Suppression of Molecular Interactions in Periodic Dielectric Structures

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We show that resonant dipole-dipole interactions are suppressed at all interatomic or intermolecular separations in periodic dielectric structures in which spontaneous emission is inhibited at the resonant optical transitions. This profoundly modifies molecular properties including donor-acceptor energy transfer, collisional dynamics, molecular spectra, and dissociation energies.

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Radiative decay is inhibited when boundary conditions impose destructive interference on spontaneously emitted radiation at the location of the emitter. This has been demonstrated for molecules near a reflecting surface[1] and for Rydberg atoms in a resonant microwave cavity.[2] Recently, it has been proposed that spontaneous emission is inhibited[3] at optical frequencies which lie within spectral bands of forbidden light propagation (photonic band gap) created in structures with sufficiently strong periodic modulation of the dielectric index.[3,4] A three-dimensional photonic band gap in a periodic dielectric structure has recently been observed experimentally at microwave frequencies.[5] The construction of appropriate structures for optical band gaps is facilitated by the recognition that deviations from periodicity still allow the existence of a pseudogap,[4] in which the density of photon states can be strongly suppressed.

In this Letter we show that a wide class of radiative, reactive, and dynamical processes is profoundly modified in molecular, quasimolecular, and excitonic systems having strong resonant optical transitions within a photonic band gap in a periodic structure. These effects are associated with the inhibition of the resonant dipole-dipole interaction (RDDI) due to the suppression of the photonic density of states. We show that RDDI is inhibited for any interatomic or intermolecular separation, including separations much shorter than the structure period and the transition wavelength. When there is an allowed mode in the gap, the RDDI spectral shift is shown to be comparable to the rate of spontaneous emission via this mode. The radiative width of this mode is determined by the effective quantization volume of the mode and its quality factor. All the aforementioned features can only be explained if RDDI is described in terms of quantum electrodynamics, namely, as photon exchange, even at separations that are normally held to be the domain of electrostatics. The effects considered are independent of the spatial distribution of molecular or excitonic systems in the periodic structure, because the gap suppresses the density of photonic *momentum* states. This should be contrasted with the sensitivity of inhibited spontaneous emission to the location of emitters and their polarizations in Fabry-Perot resonators.[2,6]

The RDDI matrix element is obtainable[7] from the multipolar Hamiltonian for a pair of two-level systems A and B having a common resonance frequency ω_n and separated by $\mathbf{R}$, when they share a single electronic excitation:

$$\Omega^{AB}(\omega_n,\mathbf{R}) = -\sum_{\mathbf{k}\lambda} (g_{\mathbf{k}\lambda})_A (g^*_{\mathbf{k}\lambda})_B e^{i\mathbf{k}\cdot\mathbf{R}}[(\omega_{\mathbf{k}}-\omega_n)^{-1}+(\omega_{\mathbf{k}}+\omega_n)^{-1}]$$
$$\rightarrow -\sum_{i,j} (\mu_A)_i (\mu^*_B)_j (\hbar\pi^2)^{-1} \int d\Omega_{\hat{\mathbf{k}}} (\delta_{ij}-\hat{\mathbf{k}}_i\hat{\mathbf{k}}_j) \frac{k^2\omega_{\mathbf{k}}^2 \cos\mathbf{k}\cdot\mathbf{R}}{\omega_{\mathbf{k}}^2-\omega_n^2} \frac{d\omega_{\mathbf{k}}}{d\omega_{\mathbf{k}}/dk}. \quad (1)$$

Here $(g_{\mathbf{k}\lambda})_n = (2\pi\omega_{\mathbf{k}}\mu_n\cdot\hat{\epsilon}_{\mathbf{k}\lambda}/\hbar V)^{1/2}$ expresses the coupling of the dipole moment μ_n to a field mode having frequency $\omega_{\mathbf{k}}$, wave vector $\mathbf{k}$, and polarization vector $\epsilon_{\mathbf{k}\lambda}$, and V is the quantization volume. The summation over all possible $\mathbf{k}$ and λ becomes an integral for large V, with i,j denoting Cartesian components. As for electronic band gaps,[8] the density-of-states factor $d\Omega_{\hat{\mathbf{k}}}k^2/(d\omega_{\mathbf{k}}/dk)$ in Eq. (1) vanishes on the energy surface $\omega_{\mathbf{k}}=\omega_n$ within a gap, as a result of the discontinuity of $\omega_{\mathbf{k}}$ for k at the allowed zone boundary. Contour integration about the pole then shows that the integral in Eq. (1) *vanishes independently of R.*

More insight into the suppression of RDDI for transitions within a gap may be gained by use of the alternative minimal coupling Hamiltonian (involving the vector potential), instead of the multipolar Hamiltonian. We then obtain[7]

$$\Omega^{AB}(\omega_n,\mathbf{R}) = -\sum_{\mathbf{k}\lambda} (g_{\mathbf{k}\lambda})_A (g^*_{\mathbf{k}\lambda})_B e^{i\mathbf{k}\cdot\mathbf{R}} (\omega_n/\omega_{\mathbf{k}})^2 [(\omega_{\mathbf{k}}-\omega_n)^{-1}+(\omega_{\mathbf{k}}+\omega_n)^{-1}] + V^{AB}(\mathbf{R}). \quad (2)$$

Here the purely electrostatic (R^{-3} dependent) interaction $V^{AB}(\mathbf{R})$ can be shown to be canceled by the $\omega_{\mathbf{k}}=0$ ($\mathbf{k}=0$) unretarded pole of the sum over modes, whereas the contribution of the $\omega_{\mathbf{k}}=\omega_n$ pole in this sum, which is radiative in origin, vanishes as in Eq. (1) independently of the value of $\mathbf{R}$ for ω_n in a gap.

It is surprising that the vanishing of RDDI in a gap occurs even in the electrostatic limit $k_nR\ll 1$, although this vanishing originates from index modulations on the scale $\sim k_n^{-1}$. This comes about because RDDI is mediated by photon emission from an excited atom into the structure and its reabsorption by another atom. Destructive interference of the emission, which occurs *throughout the structure,* eliminates the interaction in a gap, irrespective of the separation between the atoms and their location within the structure.

The dipole-dipole interaction matrix associated with an allowed mode within the gap with spectral width Δ, wave vector $\mathbf{k}_n$, and frequency $\omega_{\mathbf{k}}\simeq\omega_n$ is

$$\Omega_n^{AB}(\mathbf{k}_n,\mathbf{R})\simeq -V^{-1}\sum_{i,j}\frac{(\mu_A)_i(\mu_B^*)_j}{\hbar}(\delta_{ij}-\hat{\mathbf{k}}_i\hat{\mathbf{k}}_j)\cos\mathbf{k}_n\cdot\mathbf{R}\{(\omega_{\mathbf{k}}-\omega_n)\omega_{\mathbf{k}}/[(\omega_{\mathbf{k}}-\omega_n)^2+\Delta^2]\}\,. \tag{3}$$

The factor in the curly brackets tends to $\omega/2\Delta=Q/2$, where Q is the quality factor of the mode, for $|\omega_{\mathbf{k}}-\omega_n|\simeq\Delta$. For diatoms excited to a definite (Σ^* or Π^*) molecular state, the commonly valid averaging of Eq. (3) over random orientations of the internuclear axis yields the following relationship between Ω_n^{AB} and the rate of spontaneous emission via the allowed mode γ_n:

$$\langle\Omega_n^{AB}\rangle=(3\gamma_n/2\pi)[j_0(k_nR)+(\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2})j_2(k_nR)]\,, \tag{4}$$

where,

$$\gamma_n=\lim_{\mathbf{k}\to\mathbf{k}_n}\langle|g_{\mathbf{k}\lambda}|^2\rangle\frac{\Delta}{(\omega_n-\omega_{\mathbf{k}})^2+\Delta^2}\to\frac{2\pi|\mu_n|^2}{3\hbar^2}\frac{\hbar\omega_n}{V\Delta}\,. \tag{5}$$

The angle θ between the dipoles and $\mathbf{R}$ in Eq. (4) is $\theta=0$ for Σ^* and $\theta=\pi/2$ for Π^2. For $k_nR\ll 1$ we obtain the upper bound $\langle\Omega_n^{AB}\rangle\simeq 3\gamma_n/2\pi$, whereas for $k_nR\gg 1$ the interaction exhibits an oscillatory decrease with k_nR (same as of the cooperative radiative decay of diatoms in vacuum[7]). Thus, whereas for transitions outside the gap RDDI at small separations is much larger than the radiative width in vacuum, γ_{vac} (Einstein A coefficient), within the gap it is seen to be suppressed to a value smaller than the rate of radiative decay via a single allowed mode γ_n. The latter is related to γ_{vac} by

$$\gamma_n/\gamma_{\text{vac}}=\tfrac{1}{2}\pi Q(c/\omega_n)^3/V\,. \tag{6}$$

This ratio becomes small whenever the effective mode volume is much larger than the cubic wavelength multiplied by its quality factor Q. Along with the vanishing of RDDI in the absence of allowed modes, the dependence of RDDI suppression on the rate of spontaneous emission via a single mode in the gap is a salient manifestation of field quantization effects on this interaction at all separations.

A clear and readily accessible signature of RDDI inhibition is the suppression of the Forster energy transfer from an excited donor to a spectrally overlapping acceptor. This rate is proportional to[9] $\langle|\Omega_n^{AB}|^2\rangle$ and will therefore be practically eliminated if the overlapping portion of the donor emission band and the acceptor absorption band is within the gap. The resulting disappearance of the acceptor fluorescence in a spectral region outside the gap would convincingly demonstrate the predicted effect.

As a consequence of the inhibition of RDDI, potential curves of excited homonuclear diatoms will change. At internuclear separations $R\gtrsim 5$ Å RDDI accounts for most of the splitting between electronically excited states of homonuclear diatoms which correspond to the atomic $S+P^*$ states. The suppression of this interaction will *eliminate* the potential barriers or dips,[10]

$$V^{AB}({}^1\Pi_w^*)=-V^{AB}({}^3\Pi_w^*)=-w\mu^2/R^3\,, \tag{7a}$$

$$V^{AB}({}^1\Sigma_w^*)=-V^{AB}({}^3\Sigma_w^*)=2w\mu^2/R^3\,, \tag{7b}$$

where $w=+$ $(-)$ stands for g (u) parity. The four distinct states in Eqs. (7a) or (7b) will then converge energetically to a common Π^* or Σ^* curve, respectively, at the aforementioned separations, where exchange splittings become exponentially small. These two curves will approach the atomic limit as R^{-6} because of the van der Waals Σ^*-Π^* splitting. This can significantly change the dissociation thresholds in many systems. For example, the threshold of ${}^1\Pi_\mu^*$ states will be lowered by 2000 cm^{-1} in Mg_2 and Zn_2 and by 900 cm^{-1} in Li_2. In general, reduced binding (due to barrier elimination) will increase the spacing between bound vibrational levels of an excited state and decrease the number of levels, while augmented binding (due to dip elimination) will produce the opposite trend. These changes will be reflected in the appropriate emission, absorption, and Raman spectra. Biexcitonic splitting in solids[11] and the strong quasistatic broadening of atomic absorption lines[12] in gases, which are caused by RDDI, will be eliminated.

The dynamics of gas-phase collisions or dissociation proceeding through excited states of homonuclear diatoms will also be affected profoundly by changes in the potentials of these states: (1) Collisional excitation transfer between resonant spin-singlet atoms $A^*({}^1P)+B({}^1S)$ will be strongly suppressed, since its probability is $\sim\sin^2(\int\Omega_n^{AB}dt)$.[12] (2) Excitation transfer between finite-structure states, e.g., the doublet states $J=\frac{1}{2}$ and

$J=\frac{3}{2}$ in a collision between identical alkali atoms $A^*(^2P_J)+A(^2S)$ proceeds, like the dissociation of A_2^* diatoms, via dynamical mixing of two or more adiabatic quasimolecular states near their crossing or pseudocrossing points.[12] These points will now be determined only by van der Waals and exchange interactions, as in collisions between *dissimilar atoms,* and will therefore be confined to short separations, $R\lesssim 3$–5 Å, instead of $R\sim 20$–50 Å as with RDDI. Consequently,[12] the suppression of RDDI will result in a much stronger nonadiabatic character of the collisions, for a given internuclear velocity.

A brief discussion of the possible realization of the effects considered is in order. RDDI suppression can be demonstrated in colloidal three-dimensionally (3D) periodic structures. The modulation of the dielectric index required for the existence of a band gap in 3D periodic structures[3,4] can be achieved, for example, with use of titania spheres in water. Sufficiently wide gaps can be produced to suppress completely typical rovibronic Franck-Condon bands or inhomogeneously broadened atomic and excitonic bands in solids or liquids. Other structures, to be described in detail elsewhere, are 1D periodic structures enclosed in 2D resonators or 2D periodic structures in 1D Fabry-Perot resonators. In these systems it is possible to have several high-quality allowed resonator modes, while the emission into all other modes is forbidden by the band gaps of the 1D or 2D periodic structures. Such structures may consist of regularly spaced pores to allow gas-phase collisions or molecular-beam propagation.

In conclusion, we have demonstrated that RDDI would be suppressed in structures possessing photonic band gaps. This would be manifested in the suppression of the Forster energy transfer, the modifications of diatomic and biexcitonic spectra, and dissociation energies due to changes in their potentials. as well as the increased nonadiabaticity of diatomic collisional and dissociative processes involving fine-structure states.

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[1]K. H. Drexhage, in *Progress in Optics,* edited by E. Wolfe (North-Holland, Amsterdam, 1974), Vol. 12, p. 165; R. R. Chance, A. Prock, and R. Silbey, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1978), Vol. 37, p. 1.

[2]R. G. Hulet, E. S. Hilfer, and D. Kleppner, Phys. Rev. Lett. **55**, 2137 (1985).

[3]E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987).

[4]S. John, Phys. Rev. Lett. **58**, 2486 (1987); S. John and R. Rangarajan, to be published.

[5]E. Yablonovitch, Bull. Am. Phys. Soc. **33**, 421 (1988).

[6]P. W. Milonni and P. L. Knight, Opt. Commun. **9**, 119 (1973).

[7]G. S. Agarwal, *Quantum Statistical Theories of Spontaneous Emission* (Springer-Verlag, Berlin, 1974).

[8]J. P. McKelvey, *Solid State and Semiconductor Physics* (Harper, New York, 1983), Chap. 8.

[9]Th. Forster, Ann. Phys. (Leipzig) **2**, 55 (1948); D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[10]H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon, Oxford, 1971).

[11]V. M. Agranovich and R. M. Hochstrasser, *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems* (North-Holland, Amsterdam, 1983).

[12]E. E. Nikitin, Adv. Chem. Phys. **28**, 317 (1975).