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Hydrogen Bonding and Electronic Transitions: The Role of the Franck–Condon Principle

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The influence of hydrogen bond formation on electronic transitions (including the n → π* blue shift phenomenon) is discussed in terms of the Franck–Condon principle. The resultant frequency shift in absorption is equal to $W_0 - W_1 + w_1$ where W_0 and W_1 are the energies of hydrogen bond formation in the ground and excited states, respectively, and w_1 is the excitation implied by the Franck–Condon principle. The necessity of combining absorption and emission data to determine $W_0 - W_1$ is noted. The available absorption data indicate that the spectral shifts caused by water are usually about twice as big as those caused by methanol, suggesting that the hydrogen bond energy of water exceeds that of methanol to a given base.

Several studies have been made of the effect of hydrogen bonding (hereafter called H-bonding) on electronic transitions. For example, the absorption of phenol near 36,000 cm.$^{-1}$ has been observed for solutions containing phenol and one of several bases.[1–4] Another large body of applicable data relates to electronic transitions of bases dissolved in either alcohol or water. These data established an empirical correlation among solution spectra (apparently first suggested by Kasha[5] and substantiated by a compilation of data by McConnell[6]) called the "n → π* blue shift phenomenon." In this correlation the absorption maximum of an n → π* electronic transition is found to shift toward higher frequency if the solvent is changed from an alkane to an alcohol (this direction of shift being defined as a blue-shift). Recently Brealey and Kasha[7] recognized and established the importance of H-bonding in this solvent effect. Yet their discussion does not recognize the role of the Franck–Condon principle. Consequently their detailed interpretations are indeed oversimplified. We shall examine this role to determine the relationship between H-bond formation and the resultant spectral changes. The present discussion applies to all electronic transitions, including but not restricted to the n → π* type.

The Franck–Condon Principle and Hydrogen Bonding.—Both McConnell[6] and Bayliss and McRae[8] have discussed in terms of the Franck–Condon principle the effect of solvation on an electronic transition. The equilibrium distances and orientations of solvent molecules around a solute molecule are dictated by the energetics of solvation. If this solute molecule makes an electronic transition, the solvation arrangement of the initial state is not necessarily the most stable for the new electronic distribution and, indeed, could be energetically repulsive. Since the solvent molecules cannot reorient during the transition (Franck–Condon principle) such a change in solvation energetics would result in a change in the energy separation of the two states (*i.e.*, there would be a solvent shift).

Bayliss and McRae[8] have attempted to enumerate the contributing factors to the solvation effects. Their treatment does not give adequate attention to the H-bonding interaction which, when present, dominates such forces as are usually described in terms of dispersion, dipole-polarizability and dipole–dipole forces. The dispersion effects are of the order of the van der Waals energy and the change of this term during an electronic transition is likely to be even smaller (as is assumed by Bayliss and McRae[8]). The comparison of dipolar and H-bonding effects is more subtle. We are here concerned with that part of the solute–solvent interaction which is attributed to the presence of permanent dipole moments in some or all of the molecular species present but which is *not* part of the specific interaction designated the H-bond. Most often, the functional groups possessing high bond dipoles will be involved in H-bond formation and any residual capacity for dipolar interactions of a non-H-bonding type will be small indeed. Experimental confirmation of these views is evident in the spectra of pyridazine in hexane–ethanol mixtures, as presented by Brealey and Kasha (their Fig. 3). This figure shows frequency invariance of band features of the pyridazine (not H-bonded) during a solvent change from pure hexane to a mixture of about 2 *M* ethanol in hexane. This indicates that this transition is little influenced by the dispersive and non-H-bonding dipolar effects that accompanied the drastic solvent change.[9] A further indication that the orientation effects associated with H-bonding far exceed those of dipolar interactions is given by the Trouton's rule constants. These constants, which contrast entropies of vaporization, are relatively close to a "normal" value (near 20–21) for polar compounds (*e.g.*, diethyl ether, 20.2; acetone, 21.9; 1,1,2,2-tetrachloroethane, 22.1) compared to the high values for H-bonding compounds (*e.g.*, methanol, 24.9; water, 26.0; ethanol, 26.9). Consequently the following discussion will ignore the dispersive and dipolar interactions. In any particular system where these neglected terms are unusually large and the H-bonding terms are small, the present treatment will then account for only that portion of the spectral perturbation due to the H-bonding.

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(1) H. Tsubomura, *J. Chem. Soc. Japan*, **73**, 841 (1952).

(2) S. Nagakura and H. Baba, THIS JOURNAL, **74**, 5693 (1952).

(3) S. Nagakura, *ibid.*, **76**, 3070 (1954).

(4) S. Mizushima, M. Tsuboi, T. Shimanouchi and Y. Tsuda, *Spectrochim. Acta*, **7**, 100 (1955).

(5) M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

(6) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(7) G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

(8) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(9) This point was noted by Dr. Sydney Leach, private communication.

In an H-bonding system, the interaction is localized at functional groups with either proton donor or acceptor properties. A solvent shift then indicates that the H-bonding properties of these functional groups in the initial state differ from the H-bonding properties of these same groups in the final state. The magnitude of the shift must be evaluated, however, in terms of the Franck–Condon principle.

Figure 1 portrays potential functions for formation of an H-bond A-H· · ·B where R is the A· · ·B distance. Figure 1a portrays the situation when the excited state forms a weaker H-bond and in Fig. 1b the excited state forms the stronger H-bond. In each case the energy separation of the non-H-bonded species ($R = \infty$) is assumed to be identical to ν_0, the energy separation in a non-H-bonding solvent of the same refractive index. The H-bond energy is designated W ($W = -\Delta H$) and the excitation energy implied by the Franck–Condon principle is labeled w. (By these definitions, W and w are always positive numbers. Of course either W_0 or W_1 could be zero.)

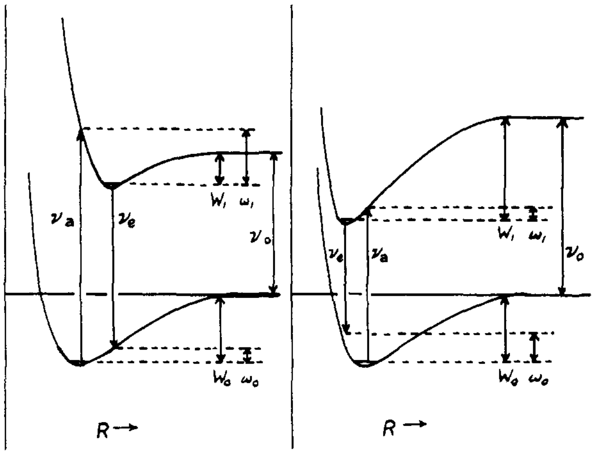

Fig. 1.—Hypothetical potential curves: energy *vs.* H-bond length: A–H...B; R = (A...B) distance; a, left, $W_0 > W_1$; b, right, $W_0 < W_1$.

There are three quantities of interest which might be experimentally accessible, ν_a, ν_e and ν_{0-0}, the frequencies appropriate to maximum of absorption, maximum of emission (*e.g.*, in a fluorescence spectrum), and the O–O transition, respectively.[10] These frequencies are related to the quantity ν_0 by the relations

$$\nu_a - \nu_0 = \Delta\nu_a = W_0 - W_1 + w_1 \qquad (1)$$

$$\nu_e - \nu_0 = \Delta\nu_e = W_0 - W_1 - w_0 \qquad (2)$$

$$\nu_{0-0} - \nu_0 = \Delta\nu_{0-0} = W_0 - W_1 \qquad (3)$$

Clearly the most interesting quantity is $\Delta\nu_{O-O}$, which gives directly the difference in H-bond energies of ground and excited states. Since the quantity W_0 (for the ground state) usually can be determined by conventional methods and is known for many systems, eq. 3 offers a measure of W_1. The determination of $\Delta\nu_{O-O}$ requires both absorption and fluorescence studies. Although such studies do not involve any new techniques, they are subject to the usual difficulties (particularly the interference of overlapping bands).[11] None of the data recorded so far give $\Delta\nu_{O-O}$ but there are a number of measurements of values of $\Delta\nu_a$'s. It is notable that w_1 and w_0 are determined if all three data, $\Delta\nu_a$, $\Delta\nu_e$ and $\Delta\nu_{O-O}$, are measured (with the reservation expressed in footnote 10).

In Fig. 1a ($W_0 > W_1$) we see that the usual expectations of potential form predict that $W_0 > w_0$ and $w_1 > w_0$. No upper limit can be set on w_1 since the steep side of the potential function could rise sufficiently fast to make $w_1 > W_1$ (as is pictured in Fig. 1a). In any event, it will only be a coincidence if $w_1 = W_1$ and we see that $\Delta\nu_a$ cannot be expected, *a priori*, to measure W_0. Since w_1 is positive, eq. 1 predicts that if $W_0 > W_1$ then $\Delta\nu_a > 0$, *i.e.*, a blue-shift which exceeds the difference $W_0 - W_1$ by w_1 will be observed in absorption. Similarly, in emission, a shift will be observed which is less than $W_0 - W_1$ by w_0 (*i.e.*, either a red shift or blue shift may be observed; in either case, the shift will be small compared to W_0). If $W_1 = 0$, no shift will be observed in emission since then $W_0 = w_0$.

In Fig. 1b ($W_0 < W_1$) the anharmonicity expectations predict that $W_1 > w_1$ and $w_0 > w_1$. Now the absorption spectrum will show a shift which is less by w_1 than the red shift implied by the negative value of $W_0 - W_1$. The emission spectrum will show a red shift exceeding $|W_0 - W_1|$ by w_0.

Turning now to the interpretation of observations, a blue shift in absorption which is comparable in magnitude to W_0 implies Fig. 1a is applicable ($W_0 > W_1$) and the blue shift *exceeds* the difference $W_0 = W_1$. If a red shift is observed in absorption then Fig. 1b is applicable ($W_0 < W_1$) and the red shift is *less than* the difference $W_1 - W_0$. If only a small blue shift is observed in absorption, either of Figs. 1a or 1b could be applicable. Similarly, in emission, a blue shift implies Fig. 1a, a large red shift implies Fig. 1b, and a small red shift is ambiguous. Under any circumstances, $\Delta\nu_a$ and $\Delta\nu_e$ bracket the quantity $\Delta\nu_{O-O} = W_0 - W_1$.

The Expected Magnitude of Spectral Shifts.—The well characterized H-bonds have energies in the range 1–7 kcal. per bond (350–2500 cm.$^{-1}$). As mentioned above, a blue shift in absorption may exceed the ground state H-bond energy, hence blue shifts are expected in the range 350–2500 cm.$^{-1}$ and occasionally larger than 2500 cm.$^{-1}$. A red shift (in absorption) should never be as large as W_0, hence should not exceed 2500 cm.$^{-1}$. Even if a much stronger H-bond is formed in the excited state, the red shift reflects only the *difference* in energies of the ground and excited state H-bonds *at an H-bond distance optimum for the ground state but not for the excited state.*

The number of H-bonds influenced by the transition is, of course, an important factor. A monobasic proton donor can form only a single H-bond,

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(10) The following discussion assumes "vertical" transitions for ν_0, ν_a and ν_e, without any consideration of transition probability as a function of configuration. It is difficult to assess this assumption, particularly for forbidden transitions which specifically depend upon vibration–electronic interaction. It is probably not a serious assumption in most cases.

(11) Kasha has pointed out that "fluorescence for n → π^* (transitions) is characteristically non-existent; or, in rare cases, is extremely weak." Private communication from Dr. M. Kasha, Florida State University.

but a base molecule can form H-bonded complexes with two or more acid molecules. Thus Barrow and Yerger[12] identified the species A_2B in the system A = acetic acid, B = triethylamine. Similarly, complexes including several HX molecules have been proposed in HX–ether systems.[13] The solvent shift would be larger in a multiple H-bond complex in accordance with the number of H-bonds affected. Similarly, more than one H-bonding functional group may be present. If these groups are equivalent because of molecular symmetry, the electron distribution must necessarily change similarly at these sites. Again the observed shift would reflect the energies of all of the H-bonds affected. For strongly bonding systems (such as a dilute solution of pyridazine in ethanol) most of the pyridazine is expected to be in the 1:2 complex form and the blue shift will be determined by the sum of the changes of the first and second H-bond energies.

Experimental Data.—For electronic transitions of bases, the expectations concerning the magnitudes of H-bonding shifts are corroborated, as is revealed in the compilation of McConnell.[6] Except for glyoxal, all shifts induced by water or alcohol are in the range -1700 to $+4000$ cm.$^{-1}$ (20 examples). Furthermore, the red (negative) shifts are generally smaller than the blue (positive) shifts, again as expected. Tables I and II list a portion of these data, those systems for which both methanol and water solvents have been studied. Table III lists the available data for transitions in proton donors. All shifts are given as $\Delta\nu_a = \nu - \nu_0$ where ν is the frequency of maximum absorption in the H-bonding solvent and ν_0 is the corresponding frequency in a suitable reference solvent. Unless noted otherwise, the data in Tables I and II are from ref. 6 and the reference solvent is in every case a paraffin hydrocarbon.

TABLE I

H-BOND SOLVENT SHIFTS FOR TRANSITIONS IN CARBONYL BASES

Base	ν_0 (cm.$^{-1}$)	Methanol $\Delta\nu_a$ (cm.$^{-1}$)	Water $\Delta\nu_a$ (cm.$^{-1}$)	Transition
Diazoacetic ester	25,500	+ 800	+1500	n-π
Acetone	35,960	+ 900 +1200[a,7]	+1900	n–π
Mesityl oxide	30,760	+1000 +1180[a,7]	+3200	n–π
Diazoacetic ester	41,000	− 550	− 600	π–π
Mesityl oxide	43,000	−1000	−1700	π–π

[a] Ethanol solvent.

TABLE II

H-BOND SOLVENT SHIFTS IN MISCELLANEOUS BASES

Base	ν_0 (cm.$^{-1}$)	Methanol $\Delta\nu_a$ (cm.$^{-1}$)	Water $\Delta\nu_a$ (cm.$^{-1}$)	Transition
Nitrosobenzene	13,000	+ 50	+ 450	n–π
Pyrazine	31,500	+ 700	+1800	n–π
Pyridazine	29,450	+2440[7]	+4000[14]	n–π

It is interesting that the shifts caused by water are invariably higher than those in methanol and in six of eight examples, roughly double. Two possible explanations are suggested: more H-bonds may be formed between solvent and solute in water than in methanol; and/or the H-bonds with water may be stronger than those with methanol. The infrared spectral data provide support for the second proposal. The shifts in the stretching frequencies of water and alcohol in basic solvents are generally considered to be related to the corresponding H-bond energies. The shifts observed for water are usually about one and a half times those for methanol, as is evident in the compilation of data presented by Gordy.[15] Thus the infrared shifts also suggest that water forms stronger H-bonds to a given base than does methanol.

TABLE III

H-BOND SOLVENT SHIFTS FOR TRANSITIONS IN PROTON DONORS

Acid	Base	ν_0 (cm.$^{-1}$)	$\Delta\nu_a$ (cm.$^{-1}$)	Ref.
Phenol	Methyl acetate	36,010	−240	2,3
Phenol	Ethyl acetate	36,010	−350	2,3
Phenol	Ether	36,010	−360	1
	Diethyl ether	36,010	−423	4
Phenol	Acetone	36,010	−397	4
Phenol	N,N-Dimethylacetamide	36,400	−500	4
Acetanilide	Diethyl ether	35,600	−189	10
Aniline	Ether		−540	11

Discussion

The Franck–Condon argument presented here implies a more complicated interpretation of the magnitude of the n $\rightarrow$ π^* "blue-shift" than the interpretation of Brealey and Kasha. Their comparison of the blue shift to the quantity W_0 is presumably based on the expectation that $W_1 = 0$ and no consideration is given to the large value of w_1 implied by the short interatomic distances of the H-bonded ground state. This suggests that the agreement between blue shift and H-bond energy found for each of the two systems pyridazine–ethanol and benzophenone–ethanol is fortuitous. This possibility is strengthened by noting that the blue shift used for pyridazine applies to a mixture containing about 25% uncomplexed pyridazine (using the K given by Brealey and Kasha), that the blue shift for benzophenone was corrected by about 20% because of overlap of an adjacent transition, and that the infrared shifts give only a coarse indication of the H-bond energy, possibly in error by as much as one kcal. On the other hand, their qualitative discussion seems to be correct. If a non-bonding electron localized on the basic functional group is transferred to an anti-bonding orbital, the change of electron density undoubtedly reduces base strength. Hence it is expected that $W_1 < W_0$ (though W_1 is not necessarily zero).

The red shifts of the π–π transitions indicate that the base strengths have been increased. This is no doubt to be attributed to a transition involving electron redistribution in the same space but

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(12) G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954).

(13) G. L. Vidale and R. C. Taylor, *ibid.*, **78**, 294 (1956).

(14) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

(15) W. Gordy, *ibid.*, **9**, 215 (1941). The approximate factor 1.5 is obtained from Gordy's data after correction for the fact that his shifts are referred to the gas state for D_2O and benzene solution for CH_3OD.

with enhanced electron density in the more peripheral portions. This is a characteristic difference of bonding and anti-bonding orbitals. Although this may be the expected behavior, again it is not necessary that every π–π redistribution give a red shift since the basic functional groups may not be affected or the nodal properties may actually deplete the electron density at the basic sites.

The red shifts observed for the proton donors may be rationalized. All of these data refer to the transitions corresponding to the $A_{1g} \rightarrow B_{2u}$ transition of benzene, a transition to an excited state containing nodal planes perpendicular to the plane of the ring. The red shift suggests that this orbital places a nodal plane through the H-bonding functional group, so as to reduce the electron density at this site. This would cause an acidic group to become a better proton donor. Aromatic acids (phenol, aniline) should display red shifts whereas aromatic bases (anisole, dimethylaniline) should display no shift in basic solvents (as is observed, see ref. 1) and a blue shift in acidic solvents (no data available).

Conclusions

It seems clear that the solvent shifts caused by H-bonding solvents contain interesting information. In addition to empirical correlations which may aid in establishing the type of transition, these solvent shifts provide clues to the locale and nature of electron redistribution in the electronic transition. Perhaps the unique aspect is the promise for understanding the electronic distribution and H-bonding properties of excited states. For this purpose absorption and emission studies should be combined, if possible, to give the shift corresponding to the O–O transition.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Equations for the Limiting Current at the Rotated Dropping Mercury Electrode[1]

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This paper describes results of a theoretical and experimental study of the relationship between the limiting current at the rotated dropping mercury electrode on the one hand and the diffusion coefficient of the electroactive species, the kinematic viscosity of the solution, and the characteristics of the electrode on the other. Two theoretical equations are derived on the basis of hydrodynamics, one for the case when no surface-active substance is present and the other for the case when such substances are present. In view of the fact that the presence of a suitable surface-active substance is necessary for most practical purposes, the relations in the presence of a capillary-active substance were studied more extensively than those in its absence. The proposed equation in the presence of surface-active compounds involves an experimentally determined numerical constant and yields satisfactory agreement between observed and calculated limiting currents in the range of 75 to 210 r.p.m., provided that an electrode of the proper dimensions is employed. At a suitable speed of rotation in the presence of a surface-active substance, the limiting current at the rotated dropping mercury electrode, as a first approximation, is proportional to $D^{2/3}(mt)^{1/2}$, while at the unrotated conventional dropping mercury electrode it is proportional to $D^{1/2}m^{2/3}t^{1/6}$. Limitations of the derived equations are discussed both from theoretical and practical viewpoints.

The rotated dropping mercury electrode (R.D.M.E.) recently developed in this Laboratory[2] is of practical importance because it allows polarographic determinations at concentrations of an order of magnitude of one smaller than with the conventional dropping mercury electrode (D.M.E.). The quantitative dependence of the limiting current upon various factors is quite different at these two electrodes. In the present paper the results of a theoretical and a systematic practical study of the factors which affect the limiting current at the R.D.M.E. are described. In order to determine the effect of the height of mercury on the limiting current, it was necessary to revise the construction of the electrode previously described.[2] The expressions derived at 25° for the average limiting current in the absence (eq. 1) and presence of a surface-active compound which completely suppresses stirring at the mercury surface (eq. 2) are

$$i_1 = 230nCD^{1/2}\{m^{2/3}t^{1/6} + 103D^{1/2}(mt)^{1/3} + 7.45U_0^{1/2}(mt)^{1/2}\} \quad (1)$$

$$i_1 = 230nCD^{1/2}\{m^{2/3}t^{1/6} + 103D^{1/2}(mt)^{1/3} + 5.76U^{1/2}\nu^{-1/6}D^{1/6}(mt)^{1/2}\} \quad (2)$$

where i_1 is the average limiting current in μa., n the number of electrons involved in the electrochemical reaction, C the concentration of the electroactive species in mM, D the diffusion coefficient in cm.^{2}/sec., m the rate of flow of mercury in mg./sec., t the drop time in sec., U_0 the uniform velocity of the solution at the surface of the mercury drop in cm./sec., U the speed of rotation of the electrode in cm./sec. and ν the kinematic viscosity of the solution in cm.^{2}/sec. In the presence of surface-active substances satisfactory agreement between calculated (eq. 2) and observed limiting currents was found only when the electrode has a relatively small orifice (<0.75 mm. in diameter) and a small distance between the orifice and center of rotation (<8.5 mm.).

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)-1516. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] W. Stricks and I. M. Kolthoff, THIS JOURNAL, **78**, 2085 (1956).