This Week's Citation Classic

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Strickler S J & Berg R A. Relationship between absorption intensity and fluorescence lifetime of molecules. *J. Chem. Phys.* **37**:814-22, 1962.
[Dept. Chemistry and Lawrence Radiation Laboratory, Univ. California, Berkeley, CA]

A formula is derived for calculating the radiative lifetime of a molecule from its absorption and emission spectra. Spectra are shown for seven organic molecules in soluion, experimental fluorescence lifetimes are reported, and the calculated and observed lifetimes are shown to agree well. [The *SCI*® indicates that this paper has been cited over 400 times since 1962.]

Stewart J. Strickler
Department of Chemistry
University of Colorado
Boulder, CO 80309

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"In February 1961, I arrived in Berkeley for postdoctoral study with Kenneth Pitzer. I started on a different project, but I also discovered that in the lab next door was a fluorescence lifetime apparatus. This was a phase-shift device constructed by Leo Brewer and his students following an earlier design by Rollefson.[1] Bob Berg, then a graduate student, had worked on the apparatus for a year and finally had it working well. He was just then trying to decide what systems to study.

"Earlier, as a graduate student with Michael Kasha, I had become interested in the nature of radiationless transitions in molecules. It occurred to me that a comparison of measured fluorescence lifetimes with lifetimes calculated from absorption intensities could provide a way to study radiationless processes competing with fluorescence. I suggested such a study to Berg and to Pitzer and Brewer, and they agreed.

"Like every student of radiation and matter, I had learned about Einstein's A and B coefficients[2] which relate fluorescence lifetime to absorption intensity in a twolevel system, i.e., an atom. I had naively assumed that Einstein's relation was all we needed for the calculation. But I soon realized that it was not applicable to molecules because they had many rotational and/or vibrational levels associated with each electronic state. However, I was able to work out a way to sum over these levels. This gave me a modification of Einstein's equation which I believed would be a good approximation for molecules.

"Berg and I then set out to test the relationship. We chose seven organic compounds known to have fluorescence quantum yields close to unity, calculated their fluorescence lifetimes, measured their lifetimes experimentally, and compared the values. We found quite good agreement between calculation and observation. The results were reported in the paper described here.

"I felt that several people had doubted whether the lifetime apparatus could actually give accurate results. The agreement we found relieved those doubts, and other lifetime studies were then undertaken. My collaboration with Berg ended at that point. I moved to Houston to continue working with Pitzer, who had become president of Rice University. Berg finished his graduate work with more lifetime measurements. After teaching at Washington University for a few years he decided to change fields, and is now practicing law in San Francisco.

"I think that this paper has been widely used because it gives a simple way to calculate the radiative lifetime or rate constant for emission from easily measured quantities for molecules whose actual lifetimes may be difficult to measure. The equation is derived in the approximation that the transition moment is independent of nuclear coordinates. This is usually a good approximation. A modified equation[3] can be used if the approximation is not valid, but it is more difficult to apply."

1. **Balley E A, Jr. & Rolleison G K.** The determination of the fluorescence lifetimes of dissolved substances by a phase shift method. *J. Chem. Phys.* **21**:1315-22, 1953.
2. **Einstein A.** Zur Quantentheorie der Strahlung. *Physik. Z.* 18:121-8. 1917.
3. **Strickler S J, Vikesland J P & Bier H D.** $^3B_1$—$^1A_1$, transition of SO_2 gas. II. Radiative lifetime and radiationless processes. *J. Chem. Phys.* 60:664-7, 1974.