Reviews

Some recent developments in pressure tuning spectroscopy*

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Pressure tuning spectroscopy has proved to be a powerful tool for studying a wide variety of electronic phenomena. In this review we present two recent examples of the application of high pressure luminescence: (1) a test of the validity of a kinetic model for the emission characteristics of molecules that emit from excited states with different degrees of charge transfer and different geometries (molecules with twisted intramolecular charge transfer (TICT)); (2) an elucidation of the mechanism for the large difference observed between the luminescence efficiencies of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(py)_2]^{2+}$ in solid media.

Key words: *N,N*-dimethylaminobenzonitrile, ruthenium complexes with pyridine and bipyridine ligands, high pressure luminescence spectra.

In this paper we review two rather recent studies in which pressure tuning spectroscopy has played a significant role in providing a definitive model for the behavior of molecules having both theoretical and potentially practical importance. In the first of these studies we test a kinetic model for the behavior of molecules that emit from two excited states with different polarities and geometries (molecules with twisted intramolecular charge transfer (TICT)). These molecules have considerable potential as molecular electronic switches and for probing local structure and intermolecular interactions in polymers, especially under stress, or in fluids like lubricants under pressure and stress. The second study was concerned with two complex compounds of very similar chemistry but with widely different luminescent efficiency. The problem was to account for the nature of this difference. These molecules have a broad spectrum of potential application in photoelectrochemical systems, in investigating electro- and chemiluminescence, and as macromolecular structure probes or photocatalysts.

Molecules with twisted intramolecular charge transfer

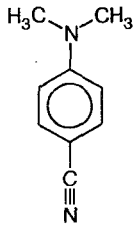
Study of molecules that can emit from two or more excited states with different geometries and polarities (TICT molecules) has become a very significant aspect of modern photophysics since it was first observed by Lippert *et al.*[1] for *N,N*-dimethylaminobenzonitrile (DMABN) in polar solvents. Later Grabowski *et al.*[2] suggested that the molecule has a planar geometry in one of the excited states, and in the other excited state,

* In 1994, Prof. H. G. Drickamer was awarded the *Honoris causa* degree by the Russian Academy of Sciences.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1195—1202, July, 1995.

1066-5285/95/4407-1149$12.50

the dimethylamino group is twisted, which indicates a large degree of charge redistribution. Although the exact form of the change in the molecular geometry is still a matter of discussion, it is clear that a larger degree of charge distribution is associated with the second excited state. At this time, this phenomenon has been observed for a large number of molecules and has been extensively discussed in the literature (>200 papers have been devoted to DMABN itself over the last five years). For recent reviews see Ref 3. We refer only to papers whose results are directly applicable to the studies presented here.



DMABN
(4-Dimethylaminobenzonitrile)

Let us consider the behavior of DMABN at a high pressure in solid polymeric media.[4] Most previous works on TICT molecules have involved liquid media at ambient pressure, although there have been a few papers using polymeric media also at ambient pressure.[5–7] In addition, there has been one earlier set of investigations of pressure effects on TICT molecules in solid media, but these compounds emitted only from one excited state.[8,9]

Here we present the results of a study of the effect of pressure on the DMABN molecule in two polymeric media, polymethylmethacrylate (PMMA) and polyethylmethacrylate (PEMA), at relatively low excitation fluxes, $<10^{12}$ ph cm^{-2} s^{-1}. To explain these results we present a model which relates steady-state data to two sets of time-dependent data over a 100 kbar pressure range, even though the experimental results depend non-monotonically on pressure.

The experimental aspects of high pressure luminescence work have been described in detail elsewhere.[10] In all of the experiments covered in this review the exciting light was the 325 nm or the 441.6 nm line of an He-Cd laser. The intensity of the beam hitting the sample was controlled by using appropriate filter combinations. In general, experiments were performed at ~295 K. All measurements were made at a concentration of the compound in a polymer of 10^{-3} mol/mol of monomer unit. At 0 kbar the emission spectrum consisted of two peaks, a relatively intense one at ~27,000 cm^{-1} (HEP) and a second peak at ~24,000 cm^{-1} (LEP) with about 20—25 % of the intensity of the HEP. The effective decay rates were ~0.35 ns^{-1} (HEP) and ~0.3 ns^{-1} (LEP). These peaks represent fluorescence from the "planar" and "twisted" forms of the excited state. As indicated above, there is still discussion about the geometry of the states involved, but we use "planar" and "twisted" to represent the excited state most like the ground state and the one involving a high degree of charge transfer, respectively. With increasing pressure a new peak appeared at ~22,000 cm^{-1}. This peak increased rapidly in intensity so that above 4—5 kbar it masked the original LEP completely. From the lifetime measurements it was evident that there was always some of the original LEP present, and it did not change significantly in intensity with pressure. The new peak had a lifetime of the order of a few s^{-1}; therefore, its origin is clearly associated with phosphorescence.

Figure 1 presents the pressure dependence of the ratio between the peak intensities. The filled-in points indicate the ratio between the two fluorescence peaks, while the open points represent the ratio of phosphorescence to fluorescence intensities. This latter ratio increased by a factor of 8—9 between ~1.5 and 100 kbar. The spectral properties of DMABN in PMMA and PEMA are essentially identical. Limited data were obtained in other polymers, *e.g.* poly(butyl methacrylate) (PBMA), poly(vinyl acetate) (PVAC), *etc.* They showed qualitatively similar results.

From the steady-state results the peak locations as a function of pressure were obtained. When the pressure increased to 100 kbar, the high energy (fluorescence) peak HEP shifted only 600—700 cm^{-1} to the low energy (red shift). The phosphorescence peak shifted even less, 200—300 cm^{-1}, to the red as the pressure increased from 5 to 100 kbar.

The data on the decay rates are given in Figs. 2 and 3. The rate of decay of the HEP is initially ~0.35 ns^{-1}

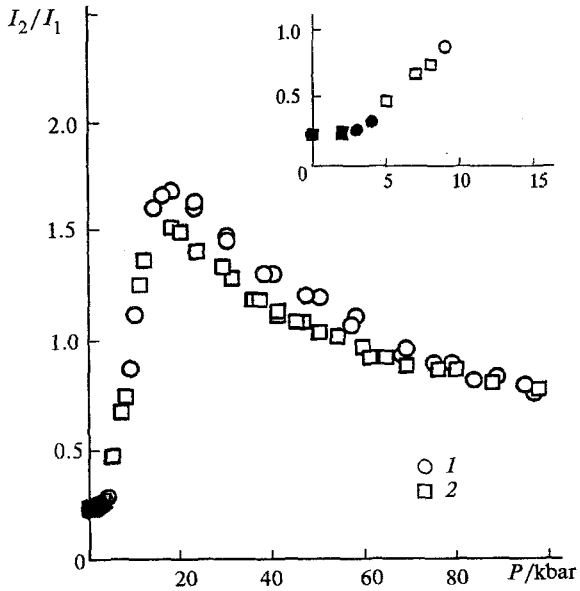


Fig. 1. Pressure dependence of the ratio of the LEP to the HEP intensities I_2/I_1 for the luminescence of DMABN in PMMA (*1*) and PEMA (*2*). The filled-in points are discussed in the text.

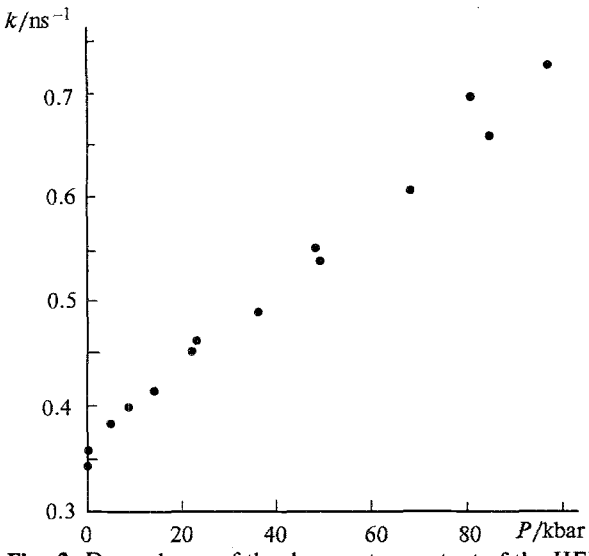


Fig. 2. Dependence of the decay rate constant of the HEP (k) on the pressure for DMABN in PMMA.

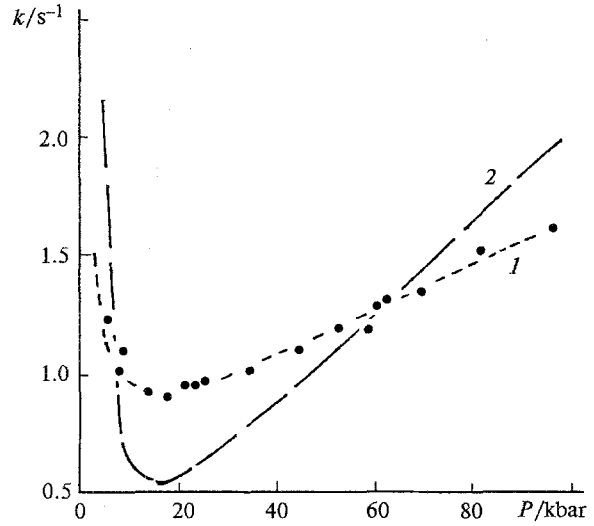


Fig. 3. Dependence of the decay rate constant of the LEP (k) on the pressure for DMABN in PMMA: the dashed line (*2*) corresponds to Eq. (3).

and increases linearly with pressure by a factor of two as the pressure increases to 100 kbar. The fluorescence at 24.000 cm^{-1} decays initially (k ~0.3 ns^{-1}) and then does not change significantly with pressure. The decay rate of phosphorescence is shown by the filled circles in Fig. 3. This rate was determined with low accuracy to be 1.5—1.8 s^{-1} at pressures below 2 kbar. The non-monotonic behavior of the intensity data and the phosphorescence decay rate make analysis particularly challenging.

A scheme of the processes observed, similar to that used by Gunther *et al.*[11] is shown in Fig. 4. In order to minimize the complexity of the subscripts, in addition to the usual spectroscopic nomenclature, the relevant states are labelled by capital letters (A, B, C, D, G, G'), and the rate constants of the transitions between these states are denoted by letter k with the corresponding subscripts.

To identify the relationships between the intensity ratios and the fluorescence and phosphorescence decay rates, the following simplifications based in part on literature data and in part on our observations can be made:

(1) The phosphorescence occurs from the planar triplet state (D), which has a modest dipole moment. It is well established that the twisted triplet state (C) is non-emissive. It decays either thermally to the ground state (k_C^{nr}) or by transforming to the planar triplet state (k_{CD}). At ambient pressure $k_C^{nr} > k_{CD}$, since no phosphorescence is observed.

(2) The transition from the planar singlet (B) to the planar triplet (D) is considered negligible at 0 kbar because of the large energy difference, 5000 cm^{-1} (k_{BD} ~ 0). Since this energy difference hardly changes with pressure it can be assumed that k_{BD} is negligible at all pressures.

(3) Since neither the fluorescence nor phosphorescence peaks shift significantly with pressure it can be assumed that $k_B = k_B^n + k_B^{nr}$ and $k_D = k_D^n + k_D^{nr}$ have negligible pressure dependences.

(4) The fluorescent lifetime observed at 435 nm does not change with pressure. One can thus neglect the pressure dependence of $k_A = k_A^r + k_A^{nr}$.

(5) The energy difference between the twisted singlet state (A) and the twisted triplet state (C) is not over 1000 cm^{-1} at 0 kbar. This conclusion is based on the usual behavior of charge transfer states, on time dependent absorption measurements, and on a number of theoretical calculations.[11,12] Since singlet excited states always shift to lower energy more rapidly than the corresponding triplet states, this energy difference decreases as the pressure increases.

By straightforward algebraic manipulations one arrives at expressions (1)—(3) for the three observables, $\frac{I_D}{I_B}$, K_B, K_D.

$$\frac{I_D}{I_B} = \frac{k_D^r}{k_A^r} \frac{k_{CD} k_{AC}}{k_D (k_C + k_{CA} + k_{CD})} \qquad (1)$$

From the discussion above, the possible pressure dependent terms are: k_{AC}, k_{CD}, k_C, and k_{CA}. There is some evidence that k_{CD} increases modestly with pressure, but since it appears in both the numerator and denominator its effect is much diminished. The k_C value should be reasonably large at 0 kbar since there is no phosphorescence under these conditions. There is no evidence concerning its pressure dependence. k_{AC} is significant at 0 kbar and most likely increases continuously as the energy difference between states A and C decreases. At 0 kbar, when the barrier to return from C to A is at least ~5 kT, the k_{CA} value is small However, it increases exponentially as the energy difference from C to A decreases. The major factor in the increase in $\frac{I_D}{I_B}$

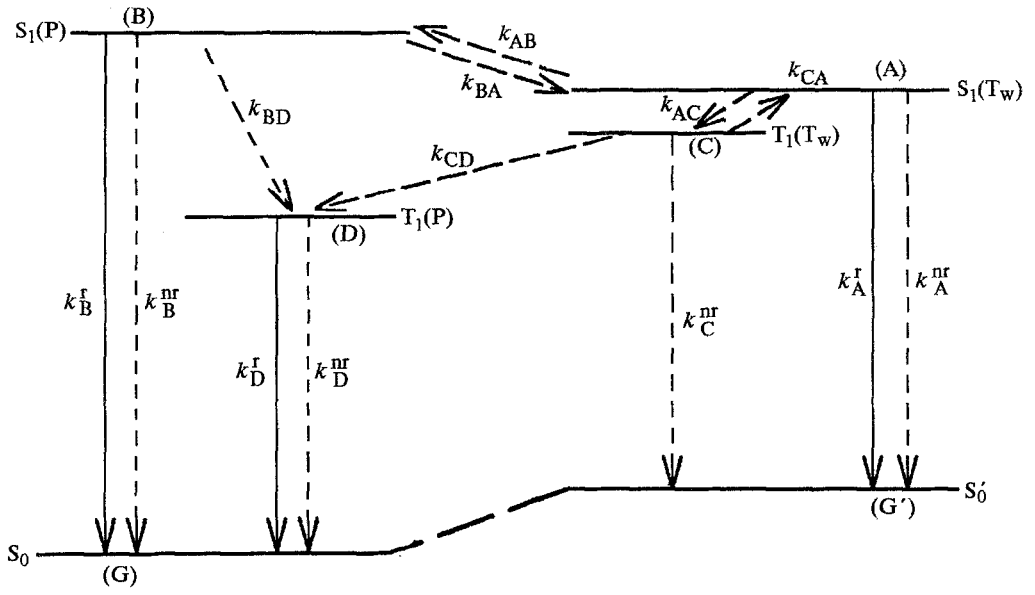


Fig. 4. Kinetic model for DMABN in polymeric media.

between 4 and 18 kbar is the increase in k_{AC}. At higher pressures the rapid increase in k_{CA} counteracts this effect. It is also possible that k_C may change with pressure.

$$K_B = k_B + \frac{I_A}{I_B}\frac{k_B^r}{k_A^r}\left[k_A + k_{AC}\left(1 - \frac{I_D}{I_B}\frac{k_A^r}{k_D^r}\frac{k_D k_{CD}}{k_{CD}k_{AC}}\right)\right] \quad (2)$$

K_B increases linearly by a factor of two as the pressure increases to 100 kbar. The terms with significant pressure dependence are k_{AC}, $\frac{I_D}{I_B}$, and $\frac{k_{CA}}{k_{CD}k_{AC}}$. From Eq. 1 it can be seen that $k_{CD}k_{AC}$ is just the pressure dependent term of the numerator in and k_{CA} is the most pressure dependent term in the denominator. Thus, one may assume that the pressure effect of the product of these factors is insignificant, and the change in K_B is due to the increase in k_{AC}. Conversely, if Eq. (2) is valid and K_B is proportional to k_{AC}, then the pressure dependence of $\frac{I_D}{I_B}$ must be given by the changes in k_{AC} and k_{CA}.

The rate of emission from the state D is given by

$$K_D = K_B \frac{k_D^r}{k_B^r}\left(\frac{I_A}{I_B}\right)^{-1}. \quad (3)$$

From the known values of K_B and $\frac{I_D}{I_B}$ we obtained a curve (Fig. 3, curve *2*) that is in relatively good agreement with the non-linear behavior observed. Not much of a definitive nature is known about the rates of crossing between planar and twisted singlet states (k_{BA} and k_{AB}). In liquids there is some evidence that the barrier is small. From our model:

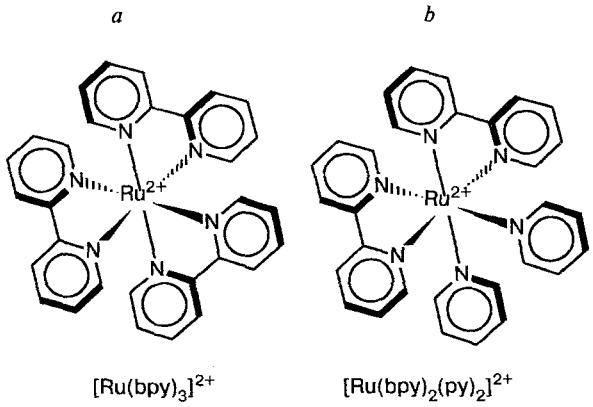
$$k_{BA} - k_{AB}\frac{I_A}{I_B}\frac{k_B^r}{k_A^r} = K_B - k_B \quad (4)$$

The only significantly pressure dependent term in this equation is K_B. It increases linearly with pressure. Thus, the rate of the transition from the planar state to the twisted state (k_{BA}) increases relative to the return rate (k_{AB}), although both terms may increase or decrease.

Overall, there is a high degree of consistency between the steady-state and time-dependent factors even though their pressure dependences are non-monotonic. This study illustrates the power of pressure tuning spectroscopy to establish the validity of a model suggested.

Polypyridine Complexes

The polypyridine complexes $[Ru(bpy)_3]^{2+}$ (TRIS) and $[Ru(bpy)_2(py)_2]^{2+}$ (BIS) (bpy = bipyridine; py = pyridine) have very closely similar structures. They absorb and emit light at very nearly the same energies, but they[13–18] differ strongly in luminescence characteristics at 0 kbar. The use of high pressure spectroscopy gives a clear explanation of this phenomena.



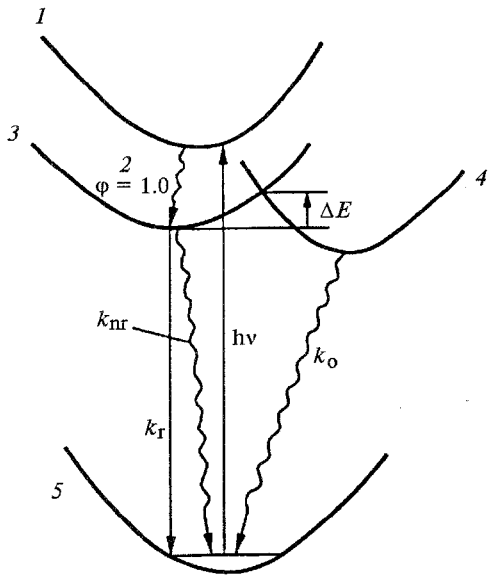


Fig. 5. Schematic energy level diagram in conformity with the model used to describe Ru^{II} complexes. ^{1}MLCT (*1*); intrasystem singlet-triplet transition (2); ^{3}MLCT (*3*); the excited crystal field state (*4*); the ground state (*5*).

The compounds were studied as crystalline solids and as solutions in polyacrylic acid (PAA) and poly(2-vinylpyridine) (PVP).[19] The excitation was carried out with the 441.6 nm line of an He-Cd laser. In the polymers the concentration was $6 \cdot 10^{-4}$ mol per mol of monomer unit. The experimental details have been published previously.[19] A common energy level diagram (Fig. 5) describes the behavior of both complexes. The excitation involves a metal to ligand charge transfer (MLCT) to give an excited singlet (^{1}MLCT), which is initially localized on a bpy ligand but can distribute itself within the triplet lifetime over several ligands. The excitation transfers to the corresponding triplet (^{3}MLCT) with practically 100 % yield ($\varphi = 1$). The return from the triplet to the ground state can occur by luminescence, by direct thermal decay, or by transfer to an excited crystal field state over an energy barrier (ΔE) followed by thermal decay to the ground state.

Table 1 presents the relative values of the luminescence intensity and the lifetimes of TRIS and BIS complexes in all three of the media. The relative values are reproducible, but, of course, it is difficult to make a quantitative comparison of efficiency in the crystal with the values in the polymers. One observes a strong medium dependence for the TRIS with much less for the BIS. We conclude that intermolecular forces are dominant for the TRIS, while for the BIS, intramolecular interactions are relatively more important. Figs. 6—8 show the peak locations as a function of pressure. A monotonic shift to lower energy is exhibited by the peaks of TRIS in all media, and this effect is more pronounced in the crystal than in the polymers. For the BIS compound in the crystal the emission energy is lower than for the TRIS, but the shift is parallel. The BIS emission in the polymers exhibits a very small blue shift at low pressure; then it parallels the TRIS shift over most of the pressure range used.

Table 1. Relative intensities and lifetimes at ambient pressure

Ru complex	Medium	Intensity		Lifetime
		Arb. units.	Normalized	ns
BIS	PVP	730	1.0	635
	PAA	790	1.1	715
	Solid	880	1.2	45
TRIS	PVP	15000	20.5	1385
	PAA	24500	33.6	1570
	Solid	4700	6.4	86

Figs. 9—11 show the pressure dependences of the relative emission intensities and the lifetimes. These values for the TRIS compound decrease monotonically as the pressure increases in all of the media. In principle, this could be due to an increase in the transfer along the non-radiative path *via* the excited ligand field state because of a decrease in ΔE (Fig. 5). However, this is unlikely as ligand field splittings increase with pressure for d^6 systems, and the red shift of the emission peak

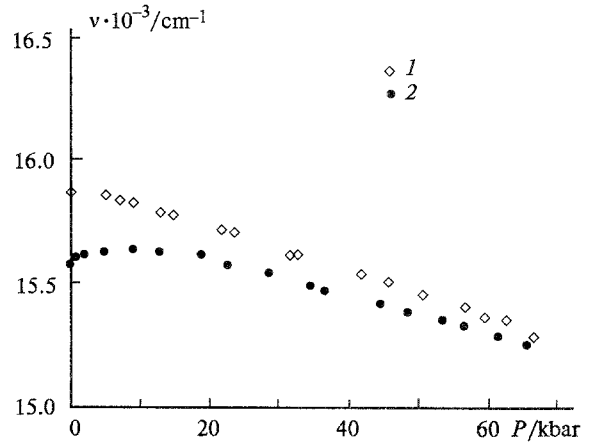


Fig. 6. Pressure dependence of the locations of the emission peaks for solutions of the complexes in PVP: $[Ru(bpy)_3]^{2+}$ (*1*); $[Ru(bpy)_2(py_2)]^{2+}$ (*2*).

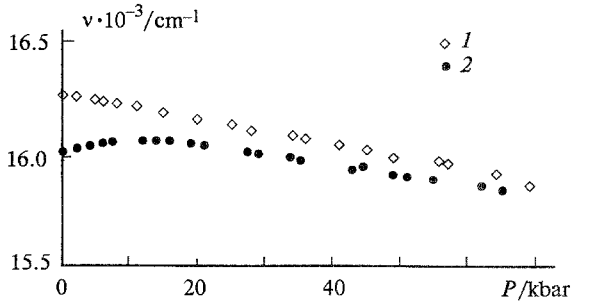


Fig. 7. Pressure dependence of the locations of the emission peaks for solutions of the complexes in PAA: $[Ru(bpy)_3]^{2+}$ (*1*); $[Ru(bpy)_2(py_2)]^{2+}$ (*2*).

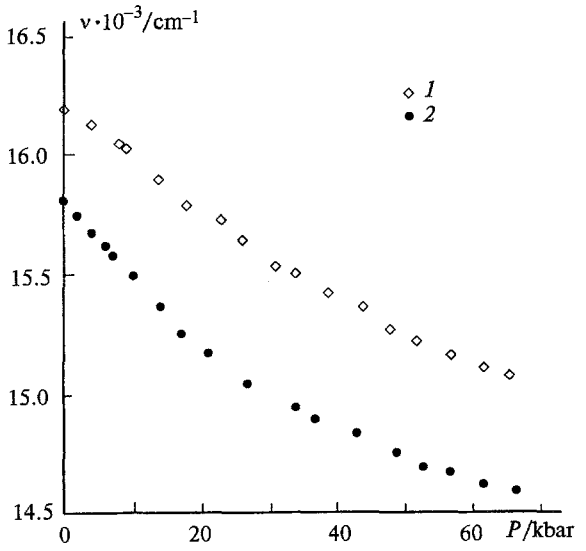


Fig. 8. Pressure dependence of the locations of the emission peaks for the crystalline solid complexes: $[Ru(bpy)_3]^{2+}$ (*1*); $[Ru(bpy)_2(py_2)]^{2+}$ (*2*).

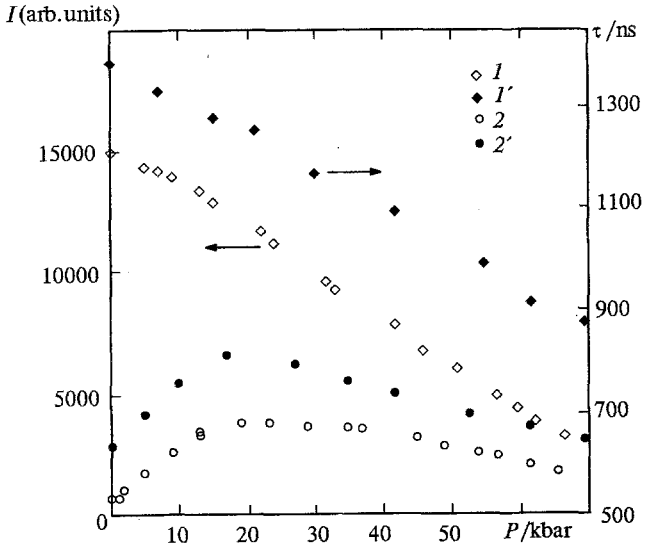


Fig. 9. Pressure dependences of relative luminescence intensities (*I*) (*1*, *2*) and lifetimes (τ) (*1′*, *2′*) for solutions of the complexes in PVP: $[Ru(bpy)_3]^{2+}$ (*1*, *1′*); $[Ru(bpy)_2(py_2)]^{2+}$ (*2*, *2′*).

indicates an increase in ΔE. The more likely path is the direct crossing to the ground state. The "energy gap law"[20] demands a linear relationship between the logarithm of the efficiency and shift of the peak. It can be seen in Fig. 12 that this rule holds well for the TRIS compound in all of the media. In this case, the logarithm of the relative luminescence yield is given as $\ln\frac{I(P)}{I(P_0)}$, where $I(P_0)$ refers to the intensity at 0 kbar.

The BIS complex exhibits a more interesting behavior. Below ~25 kbar, there is a significant increase in luminescent efficiency in all three media. At higher

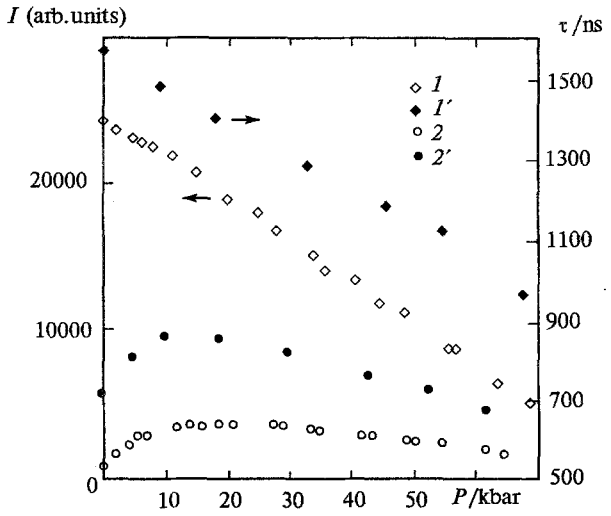


Fig. 10. Pressure dependences of relative luminescence intensities (*I*) and lifetimes (τ) for solutions of the complexes in PAA: $[Ru(bpy)_3]^{2+}$ (*1*, *1′*); $[Ru(bpy)_2(py_2)]^{2+}$ (*2*, *2′*).

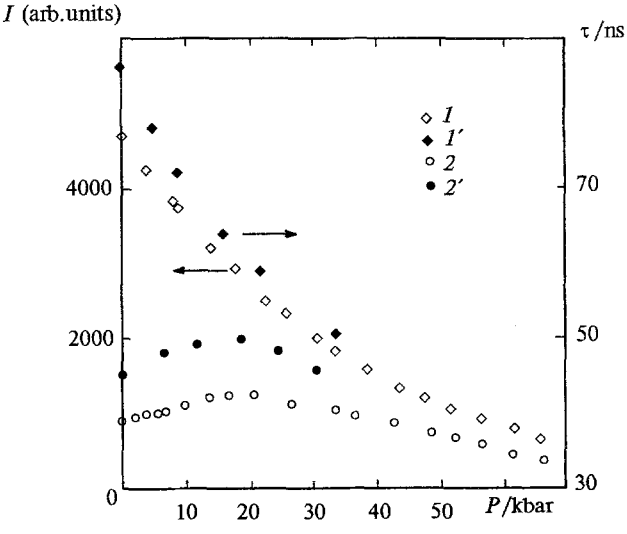


Fig. 11. Pressure dependences of relative luminescence intensities (*I*) (*1*, *2*) and lifetimes (τ) (*1′*, *2′*) for the solid crystalline complexes $[Ru(bpy)_3]^{2+}$ (*1*, *1′*); $[Ru(bpy)_2(py_2)]^{2+}$ (*2*, *2′*).

pressures the efficiency decreases. The lifetime varies as a function of pressure, mostly in parallel with the efficiency. As a result, the difference in the luminescence efficiency between the TRIS and BIS complexes decreases drastically as the pressure increases, as shown in Table 2. The behavior of the complexes beyond the point of maximum efficiency (p_{max}) obeys the energy gap rule as shown in Fig. 12, where for the BIS compound $I(0)$ refers to $I(P_{max})$.

The increase in the efficiency and lifetime below 25 kbar cannot be accounted for by the small blue shift of the emission peak (~50 cm^{-1}). In any case no blue shift is observed in the crystal. The most likely explana-

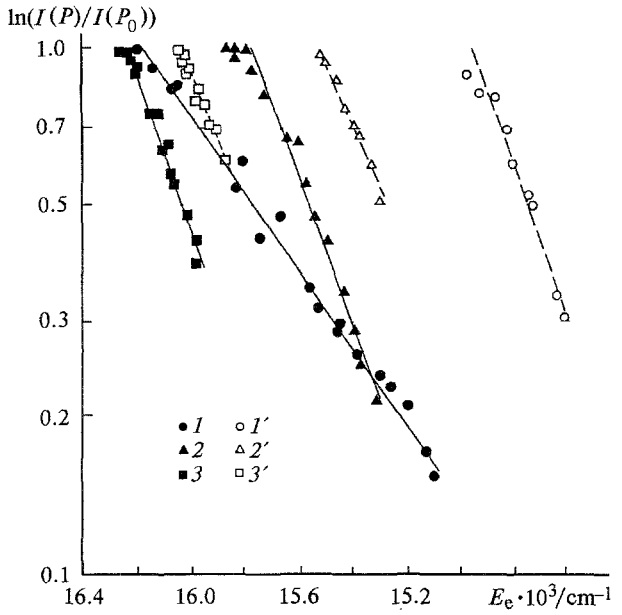


Fig. 12. Dependence of $\ln(I(P)/I(P_0))$ on the emission energy E_e: TRIS ($P(0)$ = 0 kbar) (*1—3*); BIS (*1′—3′*) (P_0 is the pressure corresponding to the maximum emission energy). Crystalline (*1*, *1′*); in PVP (*2*, *2′*); in PAA (*3*, *3′*).

Table 2. TRIS/BIS intensity ratio

P/kbar	PAA	PVP	Solid
0	31.0	20.5	5.3
65	3.2	1.9	1.5

tion lies in the compression-induced inhibition of the motion of the pyridine molecules. The excitation is initially localized on a bpy ligand, but in the time scale of the phosphorescence it spreads to the other ligands. The pyridines can undergo motions not available to the bypyridines, which accounts for the more rapid dissipation of energy and lower efficiency of the BIS molecules, as well as the intramolecular redistribution of this energy. At pressures below 25 kbar the primary effect of compression is to inhibit these extramotions and thus to increase luminescent efficiency. At higher pressure the effect of the energy gap law dominates as shown in Fig. 12.

Conclusions

These two examples of quite different phenomena illustrate how pressure tuning spectroscopy can solve scientific problems and test the validity of models of electronic phenomena in solid state physics.

It is a pleasure to acknowledge the continuing support of the Materials Science Division of the Department of Energy (Contract DEFG02-91ER45439).

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Received January 10, 1995