THEORY OF HIGHER MULTIPOLE CONTRIBUTIONS TO TWO-PHOTON ABSORPTION PROCESSES*

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With the advent of the laser, the observation of two-photon absorption processes at optical frequencies has become possible.[1-4] It has recently been suggested[5] that the two-photon absorption in anthracene is due to the higher multipole interactions, and that the coherence of the laser light plays an essential role in this process. In this Letter we wish to clarify the theory of the higher multipole contributions to two-photon processes, as well as the role of coherence. Our conclusions are that the higher multipole contributions are negligible, and that the single-molecule two-photon absorption cross section is the same for coherent and incoherent incident light.

In time-dependent perturbation theory based on the Hamiltonian

$$H=H_0-(e/mc)\vec{A}\cdot\vec{p}+(e^2/2mc^2)\vec{A}^2, \tag{1}$$

two-photon processes result in first order from the $\vec{A}^2$ term, and in second order from the $\vec{A}\cdot\vec{p}$ term. When one replaces by 1 the phase factors $\exp(ikx)$ in all the quantities $\vec{A}$ appearing in the expression for the final-state amplitude for a given radiation process, the electric-dipole contribution to that process is obtained. For two-photon processes this contribution will be called the $E1E1$ term. Iannuzzi and Polacco[5] suggest that, for coherent light, a contribution of the same order of magnitude as the $E1E1$ term arises from the terms in $\vec{A}^2$ linear in x. This contribution is clearly due to the higher multipole interactions. However, a contribution of the same order of magnitude comes from the terms linear in x in the second-order contribution from the $\vec{A}\cdot\vec{p}$ term, which these authors neglect. For light propagating along x and polarized along z, the total contribution of the terms linear in x to the amplitude of two-photon absorption between the states i and f, per pulse of the laser, is given by

$$T_{fi}=-\frac{2\pi r_0 I}{\hbar\omega_0 m}\langle f|mx-(p_zRxp_z+xp_zRp_z)|i\rangle, \tag{2}$$

where $r_0=(e^2/mc^2)$, $R=(H_0-E_i-\omega_0)^{-1}$, ω_0 is the frequency of the laser light, and I is the total energy per pulse per unit area at the position of the molecule. The expression (2) is valid both for coherent light, for which a wave packet description must be used, and for incoherent light described by a stationary density matrix diagonal in the photon number representation.

To see the physical significance of the result (2), one must transform to the "multipole" Hamiltonian

$$H'=H_0-\vec{\mu}\cdot\vec{E}-\vec{\mu}'\cdot\vec{B}-q:\nabla\vec{E}+\cdots, \tag{3}$$

where $\vec{\mu}$, $\vec{\mu}'$, and q are the electric dipole, magnetic dipole, and (tensor) electric quadrupole moment of the molecule. In addition to the terms written in (3), H' contains higher multipole terms and terms quadratic in $\vec{B}$ and its spatial derivatives.[6] In a perturbation calculation based on (3), the terms in the final-state amplitude quadratic in μ give the $E1E1$ contribution, and the terms proportional to $\mu\mu'$ and μq give the $E1M1$ and $E1E2$ contributions. The parity selection rule for $E1E1$ is opposite to that for $E1M1$ and $E1E2$. There are, therefore, no interference effects between $E1E1$ and the other two terms, but $E1M1$ and $E1E2$ both contribute to the same final-state amplitude. For the $E1E2+E1M1$ contribution to the final-state amplitude, per pulse of the laser, we find

$$\begin{aligned}T_{fi}'=-\frac{2\pi I}{\hbar c^2}\langle f|\omega_0(\mu_zRq_{xz}+q_{xz}R\mu_z)\\+ic(\mu_zR\mu_y'+\mu_y'R\mu_z)|i\rangle.\end{aligned} \tag{4}$$

Using the relations $(p_z)_{nn'}=im\omega_{nn'}z_{nn'}$, $zp_z-p_zz=i\hbar$, and $2\omega_0=\omega_{fi}$, one can prove that the expressions (2) and (4) are identical, $T_{fi}=T_{fi}'$. This proof is an extension of the well-known proof[7] of the equality of the corresponding amplitude for $E1E1$ scattering. The amplitude for $E1E1$ absorption is given by

$$S_{fi}=i\frac{2\pi I}{\hbar c}\langle f|\mu_zR\mu_z|i\rangle. \tag{5}$$

The two terms in (2) and those in (4) are all of the same order of magnitude, and are typically of order 10^{-1} to 10^{-3} compared to (5), the ratio being roughly x_{fi}/λ, where $\lambda = \hbar/mc$.

To estimate the higher multipole contribution to the two-photon absorption in anthracene, we describe the ${}^1B_{2u}$ band by a line-shape function $g(\omega)$, where $\int g(\omega)d\omega = 1$. Taking only the first term in (2) into account, the transition probability per pulse is given by

$$P = \left(\frac{2\pi r_0}{\hbar\omega_0}\right)^2 I^2 |x_{fi}|^2 g(2\omega_0) 2\Delta\omega, \tag{6}$$

which agrees with Eq. (6) in reference 5 except for a factor $(4\pi)^2$ arising from our use of unrationalized quantities. In reference 5 rationalized quantities are used, but the authors fail to take into account a factor 4π in the numerical value of r_0, and their value of P is therefore a factor $(4\pi)^2$ too small. According to the data given in reference 4, we have $V = 10^{-5}$ cm^3 and $I = 2\times10^9$ erg cm^{-2}. Using $|x_{fi}|^2 g(2\omega_0) = 2\times10^{-33}$ cm^2 sec, $\omega_0 = 2.7\times10^{15}$ rad sec^{-1}, and $\Delta\omega = 5\times10^7$ rad sec^{-1} (cf. reference 5), we get for the number of fluorescent photons $n = 10^{10}$, whereas experimentally[4] $n = 4\times10^{12}$. The higher multipole effect, estimated by taking only the first term in (2) into account, thus fails to account for the data by about a factor 10^2-10^3, and one must conclude that the observed effect is due to $E1E1$ transitions, as suggested by Singh and Stoicheff.[4] We emphasize that the order of magnitude of some of the quantities involved is rather uncertain, and more precise experimental data and a more reliable evaluation of the full amplitude (2), or (4), are required to settle the question.

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