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High-pressure studies of quantum tunnelling reactions

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Abstract

We use pressure as an empirical parameter to investigate quantum tunnelling reactions. Pressure modifies both the thickness and the barrier height of the potential, leading to enhancement of the tunnelling rate of many orders of magnitude. We use a high-spin–low-spin relaxation of a spin-crossover system to illustrate the phenomenon. Emphasis is placed on an ongoing project. A pair of anthracene molecules, perfectly oriented in a dianthracene lattice, undergoes photodimerization via tunnelling at low temperature. We report results for the perdeuterated system. These observations suggest the tunnelling of a formally very heavy particle.

1. Introduction

One of the cornerstones of modern chemistry is the Arrhenius equation: $\ln k = -E_a/RT$, where k is a reaction rate constant, and E_a is the activation energy. This phenomenological law has led to the development of the transition state theory of chemical reactions. According to this theory, chemical reactions proceed through a process of thermal activation. Reactants acquire thermal energy to reach a transition state at the top of an energy barrier. From this activated complex the system may proceed to form products. The barrier height is the activation energy. This physical picture leads to a linear Arrhenius plot of $\ln k$ versus T^{-1} . At lower temperature, however, a T -independent residual reaction rate is often observed. This non-Arrhenius behaviour is the hallmark of a secondary mode of reaction. Chemical reaction proceeds without scaling the energy barrier; that is, the reactants may tunnel through the barrier to form products directly. This is called a quantum tunnelling reaction. It is important in electron transfer reactions, although it plays a significant role in reactions involving heavier particles also. A tunnelling reaction is conceptually straightforward. Further, if it occurs in a single crystal, it often has very well defined reaction geometry. It therefore may be subjected to thorough analysis. In this paper, we introduce pressure as a parameter in the investigation of tunnelling reactions. Pressure reduces tunnelling distance; it also tends to modify the potential function of the system, leading to a change in the energy barrier height. Therefore, pressure may create an enormous enhancement in the dynamical rate. A few years ago we initiated a series of investigations on the hydrogen tunnelling photoreaction in the acridine/fluorene system [1]. Here, we will use a formal tunnelling reaction in a spin-crossover compound to

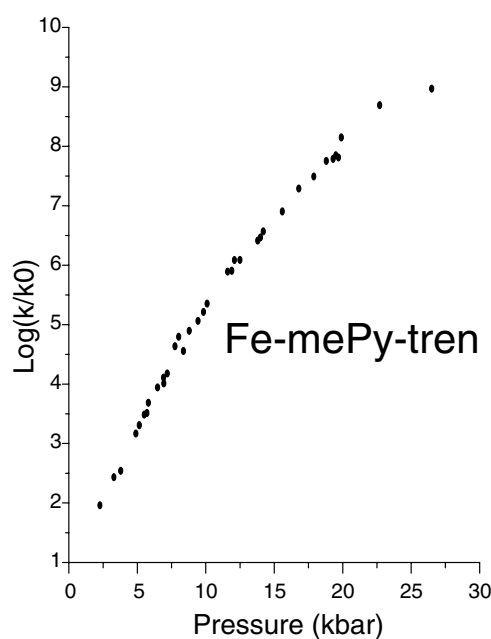


Figure 1. The HS \rightarrow LS tunnelling rate for spin-crossover compounds as a function of pressure at 10 K.

illustrate the phenomenon. This paper will conclude with a report on an ongoing project in tunnelling dimerization of anthracene.

2. An example of a spin-crossover compound

For some ferrous complexes with octahedral aza-ligands, the high-spin (HS) and low-spin (LS) states are close in energy, such that the substances cross over from LS to HS thermally: thus the name spin-crossover compounds. Through a photophysical process called ‘light-induced excited spin state trapping’ (LIESST), one may prepare the HS state by spectroscopic pumping from the LS ground state [2]. The relaxation from HS to LS is relatively slow. By changing ligands, Hauser *et al* [2] have observed a wide range of this relaxation rate. Our interest in these compounds lies in the fact that, in accord with Hund’s rule, the HS state has a much longer metal-to-ligand (ML) bond length compared with that of the LS state. Thus the HS \rightarrow LS relaxation is accompanied by a large reduction in the ML bond length. Taking the breathing normal coordinate as the reaction coordinate, the relaxation process may be construed as a tunnelling reaction. It involves tunnelling of six nitrogen atoms. Since this tunnelling is associated with a large ($\sim 20\%$) reduction in volume of the complex, we may expect a large pressure effect. The progress of this reaction may be monitored by transient absorption spectroscopy. That is, an exciting laser pulse bleaches the ground state absorption by removing the LS population to the HS state. A measurement of the recovery of this absorption conveys the lifetime of the HS state. Since we are interested in molecular tunnelling, we have focused on a dilute system of Fe(II) doped in some inert hosts.

In figure 1, we show some kinetic rate data for $[\text{Fe(II)}(\text{mepy})_3(\text{tren})](\text{PF}_6)_2$ doped in its Zn analogue [3]. Here ‘tren’ stands for tris[4-(2-pyridyl)-3-aza-3-butenyl]amine. The (mepy)₃(tren) is its 6-methyl-2-pyridyl analogue. These are hexadentate ligands forming an

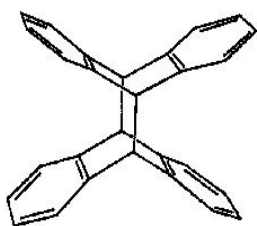
octahedral complex with the Fe(II) metal centre. It is obvious from figure 1 that the HS \rightarrow LS transition rate is enormously pressure dependent. Over a pressure range of 30 kbar, the rate has increased by nine orders of magnitude! To our knowledge this is the greatest known pressure effect on any rate process.

The physical origin of this pressure effect is primarily an increase of the energy gap between the HS and LS state. According to the Tanabe–Sugano diagram [4], for the complexes studied, the ground state is the LS 1A_1 , followed by the HS 5T_2 state. Upon compression, the ML bond length decreases, the ligand field splitting parameter $10Dq$ increases; the HS energy will be raised more than that of the LS state. This will reduce both the thickness and the height of the energy barrier for tunnelling. This picture is valid even if the HS and LS states have the same compressibility and the same breathing mode vibrational frequency. At higher pressure, the preferential compression of the ML bond length, as well as a preferential increase of the breathing frequency in the HS state relative to that in the LS state, may also make measurable contributions.

These ideas have been made quantitative [3]. For our purpose, however, it is more appropriate to take a broader theoretical perspective. One conceptual framework for rationalizing tunnelling behaviour in chemistry is the so-called golden rule approach [5]. It treats the tunnelling reaction as a radiationless transition between two spectroscopic states. The tunnelling rate therefore may be calculated by the Fermi golden rule. Thus the tunnelling rate is proportional to the product of the magnitude squared of the electronic coupling matrix element and the Franck–Condon factor (FCF). The advantage of this approach is that spectroscopic parameters serve as input to the calculation. In comparison, conventional tunnelling rate calculations tend to result in unphysical tunnelling barrier height and thickness. Although this model could be refined, its simplicity is desirable in rationalizing our results. Under compression, the tunnelling distance decreases, enhancing the FCF. Of course, the compressibility of a crystal is not linear. It tends to slow down at higher pressure. However, the reduction in distance brings about an enhanced electronic coupling which partially compensates for the compressibility non-linearity. The end result is a nearly exponential rise in tunnelling rate with increasing pressure. This is a general feature in the pressure enhancement of tunnelling reaction rate.

3. Dimerization of anthracene

Upon excitation at the near-UV band (peaking at 370 nm), anthracene (A) dimerizes to form dianthracene (A_2) with a quantum yield close to unity, provided that the topochemical orientations of the two monomers are favourable. A very clever approach for satisfying this condition was developed by Chandross and co-workers in the mid-1960s [6]. A_2 is photolysed, also with a



Dianthracene (A_2)

quantum yield near unity, by light around 245 nm. In a rigid matrix, the resultant monomer pair ($A\bullet A$) is in a perfect position for dimerization. A refinement of this scheme by Ferguson and

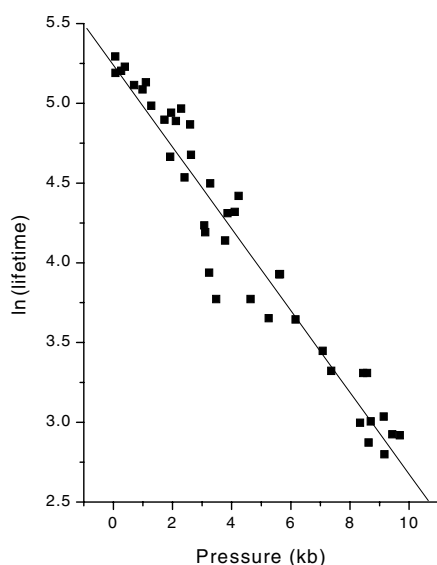


Figure 2. The fluorescence decay time (ns) of the excimer band of perdeuterated anthracene pairs in dianthracene as a function of pressure; the temperature is 2 K.

Mau (FM) is to use neat crystals of A_2 [7]. Besides gaining system uniformity by employing a crystalline sample, their use of the A_2 lattice provides a tighter and more rigid cage compared with glassy matrices. Irradiation of an A_2 crystal with 245 nm light *at room temperature* eventually leads to a steady-state concentration of $(A\bullet A)$ pairs since this wavelength also induces dimer formation [7]. Dimerization proceeds through the excimer state by thermal or tunnelling processes. Progress of the reaction may be monitored by a shortened fluorescence lifetime of the excimer (FM) band. It is greatly red-shifted from the fluorescence of the anthracene monomer. It has a lifetime up to 200 ns for the perdeuterated crystal and about 100 ns for the normal, protonated variety. Since the perdeuterated system has more favourable dynamic range both for the lifetime and pressure, we have focused our experimental effort on it.

This project is still in progress in our laboratory. Some preliminary data are shown in figure 2. It is a semilog plot of the fluorescence decay time of the orange excimer band as a function of pressure. Data were taken at 2 K with the diamond anvil cell immersed in pumped liquid helium. Compared with figure 1, these results may seem to be modest in magnitude. Nevertheless they illustrate some important features in using pressure as a parameter in investigating tunnelling reactions. As a preliminary, through some detailed investigations, we have come to the conclusion that this shortening of the fluorescence lifetime is not a result of a pressure effect enhancing the radiative probability of the excimer state. Instead, it is attributed to the quenching of fluorescence through dimerization of the perfectly oriented $(A\bullet A)$ pairs. The formation of the much shorter 9, 9' and 10, 10' covalent bonds (2.76 Å) [8] of the A_2 molecule from the typically 3.4 Å excimer separation in $(A\bullet A)$ pairs necessarily proceeds through a tunnelling mechanism under this low temperature. The results in figure 2 clearly follow a law of exponential enhancement of the tunnelling rate by pressure. It should be emphasized that, although the dynamic range is (limited by our apparatus) only e^2 , these data imply a very big effect of pressure on tunnelling. The reaction is rendered too fast to follow upon the application of a very modest pressure of 10 kbar. Indeed, skeletal data on the dimerization of normal (perprotonated) $(A\bullet A)$ pairs indicate that the reaction is

complete at a low pressure of 4 kbar. In other words, pressure enhances the kinetic rate of the perdeuterated sample much less than that of a normal sample. Beyond reinforcing the notion that this reaction is hypersensitive to the perturbation of pressure, this rather large deuterium kinetic isotope effect has a chemical implication. Namely, the formation of the dimer involves physical movement of the peripheral atoms of anthracene molecules in addition to the coming together of the 9, 9' and 10, 10' carbons. In terms of the physical phenomenon of tunnelling, the dimerization reaction is a tunnelling of a formally very massive particle through a potential barrier.

The ability of massive particles to tunnel through a barrier with a significant rate is perhaps the most important insight coming out of our pressure study of tunnelling reactions. The formal tunnelling of the spin-crossover compounds described in section 2 is another example. Other interesting systems are being investigated in our laboratory. One of these involves conformation tunnelling in porphyrins forced into a non-planar structure as a result of steric crowding. The concerted movement of atoms in the macrocyclic porphyrin again signifies tunnelling of a massive system. We have shown that pressure greatly enhanced the rate of this conformation change. However, this work has not yet reached a publishable state.

4. Conclusions

We have presented two examples of using pressure as a perturbation in studying the rate of tunnelling reactions. By reducing tunnelling distance and modifying the potential barrier, pressure brings a fruitful additional dimension to bear on this scientific problem. Tunnelling is a prevalent phenomenon in chemistry. By properly designing an experiment, chemical tunnelling of rather massive systems may be observed and investigated.

Acknowledgments

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