A-3

INTERGROUP ELECTRON TRANSFER, BACK ELECTRON TRANSFER, BACK TRANSFER QUENCHING, AND RELAXATION PROCESSES

Ron Kosloff
Department of Physical Chemistry, Hebrew University, Jerusalem, Israel

Mark Ratner
Department of Chemistry and Materials Research Center
Northwestern University, Evanston, IL 60201

ABSTRACT

For use as switching devices or as photoelectric energy converters, molecular systems must be susceptible to control of the back electron transfer rates. In natural systems (photosynthetic reaction centers), the back transfer reaction is at least 10^7 times slower than the downhill electron transfer process, but the precise roles of the quinones, chlorophylls, iron atoms, and pheophytins in controlling these relative rates are poorly understood. We focus on a much more narrowly defined theoretical problem: how to calculate rates of electron transfer between localization sites in a generalized molecular crystal model.

The model system which we consider is then one with two electron localization sites linked by a bridge (thus providing both through-bond and through-space interactions). The localization site is coupled to local vibrons through both linear (Frohlich-type) and quadratic (frequency-change) terms. This is a variation of the Holstein molecular crystal model. It is clear that a fourth timescale (other than those fixed by the vibrational frequency, the electronic coupling term, and the barrier residence time) must enter into the problem and that this relates to the relaxation processes which occur on the localization site. Once the electron has been localized at one site, it will (within the simple molecular crystal model) continue to undergo multiply periodic motions. Thus the back transfer rate, within this model, will be identical to the forward transfer rate. The achievement of switching or of photoelectric conversion is thus critically dependent upon a relaxation process, which must intervene so as to prevent the back transfer. This relaxation may be provided, for example, by diffusion, by electron energy decay in bent bands, by rapid intramolecular geometric changes (such as proton tautomerism) by strain release or by allosteric interactions.

Our calculations are performed using a semigroup approach to reckon the relaxation effects. This has several advantages over more commonly used

decoupling approximations: it is not dependent upon the assumption of weak coupling, it can include very high-order relaxation processes, and it is formally correct even when relaxation effects are stronger than the mixing terms in the molecular Hamiltonian.

Some of the results of our calculation are not unexpected: when relaxation is ignored, the Robin/Day model valency classifications and the Goodenough criterion for delocalization are recovered. Simple choices of relaxation widths reproduce the intervalence transfer line shapes given by Hush. More generally, however, we predict structure in the intervalence band and, more strikingly, in the vibrational bands. The dependence of these shapes on temperature, frequency, and coupling strength is derived straightforwardly. The Robin/Day classification must be broadened to include relaxation effects, and we can explain how systems may vary from Robin/Day II (partly delocalized) to Robin/Day III (fully delocalized) as a function of solvent, surrroundings, or temperature. Finally, and most suggestively for the purposes of this meeting, we can derive criteria for when the back-transfer process will become negligible; essentially what is required is relaxation slow enough to permit some transfer, but fast enough to damp the periodic motions effectively.

I. INTRODUCTION: THE ROLE OF BACK-TRANSFER PROCESSES IN QUENCHING

For use in molecular device applications, we require molecular species which exhibit either a charge-transfer or an energy-transfer process which can be controlled selectively. We will be concerned here primarily with electron transfer and photoexcited electron transfer processes, though similar phenomena and similar theoretical problems are encountered in proton transfer systems [1-3]. Although their application to switching devices ("rectifiers") remains uncertain [3,4], ground-state intramolecular electron transfer processes have elicited a great deal of experimental and theoretical study [5-9] in both biochemical [10] and chemical species, and a good deal is now known concerning the relevant transfer rates. Even more recently, a significant literature has been developing on the subject of excited-state electron transfer phenomena, first because of their role as quenchers of photo-excited states [11], and later because of their application to photovoltaic and photochemical energy conversion [12-14]. Both the rectification and the photoconversion applications lie clearly within the purview of this conference, and both can be vitiated if the back transfer event is not either eliminated or significantly reduced.

As an example, consider [4] the schematic rectifier circuit of reference 4; if the transfer event through the barrier between the acceptor (A) and donor (D) ends is fast enough, the molecular orbitals appropriate for discussion of electron transfer between an external circuit and either D or A ends will be linear combinations of the A and D local orbitals, and no rectification property will occur.

Similarly, Grätzel and co-workers [12] have investigated the photolysis of H_2O in a sensitized system containing methylviologen and ruthenium tris bipyridyl: they point out that "if the chemical potential of A^- and D^+ is to be used in subsequent fuel-generating proceses, it is mandatory to prevent or retard the energy-wasting back-reaction". We review their chemistry in equations (1-5):

$$S^{++} + CMV^{++} \xrightarrow{h\nu} S^{+++} + CMV^{+} \tag{1}$$

$$4S^{+++} + 2H_2O \longrightarrow 4S^{++} + 4H^{+} + O_2 \tag{2}$$

$$\underline{4CMV^{+} + 4H_2O \longrightarrow 4CMV^{++} + 2H_2 + 4OH^{-}} \tag{3}$$

$$4S^{+++} + 4CMV^{+} + 2H_2O \longrightarrow 4S^{++} + 2H_2 + 4CMV^{++} + O_2 \tag{4a}$$

$$2H_2O \xrightarrow{h\nu} 2H_2 + O_2 \tag{4b}$$

$$S^{+++} + CMV^{+} \longrightarrow S^{++} + CMV^{++} \text{ spoiler} \tag{5}$$

The sensitizer S^{++} is $Ru(bpy)_3{}^{++}$, while CMV is a methylviologen. The photoexcitation process (1) produces ionic species which (2,3) have proper redox potentials to oxidize and reduce water; the overall process starting from the photoexcited state (4a) splits water in going to the ground state, while the overall cyclic reaction (4b) is simply catalyzed photolysis of water. But if the backtransfer reaction (5) is not considerably slower than (2,3), the photolysis quantum yield will be small.

Experimentally, a number of techniques have been suggested to reduce the interfering back-transfer rates. For ground-state electron transfer systems, these have stressed the nature of the "tunneling barrier" between D and A, either in isolated molecules [4-9] or in monolayer assemblies [18]. In phototransfer, a number of rather specific schemes have been suggested, mostly involving phase barriers, and including the use of vesicles [14], micelles [18], chemical interception [17], monolayer assemblies [19,20], electrode processes [16], and even rapid reorientation [3]. From a theoretical viewpoint, the first group of schemes (barrier manipulation) can be thought of as a variation in the off-diagonal (mixing) matrix element between the two localized orbitals [5-9], while the second group (interception of the initially-transfered state) corresponds to an irreversible relaxation process which the transfer state undergoes. Although a great deal of theoretical effort has been expended in examination of the role of the mixing term [7], very little has been devoted to the relaxation effect [21]. The present paper examines how relaxation can affect both the transfer rates themselves and the experiments which probe them, particularly spectroscopic studies [6]. The relaxation processes introduce into the problem a fourth timescale beyond the three which occur in the usual polaron theory of electron transfer and in so doing they totally change the theoretical decription, just as they totally change the experimental behavior.

II. THEORETICAL DESCRIPTION OF TRANSFER DYNAMICS: CLASSIFICATION AND MODEL

The rates of intramolecular electron transfer have been addressed largely in the same language as intermolecular transfer [22], and while this should be appropriate in the case for which the rates are relatively slow, the more rapid process involved in average-valency systems requires a more general discussion including so-called nonadiabatic effects [22,23]. A useful classification was originally put forward by Robin and Day [5,24] in considering mixed-valency species. They defined class I compounds as those in which the two types of a given ion have distinct, different valence states, such as the two Ga species (Ga^{III} in tetrahedral sites, Ga^{I} in dodecahedral coordination) in $GaCl_2$. Class II behavior is exhibited by species in which the sites are similar but distinguishable; an example is provided by the two Sb sites in Cs_2SbCl_6, and these are properly called mixed-valent. Class III systems do not have distinguishable valence states; all ions behave identically, and the correct description is in terms of average valence. A standard example is provided by Krogmann's salt $K_2Pt(CN)_4Br_{.3}\cdot 3H_2O$, although several others of the charge-transfer reduced-dimensionality conductors are perhaps best thought of as average-valent [25]. A number of experimental probes have been used to study the mixed-valency species, and although class I materials are easily distinguished, the distinction between classes II and III is more difficult, and has been subject to a great deal of discussion [26]. The mixed-valence problem is highly appropriate for a discussion of back-transfer and molecular device applications, since if effective class III behavior obtains, the redox potential of the molecule will be isotropic and no rectification can be obtained (analogously, for proton transfer, a class III situation would correspond to the proton entirely delocalized along the A-H---B bond, as apparently occurs for most "strong" hydrogen bonds) [27]. For the rectification problem, then, we require a theoretical characterization in terms of the rate of intramolecular electron transfer [4]. For the excited back-transfer photoconversion devices, on the other hand, the transfer process is generally intermolecular, and simple joint diffusion of D^+ and A^- can provide the needed relaxation. (An alternative description of the transfer process can be given in terms of a pseudo-Jahn-Teller effect, in which localized sites are mixed by vibronic coupling. This model has been applied both to the electron transfer [23] and to the proton transfer [28] problems, but the important effects of relaxation have not been included.)

Experimentally, these transfer rates can be measured in favorable circumstances [29,12], but it would be very useful to have a theoretical construct which both predicts the transfer rates and relates them to experimental quantities which are easily measured (vibrational spectra, photoemission, Mossbauer, magnetic resonance) [26]. We would also like to use the theory to help design the components of a rectifier or photovoltaic/photochemical device pathway by pinpointing which characteristic parameters determine the transfer rates. In a typical experiment, for instance, Tom and Taube examine [6] the infrared behavior of $[(NH_3)_5RuNCCNRu(NH_3)_5]^{+5}$. The C≡N stretch, which is seen at 1960 cm^{-1} in the Ru^{II} species and at 2330 cm^{-1} in Ru^{III}, is measured at 2210 cm^{-1} in the mixed-valent bisruthenium complex, and this was used to argue [6] that the species is of Robin/Day Class III, since the electron is delocalized on a timescale of $(\Delta\omega)^{-1} \sim 10^{-13}$ sec. This sort of argument is attractive and is often valid, but it can be misleading, since full delocalization cannot be distinguished from rapid transfer between truly distinct sites simply by observation of the lineshape, and since relaxation effects can produce an averaged lineshape even in weakly mixed systems. In iron acetates, for example, recent work by Brown [30] shows that the Mossbauer line narrows from that corresponding to distinguishable sites to that of average valency as the temperature is raised. We should like our theory to treat the thermal effects on the transfer rates as mirrored in the lineshape.

From the viewpoint of molecular device design then, a theoretical description which includes relaxation, transfer, and vibronic coupling should permit the prediction of device characteristics (such as I/V characteristic [4] for a rectifier or the photoconversion quantum yield for a photoconverter) in terms of simple parameters characterizing the molecular subunits and surroundings. Although several theoretical discussions are available [7-9], they have not included relaxation properly, and therefore cannot correctly describe either lineshapes or the effects of the surroundings (and such important experimental variations as traps, micelles, or electrodes) on the transfer processes. We therefore give here a very simple model description for the transfer of an excitation in a homonuclear mixed-valency-type system (it could, for instance, describe optical transfer in bisruthenium systems or in oligomer subunits of one-dimensional conducting polymers or be slightly generalized to include site inequivalence, forward and backward currents in a rectifier molecule).

Our theoretical discussion of back-transfer rates then must include the local site energies of the electron or hole, the tunneling interaction between D and A sites, the vibrational motion of the ligands about a localization site, the local trapping of the valences by geometry changes in the coordination sites and local selective solvation, the changes in frequency about local sites caused by variation in effective charge as electrons transfer, and the relaxation processes which interfere with back-transfer. Adopting a one-orbital localization site model which is assumed coupled to one local vibration, the molecular hamiltonian to describe transfer may be minimally reduced to

$$H = H_{el} + H_{vib} + H_{coup} \tag{6}$$

$$H_e = E_a\sigma_a^z + E_b\sigma_a^z + t(\sigma_a^+\sigma_b^- + \sigma_b^+\sigma_a^-) \tag{7}$$

$$H_{vib} = (b_a^+b_a + 1/2)\Omega_a + (b_b^+b_b + 1/2)\Omega_b \tag{8}$$

$$H_{coup} = \gamma_a\sigma_a^z(b_a^+ + b_a) + \mu_a\sigma_a^z(b_a^+b_a) + \gamma_b\sigma_b^z(b_b^+ + b_b) + \mu_b\sigma_b^z(b_b^+b_b). \tag{9}$$

Here the electronic states on D,A are limited to two, so that the motion of an electron can be defined by spin operators. Constant terms have been omitted from (9), in which σ_a^z measures the number of excited electrons at site a, while σ_a^z promotes an electron from the ground to the excited orbital at site a. The second term describes the motion of an exciton (or of an electron in the excited state) between site a and site b. The parameter E_a is the HOMO-LUMO energy difference (roughly the optical excitation frequency) at site a, and the parameter t measures the strength of the tunneling interaction between a and b; if it is much greater than $\gamma_a{}^2/\Omega_a$, one expects the exciton to be delocalized (in the absence of relaxation) [9,31]. Thus H_{el} models an excited electron hopping between two localized excitation sites. The vibrational frequency at site a is Ω_a, and the operator $b_a{}^+$ creates one quantum of vibrational excitation at site a. The coupling term proportion to γ_a is the Frohlich linear electron-vibron coupling [32] which is responsible for metallic resistivity; it is proportional to the population of excited electrons at a given site times the vibrational displacement at that site, and is responsible for the Stokes spectral shift. Finally, the μ_a term describes the change in the vibrational energy at site a due to the presence of the excited electron. For hexammineruthenium, Ω is roughly 440 cm^{-1} and μ_a roughly 60 cm^{-1}.

(One major failing of the model (6) is that the electron density is never considered fixed on the tunneling bridge. There is experimental [6] and calculational [23] data indicating that in several Robin/Day II or III binuclear metal complexes the electronic orbitals can contain significant contributions from the bridge. Under these conditions, a more complex four-site or five-site model is useful [23]).

The hamiltonian (6) is closely related to the usual Holstein-Fröhlich molecular crystal model for electron transfer [32]. Generally one expects [9,31] localization for $\gamma^2/\Omega >> t$, delocalization for $t >> \gamma^2/\Omega$, and Robin/Day II behavior for $\Omega t \sim \gamma^2$. But such predictions can be very significantly altered by inclusion of relaxation phenomena.

III. RELAXATION EFFECTS. LINESHAPE FORMULAS.

The theoretical problem involved in the characterization of the relaxation processes is straightforward: since relaxation processes generally do not conserve the value of the energy in the hamiltonian subsystem (such as the two-site model of [6]), their effects must be reckoned differently. Although there exist a number of ad hoc or weak-coupling-limit procedures for including the effects of relaxation, the treatments of electron transfer usually neglect such terms entirely. There exists a rigorously correct method for calculating relaxation effects, which is based on a semigroup formalism and was first developed by Sudarshan [33], it is described more completely elsewhere [21,34]. If the relaxation process couples linearly to a (linear or nonlinear) hamiltonian variable V of the system, a relaxation time dependence is introduced, and the equation of motion for the dynamical variables becomes:[21]

$$\frac{dX}{dt} = i[H,X] + g\{VXV^+ - 1/2[VV^+,X]_+\} , \qquad (10)$$

where the first term is the ordinary Heisenberg evolution and the second term is the relaxation contribution; the parameter g is a strength which is nonnegative and can be evaluated in certain limits [21].

Equation (10) gives the dynamical behavior which will characterize experimental measurements of the system. The vibrational lineshape I and intramolecular electron transfer rate k are given from linear response theory by [35]

$$I(\omega) = \mathrm{Re}\int_0^\infty \exp -i\omega t \, \langle \dot{m}(t)\dot{n}(0)\rangle \, dt \tag{11}$$

$$k = \int_0^\infty \langle \dot{\sigma}_a{}^z(t) \, \dot{\sigma}_a{}^x(0)\rangle \, dt, \tag{12}$$

where the brackets indicate thermal averages and dots mean time derivatives; m is the dipole moment operator, which (if we neglect electrical anharmonicity) is proportional to vibrational displacement. Formally, then, we need merely solve the equations of motion (10) to find the correlation functions (11,12) for the model of (6). We take m proportional to $b^+ + b$, so that $I(\omega)$ can be found from solving for b(t).

The equation of motion for b, however, will involve higher-order operators on the right side, and the exact dynamics of the system [6,10] then becomes an infinite set of coupled equations. For simplicity, we assume that the relaxation process is caused by terms which couple linearly to the vibron displacement $(b^+ + b)$ and to the excitation operators $\sigma_a{}^\pm, \sigma_b{}^\pm$ (the former might correspond to a solvent quenching, and the latter to a redox process of the type indicated in eqns. (2,30). Under these conditions, the relaxation parts of the equations of motion are

$$\dot{b}^{\pm}_{rel} = -\Gamma_b$$

$$\dot{\sigma}^{\pm}_{rel} = 1/2(\alpha\pm\beta)\sigma^{\pm}$$

where the parameters α, β, Γ relate to the strengths of the relaxation processes. To solve for b, then, we perform an approximate decoupling in the vibron manifold:

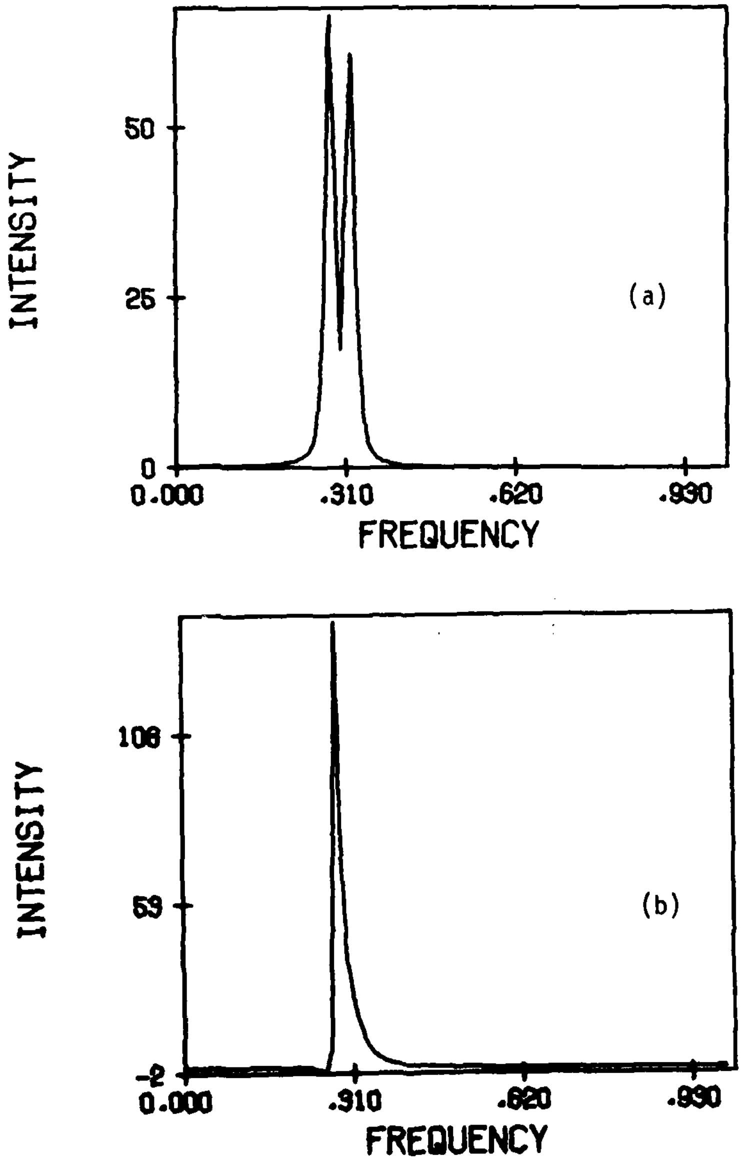
$$b_i{}^+ b_j b_k \cong \langle b_i{}^+ b_j\rangle b_k \tag{13}$$

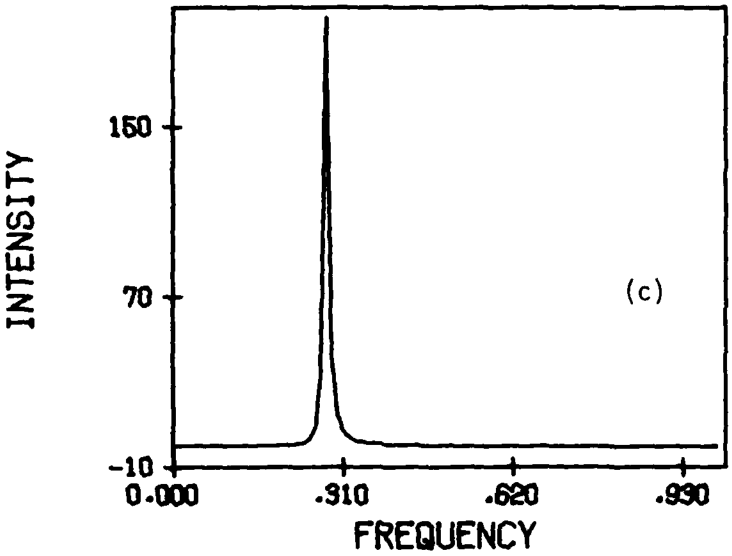
This decoupling is consonant with the thermal character of the vibron average. With the decopuling (and, for simplicity, ignoring the linear coupling γ terms of (6)), the equation of motion for b_a becomes closed in a space of six operators: b_a, $b_a\sigma_a{}^z$, $b_a\sigma_a{}^+\sigma_b{}^-$, $b_a\sigma_a{}^-\sigma_b{}^+$, $b_a\sigma_b{}^z$, $b_a\sigma_a{}^z\sigma_b{}^z$. This set of six linear coupled equations of motion can be solved by Fourier inversion and matrix diagonalization techniques, the details are given elsewhere [34].

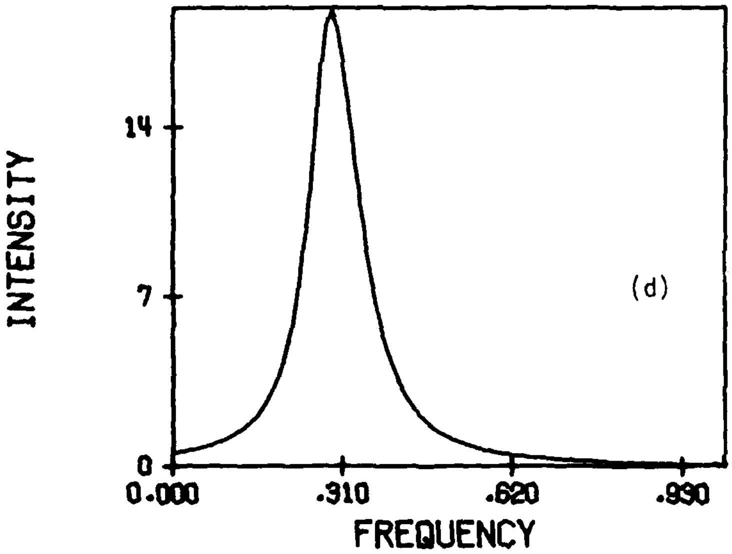
IV. RELAXATION EFFECTS, LINESHAPES, AND REMARKS

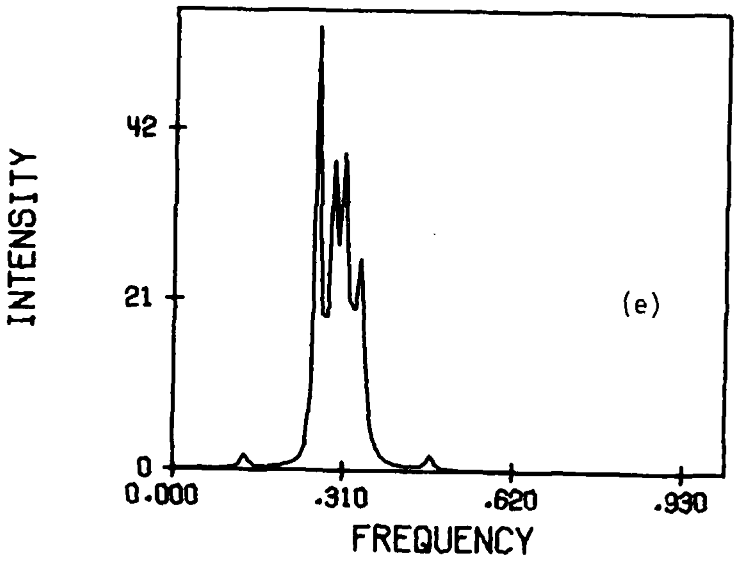
We have solved for the lineshapes $I(\omega)$ using the procedures outlined above, and present some of our computed lineshapes in figure 1. Because of the truncation (13), only six operators enter the equations of motion, and one expects at most six peaks in the vibrational lineshape. The problem is

Fig. 1. Computed vibrational lineshapes, from (6,10). The splitting of the vibrational fundamental in (a) is due to the μ coupling of (9). It collapses into a single line in (b) due to rapid exchange (the parameter t has been increased by a factor of 8), but exhibits comparable narrowing in (c) due only to relaxation (α,β were increased by a factor of 100). This can be distinguished from simple vibron lifetime broadening which is shown in (d), where Γ was increased by a factor of 10. In (e), the μ has been increased by a factor of 2 and (α,β) decreased by a factor of 10, compared to (b); it shows the full six-peak feature. Parameters for (a): $E = 1$, $\Omega = .3$, $\mu = .04$, $t = .01$, $\Gamma = .005$, $\alpha = \beta = .0001$, $T = .003$.




INTENSITY
160
70
-10
0.000
.310
.620
.930
FREQUENCY
(c)


INTENSITY
14
7
0
0.000
.310
.620
.930
FREQUENCY
(d)


42
21
0
INTENSITY
(e)
0.000
.310
.620
.930
FREQUENCY

characterized by the parameters Ω, E, t, μ, T, Γ, α, β; we choose α,β via

$$\alpha,\beta = \tau_2(T)^{5/2}(1\pm\exp -\Omega/T),$$

where the $T^{5/2}$ is a state density factor and τ_2 is a strength caused by relaxation processes of the excited electron. We present here some lineshapes for the model coupled-exciton problem; transfer rates for this system, as well as for the more interesting linearly-coupled electron transfer (rectification) problem will be published elsewhere [34].

The lineshapes show several interesting features. When t is very small, the central line about the frequency Ω splits into doublets at $\Omega\pm\mu/2$, for $T \ll E$; this is the frequency shift caused by the electron localization, and is analogous to the Ru^{II}/Ru^{III} frequency differences mentioned above. As t increases, these lines collapse into a single line at Ω; this is the behavior which Taube invokes [6] to claim Robin/Day III classification (or at least very fast transfer in a Class II system) for the cyanogen-bridged Ru_2^{5+} species discussed above. But note that a similar lineshape can be produced merely by relaxation effects; raising the temperature or lowering the relaxation time for the vibron can cause lineshapes extremely similar to that of true motional narrowing. Thus although Taube's assignment of average valence to the cyanogen-bridged mixed valence Ru species is probably correct, it is not valid to make such assignments on lineshape alone

The formal dynamics of the model (6) are not in themselves important. What is important is that the semigroup formalism allows for inclusion of relaxation processes into the calculation of rates of electron transfer processes, as well as the associated spectra. In so doing, it introduces a new time scale, the relaxation time, which can in some cases redefine the notion of localized or delocalized behavior. By predicting the transfer rates based on (10), we should be able to understand how the rates depend on tunneling barriers, trapping and quenching, and the other experimental system-surroundings interactions discussed above, and also to see how the experimental lineshapes reflect the true intramolecular dynamics. In this way, the formal transfer theory presented here may help [3] to build a better rectifier, proton storage bit, or photon trap.

ACKNOWLEDGMENTS

R.K. is grateful for the grant of a Weizmann Fellowship, and M.R. thanks the Chemistry Division of the National Science Foundation for partial support.

REFERENCES

1. P.-O. Lowdin, Adv. Quantum Chem. 2, 216 (1965); A. Aviram, P. E. Seiden, and M. A. Ratner, this conference, and references therein.

2. C. A. Taylor, M. A. El-Bayoumi, and M. Kasha, Proc. Nat. Acad. Sci. 63 253 (1969); M. Kasha, personal communication.

3. F. L. Carter, N.R.L. Memorandum Report 3960 (1969), 4335 (1980).

4. A. Aviram and M. A. Ratner, Chem. Phys. Lett. 29, 277 (1974)

5. M. B. Robin and P. Day, Adv. Inorg. Radiochem. 10, 247 (1967); N. S. Hush, Prog. Inorg. Chem. 8, 357 (1967).

6. G. M. Tom and H. Taube, J. Am. Chem. Soc. 97, 5130 (1975); H. Krentzein and H. Taube, ibid. 98, 6379 (1976) and many related papers. Also T. J. Meyer, in ref. 8 and references therein.

7. K. Y. Wong, P. N. Schatz, and S. B. Piepho, J. Am. Chem. Soc. 101, 2793 (1979); P. N. Schatz, Prog. Inorg. Chem., in press.

8. D. B. Brown, ed., "Mixed-Valence Compounds", Reidel, Dordrecht, 1980.

9. M. A. Ratner and M. J. Ondrechen, Mol. Phys. 32, 1233 (1976); J. Chem. Phys. 66, 938 (1977); M. A. Ratner, Int. J. Quantum Chem. 14, 675 (1978); M. J. Ondrechen, M. A. Ratner, and J. R. Sabin, J. Chem. Phys. 71, 2244 (1979). The notions were pioneered by J. Halpern and L. E. Orgel, Disc. Far. Soc. 29, 32 (1960).

10. G. R. Moore, R. J. P. Williams, Coord. Chem. Revs. 18, 125 (1976); E. G. Petrov, Int. J. Quantum Chem. 16, 133 (1979).

11. D. Rehm and A. Weller, Israel J. Chem. 8, 259 (1970); M. T. Indella and F. Scandola, J. Am. Chem. Soc. 100, 7733 (1978); J. Erikson and C. S. Foote, J. Phys. Chem. 82, 2659 (1980; N. Agmon and R. D. Levine, Chem. Phys. Lett. 52, 197 (1977).

12. P. A. Brugger, P. P. Infelta, A. M. Braun, and M. Grätzel, J. Am. Chem. Soc. 103, 320 (1981) and references therein.

13. E. Schumacher, Chimia 32, 193 (1978).

14. W. E. Ford, J. W. Otvos, and M. Calvin, Proc. Nat. Acad. Sci. 76, 3590 (1979).

15. C. Creutz and N. Sutin, Proc. Nat. Acad. Sci. 72, 2858 (1975).

16. M. Wrighton, Acc. Chem. Res. 12, 303 (1979).

17. S. J. Milder, R. A. Goldberg, D. S. Kliyer, and H. B. Gray, J. Am. Chem. Soc. 102, 6761 (1980).

18. H. D. Abruna, P. Denisevitch, M. Umana, T. J. Meyer, and R. W. Murray, J. Am. Chem. Soc. 103, 1 (1981).

19. H. Kuhn, J. Photochem. 10, 111 (1979).

20. H. Gerischer and J. J. Katz, Eds., "Light-Induced Charge Separation in Biology and Chemistry," Verlag Chemie, New York, 1979.

21. R. Kosloff and S. A. Rice, *J. Chem. Phys. 72*, 4591 (1980).

22. W. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald, New York, 1966; R. A. Marcus, *Ann. Revs. Phys. Chem. 15*, 155 (1966).

23. J. Linderberg and M. A. Ratner, *J. Am. Chem. Soc.*, in press.
D. E. Ellis, M. J. Ondrechen and M. A. Ratner, to be published.

24. P. Day, in ref. 8.

25. C. J. Schramm, D. R. Stojakovic, B. M. Hoffman, T. J. Marks, *Science 200*, 47 (1978); *J. Am. Chem. Soc. 99*, 280 (1977) and related work.

26. A. Ludi, in ref. 8; N. S. Hush, in ref. 8; N. S. Hush, A. Edgar, and J. K. Beattie, *Chem. Phys. Lett. 69*, 128 (1980).

27. W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," Benjamin, New York, 1968.

28. A. Witkowski, to be published.

29. S. Isied and H. Taube, *J. Am. Chem. Soc. 95*, 8198 (1973).

30. D. B. Brown, *Inorg. Chem.*, in press.

31. B. Chance et al., eds., "Tunneling in Biological Systems," Academic, New York, 1979; E. K. Kudinov and Y. Firsov, *Sov. Phys. Sol. St. 7*, 435 (1965); N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem. 78*, 2168 (1976).

32. T. Holstein, in ref. 31; also *Ann. Phys. 8*, 325 (1959).

33. V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, *J. Math. Phys. 17*, 821 (1976); G. Lindblad, *Comm. Math. Phys. 48*, 119 (1976).

34. R. Kosloff ad M. A. Ratner, to be published.

35. R. Zwanzig, *Ann. Revs. Phys. Chem. 16*, 67 (1965).