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Anomalous absorption of the ultrafast-laser supercontinuum

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The broad white-light continuum generated on the passage of ultrashort pulses of laser light through suitable media has found numerous applications in the physical, chemical, and biological sciences. Many of these are based on use of the continuum to probe the absorption characteristics of transient species, in order to obtain information on their decay kinetics. The processing of data from such experiments is generally based on the implicit assumption that the absorption of white light is subject to the normal Beer-Lambert law, in that the absorption at any particular frequency is linearly proportional to the intensity of the probe light at that frequency. In this paper it is shown that the validity of this underlying assumption should be seriously questioned. At high intensities, the uncertainty principle allows for photon pairs with differing frequencies to provide the energy for the cooperative excitation of molecules in close proximity. This nonlinear absorption, which depends on the frequency autocorrelation function and intensity of the continuum light, results in a rate of absorption which may depart significantly from the normal Beer-Lambert behavior. Hence the interpretation of continuum-probe experiments may need to be reexamined.

I. INTRODUCTION

The generation of a white-light continuum by passing mode-locked pulses of laser light through certain media was first reported by Alfano and Shapiro in 1970.[1] The phenomenon results from a process of self-phase modulation associated with intensity-dependent refraction, although a number of other mechanisms can contribute to the effect: a useful summary is provided in a recent review by Alfano.[2] Continuum generation has been shown to occur in a wide variety of materials, and is readily producible in water. The pulses of light so generated are often referred to as constituting an *ultrafast supercontinuum laser source* (USLS),[3] or *picosecond continuum* for short, since pulse durations are typically on the picosecond or femtosecond[4] time scale. The term *superbroadening* is also used to describe the continuum formation.[5]

Since the initial discovery, USLS radiation has found widespread application in the study of ultrafast photophysical processes. A number of recent experiments have focused on semiconductors, as, for example, in the study of femtosecond carrier dynamics in gallium arsenide,[6,7] and ultrafast heating in silicon.[8] Many other studies have concerned elementary photochemical and photobiological reactions such as those involved in the primary processes of photosynthesis and vision.[9–12] These studies are usually based on an adaptation of the traditional flash photolysis experiment,[13] in which transient species excited by the photoabsorption of a pump-laser pulse are probed by a continuum pulse which has traversed a variable-delay optical path. Variation of the delay thus enables the time development of the entire visible absorption spectrum to be monitored on a picosecond or femtosecond timescale.

The interpretation of results from pump-probe experiments of this kind is generally based on the apparently obvious premise that the absorption of white light produces a spectrum identical to that which would be obtained using a tunable monochromatic light source. In other words it is assumed that the sample response at any particular frequency has a direct linear dependence on the irradiance at that frequency, which is an incidental result of the Beer-Lambert law. In fact this assumption necessarily underpins *any* absorption spectrometry based on multichannel techniques. It is the purpose of this paper to demonstrate that in application to molecular materials the validity of this premise is questionable, and that the interpretation of spectra from continuum-probe experiments may therefore need more careful consideration.

The crux of the argument lies in the fact that at the high intensities associated with pump-probe experiments involving use of a picosecond or femtosecond continuum, nonlinear optical effects in the sample necessarily become very significant. In particular, a recently discovered effect known as *cooperative two-photon absorption*[14–17] can play an important part in determining the absorption characteristics of a sample. Two-photon absorption of a particular frequency normally results in the excitation of energy levels well above the limit implied by the energy of single photons, and is therefore readily distinguished from normal (one-photon) absorption.[18] It is also generally differentiated from a two-step process, involving sequential absorption, by the fact that the sample need not possess energy levels near to the energy of a single photon.

However, a *cooperative* two-photon process can result in the excitation of molecular pairs at the *mean* of two distinct photon frequencies. The energy mismatch at one molecule is thus compensated by a corresponding mismatch of opposite sign at a different molecule. The calculated absorption cross section for this process is, moreover, in the case of neighboring molecules in close proximity in the liquid or solid state, of the same order of magnitude as ordinary two-photon absorption,[16] and hence should be readily observable. The time scale over which this energy sharing can take place is determined by the energy-time uncertainty principle, and is comparable to the ultrashort duration of mode-locked pulses. A result of this nonlinear effect is a rate of absorption which departs significantly from normal Beer-Lambert behavior.

It is shown below that this type of effect may significantly affect the appearance of spectra which are obtained from pump–continuum-probe experiments using current laser intensities. Related effects may also be expected in connection with absorption of the broadband femtosecond pulses now available by the use of pulse-compression technqiues.[19–21] Other effects relating to hyperfine coupling in atoms have also recently been described, in which it is again the case that broadband laser radiation produces effects markedly different from monochromatic radiation.[22,23] It thus appears timely to consider in more general terms how laser linewidth can influence the primary mechanism for the absorption of light by atoms and molecules.

II. UNCERTAINTY CONSIDERATIONS AND CONCERTED PHOTOABSORPTION MECHANISMS

To understand the special features that can arise in connection with the absorption of *white* light, it is helpful to consider first the broad significance of the energy-time uncertainty principle for photoabsorption. As pointed out by Landau and Lifshitz[24] and discussed in detail by Rayski and Rayski,[25] this quantum-mechanical uncertainty relation has a somewhat different status from the more clearcut result for uncertainties in position and momentum. A recent paper by Finkel[26] has helpfully clarified the situation, and shows that for an average lifetime δt and an average energy displacement δE, there exists the relation

$$\delta t \delta E \geq h/4 \ . \tag{2.1}$$

The application of this result to the interaction involved in the normal photoabsorption process in which individual atoms or molecules absorb single photons is well known, and amounts to the statement that for a time interval δt, the mismatch between the energy gain of the absorber and the energy of the absorbed photon cannot exceed δE. For any normal time scale of observation, this condition ensures that only photons whose energy closely matches a transition energy of the absorber can in fact be absorbed.

The implication of Eq. (2.1) for a concerted photoabsorption process involving the coupling of two atomic or molecular excitations appears not to have received consideration, however. Experiments involving absorption from a white-light source such as the USLS provide a multitude of photon frequencies within the sample, and thus offer the possibility of a cancellation in the energy mismatches associated with absorption of photons by two separate centers. In this case, Eq. (2.1) determines the time scale within which the excess energy δE absorbed by one center needs to be conveyed to a center with a corresponding negative energy mismatch, in order to fulfill the requirement for long-term energy conservation at each center. There are, in fact, two distinct mechanisms for a concerted absorption of light based on this uncertainty principle, as detailed below.

A. Cooperative absorption

Consider first a molecule in an initial state $|i\rangle$, which undergoes a transition to an excited state $|f\rangle$ through absorption of light with circular frequency ω. If ω is off-resonant with respect to the transition frequency, there is a mismatch in energy by an amount

$$\delta E = \hbar\omega - E_{fi} \ . \tag{2.2}$$

Application of the uncertainty relation (2.1) shows that it is impossible to constrain conservation of energy over a time scale less than

$$\tau = \tfrac{1}{4}[(\omega/2\pi) - E_{fi}/h]^{-1} \ . \tag{2.3}$$

The transition is therefore allowed provided the local energy mismatch exists for a time not exceeding τ.

In the case of absorption from a white-light source, the presence of other photon frequencies within the sample provides a suitable mechanism for compensation of the energy mismatch, through absorption by a second molecule of a photon with frequency ω' given by

$$\omega' = (\omega - 2\delta E/\hbar) \ . \tag{2.4}$$

Thus by the absorption of two photons of differing frequencies from the broadband source, the total energy absorbed is $2E_{fi}$, the sum of the two molecular transition energies, and overall energy conservation is therefore achieved. From a phenomenological point of view, the overall process is thus one of *mean-frequency absorption.*

Clearly there needs to exist a mechanism for conveyance of the mismatch energy from one molecule to another (see Fig. 1), so that over longer times each molecule can individually satisfy the requirements of energy conservation. Within the framework of quantum electrodynamics, virtual photon coupling[27] provides the mechanism for cooperative absorption of this type. The concept of virtual photons originated in connection with nuclear physics,[28] where they represent the field bosons responsible not only for processes such as nucleus-electron scattering[29] but also more esoteric phenomena such as the generation of quark-antiquark pairs.[30] The formalism has nonetheless increasingly found application in chemi-

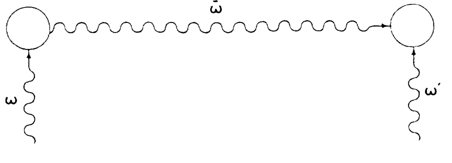


FIG. 1. The cooperative mechanism for mean-frequency absorption; each center absorbs a laser photon (frequencies ω and ω'), and the virtual photon (frequency $\tilde{\omega}$) conveys the energy mismatch.

cal physics, for example in the theory of intermolecular interactions[31–33] and the calculation of atomic energy shifts.[34,35]

By introducing the formalism of virtual photon coupling, the time scale for cooperative absorption τ can be interpreted in terms of a range of propagation for which the exchanged photon has virtual character. Thus the distance R between two molecules which cooperate in the absorption process must be subject to the condition

$$R \le R_{\max} \ge \tfrac{1}{4} hc(\hbar\omega - E_{fi})^{-1} . \tag{2.5}$$

As an example, for a circular frequency mismatch of 2.5×10^{13} Hz, we have the constraint $R_{\max} \ge 3\ \mu\text{m}$. With a smaller frequency mismatch, R can obviously become quite large, and in the limit where the mismatch is zero, there is no longer any restriction on the molecular separation. This corresponds to the case where two entirely uncorrelated absorption processes occur. The implications of this result in terms of a breakdown of the Beer-Lambert law, etc., are described in Secs. III and V.

B. Distributive absorption

A secondary mechanism for the absorption of nonresonant frequencies involves the concerted absorption of two photons by a single molecule, with virtual photon conveyance of the excess energy to the second absorber (see Fig. 2). As with conventional two-photon absorption,[18] there is no need for the first molecule to possess an energy level corresponding to the energy of *either one* of the absorbed photons, and thus no identifiable intermediate state is populated as would be the case in a two-step process. In this case, forthwith termed the *distributive* mechanism, the two absorbed photons may again have differing energies given by $\hbar\omega=(E_{fi}+\delta E)$ and $\hbar\omega'=(E_{fi}-\delta E)$, but here the excess energy absorbed by the first molecule now equals the transition energy for the second molecule, E_{fi}. The corresponding limit on the range of intermolecular distance is then given by

$$R \le R_{\max} \ge \tfrac{1}{4} hc / E_{fi} . \tag{2.6}$$

If the photon energy $\hbar\omega$ is anywhere near to the excitation energy E_{fi}, it is clear from Eqs. (2.5) and (2.6) that the distributive mechanism will only be effective over a much shorter range than the cooperative mechanism. For example, if $E_{fi}/h = 5\times10^{14}$ Hz, we have $R_{\max} \ge 0.15\ \mu\text{m}$.

Another consideration when comparing the cooperative and distributive mechanisms is a difference in the probability aspect of the two processes. At first sight, the requirement of the distributive mechanism for two laser photons to be absorbed in a concerted process at a *single* molecule appears to render the effect significantly less probable than the cooperative mechanism, which has the apparently looser requirement for two photons to be absorbed by molecules at any two *different* points in the sample. A simple statistical treatment of each process based on a Poisson distribution, the most appropriate form of distribution for laser light,[36] in fact, shows that for any given pair of molecules the conditions for the distributive process are met half as often as those of the cooperative process.[37] However, there is more than one possible pair of molecules to consider. With N molecules, there are $\frac{1}{2}N(N-1)$ pairs which can participate in a cooperative absorption process, but $N(N-1)$ to participate in a distributive process. Hence overall the photon statistics do not provide a basis for differentiating the significance of the two mechanisms. It is thus principally the difference in *range* which makes the cooperative mechanism the most significant.

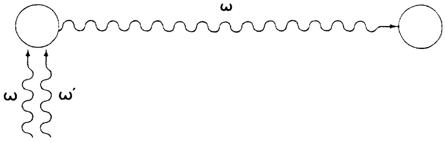


FIG 2. The distributive mechanism for mean-frequency absorption; two photons of circular frequencies ω and ω' are absorbed by a single absorber, and a virtual photon of frequency $\tilde{\omega}$ conveys the excess energy to a second absorber.

The line shape of USLS radiation is generally asymmetric, and the precise spectral distribution difficult to model theoretically.[38–42] However, experiment shows that the continuum can easily have a width of 5000 cm^{-1} centered on a frequency of 20 000 cm^{-1}. Thus, for example, two molecules with an absorption band at 20 000 cm^{-1} might together absorb a pair of photons with wave number $\omega = 17\,500\ \text{cm}^{-1}$ and $\omega' = 22\,500\ \text{cm}^{-1}$, so that in wave-number terms the mismatch would be 2500 cm^{-1}, and correspond to an energy of $\frac{1}{8}E_{fi}$. However, the highest light intensities are associated with the frequencies closer to the center of the continuum, and so it would be here that one would expect to find the strongest contributions from concerted absorption processes.

Thus, taking a typical value of $\frac{1}{20}E_{fi}$ for the mismatch, it can be seen that the acceptable range of intermolecular distance R given by Eq. (2.5) is typically 20 times that given by Eq. (2.6). The *volume* of space about any single molecule within which the passage of two photons can induce mean-frequency absorption is therefore typically $20^3 = 8000$ times larger for the cooperative mechanism than for the distributive mechanism. Since the "photon density" within a sample is directly proportional to the irradiance, it follows that observation of the distributive effect would in principle require a light source 8000 times more intense than that required for observation of the cooperative effect. In view of this result, emphasis is given to the cooperative mechanism in the development of the theory in Sec. III.

III. THEORY AND RESULTS

To place into proper perspective the detailed theory of cooperative and distributive absorption developed below, it is worth first setting down the basic equations for the normal absorption process observed with *monochromatic* light. Consider an ensemble of molecules in an initial state $|i\rangle$, certain of which are promoted to an excited state $|f\rangle$ through absorption of light with circular frequency ω_0, i.e., we have $E_{fi} = \hbar\omega_0$. Assuming that the transition is electric-dipole-allowed, the rate of (single photon) absorption is given by[43]

$$\Gamma_1=(\hbar^2 c\varepsilon_0)^{-1}\pi K_1 l(\omega_0)\ , \tag{3.1}$$

where $l(\omega_0)$ is defined as the irradiance per unit circular frequency (ω) interval at frequency ω_0, and K_1 is given by

$$K_1=|\boldsymbol{\mu}^{fi}\cdot\mathbf{e}|^2\ , \tag{3.2}$$

$\boldsymbol{\mu}^{fi}$ being the transition dipole moment for the $|f\rangle\leftarrow|i\rangle$ transition, and $\mathbf{e}$ the unit polarization vector of the incident light. To facilitate subsequent comparison with the rate equation for cooperative absorption, the above result is given in the form it takes prior to the rotational averaging which is normally performed for a randomly oriented ensemble. The single most important feature to note at this stage is the linear dependence of the absorption rate on the irradiance, a dependence which is manifest in the characteristic exponential decay of intensity with time and hence also with distance traveled through the sample (the Beer-Lambert law).

For *cooperative* absorption, consider now the concerted absorption of *two* photons with frequencies $\omega=(\omega_0+\Omega)$ and $\omega'=(\omega_0-\Omega)$, the sum of whose energies equals the sum of the $|f\rangle\leftarrow|i\rangle$ transition energies for two different molecules. The rate of absorption by the pair can be calculated using quantum electrodynamical methods based on the propagation of a virtual photon between the two centers. The virtual photon essentially mediates the conveyance of the energy mismatch $\hbar\Omega$ from one molecule to the other, as illustrated in Fig. 1. The result for the rate of cooperative absorption is given below; the derivation is outlined in the Appendix, and full details are given in Ref. 16,

$$\Gamma_{2C}=(2\hbar^2c^2\varepsilon_0^2)^{-1}\pi\int_0^\infty K_2(\omega_0,\Omega)l(\omega_0+\Omega)l(\omega_0-\Omega)d\Omega\ , \tag{3.3}$$

where

$$K_2(\omega_0,\Omega)=|e_ie_jS_{ik}^{fi}(\omega_0+\Omega)S_{jl}^{fi}(\omega_0-\Omega)\times[V_{kl}(\Omega,\mathbf{R})+\bar{V}_{kl}(\Omega,\mathbf{R})\exp(i\Delta\mathbf{k}\cdot\mathbf{R})]|^2\ . \tag{3.4}$$

The above result, the individual factors of which are described below, is essentially that given by Eq. (2.12) of Ref. 16, recast in terms of an irradiance with a large bandwidth;[44] hence the frequency-mismatch integral in Eq. (3.3). The result is simplified by the physically reasonable assumption that the two absorbed photons have the same polarization.

In Eq. (3.4), $\mathbf{R}$ is the vector displacement of one molecule with respect to the other, and $\Delta\mathbf{k}$ the difference in the wave vector of the two absorbed photons, i.e., $\Delta\mathbf{k}=(2\Omega/c)\hat{\mathbf{k}}$, where $\hat{\mathbf{k}}$ is the unit vector for the propagation direction of the incident radiation. The frequency-dependent linear susceptibility tensor S^{fi}, which is broadly similar in its structure to an electronic Raman tensor, is explicitly defined in Eq. (A10) of the Appendix, and $V(\Omega,\mathbf{R})$ represents the complex resonance retarded electric-dipole–electric-dipole coupling tensor given by[32,33]

$$V_{kl}(\Omega,\mathbf{R})=(4\pi\varepsilon_0R^3)^{-1}\{(\delta_{kl}-3\hat{\mathbf{R}}_k\hat{\mathbf{R}}_l)[\exp(i\Omega R/c)-i(\Omega R/c)\exp(i\Omega R/c)]-(\delta_{kl}-\hat{\mathbf{R}}_k\hat{\mathbf{R}}_l)(\Omega R/c)^2\exp(i\Omega R/c)\}\ . \tag{3.5}$$

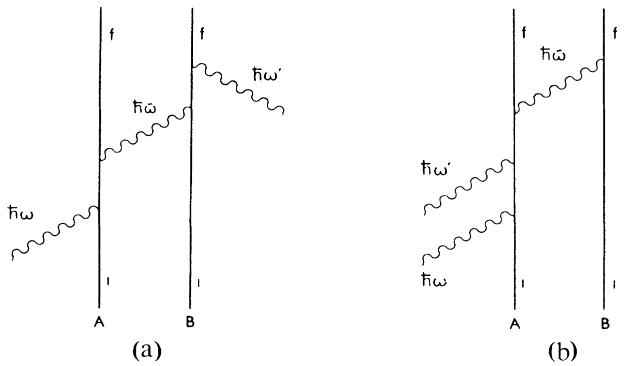
In the *near zone*, where $\Omega R/c\ll 1$, the leading term in the curly brackets dominates, and an R^{-3} dependence is obtained; at the other extreme in the *wave zone*, where $\Omega R/c\gg 1$, the last term is the most significant and a R^{-1} dependence ensues. It is interesting to note that the long-range *rate* thus has a R^{-2} dependence, reflecting the fact that the cooperative process then assumes the characteristics of Raman scattering at the first molecule followed by two-photon absorption at the second [as can be understood from the time-ordered diagram of Fig. 3(a)].

To the extent that the parameter $K_2(\omega_0,\Omega)$ in Eq. (3.3) is approximately frequency independent over any range of frequencies well away from resonance (in other words, whenever dispersion effects are small), the rate contribution Γ_{2C} has a direct dependence on the frequency-domain autocorrelation function of the incident light. Since USLS radiation is pulsed, it is useful to express the result in terms of the time dependence of the irradiance $I(t)$ through the Fourier transform,

$$l(\omega)=(2\pi)^{-1/2}\int_{-\infty}^{\infty}I(t)\exp(i\omega t)dt\ . \tag{3.6}$$

Simple manipulation of the integral in Eq. (3.3) then reveals its equivalence to the time-domain integral,

$$K_2(\omega_0)\int_{-\infty}^{\infty}I^2(t)\exp(2i\omega_0 t)dt\ . \tag{3.7}$$



(a) (b)

FIG. 3. Typical time-ordered diagrams for mean-frequency absorption; (a) represents one of the contributions to the cooperative mechanism, and (b) one of the contributions to the distributive mechanism.

Although the temporal profile and propagation characteristics of USLS pulses have recently been studied,[45] numerical results for $I(t)$ have not yet been reported in the literature.

Expressing the rate in terms of Eq. (3.7) reveals that the rate of the mean-frequency absorption process can in principle be related to the efficiency of second-harmonic generation (SHG), which is often used experimentally as a measure of the autocorrelation function of mode-locked laser light.[46] However, examination of the detailed structure of the constant $K_2(\omega_0)$ as given by Eq. (3.4) reveals a dependence on the susceptibilities of the sample molecules which is quite different from that applying to SHG. In particular, $K_2(\omega_0)$ depends on a product of the *linear* susceptibilities of two different molecules, while SHG depends on the *nonlinear* susceptibility (hyperpolarizability) of individual molecules.

It is also the case that rotational averaging of Eq. (3.3) over an isotropic distribution of molecular orientations yields a nonvanishing result, whereas a similar procedure in the case of frequency doubling leads to the well-known result that the process is forbidden in isotropic media,[47] even when multipolar interactions are taken into account.[48] Hence despite the parallel, SHG cannot be implicated in the cooperative mechanism for mean-frequency absorption. This is important since it rules out the possibility, in isotropic media, of the excitation of a pair of molecules through the absorption of *one* frequency-doubled photon.

For the *distributive* mechanism, consider now the concerted absorption of *two* photons with frequencies $\omega_0+\Omega$ and $\omega_0-\Omega$ at the *same* center. In contrast to normal two-photon absorption, the sum of the absorbed photon energies exceeds the transition energy, and the process is completed by virtual photon conveyance of the energy mismatch E_{fi} to another molecule, as illustrated in Fig. 2. In this case, using exactly similar methods, the following rate equation is obtained:

$$\Gamma_{2D}=(2\hbar^2c^2\varepsilon_0^2)^{-1}\pi\int_0^\infty K_{2'}(\omega_0,\Omega)I(\omega_0+\Omega)I(\omega_0-\Omega)d\Omega\ , \tag{3.8}$$

where

$$K_{2'}(\omega_0,\Omega)=\Big|e_ie_jX_{ijk}^{fl}(\omega_0+\Omega,\omega_0-\Omega)\mu_l^{fi}V_{kl}(\omega_0,\mathbf{R}) \times\Big[1+\exp\Big[i\sum\mathbf{k}\cdot\mathbf{R}\Big]\Big]\Big|^2\ , \tag{3.9}$$

and where $\sum\mathbf{k}$ is the sum of the wave vectors of the two absorbed photons, i.e., $\sum\mathbf{k}=(2E_{fi}/\hbar c)\hat{\mathbf{k}}$. The molecular response tensor X^{fi}, which is similar in its structure to a *hyper*polarizability tensor, is explicitly defined in Eq. (A12) of the Appendix. The appearance of the interaction tensor V once again leads to a long-range R^{-2} dependence in the rate, this time reflecting an asymptotic equivalence to *hyper*-Raman scattering at the first molecule followed by *single*-photon absorption at the second [see Fig. 3(b)]. Once again a link can be established with the autocorrelation function of the USLS light. As shown in the previous section, however, the distributive mechanism necessarily makes a far smaller contribution to the process of mean-frequency absorption, and attention is therefore centered on the cooperative mechanism below.

IV. ASSESSMENT OF THE EXPERIMENTAL SIGNIFICANCE

Assessing the significance of cooperative absorption in USLS experiments is no simple matter. To estimate the likely magnitude of the more important rate contribution represented by Eq. (3.3), we first consider the case of *neighboring* pairs of molecules, which in view of the R dependence of the interaction potential will obviously make far greater contributions to the rate than pairs of more widely spaced molecules. (This can also be regarded as a reflection of the fact that the smaller the distance traversed by the virtual photon, and hence the shorter the time scale for its existence, the greater is the tolerance of energy mismatch, in accordance with the energy-time uncertainty relation.)

Experiment alone can provide the quantitative values for the various parameters involved in Eq. (3.3). Unfortunately, no previous experiments have reported the necessary numerical values for either the intensity $I(\omega)$ or the molecular tensor $S^{fi}(\omega)$. Indeed, since the latter parameter defined by Eq. (A10) substantially differs in form from a normal two-photon absorption tensor, precise values for it will not be available until experimental measurements are made of the process here described. The only closely related molecular parameter is the frequency-dependent Raman tensor for an *electronic* transition, for which again there appear to be no numerical values in the literature. Estimation of the significance of the results presented above must therefore proceed from a different basis.

As shown in earlier work on cooperative phenomena,[14] neighboring molecules can be expected to display a cooperative absorption rate approaching the rate of two-photon absorption by individual molecules, a result which is more readily calculated. This can be argued as follows. A comparison of the short-range limit of the rate equation for cooperative absorption and the corresponding rate equation for normal two-photon absorption reveals that the former contains an additional factor of the order of $\rho=S^{fi}(\omega)/R^3$. Far from accidental resonances, the molecular tensor may be expected to be similar in magnitude to the molecular polarizability, since it is constructed in the same way from products of electric dipole transition moments divided by energy mismatch factors; see Eq. (A10). Molecular polarizabilities, at least for small molecules, have well-documented values, and are typically similar in magnitude to the cube of molecular diameter. Hence when R represents a nearest-neighbor distance, the factor ρ approaches the value of unity, and the cooperative absorption rate is thus comparable with that of conventional two-photon absorption.

It is well known that the rate of two-photon absorption depends on the square of the focused laser intensity. As long ago as 1968, Gontier and Trahin showed that in the absence of accidental resonances an intensity factor of I/I_0 is, in fact, introduced for each additional photon involved in a multiphoton excitation process.[49] The constant I_0 is a characteristic irradiance whose value depends on the sample, and in the case of atomic hydrogen equals 1.4×10^{21} W m^{-2}. This figure corresponds to an irradiance which produces an electric field equal to the Coulombic field binding the electron to the nucleus. A laser irradiance equal to I_0 thus corresponds to the situation where perturbation theory breaks down and all multiphoton processes become equally feasible. A similar treatment of molecules leads to an intensity factor per photon of $\gamma=(I/I_M)$, where I_M is an irradiance which would lead to ionization or dissociation, and would therefore have a typical value in the region[50] of $10^{18\pm4}$ W m^{-2}. This figure certainly exceeds the level of irradiance applied in most laser-excitation experiments. With this in mind, we can now compare the likely rates of conventional single-photon absorption and nearest-neighbor cooperative two-photon absorption.

Precise values for the focused irradances produced by USLS pulses seem not to be available in the literature, undoubtedly due in part to the difficulty of devising any suitable measuring device. It is also important to note that the intensity distribution across the USLS beam is not remotely like the smooth Gaussian function one normally expects for laser radiation. In fact, the self-focusing which is an intrinsic part of the supercontinuum generation process in bulk samples produces numerous filaments in which much of the light energy is contained. However, taking the figure of 10^{14} W m^{-2} as a cautious estimate of the mean continuum intensity in the pump-probe sample, integrated over the complete range of wavelengths, then even without the adoption of focusing optics the ratio γ can evidently take a value anywhere in the range $(10^{-8}\leq\gamma\leq1)$ and may even approach the value of unity. In such cases two-photon absorption becomes experimentally significant, and by extension it appears that under the same conditions the cooperative absorption process may produce important contributions to the observed spectra.

Other factors which can contribute to an increase in the extent of *cooperative* or *distributive* two-photon absorption are the involvement of non-neighboring molecules, and any enhancement of the molecular response tensors through incidental one-photon resonances.[16] Inspection of the energy denominators in expressions (A10) and (A12) for the molecular response tensors shows that resonance amplification can be expected if the molecules possess unoccupied excited states at any of the energy levels represented by dashed lines in Fig. 4. In many situations, it is therefore likely that mean-frequency absorption will play a significant role in modifying the apparent form of the absorption spectrum.

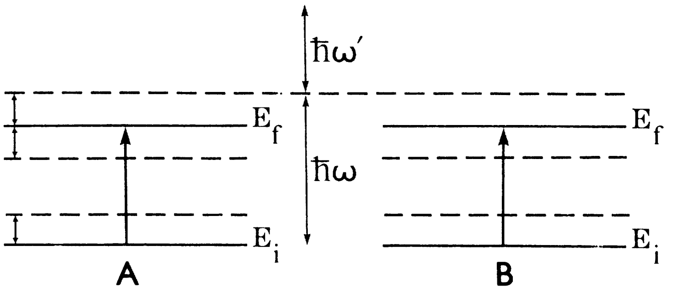


FIG. 4. Energy-level diagram for mean-frequency absorption; a resonant enhancement of the molecular response tensors, and hence a rate increase, occurs if the molecules possess unoccupied excited states at any of the energy levels represented by dashes.

V. DISCUSSION

The Beer-Lambert exponential decay law for conventional (single-photon) absorption results from the elementary relation

$$-dI(\omega,z)/dz\propto I(\omega,z)\ , \tag{5.1}$$

where z represents the distance the light has traveled through the absorbing sample. Since this is directly proportional to the propagation time within the sample, Eq. (5.1) is a result which follows directly from Eq. (3.1). It has been shown in this paper that when intense continuum light such as that provided by USLS radiation is absorbed, cooperative and distributive processes produce a correction term which necessitates the replacement of Eq. (5.1) by a result of the form

$$-dI(\omega,z)/dz \propto \left[I(\omega,z)+\chi\int K(\omega,\Omega)I(\omega+\Omega,z)I(\omega-\Omega,z)d\Omega\right]\ , \tag{5.2}$$

where $K=K_2+K_{2'}$. Clearly in this case expential decay is no longer to be expected. For the reasons discussed in the last section, it is difficult in general terms to assess the magnitude of the correction represented by the frequency integral; under optimum conditions when $\gamma\approx1$ it will clearly be comparable with the first term in the large parentheses. The most significant feature of Eq. (5.2) is undoubtedly the fact that the absorption of a sample at any given frequency is directly influenced by the intensity of light at other frequencies. Equation (5.2) thus represents an infinite set of coupled integrodifferential equations, whose solution depends on the detailed spectral distribution of the continuum light[38–42] and also the spectral response of the sample, as represented by the all-embracing constant K.

One of the most immediately obvious implications of the result is that an absorption spectrum measured with USLS light may be significantly different from the spectrum which would be observed using tunable monochromatic radiation. In particular, there should be a decrease in the apparent width of many lines in any absorption spectrum measured with USLS radiation. This is because for any sample transition of frequency ω_0, photons of appreciably off-resonant frequency $(\omega_0\pm\Omega)$ can be cooperatively absorbed and result in the excitation of two separate molecules, provided selection rules permit (see below). Hence if USLS probe absorption linewidths were used to infer the lifetimes of transient species, it would need to be realized that the true linewidths might be appreciably broader and hence the lifetimes appreciably shorter than the measurement implies. However, transient lifetimes are seldom measured this way; usually the time delay between pump and probe pulses is varied in order to directly monitor the time evolution of absorption features. The absorption mechanisms proposed in this paper have no bearing on the accuracy of this type of kinetic measurement.

The use of USLS light for probing absorption may produce other effects much more important than increased linewidth, however. This can be illustrated as follows. Consider the case of an electronic transition, in a polyatomic molecule, which displays vibronic structure associated with a certain vibrational mode. For simplicity, let us confine attention to the (0-0) band, assuming that the vibrational frequencies in the ground and excited electronic states are similar. As explained at the end of the last section, although the cooperative and distributive processes allow the absorption of *any* pair of photons whose energy sum equals that of the (0-0) excitation energies for two different molecules, the rate of each process is increased if either photon energy matches that of another transition. In particular, a pair of photons whose energies match the (0-1) and (1-0) transitions can be cooperatively absorbed and so actually result in (0-0) transitions in two separate molecules. Thus because of the resonance enhancement associated with a (0-1)-frequency photon, one should expect increased absorption at *both* the (0-1) *and* (1-0) frequencies, even if the $v=1$ level in the electronic ground state is not appreciably populated. Features of this kind have been noted in recent USLS-probe experiments on spectral hole burning in dye solutions.[51] Although it is unlikely that cooperative absorption has any direct bearing on *these* studies, in view of the large mean separation of the dye molecules in solution, it might be expected to become very much more significant in studies of molecular crystals, for example.

The cooperative and distributive absorption mechanisms described in this paper are both sensitive functions of intermolecular distance. To a point, they may be regarded as molecular *proximity* effects, a term being introduced[52] to highlight a contradistinction to the (single-photon) *collision*-induced effects which have long been familiar in gas-phase spectroscopy.[53] It is important to note that wave-function overlap is not directly implicated, since precisely the same *mechanism* applies to molecules separated by either very short or very large distances; the only difference is in the *size* of the effect. It is also worth noting that the two chemical centers involved need not be distinct molecules, but may be distinct chromophores in a single molecule, as in the classical two-group model for optical activity.[54]

The two mechanisms are associated with quite distinct selection rules. Because the virtual photon couples with each molecule by the same electric-dipole coupling as the laser photons, the cooperative mechanism requires the $|i\rangle \rightarrow |f\rangle$ transition at both centers to be allowed by two-photon selection rules, while the distributive mechanism can apply if the transition is allowed by the familiar one-photon selection rules. (In principle, it should be specified that the transition need also be three-photon allowed in view of the three distinct photon interactions which occur at the first absorber. However, with the rare exception of icosahedrally symmetric molecules, all transitions which are one-photon allowed are of necessity also three-photon allowed, so the condition is redundant.[55])

Consider, for example, the simple case of a system of centrosymmetric molecules, in which the absorption of light is normally associated with the Laporte rule and produces only parity-reversing transitions ($u \leftrightarrow g$). For the concerted absorption by a pair of such molecules, the cooperative mechanism allows for transitions that preserve parity ($g \leftrightarrow g$, $u \leftrightarrow u$), but the distributive mechanism again results in parity reversal ($u \leftrightarrow g$). In such systems, clearly only the *distributive* mechanism can affect the line shape of transitions which are normally present in the absorption spectrum. The *cooperative* mechanism may, however, result in the appearance of new spectral features, associated with population of excited states of the same parity as the ground state which are normally inaccessible. However, most absorption studies based on use of the USLS concern large molecules which lack any appreciable symmetry at the site of absorption; hence both the cooperative and distributive processes can contribute to the excitation process.

In assessing the significance of mean-frequency absorption for flash photolytic experiments based on USLS radiation, perhaps the most important factor to consider is the enormously wide range of possibilities for cooperative absorption leading to the simultaneous excitation of more than one excited state. If the sample is heterogeneous or contains more than one chemical species, there exists the even more general possibility of simultaneously exciting two chemically different species. Thus while the process discussed in this paper can be represented as

$$2A + \hbar\omega + \hbar\omega' \rightarrow 2A^* \ ,$$

there exist the more complex possibilities

$$2A + \hbar\omega + h\omega' \rightarrow A^* + A^{\ddagger} \ ,$$

and

$$A + B + \hbar\omega + \hbar\omega' \rightarrow A^* + B^{\ddagger} \ ,$$

the double dagger denoting some other excited state than that denoted by the asterisk. The last of these equations is particularly significant for flash photolytic studies of processes in complex biological systems, where A and B may even be *chemically* different chromophores within a single large molecule. The theory underlying these processes is very similar in each case, and the associated rates of absorption comparable to those estimated in the last section. However, in polyatomic molecules with complex vibronic structures, the number of pairs of transitions which can be excited through absorption of two photons with the correct energy sum may be enormously large, so that cooperative absorption may exert a very significant effect on the appearance of the absorption spectrum. The numerous possibilities for resonance enhancement of the molecular response tensors at certain frequencies should also be borne in mind.

While the type of effect described in this paper has not yet been looked for in experiments with USLS radiation, it is worth pointing out that cooperative two-photon absorption of a different but closely related kind *has* been demonstrated in a number of recent experiments with conventional laser light. Here the process is one in which two photons of *identical* frequency ω are absorbed in a process which leads to the excitation of a pair of *dissimilar* atoms or molecules. Thus the equation can be represented as;

$$A + B + 2\hbar\omega \rightarrow A^{*} + B^{\ddagger} ,$$

essentially the converse of the process described in this paper. An effect of this kind was first noted by White in 1981,[56] in studies of the laser excitation of a mixture of barium and thallium vapor. This study was followed by experiments on other atomic systems,[57,58] and following a development of the theory for application to molecular systems[14,15] the phenomenon was also noted in connection with photoinduced charge transfer between molecules in close proximity. Ku *et al.*,[59] for example, having studied gaseous mixtures of xenon and chlorine passed slowly through a laser fluorescence cell, have proposed the reaction mechanism

$$\mathrm{Xe} + \mathrm{Cl}_2 + 2\hbar\omega \rightarrow (\mathrm{Xe\text{-}Cl}_2{}^{**} \rightarrow \mathrm{Xe}^{+}\text{-}\mathrm{Cl}_2{}^{-}) \rightarrow \mathrm{XeCl} + \mathrm{Cl} ,$$

the first step of which is attributed to excitation from the van der Waals ground state to the ion-pair excited state via configurational interaction of the Xe and Cl_2. This mechanism has been further corroborated by Apkarian *et al.*, who have extended the study to charge-transfer reactions in rare-gas solids.[60,61] It has also been shown to be the predominant reaction route in the case of $\mathrm{Xe{:}Cl_2}$ van der Waals complexes generated in seeded molecular beams.[62]

In each of these cases, the underlying theory[14,15] bears a very close parallel to the mean-frequency process described in this paper, and for a given light intensity the calculated rates are accordingly very similar in magnitude. Nonetheless, the experimental observations detailed above have generally been carried out with laser light appreciably less intense than the USLS. This lends further support to the contention that cooperative effects should certainly be measurable in connection with the absorption of supercontinuum light.

In conclusion, it is worth reiterating that the anomalous absorption effects described in this paper may be manifest in any experiments which employ sufficiently high-intensity broadband radiation. To this extent, anomalies may be observable in experiments not specifically involving USLS light. In particular, the continued advances in techniques of laser pulse compression have now resulted in the production of femtosecond pulses only a few optical cycles in duration[19–21] which necessarily have a very broad-frequency spread, as the uncertainty principle shows. Thus mean-frequency absorption may have a wider role to play in the absorption of femtosecond pulses. If this is correct, it raises further questions over the suitability of absorption-based techniques for their characterization.

Note added in proof. The Lorentzian linewidth of the cooperative absorption process is readily shown to be approximately 0.64 times the ordinary absorption linewidth, if the radiation is assumed to have frequency-independent intensity over the frequency range of interest.

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APPENDIX: BASIC QUANTUM ELECTRODYNAMICAL EQUATIONS

The derivation of the rate equations given in this paper is based on the Power-Zienau-Woolley multipolar Hamiltonian for a system comprising an ensemble of molecules in the presence of radiation.[63–65] This may be expressed as

$$H = H_{\mathrm{mol}} + H_{\mathrm{rad}} + H_{\mathrm{int}} , \tag{A1}$$

where

$$H_{\mathrm{mol}} = \sum_{\xi} \left[\frac{1}{2m} \sum_{\alpha} \mathbf{p}_{\alpha}^{2}(\xi) + V(\xi) \right] , \tag{A2}$$

$$H_{\mathrm{rad}} = \tfrac{1}{2} \int \left[\frac{\mathbf{d}^{\perp 2}}{\varepsilon_0} + c^2 \varepsilon_0 \mathbf{b}^2 \right] d^3 r , \tag{A3}$$

$$\begin{aligned} H_{\mathrm{int}} = & -\frac{1}{\varepsilon_0} \sum_{\xi} \boldsymbol{\mu}(\xi) \cdot \mathbf{d}^{\perp}(\mathbf{R}_{\xi}) - \frac{1}{\varepsilon_0} \sum_{\xi} Q_{ij}(\xi) \nabla_i d_j^{\perp}(\mathbf{R}_{\xi}) \\ & - \sum_{\xi} \mathbf{m}(\xi) \cdot \mathbf{b}(\mathbf{R}_{\xi}) + \cdots \\ & + \frac{e^2}{8m} \sum_{\xi,\alpha} [(\mathbf{q}_{\alpha}(\xi) - \mathbf{R}_{\xi}) \times \mathbf{b}(\mathbf{R}_{\xi})]^2 + \cdots \\ & + \frac{1}{2\varepsilon_0} \sum_{\xi} \int |\mathbf{p}_{\xi}^{\perp}(\mathbf{r})|^2 d^3 r . \end{aligned} \tag{A4}$$

The first term, H_{mol}, represents the sum over each molecule ξ at position $\mathbf{R}_{\xi}$ of its normal nonrelativistic Schrödinger operator, $\mathbf{p}_{\alpha}$ denoting the momentum of electron α, and $V(\xi)$ the total *intra*molecular Coulombic potential energy. The subsequent term, H_{rad}, represents the radiation Hamiltonian expressed in terms of the transverse displacement field operator $\mathbf{d}^{\perp}(\mathbf{r})$ and the magnetic field operator $\mathbf{b}(\mathbf{r})$. The interaction Hamiltonian H_{int} consists of a series of terms. The first three, respectively, denote electric-dipole, electric-quadrupole, and magnetic-dipole interactions, and constitute the leading terms in an infinite multipolar series. The next term is the leading contribution to a diamagnetic interaction energy, and the last term is a field-independent contribution which is only significant for self-energy calculations. The most important feature of the system Hamiltonian expressed in this form is the absence of any *inter*molecular Coulombic energy term. As a result, all intermolecular interactions are mediated by a mutual coupling to the radiation field, associated with the concept of virtual photon exchange.

For the calculations leading to the results given in this paper, the electric-dipole approximation is employed for each molecule. The justification is the fact that provided each molecule-photon interaction is electric-dipole allowed, the contributions from other terms in H_{int} are considerably smaller in magnitude, the electric quadrupole and magnetic dipole being smaller by a factor of approximately α (the fine-structure constant) and the diamagnetic term smaller by a factor of approximately α^2. It is important to note, however, that the detailed treatment of the coupling between molecules deployed here produces results which are equivalent to the inclusion of higher-order multipole moments for the pair, as in the classical two-group theory of optical activity (see, for example, the review by Barron[54]).

Calculation of the absorption rate Γ is based on time-dependent perturbation theory, in which the basis states are product eigenstates of H_{mol} and H_{rad}, and the perturbation operator is H_{int}. The results are obtained through use of the golden rule;[66]

$$\Gamma=(2\pi/\hbar)\,|M_{fi}|^2\rho_r\ , \tag{A5}$$

in which ρ_r is the density of radiation states and M_{fi} is the matrix element connecting the initial and final states of the system. This has the perturbation expansion

$$M_{fi}=\langle f_s|H_{\text{int}}|i_s\rangle+\sum_{I_s}{}'\frac{\langle f_s|H_{\text{int}}|I_s\rangle\langle I_s|H_{\text{int}}|i_s\rangle}{E(i_s)-E(I_s)}+\sum_{\mathrm{I}_s,\mathrm{II}_s}{}'\frac{\langle f_s|H_{\text{int}}|\mathrm{II}_s\rangle\langle \mathrm{II}_s|H_{\text{int}}|\mathrm{I}_s\rangle\langle \mathrm{I}_s|H_{\text{int}}|i_s\rangle}{[E(i_s)-E(\mathrm{II}_s)][E(i_s)-E(\mathrm{I}_s)]}$$
$$+\sum_{\mathrm{I}_s,\mathrm{II}_s,\mathrm{III}_s}{}'\frac{\langle f_s|H_{\text{int}}|\mathrm{III}_s\rangle\langle \mathrm{III}_s|H_{\text{int}}|\mathrm{II}_s\rangle\langle \mathrm{II}_s|H_{\text{int}}|\mathrm{I}_s\rangle\langle \mathrm{I}_s|H_{\text{int}}|i_s\rangle}{[E(i_s)-E(\mathrm{III}_s)][E(i_s)-E(\mathrm{II}_s)][E(i_s)-E(\mathrm{I}_s)]}+\cdots\ . \tag{A6}$$

Here the summations are taken over the virtual intermediate states I_s, II_s, and III_s, the subscript s serving as a reminder that all state vectors refer to the *system* comprising both molecules and radiation; the prime on each sum indicates exclusion of the initial and final states.

In order to calculate the contributions arising from successive terms in Eq. (A6), a mode expansion of the electric displacement field operator is required;

$$\mathbf{d}^{\perp}(\mathbf{r})=i\sum_{\mathbf{k},\lambda}(\hbar ck\varepsilon_0/2V)^{1/2}[\mathbf{e}^{(\lambda)}(\mathbf{k})a^{(\lambda)}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}$$
$$-\bar{\mathbf{e}}^{(\lambda)}(\mathbf{k})a^{\dagger(\lambda)}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}]\ , \tag{A7}$$

where $a^{(\lambda)}(\mathbf{k})$ and $a^{\dagger(\lambda)}(\mathbf{k})$ are the annihilation and creation operators for the radiation mode with wave vector $\mathbf{k}$ and polarization λ. Since these operators appear linearly in $\mathbf{d}^{\perp}(\mathbf{r})$, each electric-dipole interaction can be associated with either the absorption or emission of a single photon. Consequently the first term in Eq. (A6) accounts for the usual contribution to single-photon absorption, giving the matrix element

$$M_{fi}^{1}=-i(n\hbar ck/2\varepsilon_0V)^{1/2}(\boldsymbol{\mu}^{fi}\cdot\mathbf{e})\exp[i\mathbf{k}\cdot\mathbf{R}(A_1)]\ , \tag{A8}$$

where $\mathbf{e}$ is the polarization vector of the absorbed photon, n the number of photons in the quantization volume V, and $\mathbf{R}(A_1)$ is the position vector of the absorber A_1. It is readily shown[43] that substitution of this result into Eq. (A5) leads to the result given as Eq. (3.1).

Cooperative and distributive contributions are associated with the fourth-order term in Eq. (A6), where the four photon interactions comprise the annihilation of two laser photons (ω and ω'), and the creation and annihilation of the virtual photon. All possible time orderings of these interactions need to be taken into account, and are most readily obtained by the use of time-ordered (Feynman) diagrams[67] such as those shown in Fig. 3. If the two absorbers are chemically distinguishable, there are in fact 192 diagrams to consider, resulting from the 24 permutations of the photon interaction sequences, coupled with the two possible locations (at molecule A or at molecule B) for each of the three-photon annihilations. These are divisible into two classes, one class of 96 diagrams for the cooperative mechanism, as illustrated by Fig. 3(a), and the other class of 96 for the distributive mechanism, as illustrated by Fig. 3(b).

The result of summing the contributions for the cooperative mechanism can be expressed, using the convention of implied summation over repeated indices, as follows:

$$M_{fi}^{4(a)}=\Big[-(\hbar c/4\varepsilon_0^2V^2)(n_1n_2k_1k_2)^{1/2}\exp[i(\mathbf{k}_2\cdot\mathbf{R}_1+\mathbf{k}_1\cdot\mathbf{R}_2)]e_ie_jS_{ik}^{fi}(\omega_0+\Omega)S_{jl}^{fi}(\omega_0-\Omega)$$
$$\times\sum_{\boldsymbol{\kappa},\boldsymbol{\varepsilon}}\kappa\varepsilon_k\bar{\varepsilon}_l\{[(\Omega/c)-\kappa]^{-1}\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})-[(\Omega/c)+\kappa]^{-1}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{R})\}\Big]+\{\Omega\rightarrow-\Omega\}\exp(i\Delta\mathbf{k}\cdot\mathbf{R})\ . \tag{A9}$$

Here n_1 is the number of photons and $\mathbf{k}_1$ the wave vector of the beam with frequency $(\omega_0+\Omega)$; $n_2,\mathbf{k}_2$ are the corresponding quantities for the beam with frequency $(\omega_0-\Omega)$; $\Delta\mathbf{k}=(\mathbf{k}_2-\mathbf{k}_1)$; $\boldsymbol{\kappa}$ and $\boldsymbol{\varepsilon}$ are the wave vector and polarization vector, respectively, for the virtual photon; $\mathbf{R}_1$ and $\mathbf{R}_2$ are the position vectors of the two absorbers; $\mathbf{R}=(\mathbf{R}_2-\mathbf{R}_1)$, and the second rank molecular tensor is defined by

$$S_{ij}^{fi}(\omega)=\sum_r\left[\frac{\mu_i^{fr}\mu_j^{ri}}{E_{fr}-\hbar\omega}-\frac{\mu_j^{fr}\mu_i^{ri}}{E_{ri}-\hbar\omega}\right]\ . \tag{A10}$$

In the same way the distributive contributions can be summed to give

$$M_{fi}^{4(b)}=\Bigg[-(\hbar c/4\varepsilon_0^2V^2)(n_1n_2k_1k_2)^{1/2}\exp(i\textstyle\sum\mathbf{k}\cdot\mathbf{R}_1)e_ie_jX_{ijk}^{fi}(\omega_0+\Omega,\omega_0-\Omega)\mu_l^{fi}$$
$$\times\sum_{\kappa,\varepsilon}\kappa\varepsilon_k\bar{\varepsilon}_1\{[(\omega_0/c)-\kappa]^{-1}\exp(i\kappa\cdot\mathbf{R})-[(\omega_0/c)+\kappa]^{-1}\exp(-i\kappa\cdot\mathbf{R})\}\Bigg]+\{\omega_0\to-\omega_0\}\exp(i\textstyle\sum\mathbf{k}\cdot\mathbf{R})\,, \qquad \text{(A11)}$$

where $\sum\mathbf{k}=(\mathbf{k}_1+\mathbf{k}_2)$ and the third-rank molecular tensor is given by

$$X_{ijk}(\omega_1,\omega_2)=\sum_{r,s}\Bigg[\frac{\mu_i^{ri}\mu_j^{sr}\mu_k^{fs}}{(E_{si}-\hbar\omega_1-\hbar\omega_2)(E_{ri}-\hbar\omega_1)}-\frac{\mu_i^{ri}\mu_j^{fs}\mu_k^{sr}}{(E_{fs}-\hbar\omega_2)(E_{ri}-\hbar\omega_1)}+\frac{\mu_i^{sr}\mu_j^{fs}\mu_k^{ri}}{(E_{fr}-\hbar\omega_1-\hbar\omega_2)(E_{fs}-\hbar\omega_2)}$$
$$+\frac{\mu_i^{sr}\mu_j^{ri}\mu_k^{fs}}{(E_{si}-\hbar\omega_1-\hbar\omega_2)(E_{ri}-\hbar\omega_2)}-\frac{\mu_i^{fs}\mu_j^{ri}\mu_k^{sr}}{(E_{fs}-\hbar\omega_1)(E_{ri}-\hbar\omega_2)}+\frac{\mu_i^{fs}\mu_j^{sr}\mu_k^{ri}}{(E_{fr}-\hbar\omega_1-\hbar\omega_2)(E_{fs}-\hbar\omega_1)}\Bigg]\,. \qquad \text{(A12)}$$

It should be noted that the sum over the virtual photon variables (wave vector and polarization) in Eqs. (A9) and (A11), in view of the fact that this photon does not appear in the physically observable initial or final states of the system, is in accordance with the principle of indeterminacy. The result of this summation is $(2V\varepsilon_0)V_{kl}(\omega,\mathbf{R})$, where in Eq. (A9) $\omega=\Omega$, and in Eq. (A11) $\omega=\omega_0$: $V_{kl}(\omega,\mathbf{R})$ is the resonance electric-dipole–electric-dipole coupling of the explicit form given by Eq. (3.5). Substitution of these results into the rate equation (A5), together with use of the relation $V_{kl}(-\omega,\mathbf{R})=\bar{V}_{kl}(\omega,\mathbf{R})$ and integration over the range of USLS photon frequencies, leads to the rate contributions of Eqs. (3.3) and (3.8). Full details are given in Ref. 16.

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