Pressure effects on the HS→LS relaxation in [Zn$_{1-x}$Fe$_x$(6-mepy)$_3$tren](PF$_6$)$_2$

Wei Wang and I. Y. Chan
Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254-9110

Sabine Schenker and Andreas Hauser
Département de chimie physique, Université de Genève, 30 quai Ernest-Ansermet, 1211 Genève 4, Switzerland

(Received 12 November 1996; accepted 27 December 1996)

Laser flash photolysis experiments were performed on the mixed crystal [Zn$_{1-x}$Fe$_x$(6-mepy)$_3$tren](PF$_6$)$_2$ (x = 0.00025) at 10 K in the pressure range between 1 bar and 20 kbar. An external pressure of 20 kbar accelerates the low-temperature tunneling process by almost eight orders of magnitude. © 1997 American Institute of Physics. [S0021-9606(97)02109-0]

I. INTRODUCTION

In the class of so-called iron(II) spin-crossover compounds, the ligand field strength is such that the low-spin (LS) $^1A_g$ state and the high-spin (HS) $^5T_2$ state are close in energy. Thus, whereas at low temperatures only the LS state is populated, an almost quantitative, entropy driven population of the HS state may occur at elevated temperatures. During such a spin transition most of the physical properties of the compound change dramatically. In particular there is a large change in metal-ligand bond length, $\Delta r_{HL}$, on the order of 0.2 Å$^2$–4 Concommitantly the complexes experience a large change in volume, $\Delta V_{HL}$, of typically 25 Å$^3$.

The dynamics of the HS→LS relaxation have been studied in a number of iron(II) spin-crossover compounds using various techniques. Experimental results obtained at temperatures above 150 K have generally been discussed in terms of the classical concepts of thermal activation. For [Fe(6-mepy)$_3$tren][PF$_6$)$_2$, where (6-mepy)$_3$tren stands for tris[4-[(6-methyl)-2-pyridyl]-3-aza-3-butenyl]amine, Adler et al. determined the activation energy $E^a$ and the corresponding volume of activation $\Delta V_{HL}^0$ for the HS→LS relaxation to be 416(90) cm$^{-1}$ and $-22(3)$ Å$^3$/molecule, respectively, and a volume of reaction $\Delta V_{HL}^0$ of 25(3) Å$^3$/molecule. In the diluted mixed crystal [Zn$_{1-x}$Fe$_x$(6-mepy)$_3$tren][PF$_6$)$_2$ laser flash photolysis experiments showed the HS→LS relaxation to be a thermally activated process at temperatures $\approx$100 K in accordance with the above. Below 100 K, however, there are strong deviations from classical behavior toward a much less temperature dependent tunneling process with a rate constant at 10 K of $10^{-1}$ s$^{-1}$. In this Communication we report extraordinarily large pressure effects for the low-temperature tunneling process. We discuss the experimental results within the theory of nonadiabatic multiphonon relaxation as first proposed by Buhks et al.\textsuperscript{9}

II. EXPERIMENT

Preparation of the [Zn$_{1-x}$Fe$_x$(6-mepy)$_3$tren][PF$_6$)$_2$, x = 0.00025, crystals has been reported earlier.\textsuperscript{2,9} The resulting crystals are dichroic. Under a polarization microscope they are red–violet in one polarization and orange–red perpendicular to it. The hydrostatic He-pressure cell and the cryogenic system used to achieve pressures up to 1 kbar and temperatures down to 15 K has been previously described.\textsuperscript{11,12} For higher pressures a diamond anvil cell in a gas-flow type variable temperature cryostat was used.\textsuperscript{13} The ruby fluorescence pressure calibration was made with a CCD (Princeton Instruments) detector. This procedure, eliminating the imprecision of the grating sine drive, resulted in a threefold improvement in precision over previous pressure measurements.

HS→LS relaxation curves were measured with the pump–probe technique described.\textsuperscript{9} The metal-ligand charge transfer (MLCT) band of the system was excited with the 514 line of an argon ion laser (Spectra Physics 2025) in conjunction with an acousto-optic modulator (Coherent 305), which resulted in an efficient population of the HS state, manifesting itself in a bleaching of the MLCT band. The collinear probe beam from a HeNe laser (543 nm, Polytec), after having passed through the sample, was separated from the exciting beam in a 1/4 m double monochromator (Spex 1680 B) and detected with a PM tube (Hamamatsu R928) in conjunction with a preamplifier (Analog Devices Model 341). For experiments at higher pressures, the 514 nm output of an OPO laser (Spectra Physics MOPO 730) was used for excitation and the 633 nm HeNe laser for probing in a counterpropagating geometry. The recovery of the transient bleaching was recorded with a digital scope (Tektronix TDS540A) making extensive use of its signal averaging capabilities.

III. RESULTS

Figure 1 shows the Arrhenius plots of the observed HS→LS relaxation rate constants $k_{HL}$ for [Zn$_{1-x}$Fe$_x$(6-mepy)$_3$tren][PF$_6$)$_2$ at pressures of 1 and 1000 bar. Both curves indicate a thermally activated behavior at temperatures $\approx$50 K and a much less temperature dependent tunneling process below this temperature. The experimental activation energy in the high temperature region at 1 bar as determined from a linear regression of $\ln k_{HL}$ vs $1/T$ (inset Fig. 1) for $T$=100 K is 837(23) cm$^{-1}$. An external pressure
of 1 kbar gives rise to an increase of the low-temperature tunneling rate constants of almost one order of magnitude, that is, at 15 K $k_{HL}(p=1 \text{ kbar})/k_{HL}(p=1 \text{ bar})=8.2$. At higher temperatures the increase becomes smaller, dropping to a factor of 4.8 at 45 K.

Figure 2 shows the pressure dependent low-temperature tunneling rate constants at 15 K in the pressure range between 1 bar and 1 kbar, and at 10 K between 3 and 20 kbar. They are depicted as the logarithm to the base of 10 of the ratio between the rate constants under applied pressure and under normal conditions, $\log[k_{HL}(p)/k_{HL}(p=1 \text{ bar})]$ versus pressure. The overall increase of the rate constant between 1 bar and 20 kbar is an astonishing eight orders of magnitude. The increase at low pressures is close to exponential with the above-mentioned factor of 8.2 kbar$^{-1}$, at higher pressures it gradually deviates from an exponential rise.

IV. DISCUSSION

This work combines the useful features of two previous lines of investigation on spin-crossover compounds: (1) the older work of Drickamer and Frank$^{14}$ using high pressure to shift the thermal equilibrium toward the LS state, and (2) the more specific kinetic studies by one of us.$^9$ In a recent publication,$^{15}$ Jeftić and Hauser reported a one order of magnitude increase of the HS$\rightarrow$LS relaxation rate constant in $[\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_3](\text{BF}_4)_2$, ptz=1-propyltetrazole, by applying a comparatively low pressure of 1 kbar. In the present work, intermediate pressures ranging up to 20 kbar produce an eight orders of magnitude acceleration in the relaxation rate.

To our knowledge, this is the highest dynamic range for a pressure effect on a relaxation process. Further, by working at low temperatures, attention is focussed on the nonadiabatic tunneling process from the zero-point level of the HS state.

The microscopic origin of this phenomenon is primarily the enhancement of the ligand field strength 10Dq due to the enhanced barrier height and the thickness for the tunneling potential wells: $\Delta E_{HL}(\text{ref.21})$ shows an attempt in modeling the pressure dependence of $\Delta^2_{HL}$, $\Delta_{HL}$ and $\hbar \omega$ within the Grüneisen approximation [$K=50 \text{ kbar}$ (Ref. 20), $\gamma_{\text{n}}=3$ (Ref. 21)] and a pressure coefficient for the intramolecular vibrational frequencies of 0.2 (Ref. 22) at $n_H=1$.

FIG. 1. $\ln k_{HL}(T)$ vs $1/T$ for the HS$\rightarrow$LS relaxation of the mixed crystal $[\text{Zn}_{1-x}\text{Fe}_x(6\text{-mepy})\text{tren}](\text{PF}_6)_2$ ($x=0.00025$) at 1 bar (•) and at 1 kbar (△). The dashed line (―) represents the classical Arrhenius behavior with an activation energy $E^a$ of 837(23) cm$^{-1}$ for $T>100$ K.

FIG. 2. $\log[k_{HL}(p)/k_{HL}(1 \text{ bar})]$ vs $p$ for the low-temperature tunneling process of the HS$\rightarrow$LS relaxation of the mixed crystal $[\text{Zn}_{1-x}\text{Fe}_x(6\text{-mepy})\text{tren}](\text{PF}_6)_2$ ($x=0.00025$) at 15 K (1 bar–1 kbar) (○) and at 10 K (3–20 kbar) (●). The dashed lines (—) are estimates based on the relative pressure-induced vertical displacement of the HS and LS potential wells: $n(p)=n_0+\beta_1 p+\beta_2 p^2+\Delta V_{HL}/\hbar \omega=0.45$ for $n_0$ of 0.1, and 3. The solid line (—) shows an attempt in modeling the pressure dependence of $\Delta^2_{HL}$, $\Delta_{HL}$ and $\hbar \omega$ within the Grüneisen approximation [$K=50 \text{ kbar}$ (Ref. 20), $\gamma_{\text{n}}=3$ (Ref. 21)] and a pressure coefficient for the intramolecular vibrational frequencies of 0.2 (Ref. 22) at $n_H=1$.
The question now is how are the parameters governing the low-temperature tunneling rate constant affected by external pressure. In zeroth order approximation \( \Delta r_{\text{HL}}^0 \) and thus \( S \) are not altered to any large extent by external pressure, because the metal-ligand bond is a comparatively strong bond with respect to the soft intermolecular lattice vibrations (hard sphere model of Spiering et al.\(^\text{16} \)). The zero-point energy difference \( \Delta V_{\text{HL}}^0 \), however, and therefore \( n \), depend upon pressure through the work term \( p \cdot \Delta V_{\text{HL}}^0 \):

\[
n(p) = n_0 + \beta_n p,
\]

with \( \beta_n = \Delta V_{\text{HL}}^0 / \hbar \omega \), where \( \Delta V_{\text{HL}}^0 \) is the difference in the characteristic molecular volumes between the HS and the LS state. For neat \([\text{Fe}(6\text{-mepy})_3\text{tren}][\text{PF}_6]_2\) Adler et al.\(^\text{17} \) determined \( \Delta V_{\text{HL}}^0 \) to be 25(3) \( \text{Å}^3 \)/molecule from the pressure dependence of the thermal equilibrium. A similar study on the diluted system gave a value of 22(2) \( \text{Å}^3 \)/molecule,\(^\text{18} \) which is within experimental error equal to the former. With this, a value for \( \beta_n \) of \( \approx 0.45 \text{ kbar}^{-1} \) can be estimated.

In Fig. 2 the pressure dependence of \( k_{\text{HL}}(T \to 0) \) according to Eq. (1) using Eq. (2) for the reduced energy gap as a function of pressure with the above mentioned value of \( \beta_n \) and values of \( n_0 \) of 0, 1, and 3 are shown (dotted lines). The values for \( n_0 \) of 3 and 0 reflect the upper and lower limit for a spin-crossover compound with a transition temperature below 300 K, the value of 1 may be considered typical for a transition temperature between 100 and 200 K. The experimental curve falls well within the comparatively narrow band of the limiting curves as predicted by this simple approach. However, it shows characteristic deviations from the calculated ones. The acceleration at low pressure is larger than predicted, at high pressures it levels off more rapidly. These deviations must be due to the pressure dependence of \( \Delta r_{\text{HL}} \), \( \Delta V_{\text{HL}}^0 \), and \( \hbar \omega \), and thus of \( S \) and \( n \). Qualitatively, both \( \Delta r_{\text{HL}} \) and \( \Delta V_{\text{HL}}^0 \) decrease with increasing pressure, because the ‘softer’ HS state will be compressed more than the LS state. The two quantities, however, are not directly linked. The former is governed by the force constants of the metal-ligand bond, whereas the latter involves the elastic properties of the whole crystal. Vibrational frequencies, on the other hand, generally increase with increasing pressure, the lower the frequency the more so.

At low pressures \( (p \ll 1 \text{ kbar}) \) the decrease of \( \Delta r_{\text{HL}} \) is the dominant secondary effect, because it is the direct consequence of the difference in force constants of the metal-ligand bond between the HS and the LS state, and it enters Eq. (1) exponentially via the associated pressure dependence of the Huang–Rhys parameter

\[
S(p) = S_0 \left( 1 + \frac{\delta \Delta r_{\text{HL}}(p)}{\Delta r_{\text{HL}}^0} \right)^2,
\]

where \( \Delta r_{\text{HL}}^0 \) and \( S_0 \) are the bond length difference and the Huang–Rhys parameter at zero pressure, and \( \delta \Delta r_{\text{HL}} \) is the change in \( \Delta r_{\text{HL}} \) with pressure.

For the spin-crossover system \([\text{Zn}^{2+}\text{Fe}^{3+}(\text{ptz})_3][\text{PF}_6]_2\) the relative change in metal-ligand bond length of the LS state, \( \delta r_{\text{LS}}/r_{\text{LS}} \) was found to be linear in \( p \) for \( p \) up to 1 kbar.\(^\text{12} \) From the shift of \( d-d \) absorption bands\(^\text{15,19} \) a value for \( \delta r_{\text{LS}}/r_{\text{LS}} \) of \( \approx -10^{-3} \text{ kbar}^{-1} \) can be estimated. Assuming the force constant for the accepting mode to be typically 1.5 times larger for the LS state than for the HS state,\(^\text{20} \) \( \delta \Delta r_{\text{HL}}/\Delta r_{\text{HL}}^0 \) can be estimated to be on the order of \( \approx -5 \times 10^{-3} \text{ kbar}^{-1} \). This is sufficient to enhance the acceleration of the low-temperature tunneling rate constant at low pressures from a factor of 5.6 kbar\(^{-1} \), calculated with \( \beta_n = 0.45 \text{ kbar}^{-1} \) only, to 7.6 kbar\(^{-1} \).

At higher pressures the linear dependence of \( \delta \Delta r_{\text{HL}} \) on \( p \) overestimates the change in \( \Delta r_{\text{HL}} \). Furthermore the decrease in \( \Delta V_{\text{HL}}^0 \) and the increase in \( \hbar \omega \) have to be accounted for as well. The former modifies the dependence of the reduced energy gap \( n \) on \( p \), the latter influences both \( S \) and \( n \). All effects counteract the initial enhancement of the rate constant due to the decreasing value of \( \Delta r_{\text{HL}} \). In an attempt to rationalize the present data, the pressure dependence of \( \Delta V_{\text{HL}}^0 \), \( \Delta r_{\text{HL}} \), and \( \hbar \omega \) was modelled within the Grüneisen approximation using some typical values for the bulk modulus \([50 \text{ kbar (Ref. 20)}]\), the Grüneisen parameter \((=3)\),\(^\text{21} \) and a pressure coefficient for the intramolecular vibrational frequencies.\(^\text{22} \) The solid curve in Fig. 2 was obtained, which certainly accounts for the observed trend at the higher pressures. We wish to emphasize that this curve is not the result of a fitting procedure to the data. We are currently working on a more comprehensive theoretical approach. However, the excellent emulation of the data indicates that our qualitative understanding is correct.

The single configurational coordinate model in the form resulting in Eq. (1) for the low-temperature tunneling rate constant does not consider the difference in vibrational frequencies and force constants of the two states, nor does it account for the fact that in these low-symmetry systems the actual reaction coordinate is a linear combination of several normal modes. Thus the force constant \( f \) of 2 \( \times 10^5 \text{ dyn/cm} \) and the vibrational frequency \( \hbar \omega \) of 250 cm\(^{-1} \), which together with the value of \( \Delta r_{\text{HL}}^0 \) of 0.18 Å result in the value for \( S \) of \( \approx 45 \), are to be regarded as weighted averages over the active vibrations.\(^\text{9} \) The fact that the force constants in the LS state are on average about 1.5 times larger than in the HS state,\(^\text{20} \) can easily be accounted for by calculating the Franck–Condon factors numerically for potentials having force constants for instance of 2.4 \( \times 10^5 \) and 1.6 \( \times 10^5 \text{ dyn/cm} \) for the LS and the HS state, respectively. However, in the strong coupling limit \((S>n)\) such a calculation does not significantly differ from the simple approach.

In conclusion, the eight orders of magnitude increase of the low-temperature tunneling rate constant on the application of an external pressure of 20 kbar is understood semi-quantitatively on the basis of the most simple approach to radiationless transitions. For still higher pressures \( k_{\text{HL}}(T \to 0) \) is expected to increase further to a maximum value of

\[
k_{\text{HL}}^{\text{max}}(T \to 0) = \frac{2 \pi}{\hbar \omega} \rho_{\text{HL}}^2 (2 \pi S)^{-1/2} \approx 10^{13} \text{ s}^{-1}
\]

from Eq. (1), using the Stirling formula for $n!$ and setting $n = S$. At pressures for which $n > S$, i.e., in the Marcus inverted region, $k_{HL}$ should begin to decrease again. However, pressures in excess of 100 kbar would be required to achieve an energy shift large enough to actually reach the inverted region for a spin-crossover compound.

**ACKNOWLEDGMENTS**

Part of the measurements, by S. Schenker and A. Hauser, have been performed at the Institut für anorganische und physikalische Chemie, Universität Bern, Switzerland and we thank H. U. Guétel for the use of the equipment and especially J. Jeftić for the help with the hydrostatic He-pressure cell. We also thank the Schweizerischer Nationalfonds for financial support. The Brandeis group is supported in part by the National Science Foundation (CHE-9306931), and by the Petroleum Research Fund, administered by the American Chemical Society (#27277-AC4, 3).