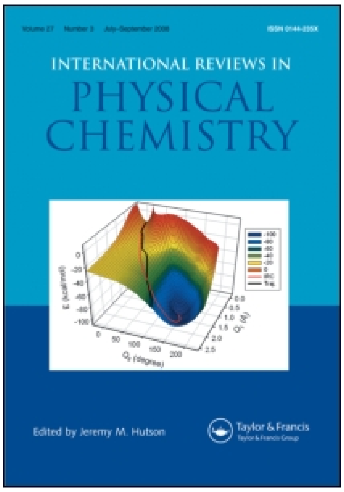

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I. Y. Chan[a]
[a] Department of Chemistry, Brandeis University, Waltham, MA, USA

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High pressure studies of the organic triplet

by I. Y. CHAN

Department of Chemistry, Brandeis University, Waltham, MA 02254, USA

High pressure up to 50 kbar generated in a diamond anvil cell has been applied to the investigation of organic molecules in their phosphorescent triplet state. Experimental techniques include specifically adapted optically detected magnetic resonance (ODMR) and optical spectroscopy. This paper reviews some of the high points of our results. On the microscopic scale there is no isotropic compression. Pressure enhances the interaction of a chromophore with its neighbours in a few specific modes according to crystalline packing. These interactions may shift the energy levels of the chromophore, or enhance the dynamical processes in the crystal. A variety of pressure-induced effects may be rationalized on this basis.

1. Introduction

The derivative of free energy versus pressure is volume, $(\partial G/\partial P)_T = V$. Any change of state involving volume changes will have a pressure-dependent equilibrium state, and a chemical process having finite activation volume exhibits a P-dependent rate. In principle, pressure ranks with temperature as a useful thermodynamic parameter. The fact that pressure is not utilized as frequently as temperature reflects its experimental difficulty. Indeed, every advance in high pressure techniques results in a phenomenal expansion in our knowledge of properties of matters under pressure. As a case in point, the availability of diamond anvil cells (DACs) in recent years has greatly popularized pressure as a fruitful experimental parameter.

The DAC technology exploits the superior hardness and mechanical strength of diamond to generate ultra-high pressure in a compact device of modest cost. A sample placed between the flat parallel faces of two diamond anvils is subject to pressure when a force pushes the opposing anvils together. The sample is contained in a small hole in a metal gasket. Application of a moderate force over a very small area generates enormous pressure. For pressures of chemical relevance (up to 50 kbar), such a device may be extremely compact. Our Merrill–Bassett cells have a thermal mass of some 60 g, allowing for liquid helium temperature experiments. Pressure is monitored by the spectral shift of the fluorescence of ruby (Jayaraman 1983).

With the experimental difficulty alleviated, pressure effects are inherently more straightforward than temperature effects. Pressure modifies the potential function of the system, and exerts a molecular perturbation in the Hamiltonian in a way analogous to an electric or magnetic field. By comparison, a temperature effect entails complicated (if well-developed) averaging among a population distribution. Further confounding the issue, temperature variation also changes the density and viscosity of the medium, whose contributions to a physical observable are hopelessly tangled. Pressure offers an alternative for investigating such effects at a fixed temperature. Similarly, pressure is conceptually simpler than many medium effects such as spectral red-shifts induced by changing solvent polarity. Indeed, a standard advocacy for pressure work is that intermolecular interaction may be enhanced without changing the chemical identity and/or the level of thermal excitation.

In the past ten years, we have made a major contribution towards introducing

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pressure as a parameter in the study of organic triplet state molecules. In so far as we were off the beaten track, many of our observations were surprising. In this paper, we review some of the high points of our work with a perspective gained by hindsight. We do not attempt to be comprehensive, and we do not deal with the question of technique which may easily be found in the literature.

2. Pressure dependence of the zero-field splitting

One area of interest made possible, or rather revived, by the DAC is magnetic resonance under high pressure. Sakai and Pifer (1985, 1986) published the design of a conventional high-field EPR apparatus and used it for ferromagnetic studies. Independently and simultaneously, we reported the first optically detected magnetic resonance (ODMR) experiment in triplet benzophenone (Sandroff *et al.* 1986). Lee *et al.* (1987) conducted proton NMR experiments in a DAC and measured T_1 and T_2 for a tumbling liquid. Since we had opened up a new area in magnetic resonance, there was no working information as to how a triplet molecule would behave under pressure. Therefore we started with the most basic characterization of a triplet—investigating the pressure dependence of its zero-field splitting (ZFS) parameters D and E. This seemingly mundane mission turned out to be interesting in its own right.

In its basic form, the ZFS originates from the dipolar interaction between the two triplet electrons. D and E respectively reflect the deviation from spherical and cylindrical symmetry of the orbital wavefunction of the triplet. Other physical interactions, however, may contribute to ZFS in a major way. Notable examples are spin–orbit coupling in carbonyls and vibronic coupling in systems with Jahn–Teller instability. In the following paragraphs, we summarize the high points of our work in each of these systems.

2.1. *The microscopic meaning of compression*

Workers under high pressure cherish the thought that compression of their sample is largely 'hydrostatic', namely, forces exerted onto the sample are normal to its surface. Thus the effect of pressure is to reduce volume. By inference, this also reduces distances in the sample. Little thought was given to how increasing the pressure affects the system at the microscopic level. This simplistic view was adequate for physicists and geochemists who worked on ionic crystals or simple molecules. Applying this idea to molecular crystals, we ran into difficulties early in our ODMR experiments. Figure 1 (Chan and Qian 1989) shows the change of *magnitude* of D for (1) benzophenone (BP) in dibromodiphenylether (DDE), (2) dichlorobenzene (DCB) in p-xylene, (3) s-tetrachlorobenzene (TCB) in durene (DR) and (4) quinoxaline in DR. We developed our high-pressure ODMR technique with BP/DDE as a test sample (Sandroff *et al.* 1986). The rise in $|D|$ was first interpreted as a consequence of the reduction of the dipolar distance of the triplet electrons. The problem was that for the next five molecules we studied (Chan and Qian 1989, 1990), $|D|$ always goes down with increasing pressure, as exemplified by the data in figure 1.

In retrospect, we may now make a general statement. On a microscopic scale, isotropic compression does not exist. Crystalline compression reduces to the enhancement of specific interactions between our spectral probe and its neighbours; whereas pressure effects on amorphous solids or liquids are manifested only as ensemble or time average. The effect of pressure on a spectral probe depends on the consequence of the specific perturbation of the probe molecule by its neighbours

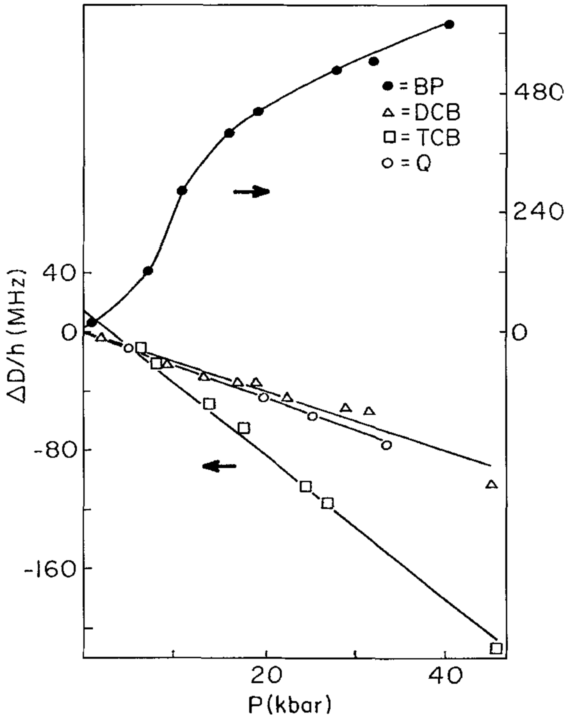

Figure 1. Pressure effect on $|D|$ for benzophenone (BP), p-dichlorobenzene (DCB), s-tetrachlorobenzene (TCB) and quinoxaline (Q). For BP use the right scale, and for the others use the left scale which is three times larger. The curve through the BP data is a visual aid only, the straight lines are the least squares fit of the respective data.

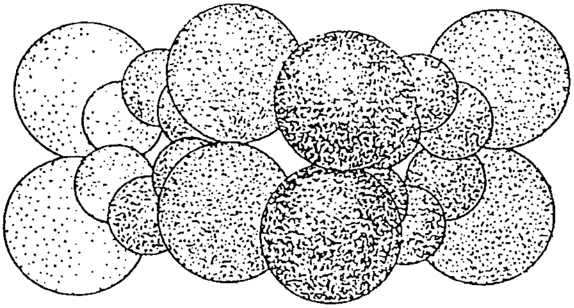

Figure 2. A packing drawing of the crystalline structure of durene. The large circles are the methyl groups, the small circles aromatic carbon. Hydrogens are not shown.

during compression. For a chemist, this chemical specificity is not an unwelcome situation. Furthermore, compression effects in molecular crystals are strongly dependent on molecular packing. This is best illustrated by considering the packing of durene molecules in the crystal (figure 2), where the two molecules in the unit cell are almost perpendicular in a herring bone structure. With the van der Waals radii of methyl and chlorine nearly equal, a TCB molecule may be represented by one of the molecules in figure 2. Upon compression, a C–Cl bond may be shortened, or more likely, be bent out of plane. As we shall see in the next section, this deformation of TCB accounts for the decrease in D. By contrast, Q is a larger two-ring aromatic molecule.

Substitution of Q in DR results in the jamming of a methyl group into the π-cloud of Q upon compression. The consequence is a redistribution of the triplet electron density in favour of the electronegative aza-atom. This leads to a reduction in *D*.

2.2. *Mesomeric effect in chlorobenzenes*

The mesomeric effect in chlorobenzenes arises from the possibility of a charge transfer promotion of an electron from the doubly-filled Cl 3p orbital of π symmetry to a LUMO of the benzene ring. This back-donation had led organic chemists to describe the C–Cl bond as a partial double bond. If the C–Cl bond is shortened, we have argued in detail that such mesomeric effects will be enhanced (Chan and Qian 1989). Bending of the C–Cl bond out of plane will induce an even greater effect, although without the aromatic symmetry it is more complicated in its consideration. In the present context, the increased back-donation leaks the triplet spin onto the Cl atoms, in effect enlarging the triplet electron cloud. Consequently the dipolar interaction decreases, leading to a lower *D*.

There are several testable predictions on this theory of pressure-enhanced mesomeric effects. These effects are independent of the position of Cl-substitution on the ring, and it is cumulative. As shown in figure 1, the pressure slope for TCB is 2·3 times that for DCB, which is in fair agreement with the theoretical prediction of a factor of two. As corroboration, we may cite the fact that the quadrupolar splitting of Cl^{35}, which may be extracted from the ODMR hyperfine structure, decreases by over 2 MHz in DCB for a pressure increase of 15 kbar. This decrease is consistent with a decrease in pπ occupancy in the chlorine, indicative of an enhancement of the mesomeric effect by pressure.

2.3. *Spin–orbit coupling in carbonyls*

In contrast to BP (figure 1), biacetyl and benzil have decreasing values of $|D|$ at higher pressure. This seemingly diverse behaviour may be explained by a unified model based upon the importance of spin–orbit coupling (SOC) in determining the ZFS in carbonyls. Figure 3 shows the energetic scheme, drawn to scale based upon spectroscopic information, for the various interactions in BP. Considering the dipolar interaction alone, the $|x\rangle$ and $|y\rangle$ spin states have higher energies. By symmetry, these spin states mix up with the $^3\pi\pi^*$ state by SOC, whereas the $|z\rangle$ couples to the much higher energy $^1\pi\pi^*$ state. The net effect of SOC is to push the $|x, y\rangle$ states below $|z\rangle$, changing the sign of *D*. Now, BP is not a planar molecule. Due to the van der Waals repulsion of the ortho-hydrogen in the two phenyl groups, the rings are twisted like a propeller. Under pressure, this twist angle will decrease, lowering the $^{1,3}\pi\pi^*$ states. The pressure effect is to push the $|x, y\rangle$ states further down relative to $|z\rangle$. For BP, this leads to an increase in $|D|$. For the other (lesser) carbonyls, the same mechanism operates, but to a lesser extent. The SOC never changes the sign of *D* in biacetyl and benzil. Pressure therefore decreases the value of $|D|$. This picture also handily explains the smaller pressure slope of $|D|$ for BP at higher pressures. Pressure flattens the phenyl twist angle, until eventually the repulsion of the ortho-hydrogen sets in. We thus observe a saturating behaviour.

A beautiful corroboration of this picture was provided by an investigation of the acetophenone (AP) system. Being a smaller molecule than BP, AP is essentially planar. As a consequence, its ππ* state is much lower compared with that of BP. For AP doped in dibromobenzene (DBB), the ππ* is the phosphorescent triplet, with the $^3n\pi^*$ state only 230 cm^{-1} above it (Cheng and Hirota 1974). An energy difference of this

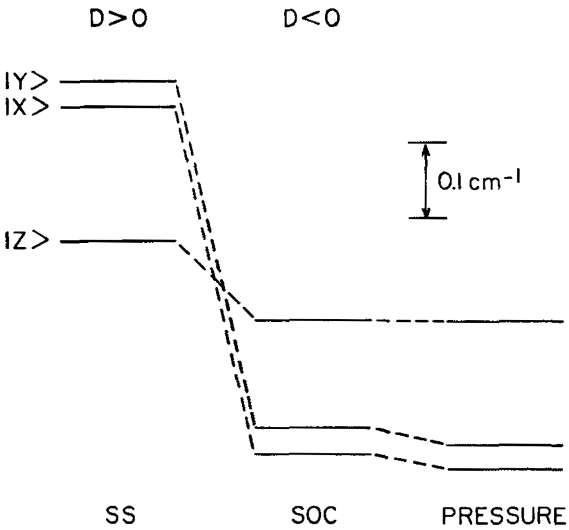

Figure 3. The various contributions to the ZFS of BP, drawn to scale based on spectroscopic information. SS: dipolar spin–spin interaction of the triplet electrons. SOC: spin–orbit coupling. Note that the SOC effect causes the ZFS parameter D to change sign.

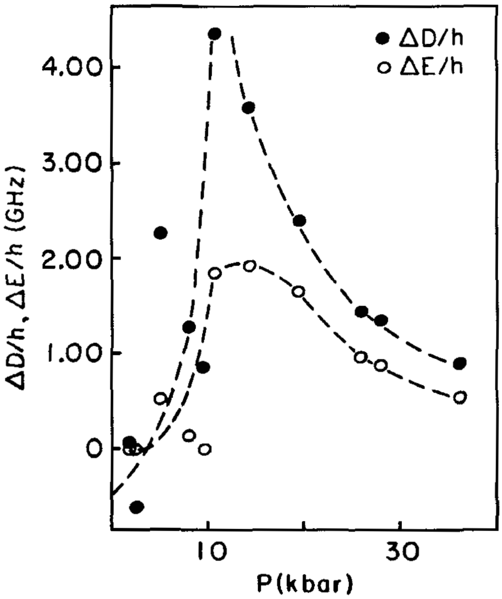

Figure 4. Pressure effect on the ZFS parameters of acetophenone in dibromobenzene. The D and E values exhibit a gigantic swing as two low-lying triplet states tune through an anticrossing. The broken curves are visual aids only.

magnitude may easily be bridged by pressure shifting of the appropriate energy levels. Now, AP is a planar molecule at ambient pressure. Upon compression, it cannot be further flattened; instead the carbonyl fragment will most probably be distorted out of the aromatic plane. The energy of the $^3\pi\pi^*$ state will increase, whereas that of the $^3n\pi^*$ state will remain largely unchanged by pressure. At a certain pressure, the two states may exhibit an anticrossing effect. As shown in figure 4, the ZFS of AP/DBB

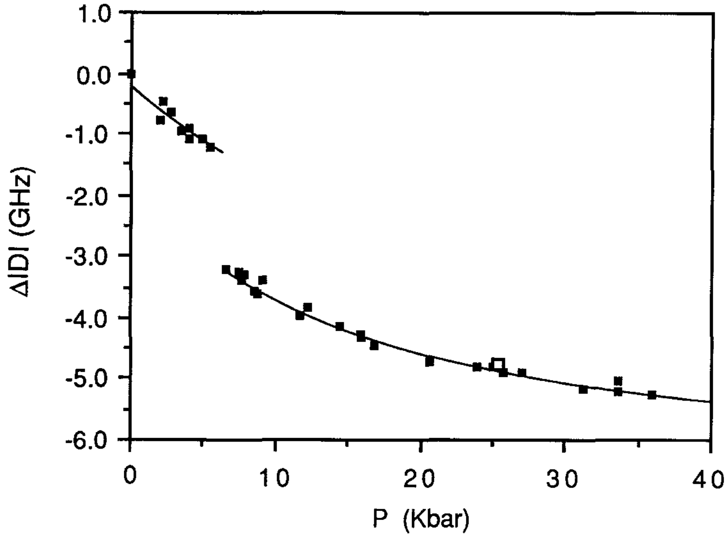

Figure 5. Pressure effect on the ZFS parameter $|D|$ for the X-trap in perdeutero-BQ. The step-change of nearly 2 GHz is due to a phase transition. The solid curve is an exponential fit after the step is removed, and the data in the two phases are fitted together.

experiences an enormous up-and-down swing around ~ 16 kbar, reflecting the rapidly changing identity of the phosphorescent triplet around an anticrossing. The measured pressure coefficient of ZFS may be up to 50 times that observed for aromatic molecules (cf figure 1).

2.4. *A pseudo-Jahn–Teller system*

p-Benzoquinone (BQ), due to the presence of two weakly-coupled carbonyl groups, has two low-lying $^3n\pi^*$ states separated by ~ 300 cm^{-1}. There is a strong vibronic interaction between them, resulting in a double-minimum potential for the phosphorescent triplet $^3B_{1g}$. We may expect a large pressure effect in such pseudo-Jahn–Teller systems. Figure 5 shows the change in $|D|$ effect by pressure in a neat perdeutero BQ crystal; other systems show similar results (Baber and Chan 1992). It suffices to mention two features of this figure: (1) There is a step change in $|D|$ at about 2 GHz resulting from a phase transition at 6 kbar. While phase transitions at elevated pressures are not uncommon, its large effect on $|D|$ illustrates the hypersensitivity of a vibronic system. (2) Meanwhile there is a gigantic reduction in ZFS, with maximum pressure slope at ambient pressures. The cause for this spectacular change by pressure is now understood (Bader and Chan 1992). Pressure causes a distortion from the D_{2h} symmetry either dynamically or statically (depending upon the system). The distortion removes the triplet spin density away from the carbonyl oxygen atoms into the ring. The accompanying electronic rearrangement greatly reduces the SOC contribution to the ZFS.

3. Phosphorescence spectroscopy

Up to the time we began working on organic triplets in a DAC, high pressure phosphorescence spectra of organic molecular crystals in the literature were generally of lower resolution (e.g. Kadhim and Offen 1967). There is no *a priori* reason why this was so but for the fact that earlier works by and large were limited to room

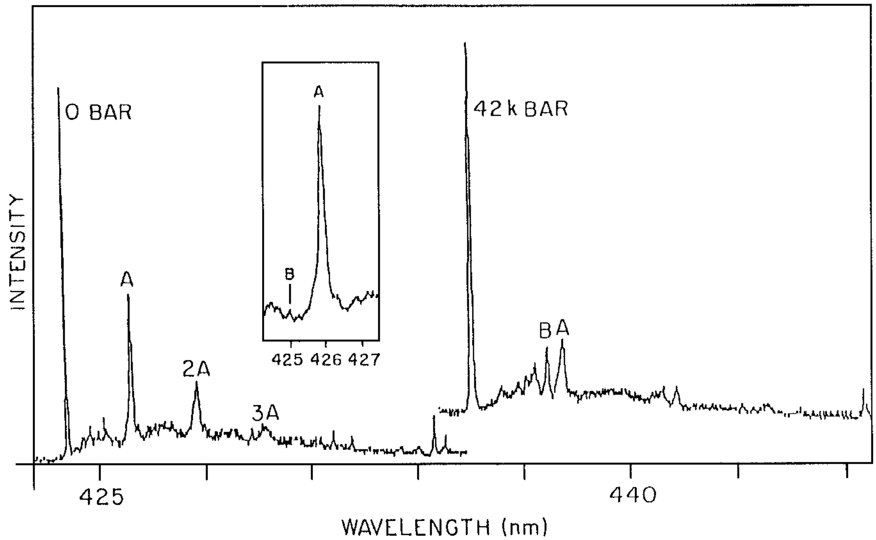

Figure 6. Phosphorescence spectra of BP/DDE at 0 and 42 kbar in the origin region. The two spectra share the same wavelength scale, but are offset vertically for clarity. A and B denote the symmetric and antisymmetric phenyl torsion modes of the same symmetry. The insert shows another 0 bar spectrum of a better signal-to-noise ratio in which the B mode may barely be seen. Temperature 2 K.

temperature or at most 77 K, due to the use of bulky pressure-containing equipment. Indeed, the fluorescence of ruby, which is widely used as a pressure calibration, is quite sharp at liquid helium temperature. In the course of our ODMR work on BP in a DAC, we found that its phosphorescence spectra stays sharp at pumped He temperature, such that we now had about 100-fold better resolution compared to the early results of Kadhim and Offen (1967). Therefore, its spectroscopy is interesting in its own right. In the next paragraph we present some features of the BP system (Chan and Chung 1988). High resolution solid state spectra of molecular crystals under pressure appear to be a general phenomenon, although some systems are understandably more vulnerable to damage during compression. Independently, Professor Chronister (1991) of UC Riverside has done much high resolution work at low temperature under pressure.

Figure 6 shows a phosphorescence spectrum at the origin region of BP/DDE taken at 42 kbar. We include in the same figure the corresponding spectrum at ambient pressure for comparison. The phosphorescence origin is greatly red-shifted by pressure, the symmetric ring-torsional mode (A) is weaker, and its overtones are no longer observable. These spectral features may be sublimed into a statement that pressure may change the Franck–Condon profile and the Debye–Waller factor. The red-shift of electronic transition energy and the increase of vibrational frequency are consistent with previous experiences in high pressure spectroscopy. Our results do show an interesting feature which is specific to the BP system. While line A is weaker, line B for the asymmetric ring-torsion gains intensity while its frequency is closer to that of line A. Lines A and B originate from the through-bond coupling of the torsional motions of the two phenyl rings. One resultant eigenstate is symmetry allowed, and the other forbidden. Pressure as a perturbation competes with this internal coupling, indeed serving to decouple the motion of the two rings. As line B becomes more allowed, its frequency becomes more nearly degenerate with that for line A. This is a pressure equivalent of the Paschen–Back effect in atomic spectroscopy.

4. Dynamical processes in solids

Pressure provides a controlled and gradual means to modify molecular distance and orientation in organic crystals. It is, therefore, a most effective way to increase short-range intermolecular interactions. With the advance of coherent spectroscopic techniques, such as spin-echoes and nonlinear laser spectroscopy, pressure should be viewed as a way to enhance dynamical processes in the condensed phase. Through pressure studies of these processes we may achieve more precise knowledge of the intermolecular potential and how it controls the observed dynamics. Our contributions in this area rest in our ability to conduct optically detected spin-echo experiments in a DAC. At the time of writing the potential of this approach has yet to be fully realized. Here, we describe the results of a three-pulse echo experiment on biacetyl (BA) and its perdeutero analogue (Chan and Qian 1991).

The phase memory time (T_M) of triplet BA-h_6 and BA-d_6 decreases by 30–40 % over a 40 kbar pressure range. Figure 7 shows a plot of this T_M as a function of reduced volume where, in the absence of compressibility data for BA, those for benzil were used. These results are consistent with the current thinking that, for organic triplets, spectral diffusion as a consequence of nuclear spin flip-flop is the dominant dephasing mechanism. The rate of flip-flop is determined by dipolar interaction between the nuclear spins, which varies with the inverse cube of the distance between two dipoles. As pressure shortens the distance between the dipoles, this rate will increase with inverse volume. Such a straightforward, perhaps trivial, effect of compression on echo decay may be expected. Our work, however, raises more questions than it answers. It is well-known that, around an electronic spin, there is a detuned sphere (DS) in which the protons are not on speaking terms with the bulk protons. The nuclear spins which are nearest to the electronic spin are subject to a hyperfine interaction. As a result, they are strongly detuned by the electronic local field, and cannot participate in the flip-flop processes with the remaining nuclei in the bulk. The radius of the DS, r_s, has been estimated by Mims (1972) as

$$r_s^3 = \frac{1}{2}\left(\frac{\gamma_e}{\gamma_n}\right)\frac{(1-3\cos^2\theta)}{n}$$

where γ_e and γ_n are the nuclear and electronic magnetogyric ratios, and n is the number density of the nuclei. The product of the volume of the DS and the number density is therefore a constant. In essence, a higher flip-flop rate also implies a greater nuclear-spin local field, requiring a more intense hyperfine field to detune it. According to this picture, pressure, by increasing the number density, reduces the volume of the DS. This results in more protons close to the electronic spin taking part in the flip-flop process. The overall effect on T_M should be quadratic with the fractional change in volume, which is not observed in our work.

Another surprising result of this work is the very small (40 %) deuteration effect on T_M observed in BA. This may be seen in figure 5, although my statement is not particularly related to pressure effects. In 1979, Van't Hof and Schmidt made a systematic study of the deuteration effect on T_2 of quinoline in durene. By successively deuterating the guest and the host, they observed a 42-fold lengthening of T_2. It was

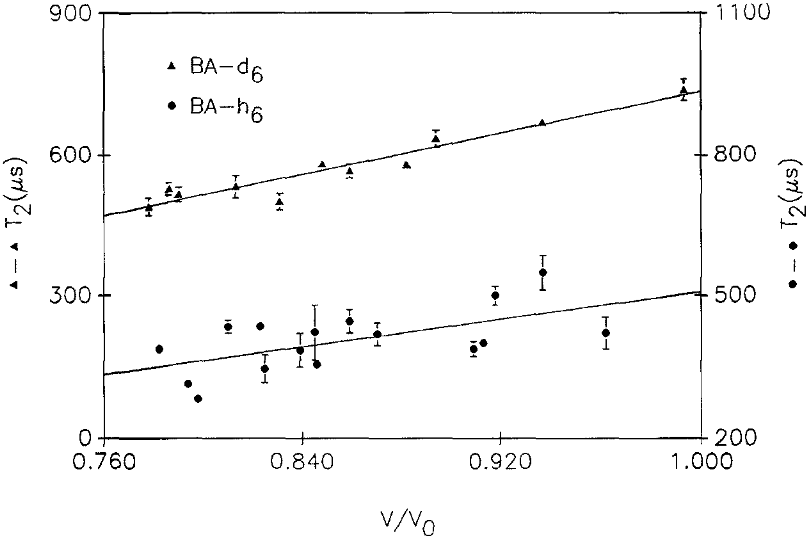

Figure 7. A plot of phase memory time T_M versus reduced volume V/V_0 for biacetyl shows a linear correlation.

mainly through their work that the importance of nuclear spin flip-flop in the dephasing of triplet spins in molecular crystals was established. From this perspective, the small deuteration effect observed in our BA work is enigmatic. We are currently conducting other experiments in order to shed some light on this phenomenon.

5. Quantum tunnelling reaction

To a chemist, the most logical extension of pressure-enhanced intermolecular dynamics is pressure-controlled chemical reactions. Indeed, activation volume information derived from P-dependence of reaction rates is a popular mechanistic tool for chemists (van Eldik *et al.* 1989). Most of these works were done in liquid solution. While such systems are chemically most relevant, the complicated nature of the solution medium makes a detailed analysis of the pressure effect on the progress of a reaction impossible. If, however, we may study a chemical reaction in a molecular crystal, the picture becomes much clearer. The position of every atom is known, and pressure enhances intermolecular interaction in a few specific modes. Therefore we have a very neat perturbation along the reaction coordinate. In recent years, we have focused on the effect of pressure on the reaction rate of a quantum tunnelling reaction, for its tunnelling nature further simplifies theoretical interpretation.

Our system is a mixed crystal of acridine-d_9 (Ac) in some isotopic species of fluorine (F). Upon photoexcitation of the Ac to its triplet state, the 9-aza atom abstracts a hydrogen atom from the methylene bridge of the F host to form a triplet radical pair (RP). This RP rapidly relaxes back to the ground states of the Ac and F nonradiatively. Thus the reaction shortens the triplet lifetime of the Ac. The progress of the reaction may then be conveniently monitored by the decay of its phosphorescence. This reaction has been extensively studied by the Stehlik group in Berlin, (Prass *et al.* 1989 and earlier references cited therein). Its reaction rate is non-Arrhenius as a function of temperature. Coupled with a large deuterium isotope effect, this observation has been interpreted as a manifestation of tunnelling of the H atom in an asymmetric double-well potential. The temperature-dependent part of the

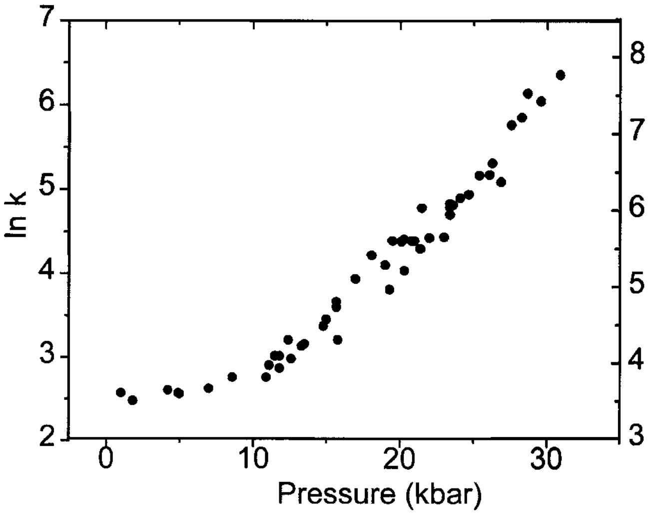

Figure 8. Phosphorescence decay rate of Ac/Fd_8H_2 at 1·4 K as a function of pressure. It is the sum of a pressure-independent intramolecular decay and an exponential rise of H-tunnelling rate.

reaction rate at low temperature is promoted by a 125 cm^{-1} libration along the *c*-axis, during which the nitrogen and the methylene are brought into a more favourable alignment.

The effect of pressure on the reaction rate may be illustrated in figure 8, where the phosphorescence decay rates of Ac/Fd_8H_2 at 1·4 K are shown (Chan *et al.* 1994). There are several important features of these data. (1) They may be interpreted as the sum of a pressure-independent intramolecular decay rate and an exponential rise in the tunnelling rate with increasing pressure. A similar exponential rise was observed at 77, 150 and 300 K, with a higher pressure coefficient attributed to a temperature-dependent compressibility of the crystal (Bomberg *et al.* 1993; Chan *et al.* 1995). Our current view is that, although a strict exponential dependence may be a numerical coincidence, an approximately exponential rise of rates with increasing pressure is a general characteristic of a tunnelling system. (2) Fitting these data to the sum of an exponential function and a constant, the tunnelling rate has increased some 2000 times over 30 kbar. The tunnelling effect is strongly pressure-dependent. (3) Until now the tunnelling rate at near-zero K is not empirically measurable due to the obscuring effect of the intramolecular decay process. By rendering the tunnelling process faster under pressure, and by observing an exponential dependence, we managed to extract the tunnelling rate at the vibrational ground state. So far there are three theoretical calculations for this quantity (Flomenblit *et al.* 1991, Chantranupong and Wildman 1991, Lavtchieva and Smedarchina 1991a, b, 1992). They are different by an order of magnitude, and at least 10 times slower than our observed rate. Thus our empirical extraction of this quantity represents a significant contribution.

Postscript: Recently we conducted a series of Raman experiments on Ac/F under pressure. Our purpose was to identify a low-frequency butterfly mode of F which might be another reaction-promoting mode. It turns out that this 99·6 cm^{-1} butterfly mode is hidden underneath a strong phonon mode under ambient pressure, but up-shifted rapidly under compression to be totally resolved. A polarization study under pressure (an experimental triumph!) establishes its identity. Although this operation does not involve the triplet state, it nevertheless illustrates the utility of pressure as a perturbation in science. Taking the computed normal coordinate of F from Cuff and Kertesz (1994), we identified yet another butterfly-like mode at 238 cm^{-1} as reaction-promoting. The fact that there are at least three promoting modes may explain why the theoretical calculations so far, assuming only the 125 cm^{-1} mode to be promoting, are off by at least an order of magnitude.

Acknowledgments

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References

BABER, J. L., and CHAN, I. Y., 1992, *J. chem. Phys.*, **96**, 5591.

BROMBERG, S. E., CHAN, I. Y., SCHILKE, D. E., and STEHLIK, D., 1993, *J. chem. Phys.*, **98**, 6284.

CHAN, I. Y., and CHUNG, W. M., 1988, *Chem. Phys. Lett.*, **150**, 437.

CHAN, I. Y., DERNIS, M. S., WONG, C. M., PRASS, B., and STEHLIK, D., 1995, *J. chem. Phys.* (in press).

CHAN, I. Y., and QIAN, X. G., 1989, *J. chem. Phys.*, **91**, 3877; 1900, *ibid.*, **92**, 929; 1991, *ibid.*, **95**, 7067.

CHAN, I. Y., WONG, C. M., and STEHLIK, D., 1994, *Chem. Phys. Lett.*, **219**, 187.

CHANTRANUPONG, L., and WILDMAN, T. A., 1991, *J. chem. Phys.*, **94**, 1030.

CHENG, T. H., and HIROTA, N., 1974, *Molec. Phys.*, **27**, 281.

CHRONISTER, E. L., and CROWELL, R. A., 1991, *Chem. Phys. Lett.*, **182**, 27.

CUFF, L., and KERTESZ, M., 1994, *J. phys. Chem.*, **98**, 12223.

FLOMEMBLIT, V.SH., MIKHEIKIN, I. D., and TRAKHTENBERG, L. I., 1991, *Dokl. Akad. Nauk. Phys. Chem.*, **320**, 695.

JAYARAMAN, A., 1983, *Rev. mod. Phys.*, **55**, 66.

KADHIM, A. H., and OFFEN, H. W., 1967, *J. chem. Phys.*, **47**, 1289.

LAVTCHIEVA, L., and SMEDARCHINA, Z., 1991a, *Chem. Phys. Lett.*, **184**, 545; 1991b, *ibid.*, **187**, 506; 1992, *Chem. Phys.*, **160**, 211.

LEE, S. H., LUSZCZYNSKI, K., NORBERG, R. E., and CONRADI, M. S., 1987, *Rev. Sci. Instrum.*, **58**, 415.

MIMS, W. M., 1972, *Electron Paramagnetic Resonance*, edited by S. Gerschwind (New York: Plenum), p. 292.

PRASS, B., COLPA, J. P., and STEHLIK, D., 1989, *Chem. Phys.*, **136**, 187.

SAKAI, N., and PIFER, J. H., 1985, *Rev. Sci. Instrum.*, **56**, 726; 1986, *Phys. Rev.* B, **33**, 1875.

SANDROFF, C. J., CHAN, I. Y., and CHUNG, W. M., 1986, *J. chem. Phys.*, **84**, 2424.

VAN ELDIK, R., ASANO, T., and LE NOBLE, W. J., 1989, *Chem. Rev.*, **89**, 549.

VAN'T HOF, C. A., and SCHMIDT, J., 1979, *Molec. Phys.*, **38**, 309.