

# This Week's Citation Classic

Hutchison C A & Mangum B W. Paramagnetic resonance absorption in naphthalene in its phosphorescent state. *J. Chem. Phys.* 29:952-3, 1958; and, *J. Chem. Phys.* 34:908-22, 1961. [Enrico Fermi Institute for Nuclear Studies and Department of Chemistry, University of Chicago, IL]

Electron paramagnetic resonance (EPR) spectroscopy unambiguously identifies the triplet state ( $^3B_{2u}$ ) as the source of the phosphorescence of naphthalene molecules. The measured zero-magnetic field energy splitting of its three components has the value expected due to dipole-dipole interaction between the two spin-parallel electrons. [The *SCI*<sup>®</sup> indicates that these papers have been cited in more than 225 and 350 publications, respectively.]

## The Triplet Nature of the Phosphorescent State

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Billy W. Mangum came to our laboratory and joined in our search for the EPR spectrum of the metastable molecular species responsible for the well-known, long-lived phosphorescence of aromatic molecules following their irradiation with ultraviolet light. At that time, there had already been a very considerable effort devoted to this problem in our laboratory as well as by many workers elsewhere. All this research activity had its origins in the 1941 suggestion by G.N. Lewis<sup>1</sup> and his school at Berkeley, that among the possibilities for a source of the phosphorescence was a metastable triplet electronic state of the irradiated molecule. A. Terenin,<sup>2</sup> in 1943, was the first to claim very firmly that experimental and theoretical evidence indicated that the emitting species was a normal molecule in a triplet state, not a photoionized molecule, an isomer of the normal molecule, or any of the many other species proposed by numerous workers.

Lewis and M. Calvin,<sup>3</sup> in 1945, irradiated fluorescein in boric acid glass. In an extremely sensitive experimental measure-

ment, they observed light-induced reversible paramagnetism. Ten years later, D.F. Evans<sup>4</sup> showed that this paramagnetism decayed at the same rate as the phosphorescence and thus was a property of the light-emitting species or its precursor.

There was a general unwillingness to accept the view that the origin of the phosphorescence was the triplet state molecule because EPR spectroscopy, first observed by E.K. Zavoisky<sup>5</sup> at almost the same time as the Lewis and Calvin experiment, afforded the ideal tool for observing and identifying a paramagnetic species. However, for 13 years, researchers had failed to find one. In fact, in June of 1958, four months before our first publication appeared, A. Jablonski<sup>6</sup> (of "diagram" fame) published a strong and reasonable argument for a nonparamagnetic singlet state origin. When, much later, I visited E.V. Shpolski (of "matrix" fame) in Moscow, he told me of his support of the triplet state idea in arguments with Jablonski that resulted in a wager concerning the eventual outcome—the winner to receive a case of wine. When, shortly after that, Shpolski read Billy's and my paper, he telephoned Jablonski and the wine soon arrived. As a reward for our help, Shpolski presented me with an inscribed copy of his *Atomnaia Fizika*.<sup>7</sup>

Our experiment succeeded in identifying the triplet state origin because we studied naphthalene molecules held in a small number of known orientations in the external field in a durene crystal, a system devised by McClure for optical work. Previous EPR work had examined randomly oriented molecules in glasses in which the anisotropic interaction of the two electrons resulted in insufficient intensity for detection at any given field value.

The reasons for the continuing<sup>8</sup> citations of this early work are the eventual importance of aromatic triplet states in many fields of chemistry and solid state physics.

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3. Lewis G N & Calvin M. Paramagnetism of the phosphorescent state. *J. Amer. Chem. Soc.* 67:1232-3, 1945.
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7. Shpolski E V. *Atomnaia fizika*. Moscow. Gozgizd-votis-mats lit. 1963.
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