

JABLONSKI DIAGRAM REVISITED

EL DIAGRAMA DE JABLONSKI REVISTADO

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This paper deals with new approaches towards the Jablonski diagram and the ξ state concepts from the viewpoint of the relationship between electronic deactivation and vibrational relaxation processes in electronically excited species. In both concepts, vibrational relaxation precedes the electronic deactivation processes of excited molecules. The experimental data accumulated up to the present using mainly time-resolved luminescence and transient absorption spectroscopy from the field of the photophysics of transition metal compounds and different organic molecules have clearly demonstrated that even spin-forbidden electronic deactivations are in many cases faster processes than vibrational relaxation. It means that the classical Jablonski diagram indicating that electronic deactivation processes occur after vibrational relaxation should be modified. In general, electronic deactivations occur from vibrationally higher states.

Este artículo trata sobre nuevas aproximaciones al diagrama de Jablonski y los conceptos del estado ξ desde el punto de vista de la relación entre la desactivación electrónica y los procesos de relajación vibracional en especies electrónicamente excitadas. En ambos conceptos, la relajación vibracional precede a los procesos de desactivación electrónica de las moléculas excitadas. Los datos experimentales acumulados hasta el momento usando básicamente luminescencia resuelta en el tiempo y espectroscopía transiente de absorción del campo de la fotofísica de los compuestos de metales de transición y de diferentes moléculas orgánicas, han demostrado claramente que incluso las desactivaciones electrónicas de espín prohibido son, en muchos casos, más rápidas que la relajación vibracional. Ello significa que el diagrama de Jablonski clásico, que indica que los procesos de desactivación ocurren después de la relajación vibracional, pudieran modificarse. En general, las desactivaciones electrónicas ocurren desde estados vibracionales superiores.

PACS: Ultrafast processes (procesos ultra-rápidos), 82.53.-k; Born-Oppenheimer approximation (aproximación de Born-Oppenheimer), 31.30.-i; photon molecule interactions (interacciones fotón molécula), 33.80.-b

I. INTRODUCTION

When dealing with photodeactivation processes of electronically excited species it should be worth summarizing and reminding one aspect of the issue, namely the relationship of the rate constant of electronic deactivations (transitions lowering the electronic energy) and rotational-vibrational relaxation (lowering mainly vibrational energy within a given electronic state). In the history of photochemistry two solutions of the relationship have evolved, both obeying the Born-Oppenheimer approximation.

The first approach applied originally in organic photochemistry was offered by Jablonski in his original paper devoted to anti-Stokes fluorescence of dyes [1]. It is usually expressed in the form of a diagram - called Jablonski diagram - which is a graphical depiction of the electronic states of a molecule and the transitions between those states. The vertical axis of the graph represents energy increasing from the bottom (ground state or S_0) to the top (singlet and triplet excited states or S_n and T_n). The transitions between the states (like excitation, internal conversion, fluorescence, intersystem crossing, etc.) are depicted as arrows (wavy arrows for nonradiative transitions, straight ones for radiative transitions). The Jablonski diagram (Fig. 1) is usually expressed for organic molecules and their singlet and triplet states, it can be, however, generally used for inorganic

complexes too, e.g. for chromium(III) complexes and their quartet and doublet states.

Its current form can be found in many literature sources devoted to photochemistry and photophysics [2–5]. One of the characteristics of a typical Jablonski diagram is that any electronic deactivation occurs from the lowest vibrational level, i.e. vibrational relaxation precedes electronic deactivation. It is worth mentioning that Jablonski diagram in combination with Franck-Condon principles has been successfully applied in explanation of the mirror shape of absorption and emission electronic spectra.

In the 1960s Adamson elaborated an analogous approach introducing the term “ ξ -state” to characterize the state thermally equilibrated with its surroundings by the transfer of part of the vibrational energy of a populated excited state to surrounding molecules through collisions [6]. Adamson defined thexi (thermally equilibrated excited states) states as the chemically reacting species being in thermodynamic equilibrium with their surroundings and essentially high energy isomers of the ground state. By contrast, the species obtained by light absorption of wavelength around a ligand field band maximum are Franck-Condon states that have a nonthermodynamic distribution of vibrational excitations; such states are treated as pseudo pure electronic states in ligand field theory [7]. One of the experimental observations that contributed to the idea of the thexi state

was LF fluorescence, which is defined as the spin-allowed radiative deactivation occurring from a LF excited state of a coordination compound to its ground-state and involving the central atom centered orbitals [8]. Also, the Adamson's concept was based on the assumption that the thermal equilibration (i.e. vibrational relaxation) preceded the electronic deactivation processes of excited molecules. Adamson applied his concept mainly in the field of LF photochemistry of coordination compounds.

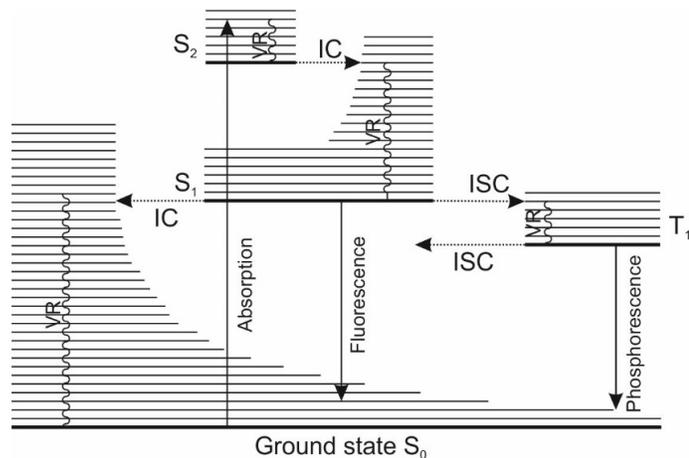


Figure 1. Jablonski diagram for organic molecules.

It should be pointed out that both - Jablonski's and Adamson's - concepts were formulated prior to introducing ultrafast flash-techniques (working in nano-, pico- and femtosecond time domain) into photochemistry and photophysics. The advent and introduction of the mentioned ultrafast techniques has documented that situation could be different, i.e. electronic deactivation is frequently a faster process than vibrational relaxation.

To support the idea, two kinds of experimental results are offered. The first one concerns photophysical deactivation processes, the other is based on photochemical deactivations.

Coordination compounds

The experimental data accumulated up to the present using mainly time-resolved luminescence and transient absorption spectroscopy from the field of the photophysics of transition metal compounds have clearly demonstrated that even spin-forbidden electronic deactivations are faster processes than vibrational relaxation. Data for iron(II) and iron(III) are gathered in several papers [9–11]. The issue of coupling of electronic deactivation and vibrational relaxation has been elaborated in detail and applied for both organic molecules and transition-metal complexes by Penfold and his coworkers [12]. They drew attention mainly to intersystem crossing processes. Instead of considering a simple ladder of states, as depicted in a Jablonski diagram, they propose to consider the more complicated spin-vibronic levels. Their main idea is that due to the strong mixing brought about by the simultaneous presence of nonadiabatic and spin-orbit coupling, the spin, electronic, and vibrational dynamics cannot be described independently [12, 13]. On the other

hand, in cases of a significant difference between the rate of electronic deactivation and vibrational relaxation, these events can be considered, in accordance with Born-Oppenheimer approximation, independent and represented as by a Jablonski diagram. A new feature is that the vibrational relaxation is preceded by faster electronic deactivation, i.e. electronic deactivation processes occur from excited vibrational states.

In the photochemistry of coordination compounds, the energy order of electronic excited states decreases stepwise typically from the energy highest intraligand (frequently ring centered $\pi\pi^*$) states, via charge transfer (both ligand to metal and metal to ligand) states, and finishing in metal-centered states. One of such examples are iron(III) complexes with a Schiff base as a ligand. In Fig. 2 structure of such complex [Fe(salen)(CH₃OH)Br] together with excitation wavelengths into different excited states is illustrated. This and other similar complexes were photochemically investigated and quantum yield of Fe(II) formation was determined [14, 15]. From the results summarized in Table 1 we can see that iron(II) is formed at any of the applied excitation wavelengths. It indicates that there must be effective communication between the excited states involving the photoredox reactive LMCT state and that the LMCT state populated in different ways must have different content of vibrational energy. This can be depicted in the sequence of deactivation processes described by equation:

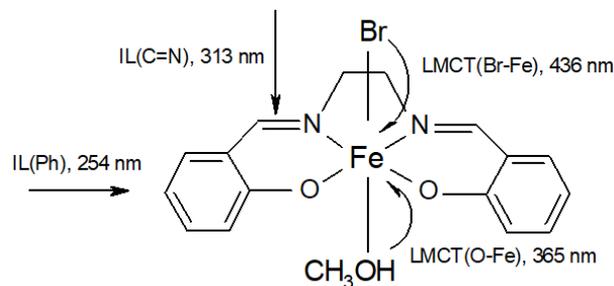


Figure 2. Schematic structure of the complex [Fe(salen)(CH₃OH)Br] and excitation data.

Table 1. Excitation wavelength, λ_{in} , populated excited state, quantum yield of iron(II) formation, $\Phi(\text{Fe}^{II})$, and order of mean vibrational energy of photoredox reactive LMCT state for the complex [Fe(salen)(CH₃OH)Br] irradiated in methanol at steady-state conditions.

λ_{in} nm	254	313	365	436
Populated excited state	IL(Ph)	IL(C=N)	LMCT (O→Fe)	LMCT (Br→Fe)
$\Phi(\text{Fe}^{II})$	0.0036	0.0031	0.00045	0.00020
Order of ν of reactive LMCT state(s)	ν	$> \nu$	$> \nu$	$> \nu$

Another interesting result of this wavelength dependence is that the step-wise decreasing in electronic energy (1) is associated with a simultaneous increase in the vibrational energy content of the photoredox reactive LMCT state. This can happen when the vibrational relaxation is slower

than electronic deactivation and any deactivation process is accompanied by the accumulation of the vibrational energy.

Based on these results we can propose a modified Jablonski diagram for the deactivation processes in [Fe(salen)XY] (X, Y – monofunctional anionic and/or neutral ligands) systems as depicted in Fig. 3.

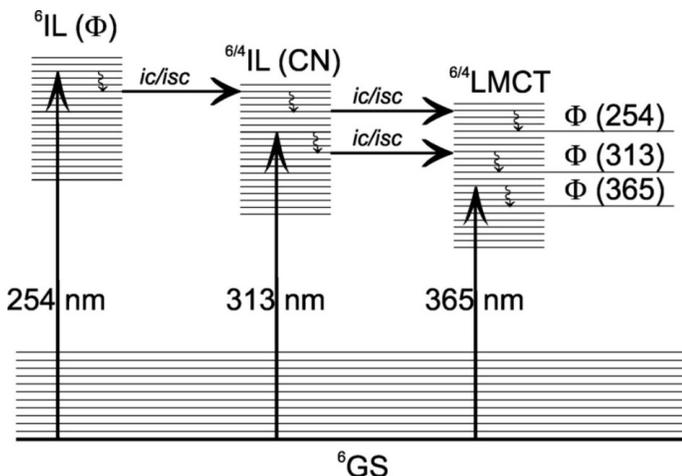


Figure 3. Modified Jablonski diagram for the deactivation processes in [Fe(salen)XY].

The femtosecond study of a similar Schiff base complex, [Fe(salpet)(CN)] ($H_2salpet = N,N$ -bis(1-hydroxy-2-benzyliden)-1,6-di-amino-4-azahexan, Fig. 4) excited at 400 nm led to the values of 338 fs, attributed to electronic deactivation in the form of intersystem crossing, and 9.09 ps, assigned to vibrational cooling and/or simultaneously occurring other electronic deactivations [16].

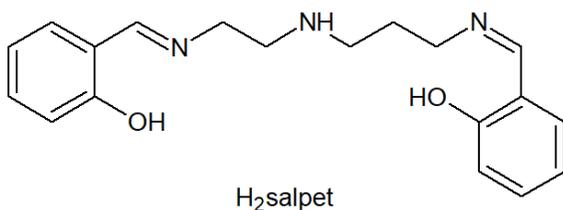


Figure 4. Structure of the ligand $H_2salpet = N,N$ -bis(1-hydroxy-2-benzyliden)-1,6-di-amino-4-azahexan.

High-spin iron(III) salicylato complexes are another example of investigated systems. Complexes with 5-sulfosalicylic acid (SSA) and all isomers of fluorosalicylic (FSA) acids as ligands were investigated. In the case of SSA all three mono-, bis- and tris complexes were prepared in solution, whereas only monofluorosalicylato complexes were investigated. In all cases data treatment yielded two relaxation times as shown in Tables 2 and 3, the first one was ascribed to electron deactivation from hot excited state and the second one to vibrational cooling of the hot ground state [17,18].

Table 2. Lifetimes of excited states of Fe(III) complexes with fluorosalicylic acid isomers.

Complex	τ_1 /ps	$\lambda_{max}(\tau_1)$ /nm	τ_2 /ps	$\lambda_{max}(\tau_2)$ /nm
Fe-3FSA	0.8±0.1	670	2.6±0.3	580
Fe-4FSA	0.5±0.1	660	2.0±0.2	580
Fe-5FSA	0.6±0.1	695	2.1±0.2	610
Fe-6FSA	0.9±0.1	645	2.8±0.4	555

Rury and Sension investigated iron (III) tetraphenylporphyrin chloride in room temperature solutions in toluene and dichloromethane [19]. Depending on the excitation wavelength and solvent they were able to determine three relaxation times. First time of 0.4 - 0.6 ps was the relaxation from the lowest-lying porphyrin singlet manifold into a LMCT state followed by a MLCT from the iron to the porphyrin on a time scale of 1.8 - 2.3 ps that produced excited 4T intermediate spin state of $Fe^{III}TPPCL$. The system relaxes back to the high spin 6A_1 ground state on a time scale of 13 - 18 ps. No vibrational cooling was observed.

Table 3. Lifetimes of excited states of Fe(III) complexes with sulfosalicylic acid.

Complex	τ_1 /ps	τ_{v2} /ps
FeSSA	0.26	1.8
$Fe(SSA)_2^{3-}$	0.1	1.4
$Fe(SSA)_2^{6-}$	0.17	1.5

In the field of ferrous complexes, different derivatives of pyridine as ligands were used. In the ultrafast study of $[Fe(bpy)_3]^{2+}$ global analysis of the transient absorption data revealed three relaxation times. The first 120 fs is the decay of the 3MLCT , the second 960 fs was identified as the population time of the 5T_2 state, and the third 665 ps was attributed as its decay time to the ground state [20]. The group of McCusker investigated excited-state dynamics in a FeII polypyridyl complexes, $[Fe(tptn)]^{2+}$ and $[Fe(tren(py)_3)]^{2+}$, where tptn is tetrakis(2-pyridylmethyl)-1,3-propylenediamine and $tren(py)_3$ is tris(2-pyridylmethyl-iminoethyl)amine. In the first complex after excitation $^1A \rightarrow ^1MLCT$ a 700 fs transition into 5T_2 was observed following by 2 ps cooling of this state and 18 ns decay to the ground state followed. The second study showed < 100 fs transition from 1MLCT into a LF manifold of 1T_2 , 1T_1 , 3T_2 and 3T_1 from which in approximately 300 fs hot 5T_2 state was formed. Vibrational cooling of this state occurred in 8 ps followed by a transition into the ground state in 60 ns [10,21,22].

Well known is the tris(acetylacetonate) chromium(III) $Cr(acac)_3$ system. It has well documented photophysical properties, high symmetry, and low quantum yield for photosubstitution (<0.01). Following the $^4A_2 \rightarrow ^4T_2$ excitation < 100 fs ISC into hot 2E occurred, that was followed by 1.1 ps vibrational cooling and final 800 ps relaxation to the ground state [23–25]. The order of $k_{VR} > k_{IC} > k_{ISC}$ that is based on the analogy from organic systems is questioned, as it does not apply to metal complexes.

Organic and organometallic compounds

Different biomolecules such as DNA bases or dyes were investigated from the broad range of organic compounds. In a study focused on ultrafast measurements of deactivation for triphenylmethane dyes, malachite green (MG), brilliant green (BG), crystal violet (CV), and ethyl violet (EV) in different solvents the multiexponential decay of the excited state was found. The times of 4.8 and 5.8 ps for CV and EV in methanol were consistent with the picture of declining vibrationally hot and/or twisted ground state, the faster time 0.54 ps in MG was attributed to fluorescence decay in MG [26,27].

A deactivation mechanism was investigated in a sunscreen constituent - oxybenzone (OB) by transient electronic and vibrational absorption spectroscopy. The energy dissipation mechanism involves ultrafast 100 fs excited enol \rightarrow keto tautomerization followed by 400 fs internal conversion relaxation processes. The cooling of the vibrationally hot ground state occurred in 5-8 ps coupled with keto \rightarrow enol tautomerization or the minor pathway of vibrational cooling to keto-form and subsequent back isomerization occurred in > 1.3 ns [28].

A delayed fluorescence was observed in dithienylbenzothiadiazole (DTBT) and a carbazole substituted derivative CDTBT (Fig. 5) was used to study the dynamics in this system.

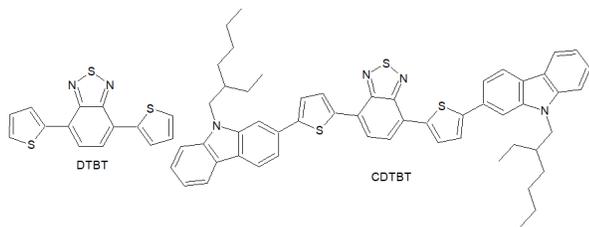


Figure 5. Structures of DTBT and CDTBT.

This study revealed a fast 300 fs IC from S_2 to hot S_1 state in DTBT followed by 33 ps cooling of this S_1 state. From this state, fluorescence occurred in 2 - 3 ns together with ISC/BISC into T_1 in 0.5 - 1 ns that was followed by 13 μ s phosphorescence. In the heavier molecule of CDTBT 3.7 ps IC from S_2 into S_1 was observed and from this hot S_1 state 2.2 ns fluorescence occurred. No cooling of this hot S_1 state was observed [29].

Investigation of the photochromic reactions (transition between the open and the closed form) of a water-soluble indolylfulgimide led to four different times. The 0.06 ps and the 0.4 ps components of the C-form can be assigned to the relaxation of the excited molecule from the Franck-Condon region and solvent reorganization. The third lifetime component (1.8 ps) was attributed to the repopulation of the ground state, while the fourth one (~ 10 ps) was associated with the vibrational cooling of the ground state [30]. Koller and coworkers investigated different indolylfulgimide derivative and found 2.0 ps deactivation of the electronic excited state which was followed by 15 - 20 ps vibrational cooling [31, 32].

Similar results were found in the studies of intramolecular vibrational relaxations. Carbonyl complexes of Re and Mn were investigated in tetrachloromethane and DMSO. The intramolecular vibrational energy redistribution (IVR) was faster in $[\text{Re}(\text{CO})_5\text{Br}]$ than in Mn complex and IVR time constants are six times faster in a polar solvent (2.8-3.9 ps) than in nonpolar solvent (20-25 ps) [33]. Electronic deactivation together with vibrational energy relaxation were observed in nickel octaethylporphyrin complex. Here in this large molecule, the IVR occurred on subpicosecond scale following by intermolecular energy transfer that occurred in ~ 10 ps. However, there are two electronic deactivation processes. One is internal conversion (< 350 fs) that forms an excited d-d state that deactivates in ~ 300 ps [34]. Investigation of IVR of cresyl

violet in methanol showed a dephasing time constant 2.4 ps and authors hypothesize that the dominant process is IVR [35]. The vibrational energy relaxation of CH2I2 in different solvents was investigated by Charvat *et al.* [36]. They found that IVR occurs on 9-10 ps timescale while intermolecular vibrational energy transfer occurred in 60 - 120 ps and was solvent and excitation energy dependent.

In many other papers investigating electron transfer processes it is problematic to find information on vibrational relaxation times. Reverse intersystem crossing (RISC) was investigated in triazine derivatives forming exciplex used in OLEDs. Rate constants for ISC were around $3 \cdot 10^7 \text{ s}^{-1}$ and for RISC $\approx 10^5 \text{ s}^{-1}$ [37]. Aizawa *et al.* investigated RISC in organic donor-acceptor molecules. For 3-(2,7-dibromo-9,9-dimethylacridan-10-yl)xanthone and 3-(3,7-dibromo-phenoxazin-10-yl)xanthone they calculated and confirmed by measurements kRISC to be $8.7 \cdot 10^5 \text{ s}^{-1}$ and $2.6 \cdot 10^7 \text{ s}^{-1}$ [38]. Photoexcitation of formyluracil and formylcytosine showed $S_1 \rightarrow T_2$ transition 1950 fs to be rate determining step, followed by hopping transitions between T_2 and T_1 states with time constants 4 and 17 fs. Formylcytosine first revealed rapid initial equilibrium in singlet manifold with time constants fs and 5 fs for $S_1 \rightarrow S_2$ and $S_2 \rightarrow S_1$, followed by rate determining step $S_1 \rightarrow T_2$ transition in 3559 fs. The subsequent IC $T_2 \rightarrow T_1$ occurred in 150 fs [39].

Calculations of Valiev *et al.* for different organic and organometallic compounds show different values of radiative and nonradiative rate constants. Values for certain molecules differed from experimental data due to inaccurate FC and adiabatic approximations [40]. Vennapusa *et al.* investigated receiver triplet state in carbonylpyrenes. They found out first occurs ultrafast IC from vibronically coupled higher S_n states to S_1 followed by ISC to T_4/T_5 receiver state followed by IC into lower states. Lifetimes of receiver triplet states in substituted pyrenes were 24, resp. 15 fs [41].

II. CONCLUSIONS

Based on the above data the following conclusions can be formulated. The concept of the excited state and Jablonski diagram was introduced before the invention of ultrafast techniques. The concept was in accord with the Born-Oppenheimer approximation. The data shows that the Jablonski diagram in its traditional form may not be fully valid, particularly in the case of coordination compounds. The original Jablonski diagram illustrates processes in organic molecules. However, in general even in such molecules the rate of electronic deactivations, spin-forbidden singlet-triplet intersystem crossing including, is higher than that of vibrational cooling. Processes occurring in open-shell transition metal complexes [42] were not involved and discussed. The relationship between vibrational relaxation and electronic deactivation processes was discussed in detail in the pioneering papers of McCusker *et al.* [21-24] who, based on experimental investigation, clearly documented that both IC and ISC processes in some Fe(II) complexes are much faster than vibrational relaxation. The selection rules that apply to organic compounds dealing with spin-forbidden processes

are not so strict for transition metal compounds. The result of this is that a rate constant of intersystem crossing is higher than that of internal conversion and electronic deactivation processes are faster compared to vibrational relaxation.

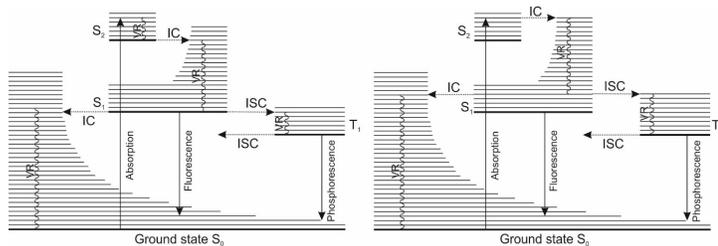


Figure 6. Original and modified Jablonski diagrams.

The better depiction of the Jablonski diagram for organic molecules, which can be used also for coordination compounds, that reflects current results is one shown in Fig. 6. There can be seen that only partial vibrational relaxation of excited states occurs and from this hot Franck-Condon states electron deactivation occurs.

ACKNOWLEDGMENTS

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