# This Week's Citation Classic

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**McClure D S.** Tripletsinglet transitions in organic molecules. Lifetime measurements of the triplet state. *J. Chem. Phys.* **17**:90513 1949.
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**The lifetimes of phosphorescence of a wide variety of organic molecules in rigid organic glasses at 77°K were measured. The effect of heavy atoms on the decay times was demonstrated, thus securely identifying the phosphorescence as a triplet to singlet transition. The long lifetimes of the aromatic molecules were shown to be anomalous. [The *SCI*® indicates that this paper has been cited over 450 times since 1961.]**



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"The paper showed what factors control the phosphorescence lifetimes of organic molecules, and it gave a considerable number of measured values for comparison with the theory. The 'atomic number effect' was demonstrated for the first time. Phosphorescence is now known to be a radiative triplet to singlet transition and is nominally forbidden because an electron spin must be reversed in the process. It only becomes permitted to the extent that spinorbit coupling causes a breakdown of the distinction between triplet and singlet states. This breakdown is larger the larger the atomic number of the heaviest atom in the electronically excited system; hence the atomic number effect. The existence of this effect constitutes a good proof that phosphorescence is indeed a triplet to singlet transition.

"Knowing what the tripletsinglet decay times should be enabled me to realize that the aromatic molecules had anomalously long lifetimes. These were explained in a later paper by me[1] and in one by Mizushima and Koide.[2]

"This paper was based on my PHD thesis and the work was done in the department of chemistry at the University of California at Berkeley during 1946 and 1947. When I arrived at Berkeley, I decided in the first week that I wanted to do my work with G. N. Lewis. Michael Kasha had finished his PhD with Lewis by that time and was Lewis' righthand man. He became very important to me especially as Lewis died only a few months later. George Gibson took over the group and became a beloved and inspiring leader. Michael suggested that it would be important to measure the lifetimes of the phosphorescence of molecules. The famous Lewis and Kasha papers had already been published, and I remember reading them when they first appeared.[3,4] The Gibson group, Robert Nauman (now at Louisiana State University), Michael Kasha (Florida State University), Harrison Shull (provost at Rensselaer Polytechnic Institute), and I, met weekly with Gibson. I remember lively discussions, wild ideas, and careful study of fundamentals, including a detailed study of Wigner's *Gruppentheorie* in the original German edition.

"An important contribution to the paper was made by David Bohm of the physics department, who taught the Gibson group about spinorbit coupling in atoms.

"Another important factor was the chemistry department's organic storeroom which was stocked with chemicals from all major suppliers and was open to graduate students for browsing. Equally important at the start was the excellent shop run by Joe Martin, which turned things out in days, not weeks.

"This paper is cited for several reasons: it gave a large amount of good data; the data led to simple theoretical ideas which permitted estimates in new cases; and there were many halfbaked ideas for others to improve on."


1. **McClure D S.** *J. Chem. Phys.* **20**:682-6, 1952.
2. **Mizushima M & Koide S.** *J. Chem. Phys.* **20**:765-9, 1952.
3. **Lewis G N & Kasha M.** *J. Amer. Chem. Soc.* **66**:2100-16, 1944.
4. .....*J. Amer. Chem. Soc.* **67**:994-1003, 1945.