conclusion is that the C–X bond in the transition state changes from a nearly neutral C–Cl bond for HCl loss to a C–F bond that has significant charge separation between the C and the F when HF is eliminated. Trends in the carbon–hydrogen and the carbon–halogen bond dissociation energies as chlorines or fluorines are substituted for the hydrogens of haloethanes parallels the variation of the E_0(HCl) and E_0(HF), respectively.

Regardless of the reasons for the change in the E_0's with halogenation, it is clear that caution must be exercised when extrapolating trends in a set of data to predict properties of the chlorofluorocarbons. In addition, further experimental and theoretical work is certainly needed to help unravel the intricacies of substituents effects at both the α- and β-carbons. To this end we have begun work with chemically activated $CFCl_2CH_3$ to determine if the E_0's for loss of HCl and HF agree with the above conclusions. Additional data on the strength of C–H and C–X bonds for the haloethanes would be very useful in verifying the correlation between E_0(HX) and the bond dissociation energies.

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Appendix

The average energy, $\langle E\rangle$, for CF_2ClCH_3 was calculated from the enthalpies of formation of CF_2ClCH_3, CF_2Cl, and CH_3. The $\Delta H_f(CF_2ClCH_3) = -128.8$ kcal/mol, recommended by Buckley and Rogers,[46] was used, which is in good agreement with the experimental value of -126.6 kcal/mol of Papina and Kolesov.[48] Conversion to 0 K gave $\Delta H_f^\circ = -125.8$ kcal/mol. For the methyl radical the ΔH_f at 0 K is 35.9 kcal/mol.[49] The ΔH_f^{298} (CF_2Cl) was estimated from the C–H bond dissociation energy of CF_2ClH and the ΔH_f of the H atom and CF_2ClH. The D(R–H) was determined from trends in the dissociation energies of several halomethanes reported by Tschuikow-Roux and Paddison.[42] The estimated D_0^{298} (CF_2Cl–H) = -101 kcal/mol together with ΔH_f^{298} (CF_2ClH) = -115.1 kcal/mol[50] gave $\Delta H_f^{298}(CF_2Cl) = -66.2$ kcal/mol. This value is somewhat lower than the -64.2 kcal/mol (298 K) reported by Kerr[51] but is in excellent agreement with -66.5 kcal/mol (298 K) estimated by Lee and co-workers[52] from analysis of trends in the carbon–chlorine bond dissociation energies of chlorofluoromethanes. Conversion to 0 K gave $\Delta H_f^\circ(CF_2Cl) = -65.3$ kcal/mol. The $\Delta H_{rxn}(CF_2ClCH_3)$ was calculated to be -96.4 kcal/mol. Finally, the $\langle E\rangle$ of 101.1 kcal/mol was obtained by combining $\Delta H_{rxn}(CF_2ClCH_3)$ with a 1 kcal/mol activation energy for radical combination and 3.7 kcal/mol thermal energy of CF_2ClCH_3.

Similarly, the $\langle E\rangle$ value of 102 kcal/mol was obtained for $CF_2Cl + CD_3 \rightarrow CF_2ClCD_3$ by assuming that $\Delta H_f^{298}(CF_2ClCD_3) = \Delta H_f^{298}(CF_2ClCH_3)$, using $\Delta H_f^\circ(CD_3) = 35.9$ kcal/mol[48] and the same thermal energy as CF_2ClCH_3.

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(48) Papina, T. S.; Kolesov, V. P. *Vestn. Mosk. Univ. Ser. 2: Khim.* **1978**, *19*, 500.

(49) Pamidimukkala, K. M.; Rogers, D.; Skinner, G. B. *J. Phys. Chem. Ref. Data* **1982**, *11*, 85.

(50) *JANAF Thermochemical Tables*; Stull, D. R., Prophet, H., Eds.; The Dow Chemical Company: Midland, MI, 1970.

(51) Kerr, J. A. *CRC Handbook of Bimolecular and Termolecular Gas Reactions*; CRC Press: Boca Raton, FL, 1981; Vol. I, p 269.

(52) Krajnovich, D.; et. al. *J. Chem. Phys.* **1982**, *77*, 5977.

Theory of Charge-Transfer Spectra in Frozen Media

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Absorption and fluorescence maxima of charge-transfer spectra in frozen media are treated, noting that only some of the nuclear motions for liquid medium are frozen in corresponding solid or glassy phase. Account is taken of the fact that the conditions under which the static dielectric constant of the frozen phase is measured do not usually correspond to those in which the initial state of the solute system is prepared. Expressions for the maxima are obtained in terms of the optical and static dielectric constants of the liquid and frozen (solid or glassy) phases. Comparison of Stokes shifts $h\nu_a - h\nu_f$ at conventional fluorescence times in frozen media with Stokes shifts at picosecond or subpicosecond times in liquid media would be of interest.

Introduction

The effects of polarity of the solvent on charge-transfer (CT) spectra have been of considerable interest in recent decades. Molecules in which the intramolecular charge transfer is largely associated with a change of dipole moment[1,2] have been the subject of intensive study, as have CT spectra of mixed-valence complexes.[3,4] In the most frequently used theoretical treatments for these systems, the solvent has been treated as a dielectric continuum, characterized by its static and optical dielectric constants.[1-4] The effect of the polar solvent medium on the spectra has been described, applying the Franck–Condon principle to the spectral transition.[1-4] The studies have normally been for liquid media.

Recently, a very interesting study was published by Hammack et al.[5] on the charge-transfer spectrum of a mixed-valence complex in a frozen medium

$$\mathrm{(bpy)_2ClRu^{II}(pz)Ru^{III}Cl(bpy)_2^{3+}} \xrightarrow{h\nu_{CT}} \mathrm{(bpy)_2ClRu^{III}(pz)Ru^{II}Cl(bpy)_2^{3+}} \tag{1}$$

where bpy is 2,2′-bipyridyl and pz is pyrazine. These authors varied the dielectric constant of the existing phase in the vicinity of the liquid–solid phase transition point of the solvent, by varying the static pressure. The phase transition itself was accompanied by a marked change in the static dielectric constant in the case

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† Contribution No. 8067.

(1) Early examples of the use of the dipole in a sphere model for treating spectral shifts of polar solutes in polar solvents include: Ooshika, Y. *J. Phys. Soc. Jpn.* **1954**, *9*, 594. Lippert, E. *Z. Naturforsch.* **1955**, *10a*, 541. Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690; **1956**, *29*, 465. Numerous examples have appeared since.

(2) Marcus, R. A. *J. Chem. Phys.* **1963**, *39*, 1734; **1965**, *43*, 1261; *J. Phys. Chem.* **1989**, *93*, 3678.

(3) Cf., Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391; *Electrochim. Acta* **1968**, *13*, 1005.

(4) A recent paper on the application of the dielectric continuum model to charge-transfer spectra of mixed valence ions is that of: Brunschwig, B. S.; Ehrenson, S.; Sutin, N. **1987**, *91*, 4714.

0022-3654/90/2094-4963$02.50/0

of polar solvents, e.g., for nitrobenzene from about 35 for the liquid to about 3.4 for the solid. Yet the charge-transfer spectral maximum showed very little change, a factor of 5 or 10 less than expected from the standard formula (given by eqs 2 and 4 below).

At first glance this result seems to conflict with existing theory.[5] However, Worl and Meyer[6] correctly explained the apparent discrepancy, making use of eqs 2 and 3 below. They noted that for the charge-transfer absorption maximum the ensemble of orientations of the solvent dipoles about the solute molecule prior to freezing was similar to that after freezing (the extent of similarity depending on the rate of cooling, of course). For sufficiently rapid cooling the various terms in eqs 2 and 3 would be largely unchanged by this phase transition. They then supplemented this observation with a further study of their own on the metal to ligand charge-transfer absorption and fluorescence spectra of (bpy)-$Re(CO)_3Cl$ in the vicinity of a glass–liquid phase transition of a methanol–ethanol solution, induced now by a change of temperature instead of pressure. Their results further documented their explanation.[6]

In the present paper we formalize and extend the discussion of ref 6, by giving an explicit expression for the charge-transfer spectra for frozen media, and also allowing for the fact that only part of the dielectric polarization arising from the nuclear coordinates is "frozen" in the glass or solid phase. For example, the static dielectric constant of the frozen phase of a polar solvent is usually[7] well below that of the liquid but still above that of the optical value (square of the refractive index).

One feature, also encountered in ref 5, in the application of standard formulas[1-3,6] to frozen media, and which we treat in the next section, is that the conditions of the solvent in which the charge-transfer system is prepared do not correspond to the conditions used for measurement of the "static" dielectric constant of the frozen phase.

Theory

The frequency ν_a of the absorption maximum for a charge-transfer spectrum, as derived in ref 2, is given by

$$h\nu_a = \lambda_0 + \lambda_i + \Delta G^\circ \qquad \text{(liquid)} \qquad (2)$$

where

$$\lambda_0 = G_{1-0}{}^{op} - G_{1-0} \qquad (3)$$

Here, G_{1-0} is the polar solvational contribution of a hypothetical equilibrium system with the charge distribution of the solute equal to $\rho_1 - \rho_0$, the difference of the charge distributions in the initial (ρ_0) and final (ρ_1) electronic states of the solute, and $G_{1-0}{}^{op}$ is the same as the latter but for a solvent which responds to the charges only via its electronic dielectric polarization.[2] λ_i denotes the intramolecular vibrational contribution. For a mixed-valence complex in which each of two charges is regarded as being in its own sphere (radii a_1 and a_2), with a center-to-center separation distance R between the spheres, λ_0 is given by[2,3]

$$\lambda_0 = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (4)$$

where D_{op} and D_s are the optical and static dielectric constants of the solvent.

For the fluorescence maximum ν_f in liquid media there is a Stokes shift, $2(\lambda_0 + \lambda_i)$,[1-3,8] and so we have[2]

$$h\nu_f = -\lambda_0 - \lambda_i + \Delta G^\circ \qquad \text{(liquid)} \qquad (5)$$

One problem encountered in applying eqs 2, 4, and 5 to charge-transfer spectra in frozen media is, as already noted, that the measurements of the charge-transfer absorption spectrum in a frozen medium are made under conditions quite different from those used to measure the static dielectric constant of that medium. In the case of the absorption spectrum, the solvent dipoles in the liquid are oriented around the initial charge distribution of the solute ρ_0 prior to freezing, as noted by Worl and Meyer.[6] The subsequent freezing of the solvent by an increase of pressure, as in ref 5, or by a decrease in temperature, as in ref 6, presumably does little to change these orientations in the immediate vicinity of the transition point, if the cooling is not too slow. In this instance, a frozen solvent (solid or glass) really behaves, from the point of view of the charges, as a medium with a static dielectric constant D_s given by the value for the liquid, not for the solid[5] or glass.[6] A more comparable measurement of D_s would arise if the measurement of D_s were made as in the following *thought experiment*, a static experiment, rather than in the conventional manner using ac methods, namely, the plates of a capacitor would first be charged, the polar solvent serving as the dielectric fluid. A measurement of the potential difference and the charge on the capacitor plates would then yield the capacity and hence D_s. If, in the presence of this charge on the plates, the pressure were now applied and the liquid thereby frozen, the dielectric polarization would be expected to be approximately unchanged. One would therefore have approximately the same D_s as for the liquid state, rather than the much lower value usually obtained for D_s for the frozen phase by a standard ac measurement. An analogous experiment, involving temperature rather than pressure changes in the presence and absence of an applied field, has been performed.[8] While no D_s's were determined, effects of the above type occurred.[8]

In summary, the usual measurements of D_s for a frozen polar medium do not yield the D_s appropriate to the customary conditions in which the charge transfer absorption spectrum in that medium is measured. One simple approximate expedient for the theory in this case would be to replace the D_s in the $D_{op}^{-1} - D_s^{-1}$ in eq 4 by the value where the actual equilibration of the solvent dielectric polarization for the initial electronic state occurred. However, this step would be not quite correct: only part of the polarization due to the nuclear coordinates is frozen when the solid or glass is formed. We treat this aspect of the problem first.

We denote that part of λ_0 which is frozen when solid or glass is formed by $\lambda_{0,0}$ (i.e., $\lambda_{0,0}$ is the same for the liquid and solid phases) and the remainder by $\lambda_{0,i}$, and obtain expressions for these quantities below. Typically, both arise from the nuclear motions. It may happen that $\lambda_{0,0}$ arises largely from the orientations of the solvent dipoles and $\lambda_{0,i}$ largely from the vibrational polarization of the solvent molecules, but we need not specify their physical nature. They will simply be called the $\lambda_{0,0}$ and $\lambda_{0,i}$ polarizations. Operational expressions for $\lambda_{0,0}$ and $\lambda_{0,i}$ are given below by eqs 6 and 8 and, in terms of specific dielectric constants, by subsequent expressions.

Equation 2 represents the ensemble-averaged energy (and free energy) difference between two systems having charge densities ρ_0 and ρ_1 of the solute, both systems having the same orientation–vibration dielectric polarization of the medium (since all nuclear coordinates are held in a fixed distribution determined by ρ_0) but having in each case an electronic dielectric polarization which adapts itself to the existing charge distribution, ρ_0 or ρ_1, and to the remaining, fixed part of the dielectric polarization.[2,9]

We shall need later an analogous quantity for two electronic states having the same $\lambda_{0,0}$ polarization but having a $\lambda_{0,i}$ polarization which, like the electronic polarization above, has adapted itself to the existing charge distribution and to the remaining (i.e., $\lambda_{0,0}$) polarization. An expression for this free energy difference can be readily derived. We let $\Delta G_{solv}(0)$ be the polar contribution to the solvational free energy difference between the states 0 and

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[5] Hammack, W.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Chem. Phys. Lett.* **1986**, *132*, 231. Cf.: Drickamer, H. G. *Annu. Rev. Mater. Sci.*, in press.

[6] Worl, L. A.; Meyer, T. J. *Chem. Phys. Lett.* **1988**, *143*, 541.

[7] The phase transition of liquid water to ice is an exception, the D_s of the two phases being fairly similar. [Cf.: Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973; Chapter 4.] Evidently the protonic rearrangements responsible for D_s, involved in the breaking of hydrogen bonds for example, are, unlike the case of dipole reorientation in nonaqueous liquids, not appreciably altered by the freezing. For many other liquids there is a marked drop in D_s on freezing, e.g.: Landolt-Börnstein. *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, 6th ed.; Hellewege, K. H., Hellewege, A. M., Eds.; Springer Verlag: Berlin, 1959; Vol. 2, Part 6, pp 692–704.

[8] Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1969**, *75*, 2408. Cf. Figure 1 and the associated discussion on unradiated MTHF.

[9] Cf., Marcus, R. A.; Sutin, N. *Comments Inorg. Chem.* **1986**, *5*, 119.

1, at a fixed orientation–vibration polarization, fixed by the charge density ρ_0. Then $\Delta G_{\text{solv}}(0)$ equals λ_0 and is given by eq 3.[2] If $\Delta G_{\text{solv}}(0,0)$ denotes, instead, the polar contribution to the solvational free energy difference when only the $\lambda_{0,0}$ polarization is held fixed, the latter determined by ρ_0, a corresponding derivation shows that $\Delta G_{\text{solv}}(0,0)$ equals $\lambda_{0,0}$ where, instead of eq 3

$$\lambda_{0,0} = G_{1-0}{}^{\text{F}} - G_{1-0} \tag{6}$$

and $G_{1-0}{}^{\text{F}}$ is the same as $G_{1-10}{}^{\text{op}}$ but now for a medium which responds to $\rho_1 - \rho_0$ via the polarizability of the frozen medium, i.e., by both the electronic plus the $\lambda_{0,i}$ polarization. Of particular interest is the fact that this $\Delta G_{\text{solv}}(0,0)$ represents the polar contribution to the solvational free energy difference between the emitting state in the frozen medium and the initial (ρ_0) absorbing state.

We introduce the component $\lambda_{0,i}$ to λ_0 by the expression

$$\lambda_0 = \lambda_{0,0} + \lambda_{0,i} \tag{7}$$

where, from 3 and 6,

$$\lambda_{0,i} = G_{1-0}{}^{\text{op}} - G_{1-0}{}^{\text{F}} \tag{8}$$

We now consider the situation in the frozen medium. In ref 4, the initial system was prepared at some pressure P_e just below the pressure P_F required for freezing. Some of the nuclear motions in the liquid adapt themselves at P_e to the charge distribution ρ_0, and their behavior is presumably only slightly altered by the freezing. Thus, the $\lambda_{0,0}$ which will appear below in the expression for $h\nu_\alpha$ in the frozen medium will be that at this pressure P_e, rather than at the prevailing pressure P. Similar remarks apply to the glassy system in ref 6, where part of the nuclear motion in the frozen system adapted itself to ρ_0 at a temperature T_e just above the glass transition temperature T_g.

Both these experiments can be treated then, at any T and P, by using eqs 2, 7, and 8 for the frozen medium, but with $\lambda_{0,0}$ replaced by its value at the equilibration condition (T_e,P_e). Thereby, we have

$$h\nu_a(T,P) = \lambda_{0,0}(T_e,P_e) + \lambda_{0,i}(T,P) + \lambda_i(T,P) + \Delta G^\circ(T,P) \quad \text{(frozen)} \tag{9}$$

We consider next the fluorescence. The Stokes shift is twice that part of λ which relaxes (this result is implicit in refs 2 and 9), and the latter equals $2(\lambda_{0,i} + \lambda_i)$ in the frozen solvent case, since the $\lambda_{0,0}$ no longer participates in the relaxation. Thus,

$$h\nu_f(T,P) = \lambda_{0,0}(T_e,P_e) - \lambda_{0,i}(T,P) - \lambda_i(T,P) + \Delta G^\circ(G,P) \quad \text{(frozen)} \tag{10}$$

Equations 9 and 10 neglect changes, if any, in the orientations of the solvent dipoles during the actual solidification of the solute–solvent system. They also presume a situation in which the lifetime of the excited electronic state in the frozen medium is not long enough for solvent orientation relaxation to occur. The equations are applied in the next section.

Applications

We first use eqs 6 and 8 to obtain values of $\lambda_{0,0}$ and $\lambda_{0,i}$ for two commonly used models. For the two-sphere model which led to eq 4, eqs 6 and 8 yield, as in the Appendix

$$\lambda_{0,0} = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{\text{s,F}}} - \frac{1}{D_{\text{s}}}\right) \tag{11}$$

$$\lambda_{0,i} = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{s,F}}}\right) \tag{12}$$

and $D_{\text{s,F}}$ is the static dielectric constant of the frozen phase. To obtain added insight into the various physical contributions to $D_{\text{s,F}}$ it would be useful to compare in each case this static value with the value of the dielectric constant D_{ir} of the liquid in the infrared region near the phase transition point. (See, however, ref 7 for the case of the ice–water phase transition.)

Another commonly used model is that of a dipole in a sphere, used for example in ref 6 for metal to ligand charge-transfer absorption and emission and used in many other situations.[1,2] In that model, λ_0 is given by[1,2,6]

$$\lambda_0 = \frac{(\Delta\mu)^2}{a^3}(f(D_{\text{op}}) - f(D_{\text{s}})) \tag{13}$$

where $\Delta\mu$ denotes the vector difference of dipole moments between the initial and final electronic states, the solute molecule is treated as a sphere of radius a, and

$$f(D) = -\frac{D-1}{2D+1} \tag{14}$$

Once again, λ_0 would be written as in eq 5, where now

$$\lambda_{0,0} = \frac{(\Delta\mu)^2}{a^3}[f(D_{\text{s,F}}) - f(D_{\text{s}})] \tag{15}$$

$$\lambda_{0,i} = \frac{(\Delta\mu)^2}{a^3}[f(D_{\text{op}}) - f(D_{\text{s,F}})] \tag{16}$$

We consider next some applications of the preceding results.

For the charge-transfer absorption maximum in eq 1, we compare eqs 2 and 7 with eq 9, noting that $\lambda_{0,0}$ is the same for both liquid and solid phases and that $\lambda_{0,i}$ and λ_i are expected to vary relatively little with pressure in the immediate vicinity of P_F. It follows from these equations that $h\nu_\alpha$ should be essentially unchanged by the phase transition at $P = P_F$. This result was, in fact, the one discovered experimentally by Hammack et al.[5]

We consider next the data of Worl and Meyer.[6] They studied the metal to ligand charge-transfer spectrum, $d_\Pi(\text{Re}) \rightarrow \Pi^*(\text{bpy})$, for the molecule $(\text{bpy})\text{Re(CO)}_3\text{Cl}$:

$$(\text{bpy})\text{Re}(d_\Pi)(\text{CO})_3\text{Cl} \xrightarrow{h\nu_a} (\Pi^*\text{bpy})\text{Re}(\text{CO})_3 \tag{17}$$

They found that the absorption spectrum maximum ν_a in an ethanol–methanol medium was largely the same at temperatures just above and just below the glass transition temperature T_g. The fluorescence maximum ν_f, however, did change. From their data an estimate can be made of some λ's: The fact that $h\nu_a$ was largely unchanged when T was lowered below T_g has, as Worl and Meyer noted,[6] an explanation similar to their explanation for the similar result of Hammack et al.[5] for the ν_a of the process in eq 1 and is consistent with eqs 2, 7, and 9. We consider next the Stokes shift $h\nu_a - h\nu_f$. For temperatures below T_g in ref 6 it was ca. 8400 cm^{-1}, while above T_g it was about 10 800 cm^{-1}. The Stokes shift for the frozen medium is, according to eqs 9 and 10, $2(\lambda_{0,i} + \lambda_i)$, so that $\lambda_{0,i} + \lambda_i$ equals 4200 cm^{-1}. Above T_g the Stokes shift equals, according to eqs 2, 7, and 10, $2(\lambda_{0,0} + \lambda_{0,i} + \lambda_i)$. Thus, $\lambda_{0,0}(T_e)$ is about (1/2)(10 800 − 8,400) or 1200 cm^{-1} for this system. The relative values of $\lambda_{0,0}$ and $\lambda_{0,i}$ can be estimated by using a model such as that given in eqs 14–16 when D_{op}, $D_{\text{s,F}}$, and D_{s} are all known, where $D_{\text{s,F}}$ is the static dielectric constant of the glass, a 4:1(v/v) ethanol:methanol system. In the particular case that $D_{\text{s,F}}$ is about twice D_{op} and that $D_{\text{s}}(T_e)$ is much larger than both, $\lambda_{0,0}$ and $\lambda_{0,i}$ would be comparable in value., namely roughly 1200 cm^{-1}. In that case, the above results would yield a $\lambda_i \sim 3000$ cm^{-1}. However, to obtain an improved value for λ_i, measurements of the D's for the actual solvent system are needed.

With modern experiments involving femtosecond and picosecond techniques, it may also be possible to obtain some of the λ's independently. For example, when the two given electronic states are involved in both the absorption and the fluorescence, the Stokes shift $h\nu_\alpha - h\nu_f$ for times before "orientational" relaxation in the polar liquid occurs will equal a quantity which can be called $2(\lambda_{0,i}{}^{\text{ir}} + \lambda_i)$. This $\lambda_{0,i}{}^{\text{ir}}$ is given by eq 8 but with $G_{1-0}{}^{\text{F}}$ replaced by $G_{1-0}{}^{\text{ir}}$, the solvational free energy when only the vibrational and electronic polarization of the liquid have responded to $\rho_1 - \rho_0$. (E.g., in eqs 12 and 16 $D_{\text{s,F}}$ is replaced by the dielectric constant D_{ir} of the liquid in the infrared region.) This Stokes shift can then be compared with that found at more conventional times in frozen media, $2(\lambda_{0,i}$

+ λ_i), for the same system, to see if they are comparable. In the case of an ice–water system[10] the two Stokes shifts would be expected to differ, since the value of D_{ir} for the liquid is ∼4–5 (e.g., for times shorter than ∼3 ps[9]). This D_{ir} is very different from the D_s of ice of 90 or more.[7]

On a related point it is interesting to inquire whether for a mixed-valence complex for which $\Delta G° = 0$, such as in eq 1, it would be possible to observe fluorescence on the usual time scale, in frozen media. (Only a two-electronic-state system is considered here. Rapid internal conversion to a third state by successful competition with the above relaxations could also yield an emission.) According to eq 10 fluorescence at the usual (nanosecond) observational time would occur if $\lambda_{0,0}(T_e,P_e)$ exceeded $\lambda_{0,i} + \lambda_i$, the latter evaluated at (T,P) in the frozen system. For nitrobenzene,[5] $D_s = 36.4$ and $D_{s,F} = 3.37$. D_{op} for the solid at the temperature studied (25 °C) is apparently not known,[5] but that of the liquid is estimated to increase by perhaps 14–28% on freezing.[5] If it is about 3.0, eqs 11 and 12 would yield $\lambda_{0,i}/\lambda_{0,0} \sim 0.2$. For fluorescence to be observable in the frozen case, and indeed in picosecond or subpicosecond experiments for the liquid, the λ_i in eq 10 would need to be small enough in the system studied. Weakness of the electronic coupling in the mixed-valence complex, and competition with nonradiative processes, might also make observation of the fluorescence difficult.

We have not considered in the calculations here of the Stokes shift $h\nu_\alpha - h\nu_f$ a situation which sometimes occurs: The final charge distribution in the absorption may differ from the initial charge distribution in the emission. Such differences can occur either because emission results from some third electronic state or because the environmental relaxation has modified the postabsorption charge distribution due to a mixing with a nearby electronic state. Some evidence for the latter appeared in the work of Drickamer and co-workers[11] in which they found changes in the radiative decay constant at $P = P_F$, particularly with polar solvents, that were not explained by changes in refractive index alone.[11]

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Appendix. Derivation of Eqs 11, 12 and 15, 16

As an example we use eq 6 to derive eq 11 (compare also ref 2). For a two-sphere system we denote the initial charges by e_1^r and e_2^r (this is state 0) and the final charges by e_1^p and e_2^p (state 1). Then the charge density $\rho_1 - \rho_0$ corresponds to $e_1^p - e_1^r$, which we shall call Δe, for the first ion, and $e_2^p - e_2^r$, which is $-\Delta e$, for the second ion.

Then G_{1-0} is given by

$$G_{1-0} = -\frac{(\Delta e)^2}{2a_1}\left(1 - \frac{1}{D_s}\right) - \frac{(\Delta e)^2}{2a_2}\left(1 - \frac{1}{D_s}\right) - \frac{(\Delta e)^2}{D_s R} \qquad (A1)$$

where the first term is the Born solvation free energy of ion 1 having a charge density ρ_{1-0}, the second is that of ion 2 with its ρ_{1-0} charge density, and the last term is the Coulombic interaction between two such charges. G_{1-0}^F is the same as in eq A1 but with D_s replaced by $D_{s,F}$. Equation 11 immediately follows from eqs 6 and A1.

For the solvation free energy G of a dipole μ in a medium of dielectric constant[12]

$$G = -\frac{\mu^2}{a^3}\,\frac{D - 1}{2D + 1} \qquad (A2)$$

and μ^2 is $\mu\cdot\mu$. With the replacement of μ by $\mu_1 - \mu_0$ and D by, respectively, $D_{s,F}$ and D_s, eq 16 follows from eqs 6 and A2.

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(10) Hasted, J. B. Reference 7, p 295.

(11) Salmon, O. A.; Drickamer, H. G. *J. Chem. Phys.* **1982**, *77*, 3329, 3337. Cf., also: Politis, T. G.; Drickamer, H. G. *Ibid.* **1981**, *75*, 3203.

(12) E.g.: Böttcher, C. J. F. *Theory of Electrical Polarization*; Elsevier: Amsterdam, 1973; p 145, which also includes the case of a polarizable point dipole.

Convective Effects on Chemical Waves. 1. Mechanisms and Stability Criteria

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We consider the effects of convection on chemical waves in which density gradients result from the exothermicity as well as from the isothermal volume change of the reaction. If the signs of the enthalpy (ΔH) and volume (ΔV) of the reaction are opposite, then simple convection will occur, and the increase in the front propagation velocity will be equal to the velocity of the convective fluid flow. If the signs are the same, then simple convection will not occur. Instead multicomponent convection may be present, even though the overall density gradient may appear to be stable. The stability conditions for both mechanisms as functions of ΔH and ΔV and of the direction of front propagation (ascending, descending or horizontal) are analyzed. The effect upon the form of the wave front is also described. We also analyze convection in horizontally and vertically propagating trigger waves in the Belousov–Zhabotinskii reaction.

I. Introduction

An autocatalytic reaction in an unstirred vessel can support a constant-velocity wave front resulting from the coupling of diffusion to the chemical reaction. A flame front is a common example in which heat is the autocatalytic species that diffuses into unreacted regions, stimulating a reaction that produces more heat. Numerous reactions in solution have been described in which a front of chemical reactivity propagates through the medium from the site of an initial concentration perturbation.[1-10]

Such behavior can play an important role in testing reaction mechanisms. For example, observations of wave front velocities

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