Vol. A71 (198?) ACTA PHYSICA POLONICA No 5

116

# FIFTY YEARS OF THE JABŁOŃSKI DIAGRAM*

By M. Kasha[†]

Institute of Molecular Biophysics and Department of Chemistry, Florida State University[**]

*(Received October 21, 1986)*

A thematic comparison is made of ten theories of classical optics, based on electromagnetic and kinetic theory, and the translation of these theories into quantum mechanical language and format. These basic theories cover the range from primary photochemical laws (Grotthus–Draper Law; Einstein Photochemical Equivalence Principle), to empirical fluorescence laws (Stokes' Shift; Levshin's Law of Mirror Image Symmetry), to fundamental spectroscopic principles (Franck Principle; Jabłoński Diagram). Each of these theories is shown to have had a fundamental role in the development of the photochemistry and spectroscopy of polyatomic molecules, and each survives today in its contemporary Quantum Mechanical format.

PACS numbers: 32.50.+d, 33.50.-j, 78.55.-m, 82.50.-m

## 1. *Researches of Aleksander Jabłoński*

Aleksander Jabłoński was one of the pioneers in the development of the field of *molecular photophysics*. He made contributions to the understanding of the kinetics of excitation of dyestuff molecules, the polarization and anisotropy of their luminescence, solvent perturbation effects on molecular excitation, and radiation mechanisms. His works, including his studies on pressure-broadening of spectral lines, are classics in the field [1–5] and have had a profound influence on the development of the understanding of the optical and spectroscopic properties of molecular systems.

A comprehensive overview of Aleksander Jabłoński's work in molecular luminescence appears in his 1936 paper [6] presented at the International Conference on Photoluminescence in Warsaw, May 1936 (Pringsheim's introduction names it the World's first international conference on the subject). The names of the conferees cover the whole range of the World's most prominent scientists of the time, working on spectroscopic phenomena.

---

[*] Presented at the International Symposium on Molecular Luminescence and Photophysics, Toruń, Poland, September 2–5, 1986.

[†] Work done under Contract No. DE-AS05-78EV05855 between the Division of Biomedical and Environmental Research, U. S. Department of Energy, and the Florida State University.

[**] Address: Institute of Molecular Biophysics and Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3015, USA.

Jabłoński's paper discusses vibrational structure of molecular transitions, the Stokes rule of fluorescence shifts, mirror symmetry of fluorescence and absorption, and especially, polarization of molecular electronic transitions. All of the discussion is oriented toward the properties of dyestuff molecules.

Inexplicably, Jabłoński's now classic and most influential papers [1, 2] (1933–1935, on the "Jabłoński Diagram") are not cited in this *Acta Physica Polonica* paper (submitted March 15, 1936). This paper is a mathematical summary of Jabłoński's concepts, with quantum mechanical cognizance. His now famous diagram does not appear in this paper, nor any of his elegant analyses of the kinetics of excitation. Perhaps the spectroscopic uncertainties in the minds of physicists of the time on the nature of electronic states of molecules, uncertainties which persisted until a late date, cautioned Jabłoński against considering a quantum mechanical translation as being premature. These 1933 and 1935 papers on the "Jabłoński Diagram" therefore will be discussed in their full historical perspective in the last sections of the present paper.

Jabłoński's researches bridged the gap between classical optics, — based on the theories of kinetics and electromagnetism, — and contemporary spectroscopy — based on theories translated into modern format by quantum mechanics. It seems appropriate as a background to the influence of Jabłoński's contributions, and as a perspective on our subject, to review the development of molecular photophysics in terms of ten theories of photochemistry and spectroscopy which have undergone parallel translations into quantum mechanical format.

## 2. *Spectroscopic theories from classical optics to quantum mechanics*

Ten spectroscopic and photochemical theories which have established and shaped the outlines of the discipline of molecular photophysics will be reviewed succinctly in this Section. A thematic summary of these is given in the accompanying Chart, which epitomizes the original name and content of each idea on the basis of classical concepts, and compares each with its contemporary format translated by the ideas of quantum mechanics.

Many of the ideas were introduced in merely verbal terms, with no mathematics, and frequently no diagram. But the principle stated proved to be so fundamental, that the concept has persisted to the present day. For example, the Grotthus–Draper law established the distinction between *coherent and incoherent* scattering. Stokes' qualitative observations established a quantitative nomenclature criterion. The Einstein contributions, derived from kinetic analysis of radiation equilibrium, led to fundamental concepts of photochemistry, intensities of transitions, laser physics, and paved the way toward the concepts of matrix elements of operators in quantum mechanics.

A dramatic example of the importance of a simple statement of a new concept and its later evolution into a powerful quantitative spectroscopic tool is the Franck principle. Franck's writing is very diffuse, and no mathematics was used. He stated that just as a pendulum rests momentarily at a turning point in its swing, so a molecular oscillator must also; therefore the most probable time for an electronic jump for a vibrating molecule is at the classical turning points. One searches in vain for a good diagram in Franck's

CHART

# SPECTROSCOPIC THEORIES FROM CLASSICAL OPTICS TO QUANTUM MECHANICS

| CLASSICAL OPTICS, KINETICS | QUANTUM MECHANICS |
|---|---|
| **Grotthus-Draper law of photochemistry**<br>Absorption required for photochemistry, in contrast to scattering, refraction | **Quantum electronic jumps**<br>Specific chemistry for each excited state species, orbital configuration |
| **Stokes fluorescence-shift rule**<br>Stokes (fluorescence lower $\bar{\nu}$ than absorption)<br>Anti-Stokes (emission higher $\bar{\nu}$ than absorption) | **Shift of band origin**<br>Dielectric relaxation, proton-transfer, Raman, ... shifts<br>Shift of band maximum<br>Franck-Condon shift |
| **Einstein photochemical equivalence principle**<br>Unit quantum yields as limiting case | **Bipartition of excitation**<br>Intersystem crossing<br>Non-integral quantum yield limit |
| **Einstein transition probabilities**<br>$A_{12}$, $B_{21}$, $B_{12}$: relation of absorption and emission rate constants for radiation equilibrium | **Q.M. transition probability**<br>Matrix elements of the electric dipole, ... polarizability, ... etc., operator |
| **Selenyi wide angle interference**<br>Electromagnetic radiation mechanism (electric dipole, electric quadrupole, magnetic dipole, ...) | **Q.M. multipole transition probability**<br>Matrix elements of the multipole operator (electric dipole, electric quadrupole, magnetic dipole, ...) |
| **Spectral line broadening**<br>Doppler broadening | **Q.M. mechanism of line broadening**<br>Uncertainty broadening |
| **Levshin's law of mirror image symmetry**<br>Apparent relation of absorption to fluorescence envelope | **Vibrational envelope inversion**<br>Vibrational frequency changes<br>F-C intensities |
| **Franck principle**<br>Electronic jump at turning points of oscillation<br>Discrete spectra and continuum limit | **Franck-Condon principle**<br>Separation of electronic and nuclear wave function (motions)<br>Most probable vibronic intensity at maximum in vibrational eigenfunction overlap |
| **Franck-Rabinowitch solvent cage**<br>Kinetic inequalities for collisions and encounters | **Spectroscopic solvent-cage theory**<br>Born-Oppenheimer separation of solvent cage nuclear motion and solute nuclear motion |
| **Jabłoński diagram**<br>Metastable states of dyes<br>Origin of thermally activated phosphorescence of dyes | **Electronic energy level diagram**<br>Separation of singlet, triplet, ..., manifolds<br>Singlet-triplet splits |

papers, and the verbal statements are diffuse — but the logic of Franck's concept is sharp: electronic jumps and vibrational motion are separable.

Then comes Edward Condon, as a graduate student equipped with harmonic oscillator quantum mechanics, who accidentally learns of Franck's pendulum concept from Hertha Sponer, Franck's student visiting California. An elegant formalism develops, and we now have the Franck–Condon Principle in full quantum mechanical regalia. Now we understand the role of interference (Condon's "internal diffraction") of the vibrational eigenfunction wave patterns in the characteristic "Franck–Condon" overlaps, and learn that only at very high quantum numbers does the probability become significant of finding a molecular oscillator at a classical turning point. A spectroscopist who does not say or think Franck–Condon ten times a day is not thinking about spectroscopy. Was the Condon electronic-vibrational eigenfunction separability justified? Some years later Born and Oppenheimer explored the meaning of the assumed separability. So from the verbal classical principle of James Franck has evolved one of the most powerful and quantitative quantum mechanical principles of modern spectroscopy.

We now turn to the background of the Jabłoński Diagram, and its statement, and its subsequent evolution into a form which is the universal basis of spectroscopic and photochemical researches today.

(The author will publish the twenty diagrams associated with the Chart with accompanying exposition and references in another place.)

## 3. *The Jabłoński diagram*

If we take atomic spectroscopy as an example, a science highly developed both experimentally and via quantum mechanical theory by 1935, we could wonder why the development of molecular spectroscopy did not follow in a parallel fashion. Indeed, the *Grotrian Diagrams* [7–9] (1928) of atomic spectroscopy are rather parallel to those of contemporary molecular electronic spectroscopy (it was Grotrian who introduced the idea of separating states of different multiplicity into different columns in energy level diagrams). But polyatomic molecules behave very differently from atoms. Atoms were usually studied in their dilute vapor states, and the whole range of $Z$, the atomic number, was available. In fact, the diagrams most like those for molecules in a general sense are those for atoms of high atomic number [8, 9].

Some of the most powerful physicists (E. Teller, J. Franck), and photochemists (R. Livingston, E. Rabinowitch) were quite baffled by the molecular phosphorescence phenomena in this 1930–1940 period. Molecular phosphorescence had been observed qualitatively by J. Dewar (1889) and P. Borisov (1905), and spectroscopically in extensive studies by J. von Kowalski (1911 and earlier). But these studies were invariably for the solid state, and frequently for dyes embedded in solid matrices or adsorbed on surfaces. There was thus a tendency to associate the phenomenon of phosphorescence of these "phosphors" with the phenomena of phosphorescence of complex inorganic doped phosphors. Indeed, in his 1936 Symposium paper, Jabłoński [6] begins the paper with a definition in which *the surrounding embedding-medium molecules and the dissolved dyestuff molecule together* *form a "dyestuff-center"*. This concept of the essentiality of the solid-state medium for the observation of phosphorescence, together with the facile occurrence of phosphorescence in molecules containing no heavy (i.e., high Z) atoms, constituted a severe intellectual block on the recognition of low-lying metastable states of molecules as an intrinsic property of isolated organic molecules in general.

The first deductions on metastable electronic states of molecules out of the context of solid state embedding came in the 1931–2 researches of H. Kautsky. Kautsky was a brilliant experimenter who demonstrated the existence of metastable states of dyes in fluid solutions as intermediates in photosensitization [10]. His verbal accounts were lacking in quantitative data or diagrams, so this part of his work did not attract the attention of contemporaries which it deserved. Most of Kautsky's researches were for dyes adsorbed on gels as sensitizers.

Aleksander Jabłoński immediately analyzed Kautsky's experiments for dyes adsorbed on surfaces, and wrote his famous note to *Nature* (1933), giving the first presentation of his famous diagram (Fig. 1) for dye molecules. This diagram clearly introduces a metastable level M as an *intrinsic* electronic state of a dye, with M–N transitions of very small probability.

Because Jabłoński was interpreting directly the excitation properties of *dye* molecules, he realized that the F–M state separation was small enough to permit thermal activation to F from M, thus leading to a second pathway for depopulation of M. He called the M → F → N process a phosphorescence, and Lewis, Lipkin, and Magel [11] made quantitative studies of this as a room temperature "α-phosphorescence" for dyes (dissolved in boric acid or in glucose glass); these authors named the direct M → N emission as a "β-phosphorescence". (Today the "α-phosphorescence" is recognized as the "delayed fluorescence" of a dye molecule.)

Jabłoński's first Note [1] contains a prescient observation on the enhancement of the

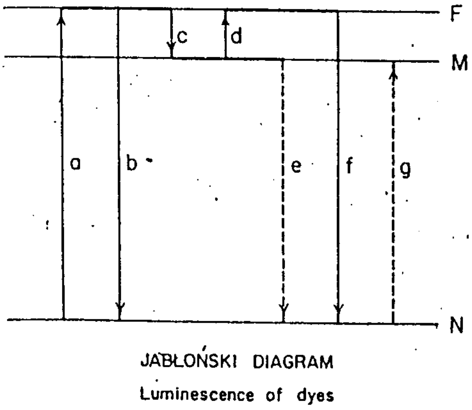

Fig. 1. Lowest electronic energy levels of a dye molecule. N — ground level, F — fluorescent level, M — metastable level. Transitions: *a* — absorption, *b* — fluorescence, *c* — transition to the metastable level, *d* — thermal excitation, *e* and *df* — phosphorescence, *g* — absorption of very small intensity

N–M probability "under the influence of disturbing fields" of the surrounding molecules of the solvent. This could be taken as an early vision of phenomena such as the external heavy atom effect [12].

The *Nature* Note [1] contains a curious error: "In solutions, practically all of the molecules which have reached the level M in any possible way will be quenched. Therefore the absorption band N → M must be completely inactive". This seems to weaken Jabłoński's concept of M being an intrinsic electronic state of a molecule. Such a state will always have an intrinsic M ↔ N transition probability. The intrinsic transition probability for emission is given by intrinsic mean life-time, not by quantum efficiency of emission. Thus a state quenched by whatever process, is still intrinsically a state which can be excited and which exists, however short its ambient lifetime. Thus, the N → M absorption would not be quenched, even if the emission is quenched. The same error has plagued many subsequent authors.

The Note [1] of 1933 was followed by a quantitative exposition of the consequences of the diagram, suggested by Jabłoński for the properties of dye molecules, in his comprehensive 1935 paper in *Zeitschrift für Physik* [2].

Jabłoński's 1935 *Z. Physik* paper [2] is elegant for the logical exposition and the mathematical analysis derived from the simple elements of the diagram he proposed. Starting with the simple rate equation for the disappearance of molecules in the metastable state M, he deduced formulas for the lifetime of M-state molecules with thermal activation to state F, and without thermal activation to state F (i.e., the low temperature limit); formulas for the fluorescence (F → N) quantum yield, and the phosphorescence (M → N) quantum yield; and a formula for the phosphorescence exponential decay law, based on intrinsic *molecular* parameters.

Some key sentences from Jabłoński's exposition summarize his main points:

> "We assume that in the case an 'energetically isolated' dye molecule is phosphorescence-capable, then in this molecule there must exist at least one metastable level."
>
> "The transitions between the ground level N and the metastable level M can occur only with a small probability (as, e.g., by forced dipole radiation or quadrupole radiation)."
>
> "... thus the level M is for the greater part reached by a detour through F (since the N → M absorption is extra-ordinarily weak)."

Jabłoński repeats the error of his Note [1] concerning the quenching of the N → M absorption in the presence of M-state luminescence quenching, as discussed above.

Jabłoński missed the idea of the *intersystem crossing ratio* [13] as an intrinsic molecular property which would permit a variation of M-state yields depending on the molecule. Even in dyes this is an observable variable, e.g., in comparing the luminescence properties of fluorescein anion, with those for corresponding erythrosine and rose bengal species. Instead, he writes an expression for quantum yields $\eta_F \gg \eta_P$ (based on a classical quenching law, using the corresponding mean lifetime inequality $\tau_P \gg \tau_F$), obviously not a correct deduction.

Nevertheless, overlooking these interesting but small pitfalls of his paper in the perspective of 50 years of hindsight(!), the Jabłoński 1933 Note and 1935 paper stand as giant steps in the transformation, of a long history of qualitative luminescence observation, into the beginnings of a quantitative science of molecular photophysics. Jabłoński appropriately ends his paper with the statement, "... by these deliberations the phenomena of photoluminescence have lost some of their mysterious character."

### 4. *The multiplicity problem: the triplet state*

The metastable electronic level M in the Jabłoński Diagram was described as giving rise to a "*quadrupole radiation or a forced dipole radiation*", concepts derived from classical electromagnetic theory. We cannot decipher uniquely today what Jabłoński meant by '*forced dipole radiation*', because all of the possibilities seem inappropriate: a wave superposition giving rise to a forbidden component; a fortuitous cancellation of electric-dipole matrix elements forcing an allowed transition to become forbidden; induced emission ($B_{21}I$) (ruled out by the spontaneous exponential decay); a perturbed magnetic dipole transition. But on the higher multipole question, the answer is definitive: the electromagnetic radiation mechanism of dyestuff phosphorescence is *electric dipole*. This was demonstrated by Weissman and Lipkin (1942) [14] in a beautiful execution of the Selenyi Wide Angle Interference Experiment, using the Selenyi theory. For acid fluorescein dye in phosphoric acid glass at 95 K, with a mean lifetime of some 3 sec, the interference pattern for an electric dipole mechanism was observed for the phosphorescence, as a prototype example.

Now we turn to the generalization of the Jabłoński Diagram and the full development of quantum mechanical consequences. Lewis and Kasha [15] made the definitive step [16] of assigning the phosphorescence of molecules to the lowest triplet-singlet transition (*Phosphorescence and the Triplet State*, 1944). Their spectroscopic study of 89 molecules established (a) the universality of the molecular phosphorescence phenomenon, (b) the intrinsic molecular nature of the phosphorescence, (c) the independence of the phosphorescence on the medium used, (d) the wide variations of phosphorescence mean lifetimes (independent of the rigid glass quantum yield).

Lewis and Kasha concentrated on simple organic molecules, largely avoiding dyes with their special energetics. Thus, Fig. 2 represents the general Electronic State Diagram for a polyatomic molecule with the generally observed large lowest $S_1$–$T_1$ separation (and with the Grotrian arrangement of multiplicities). Thus, the special conditions which Jabłoński dealt with in dyes, namely M → F, i.e., $T_1 \rightarrow S_1$ thermal excitation, no longer prevails. Lewis and Kasha, however, did relabel the Jabłoński Diagram for *acid fluorescein dye* of the 1941 paper [11] as a Jabłoński Diagram with triplet and singlet levels designated. Since their 1944 paper, the general Electronic State Diagram for any polyatomic molecule has often been called a Jabłoński Diagram.

Lewis and Kasha extended their first research with two others, one in 1945, *Phosphorescence in Fluid Media and the Reverse Process of Singlet-Triplet Absorption*, [17] and one in 1949 on a quantitative determination [18] of the magnetic moment of acid fluorescein

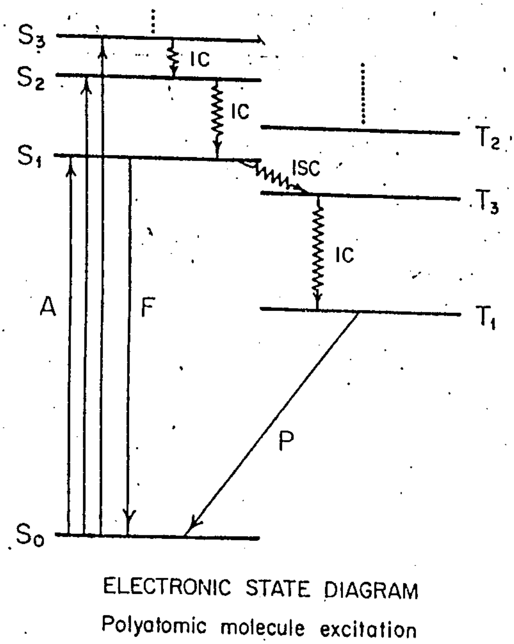

Fig. 2. General electronic energy level scheme for a polyatomic molecule. *Radiationless transitions*: IC — *internal conversion*; ISC — *intersystem crossing*. *Radiative transitions*: A — absorption, F — fluorescence, P — phosphorescence. *Energy relation*: $T_i < S_i$ for each electron orbital configuration

dye in its triplet state. These two papers should have settled many questions on the triplet state assignment [19].

Quantum mechanical concepts were now brought to bear on the triplet state assignment, and all of the qualitative and quantitative consequences were explored. It was shown from the Q. M. theory of spin-orbital interaction that the $Z$-dependence on triplet state lifetimes was operative (1949) [20] that the $Z$-dependence of intersystem crossing (the radiationless $S_1 \rightarrow T_1$ transition) prevailed (1950), [13, 21] that environmental $Z$-effects could be seen for $S_0 \rightarrow T_1$ absorption (1952), [12] that planar aromatics with their small S. O. matrix elements could have extraordinarily long triplet state intrinsic lifetimes (seconds), [22] and that ESR triplet multiplet spectroscopy could be observed in oriented crystal matrices (1958) [23] and in glasses (1959) [24].

There was however a great reluctance to accept [16] the triplet state assignment in organic molecules. It is generally known that Jabłoński could not accept his M state to be a triplet state. But even a decade after the Lewis and Kasha 1944 paper there was wide diffidence, so Jabłoński did not stand alone. The rigid glass matrix technique aroused suspicion, and the idea of a radiationless intersystem crossing [13] was not fully understood. Even though the Lewis and Kasha 1945 paper stressed the possibility of observing triplet states in fluid media, the generality of this concept awaited a more powerful attack.

The work of George Porter and associates [25, 26] brought the triplet state to the world of chemistry as a chemical species of reality, one whose particular chemistry and spectroscopy could be studied. The advent of flash photolysis and flash spectroscopy, which made study of transient species with lifetimes of a microsecond to a nanosecond a standard observation, had an enormous influence on the application of triplet state information to photochemistry.

## 5. Conclusion

The Jabłoński Diagram for dye molecule photoluminescence and kinetics of excitation transformed a vast accumulation of a diffuse set of observations into the beginnings of an exact science of molecular photophysics. Although some quantitative macroscopic laws of luminescence had been developed previously, the Jabłoński Diagram turned attention to molecular parameters, and expression of physical macroscopic behavior in terms of these.

The subsequent generalization of the Jabłoński Diagram by spectroscopic studies on a quantum mechanical basis has led to the Molecular Electronic State Diagram for polyatomic molecules in general, with its triplet and singlet multiplicities, radiationless pathways, orbital assignments, and relaxation mechanisms.

Paralleling the evolution of other theories from classical optics based on kinetics and electromagnetism, the power of a pivotal quantitative starting point as it evolved into a quantum mechanical translation, has been amply demonstrated by the influence of the Jabłoński Diagram.

## REFERENCES

[1] A. Jabłoński, *Efficiency of Anti-Stokes Fluorescence in Dyes*, *Nature* 131, 839 (1933).
[2] A. Jabłoński, *Über den Mechanismus der Photolumineszenz von Farbstoffphosphoren*, *Z. Physik* 94, 38 (1935).
[3] A. Jabłoński, *Polarized Photoluminescence of Adsorbed Molecules of Dyes*, *Nature* 133, 140 (1934).
[4] A. Jabłoński, *On the Notion of Emission Anisotropy*, *Bull. Acad. Pol. Sci. Ser. Sci. Math. Astron. Phys.* 8, 259 (1960).
[5] A. Jabłoński, *General Theory of Pressure Broadening of Spectral Lines*, *Phys. Rev.* 68, 78 (1945).
[6] A. Jabłoński, *Über einige Eigenschaften der in festen und flüssigen Medien eingebetten Molekule*, *Acta Phys. Pol.* 5, 271 (1936).
[7] W. Grotrian, *Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen*, Springer Verlag, Berlin 1928.
[8] G. Herzberg, *Atomic Spectra and Atomic Structure*, transl. by J. W. T. Spinks, Prentice-Hall, Inc., New York 1937, p. 77.
[9] G. K. Rollefson, M. Burton, *Photochemistry and the Mechanism of Chemical Reactions*, Prentice-Hall, Inc., New York 1939, p. 15.
[10] Kautsky did not distinguish between intrinsic metastable state population versus metastable state population induced by dye dimerization. Cf. M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* 11, 371 (1965).
[11] G. N. Lewis, D. Lipkin, T. T. Magel, *A Study of the Phosphorescent State*, *J. Am. Chem. Soc.* 63, 3005 (1941).
[12] M. Kasha, *Collisional Perturbation of Spin-Orbital Coupling and the Mechanism of Fluorescence Quenching. A Visual Demonstration of the Perturbation*, *J. Chem. Phys.* 20, 71 (1952).

[13] M. **Kasha**, *Faraday Soc. Discussion* No. 9, 14 (1950). The author's data on *intersystem crossing ratio* were first published with permission by D. S. McClure, Table. VI. Cf. Ref. [21].

[14] S. I. **Weissman**, D. **Lipkin**, *J. Am. Chem. Soc.* 64, 1916 (1942).

[15] G. N. **Lewis**, M. **Kasha**, *Phosphorescence and the Triplet State, J. Am. Chem. Soc.* 66, 2100 (1944).

[16] For a perspective on the evolution of this topic: Cf. M. **Kasha**, *The Triplet State — An Example of G. N. Lewis Research Style, J. Chem. Educ.* 61, 204 (1984).

[17] G. N. **Lewis**, M. **Kasha**, *Phosphorescence in Fluid Media and the Reverse Process of Singlet-Triplet Absorption, J. Am. Chem. Soc.* 67, 994 (1945).

[18] G. N. **Lewis**, M. **Calvin**, M. **Kasha**, *J. Chem. Phys.* 17, 804 (1949).

[19] M. **Kasha**, *Chem. Rev.* 41, 401 (1947).

[20] D. S. **McClure**, *J. Chem. Phys.* 17, 905 (1949).

[21] M. **Kasha**, *Radiat. Res.* Supplement 2, 243 (1960).

[22] D. S. **McClure**, *J. Chem. Phys.* 20, 682 (1952).

[23] C. A. **Hutchison**, Jr., B. W. **Mangum**, *J. Chem. Phys.* 29, 952 (1958).

[24] J. A. van der **Waals**, M. S. de **Groot**, *Mol. Phys.* 2, 333 (1959).

[25] G. **Porter**, M. W. **Windsor**, *Disc. Faraday Soc.* 17, 178 (1954); *Proc. R. Soc. London* A245, 238 (1958).

[26] G. **Porter**, F. W. **Wright**, *Trans. Faraday Soc.* 51, 1205 (1955).