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# Six-wave mixing: secular resonances in a higher-order mechanism for second-harmonic generation

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**Abstract.** A six-wave mechanism for second-harmonic generation in isotropic or microscopically disordered media is presented. This mechanism allows the signal to be sustained by molecules of all symmetry types and may also operate in isotropic fluids. A detailed derivation and first explicit result is given for the nonlinear optical susceptibility, solving the problem of secular response.

## 1. Introduction

High-order (beyond four-wave) optical nonlinearity is an area that has recently attracted great interest [1–10]. This can partly be attributed to intrinsic novelty, given the advanced stage of theoretical development and the large number of experimental studies on lower orders—but there are other reasons too. One is that such processes have emerged as possible contributors to the production of optical second harmonics and sum frequencies even in isotropic or otherwise randomly ordered systems such as glasses or solutions [4–6, 11]. The specific six-wave mechanism for optical second-harmonic generation (SHG) to be discussed here engenders a coherent harmonic even in systems with inversion symmetry, such as isotropic fluids or microscopically disordered solids. This is in direct contrast to the preclusion, through any multipolar three-wave mechanism, of a coherent second harmonic in any system where the conversion sites are randomly oriented [12–15]. Specifically, through a six-wave mixing (SWM) process, a finite SHG signal can emerge irrespective of local or bulk symmetry, in the absence of any static or optically induced fields. This direct SWM is similar to the perturbational methods employed by Steffen *et al* [16, 17] in describing scattering events, differing in that our signal in particular is the first harmonic.

The first observation in 1981 [18] of a (time-delayed) second harmonic in an optical fibre possessing inversion symmetry attracted little interest until a similar result was reported five years later [19]. The realization that the onset of the effect exhibited a time delay (the delay being typically a few hours), and that it could be accelerated by simultaneous application of the harmonic, was first reported by Stolen and Tom [20]. Other groups have since reported similar observations [21–23]. It was shortly after discovering this ‘seeding’ effect that the process was first postulated as a six-photon interaction [24, 25]. It has since been shown that simultaneous exposure to both the fundamental and the harmonic frequencies creates a periodic static electric field that removes the symmetry of the bulk [26]. The optical encoding in the glass thereby engenders an effective non-zero second-order susceptibility.

More recently there have been reports [4, 5] of harmonics emerging in organic dye solutions through optical poling. There are, however, significant differences to the

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semipermanent optical encoding in glasses. The generation in solution of a second harmonic must follow poling, within the time scale for rotational relaxation, and for this reason has to be associated with a fifth-order molecular susceptibility rather than any effective second-order susceptibility. Direct SWM, however, leads to second-harmonic emission without any requirement for light-induced anisotropy. It is, moreover, a process that is invariably permitted irrespective of molecular symmetry. In an earlier analysis [6] it was shown how such a process plays a significantly more important role for SHG than any mechanism based on optically induced fields. Furthermore, the degree of harmonic depolarization associated with SWM accords with that found experimentally [27].

In this paper, we present a fully microscopic theory of the six-wave mechanism for SHG in isotropic media, solving the problem of secular resonance, and so obtain for the first time a result for the signal intensity cast in terms of an explicit formula for the corresponding molecular susceptibility.

## 2. Theory

Using the microscopic theory of molecular quantum electrodynamics (QED) as our basis [28, 29], probability amplitudes can be developed using familiar perturbation techniques and time-ordered diagrams of the form illustrated in figure 1. For each diagram the initial and final system states are expressible in product form $|mol\rangle|rad\rangle$, as

$$|I\rangle = |0\rangle|n(\boldsymbol{k},\lambda), 0(\boldsymbol{k}',\lambda'), 0(\boldsymbol{k}'',\lambda'')\rangle \tag{1}$$

$$|F\rangle = |0\rangle|(n-4)(\boldsymbol{k},\lambda), 1(\boldsymbol{k}',\lambda'), 1(\boldsymbol{k}'',\lambda'')\rangle. \tag{2}$$

The radiation field initially consists of $n$ photons of the laser pump at the fundamental frequency $\omega$, with wavevector $\boldsymbol{k}$ and polarization $\lambda$; in the final state there are $(n-4)$ pump photons and two signal photons having wavevectors $\boldsymbol{k}'$, $\boldsymbol{k}''$ and polarizations $\lambda'$, $\lambda''$, with energy conservation expressed through $4\overline{h}ck - \overline{h}ck' - \overline{h}ck'' = 0$. Five intermediate states are transcended and the sixth-order transition operator, $M_{FI}$, is given by

$$M_{FI} = \sum_{R,S,T,U,V} \frac{\langle F|H_{\rm int}|V\rangle\langle V|H_{\rm int}|U\rangle\langle U|H_{\rm int}|T\rangle\langle T|H_{\rm int}|S\rangle\langle S|H_{\rm int}|R\rangle\langle R|H_{\rm int}|I\rangle}{(E_{IV}+{\rm i}\Gamma_V)(E_{IU}+{\rm i}\Gamma_U)(E_{IT}+{\rm i}\Gamma_T)(E_{IS}+{\rm i}\Gamma_S)(E_{IR}+{\rm i}\Gamma_R)} \tag{3}$$

where $H_{\rm int}$ is the dipole interaction Hamiltonian;

$$H_{\rm int} = \varepsilon_0^{-1}\boldsymbol{\mu}\cdot\boldsymbol{d}^{\perp}. \tag{4}$$

Here $\boldsymbol{d}^{\perp}$ is the microscopic transverse displacement electric field and $\boldsymbol{\mu}$ the molecular dipole-moment operator. In the denominators of equation (3) the energy differences $E_{IX} = E_I - E_X$ relate to system intermediate energies $E_X$ $(X = R, S, T, U, V)$ as given explicitly in table 1. A tilde is introduced to denote complex molecular energies directly incorporating the damping explicitly featured in equation (3), setting $\tilde{E}_{x0} \equiv E_{x0} - {\rm i}\Gamma_x$ with the sign determined by time-reversal considerations [30]. As an example, the matrix element associated with the first of the time-ordered diagrams in figure 1, using the expansion for the transverse displacement electric field [29] leads to the following result for harmonic conversion at a site with position vector $\boldsymbol{R}$:

$$\begin{aligned} M_{FI}^{(\rm i)} = \sum_{r,s,t,u,v} \left(\frac{\overline{h}c}{2\varepsilon_0 V}\right)^3 & k^2\sqrt{k'}\sqrt{k''}(\bar{e}_i'' e_j e_k \bar{e}_l' e_m e_n)(\mu_i^{0v}\mu_j^{vu}\mu_k^{ut}\mu_l^{ts}\mu_m^{sr}\mu_n^{r0}) \\ & \times\sqrt{n}\sqrt{n-1}\sqrt{n-2}\sqrt{n-3}\,{\rm e}^{{\rm i}(4\boldsymbol{k}-\boldsymbol{k}'-\boldsymbol{k}'')\cdot\boldsymbol{R}} \\ & \times[(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{t0}-2\overline{h}\omega+\overline{h}\omega') \\ & \times(\tilde{E}_{u0}-3\overline{h}\omega+\overline{h}\omega')(\tilde{E}_{v0}-4\overline{h}\omega+\overline{h}\omega')]^{-1} \end{aligned} \tag{5}$$

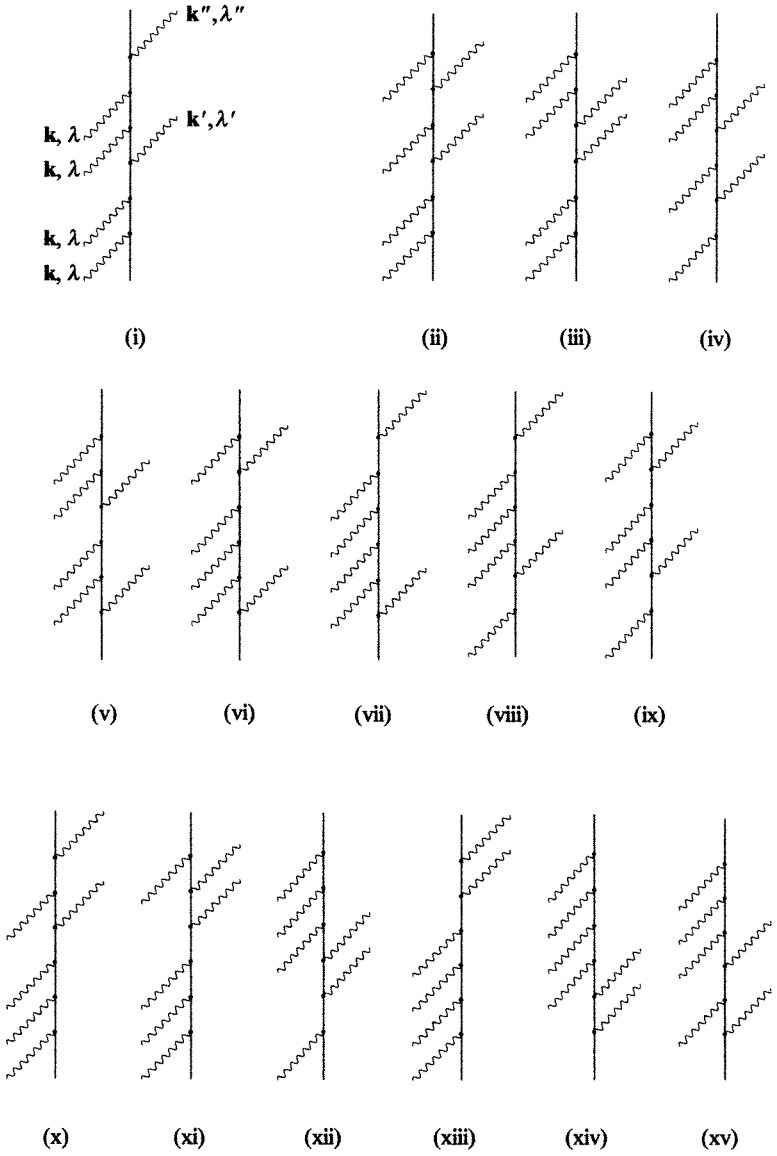


**Figure 1.** Time-ordered diagrams for SWM. The two emergent photon modes can be reversed for 15 other time-orderings.

with the unit vectors $\boldsymbol{e}$ and $\boldsymbol{e}'$ representing the incident and signal radiation polarization vectors respectively. The full probability amplitude is the sum over all possible time orderings, giving;

$$M_{FI} = \left(\frac{\bar{h}c}{2\varepsilon_0 V}\right)^3 k^2\sqrt{k'}\sqrt{k''}\sqrt{n}\sqrt{n-1}\sqrt{n-2}\sqrt{n-3}(\bar{e}''_i e_j e_k \bar{e}'_l e_m e_n)\chi^{(5)}_{ijklmn} \mathrm{e}^{\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{R}}. \qquad (6)$$

Here $\Delta\boldsymbol{k} = 4\boldsymbol{k} - \boldsymbol{k}' - \boldsymbol{k}''$ is the wavevector mismatch and the molecular susceptibility $\boldsymbol{\chi}^{(5)}$, fully represented by the 720 (6!) terms permitted on full permutation of the photon indices

$i, j, k, l, m$ and $n$, is neatly expressible in the compact form [31]:

$$\begin{aligned}\chi^{(5)}(-\omega'', -\omega'; \omega, \omega, \omega, \omega) = \sum_{\pi} \sum_{r,s,t,u,v} \{&(\mu^{0v}_{\pi(6)}\mu^{vu}_{\pi(5)}\mu^{ut}_{\pi(4)}\mu^{ts}_{\pi(3)}\mu^{sr}_{\pi(2)}\mu^{r0}_{\pi(1)}) \\ &\times[\{\tilde{E}_{r0} + \overline{h}\eta_{\pi(1)}\omega_{\pi(1)}\}\{\tilde{E}_{s0} + \overline{h}(\eta_{\pi(1)}\omega_{\pi(1)} + \eta_{\pi(2)}\omega_{\pi(2)})\} \\ &\times\{\tilde{E}_{t0} + \overline{h}(\eta_{\pi(1)}\omega_{\pi(1)} + \eta_{\pi(2)}\omega_{\pi(2)} + \eta_{\pi(3)}\omega_{\pi(3)})\} \\ &\times\{\tilde{E}_{u0} + \overline{h}(\eta_{\pi(1)}\omega_{\pi(1)} + \eta_{\pi(2)}\omega_{\pi(2)} + \eta_{\pi(3)}\omega_{\pi(3)} + \eta_{\pi(4)}\omega_{\pi(4)})\} \\ &\times\{\tilde{E}_{v0} + \overline{h}(\eta_{\pi(1)}\omega_{\pi(1)} + \eta_{\pi(2)}\omega_{\pi(2)} + \eta_{\pi(3)}\omega_{\pi(3)} \\ &+\eta_{\pi(4)}\omega_{\pi(4)} + \eta_{\pi(5)}\omega_{\pi(5)})\}]^{-1}. \end{aligned} \tag{7}$$

In equation (7) the sign of the photon label $\eta_{\pi(n)} = +1$ or $-1$ for emission or absorption respectively. The sum over $\pi$ leads to the 30 unique permutations (as illustrated upon reversal of the signal photons in figure 1). For example, the term for which $\pi(1) = n$, $\pi(2) = m$, $\pi(3) = l$, $\pi(4) = k$, $\pi(5) = j$ and $\pi(6) = i$ has the energy denominator $[(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{t0}-2\overline{h}\omega+\overline{h}\omega')(\tilde{E}_{u0}-3\overline{h}\omega+\overline{h}\omega')(\tilde{E}_{v0}-4\overline{h}\omega+\overline{h}\omega')]$, corresponding to the following temporal ordering: absorptions $n$ and $m$ ($\omega$), emission $l$ ($\omega'$), absorptions $k$ and $j$ ($\omega$) and finally emission $i$ ($\omega''$).

The structure of the $\boldsymbol{\chi}^{(5)}$ tensor has particular interest for the case of exact SHG ($\omega' = \omega''$). At first sight, problems appear to arise in connection with the molecular intermediate state $|t\rangle$, since terms corresponding to the molecular ground state $|0\rangle$ yield energy denominators, $E_{TI}$, carrying radiation-free terms of the form $E_{00} - \mathrm{i}\Gamma_0 = -\mathrm{i}\Gamma_0$. Since the ground-state lifetime represented by $\Gamma_0^{-1}$ is considered infinite, a divergent response is suggested. There are 18 individual terms that can result in the form, $\tilde{E}_{t0} \equiv E_{t0} - \mathrm{i}\Gamma_t$, as can be seen from table 1, with $\omega' = \omega'' = 2\omega$. It is these terms associated with secular resonance that have to be further analysed to identify the correct, finite response.

To approach the problem it is convenient to take the limiting case of the two-colour emission:

$$\left.\begin{aligned}\omega' &= 2\omega + \delta \\ \omega'' &= 2\omega - \delta\end{aligned}\right\}, \tag{8}$$

where $\delta$ is considered a small, positive frequency tending to zero for SHG. It is then expedient to effect a further separation of the tensor into a sum of two terms, one containing all 18 problematic secular denominators, for which $|t\rangle = |0\rangle$, and the other, all remaining terms, $|t\rangle \neq |0\rangle$;

$$\chi^{(5)}_{ijklmn} = \{\chi^{(5)}_{ijklmn}\}_{|t\rangle=|0\rangle} + \{\chi^{(5)}_{ijklmn}\}_{|t\rangle\neq|0\rangle}. \tag{9}$$

The combinatorial properties of the 30 summands in the matrix element include 18 permutations of the two groups of three indices $(i, jk)$ and $(l, mn)$. There is no loss of generality in implementing this subset permutation since the same index symmetry is already embodied in the polarization product in equation (5). A consequence of the exchange of indices $(i, jk) \leftrightarrow (l, mn)$ in the sum, equation (7), is that the dummy intermediate-state labels suffer a similar transformation $v \leftrightarrow s$ and $u \leftrightarrow r$. Exploiting this feature allows analysis to proceed more easily in establishing common factors in the expressions to follow. Explicitly, the subset of 18 terms can be represented in the concise form

$$\{\chi^{(5)}_{(i,jk)(l,mn)}\}_{|t\rangle=|0\rangle} = \sum_{\pi} \sum_{r,s,u,v} \left\{ \frac{1}{\{\overline{h}(\eta_{\pi(1)}\omega_{\pi(1)} + \eta_{\pi(2)}\omega_{\pi(2)} + \eta_{\pi(3)}\omega_{\pi(3)})\}} \right.$$

$$\times(\mu^{0v}_{\pi(6)}\mu^{vu}_{\pi(5)}\mu^{u0}_{\pi(4)}\mu^{0s}_{\pi(3)}\mu^{sr}_{\pi(2)}\mu^{r0}_{\pi(1)})\Big\}$$
$$\times[\{\tilde{E}_{r0}+\overline{h}\eta_{\pi(1)}\omega_{\pi(1)}\}\{\tilde{E}_{s0}+\overline{h}(\eta_{\pi(1)}\omega_{\pi(1)}+\eta_{\pi(2)}\omega_{\pi(2)})\}$$
$$\times\{\tilde{E}_{u0}+\overline{h}(\eta_{\pi(1)}\omega_{\pi(1)}+\eta_{\pi(2)}\omega_{\pi(2)}+\eta_{\pi(3)}\omega_{\pi(3)}+\eta_{\pi(4)}\omega_{\pi(4)})\}$$
$$\times\{\tilde{E}_{v0}+\overline{h}(\eta_{\pi(1)}\omega_{\pi(1)}+\eta_{\pi(2)}\omega_{\pi(2)}+\eta_{\pi(3)}\omega_{\pi(3)}+\eta_{\pi(4)}\omega_{\pi(4)}+\eta_{\pi(5)}\omega_{\pi(5)})\}]^{-1}. \tag{10}$$

The first term (i) is given explicitly by

$$\{\chi^{(5)}_{(i,jk)(l,mn)}\}^{(\mathrm{i})}_{|t\rangle=|0\rangle}=\sum_{s,r,v,u}\left\{\frac{1}{(\overline{h}\omega'-2\overline{h}\omega)}\right\}\times\left[\frac{\mu^{0v}_i\mu^{vu}_j\mu^{u0}_k\mu^{0s}_l\mu^{sr}_m\mu^{r0}_n}{(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{u0}-3\overline{h}\omega+\overline{h}\omega')(\tilde{E}_{v0}-4\overline{h}\omega+\overline{h}\omega')}\right] \tag{11}$$

with the same temporal ordering as given earlier. The first index-reversed contribution, $(i,\,jk)\leftrightarrow(l,mn)$, and hence the tenth term (x) in the above sum equation (10), is similarly

$$\{\chi^{(5)}_{(i,jk)(l,mn)}\}^{(\mathrm{x})}_{|t\rangle=|0\rangle}=\sum_{s,r,v,u}\left\{\frac{1}{(\overline{h}\omega''-2\overline{h}\omega)}\right\}\times\left[\frac{\mu^{0s}_l\mu^{sr}_m\mu^{r0}_n\mu^{0v}_i\mu^{vu}_j\mu^{u0}_k}{(\tilde{E}_{u0}-\overline{h}\omega)(\tilde{E}_{v0}-2\overline{h}\omega)(\tilde{E}_{r0}-3\overline{h}\omega+\overline{h}\omega'')(\tilde{E}_{s0}-4\overline{h}\omega+\overline{h}\omega'')}\right] \tag{12}$$

where each energy denominator factor is also transposed with respect to its index reversed counterpart (cf equation (11)). The sum can be expressed concisely, substituting for $\omega'$ and $\omega''$ through equation (8), as

$$\{\chi^{(5)}_{(i,jk)(l,mn)}\}^{(\mathrm{i})+(\mathrm{x})}_{|t\rangle=|0\rangle}=\sum_{r,s,u,v}\frac{1}{(+\delta)}\times\left[\frac{\mu^{0v}_i\mu^{vu}_j\mu^{u0}_k\mu^{0s}_l\mu^{sr}_m\mu^{r0}_n}{(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{u0}-\overline{h}\omega+\delta)(\tilde{E}_{v0}-2\overline{h}\omega+\delta)}-\frac{\mu^{0v}_l\mu^{vu}_m\mu^{u0}_n\mu^{0s}_i\mu^{sr}_j\mu^{r0}_k}{(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{u0}-\overline{h}\omega-\delta)(\tilde{E}_{v0}-2\overline{h}\omega-\delta)}\right]. \tag{13}$$

As the intermediate states $v,u,s,r$ are summed over the same basis set, it is permissible to effect the interchange $l,mn\leftrightarrow i,jk$, allowing the factorization of the transition dipole product;

$$\{\chi^{(5)}_{(i,jk)(l,mn)}\}^{(\mathrm{i})+(\mathrm{x})}_{|t\rangle=|0\rangle}=\sum_{r,s,u,v}\frac{(\mu^{0v}_n\mu^{vu}_m\mu^{u0}_l\mu^{0s}_k\mu^{sr}_j\mu^{r0}_i)}{(+\delta)}$$
$$\times[\{(\tilde{E}_{r0}-\overline{h}\omega-\delta)(\tilde{E}_{s0}-2\overline{h}\omega-\delta)(\tilde{E}_{u0}-\overline{h}\omega)(\tilde{E}_{v0}-2\overline{h}\omega)\}$$
$$-\{(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{u0}-\overline{h}\omega+\delta)(\tilde{E}_{v0}-2\overline{h}\omega+\delta)\}]$$
$$\times[(\tilde{E}_{r0}-\overline{h}\omega)(\tilde{E}_{s0}-2\overline{h}\omega)(\tilde{E}_{u0}-\overline{h}\omega)(\tilde{E}_{v0}-2\overline{h}\omega)(\tilde{E}_{r0}-\overline{h}\omega-\delta)$$
$$\times(\tilde{E}_{s0}-2\overline{h}\omega-\delta)(\tilde{E}_{u0}-\overline{h}\omega-\delta)(\tilde{E}_{v0}-2\overline{h}\omega-\delta)]^{-1}. \tag{14}$$

A common factor of $\delta$ emerges from the numerator, cancelling with the factorized $\delta$ from the denominator; taking the limit $\delta\rightarrow 0$ then correctly gives the finite contribution from the sum of the two terms (i) + (x).

**Table 1.** Intermediate energies associated with each of the time-ordered diagrams of figure 1. Lower-case subscripts refer to molecular state energies, the tilde allowing the possibility of complex energies to fully incorporate damping—see text.

| Diagram | $E_{RI}$ | $E_{SI}$ | $E_{TI}$ | $E_{UI}$ | $E_{VI}$ |
|---|---|---|---|---|---|
| (i) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - 2\bar{\hbar}\omega)$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 4\bar{\hbar}\omega + \bar{\hbar}\omega')$ |
| (ii) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - 2\bar{\hbar}\omega)$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (iii) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - 2\bar{\hbar}\omega)$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (iv) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (v) | $(\tilde{E}_{r0} + \bar{\hbar}\omega')$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (vi) | $(\tilde{E}_{r0} + \bar{\hbar}\omega')$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (vii) | $(\tilde{E}_{r0} + \bar{\hbar}\omega')$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 4\bar{\hbar}\omega + \bar{\hbar}\omega')$ |
| (viii) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 4\bar{\hbar}\omega + \bar{\hbar}\omega')$ |
| (ix) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (x) | $(\tilde{E}_{r0} + \bar{\hbar}\omega')$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - \bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{u0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (xi) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - 2\bar{\hbar}\omega)$ | $(\tilde{E}_{t0} - 3\bar{\hbar}\omega)$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 4\bar{\hbar}\omega + \bar{\hbar}\omega')$ |
| (xii) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - 2\bar{\hbar}\omega)$ | $(\tilde{E}_{t0} - 3\bar{\hbar}\omega)$ | $(\tilde{E}_{u0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (xiii) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega + \bar{\hbar}\omega')$ | $(\tilde{E}_{t0} - \bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{u0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |
| (xiv) | $(\tilde{E}_{r0} - \bar{\hbar}\omega)$ | $(\tilde{E}_{s0} - 2\bar{\hbar}\omega)$ | $(\tilde{E}_{t0} - 3\bar{\hbar}\omega)$ | $(\tilde{E}_{u0} - 4\bar{\hbar}\omega)$ | $(\tilde{E}_{v0} - 4\bar{\hbar}\omega + \bar{\hbar}\omega')$ |
| (xv) | $(\tilde{E}_{r0} + \bar{\hbar}\omega')$ | $(\tilde{E}_{s0} - \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{t0} - \bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{u0} - 2\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ | $(\tilde{E}_{v0} - 3\bar{\hbar}\omega + \bar{\hbar}\omega' + \bar{\hbar}\omega'')$ |

This technique can be applied to all 18 terms (nine pairs) of equation (10). The reduced set of nine summed contributions derived from equation (10) reveals the correct form of the finite result from the secular contribution to SHG. The complete expression for the finite secular terms of the molecular susceptibility, $\{\chi^{(5)}_{(i,jh)(l,mn)}\}_{|t\rangle=|0\rangle}$, is given by the sum;

$$\{\chi^{(5)}_{(i,jh)(l,mn)}(\xi)\}_{|t\rangle=|0\rangle} = \sum_{r,s,u,v}\sum_{p=1}^{9} \mathrm{X}^{(p)}_{(i,jh)(l,mn)}, \tag{15}$$

where the individual terms, $\mathrm{X}^{(p)}_{(ij,k)(lm,n)}$, are explicitly

$$\begin{aligned}
\mathrm{X}^{(1)}_{(i,jk)(l,mn)} &= \{(\mu_i^{0v}\mu_j^{vu}\mu_k^{u0}\mu_l^{0s}\mu_m^{sr}\mu_n^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} + 3\tilde{E}_{v0}\tilde{E}_{u0}\overline{\hbar}\omega + 2\tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega + 3\tilde{E}_{v0}\tilde{E}_{r0}\overline{\hbar}\omega + 3\tilde{E}_{u0}\tilde{E}_{s0}\overline{\hbar}\omega \\
&\quad +4\tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega + 3\tilde{E}_{s0}\tilde{E}_{r0}\overline{\hbar}\omega - 5\tilde{E}_{v0}(\overline{\hbar}\omega)^2 - 8\tilde{E}_{u0}(\overline{\hbar}\omega)^2 \\
&\quad -5\tilde{E}_{s0}(\overline{\hbar}\omega)^2 - 8\tilde{E}_{r0}(\overline{\hbar}\omega)^2 + 12(\overline{\hbar}\omega)^3] \\
&\quad \times[(\tilde{E}_{r0} - \overline{\hbar}\omega)^2(\tilde{E}_{s0} - 2\overline{\hbar}\omega)^2(\tilde{E}_{u0} - \overline{\hbar}\omega)^2(\tilde{E}_{v0} - 2\overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{16}$$

$$\begin{aligned}
\mathrm{X}^{(2)}_{(i,jk)(l,mn)} &= \{(\mu_j^{0v}\mu_i^{vu}\mu_k^{u0}\mu_l^{0s}\mu_m^{sr}\mu_n^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} + 3\tilde{E}_{v0}\tilde{E}_{u0}\overline{\hbar}\omega + 2\tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega + 3\tilde{E}_{v0}\tilde{E}_{r0}\overline{\hbar}\omega + \tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega \\
&\quad -5\tilde{E}_{v0}(\overline{\hbar}\omega)^2 + \tilde{E}_{u0}(\overline{\hbar}\omega)^2 + \tilde{E}_{s0}(\overline{\hbar}\omega)^2 + \tilde{E}_{r0}(\overline{\hbar}\omega)^2 - 3(\overline{\hbar}\omega)^3] \\
&\quad \times[(\tilde{E}_{r0} - \overline{\hbar}\omega)^2(\tilde{E}_{s0} - 2\overline{\hbar}\omega)^2(\tilde{E}_{u0} - \overline{\hbar}\omega)^2(\tilde{E}_{v0} + \overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{17}$$

$$\begin{aligned}
\mathrm{X}^{(3)}_{(i,jk)(l,mn)} &= \{(\mu_j^{0v}\mu_k^{vu}\mu_i^{u0}\mu_l^{0s}\mu_m^{sr}\mu_n^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} + 3\tilde{E}_{v0}\tilde{E}_{u0}\overline{\hbar}\omega - \tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega + \tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega - 3\tilde{E}_{s0}\tilde{E}_{r0}\overline{\hbar}\omega \\
&\quad +4\tilde{E}_{v0}(\overline{\hbar}\omega)^2 + \tilde{E}_{u0}(\overline{\hbar}\omega)^2 + \tilde{E}_{s0}(\overline{\hbar}\omega)^2 + 4\tilde{E}_{r0}(\overline{\hbar}\omega)^2] \\
&\quad \times[(\tilde{E}_{r0} - \overline{\hbar}\omega)^2(\tilde{E}_{s0} - 2\overline{\hbar}\omega)^2(\tilde{E}_{u0} + 2\overline{\hbar}\omega)^2(\tilde{E}_{v0} + \overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{18}$$

$$\begin{aligned}
\mathrm{X}^{(4)}_{(i,jk)(l,mn)} &= \{(\mu_j^{0v}\mu_k^{vu}\mu_i^{u0}\mu_m^{0s}\mu_l^{sr}\mu_n^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega - 3\tilde{E}_{v0}\tilde{E}_{r0}\overline{\hbar}\omega - 2\tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega \\
&\quad -3\tilde{E}_{s0}\tilde{E}_{r0}\overline{\hbar}\omega + \tilde{E}_{v0}(\overline{\hbar}\omega)^2 + \tilde{E}_{u0}(\overline{\hbar}\omega)^2 + \tilde{E}_{s0}(\overline{\hbar}\omega)^2 - 5\tilde{E}_{r0}(\overline{\hbar}\omega)^2 + 3(\overline{\hbar}\omega)^3] \\
&\quad \times[(\tilde{E}_{r0} - \overline{\hbar}\omega)^2(\tilde{E}_{s0} + \overline{\hbar}\omega)^2(\tilde{E}_{u0} + 2\overline{\hbar}\omega)^2(\tilde{E}_{v0} + \overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{19}$$

$$\begin{aligned}
\mathrm{X}^{(5)}_{(i,jk)(l,mn)} &= \{(\mu_j^{0v}\mu_k^{vu}\mu_i^{u0}\mu_m^{0s}\mu_n^{sr}\mu_l^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} - 3\tilde{E}_{v0}\tilde{E}_{u0}\overline{\hbar}\omega - 4\tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega - 3\tilde{E}_{v0}\tilde{E}_{r0}\overline{\hbar}\omega - 3\tilde{E}_{u0}\tilde{E}_{s0}\overline{\hbar}\omega \\
&\quad -2\tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega - 3\tilde{E}_{s0}\tilde{E}_{r0}\overline{\hbar}\omega - 8\tilde{E}_{v0}(\overline{\hbar}\omega)^2 - 5\tilde{E}_{u0}(\overline{\hbar}\omega)^2 \\
&\quad -8\tilde{E}_{s0}(\overline{\hbar}\omega)^2 - 5\tilde{E}_{r0}(\overline{\hbar}\omega)^2 - 12(\overline{\hbar}\omega)^3] \\
&\quad \times[(\tilde{E}_{r0} + 2\overline{\hbar}\omega)^2(\tilde{E}_{s0} + \overline{\hbar}\omega)^2(\tilde{E}_{u0} + 2\overline{\hbar}\omega)^2(\tilde{E}_{v0} + \overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{20}$$

$$\begin{aligned}
\mathrm{X}^{(6)}_{(i,jk)(l,mn)} &= \{(\mu_j^{0v}\mu_i^{vu}\mu_k^{u0}\mu_m^{0s}\mu_n^{sr}\mu_l^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} - 3\tilde{E}_{v0}\tilde{E}_{u0}\overline{\hbar}\omega - \tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega - 3\tilde{E}_{u0}\tilde{E}_{s0}\overline{\hbar}\omega - 2\tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega \\
&\quad +\tilde{E}_{v0}(\overline{\hbar}\omega)^2 - 5\tilde{E}_{u0}(\overline{\hbar}\omega)^2 + \tilde{E}_{s0}(\overline{\hbar}\omega)^2 + \tilde{E}_{r0}(\overline{\hbar}\omega)^2 + 3(\overline{\hbar}\omega)^3] \\
&\quad \times[(\tilde{E}_{r0} + 2\overline{\hbar}\omega)^2(\tilde{E}_{s0} + \overline{\hbar}\omega)^2(\tilde{E}_{u0} - \overline{\hbar}\omega)^2(\tilde{E}_{v0} + \overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{21}$$

$$\begin{aligned}
\mathrm{X}^{(7)}_{(i,jk)(l,mn)} &= \{(\mu_i^{0v}\mu_j^{vu}\mu_k^{u0}\mu_m^{0s}\mu_n^{sr}\mu_l^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&\quad -\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} - 3\tilde{E}_{v0}\tilde{E}_{u0}\overline{\hbar}\omega - \tilde{E}_{v0}\tilde{E}_{s0}\overline{\hbar}\omega + \tilde{E}_{u0}\tilde{E}_{r0}\overline{\hbar}\omega + 3\tilde{E}_{s0}\tilde{E}_{r0}\overline{\hbar}\omega \\
&\quad +\tilde{E}_{v0}(\overline{\hbar}\omega)^2 + 4\tilde{E}_{u0}(\overline{\hbar}\omega)^2 + 4\tilde{E}_{s0}(\overline{\hbar}\omega)^2 + \tilde{E}_{r0}(\overline{\hbar}\omega)^2] \\
&\quad \times[(\tilde{E}_{r0} + 2\overline{\hbar}\omega)^2(\tilde{E}_{s0} + \overline{\hbar}\omega)^2(\tilde{E}_{u0} - \overline{\hbar}\omega)^2(\tilde{E}_{v0} - 2\overline{\hbar}\omega)^2]^{-1}\}
\end{aligned} \tag{22}$$

$$\begin{aligned}
X^{(8)}_{(i,jk)(l,mn)} = \{&(\mu_i^{0v}\mu_j^{vu}\mu_k^{u0}\mu_m^{0s}\mu_l^{sr}\mu_n^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&-\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} + 2\tilde{E}_{v0}\tilde{E}_{s0}\bar{h}\omega + 3\tilde{E}_{u0}\tilde{E}_{s0}\bar{h}\omega + \tilde{E}_{u0}\tilde{E}_{r0}\bar{h}\omega + 3\tilde{E}_{s0}\tilde{E}_{r0}\bar{h}\omega \\
&+\tilde{E}_{v0}(\bar{h}\omega)^2 + \tilde{E}_{u0}(\bar{h}\omega)^2 - 5\tilde{E}_{s0}(\bar{h}\omega)^2 + \tilde{E}_{r0}(\bar{h}\omega)^2 - 3(\bar{h}\omega)^3] \\
&\times[(\tilde{E}_{r0} - \bar{h}\omega)^2(\tilde{E}_{s0} + \bar{h}\omega)^2(\tilde{E}_{u0} - \bar{h}\omega)^2(\tilde{E}_{v0} - 2\bar{h}\omega)^2]^{-1}\} \qquad (23)
\end{aligned}$$

$$\begin{aligned}
X^{(9)}_{(i,jk)(l,mn)} = \{&(\mu_j^{0v}\mu_i^{vu}\mu_k^{u0}\mu_m^{0s}\mu_l^{sr}\mu_n^{r0})[-\tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{s0} - \tilde{E}_{v0}\tilde{E}_{u0}\tilde{E}_{r0} - \tilde{E}_{v0}\tilde{E}_{s0}\tilde{E}_{r0} \\
&-\tilde{E}_{u0}\tilde{E}_{s0}\tilde{E}_{r0} + 2\tilde{E}_{v0}\tilde{E}_{s0}\bar{h}\omega - 2\tilde{E}_{u0}\tilde{E}_{r0}\bar{h}\omega + \tilde{E}_{v0}(\bar{h}\omega)^2 \\
&+\tilde{E}_{u0}(\bar{h}\omega)^2 + \tilde{E}_{s0}(\bar{h}\omega)^2 + \tilde{E}_{r0}(\bar{h}\omega)^2] \\
&\times[(\tilde{E}_{r0} - \bar{h}\omega)^2(\tilde{E}_{s0} + \bar{h}\omega)^2(\tilde{E}_{u0} - \bar{h}\omega)^2(\tilde{E}_{v0} + \bar{h}\omega)^2]^{-1}\}. \qquad (24)
\end{aligned}$$

To find the rate $\Gamma$, and thereby the intensity of the second harmonic associated with SWM, Fermi's Golden Rule is used [32]. The rate can be cast in terms of the pump irradiance $I_\omega = n\bar{h}c\omega/V$, as:

$$\begin{aligned}
\Gamma = \frac{2\pi}{\bar{h}}&\left(\frac{\bar{h}c}{2\varepsilon_0 V}\right)^6\left(\frac{V}{n\bar{h}c^2k}\right)^4 I_\omega^4(n)(n-1)(n-2)(n-3)k^4k'k'' \\
&\times\left|(\bar{e}_i''e_je_k\bar{e}_l'e_me_n)\sum_\xi^N \chi^{(5)}_{(i,jk)(l,mn)}(\xi)\mathrm{e}^{\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{R}_\xi}\right|^2\rho_F \qquad (25)
\end{aligned}$$

where the sum over molecules labelled $\xi$ represents the coherent addition of signals from each conversion site and where $\rho_F$ is the density of final radiation states. The result may immediately be generalized to accommodate an incident laser field more realistic than a simple Fock state. This leads to the replacement of the number state factors $n(n-1)(n-2)(n-3)$ and $n^4$ by their expectation values, $\langle n(n-1)(n-2)(n-3)\rangle$ and $\langle n\rangle^4$ [29], the rate now taking the form

$$\Gamma = \frac{\pi\bar{h}}{32\varepsilon_0^6c^2V^2}\bar{I}_\omega^4 g^{(4)}k'k''\left|(\bar{e}_i''e_je_k\bar{e}_l'e_me_n)\sum_\xi^N \chi^{(5)}_{(i,jk)(l,mn)}(\xi)\mathrm{e}^{\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{R}_\xi}\right|^2\rho_F, \qquad (26)$$

where $\bar{I}_\omega$ is the mean irradiance of the pump and $g^{(4)}$ its degree of fourth-order coherence,

$$g^{(4)} = \frac{\langle n(n-1)(n-2)(n-3)\rangle}{\langle n\rangle^4}. \qquad (27)$$

As the rate equation (26) represents the collective response of the $N$ molecular centres and the summation over the molecules is inside the modulus squared, the signal contains $N^2$ contributions, of which $N$ are diagonal (single-centre) and the other $(N^2 - N)$ off-diagonal. To take account of the tumbling motions experienced by each molecular centre, as for example in a molecular fluid, or indeed the random orientations of sites in any other microscopically disordered condensed phase, it is convenient to rewrite equation (26) explicitly as a sum of the diagonal and off-diagonal terms;

$$\begin{aligned}
\Gamma = \frac{\pi\bar{h}}{32\varepsilon_0^6c^2V^2}&\bar{I}_\omega^4 g^{(4)}k'k''\left\{\sum_\xi^N|(\bar{e}_i''e_je_k\bar{e}_l'e_me_n)\chi^{(5)}_{(i,jk)(l,mn)}(\xi)|^2\right. \\
&+\left[(\bar{e}_i''e_je_k\bar{e}_l'e_me_n)(e_o''\bar{e}_pe_q\bar{e}_r'e_s\bar{e}_t)\right. \\
&\left.\left.\times\sum_\xi^N\sum_{\xi'\neq\xi}^N \chi^{(5)}_{(i,jk)(l,mn)}(\xi)\bar{\chi}^{(5)}_{(o,pq)(r,st)}(\xi')\,\mathrm{e}^{\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{R}_{\xi\xi'}}\right]\right\}\rho_F \qquad (28)
\end{aligned}$$

The leading diagonal (incoherent) terms are independent of any directive phase factors. These terms differ markedly from the off-diagonal (coherent) terms, dependent through the phase factor $\exp[\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{R}_{\xi\xi'}]$ on the relative molecular displacements $\boldsymbol{R}_{\xi\xi'}\equiv\boldsymbol{R}_{\xi}-\boldsymbol{R}_{\xi'}$ and for which wavevector matching $\Delta\boldsymbol{k}\cong 0$ leads to the well known $\mathrm{sinc}^2$ dependence. The two contributions, incoherent and coherent, can be compared with similar expressions for the conventional second-harmonic process [33]; a key difference in the results presented here is that, as will be shown, the off-diagonal (coherent) terms persist in an isotropic medium.

The isotropic averages required by equation (28) for randomly oriented fluids must be separately implemented on the incoherent and coherent contributions, since they invoke a twelfth-rank and sixth-rank average tensor response respectively—thus, only even-rank averages are performed in the case of SWM. For the more familiar three-wave SHG process, the sixth-rank average yields a non-zero result for the incoherent signal whereas the third-rank average vanishes, as has been shown elsewhere [13]. The isotropic average for the coherent SWM term is represented by

$$(\eta_N - N)|\langle(\bar{e}''_i e_j e_k \bar{e}'_l e_m e_n)(\chi^{(5)}_{(i,jk)(l,mn)})\rangle|^2$$
$$= (\eta_N - N)|(\bar{e}''_i e_j e_k \bar{e}'_l e_m e_n)(\chi^{(5)}_{(\lambda,\mu\nu)(o,\pi\rho)})\langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{lo} l_{m\pi} l_{n\rho}\rangle|^2 \tag{29}$$

where the $l_{i\lambda}$ represent the direction cosines linking the site- and radiation-centred frames of reference, $\eta_N$ is defined as the coherence factor,

$$\eta_N = \left|\sum_{\xi}^{N}\exp(\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{R}_{\xi})\right|^2, \tag{30}$$

and all other terms are as previously defined. From the isotropic averages the sixth-rank average required in equation (29) consists of products of Kronecker deltas only [34], and the coherent harmonic therefore survives. This is irrespective of the molecular (conversion site) symmetry as $\boldsymbol{\chi}^{(5)}$ itself, again unlike $\boldsymbol{\chi}^{(2)}$ for conventional SHG, is supported by all point groups. Thus the ensemble rate of coherent second-harmonic production through SWM can be expressed by

$$\langle\Gamma\rangle = \frac{\pi\bar{h}}{32\varepsilon_0^6 c^2 V^2} I_\omega^4 g^{(4)} k' k''\{(\eta_N - N)|(\bar{e}''_i e_j e_k \bar{e}'_l e_m e_n)(\chi^{(5)}_{(\lambda,\mu\nu)(o,\pi\rho)})\langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{lo} l_{m\pi} l_{n\rho}\rangle|^2\}\rho_F. \tag{31}$$

Compared to this, signal contributions associated with the incoherent process will be insignificant and can, unless there is gross violation of the wavevector matching, safely be ignored.

In regions of strong dispersion where wavevector matching can only be achieved in a non-collinear beam geometry, it may prove experimentally expedient to stimulate emission by a secondary input $I_{\omega'}$. The signal output at frequency $(4\omega - \omega')$ will then emerge in a direction determined by the wavevector matching condition, yet without requiring the levels of input intensity that could produce optical poling. This experimental set-up also ensures that the collected signal is derived from the specific SWM process under consideration—the envisaged signal geometry is illustrated in figure 2. The signal intensity is now also

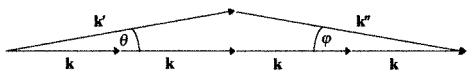


**Figure 2.** The arrows indicate the wavevectors for pump, $\boldsymbol{k}$, probe, $\boldsymbol{k}'$, and signal, $\boldsymbol{k}''$, for SWM.

proportional to the intensity of the input harmonic through $I_{\omega'} = n\bar{h}c^2k'/V$, given that the occupation number of the probe beam is sufficiently large for the approximation, $(n+1)(\boldsymbol{k}', \lambda') \approx n(\boldsymbol{k}', \lambda')$ to be valid. Utilizing the expression for the density of final radiation states $\rho_F = k'^2\,\mathrm{d}\Omega V/(2\pi)^3\bar{h}c$ [28], the rate equation (31) can be re-expressed as a signal radiant intensity $I_{\omega''}(\mathrm{Wsr}^{-1})$, where $I = \bar{h}ck''\,\mathrm{d}\Gamma/\mathrm{d}\Omega$, $\mathrm{d}\Omega$ is an element of the solid angle around the signal wavevector $\boldsymbol{k}''$; assuming the magnitude of the wavevectors, $\boldsymbol{k}'$ and $\boldsymbol{k}''$, are both approximately $2\omega/c$, we obtain:

$$I_{\omega''} = \frac{\omega^4}{16\pi^2\varepsilon_0^6c^8}\bar{I}_{\omega'}\bar{I}_{\omega}^4 g^{(4)}\{(\eta_N - N)|(\chi^{(5)}_{(\lambda,\mu\nu)(o,\pi\rho)})(\bar{e}''_i e_j e_k \bar{e}'_l e_n e_m)\langle l_{i\lambda}l_{j\mu}l_{k\nu}l_{lo}l_{m\pi}l_{n\rho}\rangle|^2\}. \quad (32)$$

By explicit implementation of the rotational average, exploiting the index symmetry of the incident-pump photon polarization vectors, we then have;

$$I = \frac{\omega^4}{560\pi^4\varepsilon_0^6c^8}\bar{I}_{\omega'}\bar{I}_{\omega}^4 g^{(4)}(\eta_N - N)|[\{6(\boldsymbol{e}\cdot\bar{\boldsymbol{e}}')(\boldsymbol{e}\cdot\bar{\boldsymbol{e}}'') - 2(\bar{\boldsymbol{e}}'\cdot\bar{\boldsymbol{e}}'')\}\chi^{(5)}_{(\lambda\mu\mu\nu)\lambda\nu}$$
$$-\{2(\boldsymbol{e}\cdot\bar{\boldsymbol{e}}')(\boldsymbol{e}\cdot\bar{\boldsymbol{e}}'') - 3(\bar{\boldsymbol{e}}'\cdot\bar{\boldsymbol{e}}'')\}\chi^{(5)}_{(\mu\mu\nu\nu)\lambda\lambda}]|^2 \quad (33)$$

As shown previously [6], SWM in frequency regions where Kleinman index symmetry holds for the nonlinear susceptibility tensor, which in practice suggests working with low frequencies, leads to the conclusion that the emergent harmonic, collinear with the pump beam, retains as much as 96% of the pump polarization, as follows from equation (33). Nonetheless equation (33) is a more general result, applicable over all frequency regions and also catering for off-axis emission. As such it may be exploited for the evaluation of the tensor parameters. For example, when the probe and signal beams are at angles $\theta = 30^\circ$ and $\varphi = -30^\circ$ relative to the pump beam respectively, the second tensorial parameter of equation (33) does not contribute to the signal intensity. Therefore the magnitude of $\chi^{(5)}_{(\lambda\mu\mu\nu)\lambda\nu}$ is directly obtainable from this particular experimental geometry.

## 3. Conclusion

Analysis of the SWM mechanism for SHG reveals that a finite harmonic can be sustained irrespective of molecular or bulk symmetry. It has been shown in detail how to identify the correct form of the fifth-order molecular susceptibility, resolving the apparent infinities associated with secular resonance. Experimental observation of the signal is expected to be contingent on satisfying the wavevector matching conditions of the overall process. In this case the signal would propagate collinearly with the pump. However, for experimental purposes the introduction of a probe beam into the fluid sample allows the signal to be detected away from the pump propagation direction by forcing one of the signal photons into a radiation mode with a well defined wavevector. The signal then emerges in an equally well defined, unoccupied radiation mode.

The issues raised by taking the limit $\omega'' \to \omega'$ are evidently complex and merit further discussion. The emergence of degeneracy as two states become energetically equivalent is familiar enough in quantum mechanics. Here, however, it is not the states of the radiation field but the modes to which they belong that merge into a non-degenerate unity, $|\boldsymbol{k}'', \lambda''\rangle \to |\boldsymbol{k}', \lambda'\rangle$. This is closely akin to the common treatment in the theory of SHG as a limiting case of SFG, though that is a case where the detailed issues have seldom received the attention they deserve because classical rather than quantum-field theoretic treatments are the norm. The physical distinguishability of photons with marginally different propagation vectors—for convenience assuming that the photon polarizations are nearly identical, is

linked with the coherence volume, as recently discussed by Mandel and Wolf [35]. For SWM, as with SHG, the coherence volume for the output radiation will be of the same order of magnitude as the input—though marginally smaller, reflecting a line width broadened in the frequency domain. For typical input line widths both coherence volumes are nonetheless considerably larger than the physical volume in which frequency conversion takes place, and the SWM output can therefore be treated as a single mode of radiation.

Over most optical frequency ranges, the SWM process, with its intrinsic ability to sustain a second harmonic in all symmetry species, offers more opportunities than conventional SHG for the exploitation of (non-secular) resonances. Inspection of the time-ordered diagrams of figure 1 (x), (xi) and (xiii), for example, readily shows their potential for enhancement associated with three- and four-photon resonances. The greater density of molecular (vibronic) states at higher energies will generally afford a greater likelihood of exploiting such resonances, typically offering several orders of magnitude signal enhancement. Finally, it may be noted that the six-wave process, once experimentally characterized, affords an excellent test for the computation of nonlinear optical susceptibilities using state-of-the-art software. The refinement of such computational methods, now achievable through solving the problem of secular behaviour, is of key significance for the further development of nonlinear optical devices.

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