CHROMOGENIC MATERIALS, PIEZOCHROMIC

1. Introduction

In its most general sense piezochromism is the change in color of a solid under compression. There are three aspects of the phenomenon.

The first is, in a sense, trivial, but it is very general. The color of a solid results from the absorption of light in selected regions of the visible spectrum by excitation of an electron from the ground electronic state to a higher level. If the two electronic energy levels are perturbed differently by pressure, compression results in a color change. This is the basic definition of pressure tuning spectroscopy. Examples include, among others, increased splitting of the *d* orbitals of transition-metal ions in complexes with pressure, the shift to higher energy of a color center (a vacancy containing an electron) in an alkali halide or glass environment, and a change in the relative energy of bonding and antibonding orbitals as pressure increases. This last phenomenon depends on the relative importance of intra- and intermolecular interactions. The compression of a bond increases the difference in energy between bonding and antibonding orbitals. On the other hand, the attractive van der Waals interactions between molecules are generally stronger around an excited molecule. Where the latter interaction dominates, one observes a shift to lower energy (red shift) of these excitations. Further examples of this include the energy associated with the transfer of an electron in an electron donor–acceptor complex and the difference in energy between the top of the valence band and bottom of the conduction band, ie, the absorption edge, in insulators and semiconductors.

These excitations are widely used to characterize electronic states and excitations, to test theories about electronic phenomena, and to delineate the nature of local sites in glasses, disordered solids, intercalates, etc. However, this aspect of changing color with pressure is so general that it is not satisfactory for defining piezochromism.

A second aspect involves a discontinuous change of color when a crystalline solid undergoes a first-order phase transition from one crystal structure to another. The most obvious example is the change of the absorption edge. For example, CdS changes from yellow to deep red at 2.7 GPa (27 kbar) when the crystal structure changes from wurtzite to sodium chloride (face-centered cubic). CdSe, ZnS, ZnSe, and ZnTe undergo similar transitions with distinct color changes at pressures from 5–15 GPa (50–150 kbar). First-order phase transitions involving alterations in crystal structure only can change the electronic excitation energy associated with almost any kind of electronic process provided the two electronic states interact differently with the changing environment. However, for most molecular crystals at modest pressures, the coupling between the electronic states of the molecule and the lattice modes is rather small so these perturbations are usually not large, with few exceptions.

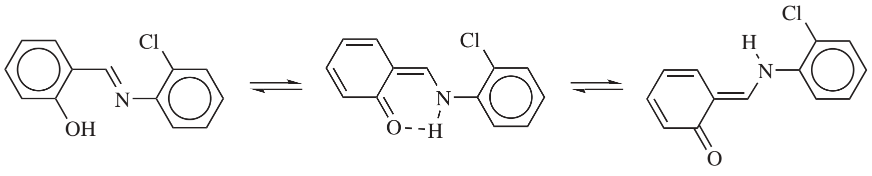
The phenomenon of most interest is a change in color of a solid as a result of a change in the molecular geometry of the molecules that make up the solid. The color change takes place because the change in geometry alters the relative energy of different electronic orbitals, and therefore the electronic absorption spectrum. Frequently it rearranges the order of these orbitals or provides new combinations of atomic orbitals because of symmetry changes. The rearrangements may be discontinuous at a given pressure, may occur over a modest range of pressures, or may occur gradually over the whole range of available pressure as for chemical equilibria in solution (1,2). A few examples, together with the principles or generalizations that arise from them, are discussed.

Piezochromism has been observed in a wide variety of materials. Three classes which illustrate well some of the generalizations that have been developed are organic molecules in crystals and polymer films, metal cluster compounds, and organometallic complexes of Cu(II).

2. Principal Piezochromic Systems

2.1. Organic Molecules in Crystals and Polymer Films.

The prototypes of piezochromic organic molecules are the salicylidene anils, eg, *N*-salicylidene-2-chloroaniline (3–5). At ambient pressure in the crystalline state they are either photochromic or thermochromic, but never both, depending on the side groups on the aromatic rings. When dissolved in a polymer film they are photochromic. The ground state has an OH group opposite a nitrogen on the adjacent ring, thus it is called the “enol” form. When heated, the thermochromic compounds exhibit an absorption in the visible spectrum which corresponds to a transfer of the H from O to N without other change of molecular geometry. This is the “*cis*-keto” form. The photochromic molecules, upon irradiation at low temperature, develop an absorption assigned to the “*trans*-keto” form.



enol ("OH form") *cis*-keto ("NH form") *trans*-keto ("NH form")

With increasing pressure at 25°C the *cis*-keto form is stabilized *vis á vis* both the enol and *trans*-keto isomers so that both thermochromic and photochromic materials exhibit the same type of piezochromism, but in different degrees. The conversion increases continuously with pressure, much like the changing of chemical equilibrium in liquid solution with pressure.

Two principles are illustrated here. In this case, increasing pressure and temperature favor the same process. With increasing temperature the possibility of crossing a barrier of a given height increases. With increasing pressure the potentials well-associated with the two states are perturbed differently. This perturbation can either augment or oppose the effect of increasing temperature, ie, temperature and pressure are not in general conjugate variables as is frequently assumed. Change in bond length or molecular geometry is induced by hydrogen transfer. This illustrates the point that changes in intermolecular interaction and packing are more likely to determine the amount of piezochromic or other reaction introduced by pressure than are differences in molecular geometry. Other piezochromic reactions have been observed in spiropyrans and bianthrones. The changes in molecular configuration are different, but no further principles are derived.

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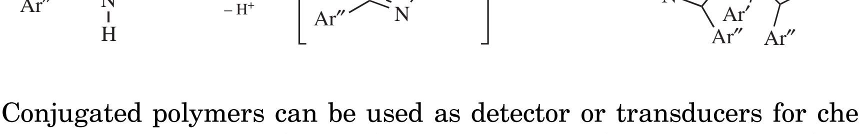
Photogenerated and cryotrapped unstable radical species of photo- thermo-, and piezochromic hexaarylbiimidazolyl (HABI) derivatives are characterized by *in situ* X-ray cristallography. Low-temperature photolysis of *o*-Cl-HABI (2-chlorohexaarylbiimidazole) crystals generate radical pairs while retaining crystallinity. On the other hand, a pair of HABI transforms into a complex of two lophyl radicals and a piezodimer upon the photolysis (6). The piezodimer is only stable below −20°C (7), the structure of which was studied by ^{1}H nmr spectroscopy (8).



Conjugated polymers can be used as detector or transducers for chemical or physical information. Thermochromism, solvatochromism, piezochromism, photochromism, biochromism for optical transducers are discussed together with conformational and electrostatic effects for electrochemical transducers (9).

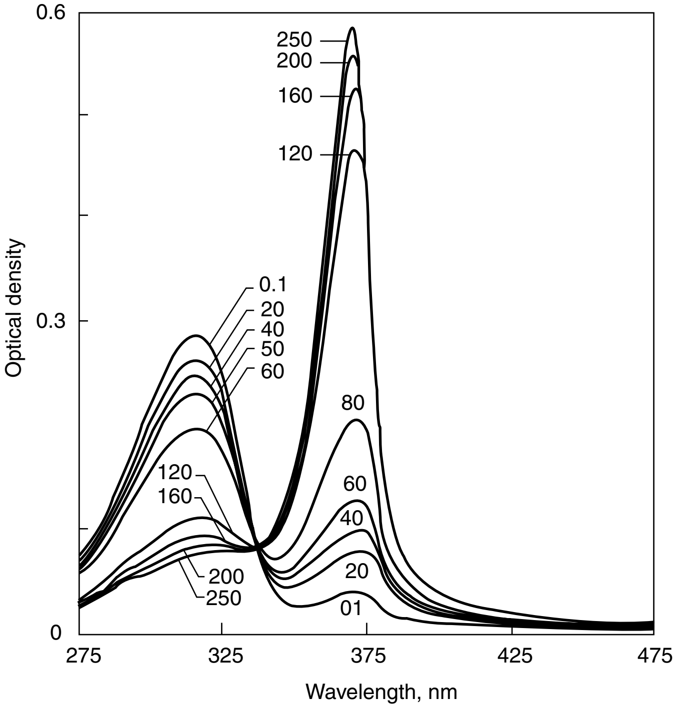


Fig. 1. Variable-pressure solid-state uv absorption spectra of poly(di-*n*-hexylsilylene) at 46°C (pressure units in MPa) (10).

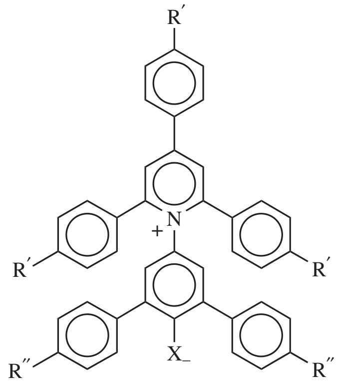
The polysilylenes exhibit complex solid-state structures and electronic properties. The solid-state conformational structure of symmetrically substituted poly(di-*n*-alkylsilylenes) are described (10) (Fig. 1).

Comparisons between the different structures and their respective uv absorption characteristics demonstrate that the relationship is complex and aspects of molecular geometry beyond chain conformation must be considered. The thermochromic and piezochromic behaviors of polysilylenes are tightly linked. The all-*trans* conformation of the silicon backbone is associated with both phenomena (11,12). Polysilylene copolymers present a well-ordered structure and exhibit absorption characteristics similar to the crystalline phases of the corresponding homopolymers.

2,2,4,6-Tetraphenyldihydro-1,3,5-triazine, 2,4,4,6-tetraphenyl-1,4-dihydropyridine and related heterocycles exhibit photochromism, thermochromism, and piezochromism in the solid state (13).

A series of 3-acridinol derivatives having a hydroxyl group at 3-position of a acridine nucleus showed an absorption at about 460 nm in protic solvents and piezochromism. AM1 and PPP molecular calculations clarified that in protic solvents the lactam form of acridinol is more stable rather than the lactim form. It was proved that the piezochromic phenomenom of 9-phenyl and 9-methyl-3-acridinols occur with an intermolecular hydrogen transfer from oxygen to nitrogen under applied pressure by means of x-ray crystallography and ir analysis (14).

Application of external pressure to solutions of betaines (1) and (2) produces in all solvents used a hypsochromic shift of their long-wavelength CT absorption band (15–19).



(**1**) $R' = R'' = H$, $X = O$
(**2**) $R' = R'' = CH(CH_3)_2$, $X = O$
(**3**) $R' = SO_2CH_3$, $R'' = H$, $X = O$
(**4**) $R' = R'' = H$, $X = S$

For example, the uv/vis absorption maximum of (**1**) in ethanol is shifted hypsochromically by −27 nm (from $\lambda_{max} = 547$ to 520 nm) by increasing the external pressure up to 10 kbar (9869 atm) (118). This corresponds to an increase in the $E_T(30)$-value of ethanol by 2.7 kcal/mol. Thus, solvent polarity is pressure dependent. The reason for this new type of piezochromism (“negative piezosolvatochromism”) lies again in the differential solvent-mediated stabilization of the dipolar electronic betaine ground state, relative to its less dipolar excited state, with increasing external pressure. The range of piezochromism is different from solvent to solvent. The pressure-dependent absorption energies of (**1**) and (**2**), dissolved in one solvent under study, correlate well with the dielectric function $(\varepsilon - 1)/(\varepsilon + 2)$ of this solvent, which also increases with compression. This seems to indicate that only nonspecific betaine-solvent interactions that occur are, to first order, constant with pressure-at least for the alcoholic HBD solvents used (18).

2.2. Coordination Compounds and Metal Cluster Compounds.

Compounds with metal–metal bonds stabilized by appropriate ligands constitute a second class of materials where a number of cases of piezochromic behavior have been observed (1,20–22). Compounds involving a Re–Re bond stabilized either by eight halides or by bridging (bidentate) ligands, such as the pivalate ion, are two well-established cases. Octahalodirhenates, Re $_2X^{2-}{}_8$ (X = Cl, Br, I), in crystals with a number of counterions, exhibit an absorption peak which corresponds to an excitation from a bonding to antibonding orbital with angular momentum two around the bond (δ orbital). When pressure is applied to the iodide a new peak grows in at a lower energy. It is associated with the rotation of the iodides on opposing Re ions from an eclipsed (directly opposite) to a staggered (not necessarily 45°) position. The reduced repulsion between opposing I^- ions more than compensates for the weakened metal–metal bond. The amount of conversion is continuous with increasing pressure.

In the case of the bridged complexes, the process involves changing from a bidentate to a monodentate configuration. For these systems the mode of transformation is variable. In close-packed crystals the rearrangement is a first-order process, ie, it occurs discontinuously at a fixed pressure. For slightly less close-packed crystals the transformation occurs over some range of pressure, eg, 2–3 GPa (20–30 kbar). In the language of physics the process corresponds to a higher order phase transition. When the molecules are dissolved in polymer films the reaction is continuous (stochastic) over the entire range of available pressure. These studies illustrate the importance of the environment on the extent of cooperativity involved in pressure-induced molecular geometry changes and thus on piezochromism.

Complexes involving larger metal clusters, eg, Au_9 or Au_2Rh_4, also undergo piezochromic rearrangements with rather dramatic changes in the absorption spectrum, and well-defined changes in molecular structure (22,23).

2.3. Organometallic Complexes of Cu(II). Complexes of Cu(II) occur in a wide variety of distorted geometries. The d^9 configuration is stabilized by distortions from a high to a slightly lower symmetry, ie, the Jahn-Teller effect (1,20,24,25). Cu(II) complexed to organic molecules such as ethylenediamine derivatives lie in a square planar configuration of nitrogens from the organic molecules. If the axial ligands are far off or not aligned the Cu(II) retains this four-coordinate geometry in the solid state. When these axial ligands are sufficiently close the system becomes six coordinated with definite changes in the ordering of the electronic orbitals and thus in the visible spectrum. In the crystalline state the rearrangement from four to six coordinated is apparently a first-order transition, whereas when dissolved in a polymeric matrix, the transformation occurs over a range of 3–5 GPa (30–50 kbar). This is then another example of the importance of the environment on the pressure dependence of the rearrangement.

Cu(II) complexed to four Cl^- ions can adopt arrangements from tetragonal to square planar. The latter arrangement gives maximum Cu–Cl bonding; the former minimizes the Cl–Cl repulsion. In practice, complexes occur near both extremes and with almost all intermediate arrangements. The geometry of a given complex is determined by the counterion. Strongly hydrogen bonding counterions draw off electron density from the Cl^- and favor square planar symmetry. With pressure one finds that both nearly square planar and nearly tetrahedral complexes distort toward an intermediate symmetry with clear-cut changes in the electronic absorption spectrum. These transformations occur over relatively short ranges of pressure ~1.5–2.5 GPa (15–25 kbar). The principle illustrated here is that at high compression the economy of best geometric packing overcomes the weaker van der Waals and hydrogen bonding forces.

Piezochromic effects have been observed in a variety of other Cu(II) complexes. In some cases it can be shown that the structures of a series of related complexes follow a reaction pathway with the structure of one complex at, eg, 8 GPa (80 kbar) corresponding to that of a related complex at, for example, 2 GPa (20 kbar). The changes in color of the complex, of course, follow the same sequence.

3. General Aspects and Conclusion

In general there appear to be two modes by which pressure induced isomerizations and consequently, piezochromism, can occur. There can be a transformation from one distinct conformation to another as a result of the relative stabilization of the potential well associated with conformation B with respect to that of A. This process may be either an equilibrium process, if the energy barrier is small, or involve a first- or higher-order phase transition depending on the extent of cooperativity demanded by the type of transformation and the environment. Such transformations are characterized by a change in the electronic character of the ground state. If there is no distinct change in the electronic character of the ground state, a series of compounds may follow each other along a reaction pathway as they undergo a similar piezochromic transformation over different pressure ranges.

In the foregoing discussion polymers have been used as a medium for small molecules in comparison with the crystalline state. It has also been observed that there are changes in polymer geometry and various rotational motions introduced by pressure (26–30). These are at times reflected in the absorption spectrum (usually in the ultraviolet) or in the emission spectrum and are a form of piezochromism.

The examples of piezochromism discussed so far involve rather well-established changes of molecular geometry. There are examples of pressure-induced changes in the electronic ground state with resultant changes in the electronic absorption spectrum where the changes in molecular geometry are not well established. One example involves intramolecular or intracomplex charge transfer (31–36). At ambient pressure this process takes place by optical excitation. At sufficiently high pressure the charge-transferred state may be stabilized sufficiently to become the ground state of the system with a different electronic absorption spectrum, but where the geometry changes are not well defined. In most transition-metal complexes the metallic ion exists in the state of maximum multiplicity “high spin” according to Hund’s rule. With compression, the splitting of the *d* states may become sufficient to establish a spin paired “low spin” ground state with resultant changes in the electronic absorption spectrum (37–39). Again, the changes in molecular geometry are not well established.

Pressure can also induce a change in the spin state of a transition-metal ion in a molecule or crystal with resultant change in the spectrum. The usual change observed is from high to low spin, but the inverse transition has been observed in some cases.

The systematic study of piezochromism is a relatively new field. It is clear that, even within the restricted definition used here, many more systems will be found which exhibit piezochromic behavior. It is quite possible to find a variety of potential applications of this phenomenon. Many of them center around the estimation of the pressure or stress in some kind of restricted or localized geometry, eg, under a localized impact or shock in a crystal or polymer film, in such a film under tension or compression, or at the interface between bearings. More generally it conveys some basic information about inter- and intramolecular interactions that is useful in understanding processes at atmospheric pressure as well as under compression.

Good thin piezochromism film (40) of rare earth compounds, with controlled stoichiometry can be grown by co-evaporation of the elements (eg, SmS) (41,42).

BIBLIOGRAPHY

"Chromogenic Materials, Piezochromic," in *ECT* 4th ed., Vol. 6, pp. 332–337, by H. G. Drickamer, University of Illinois; "Chromogenic Materials, Piezochromic" in *ECT* (online), posting date: December 4, 2000, by H. G. Drickamer, University of Illinois.

CITED PUBLICATIONS

1. H. G. Drickamer, in R. Pucci and J. Picatto, eds., *Molecular Systems under High Pressure*, North Holland Press, New York, 1991, p. 91 and references therein.
2. J. Du, R. Li, C. Chem and Z. Zhou, *Grongneng Cailiao* **30**, 133 (1999).
3. D. L. Fanselow and H. G. Drickamer, *J. Chem. Phys.* **61**, 4567 (1974).
4. E. N. Hochert and H. G. Drickamer, *J. Chem. Phys.* **67**, 6168 (1977).
5. Z. A. Dreger and H. G. Drickamer, *Chem. Phys. Lett.* **179**, 199 (1990).
6. M. Kawano, *Nypon Kessho Galskaishi* **43**, 164 (2001).
7. D. M. White and J. Sinnemberg, *J. Am. Chem. Soc.* **88**, 3825 (1966).
8. H. Tamino, T. Kondo, K. Okada and T. Goto, *Bull. Chem. Soc. Jpn.* **45**, 1474 (1972).
9. M. Leclerc, *Advanced Materials* **11**, 1491 (1999).
10. F. C. Schilling, A. J. Lovinger, D. Davis, F. A. Bovey, and J. M. Zeigler, *J. Inorg. Organomet. Polymers* **2**, 47 (1992).
11. F. C. Schilling, F. A. Bovey, D. Davis, A. J. Lovinger, R. B. Macgregor, Jr., C. A. Walsh, and J. M. Zeigler, *Macromolecules* **22**, 4645 (1989).
12. J. F. Rabolt, K. Song, H. Kuzmany, R. Sooriyakumaran, G. Fickes, and R. D. Miller, *Macromolecules* **23**, 3870 (1990).
13. K. Maeda, *React. Mol. Cryst.* 248, 273 (1993).
14. K. Natsukawa, H. Nakazumi, and M. Matsui, *Senryo to Yakuhim* **40**, 300 (1995).
15. C. Reichardt, *Chem. Soc. Rev.* 147 (1992).
16. K. Tamura and T. Imoto, *Bull. Chem. Soc. Jpn.* **48**, 369 (1975).
17. J. V. Ionanne, D. A. Palmer, and H. Kelm, *Bull. Chem. Soc. Jpn.* **51**, 463 (1978).
18. W. S. Hammack, D. M. Hendrickson, and H. G. Drickamer, *J. Phys. Chem.* **93**, 3483 (1989).
19. Y. Ikushima, N. Saito, and M. Arai, *J. Phys. Chem.* **96**, 2293 (1992).
20. H. G. Drickamer and K. L. Bray, *Intern. Rev. of Phys. Chem.* **8**, 41 (1989) and references therein.
21. J. K. Grey and I. S. Butler, *Coordination. Chem. Rev.*, 219, 713 (2001).
22. J. L. Coffer, J. R. Shapley, and H. G. Drickamer, *Inorg. Chem.* **29**, 3900 (1990).
23. K. L. Bray, H. G. Drickamer, D. M. P. Mingos, M. J. Watson, and J. R. Shapley, *Inorg. Chem.* **30**, 864 (1991).
24. H. G. Drickamer and K. L. Bray, *Acc. Chem. Res.* **23**, 55 (1991) and references therein.
25. B. Scott and R. D. Willett, *J. Am. Chem. Soc.* **113**, 5253 (1991).
26. K. Song, R. D. Miller, G. M. Wallraff, and J. F. Rabolt, *Macromolecules* **24**, 4084 (1991).

27. J. F. Rabolt and co-workers, *Polym. Prep.* **31**, 262 (1991).
28. R. A. Nallicheri and M. E. Rubner, *Macromolecules* **24**, 517 (1991).
29. K. Song, H. Kuzmany, G. M. Wallraff, R. D. Miller, and J. F. Rabolt, *Macromolecules* **23**, 3870 (1990).
30. G. Cryssomallis and H. G. Drickamer, *J. Chem. Phys.* **71**, 4817 (1979).
31. W. H. Bentley and H. G. Drickamer, *J. Chem. Phys.* **42**, 1573 (1965).
32. V. C. Bastron and H. G. Drickamer, *J. Solid State Chem.* **3**, 550 (1971).
33. R. B. Ali, P. Banerjee, J. Burgess, and A. E. Smith, *Trans. Met. Chem.* **13**, 106 (1988).
34. R. B. Ali, J. Burgess, and Guardano, *Trans. Met. Chem.* **13**, 126 (1988).
35. J. Burgess, *Spectrochim Acta* **45A**, 159 (1989).
36. M. Matsui, K. Shibata, and H. Muramatsa, *Bull. Chem. Soc. Jpn.* **63**, 1845 (1990).
37. Y. Kitamara, T. Ito, and M. Kato, *Inorg. Chem.* **23**, 3826 (1984).
38. H. T. Macholt, R. Van Eldik, H. Kelm, and H. Elias, *Inorg. Chim. Acta.* **104**, 115 (1985).
39. K. L. Bray and H. G. Drickamer, *J. Phys. Chem.* **94**, 7037 (1990).
40. C. B. Greenberg, *Thin Films Solid* **251**, 81 (1994).
41. R. Suryanarayanam and G. Brun, *Thin Films Solid* **35**, 263 (1976).
42. R. Suryanarayanam, *Phys. Status Solii B* **85**, 9 (1978).

A. SAMAT
R. GUGLIELMETTI
Université de la Mediterannée