



EXCITED STATES

EDITED BY

Edward C. Lim

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EXCITED STATES

VOLUME 3

Edited by **EDWARD C. LIM**

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Two-Photon Molecular Spectroscopy in Liquids and Gases

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I. Introduction

This chapter is a didactic treatment of the theory of simultaneous two-photon absorption spectroscopy from a point of view concerned primarily with molecular gases and liquids. The basic theoretical quantity is shown to be an *absorption tensor*, as contrasted with the *absorption vector* of one-photon spectroscopy. The parity selection rules of the two-photon tensor operator are complimentary to those of the one-photon vector operator, allowing one to detect excited states that are “hidden” to one-photon methods by their symmetry. We show that the pattern of the absorption tensor is controlled by the symmetry of the molecule and by the symmetry species of the two states involved in the transition. A table of tensor patterns determined by group theoretic methods is presented, and their use in crystal spectroscopy is briefly discussed.

The use of these tensors in the spectroscopy of liquid solutions rests upon the orientation average of the tensor formulas. This average is carried out, and it is shown how a dependence upon the polarization of the two absorbed photons survives the averaging process. The relation to polarization effects in Raman scattering is pointed out explicitly, and a graphical representation of the polarization effects is presented.

In the two-photon spectroscopy of gases, individual rotational lines can be resolved and the classical orientation average is no longer adequate to explain all the observed effects. We show how to divide the *Cartesian tensors* into their *irreducible components*, greatly facilitating the rotational problem. For an asymmetric rotor 25 rotational branches can appear in each vibronic line, as in Raman scattering. However, molecular symmetry causes many of the possible branches to vanish producing rotational contours of distinctive shape for various different transition species. For the symmetric top, these contours may be calculated by a rapid and compact computer algorithm, and the computed lineshape may be matched to the observed lineshape by varying the input parameters. Finally, we show how one may rapidly compute the irreducible tensors for the 32 point groups in “pyramid form,” and then use the pyramid pattern to predict the rotational branch structure. One exemplary calculation is presented and compared to experiment.

II. Phenomenology and Applications

Two-photon absorption spectroscopy has now survived its infancy and seems assured of growing into a mature branch of science. It is the study of a

nonlinear optical phenomenon which was unknown in classical physics and unobservable until the invention of the laser. The most visible manifestation of the process is the production of violet fluorescence in many colorless materials, following excitation with a pulse of visible red laser light. It is thus superficially similar to frequency doubling, but differs in that the fluorescence is downshifted from twice the laser frequency by molecular relaxation and is emitted in all directions with a lifetime characteristic of the molecular absorber. The fluorescence intensity is proportional to the square of the laser intensity, in the absence of any saturation effects, and it is proportional to the concentration of absorbing molecules. Two-photon absorption also occurs, of course, in materials that do not fluoresce, and can be detected by attenuation of the exciting beam, or by thermal, acoustical, or ionization effects in the sample.

The theoretical model of the phenomenon (Göppert-Mayer, 1931) is that two photons of the intense exciting light are absorbed simultaneously in the same quantum act, raising the molecule to an excited state at an energy equivalent to that of two photons. From this it decays like any excited state, either nonradiatively to the ground state, or to a fluorescing state and thence to the ground state. Alternatively, it may undergo photochemical change.

Interest in this phenomenon appears to be increasing for a variety of different reasons.

1. The selection rules for the two-photon absorption permit one to create excited states that cannot be created by one-photon methods (Kaiser and Garret, 1961). In the electric dipole approximation, one-photon absorption can excite transitions in which the transition density $\psi_g^*(\mathbf{r})\psi_f(\mathbf{r})$ (for the transition ground \rightarrow final) has a component which transforms under symmetry operations like x , y , or z ; two-photon absorptions excite transition densities which contain components transforming like the quadratic products x^2 , y^2 , z^2 , xy , yz , zx . In molecules with center-of-inversion symmetry this leads to a reversal of the usual parity rules: with ground state of even parity under coordinate inversion, the two-photon excited states are also of even parity, while the one-photon excited states are odd.

Two-photon absorption can also create two-electron excitations in molecules with or without symmetry, while such states are quite strictly forbidden for one-photon absorption.

2. Two-photon spectra of gases may be obtained free of Doppler broadening by a counter-propagating beams method (Vasilenko *et al.*, 1970; Cagnac *et al.*, 1973; Biraben *et al.*, 1974; Levenson and Bloembergen, 1974; Pritchard *et al.*, 1974; Hänsch *et al.*, 1974), so that direct measurement of natural linewidths in complex molecules appears to be imminent. This is of great interest to those concerned with radiationless processes in molecules.

The extreme accuracy of frequency measurements made possible by this method offers a broad field of research into delicate molecular perturbation effects hitherto undetectable.

3. Two-photon excited states lie at twice the energy of the individual photons, so a great stretch of "vacuum ultraviolet" energies (equivalent of 2000 to 1000 Å) is available using photons in the more accessible range 4000 to 2000 Å. Crystals for frequency doubling down to nearly 2000 Å have recently become available and appear very promising in this application.

4. Multiphoton ionization (MPI) processes will occur at any frequency in any material when the optical power is high enough. Ion currents of only a few charges per second are detectable, and the ionization effect can be saturated at obtainable powers even in very unfavorable cases (He atoms by near infrared light). Therefore, it would appear that we have at hand a new method of detecting and characterizing extremely small amounts of material in the form of a rarefied gas. Experience so far with three-, four-, and five-photon ionization in molecules (Johnson, 1975a, b) shows that the two-photon excited states play an important role as resonant intermediate states in the ionization pathway. In fact, the three-photon ionization spectrum of benzene (which is easily saturated using a nitrogen-laser-pumped dye laser) mimics the two-photon excitation spectrum remarkably closely through this resonant effect. Therefore, we may expect that the characterizing spectrum in any MPI analytical method will often be basically a two-photon absorption spectrum.

5. It is often difficult to investigate liquids and solids at energies above the one-photon absorption edge because the incident light may be completely attenuated by the first few molecular layers of the sample. One-photon spectroscopy must then rely on the spectra of thin films or upon reflection spectra from surfaces, both of which involve many uncertainties. However, the material may be quite transparent at half the excitation energy in question, so the two-photon spectrum will accurately reflect properties of the bulk material.

6. Polarization methods available in two-photon spectroscopy (McClain, 1971) make it possible to identify transition symmetries in solid, liquid, and gaseous samples by completely empirical means. There is no analog of this in the one-photon spectroscopy of liquids and gases, where assignment procedures often rely heavily on theoretical models. Therefore, where spectral features can be seen by both one- and two-photon methods, it may be expected that useful corrections of wrongly assigned features will sometimes be possible, leading ultimately to theoretical refinements.

7. Finally, experiments in many laboratories (Robinson, 1976) have shown that very strong infrared light can initiate or modify chemical reactions through a mechanism not yet entirely clear, but which can be used for

isotope separation because of its sharp frequency dependence. Multiphoton absorptions of the kind considered in this chapter are exactly forbidden for a perfect harmonic oscillator, but the mechanism may involve resonant multiphoton interaction between infrared photons and the anharmonic part of the bond potential. If so, the analysis we present of rovibronic two-photon absorption will bear on the mechanism.

III. Reviews

The most recent general review of two-photon spectroscopy is that of Mahr (1975), which is highly recommended as a sequel to the present more detailed and elementary treatment. Multiphoton ionization research was reviewed by Bakos (1974). Until very recently workers in MPI have concentrated exclusively on atoms.

A number of older reviews are also referenced for the reader's convenience (Bonch-Bruerich and Khodovoi, 1965; Peticolas, 1967; Mahr, 1968; Bredikhin *et al.*, 1973; McClain, 1974).

IV. Basic Physics of Two-Photon Absorption

We begin now a didactic presentation of the basic physics of two-photon absorption by molecules, with special attention to the consequences of molecular symmetry and optical polarization. Much of the material brought together here (McClain, 1971; Monson and McClain, 1970, 1972) is scattered throughout the literature of the past few years, while other parts of it first appeared more than 40 years ago in Placzek's treatment of Raman scattering (Placzek and Teller, 1933). We believe that a useful purpose is served in bringing it all together in one place, and in rederiving Placzek's results by modern irreducible tensor methods which have developed so beautifully since his original presentation.

A. Perturbation Treatment

1. General Theoretical Basis

We shall begin with semiclassical perturbation theory (Schiff, 1955) for the interaction of radiation and matter, and carry it to second order to obtain a formula that seems to represent correctly all two-photon effects so far observed. We shall cut away all terms predicting small (but interesting)

side effects, such as magnetic dipole or electric quadrupole terms. For these, the reader is referred to Mahr's treatment (1975).

We take the Hamiltonian of the material to be

$$\mathcal{H}^0 = \sum_i \frac{1}{2m_i} \mathbf{p}_i \cdot \mathbf{p}_i + V \text{ (pairs)} \quad (1)$$

with stationary solutions

$$\psi_k^0(\mathbf{r}, t) = u_k^0(\mathbf{r})e^{-i\omega_k t} \quad (2a)$$

such that

$$\mathcal{H}^0 u_k^0(\mathbf{r}) = \hbar\omega_k u_k^0(\mathbf{r}) \quad (2b)$$

The electromagnetic field is represented by its vector potential

$$\mathbf{A}(\mathbf{r}, t) = A_0 \mathbf{e} \exp i(-\mathbf{k} \cdot \mathbf{r} + \omega t + \phi) \quad (3)$$

where A_0 is a real amplitude, \mathbf{k} is the real wave vector ($|\mathbf{k}| = 2\pi/\lambda$), and \mathbf{e} is a complex polarization vector of unit length, such that $\mathbf{e} \cdot \mathbf{e}^* = 1$. We include an explicit phase factor ϕ in the wave so that \mathbf{e} may obey certain conventions: when the polarization is linear, \mathbf{e} is to be taken as a real vector; when polarization is circular or elliptical, \mathbf{e} has one component real and one imaginary (and one zero component in the direction of \mathbf{k} , since polarization and propagation must be perpendicular). The electric field is given (in the MKSA unit system) by

$$\mathbf{E}(\mathbf{r}, t) = \text{Re}\{-\partial\mathbf{A}/\partial t\} \quad (4)$$

so for instance, taking $\mathbf{e} = 2^{-1/2}(1, i, 0)$ and $\mathbf{k} = (0, 0, k)$ we have

$$\mathbf{E}(\mathbf{r}, t) = A_0 \omega 2^{-1/2} [\sin(-kz + \omega t + \phi), \cos(-kz + \omega t + \phi), 0] \quad (5)$$

Hence the polarization vector $2^{-1/2}(1, i, 0)$ represents a circularly polarized wave.

In the presence of the electromagnetic field, the Hamiltonian of the electrons in the material becomes

$$\mathcal{H} = \sum_i \frac{1}{2m} (\mathbf{p}_i - q\mathbf{A}(\mathbf{r}_i, t))(\mathbf{p}_i - q\mathbf{A}(\mathbf{r}_i, t)) + V \text{ (pairs)} \quad (6)$$

where $-q$ is the electronic charge (in coulombs), and m is the electronic mass. For a single particle this is

$$\mathcal{H}_i = \frac{1}{2m} (\mathbf{p} \cdot \mathbf{p} - \mathbf{p} \cdot q\mathbf{A} - q\mathbf{A} \cdot \mathbf{p} + q^2 \mathbf{A} \cdot \mathbf{A}) + V_i \quad (7)$$

where V_i is an effective potential.

* Now $\mathbf{p} \cdot \mathbf{A} = -i\hbar \nabla \cdot \mathbf{A}$ and $\nabla \cdot \mathbf{A}\psi = \psi \nabla \cdot \mathbf{A} + \mathbf{A} \cdot \nabla\psi$. Therefore one term drops out immediately: $\nabla \cdot \mathbf{A} = \mathbf{k} \cdot \mathbf{A} = 0$ because the propagation vector \mathbf{k} is always perpendicular to \mathbf{e} and therefore to \mathbf{A} . Hence

$$\mathcal{H}_i = \frac{1}{2m} (\mathbf{p} \cdot \mathbf{p} - 2q\mathbf{A} \cdot \mathbf{p} + q^2\mathbf{A} \cdot \mathbf{A}) + V_i \quad (8)$$

2. Justification and the Use of Perturbation Theory

We shall now investigate the relative sizes of $\mathbf{p} \cdot \mathbf{p}$, $2q\mathbf{A} \cdot \mathbf{p}$, and $q^2\mathbf{A} \cdot \mathbf{A}$ by interpreting this equation semiclassically. We rewrite it as

$$\mathcal{H}_i = \frac{p^2}{2m} \left(1 - 2 \frac{qA}{p} + \frac{q^2 A^2}{p^2} \right) + V_i \quad (9)$$

where it is clear that the perturbation is $(1 - qA/p)^2$, and qA/p is a dimensionless parameter that should be small compared to 1 if perturbation theory is to hold. As a representative value of p we take the momentum of an electron in the first Bohr orbit of the hydrogen atom. Taking $a_0 =$ the Bohr radius $= 5.3 \times 10^{-11}$ m and using $\lambda_e = 2\pi a_0$ and $p_e = h/\lambda_e$ we find $p_e = 2 \times 10^{-24}$ kg m sec⁻¹.

To evaluate qA we must relate A to the power density P (W/m²) of the light, which is given by the real part of the complex Poynting vector (Stratton, 1941)

$$\mathbf{P} = \frac{1}{2}\mathbf{E} \times \mathbf{H}^* \quad (10)$$

Now $\mathbf{E} = -\partial\mathbf{A}/\partial t$ and $\mathbf{H} = (1/\mu_0)\mathbf{B} = (1/\mu_0)\nabla \times \mathbf{A}$. For the harmonic plane wave

$$-\partial\mathbf{A}/\partial t = -i\omega\mathbf{A} \quad (11)$$

and

$$\nabla \times \mathbf{A} = -i\mathbf{k} \times \mathbf{A} \quad (12)$$

so

$$\mathbf{P} = (\omega/2\mu_0)\mathbf{A} \times (\mathbf{k} \times \mathbf{A}^*) \quad (13)$$

or by vector identity (again using $\mathbf{A} \cdot \mathbf{k} \equiv 0$),

$$P = |\mathbf{P}| = \frac{\omega}{2\mu_0} (\mathbf{A} \cdot \mathbf{A}^*) |\mathbf{k}| = \frac{\omega^2 A_0^2}{2\mu_0 c} \quad (14)$$

Using $\omega = 2\pi\nu$, $k = 2\pi/\lambda$, and $\lambda\nu = c$ we convert this to the more useful form

$$A_0^2 = (2\mu_0 c/\omega^2)P = (\mu_0/2\pi^2 c)\lambda^2 P \quad (15)$$

where A_0 is in $\text{kg m sec}^{-1} \text{C}^{-1}$, $\mu_0 = 4\pi \times 10^{-7} \text{ kg m C}^{-2}$, $c \simeq 3 \times 10^8 \text{ m sec}^{-1}$, λ is in meters, and P is in W m^{-2} . Taking $\lambda = 3000 \text{ \AA} = 3 \times 10^{-7} \text{ m}$, $P = 1 \text{ W m}^{-2}$, and $q = 1.6 \times 10^{-19} \text{ C}$ we have $qA_0 = 8 \times 10^{-34} \text{ kg m sec}^{-1}$. This is in the same units as momentum, and the perturbation ratio qA_0/p is about 10^{-10} for a hydrogenic electron in room light. Even when $P = 100 \text{ MW mm}^{-2} = 10^{14} \text{ W m}^{-2}$, qA_0/p is only about 10^{-3} . However, at powers of about 10^{16} W m^{-2} , it is known from multiphoton ionization experiments (Bakos, 1974) that formulas based on perturbation theory begin to fail. Above that power electronic structure is seriously distorted even without the help of a molecular resonance, and much more elaborate calculations must be undertaken. However, the two-photon phenomena we hope to describe by perturbation theory occur at powers of a few kilowatts focused into a tenth of a square millimeter (10^{10} to 10^{11} W m^{-2}), so it seems clear that we may take the term $2q\mathbf{A} \cdot \mathbf{p}$ in (8) as a perturbation on $\mathbf{p} \cdot \mathbf{p}$, and dismiss the term $q^2 \mathbf{A} \cdot \mathbf{A}$ as being too small to worry about. We therefore declare the perturbation Hamiltonian to be

$$\mathcal{H}' = -\sum_i \frac{q}{m} \mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{p}_i \quad (16)$$

The standard perturbation treatment is to expand the perturbed ground state wave function as

$$\psi_g^{\text{true}}(\mathbf{r}, t) = \sum_k a_k(t) u_k^0(\mathbf{r}) e^{-i\omega_k t} \quad (17)$$

where $a_k(t)$ must be found by an iterative approach $a_k(t) = a_k^{(0)}(t) + a_k^{(1)}(t) + \dots$. The starting point is assumed to be $\{a_g^0 = 1, \text{ all other } a_k^0 = 0\}$, and the successive corrections are found by solving the equations

$$\frac{d}{dt} a_k^{(s+1)} = (i\hbar)^{-1} \sum_n \mathcal{H}'_{kn}(t) a_n^{(s)}(t) e^{-i\omega_{kn} t} \quad (18)$$

where

$$\mathcal{H}'_{kn}(t) = \frac{q}{m} \int u_k^0(\mathbf{r}) \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{p} u_n^0(\mathbf{r}) d\tau_r,$$

or in the electric dipole approximation

$$\mathcal{H}'_{kn}(t) = qA_0 \omega_{kn} \int u_k^0(\mathbf{r}) (\mathbf{e} \cdot \mathbf{r}) u_n^0(\mathbf{r}) d\tau_r = qA_0 \omega_{kn} \langle k | \mathbf{e} \cdot \mathbf{r} | n \rangle$$

in which $\omega_{kn} = \omega_k - \omega_n$. The first iterative solution is

$$\psi_g^{(1)}(\mathbf{r}, t) = \psi_g^{(0)}(\mathbf{r}, t) + \sum_k \frac{qA_0}{i\hbar} \omega_{kg} [\mathbf{e} \cdot \langle g | \mathbf{r} | k \rangle] u_k^0(\mathbf{r}) \left(\frac{\exp[i(\omega_{kg} - \omega)t]}{\omega_{kg} - \omega} \right) \quad (19)$$