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Localization in excited states of molecules. Application to $[\mathrm{Ru(bpy)_3}]^{2+}$

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ABSTRACT

The properties of electron or exciton localization have been analyzed in solid state physics. Similar concepts can be applied to molecular systems, like $[Ru(bpy)_3]^{2+}$. It is shown that an energy stabilization of the lower excited states through delocalization (order of 10^3 cm^{-1}, mainly through the $Ru4d - bpy\pi^*$ mixing) has to be exceeded by a stabilization energy, which results from a nuclear rearrangement ΔQ, in order to lead to a localization. ΔQ must be very pronounced. Highly resolved emission spectra demonstrate that this is not the case. A series of different experimental results, all based on low-temperature, highly resolved spectra, show that an electron localization does not occur in the lower excited states of $[Ru(bpy)_3]^{2+}$ in the investigated matrices.

1. INTRODUCTION

The properties of the excited states of $[Ru(bpy)_3]^{2+}$ have been discussed often in connection with a possible localization of an electron on one of the three *bpy*-ligands. We believe that this problem has not always been clearly defined and therefore led to several misinterpretations. Consequently, it seems to be worthwhile to discuss some basic concepts concerning the physical implications related to a process of localization. Analogous models have been developed in solid state physics for the localization mechanisms of excitons (selftrapping) and of electrons (localized polarons).[1-5] It will be the subject of this paper to outline shortly that the concepts of these models are transferrable to molecular systems. Further, we want to present simple estimates which allow to decide whether a localization occurs for a symmetric $[Ru(bpy)_3]^{2+}$ complex with a D_3 ground state symmetry or not. Moreover, these estimates will be compared to experimental results.

2. LOCALIZATION / DELOCALIZATION

At first, we have to discuss the relevant time scales. An electronic absorption process from the ground into the excited state occurs within about 10^{-15} s. During this short time the nuclear positions of the chromophore and of its surrounding molecules may be regarded as not being shifted from those of the electronic ground state. However, an altered charge distribution in the excited chromophore polarizes also the electronic structure of the environment on the same time scale. In general, this leads to a force field, which tends to reorient the affected nuclei. Under the assumption that the electronic excitation in the

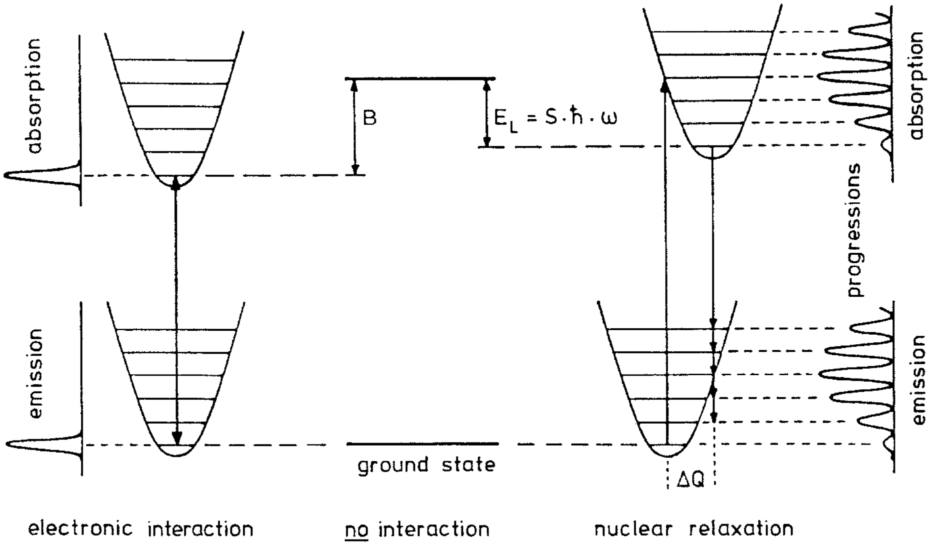

Figure 1: Schematic energy balance and shift of a representative nuclear coordinate ΔQ with its influence on optical spectra for the delocalized and the localized excited state charge density, respectively. The stabilization energies E_L (due to nuclear relaxation ⇒ localization) and B (due to electronic interaction ⇒ delocalization) are compared to the hypothetical case of no interaction.

unrelaxed situation would be confined long enough to the region of one ligand, a nuclear relaxation might occur, resulting in a localized (or selftrapped) state with the stabilization energy E_L relative to the unrelaxed situation.(Fig.1) The time, the excitation would have to stay in that region, should be at least as long as the time which is necessary for vibrational movements, say $\Delta t = 10^{-12}$ s. The shift of the nuclear coordinates by ΔQ (Q is a representative normal coordinate) can lead to a symmetry reduction. According to the size of ΔQ the maximum of the emission will be Stokes shifted relative to the maximum of the corresponding absorption and the spectra will exhibit a vibrational progression. The stabilization energy is given by $E_L = \hbar\omega \cdot S$ (Fig. 1 and e.g. [6]), where $\hbar\omega$ is the energy of the vibrational mode of the progression and S is the Huang-Rhys factor describing the number of coupling accepting modes. S can be estimated directly from the shape of a progression in the emission spectrum. The potential hypersurface of the localized state will most likely exhibit somewhat altered vibrational force constants (neglected in Fig.1) and probably show a stronger coupling to the surroundings compared to the unrelaxed state. In addition, an excited state degeneracy may be lifted.

If the electronic interaction between the three ligands and the metal could be neglected, then the localization would occur without any question. The electronic excitation will take place on that ligand which accidentally absorbs. Each of the three ligands has an equal probability for this process. Due to the (assumed) absence of an electronic interaction the charge distribution of the excited state is confined for sufficiently long time to the marked ligand in order to allow a nuclear relaxation. This process would be connected with the discussed features, which would be displayed in the measured spectra.

In a more realistic view an electronic interaction cannot be ignored, and it is directly related to the delocalization of the excited electron. For example, in $[Ru(bpy)_3]^{2+}$ the direct "through-space" *bpy-bpy* interaction energy is assumed to be very small and might be in the order of only one cm^{-1}. But the indirect *bpy-bpy* interaction mediated by the metal is appreciably larger. Especially, the $Ru4d - bpy\pi^*$ mixing leads to a very pronounced stabilization (specified as B in Fig.1) of the lower excited states in the delocalized situation. [This type of stabilization, also called back bonding, follows from the $e(d)$-$e(\pi^*)$ mixing.] Using ref. [7], it is possible to estimate that the size of the stabilization energy B through the delocalization is of the order of 10^3 cm^{-1}. For this case (delocalized excited state) we do neither expect any important alteration of nuclear coordinates nor of the vibrational force constants through the excitation.

Thus, the question whether a localization occurs or not depends on the balance of the corresponding stabilization energies. For $B > E_L$ the energy gain by an electronic delocalization is larger than the one, which is obtainable by a nuclear rearrangement. On the other hand, for $E_L > B$ a localization is preferred.

Very interesting is the case, when E_L exceeds B only slightly. This represents the lower limit, which is required for the occurrence of a localization. But a further condition has to be fulfilled. It is connected with the distinctness of the nuclear relaxation. We have to take into account that the localization of the excited electron may occur on every *bpy*-ligand with an equal probability. Thus, in the case of an electronic interaction between neighboring ligands the excited electronic charge distribution coupled to a certain deformation can still be delocalized. Or with other words (in a slightly different model), a sufficiently large interaction with neighboring ligands induces a ligand to ligand movement or hopping of this deformation.[1-4] The moving excitation takes the nuclear displacements of "its" environment with it. It is "dressed" by the local polarization. (This is in analogy with a moving polaron.) However, the value of the resulting stabilization energy B_L may be reduced drastically with respect to B. B_L describes the coupling of these electronic states being connected to a nuclear deformation. B_L is determined - mainly following Toyozawa[4] - by a product of the pure electronic energy B and a reduction factor due to the nuclear deformation. This reduction factor can be expressed by the square of an overlap integral of the wavefunctions of the distorted $\chi(Q-\Delta Q)$ and the undistorted $\chi(Q)$ zero-point vibrational states of the harmonic oszillators. Further, it can be shown that this reduction factor $|<\chi(Q-\Delta Q) \mid \chi(Q)>|^2$ is equal to e^{-S}, in the low temperature limit in which we are interested here. S is the Huang-Rhys factor (from [4] and [6]). Thus, we obtain $B_L = B \cdot e^{-S}$. With the Heisenberg uncertainty principle, $\Delta E \cdot \Delta t \approx \hbar$ - identifying ΔE with B_L - and with $\Delta t \approx 10^{-12}$ s (required time the excited electron has to stay on one ligand to allow a complete nuclear relaxation) we obtain for the Huang-Rhys factor $S \approx ln[B/\hbar \cdot 10^{12}$ s].

It is very illustrative to apply this result to $[Ru(bpy)_3]^{2+}$. Taking as lower limit for the stabilization energy $B \approx 10^3$ cm^{-1}, we obtain a Huang-Rhys factor of $S \approx 5$ as lower limit for a localized situation. This estimate implies that the shifts ΔQ of the nuclear positions of the (localized) excited state relative to those of the ground state have to be relatively large in order to allow the formation of localized excited states. Their occurrence should be seen (for example) in the emission spectrum by a very distinct progression, of which the fifth ($S \approx 5$) vibrational member is the largest one.

The process of a localization and the corresponding rearrangement of nuclear positions, which we discussed, would occur in the time scale of ps but the emission lifetime of $[Ru(bpy)_3]^{2+}$ (at $T = 2$ K) is about eight orders of magnitude longer. Therefore, even a very small interaction (B_L), which couples the different ligands, would induce many hopping processes during the lifetime τ (e. g. $B_L = 0.5$ cm^{-1} corresponding to $\Delta t \approx 10^{-11}$ s implies 10^7 hopping processes during τ). Thus, the deformation is not confined to a specific ligand. However, in a usual cw-emission spectrum (time scale of the electronic transition 10^{-15} s) the hopping process between completely relaxed positions would not be seen and the spectrum would display the properties of the deformed (localized) excited state.

3. EXPERIMENTAL RESULTS

The presented model allows to predict several distinctly different spectroscopic properties for the localized excited state compared to the delocalized case.(Table I)

Table I: Comparison of expected spectroscopic properties for a localized charge distribution in the excited state of $[Ru(bpy)_3]^{2+}$ compared to those of a delocalized situation.

Localized excited state	**Delocalized excited state**
Distinct distortion from the D_3 ground state symmetry	Same D_3 symmetry in the ground and excited states
Degeneracies should be lifted	Degeneracies possible
Stabilization energy due to localization $E_L > B$	Stabilization energy due to delocalization (e. g. back-bonding) $B \approx 10^3$ cm^{-1}
Distinct shift ΔQ on at least one normal coordinate in the excited relative to ground state $\Rightarrow$ strong progression	Relatively small shifts of the nuclear coordinates $\Rightarrow$ no or weak progression(s)
Changes of vibrational force constants	Similar vibrational force constants
Dependence of spectroscopic properties on the orientation of the magnetic field $\vec{B}$ relative to the $\vec{C}_2$ axes (Fig. 3b)	No orientation dependence for a magnetic field $\vec{B} \perp \vec{C}_3$

It is subject of this section to discuss shortly the different properties. This can successfully be carried out with the aid of highly resolved spectra. The usually registered broad band spectra would not allow to extract the required information, they could even lead to misinterpretations (e. g. see [8]).

Fig. 2 reproduces the highly resolved emission of $[Ru(bpy)_3]^{2+}$ in $[Zn(bpy)_3](ClO_4)_2$. At $T = 1.2$ K the origin line $|I\rangle \rightarrow |0\rangle$ dominates the spectrum but also a large number of vibronic sidebands can be resolved. Every vibronic component as well as the origin line couple to a series of lattice phonons. A superposition of these connected with an inhomogeneous broadening seems to be mainly responsible for the broad background. It is evident that no distinct progression occurs. The largest observable Huang-Rhys factor

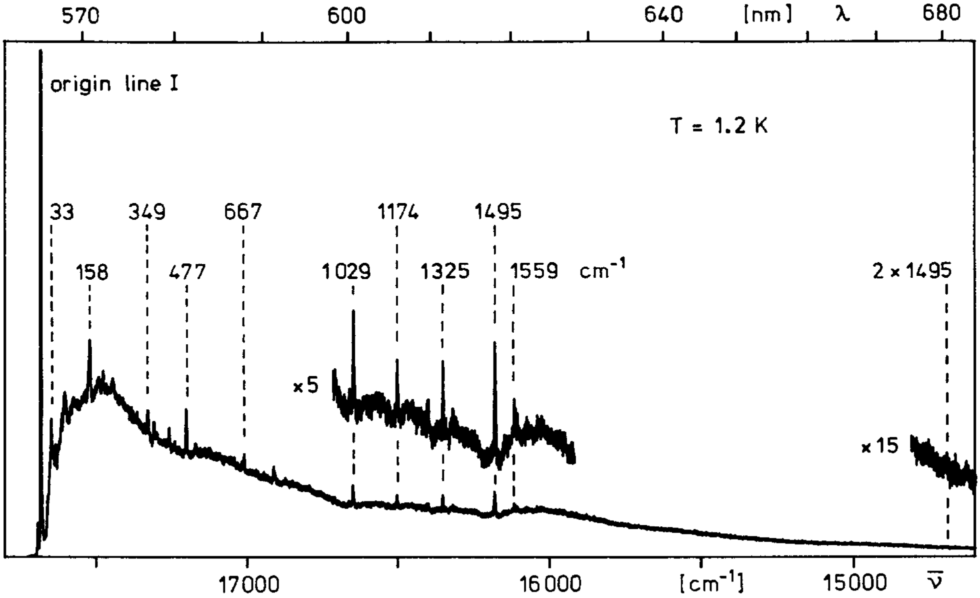

Figure 2: Low temperature emission of $[Ru(bpy)_3]^{2+}$ ($\approx$ 1 % mole/mole in $[Zn(bpy)_3](ClO_4)_2$). The given energies of vibrational modes refer to the origin I.

for the coupling to intra-molecular vibration is $S \approx 0.1$! Further, the energy position of the origin line is exactly the same in absorption and emission.[9-11] This implies that an energy shift of the electronic state does not take place between $\approx 10^{-15}$ s (time of the absorption process) and about several $10^2 \mu s$ (emission lifetime). These results are not compatible with the predictions for a localized model.

The same conclusion can also be derived from a comparison of the spectroscopic properties of the protonated and per-deuterated $[Ru(bpy)_3]^{2+}$. Upon deuteration most of the vibrational frequencies of the complex are reduced[12,13], including the zero-point vibrational energies. Thus, in the case of (on the average) smaller vibrational force constants in the excited electronic state compared to the ground state one observes a blue-shift of the corresponding origin. Its amount characterizes the extent of changes of the force constants. For $[Ru(bpy)_3]^{2+}$ one finds a blue-shift of the origin line I of 40 cm^{-1} (1.7 cm^{-1}/proton). This relatively small value points to small and unimportant differences of the vibrational energies in the excited state relative to those in the ground state. For comparison, in benzene with different excited and ground state frequencies the blue-shift of the lowest $\pi \rightarrow \pi^*$ transition amounts to 198 cm^{-1} (33 cm^{-1}/proton), while in $[Cr(NH_3)_6]^{3+}$ with similar hypersurfaces of ${}^4A_{2g}(t_{2g}^3)$ and ${}^2E_g(t_{2g}^3)$ a blue-shift of 15 cm^{-1} (0.8 cm^{-1}/proton) is observed. Using the data of ref. [12], one can estimate a blue-shift for the assumed localized excited situation of about $2 \cdot 10^2$ cm^{-1} (26 cm^{-1}/proton referring to the 8 protons of the reduced bpy). This value is not compatible to the experimental facts.

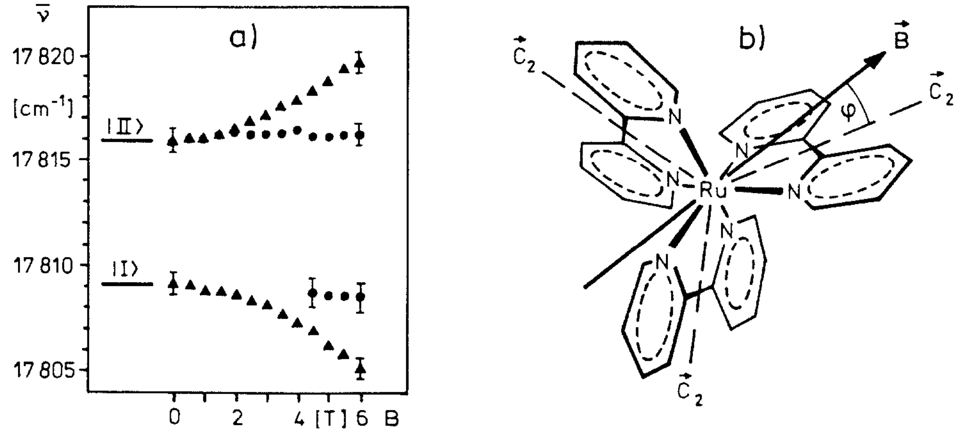

Figure 3: (a): Magnetic-field dependent splittings of the two lowest excited states in single-crystal $[Ru(bpy)_3](PF_6)_2$ (from[11]). (b): Orientation of the magnetic field $\vec{B}$ relative to the $\vec{C}_2$ axes of the complex ($\vec{B} \perp \vec{C}_3$). Changes of the angle φ do not influence the spectroscopic properties.

Interestingly, the blue-shift of the origin line $|I\rangle \leftrightarrow |0\rangle$ is identical in absorption (time scale $\approx 10^{-15}$ s) as well as in emission up to a time of ms. This allows to conclude that in the excited state no changes of force constants occur during 10^{-15} to 10^{-3} s, which is equivalent to their exclusion.[13]

The application of the zero-field ODMR spectroscopy to the *two* lowest excited states of $[Ru(bpy)_3]^{2+}$ ($|II\rangle$ lies 7 to 9 cm^{-1} above $|I\rangle$ depending on the matrix) reveals that these states exhibit zero-field splittings of the order of 0.1 cm^{-1}.[14] (The ODMR spectroscopy is similar to the ESR method but is applied to the excited states by measuring changes of the emission intensities upon microwave irradiation.) These experimental results show that the investigated electronic states are (nearly) degenerate.

Application of a high magnetic field $\vec{B}$ with $\vec{B} \perp \vec{C}_3$ results in a splitting of these states up to 3.5 cm^{-1} (at 6 T), which yields further evidence that these two states are indeed (nearly) degenerate at $B = 0$ T.[11] (Fig. 3a) An important additional result with respect to the question of localization is deducible from measurements of the emission properties for different angles of the magnetic field relative to the $\vec{C}_2$ axes.(Fig. 3b) In a localized situation (assuming two non-degenerate excited states) the special orientation $\vec{B} \parallel \vec{C}_2$ would lead to four origin lines due to the different orientations of $\vec{B}$ relative to the $\vec{C}_2$ axis intersecting the reduced *bpy*. Two of the lines would be connected with the ligand in direction of $\vec{B}$, while the two other lines would correspond to *either one* of the other two ligands in case of localization on one of these. Further, in this case the different orientations of $\vec{B}$ relative to the two positions of the assumed localization would lead to two distinctly different magnetic field-induced mixings between the states $|I\rangle$ and $|II\rangle$.[15] This should result in a distinct bi-exponential emission decay at low temperature with two lifetimes in the order of 10 to 100 μs. Moreover, in the range of $0 < \varphi < 30°$ one

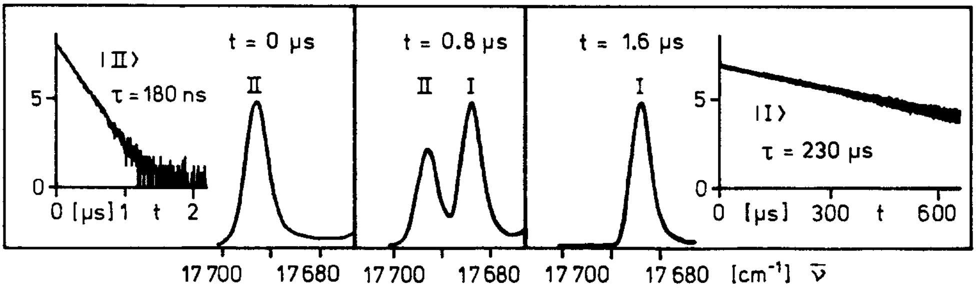

Figure 4: Time-resolved emission (linear intensity scales) of the electronic origin lines I and II at the given delay times t (time window $\Delta t = 50$ ns). The decay curves (ln intensity scales) are registered at the spectral positions of the origins.

would expect to find six origin lines. Again, the experimental evidence is at variance with this localized model but fits perfectly to a delocalized description[11]: A change of the angle φ of $\vec{B}$ relative to $\vec{C}_2$ (Fig. 3b) in steps of $\approx 5°$ did not reveal any effect neither on the splitting properties nor on the emission lifetime, which was mono-exponential on the μs time scale ($T = 1.8$ K) for all angles up to 6 T.

The time evolution of the emission spectra below 10 K on the sub-μs time scale was discussed in connection with a localization.[16] However, relatively slow relaxation processes – lying in the order of several ns at low temperatures – are general features of compounds possessing closely spaced (several cm^{-1}) electronic states, irrespectively of the nature of the involved states. Thus, these properties *cannot* be used to argue with regard to excited states symmetries. Fig. 4 shows the time-dependent emission spectra at $T = 1.2$ K in the region of the electronic origins of isolated $[Ru(bpy)_3]^{2+}$ in $[Zn(bpy)_3](ClO_4)_2$ at different delay times t. Also shown are the 1.2 K decay curves measured at the positions of the two origins. $|II\rangle$ decays mono-exponentially with a lifetime of 180 ns. Due to the spectral overlap of the emission from $|I\rangle$ and $|II\rangle$, the decay curve at the position of the origin line $|I\rangle \rightarrow |0\rangle$ is bi-exponential (not shown in Fig.4). The short component is caused by the overlapping emission of $|II\rangle$, while the long component reflects the lifetime of 230 μs of $|I\rangle$. Since the low-temperature (1.2 K) decay of $|II\rangle$ is much *faster* than at higher temperatures (thermal repopulation), it is concluded that the former decay is dominated by the transition $|II\rangle \rightarrow |I\rangle$. This is ascribed to a direct, relatively slow phonon relaxation (compared to the usual time of relaxation of $\approx 10^{-12}$ s)[17], a process which is for instance studied in detail in ruby[18].

4. CONCLUSION

An intra-molecular electronic interaction can lead to a larger energy stabilization of a delocalized state than a nuclear relaxation, which would lead to a localized state. It is pointed out, focusing on $[Ru(bpy)_3]^{2+}$ that the $Ru4d - bpy\pi^*$ mixing may result in an appreciable energy stabilization resulting in a delocalization. For example, the stabilization through "back bonding" is connected to this property.

The expected spectroscopic properties of a molecule with a localized electronic charge in the excited state are compared to those with a delocalized state. A spectroscopic analysis of $[Ru(bpy)_3]^{2+}$ in single-crystal matrices shows clearly that the lowest excited states cannot be regarded as being localized. This result is at least relevant for the three lowest excited states of $[Ru(bpy)_3]^{2+}$. (It holds also for $[Os(bpy)_3]^{2+}$[13].) Consequently, the reported localization behavior of $[Ru(bpy)_3]^{2+}$ (e. g. see [19]) should be carefully checked whether it is connected (a) to higher-lying excited states, (b) to external distortions, for example introduced by unsymmetrically acting solvent molecules, and/or (c) to high excitation density effects. On the other hand, a localization might still occur *intrinsically* in transition metal complexes with a relatively small delocalization-inducing energy stabilization. For example, this could occur for $3d^{10}$ systems, like $[Zn(bpy)_3]^{2+}$.

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