

The Triplet State

An Example of G. N. Lewis' Research Style

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In the last two years of his life, between the ages of 68 and 70, Gilbert N. Lewis brought to fruition and focus his long-germinating ideas on the triplet states of molecules. I had the great fortune to be his collaborator in this research. These researches, published in two papers in the *Journal of the American Chemical Society* in 1944 and 1945, were destined to have a profound effect on the course of the subsequent development of molecular spectroscopy and photochemistry. However, the influence was not instantaneous, since more than a decade was required to overcome the negative pressure of prestigious opponents (Franck, Teller, Livingston, Rabinowitch) and to unravel the complexities and misunderstanding of earlier research.

In this presentation I shall examine in retrospect the background of ideas against which Lewis' last researches were done, report my personal interactions with him in the hope of revealing his personality and *joi de vivre*, reflect on some general observations and views of Lewis on the conduct of scientific research, give an analysis of a unique habit of Lewis' writing of *research previews*, and indicate through his personal research memoranda to me his intensity of research interest and activity in the last years of his life.

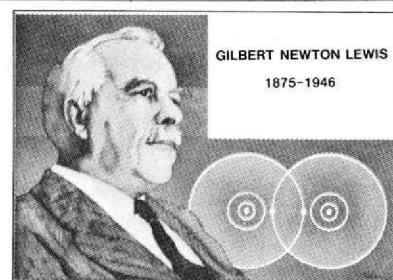
Historical Perspective on Molecular Triplet States

A spectroscopist today is easily baffled by any indication that observing triplet states of organic molecules constitutes in any way a difficulty or a mystery or puzzle. The evolution of the observations and understanding of polyatomic molecule singlet-triplet transitions took a quite different path than the development of atomic and diatomic spectroscopy. The knowledge of the latter subjects led Sponer and Teller (1941) (1) to the view

As in the case of atoms we have, in first approximation, the selection rule that only states of the same multiplicity combine with each other. Intercombinations occur with appreciable intensity only if the molecule contains some heavier atoms.

Such a background sets the stage for the expectation that in molecules with low *Z* (or "light") atoms, such as C, N, O, and H, no singlet ↔ triplet transitions are to be observed. Here we can state at once the origins of the dilemma

- (1) Radiationless transitions are essentially absent in atoms and diatomic molecules and are known today to be simply the common phenomenon in polyatomic molecules; thus, in polyatomics a prevalent mode of excitation of highly forbidden states (e.g., triplets) is abundantly available.
- (2) The terms "high intensity" and "high transition probability" carry an implication of a direct correlation. But "intensity" of emission is measured by quantum yield, so that "forbidden" triplet state of low transition probability (measured by long mean lifetime) can be observed with high "intensity" (measured by high quantum yield) in polyatomic molecules.
- (3) The original observations on phosphorescence emission of organic molecules were made for rigid glass solutions (organic solvent mixtures frozen to glass at 90 K or 77 K). Most of the early interpreters of the phosphorescence phenomena of organic molecules were preoccupied with "clamping of unusual conformations (tautomers) by the rigid glass medium"—which in those days seemed so essential to the observation of the long-lived luminescence.



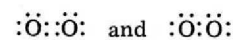
Confusion concerning the three items just mentioned abounds in the literature before 1944 and had a considerable momentum afterward. We shall examine some of the key contributions to the general background in the various authors' own words and diagrams to indicate the gradually developing tapestry of uncertainty against which the work that Lewis and I published in 1944 was hung.

G. N. Lewis on Triplet Ethylene and Singlet Oxygen

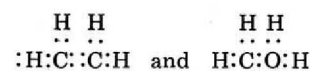
Lewis began to think about electron arrangements in ethylene and molecular oxygen on the basis of electron pairing long before any other researcher, as a consequence of his early electronic structure models. Because ethylene triplet and oxygen molecule singlet states are so intertwined with general thoughts about the triplet states of molecules and their quenching (involving singlet molecular oxygen), it is of interest to cite Lewis' developing ideas on these species.

In his 1916 paper, "The Atom and the Molecule" (2), Lewis states in considering interactions of oxygen and ethylene

These two forms of oxygen (which of course may merge into one another by continuous graduations) can be represented as



and the two forms of ethylene as



These are clear Lewis electron-dot representations of singlet and triplet arrays for the molecules. A later statement (1924) clarifies the issue of their representing discrete states

The enormous difference in magnetic properties between the oxygen molecule and other molecules to which we attribute double bonds seems to support the idea that the change from a non-magnetic to a magnetic molecule is not a gradual process, but that the molecule must possess at least one unit of magnetic moment or no magnetic moment at all.

This paper (3) is titled "The Magnetochemical Theory" and was the first to present in effect an electron spin restriction on molecular interaction, a topic very much alive today. Lewis did not speculate on the spectroscopic implications of his normal and "diradical" configurations.

H. Kautsky: Sensitization Mechanisms by Molecular Metastable States and by Singlet Oxygen

The German photochemist Kautsky wrote a long series of qualitative papers which reported ingenious experiments describing metastable excited states involved in photosensitization processes.

Metastable states of molecules were cited in one series of papers (4) in which Kautsky, et al. demonstrated effectively that sensitization of molecules (energy transfer) by *dyes* is facilitated by aggregation of the dye molecules. Kautsky mistakenly thought that aggregation was a *necessary* precondition for metastable state excitation, failing to distinguish between *intrinsic* metastable state excitation and *induced*

metastable state excitation. The nature of the metastable state of dyes adduced by Kautsky was not alluded to. His diffuse writings, merging many discrete phenomena and interpretations, had no diagrams or quantitative data.

Singlet molecular oxygen was cited by Kautsky et al. (5) in another series of papers in which the excited singlet molecular oxygen species, generated by energy transfer from metastable states of dyes, were considered the active intermediate in photooxidation. This interpretation was lost until its recent belated and fiery revival (6-8).

Singlet-Triplet Spectrum of Ethylene

In an early paper (9) C. P. Snow and C. B. Alsopp presented a seemingly authentic weak absorption spectrum of various ethylenes, interpreted as representing the singlet-triplet absorption. This observation escaped particular attention at the time and proved to be ten times too intense to be genuine (10). The singlet-triplet absorption was found by C. Reid in 1950 (11), the extraordinarily weak absorption observed from 31,000 to 37,000 cm^{-1} at 120 K requiring a 1.4-m path of liquid ethylene.

Robert Mulliken visited Berkeley sometime in 1942 and gave a talk about molecular orbitals of ethylene. G. N. Lewis told his research student Jacob Bigeleisen¹ afterwards, "You know, those triplet states that Mulliken was talking about in ethylene are probably the phosphorescent state." So Lewis had triplet states of organic molecules like ethylene very much on his mind.

Jablonski Diagram for the Lowest Metastable State of Dyes

Jablonski, the Polish theoretical physicist, published an interpretation (12) of some of the Kautsky observations on the metastable states of dyes and other known physical observations on dye-phosphors (dye molecules dissolved in sugar glasses and boric acid glasses). He ignored the aggregation phenomena which confused Kautsky and treated only the intrinsic properties of dye molecules. A replica of his diagram

is labelled I in Figure 1. His states are labelled *N*, normal; *F*, fluorescent; *M*, metastable. Jablonski could never accept the *M* state as a triplet state, and even as late as 1958 (13) he still tried to account for this state as a singlet excited state of low probability! Key quotations from his first papers (12) clearly reveal the concepts of (1) an intrinsic electronic metastable state, and (2) attempts to interpret the forbiddenness of transitions by multipole or other than singlet-triplet mechanisms:

We assume in the case that an "energetically isolated" dye-molecule is phosphorescence-capable, then there must exist in this molecule at least one metastable level.

The transition between the ground level *N* and the metastable level *M* can occur only with small probability (as for example by forced dipole radiation or quadrupole radiation). If there exists somewhat above the level *M* and unstable level *F*, which combines with the ground level *N* (only this case will be discussed in detail here), then will the level *M* in greater part be reached by a detour through *F*.

Jablonski was entirely concerned with the mechanism of *photoluminescence processes of dyes*, stressing a kinetic derivation of the thermal activation of the *F* (fluorescent) level from the *M* (metastable) level. It could be said that his treatment would not apply to polyatomic (non-dye) molecules in general, since the large excited singlet-triplet energy gap would preclude Jablonski's kinetic treatment, aside from his failure to accept the triplet designation of the metastable state of molecules. Later use of the "Jablonski Diagram" fails to recognize the limitations of his interpretations.

Franck and Livingston Tautomeric Metastable Model

The use of glassy media and adsorbed states in the study of the phosphorescence of dye molecules was a major preoc-

¹ Personal communication.

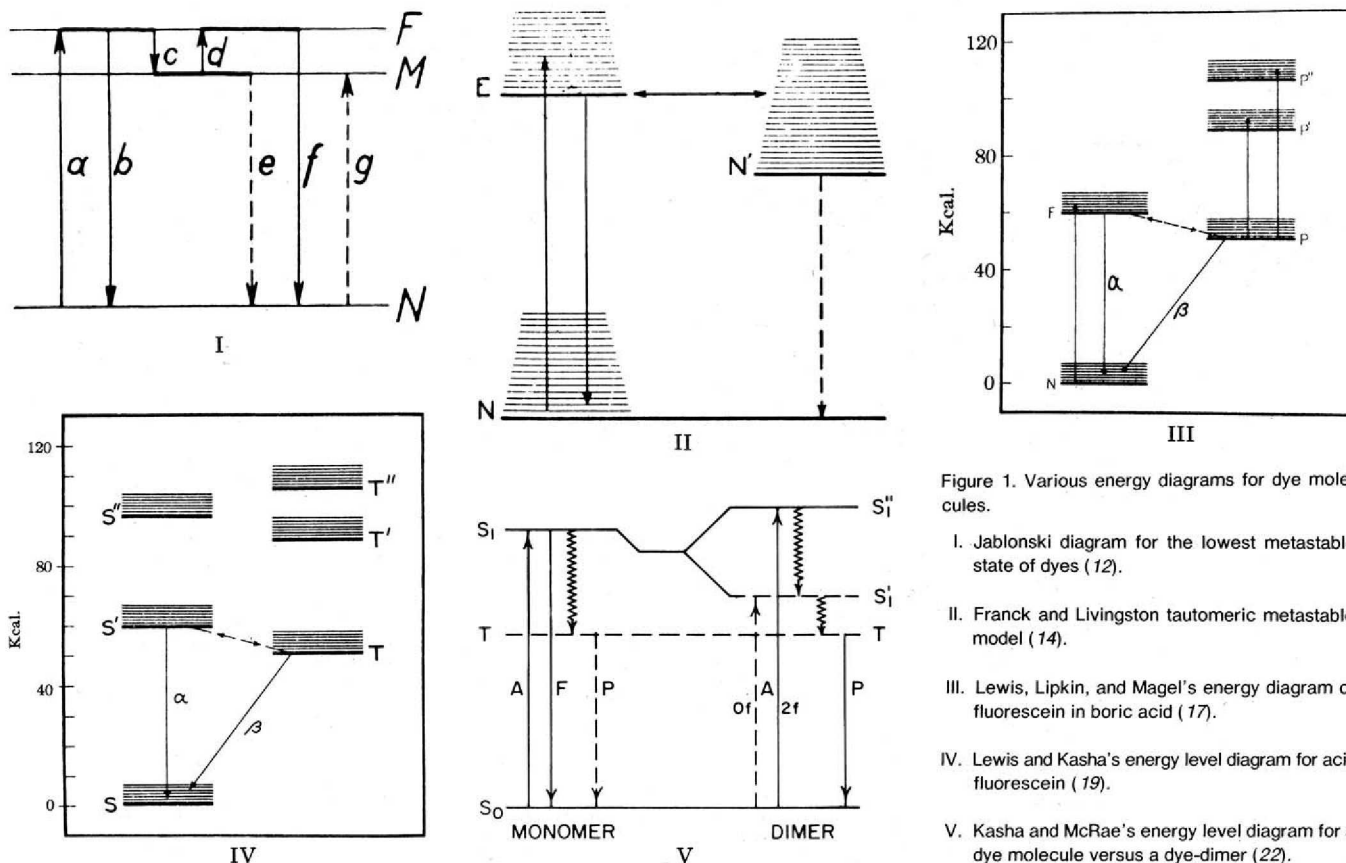


Figure 1. Various energy diagrams for dye molecules.

I. Jablonski diagram for the lowest metastable state of dyes (12).

II. Franck and Livingston tautomeric metastable model (14).

III. Lewis, Lipkin, and Magel's energy diagram of fluorescein in boric acid (17).

IV. Lewis and Kasha's energy level diagram for acid fluorescein (19).

V. Kasha and McRae's energy level diagram for a dye molecule versus a dye-dimer (22).

cupation of all authors writing on the subject before 1944. Thus in 1941 James Franck and Robert Livingston (14) presented the idea of a tautomer of the normal molecule rigidly clamped by the environmental medium:

Many of the apparently conflicting facts of the photochemistry as well as of the phosphorescence and the fluorescence quenching of dyes can be given a rational and unified interpretation if it is assumed that an electronically excited dye molecule can go over, by a process of internal conversion, to the electronic ground state of a reactive energy rich tautomer.

The Franck and Livingston diagram is reproduced as II in Figure 1. A potential curve model later given by Förster (15) for the Franck-Livingston model suggests the seemingly unsurpassable difficulty of generating a radiative phosphorescence by their scheme. Later experiments that I performed (16) on perchlorinated aromatics, which can experience no tautomerism but still possess phosphorescence, did not persuade Franck and Livingston to abandon their scheme.

Lewis, Lipkin, and Magel Study of Fluorescein Phosphorescence

In 1941 a general study of the phosphorescent state of acid fluorescein dye was published by G. N. Lewis and his colleagues (17). One of the main themes of this paper was the quantitative corroboration of the Jablonski thermal activation scheme for the $M \rightarrow F$ decay path. Their diagram is reproduced as III of Figure 1 and was labelled "Energy diagram of fluorescein in boric acid." The Lewis, Lipkin, Magel paper presents ambivalent interpretations of the P (phosphorescent) state

There seem to be but two reasonable assumptions as to the nature of the phosphorescent state.

The first assumption is that a molecule in the F state changes from a state of electronic excitation to a very highly excited vibrational state of the N state The new molecule could now be regarded as a geometrical isomer of the normal molecule

The second reasonable assumption is that in the P state the atomic configuration is approximately the same as in the N state, but that one is an electromer of the other, such as a triplet state (biradical), which now has a low probability of returning to the normal state because of quantum inhibitions.

Lewis, like his contemporaries writing on the subject, was also preoccupied with the rigid glass environmental effects, and he wrote (17) colorfully on this aspect:

We could think of the P molecules as held by the rigid medium in their unstable configuration, as though by the jaws of a powerful trap.

The Lewis, Lipkin, and Magel research (17) contained two experimental observations which were to have a powerful effect on later researches.

- (1) The saturation curve for phosphorescence of fluorescein dye in boric acid glass was to prove fundamental to later studies of photomagnetism, since triplet state population inversion with respect to the ground state was demonstrated.
- (2) The absorption spectrum of the P state was observed, opening the door to many later triplet-triplet absorption spectral studies and to the triplet state flash-spectroscopy kinetic techniques.

Terenin on Photochemical Processes in Aromatic Compounds

Terenin, the Russian photochemist, wrote a long descriptive review interpreting and correlating previous researches in photochemistry and luminescence studies in dyes and simpler aromatics (18). This paper heavily depended on the Lewis, Lipkin, and Magel (17) study and generously references the latter. Terenin presented no spectra of phosphorescences of organic molecules, and his paper gave no energy level diagram for metastable electronic levels of a molecule. His words show some of the same ambivalence as Lewis, Lipkin, and Magel:

Several suggestions have been so far advanced as to the nature of this metastable state in dyes, *viz.*

- (a) a highly endothermic and reactive dye tautomer, formed by the transposition of a "labile" hydrogen atom;
- (b) a geometrical isomer or distorted dye molecule formed as a result of a strong vibration, imparted to the molecule in its radiationless transit to the ground state, the abnormal configuration being stabilized by the environment, acting like "jaws";
- (c) an electromer of the dye, in particular, a triplet state or biradical, from which the transition to the ground level is being prohibited by selection rules.

Terenin rules out tautomerism on the basis of energy consideration and then states

It is, in our opinion, the alternative, mentioned under (b), which, supplemented by the viewpoint (c), can account for the main facts.

Terenin, like his predecessors, was preoccupied by the rigid glass environment problems, and concludes

The molecular modification of abnormally long life, which we have denoted \bar{F} , should correspond to a definite electronic configuration of the compound, differing from that of the excited state $^1I^*$. We assume, furthermore, that it is stabilized by the formation of hydrogen bonds with the environment. The rigidity of the medium, emphasized by G. N. Lewis and co-workers [(17)], has, in our opinion, not only a purely mechanical meaning [emphasized by Lewis], but also a chemical implication, *viz.* the formation of "hydrogen bridges," participating to some extent in the resonating structures of the compound and "smoothing" the way from $^1I^*$ to \bar{F} ; we should rather speak of an "incipient tautomerism" of the molecule, in this connection.

Terenin's appraisal (18) seems to be at about the same status of uncertainty as that of Lewis, Lipkin, and Magel (17). Although apparently taking geometrical isomerism, triplet assignment, and tautomerism with H-bonding in concert, Terenin did start seriously discussing electron spin configurations of triplets. His discussions of triplet aromatic molecules together with singlet and triplet oxygen configurations show unusual prescience.

Lewis and Kasha Molecular Triplet State Assignment

In our first paper in 1944 Lewis and I (19) made the unambiguous jump to assign the lowest excited metastable state of organic molecules as an intrinsic triplet electronic state. Our broad study of spectra of 89 molecules reported the great generality of the phosphorescence phenomenon, and we established the independence of the triplet-singlet emission from the nature of the medium by using a variety of rigid glass solvents. The detailed story of the personal interaction between myself, a young graduate student, and Lewis, who was doing his last piece of major research, to produce both the data and its theoretical interpretation will be told in a later section of this paper.

The energy level diagram which we proposed is reproduced as IV of Figure 1, with explicit labelling of singlet and triplet manifolds. This diagram is an explicit relabelling of the Lewis, Lipkin, Magel diagram, III. Since the latter diagram was for data on acid fluorescein in boric acid glass, we unwittingly performed a disservice to the literature by labelling IV as "Jablonski diagram for fluorescein in boric acid glass," intending to stress the α -phosphorescence (thermally activated $T-S' \rightarrow S$) versus the spontaneous β -phosphorescence ($T \rightarrow S$) (the primes also not corresponding properly to excited configuration singlets!). In view of the relation of Jablonski's contribution, this diagram should be properly labelled "Energy level diagram for acid fluorescein."

McRae and Kasha Exciton Intersystem Crossing Diagram

We return in concluding this section to the Kautsky dilemma: intrinsic metastable states of dyes versus dimerization-induced metastable states. Theo Förster in 1946 accepted the gauntlet thrown down by the Kautsky experiment and

showed (20) that by dipole-dipole coupling of parallel-transition-moment dimers a forbidden (metastable) *singlet*-state for the dimer should arise. He assumed this to be the metastable level ascribed by Kautsky to *both* phosphorescence and photosensitization (our 1944 paper was still not available to Förster because of World War II dislocations). Förster later (21) adopted our triplet state model for the metastable state.

McRae and I (22, 23), pursuing Szent-Györgyi's experiments on dye phosphorescence enhancement in frozen water versus frozen alcohol glass, approached the dye-dimerization problem by molecular exciton theory. Our diagram is given in Figure 1 as V, showing that for a dye molecule singlet-singlet fluorescence dominates the luminescence, whereas in the dye-dimer (in water) the metastable singlet exciton state radiationlessly goes over completely to the triplet state, giving phosphorescence dominance in the dimer. Thus, we effectively explained the Kautsky dilemma, and in effect, combined Förster's two diagrams into one.

Research with G. N. Lewis²

First Contacts

When I came to Berkeley in February, 1943, G. N. Lewis was 68 years old and had recently stepped aside as dean of the College of Chemistry; I had just turned 22. I had come as a graduate student determined to work with Lewis, as he was certainly the best known physical chemistry professor then at the University of California at Berkeley. The chemistry graduate students were required to select a professor before the end of their first semester and to commence research in that term. I went through the obligatory list of interviews in *pro forma* routine, saving Lewis for the last. My first hour with Lewis was impressive. I must have appeared nervous, for Lewis said, "Now don't think I'm going to embarrass you by asking you a lot of detailed questions about physical chemistry. I would just like to tell you about some of the interesting research which we have been thinking about recently."

Lewis then proceeded to talk with excitement about the phosphorescence studies done with David Lipkin and Theodore Magel and the absorption and photochemical studies just then being completed with Jacob Bigeleisen, who overlapped with me for the month of May of 1943. Lewis and Calvin had developed earlier a semi-classical theory of light absorption in dye molecules, and Lewis and Bigeleisen had done both some elegant polarization studies of *x*-band and *y*-band molecular coordinate resolution of the electronic transitions as well as related photochemical studies.

Lewis had his mind on a new class of dye molecules, the large polycyclic quinones (like pyranthrone, violanthrone), and suggested that I measure their absorption spectra carefully. Bigeleisen gave me a master's introduction to what was probably the Chemistry Department's sole electronic instrument, the battery-operated Beckman DU Spectrophotometer, housed in the Old Chemistry Building. Having learned its operation (and idiosyncrasies), I proceeded to measure absorption curves of my dyes. The instrument scale started at 2000 nm (then $m\mu$), and so did my readings.

An Intensive Month of Spectrophotometry

I measured several curves one week from 2000 nm (hardly knowing that I was in a forbidden region of the infrared), to 200 nm, the other limit of the instrument. No one in the laboratory had done this before (as all sensible operators started at 750 nm—the visible limit), and Lewis was astonished to see,

that in addition to a strong absorption band expected in the visible region, I had found an *unexpected* characteristic strong band in the middle of the near infrared for each dye I had studied.

Lewis began to speculate: what could this new electronic band be? He soon had an explanation. The polycyclic quinone dyes which we were studying could be described as large planar *oval* or *round* molecules. Lewis thought: "Could it be that we have found the low-energy *circular* oscillation of electrons, in addition to the higher energy *x* and *y* Cartesian oscillation of the previous type?" The test was then to study as many linear absorbing molecules as could be found: a *carotene* or *lycopene*. Special samples were obtained from Professor Zechmeister of Cal Tech. While waiting a week or two, I added to our list of new spectra.

The absorption curves for the "linear" electronic systems (carotenes) revealed once again strong electronic bands in the near infrared region, characteristically mimicking the visible absorption bands of the molecule, as in previous "round molecule" cases. Each molecule showed a typical vibrational envelope, band width, and spectral position, analogous to its strong characteristic visible absorption.

When Lewis saw that the Beckman Spectrophotometer gave these results on linear molecules as well, he said,

"Take Me To Your Spectrophotometer!"

Lewis asked me to explain the various components and their operation. He had me unscrew the phototube and cell compartments, exposing the exit slit of the spectrometer.

Then he said,

"Set the monochromator dial for 550 $m\mu$,"

and poised himself in line with the exit beam.

He said,

"I see GREEN."

Then,

"Set the monochromator for 600."

He said,

"I see YELLOW."

Then,

"Set the monochromator for 700."

He said,

"I see RED."

Then,

"Now, set the monochromator for 1,000 $m\mu$."

With excitement,

"Aha! I am the first man to see the INFRARED. And it is GREEN!"

Lewis had suspected that the monochromator was misbehaving, and we quickly saw that the *whole of the visible spectrum* could be seen on this instrument by scanning the near infrared from 750 to 2,000 $m\mu$. Thus, any visible dye would show an *illusory* absorption spectrum on the background of this scattered light, apparently reflected off the instrument wall. There are probably some false curves in the earlier literature based on this error. Lewis taught me to be wary of instrumental performance.

Phosphorescence and the Triplet State

Lewis held a daily research conference with me at 11:00 a.m., usually lasting an hour. Each session launched major plans to be carried out that very afternoon and evening. By the end of such an hour, a whole strategy for the day was mapped out. No apparatus was too complicated to be assembled that day, at least in a preliminary form. Of course, I had an enormous advantage over other graduate students since

² This and the sections of this report designated with an asterisk are taken from Kasha, M., "Four Great Personalities of Science—G. N. Lewis, J. Franck, R. S. Mulliken, and A. Szent-Györgyi," Scientific Essays, Tokyo Science University Lectures, 1979, to be published.

Lewis could call on any and all shop men for instant service.

After the month's debacle with the dye spectra, Lewis and I both wanted a refreshing change. I suggested phosphorescence had many puzzles to resolve. Lewis agreed, and said, "Have the shop build a phosphoroscope." Lewis then left for a month's vacation. It was the first day of June 1943, and Bigeleisen had two or three days left in Berkeley. "Jake, what is a phosphoroscope?" I asked. He was furious that I had not used the library. "Look it up!" was his answer. I studied the idea of the Becquerel phosphoroscope, and designed one with parallel discs and had it built the next day. Bigeleisen's parting suggestion to my question "What shall I study?" was: "Try carbazole, it seems to have a very long-lived blue-violet phosphorescence." This suggestion proved to be worth its weight in gold. In the Lewis inner laboratory, where the old brass-tube and mahogany-wood-boxed Medium Hilger Quartz Spectrograph was housed, was a score of large desiccators containing boric acid and dextrose glass phosphor slabs made with various dyes as solutes (from the 1941 work of Lewis, Lipkin, and Magel). All of these dye "phosphors" exhibited broad-structureless phosphorescence. If I had also studied only dyes, our work may never have developed the direction and significance that it did subsequently.

The carbazole molecule spectrum was astonishing, even to me as a beginning spectroscopist. The spectrum consisted of numerous marvelously detailed "sharp" bands. I don't know how I contained my excitement. I probably showed my spectrographic plates to everyone in the building. Jacob Bigeleisen had left before I got a spectrum. Lewis was away for a month. I was the only graduate student in his laboratory. Having just finished Harvey White's Atomic Spectra and Structure course in the Physics Department, the excitement of spectroscopy was in me. That month I ran through several dozen molecular samples: naphthalene, benzophenone, anthraquinone, benzaldehyde, nitronaphthalene, etc. Every molecule showed characteristically "sharp" banded structure. All of these were studied in EPA glass at 90 K (we had only liquid air as a coolant). The bands observed were very numerous and highly structured compared with any of the dye spectra which had been obtained in the laboratory before.

Lewis was delighted and excited by the result when he returned. Our work was now turned fully to a broad exploration of the phosphorescence of organic aromatic molecules in rigid glass solution at low temperature. My phosphoroscope, vacuum sublimers, and vacuum stills ran 24 hours a day for the year. At the end of that first summer I was allowed to give a research seminar on the preliminary observations. Admittedly, the presentation was somewhat repetitive in that I tried to show how virtually every molecule we studied showed a characteristic low-temperature phosphorescence—especially if the molecules were non-fluorescent. The rest of that year was spent in an intensive study of the phosphorescence of over 100 different molecules.

In July of 1944 our work was ready to be written up. The procedure used in writing this long paper is worth recording—as it at first startled me. Lewis seated me comfortably in the wide-armed, high-backed wicker chair which greeted all his guests, with pad and paper in my hand, and dictated the paper in perfect flowing English from beginning to end! I was allowed little interruptions here and there, with an occasional slight change of perspective, but on the whole that first paper (entitled "Phosphorescence and the Triplet State (19)") was already in Lewis' mind. How could he do it? I wondered. Then I realized that everything had been discussed endlessly in the laboratory, and finally, as Lewis puffed his cigar and paced up and down Gilman Hall and across campus, the perfect phrasing of each thought was developed. And when we sat down together, he was ready!

It is odd in retrospect that "Phosphorescence and the Triplet State" should have to come as late in 1944 as a secure

molecular correlation. In atomic spectroscopy and diatomic spectroscopy there was no difficulty with assigning multiplicities and observing forbidden transitions. I believe that one of the retardations on the understanding of polyatomic triplet states was the fact that the techniques used for observation of molecular phosphorescence, solid solutions in rigid glass matrices, impinged on the doped-inorganic-impurity phosphors, and the suspicion carried over that the strange rigid-glass media those Berkeley chemists were using could involve analogous solid state phenomena. It is hard to believe today the general negativism and even hostility which greeted the presentation of this work. It took 10 years to overcome early prejudices before the phosphorescence of molecules assigned as the lowest triplet \rightarrow singlet transition became universally accepted as it is today. Certainly the Lewis and Kasha study showed that phosphorescence was an intrinsic molecular characteristic, independent of the medium or solvent used. Probably, aside from the novelty of the spectroscopic technique, the lack of comprehension of the role of radiationless processes in polyatomic molecules was the other source of diffidence.

In the second year of my work with Lewis, World War II was in its intensive final stages, and I was permitted to remain in Berkeley only if I joined a wartime research project. I easily made the timely decision to take on the heavy extra burden in order to continue with Lewis. So in this second year, Lewis and I saw each other each evening and Saturdays, and frequently on Sundays. We averaged six hours a day together in our whole period of two and one-half years of contact. Our first paper was written in July and August 1944 in the evening hours between 7 and 11 p.m. Meanwhile, our attention had turned to singlet-triplet absorption studies, and a paper was published in June 1945 entitled "Phosphorescence in Fluid Media and the Reverse Process of Singlet-Triplet Absorption" (24). In February 1945 I had completed my PhD degree on the basis of these two researches.

G. N. Lewis Daily Research Memoranda

In June 1943 the research on phosphorescence of organic molecules in low-temperature rigid glass solvents had started in earnest. It may not be out of place to give some indications of the intensity of this research and the pressures which produced such a concentrated effort. The world was at war and academic research in universities was under severe restriction from every side. In 1943 I was still eligible for deferment from Army conscription since I was a teaching assistant in general chemistry, teaching especially the large groups of Navy Medical Corps students. There was a realization that all of the few graduate students of chemistry would rather soon take up war work of one kind or another. Perhaps that contributed to the pace of work as much as anything.

In interviewing me a few months earlier, Lewis gave a fair, thoughtful appraisal of our future relationship. He said, "You don't know me, and I don't know you. Let us say you start an apprenticeship, and in a month or so, for any reason, if you don't like working with me, or I don't like working with you—then we can part freely without friction on either side." We immediately worked so well together that the apprenticeship was never mentioned again.

Lewis had asked no questions about my background, but two of my past experiences prepared me especially well for the intensive period ahead. In my teen years I was in effect the apprentice of a Pennsylvania carpenter and cabinet maker of unusual skill. I was his "man Friday." Every evening I was his instant assistant, knowing every tool, knowing every piece of stock in his shop. I could tell by his glance what he wanted next, hardly more than a nod being necessary. In working with Lewis, I developed the same relationship. In our many hours together each afternoon, I knew his favorite optical filters, his favorite optical accessories. Our work went swimmingly, and we had much good humor between us.

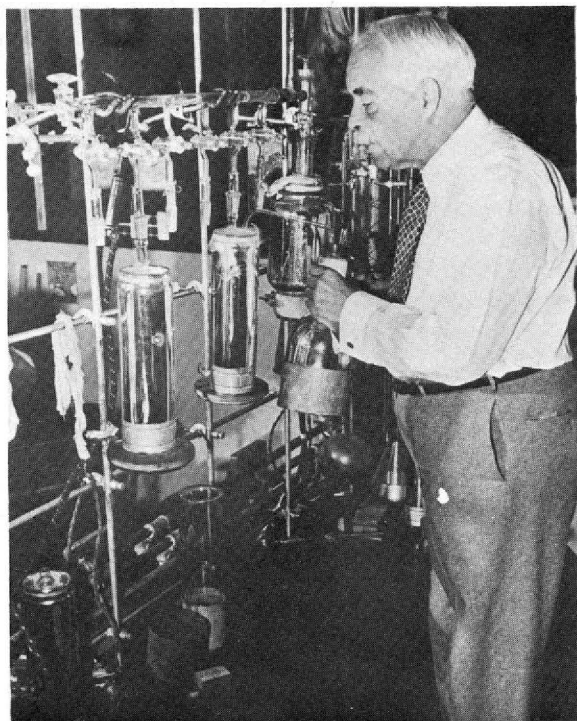


Figure 2. Lewis at vacuum line in laboratory on the third floor of Gilman Hall at the time in 1940's when he was conducting research on color and the triplet state.

My second experience of which Lewis had no inkling was my two and one-half years employment at the Merck Research Laboratories in Rahway, N. J. While going to The Cooper Union Night School of Engineering in New York City, I worked first with the famous chemist Karl Folkers on erythrina alkaloid extraction from poison beans, and fractionation of the alkaloid components. My triumph was the separation of 1.5 g of crude alkaloid into 14 pure alkaloid components by microcrystallization techniques. In my second year I did microbioassays for the entire research laboratory, whose staff was in hot pursuit of a then unknown vitamin, pantothenic acid. I worked on every aspect of this (at the age of 18-19): pilot plant isolation, synthesis of intermediates, and the daily bioassays (*Lactobacillus casei* growth curves). The excitement of pursuing an elusive research goal, and the pressure of the responsibility of the daily bioassay coupled with night school engineering studies tuned my working habits to the intense regime tacitly demanded by Lewis.

Our daily routine started when Lewis appeared in his office at 11 a.m. for our 1-hr lecture-discussion at the blackboard. The afternoon's work now outlined, he went to the Faculty Club, with the expectation that upon his return at 2 p.m. the new experiments would be ready. Quite often this meant a major feat of glassblowing, metalwork, carpentry, electrical wiring—especially if apparatus had to be moved into the building corridor as it occasionally was. Several shop people would be working furiously to get things ready. From 2 until 5 or 6 p.m. wild, rough experiments would be done. (Figure 2 shows Lewis doing vacuum line work from this period.) Then Lewis would take his departure with the comments: "Very Good! Very Interesting! Just polish up the measurements a bit and we'll study them in the morning." After a quick dinner I would return to the lab and frequently work until midnight on the expected polishing of the afternoon's work. In the morning, with a lot of neat curves, spectral plates, tables of data laid before him, Lewis would say: "Well, we did very well yesterday afternoon, didn't we?!"

Lewis would scribble notes to me if we somehow missed each other. I saved these in a file so that I would not forget to carry out any requests. Then later I realized they could be of historical interest, so I still possess what I recall to be the

complete set. They are scribed in soft pencil on yellow paper. Unfortunately, most are undated, but the research they describe allows their sequential arrangement. The few that I dated at the moment are indicated. They tell a fascinating story of Lewis' intense interest in our rapidly evolving project.

Our first molecule of special interest was carbazole because of its "sharp" bands. By the strangest coincidence the two strongest vibrational peaks of the phosphorescence of carbazole coincided almost exactly with the 4047 and 4358 Å lines of our 1-kW AH6 high-pressure, mercury-exciting light. Lewis at first thought we had some super-enhanced Raman scattering. In a rather dramatic experiment using a powerful Mg-cored carbon arc, with the beam transported across 5m of laboratory and with our phosphoroscope flashing (everyone in Gilman came to see the big experiment), we quickly found that even with farther UV excitation the same carbazole phosphorescence bands resulted. We did every kind of experiment to prove that our previously unobserved carbazole bands were unique, real, and characteristic. Lewis left me the following message.

I think the most important next thing is to get the fluorescence of carbazole in liquid air - it may take a very long exposure but the overexposure of the phosphorescence is too far away to bother.

gnl

I think the most important next thing is to get the fluorescence of carbazole in liquid air—it may take a very long exposure but the overexposure of the phosphorescence is too far away to bother.

GNL

We then began systematically to study all sorts of typical organic structures:

After dinner the whole still should be at room temperature. Remove inner part - scrape off what you want of the naphthalene - and replace inner part in still

gnl

After dinner the whole still should be at room temperature. Remove inner part—scrape off what you want of the naphthalene—and replace inner part in still

GNL

We began to recognize quickly that we could tell purity of our compounds from the simplicity and beauty of the phosphorescence bands. Naphthalene usually showed a ghost spectrum to higher frequency, which I could only get rid of by crystallization from ethanol, whereas sublimation seemed to concentrate the impurity. I later diagnosed the volatile impurity to be benzothiophene.

The very large polycyclic quinone vat dyes were still on Lewis' mind, but running concentrated H₂SO₄ as a glass solution of the polycyclic quinones at 90 K gave very complex bands.

7/4/43
 When you do the vat
 dyes in H_2SO_4 I suppose
 you will use the 9000 Å plates
 if there is phosphorescence
 GNL

7/6/43
 When you do the vat dyes in H_2SO_4 I suppose you will use the 9000 Å plates if there is phosphorescence

GNL

Lewis got very interested in the vibrational structure and had Linus Pauling pay a visit. Pauling then wrote a communication for the *Journal of the American Chemical Society* at Lewis' suggestion using our data.

Can I have the first
 4 values of β -chlor β -Brom β -Iodo
 and α -chlor for this evening, GNL

Can I have the first 4 values of β -chlor β -Brom β -Iodo and α -chlor for this evening, GNL

We began to study molecules with unsaturated functional groups (nitro-, carbonyl-, etc.) and began to observe the uniquely short lifetimes and simpler spectra of their phosphorescences (they were later recognized as n, π^* triplet emissions).

I think I would
 like one photo graph
 of 2-nitro-fluorene
 GNL

I think I would like one photograph of 2-nitro-fluorene

GNL

Lewis was toying with ideas of O_2 perturbation, but we did not succeed in accomplishing any definitive work on this, since when our solvents were frozen in glass, the perturbation effects were negated. (This dilemma plagued me for several years until I thought of the singlet-triplet absorption experiment in ethyl iodide solvents.) The data of this memorandum reminds me that I had Christmas day off from research that month, but it was very lonely because my family was 3000 miles away and my brother was fighting tanks in Europe.

I think this is the filter we want—511. with a yellow filter on the other side. $CuSO_4$ should also be used.
 Perhaps, when I come in tomorrow we will try the effect of O_2 . We shall want fluorescein and eosin in slightly alkaline alcohol

12/27/43

I think this is the filter we want—511. with a yellow filter on the other side. $CuSO_4$ should also be used.

Perhaps, when I come in tomorrow we will try the effect of O_2 . We shall want fluorescein and eosin in slightly alkaline alcohol

We kept up the oxygen quenching experiments; we continued extending our repertoire of spectral types of phosphorescence.

My experiments were interesting, and I want to try them all again in your presence.
 In the meantime start subliming in vacuo a little dinitro-diphenyl.
 GNL

12/28/43

My experiments were interesting, and I want to try them all again in your presence.

In the meantime start subliming in vacuo a little dinitro-diphenyl

GNL

We spent quite a bit of time looking at simple molecules, discussing literature ideas on triplet ethylene especially. The ethylene experiment was done badly, since we did not check if any light was absorbed. The high-pressure arc probably was unsuitable as an excitation source.

Regrease main stopcock on vac line.
 Tried two tubes of C_2H_2 —no phosph. to speak of.
 This tube is SO_2 Brilliant green phosph! one of the shortest half lives we have seen. No good bands

Regrease main stopcock on vac line.

Tried two tubes of C_2H_2 —no phosph. to speak of.

This tube is SO_2 Brilliant green phosph! one of the shortest half lives we have seen. No good bands

We were aware of the wavelength problem, but had no better luck with the next larger polyene.

Butadiene—no phosph.!

Butadiene—no phosph.!

Polyenes turned out to be elusive for a long time afterward.

In about February 1944, a big personal decision loomed: join the U. S. Army, go to Central America on a Signal Corps project, or join the Manhattan District (Plutonium Project) in Berkeley. Lewis expressed his hope that I would do the last, and I did without hesitation, as I could continue working with him evenings, Saturdays, and Sundays. The Plutonium Project work was very demanding, and was also emotionally driven, since we were able to secure secret German war reports on their project. Consequently, we were dedicated to this work, and I remember 60–65-hour workweeks being normal. Then I worked with Lewis from 7 until 10, 11, or 12 p.m. (and he

came in regularly each evening) and every Saturday morning and afternoon. On Sundays I worked alone.

At the end of our first year of research on phosphorescence I had recorded the spectra of more than 100 molecular species. Eighty-nine of these were published, and very few proved to be erroneous—in spite of the lack of refined techniques of chromatography, VPC, IR, NMR, mass spectrometry, etc. available today.

In about July 1944 we began to write our first paper, and we started exploring singlet-triplet absorption. Looking at the long-wavelength edge of dye spectra proved difficult and futile. We began to look at the absorption spectra in long tubes, first in a 1-m cell, then in a 5-m optical cell rigged up in the corridor in front of our spectrometer.

First of all we must try, in our long tube, all sort of pure liquids—such as toluene, alcohol (either ethyl or methyl) etc.

First of all we must try, in our long tube, all sort of pure liquids—such as toluene, alcohol (either ethyl or methyl) etc.

GNL

Otto Redlich, of the Redlich-Teller vibrational frequency product rule, was living in Berkeley, and was called in for expert advice. I believe it was he who suggested to Lewis that the weak bands we were finding in 5 m of liquid benzene in the visible and near UV (!) were really IR overtone bands.

Unfortunately it is now pretty sure that our bands are an extension of the molecular bands of benzene—but do benzene and perhaps dichlorethylene and acetone in the long tube anyway.

Unfortunately it is now pretty sure that our bands are an extension of the molecular bands of benzene—but do benzene and perhaps dichlorethylene and acetone in the long tube anyway.

GNL

Nevertheless, the observation of the IR overtone bands gave us confidence that the 3400 Å region weak absorption bands found in liquid benzene were indeed *electronic* bands, which could be correlated with our triple-singlet emission bands found for benzene commencing in the same region.

Lewis knew Otto Redlich on two grounds. First, Jacob Bigeleisen had got his MS degree with Redlich at Washington State in Pullman for a Raman study of the dissociation of nitric acid—then he came to Berkeley and proved to be one of Lewis' best students Lewis ever had. The second was an instance which occurred when I was in the laboratory and a dark-haired, robust Austrian gentleman appeared at my door and said with a heavy accent, "Where may I find the Herr Doktor Professor Lewis?" As it happened, Lewis was sitting on the floor with a bucket containing dry ice chips within

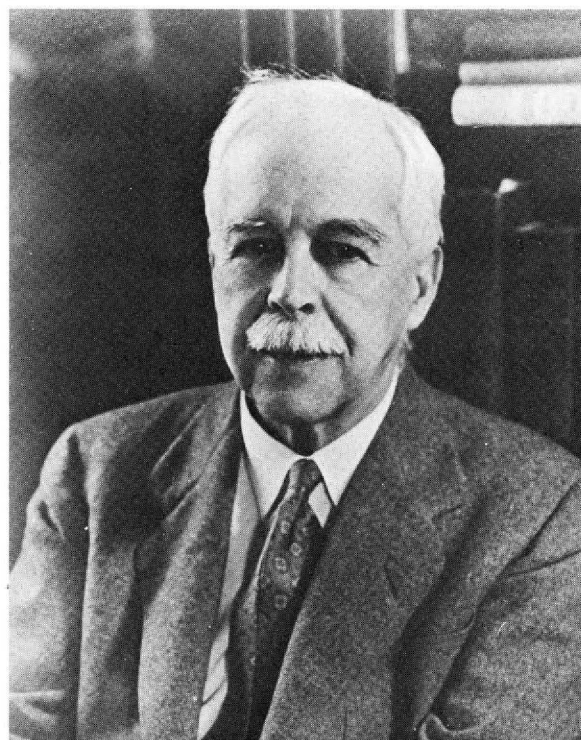


Figure 3. G. N. Lewis on his 70th birthday. Photo by author.

which he was opening an ampule of β -carotene obtained from Zechmeister ("Open in an O_2 -free atmosphere"). So I said, "This is Professor Lewis," pointing to Lewis in a frog-like pose on the floor. Redlich was visibly embarrassed but introduced himself. Lewis exclaimed to me, "Oh, this is the man who improved my book!" Redlich had added a chapter on statistical thermodynamics to the German edition of Lewis and Randall. Redlich again blushed with embarrassment.

As we began to think harder about singlet-triplet absorption and to develop the Einstein A/B relationship, we initiated a study of shorter-lived phosphorescent molecules for their correspondingly enhanced singlet-triplet absorptions

I think benzophenone is the most important substance to get absorption of in long tube—perhaps only 20 cm.

I think benzophenone is the most important substance to get absorption of in long tube—perhaps only 20 cm.

In November 1944 we were well into our singlet-triplet absorption studies, and Lewis personally began preparing some nitrosoalkanes, which had a beautiful blue color. The absorption we thought to be singlet-triplet, but this has proved to be wrong. I believe that the phosphorescences (IR) are, however, triplet-singlet.

Kasha,
 Your sample of brom nitroso propane
 is in quartz tube in L.A.
 It is clear and you could get
 absorption curve if you wish
 GNL
 The Proof has come!

Kasha,

Your sample of bromnitrosopropane is in quartz tube in L.A. [liquid air] It is clear and you could get absorption curve if you wish

G.N.L.

The Proof has come!

The proof of our first paper was very thrilling to receive. In December 1944 after the paper appeared in the *Journal of the American Chemical Society* Sam Weissman took the trouble to write Lewis a congratulatory letter on the paper. Lewis esteemed Weissman very highly, and his letter, stating that the phosphorescence and triplet state paper was "like a breath of fresh air," gave Lewis immense joy and satisfaction. He went around Gilman Hall with a fresh new smile for a week.

I am sure that Lewis was very fascinated by the color effects in optical phenomena. He loved making the nitrosocompounds, and the deep sky blue color was very beautiful.

Tubes are on Vac Bench
 Take your choice of the blue
 ones and disregard the
 quartz one, which is my stock,
 GNL

Tubes are on Vac Bench Take your choice of the blue ones and disregard the quartz one, which is my stock

GNL

In about January 1945 our work on singlet-triplet absorption was coming to an end, and we began to write our second paper. Nitroso compounds' absorptions are displayed prominently in this work.

Kasha:
 $(\text{CH}_3)_2\text{C} \begin{smallmatrix} \text{NO} \\ \text{Br} \end{smallmatrix}$ in Dewar
 I hope the ice doesn't
 matter. If it does put
 it in cold acetone. Don't
 worry about lack of meniscus,
 GNL

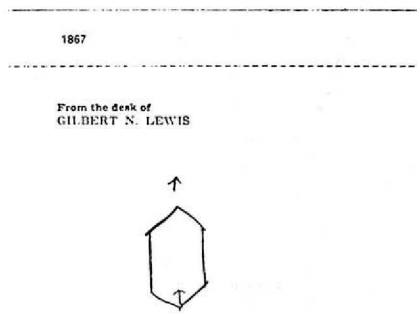
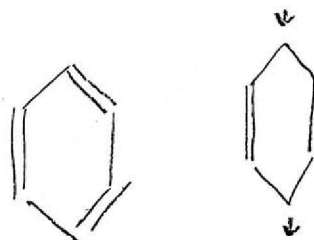
Kasha:
 $(\text{CH}_3)_2\text{C} \begin{smallmatrix} \text{NO} \\ \text{Br} \end{smallmatrix}$ in Dewar
 I hope the ice does not matter. If it does put it in cold acetone.
 Don't worry about lack of meniscus

GNL

The singlet-triplet absorption paper (24) was a landmark paper in correlating absorption spectroscopy with phosphorescence as a further spectroscopic proof of the intrinsic electronic character of the phosphorescent state as a triplet state. Although later research revealed far better examples of singlet-triplet absorption bands (we were hindered by lack of knowledge of spin-orbital Z-effects, which never entered our discussions), this work initiated the direct spectroscopic study of triplet states.

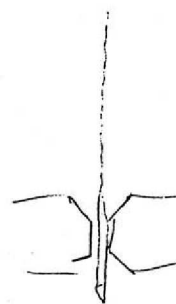
By the end of February 1945 my work with Lewis was completed, my dissertation accepted, and all my energies were devoted to an intensive phase of the Plutonium Project for the rest of 1945.

Lewis began thinking about the consequences of triplet state spin properties quite early. His sketches of the spin orientations for the triplet state began popping up in the laboratory, one on his personal note pad.



A dated sketch (July 18, 1944) shows that at a time near completion of our first triplet state paper, in discussing the expected magnetic properties of the triplet state he had sketched a Guoy balance.

July 18, 1944



Starting in March 1945, Melvin Calvin as our local paramagnetism expert worked with Lewis on an attempt to measure the paramagnetism of acid fluorescein in its phosphorescent state. A communication was submitted by them June 16, 1945 and published in the *Journal of the American Chemical So-*

ciety (25). They indicated a qualitative deflection into the magnetic field in the right direction for the illuminated half of the sample, but immediately afterwards observed a contrary deflection. In January 1946, the main part of my plutonium research completed, I was able to join Lewis full time on this photomagnetism determination. Lewis died shortly afterwards (March 23, 1946), and I, with Melvin Calvin's occasional over-viewing, was able to complete a quantitative determination. The mathematical analysis was due almost entirely to Lewis, but it took a major effort on my part, with cogent help from William Gwinn and Harrison Shull at two points, to bring the calculation to a conclusion. Also, it took me two years of meticulous physical experimentation to unravel the side effects, eliminate them, and to refine the laborious quantitative steps in the measurement. In our final day at the 20,000-Gauss magnet, the reproducibility of the Theorell boom displacement in the beam, its dependence on light intensity, and return to zero displacement in the dark, made Calvin exclaim, "G. N. would have loved to be here today! He would have loved this experiment!" I wrote up the paper, and it was submitted in 1949 to the *Journal of Chemical Physics*, as a joint paper by Lewis, Calvin, and Kasha (26). An elegant refinement of this work was published in 1964 by Jousset-Dubien and Lesclaux (27).

Gilbert Lewis' Research Style

Mathematical Prowess

At the blackboard during our conferences, at first in our morning sessions and later in the evening sessions, Lewis' powerful analytical and intuitive scientific prowess shone through. There were two rather detailed mathematical problems that we worked on, one being the derivation, from the Einstein *A* and *B* coefficient relations, of the integrated absorption-lifetime equation used in our second paper (we did not know that R. C. Tolman had done this earlier). The other was laying the analytical groundwork for a detailed photomagnetism study which I completed with the over-viewing and help of Melvin Calvin after Lewis' death (26). I was at the blackboard groping with a difficult step a couple of times, and Lewis seized the chalk and quickly showed in a few powerful steps a way to its resolution. Although Lewis had published some highly mathematical papers in his career (e.g., on relativity theory with Edwin Bidwell Wilson; statistical thermodynamics with Joseph Mayer), his later years were spent on rather qualitative experimental studies. But the old ability was very much in evidence, hiding just beneath the surface.

Overcoming Logical Barriers

A special trick was used by Lewis when we got boxed into a logical impasse, and it proved to be very effective. It did happen quite frequently that our series of logical steps in some argument or development carried us seemingly to a stone wall: $A \rightarrow B \rightarrow C \rightarrow D \rightarrow \parallel$. Lewis would realize this, and he would say, doing almost a little dance around a semi-circle \curvearrowright as if to look at an object from behind: "Let's look at it backwards!" So the argument was disassembled $D \rightarrow C \rightarrow B \rightarrow A$, and then suddenly it seemed clear that the steps should have been $A \rightarrow B \rightarrow C \rightarrow D' \rightarrow E \rightarrow$ solution, the blind alley becoming magically revealed by unraveling and reexamining the steps in the logic.

A Delayed Love Affair with Organic Molecules

Lewis died of a heart attack working one Saturday morning in the spring of 1946 at his favorite place in the laboratory, the vacuum bench. He had just passed his 70th birthday. Lewis loved to vacuum distill liquids from one flask to another, to sublime materials into reaction vessels, to watch color changes as reactions took place. The turning of the stopcocks, freezing samples with liquid-air Dewars, warming up a solution with a water bath, or even with a match which had just lit another

cigar, these were all part of the visual physical chemistry that Lewis enjoyed most. He confessed to me that organic molecules had been his special joy in his later years, and how, because he had failed a course in organic chemistry at Harvard as a student, he had developed a lifetime dislike of organic molecules—much to his later regret and chagrin.

Cautions on Heavy Instrumentation

Lewis had strong feelings against a researcher becoming too attached to a large instrument or heavy research machinery. Although he admired and made use of heavy instrumentation at times, he felt that someone who developed such instrumentation was inclined to become a slave to and an exponent of the instrument or machine. He preferred to be free to wander among available techniques and to wonder about ideas and not be tied to one technique. For somewhat analogous reasons he was prejudiced against complicated chemical syntheses as an aid to physical chemical research. He admired researchers who could make molecules, but he preferred to leave this to others so that he could devote himself maximally to developing and testing physico-chemical theories. He believed that if a theory was general enough, there should be ample scope for the physical chemist to select a suitable sample from the chemical storerooms to test it.

Gilbert Newton Lewis' Last Day

I was working with G. N. Lewis on the Saturday afternoon, March 23, 1946, when he died, and I find it worth recording the events of the last day of his life, particularly because there has been misinterpretation of the circumstances of his death.

The Saturday morning was a particularly sunny one scientifically speaking. We had an unusually fruitful discussion, and I especially remember being filled with so many ideas on research that they seemed enough to sustain a year of work. I had some new ideas on triplet-triplet absorption, and Lewis described more of his ideas on photomagnetism which I was then to undertake.

Lewis had a particular experiment he planned to do by himself at the vacuum bench that afternoon. A few days before, he had read in the latest issue of *Transactions of the Faraday Society* a paper which he showed me containing a graph indicating that the dielectric constant of liquid hydrogen cyanide changes by a factor of over 100 in a certain accessible temperature range. Lewis said, "That would be a very interesting medium in which to test the effect of dielectric constant on the color of dyes!" He planned that experiment for late Saturday afternoon.

Lewis went to lunch with a distinguished guest and returned at 2 p.m. It was unusual for Lewis to go to the Faculty Club on a Saturday. When he returned, he went to his vacuum bench lab, which was at the opposite end of the hall from his office, my laboratory being in between.

I was working on the spectrophotometer in my laboratory. About every 20 minutes or so I walked by to see if everything was all right. Around 4 p.m. when I passed the vacuum bench room on my way downstairs, I glanced in and noticed Lewis missing. I began to step into the laboratory and got a noticeable whiff of HCN. Stepping back into the hall I saw Lewis' feet just visible behind the bench. I gave out a yell to the lab at the end where I knew Daniel Cubicciotti was probably working, and I ran toward the hood with my nose clamped shut with my left hand. I threw a brick, which we kept as a weight in the fume hood, through the window. Returning to the hall I noticed the bottle of sodium bicarbonate in the hood, and rushed into the lab again, and covered the liquid on the vacuum bench table with bicarbonate, the active bubbling of which suggested that liquid HCN had just spilled out. Shortly afterwards Cubicciotti and I dragged Lewis into the hall and called for medical help. He had a serious welt in the middle of his forehead, indicating that he had fallen forward and hit

his head on a vacuum bench clamp. Lewis was dead on arrival in the University Hospital, and a medical autopsy indicated clearly that he had died of a heart attack. We concluded that many minutes after he had died, the pressure had built up in the container of liquid HCN, from which the Dewar had been removed, and the vessel dropped to the vacuum bench, spilling the contents.

Lewis' death was a very traumatic experience for me, and because that evening I was previously invited to have dinner with Otto Redlich and his wife, I tried to cancel the visit. Redlich prevailed, and I owe a great deal to him for the warm, considerate, thoughtful conversation that ensued that evening.

Reception and Verifications of Triplet State Theory

The American Chemical Society had planned a research symposium honoring G. N. Lewis to be held December 30 and 31, 1946, at Northwestern University in Chicago, but his death changed the meeting plans. As his last research student to complete work under his direction, I was invited to present the work on the triplet states of molecules.

My presentation was the first of the meeting, and I was allowed approximately 20 minutes. I knew that a very strong challenge was to be presented by James Franck, but I had not expected that two hours of rebuttal of our work had been planned by Franck, followed by Robert Livingston, Eugene Rabinowitch, and Edward Teller. Each demonstrated the impossibility of the Lewis and Kasha triplet state interpretation on the basis of his knowledge, and Teller's detailed mathematical development of the theory of spin-orbital interaction seemed particularly devastating. I report in another place³ more details of this interesting confrontation and of Franck's prior meeting and relationship to Lewis. Robert Mulliken, whom I met at this meeting, tried to defend our thesis. The conference committee seemingly was suspicious of my paper, I now realize, for although my paper (16) was presented first in the program, it appeared last in the published volume!

At the Faraday Society Discussion in 1949 I presented (28) my own new work on intersystem crossing, the radiationless transition leading to triplet excitation, and a kinetic analysis of the rates of radiationless processes with and without spin. James Franck, a medalist at that meeting, was there to oppose the triplet state idea again. Often repeated was the criticism voiced by Radinowitch (1956) (29):

The hypothesis of metastable (triplet) electronic states of organic molecules has been revived by Lewis and Kasha (1944); however, it seems that if the rule which prohibits singlet-triplet transitions does not preclude the formation of the triplet state from the excited singlet state within 10^{-7} sec., it is unlikely to delay its transformation into the singlet ground state for as long as several seconds or even minutes.

It is obvious that these critics (which included Franck and Teller) had not considered the implications of intersystem crossing, whose kinetic analysis (28) so clearly indicated an answer to the criticism.

Several spectroscopic elements were provided which finally settled all suspicion concerning the validity of triplet state assignment to organic molecule phosphorescence. The main electronic spectral proof lay in the Z-effect, since atomic number of substituents could be used for proof of spin-orbital perturbation. Learning about the quantum mechanics of spin-orbital interaction from David Bohm in Berkeley in 1948, I was able to show the Z-effect in intersystem crossing (28, 30), and Don McClure immediately afterward was able to show the Z-effect on phosphorescence lifetimes (31). A review (32) of "Spin Intercombinations in Molecules" in 1956 revealed that Terenin still believed that external "paramagnetic perturbations" were essential to induce triplet state emission.

³ See reference in footnote 2.

Chronology of Key Discoveries in Triplet State Molecular Spectroscopy

Year	Author(s)	Reference	Research
1944	Lewis and Kasha	(19)	Phosphorescence assigned as T → S
1945	Lewis and Kasha	(24)	Singlet-triplet absorption
1949	Lewis, Calvin, Kasha	(26)	Paramagnetism of triplet state
1949	McClure	31)	Z-effect on phosphorescence lifetimes
1950	Kasha	(28)	Z-effect on intersystem crossing Kinetics of radiationless transitions Uniqueness of emitting states
1952	Kasha	(39)	Environmental Z-effects on triplet states
1958	Hutchison and Mangum	(33)	EPR absorption of triplet state (crystals)
1959	van der Waals and de Groot	(34)	EPR absorption of triplet state (glasses)

The difficulties of finding a triplet state EPR signal probably delayed full acceptance of triplet state ideas, but they were finally resolved by the work of Hutchison and Mangum in 1958 (!) (33) and van der Waals and de Groot in 1959 (34). The subject of "Magnetic Properties of Triplet States" was reviewed in 1979 by Pratt (35).

Dellinger and Kasha (36) returned recently to the problem of vibrational potential effects which so dominated discussion before 1944 and concluded that only such large amplitude motions as phenyl ring torsion would be inhibited by rigid glass solvent cages. So all of the early preoccupation with specific glass effects (aside from diffusional quenching) seems to have been unnecessary.

Today triplet state studies of molecules have advanced to highly refined stages, as exemplified in symposia (1967) (37) and research treatises (1969) (38). The key historical steps in the evolution of experiments and interpretation of triplet states of organic molecules are summarized in the table.

Gilbert Lewis' Research Previews*

Gilbert Lewis' career, rich as it was in permanent contributions to the understanding of physical chemistry, also had a most unorthodox pattern, not noted especially by anyone until now, but one which was typical of Lewis and which had a profound effect on his intellectual fertility and freshness through his whole scientific life. *Lewis previewed a research field in print, using his own analysis, sometimes without an exhaustive literature review, before embarking upon research in it.* Most scientists think of reviewing a subject in print at the end of a long study and research period. Lewis told me he thought that approach could stifle originality. If a scientist got an absolutely thorough knowledge of the literature before doing research, he was likely to acquire many of the prejudices and mental blocs of his predecessors.

For example, in the beginning of his career he wrote a paper, "Outlines of a New System of Thermodynamic Chemistry" (40) in which the physical thermodynamic laws were applied to physico-chemical problems. This was the origin of Lewis' concepts of activity, activity coefficients, fugacity, partial molal free energy, etc.

Lewis told me that not long after completing his PhD at Harvard, he took a two-year appointment in Manila (as head of the Philippine Bureau of Weights and Measures) 1904-5—a most unorthodox start for a scientific career—so that he could think for himself. He worked his way through Walther

Nernst's "Physikalische Chemie" ("correcting all of the mistakes"), hiked his way around the volcanos and countryside of Luzon, and acquired a lifelong taste for Philippine cigars. Lewis then published his chemical thermodynamics overview paper and followed this with about 15 years of research on chemical thermodynamics, culminating in the classic work, "Thermodynamics and the Free Energy of Chemical Substances" (41). Publication of this book marked the essential close of Lewis' researches in chemical thermodynamics; he then turned his attention to other areas. His later works on statistical thermodynamics belong to another period of his work.

Lewis did indeed change research fields abruptly through his career, usually prefacing a research period with his characteristic penetrating research-proposal-overview paper. His later interest in isotopes could have been presaged by his paper, "The Chemistry of the Stars and the Evolution of Radioactive Substances" (42). Starting in 1933 he wrote an extensive series of papers on heavy hydrogen and heavy water, a paper on lithium isotopes, and several papers on neutron physics, culminating in "The Genesis of the Elements" (43).

Lewis' interest in valence theory began with a precocious master's thesis, "The Electron and the Molecule" (Harvard, 1898). I saw a copy of this once in Lewis' office, and I have a clear recollection of its title. I never had the chance to examine it, and it is tantalizing to speculate on what it contained. Lewis' copy of it appears to be lost, and the Harvard Chemistry Library and the Harvard Widener Library have no copy. In Lewis' summary book, "Valence and the Structure of Atoms and Molecules," (44) appear replica pages from Lewis' notebooks of the early 1900's, showing his early thoughts on electron arrangement in atoms and molecules. Lewis continued the development of ideas and nomenclature concerning valence theory, especially the role of electron pairs, octets, odd electron numbers, and diradical configurations in a series of papers, with World War I interruptions, in 1913 (45) and then in 1916-17 (2). At a joint symposium of the American Chemical and Physical Societies and the American Academy of Arts and Sciences in 1917 he threw the challenge to the Bohr atom, showing that it could not explain molecular geometry (46). His chemical intuition set conditions on valency interactions for which only Quantum Mechanics was able to provide the basis.

Other research preview papers by Lewis include his paper on the electronic theory of acids and bases (47), preceding experimental work with Glenn Seaborg on the subject. "The Color of Organic Substances," (48) preceded almost a decade of research on the color and photochemistry of dyes.

Perhaps the atypical case was Lewis' work on heavy water. Lewis had discussed the possibility of heavy water (D₂O) apparently before the actual discovery of deuterium as a proven isotope. Urey used the Rydberg isotope shift in the atomic spectrum of hydrogen to prove that a new isotope of hydrogen (deuterium) existed, after an extensive program to concentrate natural deuterium. Lewis then worked furiously to establish his part of a claim to the discovery of heavy water by doing every conceivable measurement. Finally all of this work was reviewed in a comprehensive summary paper (49) uncharacteristic of Lewis' research previews.

Gilbert Newton Lewis typified the physical chemist of great intuition who was able to conceive of beautifully simple models and concepts to explain complex physical and physico-chemical phenomena. His conceptual contributions have made lasting additions to our knowledge, and his aptness for

good nomenclature has enriched our scientific vocabulary, viz., Lewis introduced the term *photon* for light quantum (50).

Gilbert Lewis once defined physical chemistry as encompassing "everything that is interesting." His own career touched virtually every aspect of science, and in each he left his mark. He is justly regarded as one of the key scientists in American history. It would be a great omission not to record the warmth and intellectual curiosity radiated by Lewis' personality. He epitomized the scientist of unlimited imagination, and the joy of working with him was to experience the life of the mind unhindered by pedestrian concerns.

Acknowledgment

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