

# This Week's Citation Classic<sup>®</sup>

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**Englman R & Jortner J.** The energy gap law for radiationless transitions in large molecules. *Mol. Phys.* 18:145-64, 1970.  
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The decay rate of excited electronic states in a large molecule or of an impurity in a solid is calculated for a model of a large number of displaced harmonic oscillators. The rate depends exponentially on the energy difference ("gap") between the initial and final electronic states. [The SCI® indicates that this paper has been cited in over 435 publications.]

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I am pleased to place on record the events that led to the publication of our 1970 paper, which has become a *Citation Classic*, since some of these deserve to be widely known. I'll start in 1958 when I was a Junior Research Fellow in the physics department of Bristol University, England, working under Maurice (M.H.L.) Pryce. There are still many who recall Pryce as an *enfant terrible* in the Pauli style. Being one of the brightest boys of the OxCam school, he not only knew all about physics but had a finger in many things (too many, in his own view. Indeed, his universality of interest cost him supremacy in any one field).

Pryce brought elegance and perfection to many theories. One day he brought me his notebook containing his calculation by a normal mode-analysis method for the optical absorption line-shape by an impurity and asked me what I could do with it. It took me over 10 years to reply to this, but he pointed out on that occasion that the zero-phonon line has a finite intensity, rising out of the continuum of the spectral band. Neither of us pursued this point then, but I recalled it, with an "Oh, my!" and a sonorous tap on my head, after R.L. Mössbauer's discovery of the effect after his name, which mathematically is equivalent to the appearance of the zero-phonon line.

The ideas surfaced in me again in 1968 when I read an important paper by M. Bixon and J. Jortner. In this work they describe the decay of excitation in large molecules in terms of an initial state and a large number of nearly equi-energetic final states, without specifying the nature of the latter states. Surely, I said to myself, these are the states that come out from the normal-mode analysis, and I wrote down the formal expression for the decay rate, applying techniques also used by R. Kubo and W.E. Lamb. I also wrote to Jortner (who was abroad) describing my ideas and to the organizers of the 20th Farkas Memorial Symposium (at the Hebrew University, Jerusalem) asking them to let me speak after the paper by Bixon and Jortner. In 1969 the Farkas symposium, always an august occasion, was honored by the presence and lectures of (now Sir) G. Porter and E. Teller, but this did not deter me from imprudently rising after Jortner's lecture, presenting the normal-mode analysis formalism, and incidentally claiming that the Bixon and Jortner theory did not belong to the limit ("high-level density") that it was stated to be. On this point I was wrong<sup>1,2</sup> because of my unjustified use of a high-temperature approximation to evaluate the essentially correct formula. This was recognized during our collaboration by Jortner, who asked me to work out the low-temperature expression. This I did by a saddle point method to arrive at what is now widely known as the "energy-gap law."

Numerous confirmations of the law exist,<sup>3</sup> and its application has been considerably extended and refined by Jortner's students and coworkers in Tel-Aviv (notably, Nitzan and Mukamel). The success of the law gave me much satisfaction, and I was pleased that the subject featured in the judges' decisions to award the prestigious Israel (1982) and Wolf (1988) prizes to Jortner. Less favorable were receptions of our paper by the original referees, one of whom wanted a shortened version and the other, none at all. (In a letter to me, Jortner called the latter critique "deadly." Ultimately, we got by with amputation and plastic surgery.)

Why is the article popular? I have been told that it is among Sir Nevill Mott's<sup>4</sup> favored papers because it explains things in simple terms.

1. Englman R. Estimation of matrix elements in radiationless transitions. *Isr. J. Chem.* 7:221-5, 1969. (Cited 2 times.)
2. Jortner J & Bixon M. Radiationless transitions in polyatomic molecules. *Isr. J. Chem.* 7:189-220, 1969. (Cited 5 times.)
3. Kivelson S & Wu W-K. Photoproduction in neutral soliton pairs in trans-(CH)<sub>n</sub>. *Phys. Rev. B—Condensed Matter* 34:5423-9, 1986.
4. Mott N F, Davis E A & Street R A. States in the gap and recombination in amorphous semiconductors. *Phil. Mag.* 32:961-96, 1975. (Cited 445 times.)