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Review

Electronically Excited States of Free Radicals

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Abstract: Formation of the excited doublet (D) and quartet (Q) states of free radicals under their photoexcitation is discussed. The relative positions of the D and Q states are compared to the positions of the photoexcited states of organic molecules (Jablonsky diagram). A number of representative cases of the excited states of free radicals detected by their transient absorption or emission are presented. A special case of the population having the lowest Q state in some radicals is discussed. A spin–statistical factor in the reactions of Q and D is debated.

Keywords: photoexcited free radicals; Jablonsky diagram; reactions with dioxygen; doublet and quartet states

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1. Introduction

Organic compounds are used in chemistry and exist in everyday life. They consist of organic molecules. The vast majority of these molecules exist in a singlet state S_0. Upon the absorption of light, a molecule reaches an excited S_1 state. S_1 can undergo intersystem crossing (ISC) and populate the lowest triplet state T_1. These processes are presented in the Jablonsky diagram [1,2] (Figure 1). Singlet states are "close shells"; they have two electrons with opposite spins on each occupied molecular orbital (MO). A triplet state has two single-occupied MO (SOMO) with parallel spins. That way, the spin angular momentum of the singlet states is $s = 0$; for the T state, $s = 1$ (The spin multiplicity is $2s + 1$. The spin multiplicity is presented as a superscript in a state notation.).

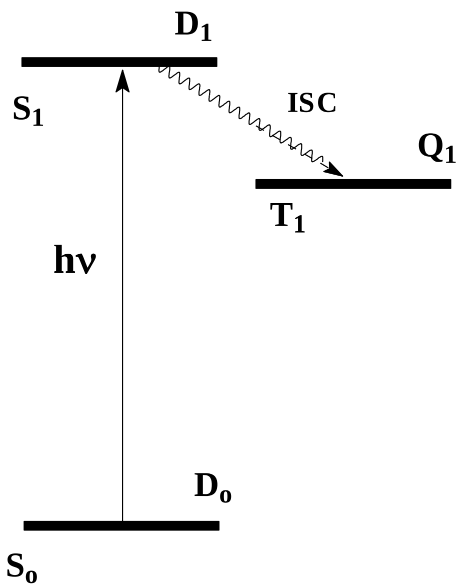


Figure 1. Jablonsky diagram for a molecule. Abbreviations of the electronic states of a molecule are presented below the horizontal lines reflecting the position of a state. An analog of the Jablonsky diagram for a radical is presented in the same diagram, with notions of the states placed above the horizontal lines.

The Jablonsky diagram is described in detail in textbooks on photochemistry [1,2]. Such books and review articles present all of the processes occurring in excited states, as well as the known rare exceptions to the diagram [1,2]. Figure 1 presents only the absorption of a light quantum and the intersystem crossing (ISC) to the T_1 state initiated by spin–orbit coupling (SOC) [3]. The probabilities of the occurrences of the processes in the excited states of molecules obviously vary from 0 to 1.

2. Doublets and Quartets

Organic free radicals ($R^\bullet$) are species with an "open shell". They have at least one SOMO. The spin state of $R^\bullet$ is $s = 1/2$, and such states are called doublets (D). Radicals with three one-electron orbitals exist in a quartet electronic state (Q), which has $s = 3/2$. Free radicals are important intermediates in many photoinduced reactions. There are cases when radicals absorb light and produce excited D_1 or Q_1 states; see below. Obviously, the chemical reactivity of the photoexcited radicals (molecules) is different from that in D_0- (S_0-) states [4].

Synthesized stable organic π-radicals have been recently reported, which are especially interesting for applications in organic light-emitting devices (OLED) due to their possibility of providing a quantum yield of luminescence of 1.0 [5]. This is one of the modern reasons for studying photoexcited free radicals.

It is logical to assume an analog of the Jablonsky scheme (Figure 1) for free radicals. SOC mixes D_1 and Q; see Figure 1. All other processes (luminescence, internal conversion, and vibrational relaxation) take place in photoexcited molecules and radicals. Luminescence from the D_1 (Q_1) state is named in the literature as fluorescence (phosphorescence), apparently due to an analogy with such processes in molecules.

Stable free radicals ($R^\bullet$) are usually colored, whereas the parent compounds (RH) are colorless. That means that D_1 lies close in energy to D_0, namely 180–300 kJ/mol above D_0 (Figure 1). For example, colorless 2,4,6-tri-*tert*-butyl phenol has a longwave absorption maximum at λ = 280 nm (370 kJ/mol), whereas the corresponding phenoxyl radical (blue aroxyl) has an analogous value λ = 626 nm (190 kJ/mol). A similar bathochromic shift of the absorption maximum holds between a parent compound (say, a ketone, a quinone) and its radical $R^\bullet$ (a ketyl radical, a semiquinone) formed by hydrogen abstraction.

Q_1 may have a higher energy than D_1; see Figure 2.

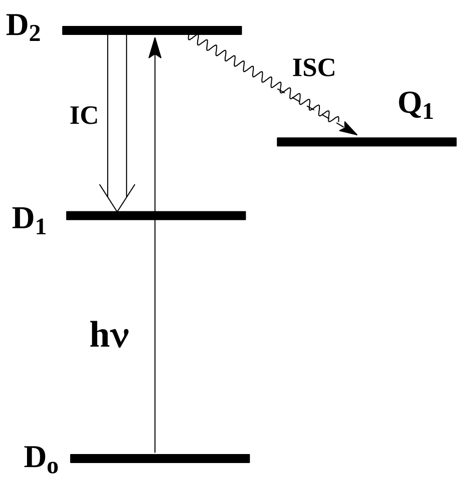


Figure 2. Possible positions of the excited states of a radical where the Q_1 state has a higher energy than the D_1 state. IC stands for internal conversion.

The formation of Q_1 requires three unpaired electrons with parallel spins, which may increase the energy of the excited $R^{\bullet *}$ compared to that of D_1 (The formation of T_1 in molecules requires only two unpaired electrons with parallel spins. The dominant role of the Pauli effect leads to a lower energy of T_1 compared to S_1 in the majority of cases [1,2]).

Thus, in a number of cases, Q_1 can be populated only after primary excitation into D_2 or D_3; see Figure 2.

Fast internal conversion (IC) from a higher $D_{2(3)}$ to a lower D_1 should lead to a low probability of the population in Q_1. This assumption allowed the authors of [2] to draw conclusions about the insignificant role of Q_1 in the photochemistry of radicals. However, there have been many reports of the experimental detection of Q_1 (Section 3 below). The observation of a relatively long-lived $R^{\bullet *}$ leads to the assumption that $R^{\bullet *}$ is in a Q_1 state; see Section 3 below.

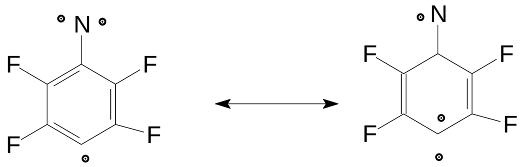
3. Excited Neutral Radicals

This brief review article does not aim to review most of the reported cases of $R^{\bullet *}$ studies. We will focus on liquid solutions of polyatomic organic radicals and radical ions at room temperature. This section presents some instructive and exemplary results of such research. Chemical transformations of $R^{\bullet *}$, except a reaction with dioxygen (Section 5), are beyond the scope of this brief article.

The excited states are usually detected by their emission spectra or transient absorption spectra.

However, we will start with a seminal publication [6] that reported a $D_0 \leftarrow Q_1$ phosphorescence of a decacyclene radical anion in a solid state at 77 K. It was assumed that Q_1 was above D_1, and the luminescence was phosphorescence. The Q_1 electronic state of this anion at 77 K was confirmed by transient magnetic resonance [7]. Photoexcited radical ions are considered in Section 4.

High-spin molecular objects are of great interest due to their potential applications in molecular magnets. It has been stated that some labile dehydrophenylnitrenes are in the ground Q state [8]. Quantum chemical calculations of the ground and excited states of several dehydrophenylnitrenes allowed the authors to obtain their geometry and distinguish between the Q and D states of these species [8]. The studied dehydrophenylnitrene system demonstrates that a fine competition between ferromagnetic Q- and antiferromagnetic D states coupling of electron spins takes place. With a single electron orbital being orthogonal to two coplanar orbitals, the relative orientation of the latter orbitals determines which mode of electron coupling prevails; see Scheme 1.

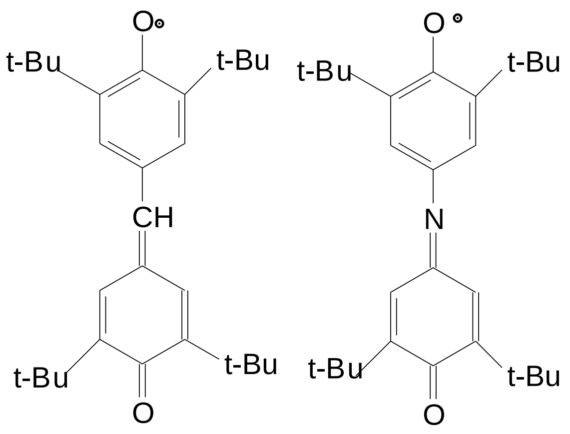


Scheme 1. Resonance structures of 4-dehydro-2,3,5,6-tetrafluorophenylnitrene. Hint to its phenylnitrene/phenyl radical (**left**) and carbene/iminyl radical (**right**) [8].

The D_1 state of benzophenone ketyl radical in a benzene solution at room temperature was observed by laser flash photolysis with time-resolved (TR) ESR and absorption spectroscopy [9]. The lifetime of this D_1 was ~2 ns [9]. It is assumed that a photoexcitation of the ketyl into D_2 led to ISC into $Q_1 \leftarrow D_2$ [9]. (Q_1 was positioned above D_1; see Figure 2). It seems that, in the case of the studied ketyl, ISC successfully competed with the $D_1 \leftarrow D_2$. The lifetime of Q_1 is relatively long, namely ~2 μs [9]. As expected, $D_0 \leftarrow Q_1$ is a relatively long process compared to $D_0 \leftarrow D_1$ in the same ketyl radical under the same conditions.

The ketyl radical of benzophenone and of its derivative were studied by two-color laser flash photolysis [10]. The first ns pulse (λ_{ex} =266 or 355 nm) generated ketyl radicals the usual way: hydrogen abstraction from a solvent. The second ps pulse (λ_{ex} = 532 nm) excited ketyls into D_1. The transient absorption and fluorescence of D_1 were measured. The lifetime of D_1 in the studied solvents varied from 0.5 to 5 ns [10]. It was noticed that D_1 had a high dipole moment of 7–10 D, which led to a significant solvent effect on D_1 [10].

Many of the compounds reported in [5] were large, stable organic radicals that emit fluorescence. Stable aroxyl (substituted phenoxyl) radicals have demonstrated transient absorption in liquid solvents in flash photolysis experiments [11]; see Figure 3. However, the fluorescence of galvinoxyl and other aroxyls has not been observed [12].



(a) (b)

Scheme 2. Chemical structures of galvinoxyl (**a**) and indophenoxyl (**b**).

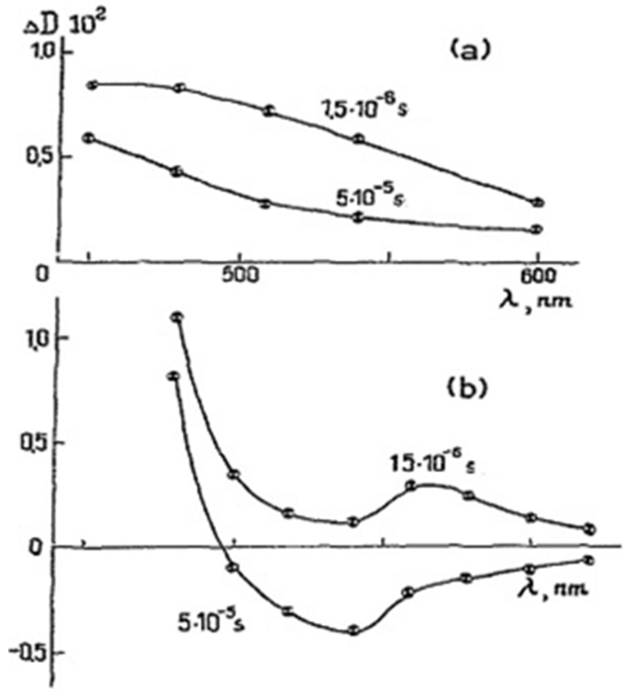


Figure 3. Transient absorption spectra, i.e., a change in the optical density ΔD vs. the wavelength, obtained under μs flash photolysis of stable aroxyl radicals (**a**) galvinoxyl and (**b**) indophenoxyl in hexane at room temperature [11]. The structures of the radicals are presented in Scheme 2 below.

Photoexcitation was performed by UV light (λ_{ex} = 260–380 nm) [11]. Quite similar spectra were observed in propan-1-ol. The spectra (Figure 3) were tentatively ascribed to the Q_1 state of the aroxyls due to their relatively long lifetime (~10 μs) [11].

The $D_{9,10} \leftarrow D_0$ transitions were observed under further study of the photochemistry of galvinoxyl with fs flash photolysis (λ_{ex} = 400 nm) [12]. However, a long-lived absorption very similar to that presented in Figure 3a was ascribed to the anions of glavinoxyl and galvinoxylate. The formation of anions in a nonpolar solvent (Figure 3) is doubtful. The photochemistry of galvinoxyl deserves further study.

Phosphoresce $D_0 \leftarrow Q_1$ was observed for phosphaethynyl radicals in solid argon [13]. The scheme of the electronic levels for this radical follows Figure 1, and the lifetime of the emission is ~0.1 s [13].

Electron spin polarization and magnetic field effects have been investigated in photoexcited organic molecules that are chemically tethered to radical fragments (nitroxyls and others) [14,15]. With TR ESR, electron spin polarization was observed in the D_1 and Q_1 states after photoexcitation of a large stable radical [15].

Scaiano, Johnson et al. performed a cycle of investigations on photoexcited transient radicals such as diphenylmethyl and others [16–18]. The radicals were generated by a laser pulse; after a short delay, the second laser pulse excited the produced radicals [16,17]. A fluorescence from D_1 was apparently observed in these experiments. The lifetime of fluorescence varied from 5 to 400 ns for polyatomic radicals in liquid non-viscous solvents at room temperature [16]. The constant k_q of quenching an excited state by dioxygen (Section 5) obtained for several $R^{\bullet *}$ [16,17,19] testified to the occurrence of Reactions (1) or (2) in the D_1 state; see Section 5. The lifetime of photoexcited diphenylmethyl radicals in common non-viscous solvents is 250 ns at 300 K [16,17]. Once more, this $R^{\bullet *}$ is in a D_1 state [16].

The excitation of perchlorodiphenylmethyl radical (PDM$^\bullet$) at λ_{ex} = 530 nm leads to the population of D_1 (lifetime τ = 31 ns), from which emission is observed ($\phi_{fl} = 1.0 \times 10^{-3}$) [20]. This state is quenched by electron donors and acceptors at a rate at or close to the diffusion control and at much slower rates by dioxygen and hydrogen atom donors. The fragmentation of PDM$^\bullet$ (ϕ_{dec} = 0.06) occurs from a higher excited doublet (D_n, n $\geq$ 2), producing intermediates that are trapped [20]. See [20] for details of the chemical reactions.

The excitation of perchlorotriphenylmethyl radical (PTM$^\bullet$) at λ_{ex} = 532 nm leads to an excited doublet, the D_1 state (lifetime τ = 7 ns) [21]. The lifetime of this state is insensitive to dioxygen, electron acceptors, and hydrogen-donating solvents. Electron donors triphenylamine, *N*,*N*-dimethylaniline, and thianthrene quench PTM$^{\bullet *}$ at diffusion-controlled rates. The cyclization of PTM$^\bullet$ to form the perchloro-9-phenylfluorenyl radical occurs with a quantum efficiency of ϕ_{cyc} = 0.3 under λ_{ex} = 365 nm irradiation [21].

Ns and ps laser flash photolysis allowed to observe $Q_1 \leftarrow D_1$ ISC of flavin radicals in DNA photolyase [22]. Thus, the electronic levels in this radical follow Figure 1; see [22] for details. The lifetime of the studied D_1 (Q_1) is 100 ps (1 µs) in an aqueous solution at room temperature [22].

Paramagnetic free radicals are efficient quenchers of the excited states of molecules [1,2]. It was observed in experiments with stable aroxyl radicals that self-quenching occurs in solutions [11]:

$$R^{\bullet *} + R^{\bullet} \rightarrow 2\, R^{\bullet} \tag{1}$$

4. Excited Radical Ions

Electronically excited radical cations and radical anions have been the subject of a number of experimental and theoretical investigations.

Stilbene (Sb) radical anions and radical cations were studied by pulse radiolysis and laser flash photolysis [23]. There were four species under investigation, namely *cis*- and *trans*-Sb$^{\bullet(+/-)*}$. It was stated that the D_2 of these species was observed [23]. Table 1 below summarizes most of the data obtained in this work:

Radical cations of polycyclic aromatic hydrocarbons (PAH) play an important role in different processes and in the environment—in particular, in astronomy [24]. PAH are easily ionized, producing radical cations PAH$^{\bullet+}$. As expected, the absorption spectra of PAH$^{\bullet+}$ are red-shifted towards the spectra of the parent PAH [24]. The excited states of 51 different PAH$^{\bullet+}$ were studied with the time-dependent density functional theory [24]. The vertical excitation energies and oscillating strengths of PAH$^{\bullet+}$ and even of PAH$^{\bullet-}$ were obtained. $\pi \leftarrow \pi$ transitions between individual π-orbitals in radical ions of PAH were considered [24].

Table 1. Properties of stilbene radical anions and radical cations in the D_2 state: lifetime (τ), rate constants of internal conversion (k_{ic}) and isomerization (k_i), quantum yield of isomerization (ϕ_i), and excitation energies (E) [1] [23].

Radical-Ion	τ, ns	$k_{ic} \times 10^{-8}$, s^{-1}	$k_i \times 10^{-9}$, s^{-1}	ϕ_i	E, kJ/mol
trans-$Sb^{\bullet-*}$	2.5 ± 1.0	4.0 ± 1.6	0	0	202
cis-$Sb^{\bullet-*}$	1.5 ± 0.4	5.6 ± 1.7	1.0 ± 0.3	0.14 ± 0.05	189
trans-$Sb^{\bullet+*}$	0.24 ± 0.05	41 ± 11	0	0	223
cis-$Sb^{\bullet+*}$	0.12 ± 0.03	29 ± 7	4.1 ± 1.0	0.49 ± 0.12	210

[1] In DMF at room temperature. See [23] for additional details.

Biphotonic laser photoexcitation (λ_{ex} = 248 nm) of different aromatic compounds (biphenyl, naphthalene, perylene, and others) and several amines in oxygenated polar solvents have led to the corresponding radical cation $R^{\bullet+}$ [25]. $R^{\bullet+}$ have obviously red-shifted spectra compared to the parent compounds and are absorbed in the visible and NIR regions. A prompt irradiation of $R^{\bullet+}$ with a second harmonic Nd:YAG laser (λ_{ex} = 532 nm) led to the excited $R^{\bullet+*}$ [25]. The studied $R^{\bullet+*}$ had a lifetime ranging from hundreds of fs to tens of ps at room temperature. The nature of $R^{\bullet+*}$ is not discussed [25]; it is probably the $D_{1(2)}$ states.

In general, excited states of multiple radicals of radical ions in the D_n state have very short lifetimes (see Sections 2 and 3) as a result of their low-lying excited state energies (energy gap law) [26–28].

A study of the dynamics of the ground state recovery of the perylene radical cation ($Pe^{\bullet+}$), of the perylene radical anion ($Pe^{\bullet-}$), and of the anthraquinone radical anion ($AQ^{\bullet-}$) was shown in [29]. Complete or partial regeneration took place after a picosecond photoexcitation of the corresponding radical ion. In boric acid glass, the excited state lifetime of $Pe^{\bullet+}$ was 35 ± 3 ps, while in concentrated sulfuric acid, it was smaller than 15 ps, the time resolution of the experimental setup [29]. The excited state lifetime of $Pe^{\bullet+}$, $Pe^{\bullet-}$, and $AQ^{\bullet-}$ generated by a photoinduced intermolecular electron transfer reaction in acetonitrile was shorter than 15 ps [29].

It is well known that molecules in excited states essentially change their redox properties [1,2]. Not surprisingly, the same holds true for radical ions. Wasielewski et al. studied the redox properties of radical anions in excited doublet states [26,27]. The radical anions of aromatic diimides have been assumed recently to be participants in different photoinduced electron transfers. The photoexcitation of these radical anions produces powerful reducing agents [26]. However, the properties of the π^*-excited D states of these radical anions remain obscure. The radical anions of three complex aromatic imides with increasingly larger π systems, namely *N*-(2,5-di-*tert*-butylphenyl)phthalimide, *N*-(2,5-di-*tert*-butylphenyl)-1,8-naphthalimide, and *N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide, as well as the three corresponding aromatic diimides [26], were produced by electrochemical reduction of the neutral molecules. The radical anions of these imides and diimides demonstrated intense visible and weaker NIR absorption bands corresponding to their $D_n \leftarrow D_0$ transitions [26]. The excited states of the radical anions were generated by fs excitation (λ_{ex} = 840 nm) into these absorption bands. Excitation of the first two radical anions mentioned above led to their decomposition, whereas excitation of the third imide and three diimides yielded transient spectra of their $D_n \leftarrow D_1$ transitions. The lifetimes of the observed D_1 states of the radical anions were all less than 600 ps and increased as the D_0–D_1 energy gap increased [26]. These results imposed constraints on the use of these excited radical anions as electron donors in electron transfer systems targeted at molecular electronics and solar energy utilization [26].

Three photoexcited cyanoanthracenes radical anions, including the radical-anion of 9,10-dicyanoanthracene, were produced by photoinduced electron transfer in liquid using femtosecond spectroscopy [30]. All three excited radical ions had 3–5 ps lifetimes due to efficient non-radiative deactivation to the ground state. The excited state of these radical anions was D_1. It is suggested that a short lifetime of D_1 does not preclude photochemical applications of cyanoanthracene radical anions [30].

It was observed that the 10-phenyl-10*H*-phenothiazine radical cation ($PTZ^{\bullet+}$) had a manifold of excited D states accessible using visible NIR light [27]. $PTZ^{\bullet+}$ could serve as super-photooxidants with excited state potentials in excess of +2.1 V vs. SCE [27]. The photoexcitation of $PTZ^{\bullet+}$ in acetonitrile with λ_{ex} = 517 nm laser pulse populated a D_n excited D state that decayed first to the unrelaxed lowest electronic excited state, $D_1{}'$ (τ < 0.3 ps), followed by relaxation to D_1 (τ = 10.9 $\pm$ 0.4 ps) [27]. D_1 finally decayed to D_0 (τ = 32.3 $\pm$ 0.8 ps) [27]. To probe the oxidative power of $PTZ^{\bullet+*}$ D_n states, $PTZ^{\bullet+}$ was covalently linked to each of three hole acceptors: perylene, 9,10-diphenylanthracene, and 10-phenyl-9-anthracenecarbonitrile, which have oxidation potentials of 1.04, 1.27, and 1.6 V vs. SCE, respectively [27]. In all three cases, photoexcitation wavelength-dependent ultrafast hole transfer occurred from the D_n, $D_1{}'$, or D_1 of $PTZ^{\bullet+*}$ to the three acceptors. The high oxidative power of the D_n state of $PTZ^{\bullet+*}$ will enable applications using this chromophore as a superoxidant for energy-demanding reactions [27].

The quantum chemical calculations (restricted coupled cluster with perturbative triples method) were used to calculate the equilibrium geometries and excitation energies of the hitherto unknown Q states in diacetylene-, triacetylene-, and benzene radical cations [31]. Spectroscopic data for the D states obtained with the same approach were found to be in good agreement with the experiment [31]. In diacetylene and triacetylene cations, there were Q states that were close to the minimum energies of the corresponding D_1 states [31].

The kinetics of the radical cations of perylene ($PE^{\bullet+}$), tetracene ($TE^{\bullet+}$), and thianthrene ($TH^{\bullet+}$), as well as the radical anions of anthraquinone ($AQ^{\bullet-}$) and tetracenequinone ($TQ^{\bullet-}$), formed by γ irradiation in low-temperature matrices ($PE^{\bullet+}$, $TH^{\bullet+}$, $AQ^{\bullet-}$, and $TQ^{\bullet-}$) or by oxidation in sulfuric acid ($PE^{\bullet+}$, $TE^{\bullet+}$, and $TH^{\bullet+}$) were investigated using picosecond spectroscopy [32]. The longest ground state recovery time measured was 100 ps. It is not surprising that the excited state lifetime of $PE^{\bullet+}$ is substantially longer in low temperatures than in sulfuric acid. The data suggest that both $PE^{\bullet+*}$ and $TE^{\bullet+*}$ probably decay by a reversible charge transfer reaction [32]. $TQ^{\bullet-}$ demonstrates fluorescence [32]. Most probably, the studied radical ions are photoexcited in the doublet state.

Electron acceptor methyl viologen (*N*,*N*′-dimethyl-4,4′-bipyridine, abbreviated MV^{2+}) plays an important role in redox reactions ($MV^{2+} \leftrightarrow MV^{\bullet+}$ [33]). Femtosecond pump-probe spectroscopy was used to investigate the excited state dynamics of the electrochemically generated $MV^{\bullet+}$ in an acetonitrile solution [34]. Excitation of the $D_1 \leftarrow D_0$ transition at λ_{ex} = 730 nm led to rapid relaxation (700 fs), generating two intermediates in the transient absorption spectra [34]. The longer-lived intermediate, with a lifetime of 16 ps, could be assigned to a vibrationally excited ground state of $MV^{\bullet+}$. Its absorption spectrum was very similar to the ground state spectrum of $MV^{\bullet+}$ in both shape and extinction coefficients but red-shifted by ~810 cm^{-1} [34]. The shorter-lived transient decayed with a characteristic time of τ = 1.0 $\pm$ 0.1 ps and was possibly also a vibrationally excited ground state. Thus, these results show that the excited D_1 state of $MV^{\bullet+*}$ in an acetonitrile solution relaxes on the fs time scale via at least one long-lived (τ = 16 ps) vibrationally excited ground state [34].

The study [35] provides evidence that the photoexcited radical cation of guanine in DNA participates in chemical reactions.

5. Quenching of Photoexcited Radicals by Dioxygen

The majority of free radicals (especially C-centered alkyl, aromatic benzyl, and others) react with dioxygen at rates controlled by diffusion in a solution. The same is expected for highly reactive $R^{\bullet*}$. The rate of a diffusion-controlled reaction estimated by the Debye formula is $k_{diff} \approx 7 \times 10^9$ $M^{-1} \cdot s^{-1}$ at room temperature (T) and a solvent viscosity of η = 1 cP [36]. In the case of a reagent with a non-zero spin, the expected rate constant of the diffusion reaction is lower: $k_q = \sigma\, k_{diff}$, where σ is the spin–statistical factor [19,36]. There are two types of quenching of $R^{\bullet *-}$, physical and chemical [19]:

$$^{n}R^{\bullet *} + {}^{3}O_2 \rightarrow {}^{2}R^{\bullet} + {}^{1}O_2\ ({}^{1}\Delta_g) \quad (2)$$

$$^{n}R^{\bullet *} + {}^{3}O_2 \rightarrow {}^{2}RO_2^{\bullet} \quad (3)$$

Photoexcited $R^{\bullet *}$ can be in the D_1 state (n = 2) or in the Q_1 state (n = 4). It is easy to obtain that, for Reactions (2) and (3), σ = 1/3 and 1/6 for n = 2 (D_1) and n = 4 (Q_1), respectively. Thus, one can expect $k_q \approx 2 \times 10^9$ (1×10^9) $M^{-1} \cdot s^{-1}$ for the quenching of $R^{\bullet *}$ for D_1 (Q_1) in Reactions (1) or (2) under T and η mentioned above (It is known that $k_{diff} \sim \eta^{-1}$; the rate constant of a reaction with fast-diffusing O_2 may have higher k_{diff}-values than those predicted by the Debye formula).

6. Conclusions

The main elementary photophysical processes in the excited free radicals are depicted in Figures 1 and 2. There is an analogy with the relevant photophysical processes in molecules (Figure 1), but the photophysics of $R^{\bullet *}$ are more complex (Figure 2). Usually, D_1 or Q_1 were observed in the experiments by their emission or absorption spectra. Additional TR ESR experiments would make such assignments more reliable. Quantum chemical calculations should help in the identification of $R^{\bullet *}$, their electronic nature and their structure as well.

It is possible to conclude that the Q_1 state has a much longer life than the D_1 state of the same radical. It is obvious that $D_0 \leftarrow Q_1$ transition occurs with a change in the spin multiplicity and is analogous to $S_0 \leftarrow T_1$ ISC or phosphorescence in molecules.

Stable nitroxyl radicals (TEMPO and others) have been widely used in chemistry research as antioxidants and as photostabilizers of polymers for many decades. To the best of our knowledge, there are no experimental data on the excited states of nitroxyls.

There are tens of colored stable free radicals that are commercially available or can be synthesized. The photochemistry of a small portion of them has been studied; see some examples in Sections 3 and 4 above. Stable radicals are valuable and convenient objects for the study of their excited states and their transformations. The first triphenylmethyl free radical discovered by Gomberg in 1900 was in equilibrium with its corresponding dimer [37]. Once more, to the best of our knowledge, there are no experimental data on the excited state of the first radical.

The high reactivity of photoexcited radicals and radical ions may find applications, such as the decomposition of environmental pollutants and light energy conversion [38]. However, a detailed picture of excited radical ions provided by spectroscopy require further clarification, especially the nature of the excited states. Laser flash photolysis (from μs to fs) and other spectroscopic and quantum-chemical calculations will shed light on the nature and reactivity of such excited species. These multidisciplinary studies will help us obtain detailed understandings of the chemistry of the higher excited states and excited intermediates [38,39].

It would be of interest to compare ESR spectra of radicals in the ground and in excited states to compare hyperfine coupling constants (HFC) and g factors. It will give information on the geometrical structure of $R^{\bullet *}$.

It is expected that a relatively long lifetime (~10 μs) in solvents at room temperature signified that $R^{\bullet *}$ is in the Q_1 state.

The measured numerical values of the rate constant k_q of quenching $R^{\bullet *}$ by O_2 give a hint as to the nature of a spin state of $R^{\bullet *}$.

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References

1. Turro, N.J.; Ramamurthy, V.; Scaiano, J.C. *Modern Molecular Photochemistry of Organic Molecules*; University Science Books: Sausalito, CA, USA, 2010.
2. Klán, P.; Wirtz, J. *Photochemistry of Organic Compounds*; Wiley: Wiltshire, UK, 2009.
3. Khudyakov, I.V.; Serebrennikov, Y.u.A.; Turro, N.J. Spin-Orbit Coupling in Free-Radical Reactions: On the Way to Heavy Elements. *Chem. Rev.* **1993**, *93*, 537. [CrossRef]
4. Melnikov, M.Y.; Smirnov, V.A. *Handbook of Photochemistry of Organic Radicals*; Begell House: New York, NY, USA, 1996.
5. Teki, Y. Excited-State Dynamics of Non-Luminescent and Luminescent π-Radicals. *Chem. Eur. J.* **2019**, *25*, 1. [CrossRef]
6. Brugman, C.J.M.; Rettschnick, R.P.H.; Hoytink, G.J. Quartet-doublet phosphorescence from an aromatic radicals. The decacyclene mononegative ion. *Chem. Phys. Lett.* **1971**, *8*, 263. [CrossRef]
7. Kothe, G.; Kim, S.S.; Weissman, S.I. Transient magnetic resonance of a photoexcited quartet state. *Chem. Phys. Lett.* **1980**, *71*, 445. [CrossRef]
8. Bettinger, H.F.; Sander, W. Dehydrophenylnitrenes: Quartet versus Doublet States. *J. Am. Chem. Soc.* **2003**, *125*, 9726. [CrossRef] [PubMed]
9. Thurnauer, M.C.; Meisel, D. Time-resolved EPR studies of the benzophenone-diphenyl ketyl radicals system. Possible evidence for quartet-doublet intersystem crossing. *Chem. Phys. Lett.* **1982**, *92*, 343. [CrossRef]
10. Sakamoto, M.; Cai, X.; Fujitsuka, M.; Majima, T. Solvent Effect on the Deactivation Processes of Benzophenone Ketyl Radicals in the Excited State. *J. Phys. Chem. A* **2006**, *110*, 11800. [CrossRef]
11. Kuzmin, V.A.; Khudyakov, I.V.; Tatikolov, A.S. Electronically-Excited States of Phenoxy Radicals. *Chem. Phys. Lett.* **1977**, *49*, 495. [CrossRef]
12. Grilj, J.; Zonca, C.; Max, L.; Daku, L.; Vauthey, E. Photophysics of the galvinoxyl free radical revisited. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6352. [CrossRef]
13. Ganesan, E.; Custer, A.-L.; Guillemin, J.-C.; Kołos, R. Unusual Quartet-Doublet Phosphorescence from the Phosphaethynyl Radical, CP. *Angew. Chem. Intern. Edn.* **2022**, *134*, e202210521.
14. Turro, N.J.; Khudyakov, I.V. Application of chemically induced dynamic electron polarization to mechanistic photochemistry. *Res. Chem. Interm.* **1999**, *25*, 505. [CrossRef]
15. Giacobbe, E.M.; Mi, Q.; Colvin, M.T.; Cohen, B.; Ramanan, C.; Scott, A.M.; Yeganeh, S.; Marks, T.J.; Ratner, M.A.; Wasielewski, M.R. Ultrafast Intersystem Crossing and Spin Dynamics of Photoexcited Perylene-3,4:9,10-bis(dicarboximide) Covalently Linked to a Nitroxide Radical at Fixed Distances. *J. Amer. Chem. Soc.* **2009**, *131*, 3700. [CrossRef] [PubMed]
16. Scaiano, J.C.; Tanner, M.; Weir, D. Exploratory Study of the Intermolecular Reactivity of Excited Diphenylmethyl Radicals. *J. Am. Chem. Soc.* **1985**, *107*, 4396. [CrossRef]
17. Scaiano, J.C.; Johnson, L.J.; McGimsey, W.G.; Wier, D. Photochemistry of Organic Reaction Intermediates: Novel Reaction Paths Induced by Two-Photon Laser Excitation. *Acc. Chem. Res.* **1988**, *21*, 22. [CrossRef]
18. Johnston, L.J. Photochemistry of Radicals and Biradicals. *Chem. Rev.* **1993**, *93*, 251. [CrossRef]
19. Darmanyan, A.P.; Gregory, D.D.; Guo, Y.; Jenks, W.S. Generation and Decay of Aryl Sulfinyl and Sulfenyl Radicals: A Transient Absorption and Computational Study. *J. Phys. Chem. A* **1997**, *101*, 6855. [CrossRef]
20. Ruberu, S.R.; Fox, M.A. Photochemical Behavior of Stable Free Radicals: The Photochemistry of Perchlorodiphenylmethyl Radical. *J. Phys. Chem.* **1993**, *97*, 143. [CrossRef]
21. Fox, M.A.; Gaillard, E.; Chen, C. Photochemistry of Stable Free Radicals: The Photolysis of Perchlorotriphenylmethyl Radicals. *J. Am. Chem. Soc.* **1987**, *109*, 708. [CrossRef]
22. Okamura, T.; Sancar, A.; Heelis, P.F.; Hirata, Y.; Mataga, N. Doublet-Quartet Intersystem Crossing of Flavin Radical in DNA Photolyase. *J. Am. Chem. Soc.* **1989**, *111*, 5961. [CrossRef]
23. Majima, T.; Fukui, M.; Ishida, A.; Takamuku, S. Stilbene Radical Anions in the Excited Doublet State. *J. Phys. Chem.* **1996**, *100*, 8913. [CrossRef]
24. Hirata, S.; Head-Gordon, M.; Szczepanski, J.; Vala, M. Time-Dependent Density Functional Study of the Electronic Excited States of Polycyclic Aromatic Hydrocarbon Radical Ions. *J. Phys. Chem. A* **2003**, *107*, 4940. [CrossRef]
25. Shkrob, I.A.; Sauer, M.C.; ALiu, A.D.; Crowell, R.A.; Trifunac, A.D. Reactions of Photoexcited Aromatic Radical Cations with Polar Solvents. *J. Phys. Chem. A* **1998**, *102*, 4976. [CrossRef]
26. Gosztola, D.; Niemczyk, M.P.; Svec, W.; Lukas, A.S.; Wasielewski, M.R. Excited Doublet States of Electrochemically Generated Aromatic Imide and Diimide Radical Anions. *J. Phys. Chem. A* **2000**, *104*, 6545. [CrossRef]
27. Christensen, J.A.; Phelan, B.T.; Chaudhuri, S.; Acharya, A.; Batista, V.S.; Wasielewski, M.R. Phenothiazine Radical Cation Excited States as Super-oxidants for Energy Demanding Reactions. *J. Am. Chem. Soc.* **2018**, *140*, 5290. [CrossRef]
28. Englman, R.; Jortner, J. Energy Gap Law for Radiationless Transitions in Large Molecules. *Mol. Phys.* **1970**, *18*, 145. [CrossRef]
29. Gumy, J.-C.; Vauthey, E. Investigation of the Excited-State Dynamics of Radical Ions in the Condensed Phase Using the Picosecond Transient Grating Technique. *J. Phys. Chem. A* **1997**, *101*, 8575. [CrossRef]
30. Beckwith, J.S.; Aster, A.; Vauthey, E. The excited-state dynamics of the radical anions of cyanoanthracenes. *Phys. Chem. Chem. Phys.* **2022**, *24*, 568. [CrossRef]

31. Komiha, N.; Rosmus, P.; Maier, J.P. Low lying quartet states in diacetylene, triacetylene and benzene radical cations. *Mol. Phys.* **2007**, *105*, 893. [CrossRef]
32. Brodard, P.; Sarbach, A.; Gumy, J.-C.; Bally, T.; Vauthey, E. Excited-State Dynamics of Organic Radical Ions in Liquids and in Low-Temperature Matrices. *J. Phys. Chem. A* **2001**, *105*, 6594. [CrossRef]
33. Turro, N.J.; Khudyakov, I.V.; Gopidas, K.R. A laser flash photolysis study of magnetic field effects in photoinduced electron transfer between Ru (bpy $)_3^{2+}$ and *N,N*-dimethylviologen in micellar solution. *Chem. Phys.* **1992**, *162*, 131. [CrossRef]
34. Häupl, M.; Lomoth, R.; Hammarström, L. Femtosecond Dynamics of the Photoexcited Methyl Viologen Radical Cation. *J. Phys. Chem. A* **2003**, *107*, 435. [CrossRef]
35. Khanduri, D.; Adhikary, A.; Sevilla, M.D. Highly Oxidizing Excited States of One-Electron-Oxidized Guanine in DNA: Wavelength and pH Dependence. *J. Am. Chem. Soc.* **2011**, *133*, 4527. [CrossRef] [PubMed]
36. Khudyakov, I.V. Transient free radicals in viscous solvents. *Res. Chem. Interm.* **2013**, *39*, 781. [CrossRef]
37. Khudyakov, I.V.; Levin, P.P.; Kuzmin, V.A. Reversible recombination of radicals. *Russ. Chem. Rev.* **1980**, *49*, 1990. [CrossRef]
38. Fujitsuka, M.; Majima, T. Reaction dynamics of excited radical ions revealed by femtosecond laser flash photolysis. *J. Photochem. Photobiol. C* **2018**, *35*, 25. [CrossRef]
39. Grill, J.; Beckwith, J.; Vauthey, E. Excited-state Dynamics of Radical Ions in Liquids. *Chimia* **2021**, *75*, 856. [CrossRef]