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Cooperative Optical Absorption in Solids*

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A discussion is given of a mechanism for resonance energy transfer in the absorption of light by a pair of neighboring ions in a crystal, as recently demonstrated by Varsanyi and Dieke. An estimate of the probability for this process is given.

A brief discussion is given of an elegant experiment by Varsanyi and Dieke[1] demonstrating a new effect in optical phenomena, namely the absorption of one photon simultaneously by two rare earth ions. The reason why this is a remakable phenomenon is that the interaction of a radiation field with matter consists of a sum of one-electron operators $\Sigma_j \boldsymbol{A}_j \cdot \boldsymbol{\nabla}_j$; where $\boldsymbol{A}_j$ is the vector potential at the position of the j^{th} electron of momentum $(\hbar/i)\,\boldsymbol{\nabla}_j$. Thus the excitation of two atoms A and B from the ground state $\psi_0\,\varphi_0$ to the doubly excited state $\psi_a\,\varphi_b$ appears impossible– if the j^{th} electron is associated with atom A, a transition ψ_0 to ψ_a can readily be imagined at the correct energy, but in this case the orthogonality of φ_0 and φ_b will cause the total transition element (00)–(ab) to vanish; similarly if the j^{th} electron is on B.

This argument, though general, is phrased in terms of the tight binding approximation; the relevance of this description is attested to both by theoretical understanding of the nature of the transitions of the shielded inner electrons, and by the experimental fact that the observed excitation energies are accurately equal to the sums of the single-ion excitation energies.

This interesting, new, and potentially useful phenomenon can readily be interpreted in terms familiar in the field of resonant energy transfer in condensed media[2]. The description proceeds as follows[3]: We imagine all interactions among all atoms (or ions) to be exactly accounted for, except those between A and B, and that complete orthogonalization of the wave functions has been accomplished. Now we apply first order, time-independent perturbation theory for the interaction between A and B, and we find admixed to the zero-order ground state (00) some components ($a'b$) and (ab'), among others. The radiation field may then induce transitions from the small admixture of ($a'b$) to (ab) through a one-electron process on A, or from (ab') to (ab) on B. On the other hand, we may imagine the field to be applied first, inducing a virtual transition from (00) to ($a'0$) [or ($0b'$)] and then allowing the AB interaction to result in a final state of (ab).

The probability of this phenomenon clearly is determined by the strength of the interaction between A and B, and relates to the atomic symmetries involved. Multipole expansions of the interaction Hamiltonian indicate how important the effects can be in particular cases. For atoms A and B near-neighbors, and for suitable atomic symmetries, the transition probability for the double transition might be as large as 10^{-2} of that for a single allowed transition. It would be observable under much less favorable circumstances, say a factor of 10^{-8}.

When the dipole-dipole interaction between A and B vanishes, the transition probability for the double transition may or may not be reduced. When it is decreased, it is not necessarily reduced by familiar factors such as $(a_0/\lambda\!\!\!^{-})^2$, as in going from electric dipole to electric quadrupole transitions (a_0 is the atomic size, λ the wavelength of light), but only by factors $(a_0/\rho)^2$, where ρ is the atomic separation. With ρ only a few a_0, we might expect some double excitations to be even more probable than single quadrupole transitions. The energy shift from the sum of single-ion excitation energies can still remain small, even with sizeable first order interactions between A and B, since this is a second order effect.

Clearly there are many ramifications of this effect for various atomic symmetries, and this abstract is intended to call attention to the experimental observation of double excitations,

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and to indicate how first order perturbation theory can avoid the restrictions of one-electron selection rules, can remove many of the atomic selection rules, and can replace the degree of forbiddenness of transitions only by factors $(a_0/\rho)^2$ rather than $(a_0/\lambda)^2$. Exchange and overlap effects can similarly be included.

The relevance to optical pumping phenomena should be emphasized. A mechanism of this type allows the preparation of excited states of the system which effectively cannot be accomplished by single-ion transitions. It can also excite with high efficiency single-ion states which will decay selectively with low or high probability to lower states.

Another potentially useful aspect of this effect is as a "photon-splitter", *i.e.*, getting two (or more) photons of lower energy out for each photon incident. This could also have important ramifications for uv light sources.

References

1 Varsanyi and Dieke: Phys. Rev. Letters **7** (1961) 442.
2 D. L. Dexter: J. Chem. Phys. **21** (1953) 836 and references contained therein.
3 D. L. Dexter: Phys. Rev. **126** (1962) 1962.

DISCUSSION

Howard, R.: Have you considered states arising from three or more neighboring ions?

Dexter, D. L.: Yes. With second order perturbation theory, without overlap, three-ion transitions can occur in the same way. They can also occur in first order perturbation theory if overlap takes place. Naturally the probability is reduced.

Iida, Y.: Will you give us general principle to see in which cases we can find such phenomena?

Dexter, D. L.: Obviously the rare earth ions are indicated, since the effect has been observed with them, but I see no reason why any transparent medium should not serve as a host matrix, such as KCl or solid argon. With a high concentration of substitutional metals such as Na, in a medium like A, I would expect the effect to appear. What would make the effect pronounced would be sharp levels, and a lot of them, so as to be sure of finding some with suitable symmetry.