Radiation–Molecule and Molecule–Molecule Interactions. A Unified Viewpoint from Quantum Electrodynamics

DAVID P. CRAIG*

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia

T. THIRUNAMACHANDRAN

Department of Chemistry, University College London, London WC1H OAJ, England

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Molecular quantum electrodynamics is the dynamics of molecules interacting with the quantized electromagnetic field. It is the theory underlying a wide range of phenomena such as ordinary absorption and emission of light, optical activity, and Rayleigh and Raman scattering, as well as a variety of nonlinear processes that have become amenable to study since the development of laser sources. Typical are harmonic generation, multiphoton absorption, hyper-Raman scattering, coherent anti-Stokes Raman scattering, and laser-induced optical activity. These processes provide new information about molecular properties such as hyperpolarizabilities and symmetries of states. It has also been recognized that the methods developed to treat interactions of radiation with molecules are adaptable in a natural way to the theory of intermolecular interactions. In this framework the coupling between molecules is mediated by virtual photons of the radiation field.

Molecular quantum electrodynamics[1-5] brings together these two apparently separate areas of chemical physics, with advantages in the treatment of each. They include superior insight into the nature of the electromagnetic field and its associated particles, the photons, as a unifying viewpoint. In this Account we describe the leading features of molecular quantum electrodynamics, show how it is used to calculate both radiation–molecule and molecule–molecule interactions, and indicate its further range in problems beyond the scope of the semiclassical method.

The Semiclassical Method

Optical and scattering processes in molecules usually in the past have been treated by methods distinct from those used for intermolecular forces, even though these forces have long been known to be electromagnetic in origin. The reason is that the widely used semiclassical theory is confined to treating the *molecular response* to a classical radiation field. That is, the radiation field is supposed to be generated externally to the system and imposed on the molecules. The molecules respond to this fixed influence, and the effects are calculable. In quantum electrodynamics the radiation field and molecules are treated as parts of a single system, each part acting on, and responding to, the other. The total energy contains molecule–molecule as well as molecule–radiation terms. Only the former are distance-dependent and so may be disentangled from the others. The need to include the reaction of the matter on the radiation field is also shown in phenomena such as quantum beats (in coherent excitation of close levels), photon polarization correlation in three-level cascades, and antibunching of photons (nonclassical interval between sequential emission of photons), where agreement with observation requires it.

The semiclassical theory is based on the interaction of a classical electromagnetic field with a quantized atomic or molecular system. The field is *prescribed*, which means that it is taken to be generated by an external apparatus of charges and currents which are not specified and are not affected by the "target" molecules. It does not appear in the Hamiltonian which, for molecules in the presence of a field, is given as the sum of molecular and interaction Hamiltonians only

$$H = H_{\text{mol}} + H_{\text{int}} \tag{1}$$

Energy is not conserved in a system so defined, because energy flow in and out of the radiation field is not included, although this does not cause difficulties in most practical applications.

The radiation field is specified through the macroscopic electric and magnetic field vectors **E** and **B**. Interactions with an electron depend on the Lorentz force **F**

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \tag{2}$$

where **v** is the particle velocity. This force is added to Coulombic forces acting on the electron to give the complete Newton's equations of motion. It should be noted that the momentum canonically conjugate to the particle displacement **q** is not the kinetic momentum $m\dot{\mathbf{q}}$ alone but becomes

$$\mathbf{p} = m\dot{\mathbf{q}} - e\boldsymbol{A}(\mathbf{q}) \tag{3}$$

where **A** is the vector potential of the electromagnetic

David Craig was born in 1919. After a first degree at the University of Sydney and Ph.D. at University College London, he has held professorships in Sydney, University College London, and at the Australian National University. His current interests are in the theory of the interaction of radiation with molecules and crystals.

T. Thirunamachandran was born in 1932. Following undergraduate work at the University of Ceylon, he obtained his Ph.D. at University College London, where he is presently Reader in Chemistry. His main research interests are in the applications of quantum electrodynamics to chemical problems with special reference to optical activity, intermolecular forces, and nonlinear optics.

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field at the particle position. The electric and magnetic field vectors are related to **A** by

$$\mathbf{E} = -\dot{\mathbf{A}}$$
$$\mathbf{B} = \text{curl } \mathbf{A} \tag{4}$$

Use of the new conjugate momentum in the molecular Hamiltonian enables the field-dependent part to be separated as the familiar interaction term:

$$H_{\text{int}} = -(e/m)\mathbf{p}\cdot\mathbf{A}(\mathbf{q}) + (e^2/2m)\mathbf{A}^2(\mathbf{q}) \tag{5}$$

The semiclassical method is a good way of calculating many important radiation–molecule processes. Its failures, which can be dealt with to a limited extent only in the neoclassical method,[6,7] arise from neglect of quantum character of the radiation field, without which spontaneous emission, and the Lamb shift, to take just two examples, cannot be calculated.

Quantization of the Electromagnetic Field

In quantum electrodynamics the molecules are coupled to an electromagnetic field subject to quantum conditions. The Hamiltonian for the field forms part of the total Hamiltonian, and energy is conserved overall. The consequences of quantization are the introduction of *photons*, the imposition of the uncertainty principle restrictions on the field vectors, and the existence of electromagnetic zero-point energy. In the passage to quantum mechanics through the Hamiltonian, the fundamental microscopic electric and magnetic fields, denoted hereafter by **e** and **b**, are again used to introduce potentials, namely, the vector potential **a**, as before, and the scalar potential ϕ. The potentials **a** and ϕ are not fully specified by the condition that they give **e** and **b** by eq 6 but may be chosen in various

$$\mathbf{e} = -\dot{\mathbf{a}} - (1/c^2)\text{grad } \phi \tag{6}$$
$$\mathbf{b} = \text{curl } \mathbf{a}$$

gauges, which are adapted to different applications. The best gauge for molecule–radiation problems is the Coulomb gauge, defined by div **a** = 0, because the scalar potential ϕ, though not zero, can be eliminated in favor of the electrostatic interaction energy as used in the construction of the molecular Hamiltonian. The total Hamiltonian is the sum of terms for molecules, radiation field, and an interaction between the two.

$$H = H_{\text{mol}} + H_{\text{rad}} + H_{\text{int}} \tag{7}$$

In this sum the molecular term is the molecular Hamiltonian familiar in particles only quantum mechanics. Thus in treating interaction with radiation, the molecular problem can be taken to be solved and the solutions to be used as basis functions for a perturbation treatment of the effect of the interaction.

For the field in the absence of matter, i.e., the free field, the vector potential **a** satisfies the wave equation

$$\left(\nabla^2 - (1/c^2)\frac{\partial^2}{\partial t^2}\right)\mathbf{a}(\mathbf{r},t) = 0 \tag{8}$$

the plane wave solutions of which are

$$\mathbf{a}(\mathbf{r},t) = \mathbf{a}_{\mathbf{k}}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{9}$$

where $\mathbf{a}_{\mathbf{k}}$ is the amplitude, **k** the wave vector, and $\omega = ck$ the frequency. Since div **a** = 0, $\mathbf{a}_{\mathbf{k}}$ is transverse to $\hat{\mathbf{k}}$ and can be expressed as a linear combination of two mutually orthogonal vectors $\mathbf{e}^{(\lambda_1)}(\mathbf{k})$ and $\mathbf{e}^{(\lambda_2)}(\mathbf{k})$, both transverse to $\hat{\mathbf{k}}$, which describe the polarization properties of **a** and, through (6), also of the electric and magnetic fields. The vector potential is then expressible as an expansion over allowed modes (**k**,λ)

$$\mathbf{a}(\mathbf{r},t) = \sum_{\mathbf{k},\lambda}\{e^{(\lambda)}(\mathbf{k})a_{\mathbf{k}}^{(\lambda)}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k})\bar{a}_{\mathbf{k}}^{(\lambda)}e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\} \tag{10}$$

where $a_{\mathbf{k}}^{(\lambda)}$ are the amplitude coefficients and the bar stands for the complex conjugate. The classical Hamiltonian for the free field can be constructed in the conventional manner within the canonical formalism

$$\mathrm{H} = \frac{\epsilon_0}{2}\int\left\{\left(\frac{\mathbf{\Pi}}{\epsilon_0}\right)^2 + c^2(\text{curl } \mathbf{a})^2\right\} \mathrm{d}^3\mathbf{r}$$
$$= \frac{\epsilon_0}{2}\int(\mathbf{e}^2 + c^2\mathbf{b}^2)\, \mathrm{d}^3\mathbf{r} \tag{11}$$

In (11), $\mathbf{\Pi}(\mathbf{r},t)$ is the momentum canonically conjugate to the vector potential $\mathbf{a}(\mathbf{r},t)$ and is

$$\mathbf{\Pi}(\mathbf{r},t) = \epsilon_0\dot{\mathbf{a}}(\mathbf{r},t) \tag{12}$$

It is straightforward to show that the Hamiltonian (11) can be expressed as

$$H = 2V\epsilon_0c^2\sum_{\mathbf{k},\lambda}k^2a_{\mathbf{k}}^{(\lambda)}\bar{a}_{\mathbf{k}}^{(\lambda)} \tag{13}$$

where V is the volume of the box within which the radiation is contained. By a change of variables, (13) can be cast into (14), each term of which has the familiar structure of the Hamiltonian for the harmonic oscillator

$$H_{\text{classical}} = \sum_{\mathbf{k},\lambda}H(\mathbf{k},\lambda) = \tfrac{1}{2}\sum_{\mathbf{k},\lambda}\{p_{\mathbf{k}}^{(\lambda)^2} + \omega^2q_{\mathbf{k}}^{(\lambda)^2}\} \tag{14}$$

where as before $\omega = ck$ and $p_{\mathbf{k}}$ and $q_{\mathbf{k}}$ have the dimensions of momentum and displacement, respectively. The Hamiltonian is that for the sum of independent one-dimensional harmonic oscillators, one for each mode (**k**,λ). The key step is now taken. Following the familiar quantization procedure for an oscillator, we get the quantum Hamiltonian for the radiation field

$$H_{\text{rad}} = \sum_{k,\lambda}\{a^{(\lambda)\dagger}(\mathbf{k})a^{(\lambda)}(\mathbf{k}) + \tfrac{1}{2}\}\hbar ck \tag{15}$$

expressed in second quantized form, with $a^{(\lambda)\dagger}(\mathbf{k})$ and $a^{(\lambda)}(\mathbf{k})$ as creation and annihilation operators for mode (**k**,λ). An important consequence of field quantization is that the energy of the ground state is not zero but is $^1/_2\sum\hbar ck$. Though the fields fluctuate about zero mean value, their squares have nonzero expectation values, associated with the zero-point energy. The vacuum fluctuations can affect the dynamics of the electrons, with effects on spontaneous emission, Lamb shift, and intermolecular interactions such as the fully retarded Casimir–Polder potential.

The quantum states of the radiation field can be specified by the number of quanta of excitation in each of the modes. The quanta, with the properties of bosons, can be considered as the field particles, namely photons.

The Coupling of Molecules and Radiation

If the molecules and the field are not coupled, the Hamiltonian is simply the sum of the molecular and

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radiation Hamiltonians. The Hamiltonian for a molecular assembly can be written, as usual

$$H_{\mathrm{mol}} = \sum_{\zeta} H_{\mathrm{mol}}(\zeta) + \sum_{\zeta<\zeta'} V(\zeta,\zeta') \tag{16}$$

where

$$H_{\mathrm{mol}}(\zeta) = \sum(\tfrac{1}{2}m_\alpha)p_\alpha^{\,2}(\zeta) + V(\zeta) \tag{17}$$

and $V(\zeta,\zeta')$ is the electrostatic interaction energy between the molecules ζ and ζ'. $\mathbf{q}_\alpha(\zeta)$ and $\mathbf{p}_\alpha(\zeta)$ are the position and momentum operators of particle α of molecule ζ and $V(\zeta)$ is the intramolecular potential energy. The radiation Hamiltonian is given by (15). The coupling between the molecules and the radiation field is introduced by the substitution

$$\mathbf{p}_\alpha^{(\zeta)} \rightarrow \mathbf{p}_\alpha^{(\zeta)} - e_\alpha \mathbf{a}(\mathbf{q}_\alpha(\zeta))$$

The Hamiltonian for the coupled system is

$$H = \sum_{\zeta}\left\{\sum_{\alpha}\frac{1}{2m_\alpha}[\mathbf{p}_\alpha(\zeta) - e_\alpha\mathbf{a}(\mathbf{q}_\alpha(\zeta))]^2 + V(\zeta)\right\} + \sum_{\zeta<\zeta'} V(\zeta,\zeta') + \frac{\epsilon_0}{2}\int\left\{\left(\frac{\mathbf{\Pi}}{\epsilon_0}\right)^2 + c^2(\mathrm{curl}\ \mathbf{a})^2\right\} \mathrm{d}^3\mathbf{r}$$

$$H = \sum_{\zeta} H_{\mathrm{mol}}(\zeta) + H_{\mathrm{rad}} + H_{\mathrm{int}} \tag{18}$$

where

$$H_{\mathrm{int}} = \sum_{\alpha,\zeta}(e/m_\alpha)\mathbf{p}_\alpha(\zeta)\cdot\mathbf{a}(\mathbf{q}_\alpha(\zeta)) + \sum_{\alpha,\zeta}(e^2/2m_\alpha)\mathbf{a}^2(\mathbf{q}_\alpha(\zeta)) + \sum_{\zeta<\zeta'} V(\zeta,\zeta') \tag{19}$$

In (19), the first two terms are field-dependent interactions. The last term consists of Coulombic interactions between the particles of ζ and ζ' and is instantaneous, i.e., nonretarded. In electrodynamics *all* interactions are retarded; any change at one center is propagated to another by the radiation field at the speed of light. It can be shown that the unretarded term $V(\zeta,\zeta')$ in (19) is cancelled out by a term in the field-dependent interaction.

An advance of central importance for problems in chemical physics has been the development of a form of Hamiltonian in which the intermolecular electrostatic terms are completely eliminated in favor of retarded interactions. This is the Multipolar Hamiltonian, which can be obtained from the minimal coupling Hamiltonian by a canonical transformation[8-10]

$$H_{\mathrm{mult}} = e^{-iS}H_{\mathrm{min}}e^{iS} \tag{20}$$

with the generator S, in the electric dipole approximation, given by

$$S = \frac{1}{\hbar}\sum_{\zeta}\mu(\zeta)\cdot\mathbf{a}(\mathbf{R}_\zeta) \tag{21}$$

Here the vector potential is given its value at the molecular center. In (21) $\mu(\zeta)$ is the electric dipole moment

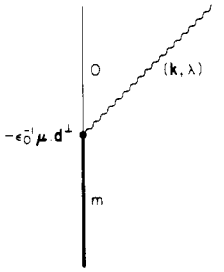

Figure 1. Time-ordered diagram for spontaneous emission.

operator for molecule ζ. The resultant Hamiltonian is of the form

$$H_{\mathrm{mult}} = \sum_{\zeta}\left\{\frac{1}{2m}\sum_{\alpha}\mathbf{p}_\alpha^{\,2}(\zeta) + V(\zeta)\right\} + \frac{\epsilon_0}{2}\int\left\{\left(\frac{\mathbf{\Pi}}{\epsilon_0}\right)^2 + c^2(\mathrm{curl}\ \mathbf{a})^2\right\}\mathrm{d}^3\mathbf{r} + \frac{1}{\epsilon_0}\sum_{\zeta}\mu(\zeta)\cdot\mathbf{\Pi}(\mathbf{R}_\zeta) + \frac{1}{2\epsilon_0}\sum_{\zeta}\int|\mathbf{p}_\zeta^{\perp}(\mathbf{r})|^2\,\mathrm{d}^3\mathbf{r} \tag{22}$$

where $\mathbf{\Pi}(\mathbf{r})$ is now given by the negative of the transverse component of the displacement vector $\mathbf{d}(\mathbf{r})$

$$\mathbf{d}(\mathbf{r}) = \epsilon_0\mathbf{e}(\mathbf{r}) + \mathbf{p}(\mathbf{r}) \tag{23}$$

The multipolar Hamiltonian has several important features. The radiation part of H_{mult} contains $\mathbf{d}^\perp$ and not $\mathbf{e}^\perp$. The electrostatic interaction term has been removed, leaving all intermolecular interactions to be radiative, by the exchange of transverse photons. The interactions are thus fully retarded. Use of the multipolar Hamiltonian leads to a striking simplification in calculations, especially of intermolecular properties.

Spontaneous Emission

A free atom or molecule in an excited state decays by emission of light, returning to the ground state. The rate of this spontaneous emission was first deduced by Einstein[11] using energy balance arguments. His derivation did not bear on the question of the mechanism of the emission. The term spontaneous is used not to mean that the emission has no cause but that the cause cannot be described in the frame of semiclassical electrodynamics. The first complete treatment is due to Dirac,[12] who showed that the process stems from the fluctuations of the quantized electromagnetic field in the vacuum state. The fluctuations perturb electron motions causing transitions and act on an excited state to give downward transitions. The initial state of the system is $|E_m;0\rangle$ where $|E_m\rangle$ is the molecular state and $|0\rangle$ represents the vacuum state of the radiation field. The final state is $|E_0;1(\mathbf{k},\lambda)\rangle$ where the molecule has dropped to its ground state and the field has an occupation number of 1 in the mode $(\mathbf{k},\lambda)$. The matrix element for the overall process is found to be

$$M_{fi} = \langle 1(\mathbf{k},\lambda);E_0|-\epsilon_0^{-1}\mu\cdot\mathbf{d}^\perp(\mathbf{R})|E_m;0\rangle$$

$$M_{fi} = i\left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2} e_i^{(\lambda)}(\mathbf{k})\mu_i^{0m}e^{-i\mathbf{k}\cdot\mathbf{R}} \tag{24}$$

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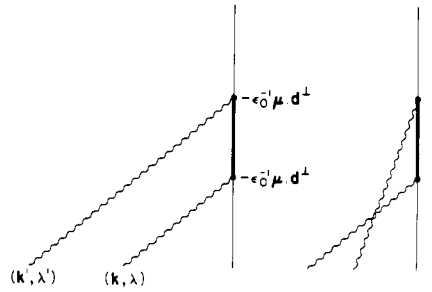

Figure 2. Graphs for two-photon absorption.

The rate of spontaneous emission after averaging over spatial directions and summing over polarizations is

$$\frac{\omega^3}{3\epsilon_0\pi\hbar c^3}|\mu^{0m}|^2 \tag{25}$$

which is the Einstein A coefficient.

The matrix element (eq 24) for spontaneous emission is connected with the time-ordered graph in Figure 1. Time flows upward. The molecule (vertical line) makes a transition from its state $|E_m\rangle$ to the ground state by the interaction $-\epsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}$, with the emission of a free photon of energy $\hbar ck = E_m - E_0$. Graphs have a general application as an easy means of listing and calculating matrix elements.

Two-Photon Absorption

The invention of lasers producing intense, coherent, monochromatic light has led to the development of multiphoton spectroscopy, including absorption, harmonic generation, laser-induced resonance fluorescence, and coherent anti-Stokes Raman scattering. The example discussed in this section is two-photon absorption from two beams. In most experiments one of the laser frequencies is kept fixed and the other tunable. Let us consider the transition $|E_m\rangle \leftarrow |E_0\rangle$ via a two-photon mechanism corresponding to the absorption of one photon from each of the two beams $(\mathbf{k},\lambda)$ and $(\mathbf{k}',\lambda')$. Energy is conserved overall:

$$E_{m0} = \hbar ck + \hbar ck' \tag{26}$$

The matrix element for the process is of second order and can be calculated with the aid of time-ordered diagrams in Figure 2. The two graphs correspond to the two possible time orderings. In graph a a $(\mathbf{k},\lambda)$ photon is absorbed first and a $(\mathbf{k}',\lambda')$ second. In graph b the order is reversed. The energies of the intermediate states are $E_r + (n-1)\hbar ck + n'\hbar ck'$ and $E_r + n\hbar ck + (n'-1)\hbar ck'$. Energy is not conserved in the intermediate states which are referred to as virtual states. The matrix element for two-photon absorption is

$$M_{fi} = \left(\frac{n\hbar ck}{2\epsilon_0 V}\right)^{1/2}\left(\frac{n'\hbar ck'}{2\epsilon_0 V}\right)^{1/2} e_i^{(\lambda')}(\mathbf{k}')e_j^{(\lambda)}(\mathbf{k})\alpha_{ij}{}^{m0}(\omega,\omega') \tag{27}$$

where $\alpha_{ij}{}^{m0}$, the frequency-dependent transition polarizability, is given by

$$\alpha_{ij}{}^{m0}(\omega,\omega') = \sum_r \left\{\frac{\mu_i{}^{mr}\mu_j{}^{r0}}{E_{r0} - \hbar\omega} + \frac{\mu_j{}^{mr}\mu_i{}^{r0}}{E_{r0} - \hbar\omega'}\right\}$$

The total absorption rate for a randomly oriented sample can be expressed as

$$\langle\Gamma\rangle = N\mathcal{I}I'B^{(2)} \tag{28}$$

where N is the number of absorbers, $\mathcal{I}$ the irradiant energy density per unit frequency of the tunable beam, I' the irradiance of the fixed frequency beam, and the molecular factor $B^{(2)}$ is given by

$$B^{(2)} = \frac{1}{120\hbar c\epsilon_0{}^2}(A\alpha_{\lambda\lambda}{}^{m0}(\omega,\omega')\bar{\alpha}_{\mu\mu}{}^{m0}(\omega,\omega') + B\alpha_{\lambda\mu}{}^{m0}(\omega,\omega')\bar{\alpha}_{\lambda\mu}{}^{m0}(\omega,\omega') + C\alpha_{\lambda\mu}{}^{m0}(\omega,\omega')\bar{\alpha}_{\mu\lambda}{}^{m0}(\omega,\omega')) \tag{29}$$

In (29) the coefficients are

$$\begin{aligned} A &= 4|\mathbf{e}\cdot\mathbf{e}'|^2 - 1 - |\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 \\ B &= -|\mathbf{e}\cdot\mathbf{e}'|^2 + 4 - |\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 \\ C &= -|\mathbf{e}\cdot\mathbf{e}'|^2 - 1 + 4|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 \end{aligned} \tag{30}$$

By choosing different polarizations for the two beams, it is possible to carry out a complete polarization study and thus characterize fully the two-photon transition.[13,14]

Similar considerations apply to two-photon emission, which is the process inverse to two-photon absorption from two beams. However, there is an important difference. The emitted photons $\mathbf{k}$ and $\mathbf{k}'$ satisfy the energy conservation condition but are otherwise unrestricted. If there are no one-photon resonances, the emission spectrum is broad and has little structure. If there are one-photon resonances, then sequential emission (two successive one-photon real emissions) is likely to be the dominant process. Two-photon emission can be stimulated by irradiating the system with monochromatic radiation at energy lower than the molecular transition energy. In this case, the additional contribution to the emission rate has the structure similar to that of Einstein's A coefficient for one-photon spontaneous emission. The additional term is

$$\frac{I'\omega^3}{18\pi\epsilon_0{}^2\hbar c^4}\alpha_{\lambda\mu}{}^{m0}(\omega,\omega')\bar{\alpha}_{\lambda\mu}{}^{m0}(\omega,\omega') \tag{31}$$

Harmonic Generation

An intense beam of light incident upon an assembly of molecules induces polarization with frequency components of multiples of the incident frequency. Harmonics appear in the scattered radiation. Second harmonic generation using crystals of KDP, potassium dihydrogen phosphate, is a common laboratory method for getting near-UV coherent radiation from a primary laser source in the visible. Another example is the generation of high harmonics of the 1.06-μm CO_2 gas laser.

The generation of the nth harmonic corresponds to the absorption of n photons of frequency ω and the emission of one photon of frequency $n\omega$. When the emission is in the forward direction, photon momentum is conserved, the process is coherent, and the rate is proportional to the square of the number of absorbers. With randomly oriented molecules, generation of harmonics of even order is forbidden and odd harmonics allowed.[15] As an example, we consider third harmonic generation. The matrix element is of fourth order and

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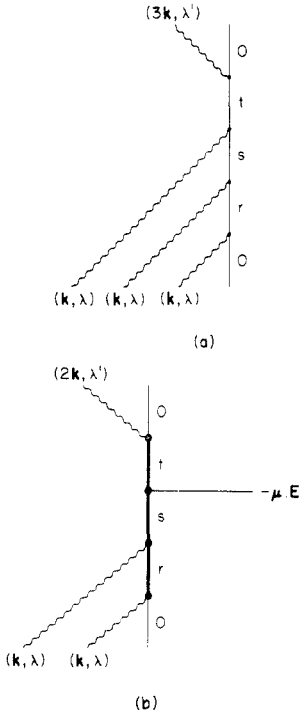

Figure 3. (a) Typical graph for third harmonic generation. (b) Typical graph for static electric field-induced second harmonic generation.

can be found with the aid of time-ordered diagrams (Figure 3). If the differences in refractive indices of frequencies ω and 3ω are ignored and random orientation is assumed, the matrix element is position independent and the total amplitude is N times the amplitude for scattering by a single molecule, N being the number of scatterers. The third harmonic radiant intensity is therefore proportional to N^2, in contrast to linear dependence for incoherent scattering. The fully averaged expression for the intensity is

$$I = \frac{81\bar{I}^3 g^{(3)} k^4 N^2}{1600\pi^2 \epsilon_0{}^4 c^2} |\mathbf{e}\cdot\mathbf{e}|^2 |\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 |\beta_{\lambda\lambda\mu\mu}|^2 \qquad (32)$$

where $\beta_{\lambda\lambda\mu\mu}$ is the fourth rank hyperpolarizability tensor, $g^{(3)}$ is the degree of third-order coherence, and $\bar{I}$ is the mean irradiance of the incident beam; $\mathbf{e}$ and $\mathbf{e}'$ are the polarizations of the incident and scattered beams.

It may be remarked that even harmonics which are forbidden in randomly oriented samples can be made allowed by applying a static electric field transverse to the direction of the incident beam.[16-18] The interaction is now made up of two terms as in (33). The first term

$$H_{\text{int}} = \epsilon_0{}^{-1} \sum_\zeta \mu(\zeta)\cdot\mathbf{d}^\perp(\mathbf{R}_\zeta) - \sum_\zeta \mu(\zeta)\cdot\mathbf{E}(\mathbf{R}_\zeta) \qquad (33)$$

in (33) represents the coupling to the radiation field and the second to the static field. The matrix element for second harmonic generation is of fourth order. A typical diagram is shown in Figure 3b where the horizontal solid line represents coupling to the static field. The radiant intensity shows quadratic dependence on the static field strength as well as the irradiance of the incident beam.

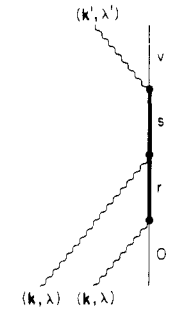

Figure 4. Typical graph for the hyper-Raman effect.

Hyper-Raman Scattering

Hyper-Raman scattering is another three-photon process. The scattered photon ω' is approximately twice the incident frequency ω. The mismatch $|2\omega - \omega'|$ usually equals a vibrational or rotational frequency of the molecule.[19] Because the selection rules are different from infrared and Raman spectra, hyper-Raman spectroscopy provides new molecular information.

The matrix element for hyper-Raman scattering associated with the vibrational transition $|0,v\rangle \leftarrow |0,0\rangle$ is easily obtained with the aid of time-ordered graphs such as in Figure 4. For the case where there are no near-resonances, the vibrational energy differences in the energy denominators can be neglected in comparison with the electronic energy differences. This makes it possible to effect closure over the vibrational manifold of the intermediate electronic states, and the matrix element can be written as

$$M_{fi} = -i\left(\frac{\hbar c}{2\epsilon_0 V}\right)^{3/2} (k^2 k')^{1/2} \{n(n-1)\}^{1/2} \bar{e}_i' e_j e_k \langle \chi_{0v} | \beta_{ijk} | \chi_{00} \rangle \qquad (34)$$

where β_{ijk} is the j,k symmetric hyperpolarizability tensor, n is the occupation number of the state of the incident beam, and $\mathbf{e}$ and $\mathbf{e}'$ are the polarizations of the incident and scattered beams. By carrying out the scattering experiment for different configurations, it is possible to make a complete assignment of the symmetry properties of the transition.[20,21]

Interactions between Molecules

The common way of dealing with the energy of interaction between two molecules A and B is to work from a Hamiltonian (eq 35) given as the sum

$$H = H_A + H_B + V_{AB} \qquad (35)$$

of the free-molecule terms H_A and H_B and an intermolecular Coulombic interaction V_{AB}. The intermolecular coupling is between all the charges of molecule A and all those of B. For neutral molecules, the leading term in an expansion of V_{AB} is the electrostatic coupling of the molecular dipole moments. The interaction V_{AB} is electrostatic, meaning that the fields of force of charges in A are felt at B instantaneously. When the charges are moving, changes in their force fields propagate likewise at infinite speed. Such influences however travel at the speed of light, so that the conventional

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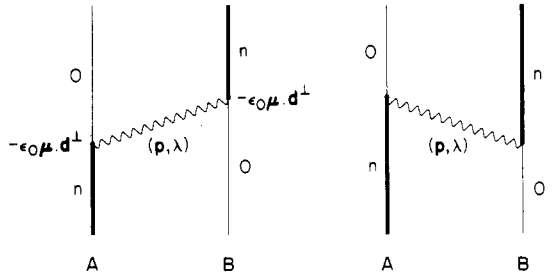

Figure 5. Graphs for resonance transfer of excitation.

picture is less and less realistic the greater the separation. At short distances, say up to a few tens of nanometers, there is no difficulty, but errors begin to appear at longer range.

A second unsatisfactory feature is that the underlying physics of intermolecular coupling, which is that it is electromagnetic in type, is not built in. Thus the role of the radiation in "conveying" or mediating the mutual influences is suppressed, and the formal affinity with other radiation processes such as absorption and emission goes unnoticed, with consequent loss of insight. We illustrate with examples of the simplest type of intermolecular coupling.

The Resonance Interaction

Resonant energy transfer between two identical molecules, one initially excited

$$A^*B \leftrightarrow AB^*$$

is of central importance in electronically excited crystals. Following light absorption, excitation is transferred rapidly to other (identical) molecules to give an exciton state, with delocalization over many centers. The time-ordered graphs for the process are given in Figure 5. They describe coupling by emission and absorption of photons, i.e., coupling via the radiation field. The molecular states are $|E_0\rangle$ and $|E_n\rangle$ for ground and excited, respectively. Here the emission and absorption steps involve virtual photons $(\mathbf{p},\lambda)$: all possible photon wave vectors $\mathbf{p}$, and polarizations λ, are summed over. The calculation gives an expression for the interaction energy, valid at all distances R beyond the touching distance.[22]

$$\Delta E = \mu_i^{0n}(A)\mu_j^{n0}(B)V_{ij}(k,\mathbf{R}) \tag{36}$$

where

$$V_{ij}(k,\mathbf{R}) = \frac{1}{4\pi\epsilon_0 R^3}((\delta_{ij} - 3\hat{R}_i\hat{R}_j) \times (\cos kR + kR \sin kR) - (\delta_{ij} - \hat{R}_i\hat{R}_j)k^2R^2 \cos kR) \tag{37}$$

In expressions 36 and 37, k is defined through $\hbar ck = E_n - E_0$, $\hat{\mathbf{R}}$ means the unit vector $\mathbf{R}/|\mathbf{R}|$. The terms within the brackets reduce in the *near-zone* ($kR << 1$) to the well-known static dipole–dipole coupling

$$\Delta E^{\text{near}} = \frac{1}{4\pi\epsilon_0 R^3}\{\mu(A)\cdot\mu(B) - 3(\mu(A)\cdot\hat{\mathbf{R}})(\mu(B)\cdot\hat{\mathbf{R}})\} \tag{38}$$

In the *far zone* ($kR >> 1$) the limiting behavior is given by

$$\Delta E^{\text{far}} = \frac{k^2R^2 \cos kR}{4\pi\epsilon_0 R^3}\{\mu(A)\cdot\mu(B) - (\mu(A)\cdot\hat{\mathbf{R}})(\mu(B)\cdot\hat{\mathbf{R}})\} \tag{39}$$

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Important features of the far-zone interaction are that the behavior with distance is as the inverse first power, with modulation by cos kR, depending on the transition frequency ck. A second feature is the angle dependences in braces in (39), which shows that the coupling is between the components of the dipole moments transverse to $\mathbf{R}$ only, whereas in the near zone all dipole components are coupled. This is an expression of the fact that the mechanism is by photon emission and absorption, involving only the transverse fields of emitter and absorber.

The complete interaction (36) with (37) is described as including retardation, in as much as all effects of one system on the other are propagated at the speed of light. At small distances the propagation time or retardation R/c is negligible small, and the behavior is that of static dipoles; but at long distances the retardation is important and the behavior is that for signals conveyed by radiation.

The Dispersion Interaction

The dispersion interaction is of great importance. It is responsible for example for most of the binding energy in crystals formed from neutral molecules with small or zero dipole moments. In its familiar form, for the near zone, it shows the inverse sixth power dependence on distance.

Molecular quantum electrodynamics allows the dispersion interaction to be treated in a straightforward way and leads to formulae applicable to all separation distances beyond overlap. A notable and important result, which has been verified experimentally, is that at the long-range limit the dispersion energy varies as the inverse seventh power of the separation distance[23-26]

$$\Delta E^{\text{far}} = -\left(\frac{23\hbar c}{64\pi^3\epsilon_0^2}\right)\frac{\alpha(A)\alpha(B)}{R^7} \tag{40}$$

where the polarizability $\alpha(A)$ is

$$\alpha(A) = \tfrac{2}{3}\sum_n \frac{|\mu^{n0}|^2}{E_{n0}} \tag{41}$$

with summation over all excited states of A.

Typical graphs are (i)–(iii) in Figure 6, together with others to complete the set of all time orderings for the two-photon virtual exchanges. After carrying through the technical steps already outlined, we arrive at a general formula for the energy of interaction applicable at all distances. For short distance we get the well-known result

$$\Delta E^{\text{near}} = -\frac{1}{24\pi^2\epsilon_0^2R^6}\sum_{r,s}\frac{|\mu^{r0}|^2|\mu^{s0}|^2}{E_{r0} + E_{s0}} \tag{42}$$

with summation over all excited molecular states.

Chiral Discrimination in the Dispersion Interaction

In the interaction between chiral (optically active) molecules the possibility exists of chiral discrimination.[27-29] If A(R) and A(S) are the enantiomeric forms

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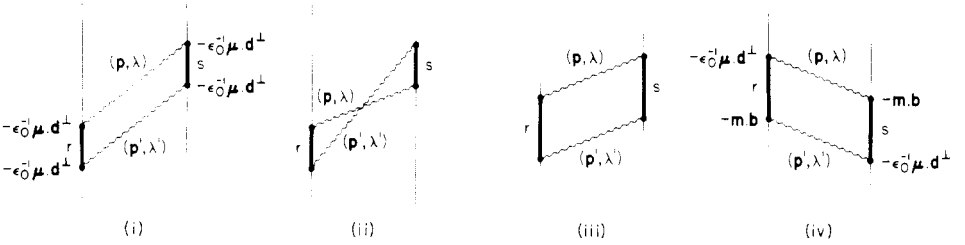

Figure 6. (i)–(iii) Typical graphs for dispersion interaction. (iv) Typical graph for dispersive chiral discrimination.

of a molecule A, the interactions A(R)–A(S) and A(R)–A(R) are in general not equal. This fact, obvious where there are close contacts between the molecules in crystals or concentrated solutions, is less easily understood at longer range, beyond overlapping distance of the van der Waals radii. A number of types of force can contain chiral information and cause discrimination, with contributions to the total interaction which vary in relative importance over the range of separations. The dispersion interaction already described, with all interactions of the electric dipole type, does not discriminate in leading order. The mixed electric–magnetic terms, with a typical graph in (iv) of Figure 6, give small energy contributions that are different for R–R and R–S pairs. The discriminating term $\Delta E_{\mathrm{E-M}}$ is

$$\Delta E_{\mathrm{E-M}} = \frac{1}{12\pi^2\epsilon_0{}^2R^6}\sum_{r,s}\frac{R^{r0}R^{s0}}{E_{r0}+E_{s0}} \tag{43}$$

where R^{r0} is the rotatory strength

$$R^{r0} = Im\mu^{0r}\cdot\mathbf{m}^{r0} \tag{44}$$

m being the magnetic dipole moment operator. The dispersive discrimination varies as the inverse sixth power of the distance. For chemically identical pairs this form of discrimination stabilizes unlike chiral pairs over like pairs.

Concluding Remarks

All radiation–molecule interactions can be treated by the methods described, including complex scatterings like CARS, and intermolecular problems such as radiation-induced modifications to intermolecular interactions.[30,31] The problems to which the methods are adapted are those in which the particles, electrons, and nuclei move slowly compared with the speed of light, allowing neglect of relativity. This is realistic for at least the outer electrons of atoms and molecules and for nuclei generally. These are responsible for most of the important phenomena in chemical physics.

Among the attractive features of the method are that the procedures for making calculations are transparent, being based on a graphical scheme enabling the required matrix elements to be enumerated and then evaluated, simply and economically, especially when the multipolar interaction is used.

The results found in molecular quantum electrodynamics are correct in all known cases. The method can be expected increasingly to be the scheme adopted to deal with new phenomena discovered with further exploitation of lasers, involving complicated multiphoton scattering, absorption, and emission steps.

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