

This Week's Citation Classic

Smith M & Symons M C R. Solvation spectra 1. The effects of environmental changes upon the ultra violet absorption of solvated iodide ions. *Trans. Faraday Soc.* 54:338-45, 1958; and, Solvation spectra 2. The nature of the electronically excited state of solvated iodide ions. *Trans. Faraday Soc.* 54:346, 1958. [University of Southampton. England]

The charge-transfer-to-solvent (CTTS) ultraviolet absorption band for iodide ions is markedly dependent upon solvent, added electrolytes, and temperature changes. These shirts are interpreted using an "electron in a box" theory for the outer regions of the excited state, and on the assumption that the cavity radius is a controlling factor. These confined excited states are compared with the ground states for solvated electrons. [The *SCI*[®] indicates that these papers, taken together, have been cited in more than 220 publications.]

Studies of Solvation Using Spectroscopy

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When I moved to a lectureship at the University of Southampton from an elementary chemistry teaching post at Battersea Polytechnic in 1953, I had very little research training and an open mind. However, I had one wide aim—to "look and see." For example, carbonium ions and free radicals were widely postulated, but no one seemed to be interested in "seeing" them. I managed to get a UV spectrometer that I thought might "see" carbocations, and I found a colleague with an ESR spectrometer that I thought might "see" radical intermediates.

Another area of great activity was ion pairing and ionic solvation—many theories and measurements, but no direct studies. Iodide ions have an intense absorption band in the UV, so maybe we could "see" them solvate and form ion pairs? Changing temperature and solvent caused dramatic shifts, and my first PhD student, Mike Smith, thoroughly enjoyed himself obtaining, and trying to rationalize, a wide range of results.

In the second paper, we used a simple particle-in-a-box theory to suggest that the excited electron was considerably "bonded" by the first layer of solvent molecules in an s-like orbital (closely resembling, in our view, the ground state of a solvated electron¹). We called such transitions "charge-transfer-to-solvent" and the initials CTTS have, to my delight, become common usage.

I think this was the first attempt to study solvation directly, using spectroscopy. Since then, we have used IR, Raman, NMR, and ESR methods to help shed light on solvation and ion pairing, with, in many cases, quite definitive results.^{2,1} I wish that these were used more widely than they are to help unravel less direct information, especially in the field of thermodynamics. In these studies, the importance of hydrogen bonding to anions became clear. This was strongly supported by combined IR and NMR studies that have enabled us to assign separate spectra to dipolar species forming one to three H-bonds,³ and, for weakly basic solutes, IR line-broadening has been observed that can lead to estimates of lifetimes in the 10⁻¹² range.⁴ Overtone infrared studies on 2u(OH) for HOD and for various alcohols have also supported these results and have led to the important concepts of specific (OH)_{free} and (lone-pair)_{free} units having high reactivity.⁵

Many groups now use spectroscopic techniques for studying solvation, and this must be why our early papers are widely cited, although I am surprised—and delighted—that they have done so well. I already realized, via this journal's study,⁶ that my work, as a whole, is highly cited. However, this is partly because of my high publication rate. It is satisfying to know that individual papers also rank highly.

My research interests have recently veered strongly into biology—a shift that is giving me huge excitement coupled with an overriding sense of awe.

The R. A. Robinson Memorial Lectureship of the Royal Society of Chemistry was given to me in 1987 because of our spectroscopic studies of solvation.⁷

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2. Infrared and NMR studies of probes in binary solvent systems. *Pure Appl. Chem.* 58:1121-32, 1986.
3. Eaton G & Symons M C R. Spectroscopic studies of the solvation of N,N-dimethyl amides in pure and mixed solvents. *J. Chem. Soc. Faraday Trans. 1* 84:3459-73, 1988.
4. Eaton G, Pena-Nunez A S, Symons M C R, Ferrario M & McDonald I R. Spectroscopic and molecular dynamics studies of solvation cyanomethane and cyanide ions. *Faraday Discuss. Chem. Soc.* 85:237-53, 1988.
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6. Garfield E. The 1,000 contemporary scientists most-cited 1965-1978. Parts 1, 2A, and 3. *Current Contents* (41):5-14, 12 October 1981; (9):5-13, 1 March 1982; (27):5-20, 5 July 1982. [Reprinted in: *Essays of an information scientist*. Philadelphia: ISI Press, 1983. Vol. 5, p. 269-78; 428-36; 591-606]
7. Symons M C R. Liquid water—the story unfolds. *Chem. Brit.* 25:491, 1989.

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