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TERMINAL REPORT

High Pressure Spectroscopy

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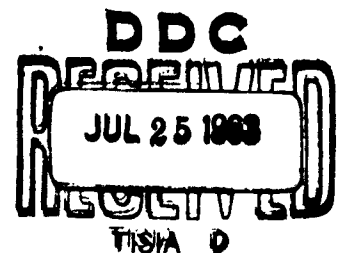
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Most of the work performed under this contract has dealt with the effects of hydrostatic pressure on the absorption spectra of non-polar aromatics in dilute solution in hydrocarbon solvents. It was originally anticipated that pressures of the order of 6 to 8 thousand atmospheres would produce some rather drastic changes in the magnitude of the intermolecular forces and that these changes would reflect in observable spectral changes. It was hoped that the ability to produce pressure changes and the resultant spectral changes in steps as small as desired would allow the changes to be followed almost continuously and thus offer optimum possibilities for interpretation, as contrasted to the abrupt change observed in going from vapor to solution. How this has worked out is described in the following pages.

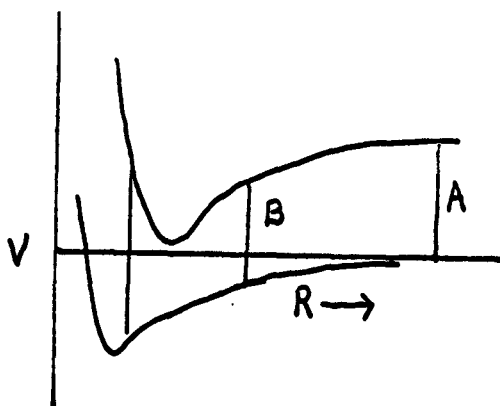
One of the first things that became apparent was that pressure changes up to those that produce solidification actually produce only small changes in the intermolecular forces. Pressures of the order of 6000 atmospheres remove 15 to 20 per cent of the free volume of the liquid and increase its density to that extent but do not seem to increase the interpenetration of charge clouds, compress charge clouds, bend bonds, change bond length, or etc. With this orientation, the effects of pressure could be qualitatively anticipated from the results of passing from vapor to solution spectra by simply adding some 20 per cent of the effect to account for the additional density change. Spectra changes that are

usually observed are those of intensity, breadth of band and frequency shift. Chako's rule would indicate an intensity change in going from vapor to solution of around 30 per cent,¹ experience indicates an even smaller change in most cases.^{2,3} This suggests that intensity changes with pressure could be measured quantitatively and profitably only with photoelectric recording equipment, which was not yet available in this laboratory. Exceptions to this statement are found in the effects of pressure on complex spectra of a number of types.^{4,5,6} Upon solution, the sharp vapor spectrum of benzene in the ultraviolet passes into the typical broad, featureless bands characteristic of a solution spectrum. The many sharp bands of a group in the vapor have broadened and overlapped to form the solution band. Little can be said about the effects of pressure on the breadth of the solution bands as a result of their complicated structure, although some work along this line did prove profitable.⁷ Thus the frequency shifts of the bands remained as potentially the more profitable source of information about pressure shift, and most of the effort expended on this project has been directed to the measurement of frequency shifts.

For the most part we were concerned with the interaction between non-polar absorbers and non-polar solvents molecules. Basically then we were dealing with the London-Van der Waals interaction between polarizable molecules. That is, an instantaneous dipole due to electronic motion in one molecule induces a dipole in a neighboring molecule and dipoles tend

to rotate in phase, lowering the energy of the system. A change in the density of the solution changes this dispersion interaction and thus the energy levels of the interacting molecules. There are two general ways of approaching the problem of evaluating the dispersion forces. One is to try to represent the interaction between two of the interacting molecules and then to sum this interaction over the effective environment. The other is to consider the absorber in a cavity of molecular dimensions in a dielectric continuum with effects representable in terms of the macroscopic properties of the continuum.

Considering the first course first, the nature of the intermolecular potential between the molecules is approximately that given in the following sketch:



At large separations the attractive forces predominate, at close separations the repulsive. The molecule in the excited

state is generally considered to be more polarizable than is the ground state simply because the electron in an outer orbit is less tightly bound. Thus the potential curve for the molecule in an excited state dips more sharply than for the ground state. A transition for the isolated molecule could be represented by A in the figure. The transition at B for the perturbed molecule is of lower energy and a red shift is observed. For absorbing molecules in a region dense with perturbers, each transition may still be thought of as being as sharp as for the isolated molecule but as occurring at a frequency dependent upon the instantaneous distribution of perturbers. Different absorbers, or a given absorber at different times, would see a different distribution of perturbers and so would undergo different frequency shifts. The average shift would correspond to the most probable perturber distribution, but the band would be broadened in accord with fluctuations in this distribution.

If the energy change per interacting pair is $V_1(R) - V_0(R)$, the total frequency shift may be expressed as

$$\Delta\nu_{01} = \int_a^{\infty} 4\pi R^2 g(R) \eta_0 [V_1(R) - V_0(R)] dR \quad (1)$$

where "a" is the minimum distance of approach of the molecules, " η_0 " the mean particle density and $g(R)$ a function that represents the probability of finding a perturber a distance R from the absorbing molecule. This uses the additive property of the dispersion forces. As will be seen later, there

are reasons for believing that the minimum separation "a" does not change appreciably with increasing density. This is in accord with the idea expressed above that an increase in density does little more than remove some of the free volume of the liquid. The distance of minimum separation would be dependent upon temperature, but doesn't change at these pressures. If, further, the pair distribution function $g(R)$ does not change with pressure, again a concept that gains support later, then the integral above is a definite integral in R and the frequency shift with density is a constant times the variation in the mean number density η_0 with density, which is also a constant. Thus the frequency shift is proportional to the density. This is not an unequivacable conclusion, since, as will be mentioned later, there are at least two reasons for believing that the frequency shift should be proportional to the square of the density. Also this is not such a simple conclusion to check as it would appear to be. The relatively short range of densities made available by compressing a liquid together with the inaccuracies in measuring the maximum of absorption of broad bands make it next to impossible to test the above result in terms of the linearity of the plot of $\Delta\nu$ vs ρ , $\Delta\nu$ vs ρ^2 appearing just as linear. How the above conclusion is shown to be correct will be presented later.

The interaction between two molecules is given by the London dispersion equation and assumes a separation large in

terms of molecular dimensions. Although there are ways of improving its applicability,⁸ these are not pertinent to the present discussion. Following Margenau and Watson,⁹ the expression of the dispersion energy, or change in energy level due to dispersion forces, is given by

$$E_0 = - \frac{3}{2} (e^4 / R^6) (\hbar^4 / M^2) \sum_k \frac{f_{0k}^A f_{0k}^B}{E_k^A E_k^B (E_k^A + E_k^B)} + S$$

where A and B refer to absorber and perturber, respectively, f_{0k} is the oscillator strength of the $0 \rightarrow k$ th transition, and E_k the energy of the k th level relative to the ground level. It is somewhat surprising really that the R-dependence cannot be checked as the density is varied because, as stated above, at any given density the interaction is averaged over the complete range of available intermolecular separations. The expression for the frequency shift of a line is then

$$\Delta\nu_{01} = (\text{const}) \rho \left[\sum_k \frac{f_{0k}^A f_{0k}^B}{E_k^A E_k^B (E_k^A + E_k^B)} - \sum_k \frac{f_{1k}^A f_{0k}^B}{(E_k^A - E_1^A) E_k^B (E_k^A - E_1^A + E_k^B)} \right]$$

where the constancy of the integral over R is assume as above. Since few of the energy levels and fewer still of the oscillator strenths are known, some approximations must be made to obtain an equation that is interpretable. If the energy levels

of the solvent are all approximated by its ionization energy and a one term polarizability equation is assumed, the polarizability of the solvent can be introduced into the equation. Further, the oscillator strength of the observed transition may be separated from the others. This leads to the expression

$$\Delta\nu_{01} = I_B^{\alpha} B^{\rho} [\text{Const}] \left[\frac{-2f_{01}^A}{(I_B)^2 - (E_1^A)^2} + \left\{ \sum_{\substack{k \neq 1 \\ k \neq 0}} \frac{f_{0k}^A}{(I_B + E_k^A) E_k^A} - \sum_{\substack{k \neq 1 \\ k \neq 0}} \frac{f_{1k}^A}{(I_B + E_k^A - E_1^A)(E_k^A - E_1^A)} \right\} \right].$$

If the oscillator strength (f_{01}^A) of the observed transition is large and the other terms cancel approximately, the frequency shift might be proportional to the observed oscillator strength. This would be a typical dispersion effect. However, if f_{01}^A is small, the remaining terms would probably be predominant and the frequency shift would be independent of f_{01}^A . This is the observed effect.¹⁰

The question of the nature of the forces acting here was obscured by Shuler's¹¹ original interpretation of the pressure shifts of benzene as due to the formation of a π -molecular complex and the continued use of this interpretation by Oksengorn.¹² It was thus of importance to be sure that the nature of the interaction was understood. A further reduction of the above equation by the introduction of the polarizability

and ionization energy of the absorber leads to the familiar form of the expression for dispersion forces

$$\Delta\nu_{01} = - (\text{const})\rho[(I_A I_B)/(I_A + I_B)]\alpha_A \alpha_B.$$

Although the approximations made in arriving at the equation are drastic, it should predict the qualitative behavior of a given absorber in a number of different diluents. This then was checked. The diluents were various gases such as He, Ne, H₂, Ar, N₂, O₂, CO₂, CO, C₂H₄, and C₂H₆. A plot of the slopes of the resulting curves, $\Delta\nu/\Delta\rho$, against the dispersion energy as calculated above showed approximate linearity.¹³ The dispersive nature of the interaction was considered to be demonstrated beyond reasonable doubt.

As mentioned above, the second broad approach to the interpretation of energy level shifts due to solvent perturbation consists of considering the absorber to be in a cavity of molecular dimensions in a field determined in part by the isotropic dielectric and in part by the molecule itself. Bayliss¹⁴ has expressed the frequency shift for non-polar absorber in a non-polar solvent as

$$\Delta\nu_{01} = \frac{k f_{01}}{a^3 \nu_{01}} \left(\frac{\eta^2 - 1}{2\eta^2 + 1} \right).$$

f_{01} is again the transition oscillator strength, η the index of refraction and "a" the radius of the molecular cavity.

McRae¹⁵ later derived a more complete expression including

dipole-dipole and dipole-induced dipole interactions which proved to be equivalent to the Bayliss relation for non-polar molecules.

If the cavity radius "a" is associated with the absorber, frequency shifts may be measured in a range of solvents and the slope of the curve $\Delta\nu$ vs $(\eta^2 - 1)/(2\eta^2 + 1)$ determined. In a given solvent the pressure shift should then be calculable, the index "n" for the different pressures calculated from the Lorentz-Lorenz expression. Here the molecular cavity is usually considered to vary inversely with the density, and since the term $(\eta^2 - 1)/(2\eta^2 + 1)$ is approximately the $(\eta^2 - 1)/(\eta^2 + 2)$ of the Lorentz-Lorenz expression, which varies directly with density, the frequency shift has been assumed to be proportional to the density squared. Here it was possible to plot $\Delta\nu$ vs $k\rho \left(\frac{\eta^2 - 1}{2\eta^2 + 1} \right)$ and $\Delta\nu$ vs $k \left(\frac{\eta^2 - 1}{2\eta^2 + 1} \right)^{1/2}$ and compare with the measured pressure shifts. It was found¹⁶ that the experimental pressure points fell near to the calculated values for the constant cavity and differed by many times the experimental error from the values predicted when the density ρ was included to account for the decrease in size of cavity with increase in pressure. In this manner, solvent shift data was used to calculate pressure shifts for polar and non-polar absorbers in polar and non-polar solvents. The agreement with experimental values was usually remarkably good. It would thus seem for the most part that the far simpler solvent work could be substituted for the high pressure work. This, however, was something that

couldn't have been known ahead of time.

It was found¹⁰ that extrapolation of the linear curves $\Delta\nu$ vs ρ back to a density $\rho = 0$ did not always yield the vapor phase wavelengths. A portion of the difficulty lay in the fact that the reference point in the band system changed from some peak of absorption near the center of the band in absorption near the center of the band in solution to something nearer the stronger shorter wavelength components in the vapor. This would indicate that the extrapolated wavelength should fall to the red side of the vapor phase wavelength. This was generally the case but differed often enough to suggest a change in slope with phase change. This effect was investigated¹⁷ by observing benzene in the gases C_2H_4 , C_2H_6 and CO_2 . Frequency shifts were measured at temperatures slightly above the critical temperature and then again over the same density range at temperatures slightly under the critical temperature. It was found that at equal densities the frequency shift was the same regardless of the phase. The slope of the curve in CO_2 changed at about liquid densities but the change was not dependent upon the phase. Thus it would seem that usually the slopes of the pressure curves were about the same as those that would be obtained by simply looking at the vapor phase wavelength and the solution wavelength and the corresponding density change. Of course, for large molecules the vapor phase wavelengths might not be attainable and extrapolation of pressure data might yield these approximately. The $\Delta\nu/\Delta\rho$

vs oscillator strength curve¹⁰ on which so much effort was expended might have been obtained with equal significance from vapor phase and solution wavelength determination which were already in the literature. Once again, though, this was known only when both sets of data became available.

Another way by which frequency shifts with density might be obtained more simply than with pressure apparatus is the use of low temperatures. Low temperature data was obtained for a number of aromatics in non-polar solvent from room temperature down to that of dry ice and acetone.¹⁸ Lower temperatures resulting in phase change to the crystalline state or rigid glass or else necessitating a change to a lighter hydrocarbon solvent introduce discontinuous and uninterpretable changes in the data and so were avoided. A comparison of frequency shift with density obtained by lowering the temperature with that obtained by raising the pressure gave interesting results. The low temperature shifts were found to consist of the usual dispersion red shift due to density increase plus a blue shift resulting from a change in the Boltzman distribution across the vibrational levels. As the temperature is lowered, the band contours sharpen and the peaks shifts to the blue as the contribution of the red bands to the structure lessens. For the weak transitions with their low dispersion force red shifts, the blue shift predominates and the observed shift of the band at low temperatures is to the blue. For the stronger transition the red shift is dominant.

In retrospect, we could have obtained much the same information as was obtained from pressure shifts by (1) solvent shifts, (2) vapor to solution shifts and (3) low temperature shifts. Although the theme of this summary seems to be "why do pressure work?," the understanding of the above relationships alone makes the effort expended in pressure work worth while. Also there were a number of basic and interesting phenomena uncovered and investigated that have not been mentioned here but are reflected in the list of publications. It is felt that much profitable information remains to be obtained from further work along these lines.

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PAPERS PRESENTED FOR PUBLICATION

1. "A Comparison of the Effects of High Pressure and Low Temperature on the Absorption Spectra of Some Condensed-Ring Aromatics."
2. "Effects of Solvent, Pressure and Temperature on the Solution Absorption Spectrum of Azulene."
3. "The Calculation of Pressure Shifts from Solvent-Shift Data."

PAPERS PUBLISHED

1. "Pressure Effects on the Ultraviolet Absorption Spectra of Some Aromatic Molecules," W. W. Robertson, O. E. Weigang, Jr., and F. A. Matsen, *Mol. Spec.* 1, 1 (1957).
2. "Phase Changes and Spectral Shifts," by W. W. Robertson and S. E. Babb, Jr., *J. Chem. Phys.*, 28, 953 (1958).
3. "Intermolecular Forces and Pressure Shifts of the Spectra of Aromatic Hydrocarbons" by W. W. Robertson, S. E. Babb, Jr., and O. E. Weigang, Jr., International Symposium, Proprietes Optiques Et Acoustiques des Fluids Comprimés Et Actions Intermoléculaires. Publications du C.N.R.S., Bellevue, France.
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