Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Charge-Transfer Spectra

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To cite this article: Robert S. Mulliken (1985): Charge-Transfer Spectra, Molecular Crystals and Liquid Crystals, 126:1, 1-7

To link to this article: http://dx.doi.org/10.1080/15421408508084149

Mol. Cryst. Liq. Cryst. 1985, Vol. 126, pp. 1-7
0026-8941/85/1261-0001/$15.00/0

Printed in the United States of America

CHARGE-TRANSFER SPECTRA

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When I learned that one of my areas of research had been selected for review at a symposium in this memorable meeting of the chemical societies of the Pacific basin nations, I, of course, felt very honored. I also felt very appreciative of the efforts of all those who have arranged it, notably, Professor Jiro Tanaka of Nagoya University, and Dr. Edward Engler of the IBM Research Laboratory at San Jose, California.

I had hoped that I could be in Honolulu for the occasion and was eager to meet old and new friends there, but I finally concluded, very regretfully, that the trip would be somewhat too strenuous. I have, therefore, asked Dr. Saburo Nagakura to read the talk that I would have given. He is an old friend whom I have often met on trips to conferences in America, and again in Japan, where he has frequently been very kind to me. In 1956-57, he himself spent some time in research at the Laboratory of Molecular Structure and Spectra in Chicago on molecular complexes, first making a thorough study of the triethylamine-iodine complex, and its spectrum: J. Am. Chem. Soc., 80, 520 (1958). Since that time he has often helped me in recommending Japanese scientists who might come to Chicago to work with me.

In my research at Chicago, I have had the cooperation of a group of physicists and chemists, including postdoctoral research associates, visiting professors, and students. One day my secretary at the time, Mr. Harvey Brimmer, a philosophy student, suggested that the group ought to have a name. So I called it the Laboratory of Molecular Structure and Spectra (abbreviated LMSS), operating within the Physics Department. Later I went over to the Chemistry Department because the spectroscopic work on molecules, although initiated by physicists, is now a field which belongs to Chemistry (or Chemical Physics).

I have long had several favorite molecules. One is iodine. My interest was, at first, in individual molecules, or one might say molecules in the vapor or gaseous state. One day, in looking over the abstracts of papers to be presented in the 1948 Spring meeting of the National Academy of Sciences in Washington, D.C., I was attracted to one by Benesi and Hildebrand, on a new absorption spectrum obtained when iodine is dissolved in benzene. Professor J.H. Hildebrand of the University of California, Berkeley, had long been an authority on the properties of solutions, and had noted, among other things, evidence that some pairs of molecules in solution stick together, forming complexes. In particular, electron donor and acceptor molecules associate as complexes. Among other complexes, iodine molecules give violet colored solutions in some solvents, brown solutions in others. This can be explained if the iodine molecules are essentially free in the violet solutions (e.g., in hexane), but in the brown solutions are in complexes with the iodine molecules as acceptors and the solvent molecules as donors. Many years ago, Hildebrand published papers along these lines

When I saw Professor Hildebrand at the National Academy of Sciences meeting, I told him of my interest in the new Benesi-Hildebrand spectrum, and said, "I bet I can explain that spectrum." Before long I published a paper in which I proposed that the spectrum is a new benzene molecular spectrum somehow created by the proximity of the iodine molecule. This was really nonsense, as I realized later. Now it so happened that the American Chemical Society had asked Hildebrand to arrange a symposium at Chicago on spectra such as this one, and he asked me to present a paper. I now set to thinking again and prepared a new paper with a modified explanation which, sad to say, was no better than the previous one. However, as I worked on the proof of the manuscript for publication, I did more agonizing and arrived at a totally new explanation which has turned out to be correct.

Before sending off the proof, I added it to the paper as a "Note added in proof". I now identified the Benesi-Hildebrand spectrum as an "intermolecular charge-transfer spectrum" of a benzene-iodine molecular complex resulting from partial transfer of an electron from the benzene to the iodine partner within the complex, which I called a "Charge-transfer Complex". (I don't remember now why I spoke of charge transfer rather than electron transfer.) I reasoned that the benzene and iodine molecules were held together in the ground state of the complex by a small amount of charge transfer, as contrasted with a nearly complete transfer in the spectroscopically excited charge-transfer state of the complex.

Subsequently, I wrote a detailed paper on the theory of charge transfer (CT) complexes and their spectra, and discussed the application of this theory to existing experimental data for a number of systems which could be identified as containing such complexes. After this, we at LMSS and others elsewhere, undertook extensive new experimental studies with molecule-pairs which form CT complexes.

Some years later (1961) Professor G. Briegleb of the University of Wurzburg published a comprehensive book on the subject, including extensive work done by him and his students. He dedicated the book to me. However, the title of his book was "Electron-Donor-Acceptor Complexes". In choosing this title, he recognized that my use of the term "charge transfer complexes" was really not appropriate because in the ground state there is usually only a little electron transfer. On the other hand, the name "charge-transfer state" is highly appropriate for the excited state, in which nearly a complete transfer of an electron has occurred. Likewise, for the spectrum corresponding to the transition from the ground state to the CT state, the term "charge-transfer spectrum" is well justified.

The work on EDA (Electron-Donor Acceptor) complexes was carried on in LMSS at Chicago's Physics Department for a number of years through the cooperation of a succession of research associates and pre-Ph.D. students. In connection with this work, I developed a systematic classification of electron-donors and acceptors. In describing complexes, I sometimes used the concepts of inner and outer complexes. Another classification was that of two-way EDA complexes, where each partner in a complex functions simultaneously as a donor and as an acceptor.

Related to the CT spectra of complexes is the observation that pairs of molecules more in contact and not bound in a stable complex often give rise to CT spectra. Dr. L.E. Orgel and I called these contact CT spectra in a paper published in J. Am. Chem. Soc., 79, 4839 (1975). Orgel and I discussed writing a book together on EDA complexes and their spectra, but we did not do this. I think because our writing styles proved too dissimilar.

Later (in 1969) Willis Person and I published "Molecular Complexes: A Lecture and Reprint Volume". Professor Person, earlier at the

University of Iowa and now at the University of Florida had spent much of 1955 and 1956 at Chicago. In the fall of 1965 I gave a lecture course on molecular complexes and their spectra with the cooperation of Professor Person. He wrote up the lectures. Jointly edited and with some revisions, they are presented in the book just mentioned. The book also contains LMSS and other published papers on DA complexes and their spectra.

The work at LMSS was for a long time on complexes dissolved in inert solvents. However, the theory I had used to interpret the experimental data really applies just to isolated, that is vapor state complexes. In particular, mixtures of aromatic hydrocarbons (e.g., p-xylene) and TCNE (tetracyanoethylene) were studied and strong CT spectra were observed. The gas-phase CT spectra are 3-20 times weaker than the corresponding solution spectra. Also, they are shifted 700-3,000 cm^{-1} to shorter wavelengths. Mr. Kroll also obtained similar results on iodine complexes of dimethylsulfur and other thio compounds. With this work, published in J. Am. Soc., 90, 1097 (1968), as a thesis, Mr. Kroll received a Ph.D. in chemistry. (Similar work has been done since in other laboratories.)

Following is a list of people who worked at LMSS on molecular complexes and their spectra:

Dr. Saburo Nagakura, Professor, University of Tokyo, on leave 1955-56.

Dr. H. Tsubomura, University of Tokyo, on leave 1959-60. Now at Department of Synthetic Chemistry, Faculty of Fundamental Engineering, Osaka University.

Dr. Akira Kuboyama, on leave 1962 from the Government Chemical Research Institute, Tsukuba.

Dr. Michiya Itoh, Research Associate 1968-69 now at Kanazawa University.

Dr. Ichiro Hanazaki, Research Associate 1969-70, now at the Institute for Molecular Science

Professor C. Reid, on leave from University of British Columbia, 1952-53.

Joe S. Ham, AEC predoctoral fellow, 1951-53. Later Ph.D. in physics.

Robert P. Lang, 1960-62, later Ph.D. in chemistry.

Dr. Jane Peters, on leave 1960-61 from Royal Holloway College, University of London.

Dr. Harden McConnell, National Research Council Postdoctoral Fellow, 1950-52, New Professor, Stanford University.

Dr. Leslie E. Orgel, Research Associate, 1955-56, from England, now at Research Institute, La Jolla, California.

Dr. J.N. Murrel, Commonwealth Fund Fellow, 1956-57.

Dr. K.H. Hausser, on leave 1956-57 from the Max Planck Institute fur Medizinische Forschung, Heidelberg.

Dr. P.A. De Maine, postdoctoral research associate, 1955-56.

Marvin Kroll, predoctoral research assistant, 1967-68, later Ph.D. in chemistry.