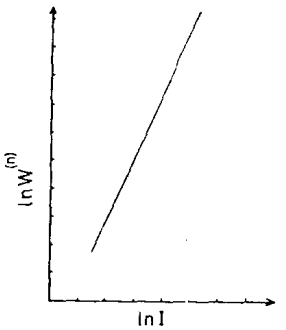

Fig. 1.2 The formal intensity law for multiphoton processes. Here I and $W^{(n)}$ denote the laser intensity and the transition probability of an n-photon process, respectively.

order term of the radiation–molecule interaction, is given as

$$W^{(2)} \propto I^2 \left| \sum_m \frac{\langle n|\boldsymbol{\mu}|m\rangle\langle m|\boldsymbol{\mu}|a\rangle}{\Delta E_{ma} - \hbar\omega_r} \right|^2, \tag{1.2.1}$$

where I is the intensity of the laser, m the virtual intermediate states, ΔE_{ma} the energy difference between the intermediate and initial states, $\boldsymbol{\mu}$ the dipole moment, and ω_r the laser frequency. Equation (1.2.1) shows that the two-photon transition probability is proportional to the square of the laser intensity. More generally, the n-photon transition probability is proportional to I^n. This is called the formal intensity law for the multiphoton transition. If no saturation occurs, one can determine the order of the multiphoton transition from the slope of the log–log plot of the transition probability as a function of laser intensity,

$$\ln W^{(n)} = n \ln I + C, \tag{1.2.2}$$

as shown in Fig. 1.2. The intensity law holds for multiphoton transitions of molecules irradiated just above the detection threshold by light from a moderately high-power laser. In multiphoton experiments in which a strong laser beam brings about saturation of the population between the relevant states, one can often see a deviation from the intensity law. This will be discussed in detail in Chapter 4.

1.2.2 Resonant Effect

When the laser is tuned and its frequency approaches a real intermediate electronic state (Fig. 1.1b), we can see a drastic increase in the two-photon absorption signal (resonance enhancement). This process is called a resonant two-photon transition. If a rigorous resonance condition were satisfied, that is, $\Delta E_{ma} = \hbar\omega_r$ in Eq. (1.2.1), then the magnitude of the transition prob-

ability would go to infinity. However, the energy levels of the intermediate states are not infinitely sharp but have widths Γ_{ma}, and the divergence of the transition can be avoided. The width originates from intra- and intermolecular perturbations and from the higher order radiation–molecule interaction. In order to take the resonant effect into account phenomenologically, we replace the real energy denominator in Eq. (1.2.1) by a complex energy denominator with the term $i\Gamma_{ma}$. If we neglect the higher order radiation–molecule interaction, Γ_{ma} is called the dephasing constant—it describes the rate of phase loss between the m and a states associated with the transition, and it may be expressed as (see Chapter 2)

$$\Gamma_{ma} = \tfrac{1}{2}(\Gamma_{mm} + \Gamma_{aa}) + \Gamma_{ma}^{(d)}, \tag{1.2.3}$$

where Γ_{mm} and Γ_{aa} are the population decay constants of states m and a, respectively, and $\Gamma_{ma}^{(d)}$ is the pure dephasing constant that originates from a molecule–perturber elastic scattering process.

It is interesting to note that the vibronic structure appearing in the resonant multiphoton transition is generally different from that in the nonresonant transition: In the former case the vibronic structure reflects the potential differences between the initial, resonant, and final states or between these states, and in the latter case the vibronic structure is mainly determined by the Franck–Condon vibrational overlap integral between the initial and final states, since energy mismatch to the intermediate states is so large that the vibronic structure of the intermediate state $|m\rangle$ may be neglected in Eq. (1.2.1). A detailed discussion of the vibronic structure in multiphoton spectra may be found in Chapter 5.

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CHAPTER 2

Theory of Multiphoton Absorption and Ionization

In this chapter we are concerned with the derivation of expressions for the transition probabilities of multiphoton absorption and ionization processes. For this purpose several theoretical methods will be presented. Readers who are already familiar with this type of derivation or who are mainly concerned with the applications of the theory may skip this chapter.

2.1 THE PERTURBATION METHOD

In this section we shall present a systematic formulation of the theory of multiphoton processes by using the time-dependent perturbation method. This method is well known and can be found in standard textbooks (Schiff, 1955) and reference books (Heitler, 1954; Louisell, 1973; Sargent *et al.*, 1974). First we shall briefly outline the time-dependent perturbation method, and then we shall show how to apply this method to multiphoton processes.

2.1.1 Time-Dependent Perturbation Theory

To solve time-dependent problems we need to be able to calculate the time evolution of the system caused by a perturbation. Thus we have to solve the wave equation, which expresses the manner in which the complete wave function Ψ changes with time,

$$\hat{H}\Psi = i\hbar(\partial\Psi/\partial t). \tag{2.1.1}$$

Let us now write the Hamiltonian operator as

$$\hat{H} = \hat{H}_0 + \lambda V, \tag{2.1.2}$$

where V is the perturbation and λ denotes the perturbation parameter. The unperturbed eigenfunctions Ψ_n^0 satisfy the equation

$$\hat{H}_0\Psi_n^0 = i\hbar(\partial\Psi_n^0/\partial t) \tag{2.1.3}$$

and are of the form

$$\Psi_n^0 = \psi_n \exp(-itE_n/\hbar), \tag{2.1.4}$$

where

$$\hat{H}_0\psi_n = E_n\psi_n. \tag{2.1.5}$$

In order to obtain a solution of Eq. (2.1.1) we expand the wave function Ψ in terms of the unperturbed basis set Ψ_n^0 (i.e., using the expansion theorem):

$$\Psi = \sum_n C_n(t)\Psi_n^0. \tag{2.1.6}$$

Substituting Eq. (2.1.6) into Eq. (2.1.1) gives (Eyring *et al.*, 1944)

$$i\hbar \frac{\partial C_n}{\partial t} = \lambda \sum_m C_m \langle \Psi_n^0 | V | \Psi_m^0 \rangle. \tag{2.1.7}$$

According to the usual practice of perturbation theory, we set

$$C_n = C_n^{(0)} + \lambda C_n^{(1)} + \lambda^2 C_n^{(2)} + \cdots. \tag{2.1.8}$$

Substituting Eq. (2.1.8) into Eq. (2.1.7) and equating the coefficients of λ^n, we find

$$\frac{dC_n^{(0)}}{dt} = 0, \tag{2.1.9}$$

$$i\hbar \frac{dC_n^{(1)}}{dt} = \sum_m C_m^{(0)} \langle \Psi_n^0 | V | \Psi_m^0 \rangle, \tag{2.1.10}$$

$$i\hbar \frac{dC_n^{(2)}}{dt} = \sum_m C_m^{(1)} \langle \Psi_n^0 | V | \Psi_m^0 \rangle, \tag{2.1.11}$$

$$i\hbar \frac{dC_n^{(3)}}{dt} = \sum_m C_m^{(2)} \langle \Psi_n^0 | V | \Psi_m^0 \rangle, \tag{2.1.12}$$

and so forth.

Equation (2.1.7) indicates that in any particular problem we shall have a set of simultaneous differential equations that can be solved to give explicit expressions for the coefficients C_n. From Eqs. (2.1.8)–(2.1.12) we can see that owing to the use of the perturbation method, these simultaneous equations are decoupled; we can solve Eqs. (2.1.9)–(2.1.12) successively. As will be shown later, the use of the ordinary perturbation method cannot take into account the damping effect (Heitler, 1954). The damping effect can be treated by using the so-called singular perturbation method (Lee *et al.* 1973; Lee and Lee, 1973) and the Green's function method described in Section 2.2.

To solve the zeroth-order equation given by Eq. (2.1.9) we need the initial condition. Suppose that the system is initially in the k state. Then Eq. (2.1.9) yields

$$C_k^{(0)} = 1, \qquad C_m^{(0)} = 0. \tag{2.1.13}$$

By substituting Eq. (2.1.13) into the first-order equation given by Eq. (2.1.10), we find

$$i\hbar \, (dC_n^{(1)}/dt) = \langle \Psi_n^0 | V | \Psi_k^0 \rangle. \tag{2.1.14}$$

For the case in which V is time independent, Eq. (2.1.14) can be integrated as

$$C_n^{(1)} = (V_{nk}/\hbar\omega_{nk})(1 - e^{it\omega_{nk}}), \tag{2.1.15}$$

where $\omega_{nk} = (E_n - E_k)/\hbar$.

Substituting Eq. (2.1.15) into Eq. (2.1.11) and carrying out the integration give

$$C_n^{(2)} = \sum_m \frac{V_{nm}V_{mk}}{\hbar\omega_{mk}} \left(\frac{1 - e^{it\omega_{nm}}}{\hbar\omega_{nm}} - \frac{1 - e^{it\omega_{nk}}}{\hbar\omega_{nk}} \right). \tag{2.1.16}$$

Similarly, we obtain the third-order result as

$$C_n^{(3)} = \sum_l \sum_m \frac{V_{nm}V_{ml}V_{lk}}{\hbar\omega_{lk}} \left[\frac{1}{\hbar\omega_{ml}} \left(\frac{1 - e^{it\omega_{nm}}}{\hbar\omega_{nm}} - \frac{1 - e^{it\omega_{nl}}}{\hbar\omega_{nl}} \right) - \frac{1}{\hbar\omega_{mk}} \left(\frac{1 - e^{it\omega_{nm}}}{\hbar\omega_{nm}} - \frac{1 - e^{it\omega_{nk}}}{\hbar\omega_{nk}} \right) \right]. \tag{2.1.17}$$

Let us now derive the expressions for the transition probabilities. In the first-order approximation, for the transition $k \to n$ we have

$$|C_n^{(1)}|^2 = (|V_{nk}|^2/(\hbar\omega_{nk})^2)(2 - 2\cos\omega_{nk}t). \tag{2.1.18}$$