Spectra of Weak Chemical Complexes. Internal Compression Effects[1]

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Abstract: Statistical mechanical calculations have shown that liquids exert internal mechanical pressures of the order 10^3 to 10^4 atm on dissolved molecules. These pressures cause very large vapor-to-liquid changes in spectra of the weak and compressible charge-transfer complexes. Hydrogen-bonded complexes are expected to be much less sensitive to internal compression. It is suggested that the internal mechanical pressure may have significant effects on a wide variety of liquid-state chemical systems. Molecules in the solid state are probably also under very high internal compression.

The internal pressure, P_i, of a liquid may be defined thermodynamically by[2a]

$$P_i \equiv \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (1)$$

For most organic liquids P_i values are in the range 2000–6000 atm.[2] Do these high pressures indicate that there is a strong mechanical compression on molecules in the liquid? And, if this compression exists, how will it affect the properties of dissolved molecules?

Hildebrand[3] has given a thermodynamic discussion of van der Waals liquids which suggests that liquid molecules may be under high compression. Bayliss and Rees[4] have considered, qualitatively, energies of solvent cages and the possible distortion of solute molecules which could produce spectral changes. Prochorow[5] has suggested an analogy between high-pressure spectral frequency shifts of molecular complexes and the "internal pressure" and shifts in liquids. Ideas of this type directly relate to the "solvent cage effects" often postulated in the literature. In order to examine these suggestions quantitatively we will make use of a statistical mechanical model of liquids.

The scaled-particle theory of hard-sphere fluids[6] has proved capable of accurately calculating properties of liquids.[7,8] Reiss[9] and his co-workers have developed an energy function, W, which gives the work required to produce a spherical cavity of radius r in a fluid, and they equate W with the energy of forming a cavity containing a solute molecule in some liquid solvent. Calculations of W compare quite well with experimental energies related to Henry's law constants, surface tensions, and heats of vaporization.[9] In their eq 1.16, Reiss, *et al.*, give W as[9]

$$W = kT\{[6y/(1-y)][2(r/a)^2 - (r/a)] + [18y^2/(1-y)^2]\,[(r/a)^2 - (r/a) + (1/4)] - \ln(1-y)\} + \pi p a^3[(4/3)(r/a)^3 - 2(r/a)^2 + (r/a) - (1/6)] \qquad (2)$$

where $r = (a + b)/2$, a = solvent molecular diameter, b = solute molecular diameter, $y = \pi a^3\rho/6$, $\rho = N/V$ = number density of solvent, p = pressure of the fluid.

We may obtain the mechanical pressure, P_M, on the solute molecule as the change in energy with respect to volume of the solute molecule, V_b

$$P_M = \left(\frac{\partial W}{\partial V_b}\right) = \frac{1}{\pi b^2}\left(\frac{\partial W}{\partial r}\right) \qquad (3)$$

Substituting W from (2) into (3) and simplifying

$$P_M = \frac{kT}{\pi b^2 a}\{[6y/(1-y)][4(r/a) - 1] + [18y^2/(1-y)^2][2(r/a) - 1]\} + p \qquad (4)$$

Equation 4 is divided into two physically distinct terms. The second term, p, is the macroscopic pressure on the liquid (about 1 atm in normal laboratory experiments). The first term, in kT, is a microscopic "internal compression" of the solute molecule due to interaction with surrounding solvent molecules; and it is seen that this interaction is a function of temperature and molecular size and packing.[10] Figure 1 shows a plot of P_M from eq 4 for various solute diameters in the solvent benzene (a = 5.27 A).[12,13] For molecules of average size the first term in (4) dominates and P_M lies between 3000 and 6000 atm. P_M decreases monotonically with increasing solute size, and for very large (macroscopic) b, P_M reduces to p.

It should be noted that P_M does not seem to be simply related to the thermodynamic internal pressure P_i.[14] This is illustrated by the following examples of P_i[2]

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(1) Supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-65.

(2) (a) W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, pp 712–713; (b) J. H. Hildebrand, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

(3) J. H. Hildebrand, *et al.*, *Phys. Rev.*, **34**, 984 (1929).

(4) N. S. Bayliss and A. L. G. Rees, *J. Chem. Phys.*, **8**, 377 (1940).

(5) J. Prochorow, *ibid.*, **43**, 3394 (1965).

(6) H. Reiss, H. L. Frisch, and J. L. Lebowitz, *ibid.*, **31**, 369 (1959).

(7) H. L. Frisch, *Advan. Chem. Phys.*, **6**, 229 (1964).

(8) H. Reiss, *ibid.*, **9**, 1 (1965).

(9) H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960).

(10) It should be noted that $y = \pi a^3\rho/6$ physically corresponds to the volume occupied by the molecules ($\pi a^3/6$) divided by the total volume (including free volume). To be physically meaningful it is required that $0 < y < 1$. Considerations of packing suggest the further restriction that $y < 0.74$.[11] This provides a good criterion for choosing measured values of a which are reasonable for liquid-phase calculations.[9] For example, from liquid densities[12] and gas-phase a values[13] one obtains for n-C_7H_{16}, y = 1.5, and for n-C_8H_{18}, y = 0.81, which indicates that these molecules are extended in vapor and more closely packed in the liquid state.

(11) See ref 7, p 268.

(12) Densities were obtained from "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964.

(13) Unless noted otherwise, molecular diameters (a, b) used are from the Lennard-Jones 6–12 values in J.O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954. pp 1110–1113.

(14) In order to avoid confusing nomenclature, the term "internal pressure" will refer only to the thermodynamic P_i in eq 1. P_M is the "mechanical pressure" and is a microscopic statistical quantity. The effect of P_M will be referred to as "internal compression."

Table I. Liquid and Vapor Spectral Properties

Complex	Liquid-phase solvent	P_M of solvent,[a] atm	ν_{max}^v, cm^{-1}	ν_{max}^l, cm^{-1}	a_c^v	a_c^l	a_{min}^l
I_2–benzene	*n*-Heptane	2310	37,300[b]	33,700[e]	1,650[b]	16,000[e]	9800[i]
I_2–ether	CCl_4	3320	42,700[b]	40,200[f]	2,100[b]	4,700[f]	. . .
I_2–ethyl sulfide	*n*-Heptane	2310	34,500[c]	33,000[g]	11,400[c]	26,400[g]	. . .
TCNE–p-xylene	Dichloromethane	2170	26,600[d]	24,100[h]	910[d]	2,770[h]	2200[j]

[a] P_M was calculated assuming the complex diameter $b = 11.0$ A (25°). [b] Reference 28. [c] Reference 30. [d] Reference 29. [e] Reference 23. [f] P. A. D. DeMaine, *J. Chem. Phys.*, **26**, 1192 (1957). [g] M. Tamres and S. Searles, Jr., *J. Phys. Chem.*, **66**, 1099 (1962). [h] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). [i] From the data of ref 23. [j] Estimated by an extrapolation of the data from footnote *h*.

and P_M (exerted on a solute with $b = 11.0$ A at 25°) in the solvents n-C_7H_{16}, CCl_4, benzene, and CS_2:[15] n-C_7H_{16} ($a = 6.7$ A), $P_M = 2310$ atm, $P_i = 2510$ atm; CCl_4 ($a = 5.88$ A), $P_M = 3320$ atm, $P_i = 3640$ atm; benzene ($a = 5.27$ A), $P_M = 1550$ atm, $P_i = 4050$ atm; CS_2 ($a = 4.44$ A), $P_M = 1470$ atm, $P_i = 5400$ atm.

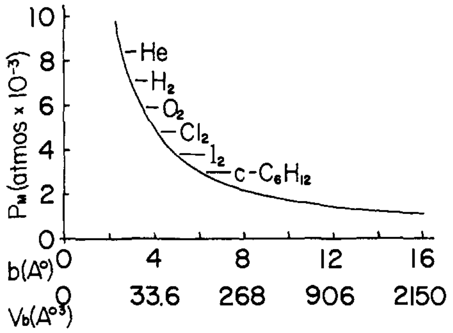

Figure 1. Mechanical pressure *vs.* solute diameter, *b*, and volume V_b, in the solvent benzene at 15°. The pressure on various solute molecules is indicated. Values of *b* were obtained from Hirschfelder, Curtis, and Bird.[13]

We have seen that liquids exert large internal compressions on dissolved molecules. The magnitude of mechanical pressures estimated by means of eq 4 can now be used in considering solvent effects on dissolved chemical complexes.[16]

Charge-Transfer Complex Spectra

Charge-transfer (CT) bands of molecular complexes[17,15] generally undergo large red shifts and intensity enhancements when the complex in solution or solid state is subjected to pressures of a few thousand atmospheres.[19–22] Ham[19] has investigated iodine aromatic complexes in solution at 2000 atm and has observed a red shift of 600 cm^{-1} from the CT band position of iodine–benzene at 34,700 cm^{-1} and a large apparent intensity increase (the complex equilibrium was not analyzed). More recently, Gott and Maisch[21] have studied solutions of aromatic–tetracyanoethylene (TCNE) complexes in detail; and they find for benzene–TCNE at 4000 atm a red shift in the CT band of 850 cm^{-1} from 26,000 cm^{-1} and an approximate doubling of the CT extinction coefficient. Similar effects are obtained with crystalline charge-transfer complexes under high pressure.[20,22] Since the values of P_M in solution at 1 atm calculated using eq 4 are of the same magnitude as the pressures (p) used in the above work, one should observe spectral effects on taking a complex from the low-pressure vapor phase into the internally compressed liquid phase which are comparable to the high-pressure changes. These effects are observed but exact experimental analysis has proven difficult.[23–27]

Experimental Background. Optical spectra of molecular complexes in the vapor phase[28–30] have recently been studied to obtain the band maximum (ν_{max}^v) and molar absorbancy index (a_c^v) for the complex charge-transfer band. Comparison with the derived values[23] for the same complexes in liquid solution (ν_{max}^l; a_c^l) gives a large red shift and indicates a very large apparent intensity enhancement on going from gas to liquid: $a_c^v \ll a_c^l$; $\nu_{max}^v > \nu_{max}^l$ (*cf.* Table I).

It can be shown, however, that the derived a_c^l systematically overestimates the true value of the complex absorbancy.[26,27] This is due to large effects of solvent competition and nonideality on the plotting procedure[23] used to obtain a_c^l. In view of this the apparent liquid-phase enhancement has been interpreted as an artifact,[26] and it has been generally assumed[26,28,30] that the corrected liquid-phase absorbancy index is approximately equal to the vapor-phase value. This interpretation may be tested if we can establish a lower bound to a_c^l.

The minimum value (a_{min}^l) of a_c^l can be obtained by measuring the absorbancy of a dilute solution (*ca.* 10^{-4} *M*) of the acceptor, A, in pure donor, D, and then calculating a_c as if A were completely complexed

$$A + D \rightleftarrows A \cdot D \tag{5}$$

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(15) Molecular diameters, *a*, are from ref 13 except for n-C_7H_{16} which was estimated from a molecular model.

(16) The effects of P_M on complicated molecular complexes will be examined. Strictly speaking, this overextends the liquid theory which was designed for simple nonpolar molecules. It is hoped that eq 4 will provide a reasonably accurate means of treating these more intricate systems. The value $b = 11.0$ A used above is about the size of complex to be examined.

(17) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

(18) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 1964.

(19) J. Ham, *J. Am. Chem. Soc.*, **76**, 3881 (1954).

(20) D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, **30**, 1518 (1959).

(21) J. R. Gott and W. G. Maisch, *ibid.*, **39**, 2229 (1963).

(22) H. W. Offen, *ibid.*, **42**, 430 (1965).

(23) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(24) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

(25) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

(26) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965).

(27) P. J. Trotter and M. W. Hanna, *J. Am. Chem. Soc.*, **88**, 3724 (1966), and references therein.

(28) F. T. Lang and R. L. Strong, *ibid.*, **87**, 2345 (1965).

(29) M. Kroll and M. L. Ginter, *J. Phys. Chem.*, **69**, 3671 (1965).

(30) J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965).

$$a_{\min}^1 = \frac{A_c}{dC_A^0} \le \frac{A_c}{dC_{AD}} \equiv a_c^1 \qquad (6)$$

where $C_A^0 \ge C_{AD}$, C_A^0 = total molar concentration of A, C_{AD} = molarity of A·D complex, A_c = charge-transfer absorbancy, d = path length. Values of $a_{\min}^1$ for two complexes are shown in Table I. It is seen that $a_{\min}^1 \gg a_c^v$ and that *the large vapor-to-liquid enhancement is a real effect*[31] *which cannot be accounted for by solvent competition in the Benesi–Hildebrand analysis.*[23,26,27]

An Explanation for Vapor–Liquid Spectra. It is proposed that these spectral effects (large red shifts and intensity increases) are made possible by the weak and highly compressible bond between A and D in the complex ground state (N_{AD}) shown in Figure 2; and that the large compressional force on A·D in the liquid reduces the bond length, r_{AD}, and thus causes the spectral shift and enhancement. An inspection of the ground and ionic excited ($E_{A^-D^+}$) states in Figure 2[32–34] shows how the red shift occurs. Mulliken has shown that the transition moment integral increases with increasing overlap[33] (decreasing r_{AD}), and this can explain the intensity enhancement.

The potential curves of Figure 2 must be consistent with spectral changes due to internal compression. Observed red shifts on compression show that the equilibrium r_{AD} of $E_{A^-D^+}$ is less than that of N_{AD} (otherwise one would expect a blue shift).[35] And the approximate constancy of band shapes on compression[19,21,29,30] suggests that the relative slopes of the $E_{A^-D^+}$ and N_{AD} curves remain nearly constant during compression.

An estimate of the magnitude of the expected red shift, enhancement, and r_{AD} compression can be made for a complex to test the validity of this explanation. The TCNE–*p*-xylene complex provides a good example because its CT band is well separated from other peaks[29] and because the experimental determination of a stronger complex is more reliable.[26,27] Approximately, in the vapor, r_{AD}^v = 3.5 A,[36] and we use the formula[37]

$$\Delta E = I - A - C \qquad (7)$$

where ΔE = energy of the CT transition, I = ionization potential of donor, A = electron affinity of acceptor, $C = ke^2/r_{AD} \approx$ Coulomb energy of the CT transition, e = fractional electronic charge transferred, $k = 1.44 \times 10^{-7}$ ev cm e^{-2}. Using the vapor-phase ΔE_v[29] and values of I and A from the literature,[17,38] eq 7 gives e = 0.90 (90% of an electron transferred). From (7), assuming I, A, and e are equal in gas and liquid

$$\Delta E_v - \Delta E_l = C_l - C_v = ke^2\left(\frac{1}{r_{AD}^{\,l}} - \frac{1}{r_{AD}^{\,v}}\right) \qquad (8)$$

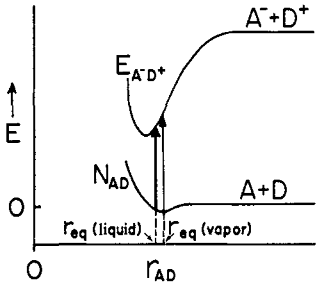

Figure 2. Ground and excited states of A·D according to Mulliken's theory.[32,33] The charge-transfer band is due to the transition $N_{AD} \rightarrow E_{A^-D^+}$. In the liquid state r_{AD} is decreased, giving a red shift and a more intense band due to increased orbital overlap.

where, v and l refer to vapor and liquid values. Substituting r_{AD}^v, e, and the experimental ΔE_v and ΔE_l into (8) gives r_{AD}^l = 3.2 A. Thus, the complex bond is compressed about 0.3 A on going from vapor into CH$_2$Cl$_2$ solution. With P_M = 2170 atm the bond compressibility is approximately 1.4×10^{-4} A/atm which may be compared to a solid-state oxalic acid hydrogen bond compressibility of *ca.* 1.5×10^{-6} A/atm.[39]

To estimate the vapor–liquid intensity increase we assume the approximate proportionalities

$$I \propto S_{EN}^2 \qquad (9)$$

$$S_{EN} \propto \exp(-r_{AD}) \qquad (10)$$

where I = intensity (proportional to a_c for constant band shape), S_{EN} = ground–excited state overlap, and r_{AD} is in atomic units. From (9) and (10) the enhancement factor for the TCNE complex is

$$(I_l/I_v) = \exp[2(r_{AD}^v - r_{AD}^l)] = 3.1 \qquad (11)$$

which compares with a_c^l/a_c^v = 3.0 from Table I. The agreement is much better than one should expect.

It is difficult to know how to treat the benzene–iodine complex since its geometry in gas and liquid is not agreed upon.[18,40] If one takes r_{AD}^v = 4.0 A (a compromise between axial and resting models),[41] then one obtains from eq 7–10 a vapor–liquid compression of 0.4 A and an enhancement factor of times 4.5 which compares to a_c^l/a_c^v = 9.7 from Table I. The experimental enhancement for iodine–benzene seems larger than one would expect and the other complexes in Table I may be more typical of CT behavior. Part of the discrepancy may be due to the difficulty of determining a CT band which is interfered with by both benzene and iodine.[28]

From the above treatment one predicts increasing CT intensities and red shifts with increasing P_M for a series of nonpolar, inert solvents.

A cursory inspection of the kT factor in eq 4 suggests that P_M should increase significantly with temperature, shifting the CT band toward the red. However, P_M is very sensitive to the decrease of density (in y) with increasing temperature. For example, assuming a solute b = 11.0 A in the solvent benzene we obtain from (4) that P_M = 1580 atm at 10° (d 0.890 g/cc[42]) and that P_M = 1500 atm at 65° (d 0.830 g/cc[42]), and we see a

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[31] This analysis may be complicated by the presence of some A·D$_2$, but the effect is so large that it probably cannot be explained except as a real enhancement.

[32] Reference 17, p 91.

[33] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[34] R. S. Mulliken, *J. Chim. Phys.*, **60**, 20 (1963).

[35] Excited-state r_{AD} for hexamethylbenzene-TCNE appears to be very close to the ground-state r_{AD} since the CT band shifts red up to about 2000 atm and begins to shift toward the blue at higher pressures.[21]

[36] This value of r_{AD}^v is taken to be 0.1 to 0.2 A greater than the interplanar spacing found in crystalline complexes of this type in J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.*, **69**, 2160 (1965).

[37] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 13.

[38] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[39] J. Reynolds and S. S. Sternstein, *J. Chem. Phys.*, **41**, 47 (1964).

[40] H. B. Friedrich and W. B. Person, *ibid.*, **44**, 2161 (1966).

[41] M. W. Hanna, *J. Am. Chem. Soc.*, in press.

[42] C. V. Suryanarayana and S. Govindaswamy, *Monatsh. Chem.*, **92**, 203 (1961).

small *decrease in* P_M with increasing T. For most systems P_M will be a very weak function of temperature and should contribute only slightly to changes in CT bands with temperature. This can easily be checked for any particular system under study.

Electrical Effects. The contribution of solvent dielectric properties to the observed shifts and enhancements has been ignored in the above discussion because these contributions in going from vapor to liquid are thought to be small compared to the observed effect.

Theories relating frequency shifts to solvent refractive index[43,44] predict small shift effects for polar molecules in nonpolar solvents which reproduce the main experimental trends.[45] However, these theories are very inaccurate in the region of low refractive index (approaching the gas phase).[46] Experimentally observed vapor–liquid shifts for simple, incompressible molecules[47] are generally small compared to the CT frequency shifts of Table I. For example, shifts for benzene, phenol, fluorobenzene, and benzotrifluoride[46] in the ultraviolet range from about 20 to 400 cm^{-1}.

Very recently, Voigt[49] has discussed some difficulties in applying dielectric theory of solvent shifts[43] to CT complexes. She obtains good empirical correlation of frequency shifts with the theoretical refractive index function,[50] but different lines are required for different sets of solvents. The problems observed by Voigt can be resolved by a qualitative consideration of internal compression effects. First, the two sets of solvents examined were saturated hydrocarbons and perfluoro compounds with the hydrocarbons showing a larger vapor–liquid red shift. Since the hydrocarbons possess attractive London forces which are much greater than those of perfluorocarbons, they can exert a larger mechanical compression on the complex yielding a larger red shift. Equation 4 for P_M would seem to be the quantitative expression of the "tightly bound solvation shells" mentioned here.[49] Second, the weaker TCNE–aromatic complexes appear to give larger red shifts which is opposite to the shift order predicted from refractive index theory used by Voigt. This trend is exactly what is expected from internal compression, however, since the weaker complexes will be more compressed yielding larger red shifts.

Classical dispersion theory predicts small (10–20%) intensity enhancements from vapor-to-liquid spectra.[44,48] However, the quantitative relationship between refractive index and intensity is inadequate,[44,54] and Mulliken and Rieke[48] suggest that vapor and liquid intensities be assumed approximately equal since the changes are small and erratic for allowed transitions. This appears to be a good approximation for simple, incompressible compounds subject only to electrical effects; it cannot be assumed for weak complexes.

It is concluded that the major part (80–100%) of vapor–liquid shifts and intensity increases of weak CT complexes is due to mechanical compression of the complex while solvent dielectric properties play only a minor role. However, it may be necessary to consider electrical properties in studying the details of spectral changes within a group of liquid solvents.

Other Properties. Any property of a complex which is sensitive to r_{AD} will show internal compression effects. For example, some complexes may show significant vapor–liquid proton nmr shifts where magnetic susceptibility effects[55,56] are sensitive to r_{AD}.

In view of the large change in CT electronic spectra brought about by compression, it is predicted that internal compression (or high external pressures) will very significantly influence photochemical or thermal reactions involving excited-state CT intermediates.[57] This may serve as a test for CT intermediates.

Hydrogen-Bonded Complexes

Another large class of complexes for which internal compression may be significant is that of the weak hydrogen-bonded systems.[58] We shall first examine the infrared stretching frequency, ν_s, of the H bond,[58] referring again to high-pressure work for guidance. Reynolds and Sternstein[59] have examined ν_s of hydrogen in O–H···O bonds of solid oxalic acid and polyvinyl alcohol to 25,000 atm. Oxalic acid at 10^4 atm shows a shift of 30 cm^{-1} toward lower frequency from the 3450-cm^{-1} ν_s band. The ν_s bands of oxalic acid and polyvinyl alcohol broaden at high pressure, and the integrated absorption appears to increase slightly. Reynolds and Sternstein estimate a compressibility for the H bond in oxalic acid polymers of 1.5×10^{-6} A/atm. This value is only very approximate since molecular compressibility is a tensor property, and it is difficult to know how the pressure is distributed in a solid. If a liquid exerts a $P_M \approx 10^4$ atm on oxalic acid, one estimates an H-bond compression of 0.015 A.

The high-pressure shifts discussed by Pimentel and McClellan have been rationalized by postulating the increased formation of polymers (with lower ν_s) at high pressures.[59] While equilibrium shifts will have some influence on ν_s, it is evident that *internal compression will cause the* ν_s *of each individual complex to red shift.* Unless the equilibrium species can be specifically analyzed, as was done by Gott and Maisch[21] for CT complexes, it will be difficult to interpret these effects. Unfortunately this analysis is quite difficult since multiple equilibria and self-association[60] must be

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(43) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(44) O. E. Weigang, Jr., *J. Chem. Phys.*, **41**, 1435 (1964). and references therein.

(45) See ref 43 on phenol blue spectra.

(46) E. A. Bovey and S. S. Yanari, *Nature*, **186**, 1042 (1960).

(47) Most simple molecules with strong chemical bonds should not be pressure sensitive. Ham[19] failed to observe any pressure effect on the spectrum of pure iodine in *n*-heptane to 2000 atm. However, Mulliken and Rieke[48] observed a vapor–liquid intensity change in cyclopentadiene opposite to theoretical prediction, and compression of the ring may have some influence.

(48) R. S. Mulliken and C. Rieke, *Rept. Progr. Phys.*, **8**, 231 (1941).

(49) E. M. Voigt, *J. Phys. Chem.*, **70**, 598 (1966).

(50) For nonpolar liquids the refractive index and P_i increase together[12,51] (along with molecular polarizability and dispersion energies[52]). Therefore, it is reasonable to expect P_M (mechanical forces) to increase with increasing refractive index in a closely related set of solvents so that one is not surprised to find correlations with refractive index.[53]

(51) C. V. Suryanarayana, *Monatsh. Chem.*, **91**, 139 (1960).

(52) W. Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, N. Y., 1957

(53). H. M. Rosenberg and D. Hale, *J. Phys. Chem.*, **69**, 2490 (1965), correlate shift with refractive index.

(54) Weigang[44] predicts that permanent solvent dipoles will contribute to a *decrease* in intensity.

(55) M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964).

(56) J. A. Pople, J. J. Bernstein, and W. G. Schneider, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 7.

(57) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965), reviews possible CT reaction intermediates.

(58) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond." W. H. Freeman Co., San Francisco, Calif., 1960.

(59) Reference 58, pp 81–82.

considered. Some data for complexed formic acid[61] indicate a red shift of ν_s from gaseous to condensed states. This may be partly due to polymer formation and partly to internal compression.

It is seen that the magnitudes of the bond compression and spectral changes expected for H bonds under P_M are much less than those observed for CT complexes. This is consistent with the fact that the stronger H bonds ($\Delta H_f^\circ \approx$ 6–8 kcal)[58] are much less compressible than relatively weak CT complex bonds ($\Delta H_f^\circ \approx$ 2–5 kcal).[18] On taking an O–H···O complex from vapor into a liquid with $P_M \approx$ 5000 to 10,000 atm, we expect a bond compression of the order 0.01 to 0.02 A and a contribution to $\Delta\nu_s$ of -20 to -40 cm^{-1},[62] coupled with a slight intensity increase (*cf.* ref 39). The expected red shift of ν_s may be rationalized in H-bond theory by the weakening of the covalent bond to hydrogen as the hydrogen atom moves closer to the field of the base.[39,63] The small intensity increase of ν_s on compression is expected from a theory of Huggins and Pimentel[63,64] which gives the oscillating dipole ($\partial\mu/\partial r$) associated with an H bond as

$$\frac{\partial\mu}{\partial r} = \frac{\partial\mu_0}{\partial r} + \frac{\partial\mu_i}{\partial r} \qquad (12)$$

where $\partial\mu_0/\partial r$ = oscillating dipole associated with H and $\partial\mu_i/\partial r$ = dipole induced in the base which increases on compression. Thus, one anticipates small but definite contributions to H-bond spectral properties from internal compression.

Proton nmr spectra are especially sensitive to H-bond formation since the bonding proton can be directly observed.[56,58] It may be possible to detect significant vapor–liquid nmr shifts due to internal compression in spite of the small decrease in H-bond length. If an H-bond contraction of 0.02 A is assumed for an amine, then the theoretical nmr results of Berkeley and Hanna[65] predict a vapor-to-liquid downfield shift of about 5 cps.

Other Systems

Comments made in this paper concerning CT reaction intermediates and the large magnitudes of P_M in solution directly relate to the question of calculating activation volumes, ΔV^*.[66–69] The compressional force on the activated complex is not just the macroscopic p applied to the system[66–68] but is approximately given by P_M of eq 4. Replacing p by P_M in the rate–pressure functions[66,68] will change the graphs and interpretations relating to ΔV^*.

Inorganic complex CT bands show significant spectral effects at high pressures, and Stephens and Drickamer[20] have determined and explained some of these. Their data indicate that inorganic complexes should show small but significant internal compression[70] spectral shifts in liquids.

Ribonuclease and poly-γ-benzyl-L-glutamate exhibit a significant enhancement of unfolding with increasing pressure up to 1400 atm.[71] The P_M on large biochemical molecules is probably of the order 500 atm[70] (at p = 1 atm), and this pressure can influence their properties.[71]

The following facts suggest that molecules in the solid state are under very high internal compression: thermodynamic P_i of solids are generally much higher than those of organic liquids;[72] CT bands of weak molecular complexes in the solid state are red-shifted relative to solution bands;[73] infrared spectra of H-bonded solids indicate stronger H-bonding interactions compared to gaseous or liquid complexes;[74] and Cr^{III} ions in a ruby crystal (a LASER) have a much higher Δ_0 splitting than in the $[Cr(H_2O)_6]^{3+}$ ion, suggesting that Cr^{III} in the solid is under large internal compression.[75]

Summary

An approach to the problem of mechanical effects of liquids on dissolved molecules has been outlined, and some examples have been considered which illustrate the wide range of systems involved. This research leads to the following considerations.

1. All liquids exert a mechanical pressure of the order 10^3 to 10^4 atm on dissolved molecules. Any molecular property which is sensitive to pressures of this magnitude will show significant internal compression effects.
2. For weak CT complexes a large red shift (1000 to 4000 cm^{-1}) and intensity enhancement (times 1.5 to 5) are predicted for the CT band on going from vapor to an inert, nonpolar liquid.
3. H-Bonded complexes will generally be much less sensitive to compression than CT complexes. However, internal compression will contribute $\Delta\nu_s \approx -20$ to -40 cm^{-1} to the vapor–liquid shift of an O–H···O bond,[76] and a small downfield nmr shift is also predicted.
4. Internal compression effects are suggested for important inorganic and biochemical systems, and data are cited which indicate that very large mechanical pressures exist within solids.

Problems involving the pressure on a molecule in solution must be treated in terms of the mechanical pressure, P_M, which has added to the macroscopic applied pressure (p) a large contribution from internal mechanical forces in the fluid (the kT term in eq 4). It is hoped that eq 4 will provide a good estimate of P_M

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(60) E. Grunwald and W. Coburn, *J. Am. Chem. Soc.*, **80**, 1322 (1958).

(61) Reference 58, pp 104, 112.

(62) See ref 58, pp 87, 88, for graphs of $\Delta\nu_s$ *vs.* H-bond length for various H bonds.

(63) Reference 58, Chapter 8, and references therein.

(64) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

(65) P. J. Berkeley, Jr., and M. W. Hanna, *J. Am. Chem. Soc.*, **86**, 2990 (1964).

(66) S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962).

(67) C. Walling and H. J. Schugar, *ibid.*, **85**, 607 (1963).

(68) C. Walling and D. D. Tanner, *ibid.*, **85**, 612 (1963).

(69) S. W. Benson and J. A. Berson, *ibid.*, **86**, 259 (1964).

(70) For H_2O (a = 2.8 A)[2a] the value of P_M from eq 4 is 2400 atm for dissolved inorganic complexes ($b \approx$ 11 A) and about 500 atm for the protein insulin ($b \approx$ 50 A)[2a] at 25°. These values represent very crude estimates since the theory was not derived for such complicated systems, but the values indicate the existence of quite significant internal compression in these systems.

(71) S. J. Gill and R. L. Glogovsky, *J. Phys. Chem.*, **69**, 1515 (1965).

(72) N. O. Smith, *J. Chem. Educ.*, **42**, 654 (1965), lists P_i values.

(73) H. Kuroda, K. Yoshihara, M. Kinoshita, and H. Akamatu, Proceedings of the International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962; *Chem. Abstr.*, **61**, 1731*f* (1964).

(74) A. V. Korshunov, L. S. Solov'ev, and V. S. Korobkov, *Spektroskopiya, Metody i Primenenie, Akad. Nauk SSSR, Sibirsk. Otd.*, 143 (1964); *Chem. Abstr.*, **62**, 8522*g* (1965).

(75) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, pp 688–689.

(76) See ref 58, p 87, for $\Delta\nu_s$ *vs.* bond length for other H bonds.

for nonpolar liquids. Explanations of vapor–liquid changes in terms of P_M may be directly tested by comparison with high-pressure experiments.

This viewpoint unifies the theoretical explanations of vapor, liquid, and high-pressure molecular properties. It also lends more general importance to high-pressure studies because molecules under high pressure are not in an unusual state. The high-pressure state is common to most chemical systems.[77]

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[77] NOTE ADDED IN PROOF. It is recognized that eq 7–10 are very approximate. For example, the change in overlap in (10) might be better approximated by Roothaan's formulas (C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951)); but, since the exact structures of a complex are unknown, it is thought that the simple calculations serve to illustrate the correct direction and approximate magnitude of CT spectral changes. Since this article was submitted, a similar explanation of gas–liquid CT spectra has been received from J. Prochorow and A. Tramer, *J. Chem. Phys.*, **44**, 4545 (1966). The spectral results given by Prochorow and Tramer are in excellent agreement with the treatment here in terms of P_M. However, it is not necessary to postulate a quasi-crystalline solvent cage since high internal compression is obtained from the assumption of an unstructured liquid. Calculations correlating CT frequencies with P_M have been completed and will be published soon.

Kinetics of Formation of N-Pyruvylideneglycinatozinc(II)[1]

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Abstract: N-Pyruvylideneglycinatozinc(II) is formed through two major pathways in the range pH 4.5–6.0. In one of these paths the rate-determining step appears to be the proton-catalyzed addition of glycinate to pyruvate followed by the splitting out of water from the carbinolamine. In the other path, zinc(II) ions appear to stabilize the carbinolamine through coordination. However, dehydration of this complex is effected through proton catalysis. In this system, the metal ions serve the role of stabilizing intermediates and products by forming complexes, but are much less effective than protons in influencing those reactions which are facilitated by a change of the charge distribution within the reactant molecules.

A series of investigations currently underway in our laboratories concerns the properties of the metal ion complexes of Schiff bases, particularly with their role in duplicating enzymatic reactions.[2] It was observed in our studies that the rates of formation of these complexes from the dissociated ligands lie in a range that is tractable for ordinary measurement. In order to fully understand the role of metal ions in catalyzing the reactions observed in nonenzymatic systems, it is necessary to have knowledge of the factors involved in their formation and dissociation. Furthermore, carbonyl addition reactions have been of interest to chemists for many years,[3] but relatively little is known regarding the kinetic effects of metal ions on these systems although their mediating effect on Schiff base formation is well recognized.[4–6] Thompson and Busch[6] have suggested that the metal ion in these systems can function as either a "kinetic template" or an "equilibrium template."

An earlier study by Nunez and Eichhorn[7] on the kinetics of formation of salicylideneglycinatonickel(II) in dioxane–water mixtures suggested that metal ions slow the rate of formation of the Schiff base. Faster rates of formation were observed when the metal ion was added to a premixed solution of salicylaldehyde and sodium glycinate than when one of these ligands was added to a solution containing the metal ion and the other ligand. In these latter experiments, evidence for a two-step mechanism was found. It was postulated that the intermediate is a ternary (mixed) complex in which the ligands are independently bound, SMG (S^- = salicylaldehyde anion, G^- = glycinate anion). This mechanism would fall into the "kinetic template" category.

Salicylaldehyde and glycinate form a stable protonated Schiff base, SGH^-,[8,9] similar to that formed in amino acid–pyridoxal[10] systems, and the faster rate of equilibration observed with the premixed ligands may merely indicate the fast proton displacement from already formed Schiff base.

$$M^{2+} + SGH^- \longrightarrow MSG + H^+$$

Furthermore, no attempt was made to control the pH of the solutions in the earlier work[7] and the release of a proton when the Schiff base complex is formed obscures an interpretation of the reaction mechanism: carbonyl addition reactions show either proton or general acid catalysis,[3] and the released proton competes

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[1] Paper VI in this series; paper V, D. L. Leussing and N. Hug, *Anal. Chem.*, **38**, 1388 (1966). This work was supported by the National Science Foundation, GP 1627. C. K. S. held an undergraduate research fellowship sponsored by The Ohio State University.

[2] D. E. Metzler, M. Ikawa, and E. E. Snell, *J. Am. Chem. Soc.*, **76**, 648 (1954).

[3] For recent discussions see, W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964); R. B. Martin, *J. Phys. Chem.*, **68**, 1369 (1964).

[4] H. Schiff, *Ann. Chem. Pharm.*, 150, 193 (1869).

[5] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

[6] M. C. Thompson and D. H. Busch, *ibid.*, **86**, 213 (1964).

[7] L. J. Nunez and G. L. Eichhorn, *ibid.*, **84**, 901 (1962).

[8] D. Heinert and A. E. Martell, *ibid.*, **85**, 183 (1963).

[9] K. Bai, unpublished results in these laboratories.

[10] D. E. Metzler, *J. Am. Chem. Soc.*, **79**, 485 (1957).