Fast intersystem crossing in transition-metal complexes

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The mechanism behind fast intersystem crossing in transition-metal complexes is shown to be a result of the dephasing of the photoexcited state to the phonon continuum of a different state with a significantly different transition metal-ligand distance. The coupling is a result of the spin-orbit interaction causing a change in the local moment. Recurrence to the initial state is prevented by the damping of the phonon oscillation. The decay time is faster than the oscillation frequency of the transition metal-ligand stretch mode, in agreement with experiment. For energies above the region where the strongest coupling occurs, a slower “leakage”-type decay is observed. If the photoexcited state is lower in energy than the state it couples to, then there is no decay.

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Introduction.— Fast intersystem crossing is an intriguing phenomenon that has puzzled many for several decades [1,2]. In a wide variety of transition-metal complexes, laser excitation creates a photoinduced excited state that decays on the order of tens to hundreds of femtoseconds into a state with often a different spin and a significant change in transition metal-ligand distance. This is generally followed by a cascade of intersystem crossings. Examples are spin crossover phenomena in divalent iron. The iron atom is generally surrounded by an organic material, such as Fe[(phen)$_2$] (NCS)$_2$ or Fe(bpy)$_3$ (bpy=bipyridine) [1,3]. In the ground state, Fe$^{2+}$ is in a low spin state. Illumination by light causes a charge transfer to the ligands, followed by a cascade of intersystem crossings, turning the singlet configuration ($S=0$) into a high-spin $S=2$ state. The high-spin state has a temperature-dependent decay time back into the low-spin state that can vary from nanoseconds up to days. Comparable crossovers have been observed in nickel compounds, where the electronic transition is followed by dissociation of the molecule [3]. These phenomena have been explored since the sixties predominantly using optical and Mössbauer spectroscopy [3]. Recent ultrafast x-ray spectroscopic measurements [4,6] have provided more detailed information on the crucial first step of the cascading process showing that the electronic transition occurs on the order of tens of fs [4] whereas the lattice relaxes on a timescale related to the transition metal-ligand stretch mode (100-200 fs) [6]. Experimental work has focused on identifying the states and relevant times scales of the intersystem crossing. Theory has followed several approaches. Study of the time-dependence generally relies on phenomenological rate equations [2,6]. Energy level diagrams have been obtained using ab initio techniques that use an adiabatic approximation [10,11], which has the disadvantage that strong coupling between states only occurs for very particular energies and transition metal-ligand distances.

This Letter focuses on the important first intersystem crossing and explains why the system decays so rapidly into states that dramatically differ in both spin and lattice parameter with quantum efficiencies close to 100%. Several types of decay depending on the relative energy positions of the states are identified.

Excitation.— Figure 1 gives a schematic diagram of the fast intersystem crossing. Initially, the system is in the ground state $|\psi_0\rangle$. It is then excited into state $|\psi_1\rangle$ from which it will decay into state $|\psi_2\rangle$. Depending on the change in coupling to the ligands, several phonons can be created in the excitation process, leading to states $|\psi_{1n}\rangle$. Although details of the initial excitation can play a role, its primary role is to create an excited state higher in energy compared to states that have a different spin.

Dephasing.— We now turn our attention to the crucial step of the fast intersystem crossing. Transitions between different spin states are accompanied by a change in lattice constant due to the conversion of $t_{2g}$ into $e_g$ electrons that repel the ligands more strongly (for example, from

FIG. 1: (color online) Schematic of fast intersystem crossing. The initial photoexcitation from state $|\psi_0\rangle$ into state $|\psi_{1n}\rangle$ occurs with minimal lattice distortion, i.e., the number of excited phonons $n$ is small. State $|\psi_{1n}\rangle$ couples to state $|\psi_{2n}\rangle$ under the excitation of phonons. The coupling strength (red curve) creates an effective phonon density of states.
LS $t_{2g}^0$ to HS $t_{2g}^1 e_g^0$). This can be described by the Hamiltonian

$$H_0 = \sum_{i=1,2} E_i c_i^\dagger c_i + \hbar \omega a^\dagger a + \sum_{i=1,2} \sqrt{\varepsilon_i} \hbar \omega n_i (a^\dagger + a), \quad (1)$$

where $E_i = E_2 + \Delta$, $E_2$ for the relative positions of states 1 and 2, respectively. The third term describes the coupling between the electrons and the lattice. Classically, this term corresponds to a constant force displacing the equilibrium position of the ligand atoms. Only the relative change in coupling is of importance. Since experimentally one observes a change in spin of $\Delta S = 1$, the coupling,

$$H_1 = V (c_1^\dagger c_2 + c_2^\dagger c_1), \quad (2)$$

is generally accepted to be due to the spin-orbit coupling.

We can diagonalize $H_0$ with a displaced-harmonic-oscillator transformation $\tilde{H}_0 = e^{\mathbf{S}} H_0 e^{-\mathbf{S}}$ with $\mathbf{S} = \sum_i n_i \sqrt{\varepsilon_i} (a^\dagger - a)$ with $g_i = \varepsilon_i / \hbar \omega$, giving

$$\tilde{H}_0 = \sum_i (E_i - \varepsilon_i) c_i^\dagger c_i + \hbar \omega a^\dagger a, \quad (3)$$

with eigenstates $|\psi_n^i\rangle$ for states $i = 1, 2$ and $n$ excited phonon modes. The transformed coupling $\tilde{H}_1 = e^{\mathbf{S}} H_1 e^{-\mathbf{S}}$ with $\tilde{V}_{nn'} = \langle \psi_n^i | \tilde{H}_1 | \psi_{n'}^j \rangle$ is no longer phonon conserving. If the change in transition metal-ligand distance in the photoexcitation is small, the prepared state is close to $|\psi_{10}\rangle$, see Fig. 1. The dominant coupling to $|\psi_{2n}\rangle$ is then $\tilde{V}_{n0}^n = e^{-g}\Phi^n / n!$ with $\Phi = \sqrt{\varepsilon_2 - \varepsilon_1}$. The strongest coupling between $|\psi_{10}\rangle$ and $|\psi_{2n}\rangle$ occurs at the maximum of the Poisson distribution for which $n \approx g$ at an energy $E_2 + g \hbar \omega = E_2 + \varepsilon_{12}$. In the calculations, we take $\hbar \omega = 30$ meV, which is a typical value for a transition metal-ligand stretching mode $^{12}$. The value of $\varepsilon_{12} = \varepsilon_2 - \varepsilon_1 = 0.2$ eV corresponds to a typical displacement of a few tenths of an Ångstrom $^{6,11}$. This energy difference also corresponds well to the observed change in wavelength of the emission features in the luminescence spectra $^{14}$. The spin-orbit coupling parameter is $V = 50$ meV, which is the atomic value calculated in the Hartree-Fock limit $^{13}$. Let us first consider $\Delta = 2\varepsilon_{12}$, when $|\psi_{10}\rangle$ coincides with this maximum, see Fig. 1. Figure 2(a) shows the time-dependence of the probability $P_1$ of finding the system in state 1, with

$$P_1 = \sum_n \langle \psi_n^1 | \tilde{H}_1 | \psi_n^1 \rangle^2,$$

and the displacement of ligands $x = \langle \psi(t) | \delta x \psi(t) \rangle$, where $x/x_1 = 1$, 0 correspond to the equilibrium positions of states 1 and 2, respectively. In the first 20 fs, we observe a rapid decrease in $P_1$ due to the dephasing of $|\psi_{10}\rangle$ into the phonon states $|\psi_{2n}\rangle$. Although dephasing is more commonly associated with coupling to a continuum $^{14}$, there are sufficient phonon states for a fast dephasing. However, the finite spacing $\hbar \omega$ between the phonon states leads to a recurrence as evidenced by the increase in $P_1$ around 140-160 fs. This recurrence is directly related to the oscillations of the ligands, where $\hbar \omega = 30$ meV corresponds to a period of 138 fs. When looking at larger times, we see a finite value of $P_1$, which does not correspond to the experimental observation of quantum efficiencies close to 100%. In addition, there is a continued oscillation of the ligands.

**Damping.**— The quantum efficiency can be dramatically improved by including damping of the phonon oscillations $^{15}$. Here we describe how to include a damping to a bath that accounts for damping mainly due to intramolecular energy redistribution $^{16,17}$. In the absence of the coupling $H_1$ relaxes the oscillations into their equilibrium states $|\psi_{10}\rangle$. Since fast intersystem crossings are experimentally known to be almost temperature independent, we take $T = 0$. The wavefunctions $|\psi(t)\rangle = \sum_{inb} \phi_{inb}^b(t) |\psi_{inb}^b\rangle$, are extended to include the possible states $b$ of the bath. The bath variables are integrated out to obtain the time-development of the occupation of state $|\psi_{inb}\rangle$. $P_{inb}(t) = \sum_{b} (\langle \psi_{inb}^b \psi(t) \rangle)^2 = \sum_{b} (\phi_{inb}^b(t))^2$. For the matrix elements of the coupling between the local states and the bath, $\langle \psi_{j,n-1}^b | \tilde{H}_{AB} | \psi_{in}^b \rangle = \sqrt{\nu_b} \delta_{ij}$, we take only the terms linear in $a$ and $a^\dagger$. The superscript $b$ in the states $|\psi_{inb}\rangle$ indicates that an additional excitation with energy $E_b$ has been created with respect to state with the original bath ($|\psi_{in}\rangle$). From the Schrödinger equation, we find for the change in coefficients due to presence of the bath

$$\frac{d\phi_{inb}^b(t)}{dt} = -i \hbar \sum_{b} \sqrt{\nu_b} \phi_{inb}^b(t), \quad (4)$$

(for clarity, we omit the subscript $B$ in the following equa-
tions). We omit processes that increase the number of phonons $n$ via processes involving $a^\dagger$ and the creation of an excitation in the bath (the rotating-wave approximation). These processes have an energy $\hbar \omega + E_b$ and are less likely than the phonon conserving excitation of energy $\hbar \omega - E_b$. Numerical calculations \cite{18} show that the probability of these processes are an order of magnitude smaller for the damping time scales under consideration in this paper. The coefficients on the right-hand side of Eqn. \ref{eq:1}, can be found from $d\varepsilon_{in}^{-1}(t)/dt = -\pi \sqrt{\nu} V_b \varepsilon_{in}(t)$. Integration gives for the change in the norm Eqn. \ref{eq:1}

$$\frac{d\varepsilon_{in}(t)}{dt} = -n \sum_b \left( \frac{V_b}{\hbar} \right)^2 \int_0^t dt' e^{-i\omega_{b,n-1}(t-t')} \varepsilon_{in}(t'),$$

where $\hbar \omega_b = E_i - \varepsilon_i + E_b$ is an eigenstate of $\hat{H}_0$ and the bath Hamiltonian. The integral is greatly simplified when using the common approximation that the sum over the bath integral can be replaced by an integral over an effective density of states. Taking a density of states $\bar{\rho}$ and coupling constant $\bar{V}$ in the region where it couples strongly, we obtain

$$\sum_b \frac{V_b^2}{\hbar^2} e^{-i\varepsilon_b(t-t')} \approx \frac{\pi \bar{\rho} \bar{V}^2}{\hbar} \delta(t-t'). \quad \text{(5)}$$

Introducing the lifetime broadening $\Gamma = \pi \bar{\rho} \bar{V}^2 / \hbar$, we obtain $d\varepsilon_{in}/dt = -n\Gamma \varepsilon_{in}(t)$ . This term shows the decrease in $\varepsilon_{in}$ with the bath unchanged in the time step. However, at the same time $\varepsilon_{in}$ can increase by the decay of the state with $n + 1$ excited phonons. By calculating the probability for $\varepsilon_{in}$ using Eqn. \ref{eq:5}, we obtain

$$\frac{dP_{in}(t)}{dt} = -2n\Gamma P_{in}(t) + 2(n + 1)\Gamma P_{n+1}(t) \quad \text{(6)}$$

The obtained rate equation can also be obtained heuristically by taking an oscillator frequency with damping $\omega - i\Gamma$ \cite{19}. The changes in the coefficients due to damping is included in the Schrödinger equation through \cite{18}

$$i\hbar \frac{d}{dt} \psi(t) = (\hat{H}_0 + \hat{H}_1)\psi(t) + \frac{i\hbar}{2} \ln P(t) \frac{d}{dt} |\psi(t)|,$$

with $P(t) = \sum_{in} P_{in}(t) |\psi_{in}(t)\rangle\langle \psi_{in}|$.

Experimentally, no oscillations of the ligands are observed indicating that the intramolecular vibrational energy distribution occurs within half an oscillation period of the stretching mode. Figure\ref{fig:2}(b) shows that the inclusion of $\Gamma^{-1} = 30$ fs causes a damping of the oscillation within a few periods (for the rest, using the same parameters as Fig. \ref{fig:2}(b)). The damping strongly suppresses the recurrence of intensity in state 1. The net result is a very fast intersystem crossing with a close to 100% quantum efficiency in good agreement with experiment. The decay time, however, is not simply related to the oscillation period of 138 fs of the phonon, but significantly smaller. A good estimate of the decay time is obtained by viewing it as a dephasing of state $|\psi_{10}\rangle$ into the phonon continuum of that $|\psi_{2n}\rangle$. The coupling strengths $V_{in0} = e^{-g^2 n}/n!$, can also be viewed as a constant coupling $V$ to a density of states, see Fig. \ref{fig:1} given by $\rho(\epsilon) = e^{-g^2}/[\hbar \omega \Gamma(\epsilon + 1)]$, with $\epsilon = E/\hbar \omega$ and where $\Gamma(\epsilon + 1)$ is the gamma function that allows calculation of the factorial for non-integer values. The lifetime broadening $\Gamma_d$ associated with the dephasing is then straightforwardly obtained \cite{14} through $\Gamma_d = \pi V^2 \rho(\Delta - \epsilon)/\hbar$. This gives a decay time of $(2\Gamma_d)^{-1} \approx 26$ fs. The exponential decay $e^{-2\Gamma_d t}$ provides a satisfactory agreement with the numerical calculation, see the dotted line in Fig. \ref{fig:2}(b). Furthermore, this rapid decay does not require the involvement of high-frequency phonon modes (150-200 meV), as was suggested earlier since the electronic and lattice relaxation occurs on different time scales.

It has also been suggested \cite{4} that the major change in transition metal-ligand distance occurs in the photoexcitation. Figure\ref{fig:2}(c) shows the calculation for that situation under the assumption that the total change is constant ($\Delta_{02} = 0.2$ eV). If there is no difference in bond length between states 1 and 2 ($\varepsilon_{12} = 0$ and $\varepsilon_{02} = 0.2$), one observes oscillations in $P_1$. Note that in this limit, phonons are created in the photoexcitation. For $\varepsilon_{12} = 0$, there is no phonon continuum but a simple coupling between the two states. When introducing a small difference in lattice between states 1 and 2 ($\varepsilon_{12} = 0.05$, see dashed line in Fig.\ref{fig:2}(c)), we do not find a fast decay nor a close to 100% quantum efficiency.

We now turn our attention to the dependence of the relative positions of states 1 and 2. When using an adiabatic approach, strong coupling between the different states only occurs for very particular energies and transition metal-ligand distances. This appears in contradiction with the prevalence of fast intersystem crossings. We demonstrate that the fast decay occurs for a relative wide energy range. In Fig. \ref{fig:3} we show the decay and change in transition metal-ligand distance for several values of $\Delta$. We take that the initially photo-prepared state is $|\psi_{10}\rangle$, i.e. the change in the lattice upon photoexcitation is small. As described above, the fastest decay occurs for $\Delta = 2\varepsilon_{12}$, see curve e in Fig. \ref{fig:3}. However, also in a region more than $\varepsilon_{12}$ wide around this point (see d and f), we see the same dephasing with the lifetime broadening following the effective density of phonon states $\rho(E)$, see the lower part of Fig. \ref{fig:3}. When going to curve g, there is an initial dephasing followed by a slower decrease in $P_1$. However, even at higher energies (h and i), where the effective phonon density of states $\rho(E)$ is so small that dephasing does not occur, the decay occurs on a timescale larger than the oscillation period of the phonons. We can understand this behavior as a “leakage” into state 2. Since the excitation is into $|\psi_{10}\rangle$, phonon damping is irrelevant for state 1. The strongest coupling to state 2 occurs at the maximum of the effective phonon density of states. For significantly large $\Delta$, we can treat $\rho(E)$ as a single state and write an effective Green’s function for
oscillator, the rate equation can be solved analytically

\[
\alpha \approx \exp(-\Gamma t) 
\]

approximately to the state 1. The effective state in the Green’s

dependence as a function of time \(t\) is given for different positions of \(\psi_{10}\) with respect to the effective phonon density of states \(\rho(E)\) of state 2, see bottom part of the figure.

state 1

\[
G^{-1}(E) = z - \frac{V^2}{z - \Delta + 2\epsilon_{12} + \alpha \Gamma} \tag{8}
\]

with \(z = E - E_2 - \Delta + i0^+\). The phonon damping \(\Gamma\) indirectly affects state 1. The effective state in the Green’s function consist of \(\psi_{2n}\) with \(n \approx \epsilon_{12}/\hbar \omega\). Phonon damping causes these state to relax into \(\psi_{2n}\), which couples very weakly to \(\psi_{10}\). This causes a decrease in \(P_1\) with an effective decay time \(\alpha V^2 \Gamma/[(\Delta - \epsilon_{12})^2 + (\alpha \Gamma)^2]\). The factor \(\alpha\) accounts for the fact that there are approximately \(g\) phonons excited. For an independent oscillator, the rate equation can be solved analytically and is equivalent to \(g\) independently decaying oscillators with one phonon excited. The time needed to obtain a 50% occupation of the \(n = 0\) state is \(1/\alpha \Gamma\) with \(\alpha^{-1} = -\ln[1 - (1/2)^1/g]\).

When state \(\psi_{10}\) is on the low-energy side of the effective phonon density of states \(\rho(E)\) (a-c in Fig. 3), we see an entirely different behavior. When \(\Delta \approx \epsilon_{12}\), states \(\psi_{10}\) and \(\psi_{20}\) are almost degenerate, and one obtains a strong coupling between them. For, \(\Delta > \epsilon_{12}\), state 1 slowly decays into state 2. For \(\Delta < \epsilon_{12}\), state 1 does not decay into state 2. At first, the asymmetry below and above the phonon continuum seems surprising since \(\rho_{10}\) can still couple to the effective phonon continuum of state 2 and one would expect leakage. However, now state 2 can easily couple back into the phonon continuum \(\psi_{1n}\) of state 1, which is now at a much lower energy (about \(\epsilon_{12}\) above \(\psi_{10}\)). The states \(\psi_{1n}\) then damp into \(\psi_{10}\).

Conclusions.— An explanation is given for the fast intersystem crossing in transition-metal systems. The large change in lattice between the states produces an effective phonon continuum leading to a fast dephasing. The change in spin is necessary since most parts of the electronic Hamiltonian do not produce an intersystem coupling. Damping of the phonon oscillation by coupling with the environment prevents a recurrence of intensity in the initially photoexcited state. We demonstrate that an intersystem crossing of tens of fs is compatible with a lattice relaxation of the order of 100-200 fs. Different regions of decay can be identified as a function of the relative energy positions of the states. The fastest decay is an effective dephasing and occurs on a smaller timescale than the oscillation period of the phonons that are involved in the process. Quantum efficiencies of close to 100% are obtained. After obtaining an understanding of the crucial initial step leading to a complete spin crossover, future research should provide a quantum-mechanical understanding of cascading effects and finally close the loop with a return to the ground state. Additionally, spectroscopic signatures of the process need to be investigated.

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