III
**Equations Describing Coherent and Partially Coherent
Multilevel Molecular Excitation Induced by Pulsed Raman Transitions**

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Abstract

This memo discusses the equations of motion used to describe multilevel molecular excitation induced by Raman transitions. These equations are based upon the time-dependent Schrödinger equation expressed in a basis of molecular energy states. We introduce a partition of these states into two sets, those that are far from resonance (and hence unpopulated) and those that are close to resonance, either by one-photon transition or two-photon (Raman) processes. By adiabatic elimination we obtain an effective Schrödinger equation for the resonance states alone. The effective Hamiltonian is expressible in terms of a polarizability operator.

We discuss a revision of the conventional adiabatic elimination procedure that takes into account the finite bandwidth of pulses by introducing time derivatives of pulse envelopes.

We consider the modifications of the equations that are needed to describe molecules arrayed (randomly) over a finite optical path. In so doing we adopt a semiclassical view in which the internal structure of a molecule is governed by quantum mechanics while the center of mass is stationary (or follows a classical trajectory), and therefore enters the theory as a (c-number) parameter.

From a time-dependent Schrödinger equation we progress, by conventional techniques, to a description of excitation by means of a density matrix. This procedure allows the introduction of relaxation processes in a phenomenological way. By this means we arrive at equations describing partially coherent (or incoherent) molecular excitation. The present memo illustrates the structure of these equations for nondegenerate systems.

The material presented here is a portion of a more extensive treatment of propagation to be presented separately.

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§III.1 The Schrödinger Equation for Pulsed Raman Excitation

Molecular excitation by radiation is well described, with the neglect of incoherence, by the time dependent (TD) Schrödinger equation. For laser radiation it is adequate to regard the radiation field at any point as a classical time-dependent electromagnetic field rather than as an operator. In the optical and infrared region of the spectrum the dominant interaction of radiation with a molecule, with center of mass at position $\mathbf{R}$, is the electric-dipole interaction $-\mathbf{d} \cdot \mathbf{E}(\mathbf{R}, t)$. The time evolution of the molecular state vector $\Psi(\mathbf{R}, t)$ for a molecule at this position is therefore governed by the TD Schrödinger equation

$$\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t) = -\hat{H}(\mathbf{R}, t) \Psi(\mathbf{R}, t) \equiv -\{\hat{H}^0 - \mathbf{d} \cdot \mathbf{E}(\mathbf{R}, t)\} \Psi(t) \quad (\text{III.1-1})$$

where H^0 is the Hamiltonian of the unperturbed molecule. The coordinate $\mathbf{R}$ may be viewed in two ways. In a fully quantum mechanical treatment of the molecule, $\mathbf{R}$ is the operator that corresponds to the center of mass coordinate. Motion of the center of mass is governed by an appropriate Schrödinger equation. We shall follow an alternative semiclassical approach in which the internal molecular structure obeys quantum mechanics but the molecule as a whole moves along a classical trajectory. In this latter view the coordinate $\mathbf{R}$ is simply a parameter. It expresses the location at which we require the value of the electric field, in the dipole approximation for the interaction energy, and in this guise it enters the Hamiltonian as a parameter (or c-number). For simplicity we consider stationary molecules. Because the field differs at different positions (due to pulse attenuation, reshaping, etc.) the statevector will be different at different positions. This parametric dependence on $\mathbf{R}$ is what we imply by the notation $\Psi(\mathbf{R}, t)$.

Pulse-Mode Expansion

Let us consider radiation that consists of time varying pulses centered about various carrier frequencies ω_λ , so that at the location of the molecule the positive frequency portion of the field has the form

$$\mathbf{E}^{(+)}(\mathbf{R}, t) = \sum_{\lambda} \mathbf{E}^{(+)}_{\lambda}(\mathbf{R}, t) = \frac{1}{2} \sum_{\lambda} \mathbf{e}(\lambda) \mathcal{E}_{\lambda}(\mathbf{R}, t) \exp(i\mathbf{k}_{\lambda} \cdot \mathbf{R} - i\omega_{\lambda} t). \quad (\text{III.1-2})$$

When the carrier frequencies approximately match Bohr transition frequencies it is often possible to introduce a multiwave rotating wave approximation amongst the molecular states that are connected by near-resonant electric-dipole transitions. Such is the conventional description of near-resonant coherent excitation. Here we consider a different situation. We want to determine the molecular state vector under the assumption that none of the carrier frequencies is near resonant with a molecular transition. In this situation excitation can be regarded as proceeding by various multi-photon transitions. Let us consider specifically (nonresonant) Raman processes. These are two-photon processes in which absorption from one frequency combines with emission into another frequency. The difference of these two frequencies matches a molecular transition frequency, but neither frequency alone is close to a

transition frequency. (Resonant Raman processes, in which the individual photons are near resonant, may be treated within the general framework of multistate dipole excitation.)

Basis Expansion

The evaluation of the molecular state vector, or wavefunction, is always done by expressing the molecular statevector in terms of some tractable set of basis states. In general, we introduce some set of molecular basis states ψ_m and write the statevector at time t for a molecule whose center of mass is at $\mathbf{R}$, as

$$\Psi(\mathbf{R}, t) = \sum_m \psi_m C_m(\mathbf{R}, t) \exp[-i\zeta_m(\mathbf{R}, t)]. \quad (\text{IV.1-3})$$

Ideally the summation goes over a complete set of molecular states. In practice we include only some finite approximation to such a set. The exponential phases $\zeta_m(\mathbf{R}, t)$ are to be chosen *a priori* with the intention of incorporating at least part of the identifiable dependence on time (and position), so that the probability amplitudes $C_m(\mathbf{R}, t)$ are more slowly varying. To simplify the present discussion we consider a fixed location $\mathbf{R}$, and omit reference to this parameter by writing $E(t) \equiv E(\mathbf{R}, t)$ and $\Psi(t) \equiv \Psi(\mathbf{R}, t)$, etc. The next section will consider the alterations needed when we consider molecules at different locations.

Molecular P and Q Basis States

We make the assumption that the electric field is sufficiently weak (and nonresonant) that neither multiphoton dissociation nor ionization occurs. Then the state vector $\Psi(t)$ is expressible, at all times, as a superposition of bound molecular basis states. These molecular states will combine rotational, vibrational, and electronic excitation. Within this basis the Hamiltonian operator becomes a discrete (albeit large) matrix. By definition, the operator H^0 becomes a diagonal matrix in this basis. The electric dipole moment operator has appreciable matrix elements only between states that differ either in electronic excitation or in vibrational excitation.

Of this large set of molecular states, most are not resonant either for one-photon or two-photon (Raman) transitions, and so they do not participate directly in the dynamics. They may be regarded as virtual states. They affect the dynamics indirectly, by contributing to the polarizability of the molecule. We wish to eliminate explicit reference to these states in our equations, and retain their properties only through appropriate parameters, the polarizability. To simplify the discussion, let us first assume that there are no near-resonant single photon transitions.

For application to Raman processes we can divide the molecular basis states into two sets. In the first set we place the ground state and those low-lying rotational (or rotational and vibrational) states that connect with the ground state either by various Raman processes. Let us call this set, the states ψ_p , the P set. For simplicity, we shall here assume that there are no nonzero matrix elements of the electric-dipole moment operator $\mathbf{d}$ between any of the P states. The remaining states form the Q set, and are denoted ψ_q . They are each orthogonal to each of the P states. These states have the properties

$$\begin{aligned}
 H^0 \psi_p &= \hbar W_p \psi_p & H^0 \psi_q &= \hbar W_q \psi_q \\
 \langle \psi_p | d | \psi_p \rangle &= 0 & \langle \psi_p | \psi_q \rangle &= 0.
 \end{aligned}
 \tag{III.1-4}$$

Here $\hbar W_p$ is the energy eigenvalue of molecular state p in the absence of the electric field $E(t)$. With the separation of basis states in this manner we can express the molecular state vector $\Psi(t)$ at all times as a superposition of the form

$$\Psi(t) = \sum_p \psi_p C_p(t) \exp(-iW_p t) + \sum_q \psi_q C_q(t) \exp(-iW_q t). \tag{III.1-5a}$$

The introduction of explicit phases iWt gives expansion coefficients $C(t)$ in the Dirac picture. The time variable t has, in the present context of the TD Schrödinger equation, an arbitrary starting point. In the larger context of propagation, it is the time relative to the arrival of a fiducial pulse of radiation at the location of the molecule.

We shall consider below the spatial variation that remains for the moment implicit. We shall see that we compare wavefunctions at different positions, as we must in the treatment of propagation, we introduce an expansion having the form

$$\Psi(\mathbf{R}, t) = \sum_p \psi_p C_p(\mathbf{R}, t) \exp(i\mathbf{K}_p \cdot \mathbf{R} - iW_p t) + \sum_q \psi_q C_q(\mathbf{R}, t) \exp(i\mathbf{K}_q \cdot \mathbf{R} - iW_q t). \tag{III.1-5b}$$

The vectors $\mathbf{K}_p$ provide adjustments to the arbitrary phase of the wavefunction, and may be chosen to simplify the equations of motion. For the present we ignore these additional phases, and concentrate on the equations for fixed position. This simplification may be viewed as the introduction of phased variables

$$C_p(t) = C_p(\mathbf{R}, t) \exp(i\mathbf{K}_p \cdot \mathbf{r})$$

with similar expression for $C_q(t)$.

Essential States

The most important of the Q states are those that have nonzero value for the electric dipole moment matrix element to one of the P -space states. Each of these particular Q states can be reached from one of the P states by the excitation produced by absorption of a single electric-dipole photon. We are concerned with non-resonant Raman processes. By hypothesis then, none of the q states are resonant for any transitions from the P states. The Q states are therefore relatively unpopulated; they are, in this sense, *virtual* states. We shall be interested in only those Q states that connect with P states by single-photon processes, and so we shall neglect all radiative processes within the Q states. This *essential states* approximation produces the equations

$$\hbar \frac{d}{dt} C_p(t) = + i \sum_q \langle p | d \cdot E(t) | q \rangle C_q(t) \exp[-i(W_q - W_p)t] \quad (\text{III.1-6})$$

$$\hbar \frac{d}{dt} C_q(t) = + i \sum_p \langle q | d \cdot E(t) | p \rangle C_p(t) \exp[-i(W_p - W_q)t]. \quad (\text{III.1-7})$$

Apart from the essential states approximation, these equations provide a complete description for molecular excitation by radiation, under the approximation that the mean wavelength of the radiation is much longer than molecular dimensions (the electric-dipole approximation), and under the assumption that spontaneous emission, as well as other relaxation phenomena, are negligible.

Adiabatic Elimination

We start from the equation for Q-state amplitudes, which we formally integrate to the expression

$$\hbar C_q(t) = i \int_{-\infty}^t dt' \sum_p \langle q | d \cdot E(t') | p \rangle C_p(t') \exp[-i(W_p - W_q)t']. \quad (\text{III.1-8})$$

We now use Fourier transform methods on the amplitude equations, with the notation $\tilde{f}(\omega)$ for the Fourier transform of $f(t)$,

$$F(t) = \int d\omega \exp(-i\omega t) \tilde{F}(\omega). \quad (\text{III.1-9})$$

In particular, we let $\tilde{E}(\omega)$ denote the vector of transforms of the vector $E(t)$ for the field at the molecule position R . We can write the solution for $C_q(t)$ as the double Fourier integral

$$\hbar C_q(t) = - \sum_p \int d\omega \int d\omega' \frac{\exp[-i(W_p - W_q + \omega + \omega')t]}{W_p - W_q + \omega + \omega'} \langle q | d \cdot \tilde{E}(\omega') | p \rangle \tilde{C}_p(\omega). \quad (\text{III.1-10})$$

These results hold, exactly, for any electric field. Our concern is with fields that describe pulses of radiation with reasonably well defined carrier frequencies, i.e. pulses whose bandwidths are narrow compared with molecular frequency differences. Specifically, let us suppose that the positive frequency part of the electric field at the molecular center of mass, $E(t)$, has the form

$$E^{(+)}(t) = \sum_{\lambda} E_{\lambda}(t) = \frac{1}{2} \sum_{\lambda} e(\lambda) \mathcal{E}_{\lambda}(t) \exp(-i\omega_{\lambda}t), \quad (\text{III.1-11})$$

This is the expression at fixed position. We shall consider below the spatial dependence that remains implicit in this expansion. In order that this pulse mode expansion be useful, the Fourier transform of $E_\lambda(t)$ must be strongly peaked within a bandwidth $\Delta\omega_\lambda$ about frequency ω_λ , and the bandwidths must be much smaller than the separation between carrier frequencies.

We now introduce the basic assumptions of nonresonant Q states:

1). We assume that the frequencies contributing to $\tilde{E}_\lambda(\omega')$ are localized around the value ω_λ , within a bandwidth $\Delta\omega_\lambda$ that is much smaller than the frequency differences $|W_p - W_q \pm \omega_\lambda|$. This approximation allows us to replace ω' by ω_λ in the denominator $(W_p - W_q + \omega' + \omega)$.

2) We assume that the frequencies contributing to $\tilde{C}_p(\omega)$ are much smaller than the frequency differences $|W_p - W_q \pm \omega_\lambda|$. This *nonresonant* approximation allows us to replace ω by 0 in the denominator $(W_p - W_q + \omega' + \omega)$. It is equivalent to the assumption that negligible population reaches the Q states.

Using these approximations we obtain the formula for the Q-state amplitude $C_q(t)$ as

$$\begin{aligned} \hbar C_q(t) = & + \sum_{p\lambda} \frac{\exp[-i(W_p - W_q)t]}{W_q - W_p - \omega_\lambda} \int d\omega \int d\omega' \exp[-i(\omega + \omega')t] \langle q | d \cdot \tilde{E}_\lambda(\omega') | p \rangle \tilde{C}_p(\omega) \\ & + \sum_{p\lambda} \frac{\exp[-i(W_p - W_q)t]}{W_q - W_p + \omega_\lambda} \int d\omega \int d\omega' \exp[-i(\omega + \omega')t] \langle q | d \cdot \tilde{E}_\lambda(\omega')^* | p \rangle \tilde{C}_p(\omega). \quad (\text{III.1-12}) \end{aligned}$$

The integrals merely reproduce the Fourier transforms of the functions $E^{(\pm)}_\lambda(t)$ and $C_p(t)$. The result can be written as a linear relationship between amplitudes [more general expressions would involve time derivatives of amplitudes],

$$C_q(t) = \sum_{p\lambda} M_{qp}^\lambda(t) C_p(t) \quad (\text{III.1-13})$$

where the time dependent coefficients are

$$M_{qp}^\lambda(t) = \left[\frac{\langle q | d \cdot E^{(+)}_\lambda(t) | p \rangle}{\hbar(W_q - W_p - \omega_\lambda)} + \frac{\langle q | d \cdot E^{(-)}_\lambda(t) | p \rangle}{\hbar(W_q - W_p + \omega_\lambda)} \right] \exp[-i(W_p - W_q)t]. \quad (\text{III.1-14})$$

These matrix elements can be written in terms of the pulse envelope functions (at fixed position) as

$$M_{qp}^\lambda(t) = \frac{1}{2} \frac{\langle q | d \cdot e(\lambda) | p \rangle}{\hbar(W_q - W_p - \omega_\lambda)} e_\lambda(t) \exp[-i(W_p - W_q + \omega_\lambda)t]$$

$$+ \frac{1}{2} \frac{\langle q | \mathbf{d} \cdot \mathbf{e}(\lambda)^* | p \rangle}{\hbar(W_q - W_p + \omega_\lambda)} \mathcal{E}_\lambda(t)^* \exp[-i(W_p - W_q - \omega_\lambda)t]. \quad (\text{III.1-15})$$

These are basically the expressions obtained by Placzek, who treated a single monochromatic wave (he used the notation M_{pq} for the matrix element $\langle q | \mathbf{M} | p \rangle$).

The Schrödinger Equation with Adiabatic Elimination

We have separated the molecular states into P states (low-lying, populated states) and essential Q states (connected by dipole transitions to P states, yet unpopulated). For the present we have neglected near resonant dipole transitions amongst the P states. We now wish to obtain for the P states equations of motion that make no explicit reference to the Q states. To do this we start from the (Dirac picture) Schrödinger equation that dictates the time dependence of $C_p(t)$ in terms of $C_q(t)$. Into this equation we substitute the adiabatic result for $C_q(t)$, Eqn. (III.1-12'). The result is the equation

$$\begin{aligned} \hbar \frac{d}{dt} C_p(t) = & \frac{i}{2} \sum_{q\lambda\lambda'} \langle p | \mathbf{d} \cdot \mathbf{e}(\lambda) | q \rangle \mathcal{E}_\lambda(t) M_{qp}^{\lambda'}(t) C_p(t) \exp[-i(W_q - W_p + \omega_\lambda)t] \\ & + \frac{i}{2} \sum_{q\lambda\lambda'} \langle p | \mathbf{d} \cdot \mathbf{e}(\lambda)^* | q \rangle \mathcal{E}_\lambda(t)^* M_{qp}^{\lambda'}(t) C_p(t) \exp[-i(W_q - W_p - \omega_\lambda)t]. \end{aligned} \quad (\text{III.1-16})$$

From the structure of the matrix $M^\lambda(t)$ as the sum of two parts, we recognize that each set of indices $q\lambda\lambda'$ produces four terms. These four terms involve four different exponential time dependences. These frequency differences fall into two classes. Two of the differences allow the possibility of resonances, when

$$W_p - W_{p'} = \omega_{\lambda'} - \omega_\lambda. \quad (\text{III.1-17})$$

When such conditions apply, the frequency difference vanishes. For neither of the remaining two frequency differences is such a resonance condition possible. These differences are always large, compared with possible values of the resonance differences. This separation into two classes of frequency increments is equivalent to separation into two classes of time scales: long (for resonance terms) and short (for non-resonant terms).

The Rotating Wave Approximation.

We now make the rotating wave approximation (RWA). That is, we separate time variations into those that are fast and those that are slow, and we average over those time variations that are fast. These rapidly varying exponentials involve the non-resonant frequency differences. Our averaging eliminates exponentials in which rapid time changes occur (i.e. exponentials in which the phase is the product of t and a large frequency increment.) In the RWA we neglect all exponentials that involve frequency combinations of the form

$$(W_q - W_p) \pm \omega_\lambda \quad \text{and} \quad (W_p - W_{p'}) \pm (\omega_\lambda + \omega_{\lambda'}).$$

We retain only the two exponentials that involve frequency differences of the form

$$(W_p + \omega_\lambda) - (W_{p'} + \omega_{\lambda'}).$$

With this approximation we can write the P-state equations as

$$\frac{d}{dt} C_p(t) = -i \sum_p W_{p'p}(t) C_p(t). \quad (\text{III.1-18})$$

The matrix $W_{p'p}(t)$ that appears here as the effective Hamiltonian (in units of frequency) has the elements

$$W_{p'p}(t) = -\frac{1}{4\hbar^2} \sum_{\lambda\lambda'q} \mathcal{E}_{\lambda'}(t)^* \mathcal{E}_\lambda(t) \exp[i(W_{p'} - W_p + \omega_{\lambda'} - \omega_\lambda)t] \\ \times \left[\frac{\langle p' | d \cdot e(\lambda')^* | q \rangle \langle q | d \cdot e(\lambda) | p \rangle}{W_q - W_p - \omega_\lambda} + \frac{\langle p' | d \cdot e(\lambda) | q \rangle \langle q | d \cdot e(\lambda')^* | p \rangle}{W_q - W_p + \omega_{\lambda'}} \right]. \quad (\text{III.1-19})$$

This expression is the final result of the adiabatic elimination: all dependence upon Q states appears in terms of intermediate states in summations. The summation includes both resonant and antiresonant denominators: the resonant terms involve $-\omega$ whereas the antiresonant terms involve $+\omega$. As is clear from the conditions needed for adiabatic elimination of the virtual states, none of the transition frequencies can be close to resonance with any of the carrier frequencies. Any such resonant states must be retained in the set of P states.

The Polarizability Tensor

The formula for the matrix elements of $W(t)$ involve both molecular properties (sums of products of dipole moments) and field properties (polarization unit vectors and amplitudes.) This expression can be simplified by introducing two second rank tensors, one that depends upon molecular properties and another that expresses field polarization characteristics.

To express molecular properties most simply we introduce the tensor operator $X(\omega, \omega')$, a dyadic defined by the equation for Cartesian components $X_{ij}(\omega, \omega')$:

$$\langle p' | X_{ij}(\omega', \omega) | p \rangle = \sum_q \left[\frac{\langle p' | d_j | q \rangle \langle q | d_i | p \rangle}{\hbar(W_q - W_p - \omega)} + \frac{\langle p' | d_i | q \rangle \langle q | d_j | p \rangle}{\hbar(W_q - W_p + \omega')} \right]. \quad (\text{III.1-20})$$

Using this dyadic we can write the effective Hamiltonian matrix elements (at fixed position) as

$$\hbar W_{p'p}(t) = - \sum_{\lambda\lambda'} E^{(-)}_{\lambda'}(t) \cdot \langle p' | X(\omega_{\lambda'}, \omega_{\lambda}) | p \rangle \cdot E^{(+)}_{\lambda}(t) \exp[i(W_{p'} - W_p)t]. \quad (\text{III.1-21})$$

To express the directional properties of the field we introduce the field polarization dyadic $\epsilon(\lambda', \lambda)$, whose Cartesian components form a tensor $\epsilon_{ij}(\lambda', \lambda)$:

$$\epsilon(\lambda', \lambda) = e(\lambda')^* e(\lambda), \quad \epsilon_{ij}(\lambda', \lambda) = e_i(\lambda')^* e_j(\lambda). \quad (\text{III.1-22})$$

We shall abbreviate the required contraction of the molecular tensor and the field tensor by the notation

$$X : \epsilon \equiv \sum_{ij} X_{ij} \epsilon_{ij} \quad (\text{III.1-23})$$

That is,

$$\langle p' | e(\lambda')^* \cdot X(\omega_{\lambda'}, \omega_{\lambda}) \cdot e(\lambda) | p \rangle = \langle p' | X(\omega_{\lambda'}, \omega_{\lambda}) | p \rangle : \epsilon(\lambda', \lambda). \quad (\text{III.1-24})$$

Using these dyadics we can write the effective Hamiltonian matrix elements as

$$\hbar W_{p'p}(t) = - \frac{1}{4} \sum_{\lambda\lambda'} \mathcal{E}_{\lambda'}(t)^* \mathcal{E}_{\lambda}(t) \exp[i(W_{p'} - W_p + \omega_{\lambda'} - \omega_{\lambda})t] \langle p' | X(\omega_{\lambda'}, \omega_{\lambda}) | p \rangle : \epsilon(\lambda', \lambda). \quad (\text{III.1-25})$$

This is the effective Hamiltonian governing time variation of P states when negligible population occurs in Q states.

The Polarizability Approximation

We require these matrix elements only for cases in which the exponentiated frequency sum is small. We can use this property,

$$W_{p'} + \omega_{\lambda'} \simeq W_p + \omega_{\lambda} \quad (\text{III.1-26})$$

in the denominators of the two-argument operator $X(\omega, \omega')$ to obtain a single-argument operator $X(\omega)$. This approximation allows us to write the energy operator (whose matrix elements give $W_{p'p}$) as dependent only on one frequency, say that of the incident photon, rather than on two frequencies (the incident and scattered photons). This approximation (Placzek's polarizability approximation) becomes an equality in the rotating wave approximation and in the Raman resonance approximation. It holds so long as the sums are not sensitive to frequency differences comparable to the Raman shifts $W_p - W_{p'}$, and so it assumes that none of the frequencies are near resonance with the Q states (this assumption is already present in the adiabatic approximation needed to derive Eqn. III.1-20). With these approximations we can express molecular properties by means of the tensor polarizability operator $X(\omega)$, a dyadic defined by

the equation for Cartesian components $X_{ij}(\omega)$:

$$\langle p' | X_{ij}(\omega) | p \rangle = \sum_q \left[\frac{\langle p' | d_i | q \rangle \langle q | d_j | p \rangle}{\hbar(W_q - W_p - \omega)} + \frac{\langle p' | d_j | q \rangle \langle q | d_i | p \rangle}{\hbar(W_q - W_p + \omega)} \right] \quad (\text{III.1-27})$$

(This is the polarizability operator of Placzek; he writes matrix elements $\langle p | M | q \rangle$ as M_{qp}). Note that the indices ij are interchanged in the second summation, and that the first sum contains the final-state energy $E_{p'} = \hbar W_{p'}$, whereas the second sum contains the initial-state energy $E_p = \hbar W_p$. These matrix elements have the property

$$\langle p' | X_{ij}(\omega) | p \rangle = \langle p | X_{ij}(-\omega) | p' \rangle^* \quad (\text{III.1-28})$$

Using this dyadic we can write the effective Hamiltonian matrix elements as

$$\hbar W_{p'p}(t) = - \sum_{\lambda\lambda'} E^{(-)}_{\lambda'}(t) \cdot \langle p' | X(\omega_{\lambda}) | p \rangle \cdot E^{(+)}_{\lambda}(t) \exp[i(W_{p'} - W_p)t]. \quad (\text{III.1-29})$$

This is a generalization of the elementary expression for the energy of an induced dipole moment,

$$H^{\text{ind}} = -\mathbf{d} \cdot \mathbf{E} = -\mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E}. \quad (\text{III.1-30})$$

The Raman Hamiltonian

The adiabatic elimination procedure, together with the polarizability approximation, gives the following expression for the matrix elements of the effective Raman Hamiltonian at fixed position:

$$W_{p'p}(t) = -\frac{1}{4\hbar} \sum_{\lambda\lambda'} \mathcal{E}_{\lambda'}(t)^* \mathcal{E}_{\lambda}(t) \exp[i(W_{p'} - W_p + \omega_{\lambda'} - \omega_{\lambda})t] \langle p' | X(\omega_{\lambda}) | p \rangle : \in (\lambda', \lambda). \quad (\text{III.1-31})$$

This is the matrix element to be used in the equation of motion for the P -state amplitudes $C_{p'}(t)$ at a given position. The matrix $\hbar W(t)$ is the effective Hamiltonian for Raman processes in the rotating wave approximation, and the envelope functions $\mathcal{E}_{\lambda}(t)$ refer to the field at the location of the molecule. In this Hamiltonian all molecular properties are parameterized by the polarizability operator $X(\omega)$, as contrasted with the dipole moment operator $\mathbf{d}$ that occurs for single-photon transitions. In place of the field unit vector of single-photon transitions, we now have a second rank tensor. And in place of a single electric field amplitude we now have the product of two amplitudes. It may be noted that the polarization approximation of Eqn. (III.1-21) allows us to introduce a molecular operator that depends upon a single frequency, rather than the two frequencies that appear in Eqn. (III.1-20).

We shall be concerned with radiation in which the modes all fall within a band of photon energies that is much smaller than the molecular excitation energies. In this situation we make no appreciable error in replacing the exact mode-dependent

operator $X(\omega_\lambda)$ by the operator $X(\bar{\omega})$ appropriate some mean frequency $\bar{\omega}$. We can therefore remove the molecular matrix element from the sum and write

$$W_{p'p}(t) = -\frac{1}{4\hbar} \langle p' | X(\bar{\omega}) | p \rangle \sum_{\lambda\lambda'} :F(\lambda', \lambda; t) \exp[-i(W_{p'} - W_p + \omega_{\lambda'} - \omega_\lambda)t]. \quad (\text{III.1-32})$$

All required properties of the field are embodied in the dyadic F , a second rank tensor with Cartesian components

$$F_{ij}(\lambda', \lambda; t) = e_i(\lambda')^* \mathcal{E}_{\lambda'}(t)^* e_j(\lambda) \mathcal{E}_\lambda(t). \quad (\text{III.1-33})$$

Only the composite properties of the field embodied in this dyadic are needed to describe Raman excitation.

The terms that we have retained here, through the RWA, have the property expressed by Eqn. (III.1-20). That is, the states p and p' are connected by two-photon resonance involving photons from modes λ and λ' . This includes the Raman-type resonances, when $W_{p'} + \omega_{\lambda'} = W_p + \omega_\lambda$, as well as the case $\omega_{\lambda'} = \omega_\lambda$ but $W_{p'} \neq W_p$.

The time dependence of $W(t)$ occurs for two reasons. First, the exponential factors express the time variation of the carrier frequencies. Second, $W(t)$ involves bilinear products of pulse-envelope amplitudes $\mathcal{E}_{\lambda'}(t)^*$ and $\mathcal{E}_\lambda(t)$ as embodied in the dyadic $F(\lambda', \lambda; t)$. These change as the pulses propagate, and so they depend both upon time and, implicitly, upon position.

The exponential phase factors that occur in the matrix $W_{p'p}(t)$ are the same sort that occur in traditional treatments of multistate excitation via single-photon transitions. In those cases one employs a rotating-wave picture rather than a Dirac picture. One makes a rotating wave approximation by retaining only those terms whose phases are null, and neglecting the large-phase terms. Here we have used the Dirac picture, rather than the rotating wave picture, so we are not guaranteed that phases will vanish. Indeed, we recognize that the phase will not vanish in the important case of a strong pump (see below).

The matrix elements $W_{p'p}(t)$ depend not only upon time, but also upon the directionality properties (the polarization directions) of a bilinear product of electric field vectors. These properties enter as the unit vectors $e(\lambda)$ and $e(\lambda')^*$, and are expressed by means of the tensor $\epsilon(\lambda', \lambda)$. The molecular dependence upon spatial orientation enters through the reference frame implicit in the dipole moment operator (a vector) $\mathbf{d}$, as expressed through the molecular tensor operator $X(\omega)$. The matrix element $W_{p'p}(t)$ involves a scalar constructed from the molecular tensor operator X and the field tensor ϵ . This is a fixed coefficient, for given molecule states p', p and given pulse modes λ, λ' .

Diagonal Elements

The diagonal elements of the matrix $W_{p'p}(t)$ have phase factors in which, by definition, the energy difference $W_{p'} - W_p$ vanishes. We therefore obtain the result

$$W_{pp}(t) \equiv \Delta_p(t) = -\frac{1}{4\hbar} \langle p | X(\bar{\omega}) | p \rangle \sum_{\lambda\lambda'} :E(\lambda', \lambda) \mathcal{E}_{\lambda'}(t)^* \mathcal{E}_{\lambda}(t) \exp[i(\omega_{\lambda'} - \omega_{\lambda})t]. \quad (\text{III.1-33})$$

In the rotating wave approximation (or the single-mode approximation) these elements require only those modes for which $\omega_{\lambda'} = \omega_{\lambda}$. When we include molecular degeneracy, as we must in treating rotational spectra, we obtain matrix elements of this same type (i.e. involving the condition $\omega_{\lambda'} = \omega_{\lambda}$) between degenerate sublevels. That is, the dynamic Stark interaction not only shifts energies but it also mixes degenerate states.

In the plane wave approximation each pulse mode is characterized by frequency and polarization. There will be a unique direction to the electric field of frequency ω_{λ} and so each frequency has a definite polarization. As a consequence, the specification of frequency may also be regarded as a specification of the polarization direction. However, the unit vectors needed for this specification may change with position, if the polarization properties change. One would need to introduce a changing basis to accommodate this change. The result would be equivalent to the summation over two preassigned vectors, as implied by the previous equation. In the simple case that no polarization change occurs, the diagonal elements in the RWA are

$$\Delta_p(t) = -\frac{1}{4\hbar} \langle p | X(\bar{\omega}) | p \rangle \sum_{\lambda} :E(\lambda, \lambda) |\mathcal{E}_{\lambda}(t)|^2 \quad (\text{III.1-34})$$

These terms represent time-dependent dynamic Stark shifts. Notice that this shift is negative.

The Schrödinger Equation

The Schrödinger equation for the probability amplitude for state p' , for a molecule at fixed position, is

$$\left[\frac{\partial}{\partial t} + i\Delta_{p'}(t) \right] C_{p'}(t) = \frac{i}{\hbar} \sum_{p \neq p'} C_p(t) \langle p' | X(\bar{\omega}) | p \rangle \sum_{\lambda\lambda'} :F(\lambda', \lambda; t) \times \exp[-i(W_p - W_{p'} + \omega_{\lambda} - \omega_{\lambda'})t]. \quad (\text{III.1-35})$$

In the RWA we retain only those terms whose exponentials are slowly varying with time.

Example: Strong Pump

As an application of the general formula for $W_{pp}(t)$, consider excitation with a single strong pump mode (P) together with Stokes (S) and anti-Stokes (A) modes. Suppose that the pump is much stronger than either of these modes, as expressed by the inequalities

$$|\mathcal{E}_S| \ll |\mathcal{E}_P|^2, \quad |\mathcal{E}_A| \ll |\mathcal{E}_P|^2 \quad (\text{III.1-36})$$

Then the diagonal elements of the effective Hamiltonian (the dynamic Stark shifts) are

$$\hbar\Delta_p(t) = -\frac{1}{4} \langle p | X(\omega_p) | p \rangle : \in (P, P) \quad |\mathcal{E}_p(t)|^2. \quad (\text{III.1-37})$$

The off-diagonal elements depend upon pump field and upon secondary fields, either Stokes or anti-Stokes. Suppose first that (final) state p' lies above (initial) state p . Then from the resonance condition we identify λ with the pump and λ' with the Stokes modes. The off-diagonal matrix element becomes

$$\begin{aligned} W_{p'p}(t) = & -\frac{1}{4\hbar} \langle p' | X(\omega_p) | p \rangle : \in (S, P) \quad \mathcal{E}_S(t)^* \mathcal{E}_P(t) \exp(-i\phi_{SP}) \\ & -\frac{1}{4\hbar} \langle p' | X(\omega_p) | p \rangle : \in (P, A) \quad \mathcal{E}_P(t)^* \mathcal{E}_A(t) \exp(-i\phi_{PA}) \\ & -\frac{1}{4\hbar} \langle p' | X(\omega_p) | p \rangle : \in (P, P) \quad |\mathcal{E}_P(t)|^2 \exp[-i(W_p - W_{p'})t]. \end{aligned} \quad (\text{III.1-38})$$

Here $\phi_{\lambda\lambda'}$ is the phase associated with modes λ and λ' ,

$$\phi_{\lambda\lambda'} = (W_p - W_{p'} + \omega_\lambda - \omega_{\lambda'})t$$

The RWA neglects the last term, proportional to $|\mathcal{E}_P|^2$. On the other hand, if (final) state p' lies below (initial) state p , then λ' is an anti-Stokes mode, and we have the expression

$$\begin{aligned} W_{p'p}(t) = & -\frac{1}{4\hbar} \langle p' | X(\omega_p) | p \rangle : \in (A, P) \quad \mathcal{E}_A(t)^* \mathcal{E}_P(t) \exp(-i\phi_{AP}) \\ & -\frac{1}{4\hbar} \langle p' | X(\omega_p) | p \rangle : \in (P, S) \quad \mathcal{E}_P(t)^* \mathcal{E}_S(t) \exp(-i\phi_{PS}) \\ & -\frac{1}{4\hbar} \langle p' | X(\omega_p) | p \rangle : \in (P, P) \quad |\mathcal{E}_P(t)|^2 \exp[-i(W_p - W_{p'})t]. \end{aligned} \quad (\text{III.1-39})$$

The RWA neglects the last term. Without making the RWA it is not possible to introduce phases that will remove all time dependence from the elements of $W(t)$.

§III.2 Corrections to Adiabatic Elimination

We have derived equations that require the polarizability operator $X(\omega_\lambda)$ evaluated at discrete carrier frequencies. Let us consider modifications that account for the finite bandwidth of the pulses. For this purpose it is useful to define the vector

$$D_{qp}(\omega) = \frac{1}{\hbar(W_p - W_q + \omega)} \langle q | d | p \rangle = -D_{pq}(-\omega)^* \quad (\text{III.2-1})$$

Then we can write the exact expression for the Q state amplitude, Eqn. (III.1-10), as the double Fourier integral

$$C_q(t) = - \sum_p \int d\omega_1 \int d\omega_2 \exp[-i(W_p - W_q + \omega_1 + \omega_2)t] D_{qp}(\omega_1 + \omega_2) \tilde{E}(\omega_1) \tilde{C}_p(\omega_2) \quad (\text{III.2-2})$$

Let us continue to assume that the molecular amplitudes are adequately described by nonresonant low frequency components, so that we can continue the approximation $\omega_2 = 0$ in the denominator of $D(\omega_1 + \omega_2)$, but let us now allow dependence on ω_1 by introducing an expansion about ω_λ : we write

$$D_{qp}(\omega_1 + \omega_2) \tilde{E}_\lambda(\omega_1) = \sum_{k=0}^{\infty} (\omega_1 - \omega_\lambda)^k D_{qp}^{(k)}(\omega_\lambda) \tilde{E}_\lambda(\omega_1) \quad (\text{III.2-3})$$

where the coefficients are frequency derivatives evaluated at the carrier frequency,

$$D_{qp}^{(k)}(\omega_\lambda) = \frac{1}{k!} \left[\left(\frac{\partial}{\partial \omega} \right)^k D_{qp}(\omega) \right]_{\omega=\omega_\lambda} \quad (\text{III.2-4})$$

Specifically we have

$$D_{qp}^{(0)}(\omega_\lambda) = D_{qp}(\omega_\lambda) = \frac{1}{\hbar(W_p - W_q + \omega_\lambda)} \langle q | d | p \rangle \quad (\text{III.2-5})$$

$$D_{qp}^{(k)}(\omega_\lambda) = \frac{1}{\hbar(W_p - W_q + \omega_\lambda)^{k+1}} \langle q | d | p \rangle = (-1)^k D_{pq}(-\omega_\lambda)^* \quad (\text{III.2-6})$$

With this procedure we obtain, in place of Eqn. (III.1-12), the equations

$$C_q(t) = - \sum_{p\lambda k} D_{qp}^{(k)}(\omega_\lambda) \int d\omega \int d\omega' \exp[-i(W_p - W_q + \omega)t] (\omega' - \omega_\lambda)^k \tilde{E}_\lambda(\omega') \tilde{C}_p(\omega' - \omega) \quad (\text{III.2-7})$$

$$- \sum_{p\lambda k} D_{qp}^{(k)}(-\omega_\lambda) \int d\omega \int d\omega' \exp[-i(W_p - W_q + \omega)t] (\omega' + \omega_\lambda)^k \cdot \tilde{E}_\lambda(\omega')^* \tilde{C}_p(\omega' - \omega).$$

The integrals differ from simple Fourier transforms of $E^{(\pm)}_\lambda(t)$ by the presence of powers of $(\omega' - \omega_\lambda)$. When we convert this equation back to the time domain we obtain

$$\begin{aligned} C_q(t) = & - \frac{1}{2} \sum_{p\lambda k} D_{qp}^{(k)}(+\omega_\lambda) \cdot e(\lambda) \exp[-i(W_p - W_q + \omega_\lambda)t] C_p(t) \left[\left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_\lambda(t) \right] \\ & \text{(III.2-8)} \\ & - \frac{1}{2} \sum_{p\lambda k} D_{qp}^{(k)}(-\omega_\lambda) \cdot e(\lambda)^* \exp[-i(W_p - W_q - \omega_\lambda)t] C_p(t) \left[\left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_\lambda(t)^* \right]. \end{aligned}$$

There are no additional time derivatives of the molecular amplitudes because of our approximation 2). The connection matrix between $C_p(t)$ and $C_q(t)$ becomes

$$\begin{aligned} M_{qp}^\lambda(t) = & - \frac{1}{2} \exp[-i(W_p - W_q + \omega_\lambda)t] \sum_k D_{qp}^{(k)}(\omega_\lambda) \cdot e(\lambda) \left[\left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_\lambda(t) \right] \\ & - \frac{1}{2} \exp[-i(W_p - W_q - \omega_\lambda)t] \sum_k D_{qp}^{(k)}(-\omega_\lambda) \cdot e(\lambda)^* \left[\left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_\lambda(t)^* \right]. \end{aligned} \quad \text{(III.2-9)}$$

This series may be regarded as an expansion in powers of the ratio of pulse bandwidth $\Delta\omega_\lambda$ to nonresonant detuning, that is, to the frequency difference between a carrier frequency and a typical pair of states from P and Q space, $|W_q - W_p + \omega_\lambda|$. For sufficiently broadband pulses, some frequencies will approach resonance and these terms will become important. (At the same time, however, population will be brought into the Q states, and our assumption of adiabatic elimination fails: we must consider Q-state dynamics.) It should be noted that although we have removed our restriction to narrow pulse bandwidth, we have continued to assume that the frequency distribution of amplitude $C_p(t)$ contains negligible resonant components. A more general procedure, without this assumption, would produce a connection of the form

$$C_q(t) = \sum_{p\lambda k} M_{qp}^{\lambda k}(t) \left[\left(i \frac{\partial}{\partial t} \right)^k C_{p_2}(t) \right]$$

The Dipole Moment

The dipole-moment expectation value is

$$\langle \mathbf{d}(t) \rangle = 2 \operatorname{Re} \sum_{\mathbf{p}'\mathbf{q}} C_{\mathbf{p}'}(t) d_{\mathbf{p}'\mathbf{q}} C_{\mathbf{q}}(t) \exp[-i(W_{\mathbf{q}} - W_{\mathbf{p}'})t] . \quad (\text{III.2-10})$$

By using the preceding formula we can eliminate the Q state amplitudes and write this as

$$\begin{aligned} \langle \mathbf{d}(t) \rangle = & - \operatorname{Re} \sum_{\mathbf{p}'\mathbf{q}\mathbf{p}\lambda k} C_{\mathbf{p}'}(t)^* C_{\mathbf{p}}(t) d_{\mathbf{p}'\mathbf{q}} \exp[-i(W_{\mathbf{p}} - W_{\mathbf{p}'})t] \\ & \times [D_{\mathbf{qp}}^{(k)}(\omega_{\lambda}) \cdot \mathbf{e}(\lambda) \exp(-i\omega_{\lambda}t) \left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_{\lambda}(t) \\ & + D_{\mathbf{qp}}^{(k)}(-\omega_{\lambda}) \cdot \mathbf{e}(\lambda)^* \exp(+i\omega_{\lambda}t) \left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_{\lambda}(t)^*] . \end{aligned} \quad (\text{III.2-11})$$

This can be rewritten as

$$\begin{aligned} \langle \mathbf{d}(t) \rangle = & - \operatorname{Re} \sum_{\mathbf{p}'\mathbf{q}\mathbf{p}\lambda} \rho_{\mathbf{pp}'}(t) \exp[-i(W_{\mathbf{p}} - W_{\mathbf{p}'} + \omega_{\lambda})t] \\ & \times \sum_k [d_{\mathbf{p}'\mathbf{q}} D_{\mathbf{qp}}^{(k)}(\omega_{\lambda}) \cdot \mathbf{e}(\lambda) + (-1)^{k+1} d_{\mathbf{qp}} D_{\mathbf{p}'\mathbf{q}}^{(k)}(\omega_{\lambda}) \cdot \mathbf{e}(\lambda)] \left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_{\lambda}(t) . \end{aligned} \quad (\text{III.2-12})$$

This expansion can be expressed in terms of derivatives of the polarization operator,

$$\begin{aligned} \langle \mathbf{d}(t) \rangle = & - \operatorname{Re} \sum_{\mathbf{p}'\mathbf{q}\mathbf{p}\lambda} \rho_{\mathbf{pp}'}(t) \exp[-i(W_{\mathbf{p}} - W_{\mathbf{p}'} + \omega_{\lambda})t] \\ & \times \sum_k \frac{1}{k!} \left[\left(i \frac{\partial}{\partial \omega} \right)^k \langle \mathbf{p}' | \mathbf{X}(\omega) | \mathbf{p} \rangle \right]_{\omega=\omega_{\lambda}} \cdot \mathbf{e}(\lambda) \left(i \frac{\partial}{\partial t} \right)^k \mathcal{E}_{\lambda}(t) . \end{aligned} \quad (\text{III.2-13})$$

We may expect that derivative terms are negligible as long as the bandwidth $\Delta\omega_{\lambda}$ is much smaller than the frequency difference between a typical P state plus carrier, $W_{\mathbf{p}} + \omega_{\lambda}$, and the lowest lying Q state. When the pulse envelope contains such (high) frequency components, Q-state excitation becomes likely and we may need to revise our assumption that Q-states do not participate in the dynamics.

The Hamiltonian

These equations are those that are produced by the Raman Hamiltonian

$$\begin{aligned}
 W_{p'p}(t) = & \frac{1}{4} \exp[i(W_{p'} - W_p)t] \sum_{kq\lambda\lambda'} d_{p'q} D_{qp}^{(k)}(\omega_\lambda) \epsilon(\lambda', \lambda) \mathcal{E}_{\lambda'}(t)^* \left[\left(\frac{i\partial}{\partial t} \right)^k \mathcal{E}_\lambda(t) \right] \\
 & + \frac{1}{4} \exp[i(W_p - W_{p'})t] \sum_{kq\lambda\lambda'} D_{qp}^{(k)}(-\omega_{\lambda'}) d_{p'q} \epsilon(\lambda', \lambda) \left[\left(\frac{i\partial}{\partial t} \right)^k \mathcal{E}_{\lambda'}(t)^* \right] \mathcal{E}_\lambda(t).
 \end{aligned}
 \tag{III.2-14}$$

This is the effective Hamiltonian to use when we wish to treat dispersion. It is the Raman Hamiltonian that is consistent with the dispersive expression for the dipole moment. It differs from the traditional Raman Hamiltonian by the presence of time derivatives of pulse envelopes. Only the term with $k = 0$ permits factorization in terms of a polarizability operator.

$$\langle p' | X(\omega) | p \rangle = \sum_q \{ d_{p'q} D_{qp}^{(0)}(\omega) + D_{qp}^{(0)}(-\omega) d_{p'q} \}.
 \tag{III.2-15}$$

§III.3 Spatial Variation of Molecular Schrödinger Equation

Let us consider the modifications that are needed when we wish to compare molecular excitation at different locations. We begin with the time-dependent Schrödinger equation appropriate to electric-dipole transitions, for a molecule with center of mass at $\mathbf{R}$:

$$\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}, t) = -i[\mathbf{H}^0 - \mathbf{d} \cdot \mathbf{E}(\mathbf{R}, t)] \Psi(\mathbf{R}, t). \quad (\text{III.3-1})$$

The electric field has the expansion

$$\mathbf{E}^{(+)}(\mathbf{R}, t) = \sum_{\lambda} \mathbf{E}^{(+)}_{\lambda}(\mathbf{R}, t) = \frac{1}{2} \sum_{\lambda} \mathbf{e}(\lambda) \mathcal{E}_{\lambda}(\mathbf{R}, t) \exp(i\mathbf{k}_{\lambda} \cdot \mathbf{R} - i\omega_{\lambda} t). \quad (\text{III.3-2})$$

We write the statevector at time t for a molecule whose center of mass is at $\mathbf{R}$, as

$$\Psi(\mathbf{R}, t) = \sum_m \psi_m C_m(\mathbf{R}, t) \exp[-i\zeta_m(\mathbf{R}, t)]. \quad (\text{III.3-3})$$

The Phases

Although in principle the phases may be chosen as arbitrary functions of space and time, in practice one assumes separability and writes

$$\zeta_m(\mathbf{R}, t) = \omega_m t - \mathbf{K}_m \cdot \mathbf{R}. \quad (\text{III.3-4})$$

The frequency ω_m may be taken as zero (thereby defining the Schrödinger picture) or as the molecular frequency ω_m corresponding to the unperturbed energy eigenvalue $\hbar\omega_m$ of state ψ_m (thereby defining the Dirac picture), or it may be taken as some combination of radiation-field frequencies (thereby defining a rotating wave picture). The latter choice allows us to remove from the Hamiltonian the time variations associated with near-resonant carrier frequencies, leaving an effective Hamiltonian that varies in time only because of slower changes in pulse envelopes. For descriptions of radiation-induced motions (such as cooling or trapping of molecules by radiation), it is often useful to incorporate into the molecular energies the center-of-mass kinetic energy $Mv^2/2$ associated with molecular center-of-mass velocity $\mathbf{v}$. When excitation is largely attributable to photon absorption (rather than collisions with massive particles), one may wish to define phases that include appropriately modified kinetic energies corresponding to internal excitation states.

The wavevector $\mathbf{K}_m$ allows us to remove a portion of the spatial variation of the Hamiltonian that originates in plane-wave carriers. It amounts to the introduction of a state-dependent center-of-mass momentum for the molecule. For molecules initially at rest in the ground state ψ_0 we would take $\mathbf{K}_0 = 0$, whereas for a moving molecule

$\hbar K_0$ may be taken as the molecular momentum Mv . The remaining excited-state values represent momentum transferred to the molecule as a consequence of photon absorption from the field. In a photon-number representation of the field differences of these vectors represent molecular momentum changes as a result of photon absorption and emission (cf. the discussion in Bernhardt and Shore, 1981). In the classical description of the fields used here, differences of wavevectors occur when we evaluate products of electric field mode amplitudes. We shall be interested in propagation along a beam. Under those circumstances the most convenient choice for K_m will be a vector along the primary propagation axis, say the z direction, so that the phase reads

$$\zeta_m(R,t) = \omega_m t - K_m z. \quad (\text{III.3-5})$$

The use of such phases is equivalent to introducing a delay time

$$T_m = \frac{K_m}{\omega_m} z \equiv \frac{z}{v_m} \quad (\text{III.3-6})$$

and writing the state-vector expansion coefficient as

$$C_m(R,t) \exp[i(K_m z - \omega_m t)] = C_m(R,t) \exp[-i\omega_m(t - T_m)]. \quad (\text{III.3-7})$$

When all of wavevectors K_m and the frequencies ω_m have a common ratio (the phase velocity v_m and the delay time T_m are independent of m), then the phase choice is equivalent to introducing a retarded time $\tau = t - T_m$ as the temporal argument of the probability amplitude: we take the local zero-point of time (at a given molecule) to coincide with the arrival of a fiducial mark moving with the phase velocity $v = \omega_m/K_m$. The expansion coefficient then becomes

$$C_m(R,t) \exp[i(K_m z - \omega_m t)] = C_m(R, \tau + T) \exp[-i\omega_m \tau]. \quad (\text{III.3-8})$$

where $\tau = t - z/v$. Although it is possible to use a different time scale for each probability amplitude (thereby introducing a different time window for each pulse), such a procedure complicates the equations of motion.

It should be stressed that the phases $\zeta_m(R,t)$ are introduced solely to simplify subsequent equations; ideally they produce amplitude functions that vary more slowly with space and time. Any injudicious choice of explicit phase will ultimately be compensated by a phase in the amplitude $C_m(R,t)$.

The Schrödinger Equation

Upon introducing these phases the expansion into P and Q states reads

$$\Psi(R,t) = \sum_p \psi_p C_p(R,t) \exp(iK_p \cdot R - iW_p t) + \sum_q \psi_q C_q(R,t) \exp(iK_q \cdot R - iW_q t). \quad (\text{III.3-9})$$

The Schrödinger equation for the P states, obtained by adiabatic elimination of the Q states, is

$$\frac{d}{dt} C_p(R,t) = -i \sum_p W_{p',p}(R,t) C_p(R,t). \quad (\text{III.3-10})$$

With the neglect of direct dipole transitions between P states the effective Hamiltonian $W(R,t)$ is due to polarizability. We introduced the polarizability operator $X(\omega)$ and the field polarization tensor $\epsilon(\lambda',\lambda)$. Upon using these tensors we obtain the expression

$$\begin{aligned} \hbar W_{p',p}(R,t) = & -\frac{1}{4} \sum_{\lambda\lambda'} \mathcal{E}_{\lambda'}(R,t)^* \mathcal{E}_{\lambda}(R,t) \langle p | X(\omega_{\lambda}) | p \rangle : \epsilon(\lambda',\lambda) \\ & \times \exp[i(W_{p'} - W_p + \omega_{\lambda'} - \omega_{\lambda})t] \exp[-i(\mathbf{K}_{p'} - \mathbf{K}_p + \mathbf{k}_{\lambda'} - \mathbf{k}_{\lambda}) \cdot \mathbf{R}] \end{aligned} \quad (\text{III.3-11})$$

In place of Eqn. (III.1-29) we have

$$W_{p',p}(R,t) = -\frac{1}{4\hbar} \langle p | X(\bar{\omega}) | p \rangle \sum_{\lambda\lambda'} :F(\lambda',\lambda; R,t) \exp[-i(W_{p'} - W_p + \omega_{\lambda'} - \omega_{\lambda})t] \quad (\text{III.3-12})$$

where the Cartesian components of the field dyadic F are

$$F_{ij}(\lambda',\lambda; R,t) = e_j(\lambda')^* \mathcal{E}_{\lambda'}(R,t)^* e_j(\lambda) \mathcal{E}_{\lambda}(R,t) \exp[-i(\mathbf{K}_{p'} - \mathbf{K}_p + \mathbf{k}_{\lambda'} - \mathbf{k}_{\lambda}) \cdot \mathbf{R}] \quad (\text{III.3-13})$$

This effective Raman Hamiltonian includes not only a time dependent phase, involving frequency differences, but also a position dependent phase, involving differences of wave vectors. For any fixed position this phase does not change with time. In simple cases, such as excitation of nondegenerate excitation chains in which each excitation link is associated with a unique carrier frequency, these phases do not affect the dynamics. In other cases the relative phases of various Rabi frequencies may profoundly affect the dynamics. (Such a case occurs in two-step excitation from $J = 0$ to $J = 1$ to $J = 0$.) When we treat propagation, it is desirable to have probability amplitudes $C_p(R,t)$ that vary slowly with position. The arbitrary vector $\mathbf{K}_p$ can be used to remove a portion of the spatial variation from the probability amplitude. Specifically, the vector $\mathbf{K}_p$ can be taken along the dominant propagation axis.

§III.4 The Density Matrix Equation

The single-molecule Schrödinger equation does not provide a description of homogeneous relaxation phenomena. (One can include effects of Doppler broadening, a form of inhomogeneous relaxation, by summing over molecular velocities.) Solutions to the Schrödinger equation are undamped oscillations (Rabi oscillations) that persist indefinitely. The Schrödinger equation does not approach a steady limit. To treat steady-state limits it is traditional to employ the density matrix. For simplicity we consider only molecules at a fixed position, and we suppress explicit mention of this position R . (To correct this omission we replace phases $W_p t$ by $W_p t - K_p \cdot R$.)

The Density Matrix

Let us consider a single species of molecule, describable by a state vector $\Psi(t)$. Quantum mechanical expectation values for an operator M have the form, for this pure state,

$$\langle M(t) \rangle = \langle \Psi(t) | M | \Psi(t) \rangle. \quad (\text{III.4-1})$$

To evaluate this expression we introduce a set of basis states, say ψ_p , for which we can evaluate matrix elements of the operator M :

$$M_{pp'} = \langle \psi_p | M | \psi_{p'} \rangle. \quad (\text{III.4-2})$$

Then we can write the pure-state expectation value in the form

$$\langle M(t) \rangle = \sum_{pp'} \tilde{\rho}_{p'p}(t) M_{pp'} = \text{Trace} \{ \tilde{\rho}(t) M \}. \quad (\text{III.4-3})$$

The density matrix $\tilde{\rho}(t)$ introduced by this equation has elements

$$\tilde{\rho}_{p'p}(t) = \langle \psi_{p'} | \Psi(t) \rangle \langle \Psi(t) | \psi_p \rangle. \quad (\text{III.4-4})$$

This equation may be regarded as the definition of the pure-state density matrix $\tilde{\rho}$, in the Schrödinger picture. When we make an expansion of the statevector in terms of basis states in the form

$$\Psi(t) = \sum_p \psi_p C_p(t) \exp(-iW_p t) + \sum_q \psi_q C_q(t) \exp(-iW_q t) \quad (\text{III.4-5})$$

as we have done, then the Schrödinger-picture density matrix is expressible as bilinear products of probability amplitudes $C_p(t)$ together with the explicitly extracted phases,

$$\tilde{\rho}_{p'p}(t) = C_{p'}(t) C_p(t)^* \exp[i(W_{p'} - W_p)t] \equiv \rho_{p'p}(t) \exp[i(W_{p'} - W_p)t]. \quad (\text{III.4-6})$$

The presence of the phase factors accompanies our use of the Dirac picture: both the

probability amplitudes $C_p(t)$ and the density matrix $\rho_{pp}(t)$ are in the Dirac picture. The diagonal elements of the density matrix provide the probability that at time t the molecule will be found in state p , given that it was in state $\psi(0)$ at time $t = 0$:

$$\tilde{\rho}_{pp}(t) = \rho_{pp}(t) = |C_p(t)|^2. \quad (\text{III.4-7})$$

The Mixed-State Density Matrix

More generally, we deal with systems that are not describable as a pure quantum state. In addition to the state labels p that suffice for a single state vector, we have additional labels that prescribe such attributes as the molecular velocity. Let us refer to these additional attributes as labelling different molecular species. (In this phraseology, molecules with different velocities are regarded as different species.) We must sum the pure-state expectation values over all possible species. The additional labels over species may be divided into two classes, namely those (a) that will appear in the molecule-radiation Hamiltonian (velocity is of this type, because it produces Doppler shifts of the interaction frequencies), and those (α) that will not so appear (such labels might refer to the properties of the environment around the molecule). Both of these labels may take discrete or continuous values. The expectation value may be written

$$\langle M(t) \rangle = \int_{a\alpha} \langle \Psi(a\alpha; t) | M | \Psi(a\alpha; t) \rangle = \int_a \mathcal{T} \text{rad} [\tilde{\rho}(a; t) M]. \quad (\text{III.4-8})$$

The mixed-state Schrödinger-picture density matrix that occurs here is a sum over those attributes α that do not appear explicitly in the Hamiltonian for the molecule-radiation system, weighted by probability $p(a\alpha)$ for the occurrence of the relevant labels $a\alpha$ in the ensemble:

$$\tilde{\rho}_{p'p}(a) = \int_{\alpha} \langle \psi_{p'} | \Psi(a\alpha; t) \rangle p(a\alpha) \langle \Psi(a\alpha; t) | \psi_p \rangle. \quad (\text{III.4-9})$$

The summation over α enables us to account for properties of the molecular environment that are not directly apparent in the molecule-radiation Hamiltonian (such as temperature and density of perturbing particles). These variables will not appear in equations of motion for the molecule. The dependence upon attributes a will remain as a parameter in the molecular equations.

The Dirac-picture mixed-state density matrix may be regarded as an average, over unobserved attributes a , of bilinear probability amplitudes:

$$\rho_{p'p}(a; t) = \{ C_{p'}(a; t) C_p(a; t)^* \} = \int_{\alpha} p(a\alpha) C_{p'}(a\alpha; t) C_p(a\alpha; t)^*. \quad (\text{III.4-10})$$

This average is not, in general, equal to the bilinear combination of two averaged amplitudes. Using the Dirac picture we write expectation values as

$$\langle M(t) \rangle = \int_a \sum_{pp'} \rho_{p'p}(a;t) M_{pp'} \exp(i(W_p - W_{p'})t). \quad (\text{III.4-11})$$

In particular, the polarization field at fixed position takes the form

$$P(t) = \mathcal{N} \int_a \sum_{pp'} \rho_{p'p}(a;t) \langle p|d|p' \rangle \exp(i(W_p - W_{p'})t). \quad (\text{III.4-12})$$

The time dependence appears in explicit phases, obtained from field-free molecular energy eigenvalues, and in the variation of the Dirac-picture density matrix. Spatial dependence is not exhibited explicitly here, but may be included.

The Density Matrix Equations

We can derive equations of motion for the density matrix. Let us consider first the pure state, and work with the Dirac picture, when we deal with the elements $\rho_{p'p}(t)$. Let us rewrite the Schrödinger amplitude equation (in the Dirac picture)

$$\frac{d}{dt} C_p(t) = -i \sum_p W_{p'p}(t) C_p(t) \quad (\text{III.4-13})$$

as an equation for the density matrix

$$\rho_{p'p}(t) = C_{p'}(t) C_p(t)^*. \quad (\text{III.4-14})$$

The matrix W that occurs here is the effective Hamiltonian. In the present situation we have in mind the Raman Hamiltonian, in the rotating wave approximation, involving bilinear products of electric field amplitudes and the molecular polarizability tensor. Upon using the Hermitian property $W_{p'p}(t) = W_{pp'}(t)^*$ we obtain the equation

$$\frac{d}{dt} \rho_{p'p}(t) = -i \sum_{p''} [W_{p'p''} \rho_{p''p} - \rho_{p'p''} W_{p''p}] \quad (\text{III.4-15})$$

These are the equations for the pure state density matrix, in the Dirac picture. By construction they are equivalent to the Schrödinger equation.

We generalize this equation to the more general case of mixed states by introducing an enlarged system including not only the single molecule of interest but an environment of other molecules. The summations over attributes α that occur in the definition of the density matrix then give rise to additional terms in the equation of motion. These additional environmental terms are almost always regarded as arising in essentially random relaxation processes occurring to the molecule. Their effect is included by adding terms to produce the equation

$$\frac{d}{dt} \rho_{p'p} = -i \sum_{p''} [W_{p'p''} \rho_{p''p}(t) - \rho_{p'p''}(t) W_{p''p}] - \sum_{p''} \Gamma_{pp''p'} \rho_{p''p}. \quad (\text{III.4-16})$$

The relaxation coefficients may be written as

$$\begin{aligned} \sum_{p''} \Gamma_{pp''p'} \rho_{p''p} &= \Gamma_{p'p} \rho_{p'p} + \delta(p', p) \sum_{p''} \rho_{p''p''} R_{p''p}. \\ \Gamma_{p'p} &= \frac{1}{2} \sum_{p''} [R_{p',p''} + R_{p,p''}] + [1 - \delta(p', p)] \gamma_{p'p} \\ &+ [1 - \delta(p, p')] \Gamma_{p'p} \rho_{p'p}(t) + \delta(p, p') \sum_{p''} \rho_{pp''}(t) R_{pp'}. \end{aligned} \quad (\text{III.4-17})$$

Here $\rho_{pp} R_{p,p'}$ denotes the rate at which population in state p changes to population in state p' as a result of all the processes that are not included in the Hamiltonian $\hat{H}_W(t)$. (These include spontaneous emission and collisional changes.) The coefficient $\gamma_{p'p}$ expresses additional processes that can produce relaxation of coherence without producing population changes.

This is the basic equation for the density matrix in the Dirac picture. It involves the damping coefficients $\Gamma_{p'p}$ and the rate coefficients $R_{p'p}$ as empirically determined parameters, and the matrix elements

$$W_{p'p}(t) = -\frac{i}{\hbar} \sum_{\lambda\lambda'} \langle p' | X(\omega_\lambda) | p \rangle : \epsilon(\lambda', \lambda) \mathcal{E}_{\lambda'}(t)^* \mathcal{E}_\lambda(t) \exp[-i(W_{p'} - W_p + \omega_\lambda - \omega_{\lambda'})t] : \quad (\text{III.4-18})$$

to be evaluated from given pulse envelope functions. In the RWA we retain only those modes whose frequencies produce a slowly varying exponential, on a time scale set by two-photon Rabi oscillations.

The general multilevel density matrix equations for degenerate levels becomes fairly complicated. We treat examples of this in a separate memo. Here let us consider some properties of nondegenerate systems.

Nondegenerate Populations and Coherences

When treating *nondegenerate* systems it often proves useful to separate the density matrix into diagonal parts (populations)

$$P_p(t) \equiv \rho_{pp}(t) \equiv \bar{\rho}_{pp}(t) \quad (\text{III.4-19})$$

and off-diagonal parts (coherences),

$$Q_{p'p}(t) \equiv \rho_{p'p}(t) \equiv \bar{\rho}_{p'p}(t) \exp[-i(W_{p'} - W_p)t], \quad \text{for } p \neq p' \quad (\text{III.4-20})$$

The populations satisfy the equation

$$\frac{d}{dt} P_p(t) = \sum_{p'} P_{p'}(t) R_{p'p} - i \sum_{p'' \neq p} [W_{pp''} Q_{p''p}(t) - Q_{pp''}(t) W_{p''p}] \quad (\text{III.4-21})$$

in which direct links to other populations occur only as a result of rate processes (that is, processes that are not described by the Hamiltonian of the matrix W). The coherences obey the equation

$$\begin{aligned} \frac{d}{dt} Q_{p'p}(t) = & -i [W_{p'p'} - W_{pp} - i\Gamma_{p'p}] Q_{p'p}(t) \\ & -iW_{p'p} [P_p(t) - P_{p'}(t)] \\ & -i \sum_{p'' \neq p, p'} [W_{p'p''} Q_{p''p}(t) - Q_{p'p''}(t) W_{p''p}] \end{aligned} \quad (\text{III.4-22})$$

Thus the coherences are coupled to differences of populations and to other coherences.

These are the equations, taken with the expressions for the elements $W_{pp'}$, that we must solve to determine the molecular response and, in turn, the polarization field. Resonant propagation, in which the polarization is expressed in terms of dipole moments, requires only off-diagonal elements of s . Raman propagation approximates the dipole moment by a polarizability, and as a result its description requires both diagonal and off-diagonal elements.

Coherence Hierarchy from Nondegenerate States

Further subdivision of the set of off-diagonal elements is often useful. Suppose that we have a *nondegenerate* system whose labels p are integers. We can then categorize the elements of the density matrix by the integer difference between subscripts:

$$\begin{aligned} Q_p^0 &\equiv P_p = \rho_{pp} \\ Q_p^1 &= \rho_{p,p+1}, \quad Q_p^{1*} = \rho_{p+1,p} \\ Q_p^n &= \rho_{p,p+n}, \quad Q_p^{n*} = \rho_{p+n,p} \end{aligned} \quad (\text{III.4-23})$$

The quantities Q_p^n may be regarded as components of a vector Q^n . The effective Hamiltonian has elements

$$W_{p+n,p}(t) = -\frac{1}{4\hbar} \langle p+n | X(\tilde{\omega}) | p \rangle \sum_{\lambda\lambda'} :E(\lambda', \lambda) \mathcal{E}_{\lambda'}(t)^* \mathcal{E}_{\lambda}(t) \exp[-i(W_p - W_{p+n} + \omega_{\lambda} - \omega_{\lambda'})t] : \quad (\text{III.4-24})$$

Suppose further that the operator X has elements only for $n = 0, \pm 1$. (The Raman case $n = 0, \pm 2$ merely requires renumbering of the states.) That is, we deal with a single excitation chain of states, with tridiagonal Hamiltonian. Then the set of density matrix equations for populations reads

$$\begin{aligned} \frac{d}{dt} P_p(t) = & \sum_{p'} P_{p'}(t) R_{p'p} - i[W_{p,p-1} Q_{p-1}^1(t) - Q_{p-1}^{1*}(t) W_{p,p-1}^*] \\ & - i[W_{p,p+1} Q_p^{1*}(t) - Q_p^1(t) W_{p,p+1}] \end{aligned} \quad (\text{III.4-19})$$

The equations for coherences are

$$\begin{aligned} \frac{d}{dt} Q_p^1(t) = & -i[W_{p,p} - W_{p+1,p+1} - i\Gamma_{p,p+1}] Q_p^1(t) \\ & - iW_{p,p+1} [P_{p+1}(t) - P_p(t)] - i[W_{p,p-1} Q_{p-1}^2(t) - W_{p+2,p+1} Q_p^2(t)] \end{aligned} \quad (\text{III.4-20})$$

and, for $n > 1$,

$$\begin{aligned} \frac{d}{dt} Q_p^n(t) = & -i[W_{pp} - W_{p+n,p+n} - i\Gamma_{p,p+n}] Q_p^n(t) \\ & - i[W_{p,p+1} Q_{p+1}^{n-1}(t) - W_{p+n-1,p+n} Q_{p+n-1}^{n-1}(t)] \\ & - i[W_{p,p-1} Q_{p-1}^{n+1}(t) - W_{p+n+1,p+n} Q_{p+n+1}^{n+1}(t)] \end{aligned}$$

Thus we obtain a coupled hierarchy in which the vector Q^n is coupled to the vectors Q^{n-1} and Q^{n+1} . When the excitation is sufficiently weak, these additional equations may be neglected, and we consider only equations for the populations P_p and the coherences Q_p^1 .

Example: Strong Pump

Let us consider the example of a strong pump P together with Stokes S and anti-Stokes A waves. We have

$$\begin{aligned} W_{p+1,p}(t) = & -\frac{1}{4\hbar} \langle p+1 | X(\tilde{\omega}) | p \rangle :E(P, S) \mathcal{E}_P(t)^* \mathcal{E}_S(t) \exp[i(W_{p+1} - W_p + \omega_P - \omega_S)t] : \\ & - \frac{1}{4\hbar} \langle p+1 | X(\tilde{\omega}) | p \rangle :E(A, P) \mathcal{E}_A(t)^* \mathcal{E}_P(t) \exp[i(W_{p+1} - W_p + \omega_A - \omega_P)t] : \end{aligned}$$

Degeneracy

When degeneracy is present, as it is when one considers transitions between rotational levels, the hierarchy equations provide a framework of linkages that must be modified by including, for each n , a set of sub-components. We will discuss this situation separately, using the method of state multipoles.