

McRae E G. Theory of solvent effects on molecular electronic spectra. Frequency shifts. *J. Phys. Chem.* 61:562-72, 1957.
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The paper gave formulas relating the electronic absorption spectra of molecules in solution to the corresponding gas-phase spectra. [The SC1® indicates that this paper has been cited in over 505 publications.]

Solvation Effects in Molecular Spectroscopy

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July 15, 1988

My paper originated in an undergraduate student project at the University of Western Australia. The four-year bachelor-of-science course required a piece of research and a thesis. My major was physical chemistry, and my research topic was the "solvent effects" on the visible and near-ultraviolet absorption spectra of organic molecules, that is, the differences between the spectra of the same molecule in dilute solution in different solvents. I was one of the several students to work on these solvent effects. The program was initiated and supervised by Noel S. Bayliss, the chairman of the chemistry department. Bayliss devoted a great deal of thought and effort not only to his research speciality—molecular spectroscopy—but also to the teaching of chemistry at all levels. The solvent-effect program was well chosen from an educational viewpoint. Besides giving students some practical experience at minuscule cost, it neatly illustrated some of the things we were learning about in class: the solvent-induced frequency shift of an electronic absorption band derives from the difference between the solute-solvent interaction energies for the ground and excited states of the solute; these interactions derive chiefly from the dispersion forces and the permanent molecular dipole forces, together with hydrogen bonding; the electrostatic field at the solute, attributable to hydrogen bonding or to the permanent dipoles of the solvent molecules, is the same in the ground and excited states (the Franck-Condon principle).

We observed a variety of solvent effects, ranging from a ubiquitous, small "red shift" (a solvent-induced displacement of the absorption band to lower frequency relative to the vapor spectrum) to much larger, superimposed red or blue shifts for polar molecules in polar solvents. As a rule the magnitudes of these

superimposed shifts increased with increasing solvent polarity, but one interesting exception was known at the time: for highly polar merocyanine dyes dissolved, for example, in acetone-water mixtures, the incremental shift on making the solvent more polar by adding water was first to the blue and subsequently to the red.

For the most part, the origins of these frequency shifts seemed easy enough to understand semiquantitatively on the basis of dipole and hydrogen-bonding interactions, but there were a couple of facts that did not fit into the simplest picture. One problem was that while the small red shift had already been explained by Bayliss as due to the dispersion forces, the theoretical expression he derived indicated a far stronger dependence on the intensity of the transition than was actually observed. The other inconvenient fact was the nonmonotonic behavior of the merocyanines.

When I went to Florida State University for graduate study in physical chemistry, I found that my supervisor, Michael Kasha, knew a lot about solvent effects and was using solvent effects to distinguish between different kinds of electronic transitions. With Kasha's encouragement I continued to think about frequency shifts and finally managed to fit all the facts into a consistent pattern. The Bayliss formula^{1,2} for the dispersion red shift was basically right for strong transitions, but for weak transitions it failed to take account of the indirect effect of other, stronger transitions. The nonmonotonic dependence of merocyanine spectra on solvent polarity was explained by the superposition of effects of the permanent-permanent and permanent-induced dipole interactions. These interactions induce shifts in opposite directions and with different dependences on solvent polarity.

My paper describing these results was the first for which I was responsible, and I soon left the field of molecular spectroscopy. Until recently, I was not aware that my paper had been cited often. I do not know why it should have been, and I am reluctant to check lest it has been found a particularly instructive example of some egregious error. But I am pleased that my student effort has proved worthy of citation, whatever the reason may be, and I am grateful to Bayliss and Kasha for setting me on the path to worthwhile effort in research.

[Editor's note: A recent article citing this Citation Classic is reference 3.]

1. Bayliss N S. The effect of the electrostatic polarization of the solvent on electronic absorption spectra in solution. *J. Chem. Phys.* 18:292-6, 1950. (Cited 275 times.)
2. Bayliss N S & McRae E G. Solvent effects in organic spectra. Dipole forces and the Franck-Condon principle. *J. Phys. Chem.* 58:1002-6, 1954. (Cited 350 times.)
3. Johnston K P & Haynes C. Extreme solvent effects on reaction-rate constants at supercritical fluid conditions. *AIChE J.—Amer. Inst. Chem. Eng.* 33:2017-26, 1987.

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