

# Theoretical Studies of the Kinetics of Planar-Tetrahedral Equilibration in Nickel(II) Complexes. 2. Reaction Probabilities and Rate Constants

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**Abstract:** The kinetics of the equilibration of planar spin-singlet and tetrahedral spin-triplet species of Ni(II) complexes are described using two different but related theoretical approaches. Both employ simplified potential energy curves in a twisting coordinate together with the Landau-Zener model for transitions at curve crossings. First, the number of approaches to a crossing needed per second in order for the half-life of a given spin state not to exceed approximately  $10^{-6}$  s is calculated. The resulting value of  $\sim 10^{12}$  is compatible with estimated torsional frequencies. Second, the general method of analyzing kinetic networks known as dynamical systems theory is outlined and applied to the description of chemical relaxation such as occurs in experiments where the thermal equilibrium between planar and tetrahedral species is disturbed. Eigenvalues (decay constants) and eigenvectors for displacements from equilibrium are calculated for a number of model kinetic systems having the cyclic symmetry characteristic of the interconversion of the structures of Ni(II) complexes along non-bond-rupturing bending and twisting coordinates.

## I. Introduction

In the first article of this series,<sup>1</sup> hereafter denoted as I, we briefly reviewed the experimental evidence for the rapid interconversion of "planar" spin-singlet and "tetrahedral" spin-triplet species of certain four-coordinate complexes of Ni(II). We then introduced "global" bending and twisting coordinates which connect these structures, and presented potential energy curves in these coordinates as calculated using an extended crystal-field model. Although there are a total of 14 levels (components of multiplets) which are mixed with the lowest spin-singlet when spin-orbit coupling is introduced in  $D_2$  symmetry, only three of these, namely, the  $A_1$  ( $J = 0$ ) and E ( $J = 2$ ) levels of the lowest  ${}^3T_1$  multiplet of a tetrahedral species, actually cross the lowest spin singlet when spin-orbit coupling is omitted. Thus, only this smaller number of levels is considered in the analysis which follows. The potential energy curves shown in Figure 6-8 of I as functions of the angles  $\Phi$  and  $\theta$  are quite different for these three levels, and in fact the curves suggest that a planar structure may be the preferred structure for the  ${}^3B_{2g}$  multiplet (notation for  $D_{4h}$  symmetry), but not for the other low-lying triplet components. However, it should be recalled that the potential energy curves in I do not include any ligand-ligand repulsions, so that they should be used to compare energies of different states at a given geometry rather than to compare energies of a given state at different geometries. In order to explore more easily the "curve-hopping" description of the interconversion kinetics we now introduce simple empirical potential energy functions which have the qualitative features of the curves in the angle  $\Phi$  shown in Figures 6 and 7 of I, but which correspond to more realistic values of the activation energy defined as the difference between the energy at the crossing of singlet and triplet curves and the minimum energy for the more stable species.

## II. Simplified Potential Energy Curves

For complexes of the  $Ni(L-L)_2$  and  $Ni(L-L)X_2$  types, the relevant internal motion is that through the angle  $\Phi$  as defined in I. If the bidentate ligands are symmetric, the potential energy is twofold in a twist angle  $\alpha = 2\Phi$ . For the singlet state we write on the approximate form

$$V_S(\alpha) = a[1 - \cos(2\alpha)] \quad (1)$$

where  $\alpha = \pi/2$  and  $3\pi/2$  for the twisted structures of  $T_d$  or  $D_{2d}$  symmetry [nonplanar structures of  $C_{2v}$  symmetry for  $Ni(L-L)X_2$ ] with energy  $2a$ , and  $\alpha = 0$  and  $\pi$  for the planar structures of  $D_{2h}$  or  $D_{4h}$  symmetry [planar structures of  $C_{2v}$  symmetry for  $Ni(L-L)X_2$ ], with energy zero. Alternatively, as displayed in Figures 1 and 3 of I, the potential energy may be viewed as fourfold in  $\Phi$ . For some component of the triplet state, we similarly write

$$V_T(\alpha) = b + c[1 + \cos(2\alpha)] \quad (2)$$

The energy of the triplet at the *planar* geometry is  $b + 2c$ , while the energy at the *twisted* geometry is  $b$ , which is also the adiabatic energy difference between the triplet and singlet minima. From the crystal-field results in I we saw that different components of the tetrahedral  ${}^3T_1$  term will give rise to curves of the approximate form of eq 2, but with different values for the parameters  $b$  and  $c$ . Some components, in fact, may have energy minima for a planar rather than a twisted geometry. For purposes of illustration we will consider only a single curve of the form of eq 2, with parameters appropriate to some component which "connects" to the singlet when spin-orbit coupling is "turned on".

In general eq 1 and 2 do not intersect at  $\alpha = \pi/4$  ( $\Phi = \pi/8$ ), but instead at  $\alpha_0$  given by

$$\cos(2\alpha_0) = (a - b - c)/(a + c) \quad (3)$$

where

$$V_S = V_T = a(b + 2c)/(a + c) \quad (4)$$

The introduction of spin-orbit coupling replaces this crossing by an avoided crossing described by the solution of a  $2 \times 2$  secular equation using eq 1 and 2 as diagonal elements. A simple functional form which has the essential features of the lower root of such an equation is given by the twofold form

$$V_0(\alpha) = d[1 - \cos(2\alpha)] + e[1 - \cos(4\alpha)] \quad (5)$$

which has local minima of zero at  $\alpha = 0$  and  $2d$  at  $\alpha = \pi/2$ . There is a maximum at  $\cos(2\alpha) = -d/2e$ , at which  $V_0(\alpha) = (d + 4e)^2/8e$ . We may fit eq 5 to eq 1 and 2 by requiring that  $V_0 = V_S$  and  $V_0'' = V_S''$  at  $\alpha = 0$  (double primes denote second derivatives with respect to  $\alpha$ ), and that  $V_0 = V_T$  and  $V_0'' = V_T''$

at  $\alpha = \pi/2$ . Thus

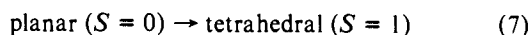
$$\begin{aligned} d &= b/2 = (a - c)/2 \\ e &= (a + c)/8 \end{aligned} \quad (6)$$

The relationship  $b = a - c$  reduces to two the number of independent parameters in eq 1 and 2. In this case from eq 3 and 4 we find  $V_S = V_T = d + 4e = a = b + c$  at  $\alpha = \pi/4$ ;  $V_0$  is  $2e$  below this crossing of the unperturbed curves.

As an example we use the experimental data<sup>2</sup> for Ni(dpp)Cl<sub>2</sub>, setting  $V_0$  or  $V_T$  at  $\alpha = \pi/2$  equal to  $\Delta H^\circ = 1.7 \pm 0.2$  kcal/mol =  $b$ , and  $V_S$  or  $V_T$  at  $\alpha = \pi/4$  equal to  $\Delta H_t^\ddagger = 8.4 \pm 0.2$  kcal/mol =  $a$ . Thus  $d$  and  $e$  equal 0.85 and 1.89 kcal/mol, respectively. Figure 1 shows  $V_S$ ,  $V_T$ , and  $V_0$  vs.  $\alpha$  for this parametrization. The maximum in  $V_0$  is approximately 3.8 kcal/mol below the crossing of  $V_S$  and  $V_T$ , reducing the effective activation energy by about twice the spin-orbit energy of  $\zeta(3d) = 1.86$  kcal/mol for Ni(II). Thus the simple form of eq 5 has led to a somewhat exaggerated difference between  $V_0$  and the intersection of  $V_S$  and  $V_T$ . An alternate parametrization is to set  $\Delta H_t^\ddagger$  equal to the maximum in  $V_0$ , thus giving a "correct" activation energy. This latter choice yields parameters of  $d$  and  $e$  equal to 0.85 and 3.76 kcal/mol, respectively, with the maximum in  $V_0$  occurring at an angle slightly greater than  $\pi/4$ , namely, at  $\alpha = 0.259\pi$ , where  $\cos(2\alpha) = -d/4e$ .

### III. Landau-Zener Transition Probabilities and Spin Lifetimes

Let us assume that a good potential energy function in  $\theta$  and  $\Phi$ , or just in  $\Phi$  for monobidentate or bisbidentate complexes, is available, either from molecular orbital calculations, ligand field calculations, or by an empirical fit of forms such as those described in the previous section to experimental data. The question now is how to describe the kinetics of the process



or of its reverse. Since the reduced moments of inertia are large, so that "torsional" vibrational spacings are small compared to  $kT$  at room temperature, it is reasonable to employ insofar as possible a classical picture of the motion on the potential energy surface. The intersecting sinusoidal curves in the variable  $\Phi$  as described in the previous section lead to an interesting "roller-coaster" picture of the intramolecular motion and spin conversion. If the energy  $E$  in the torsional mode is less than the potential energy  $V(\Phi)$  at the crossing, no conversion can occur, and the system merely oscillates quasi-harmonically in either the singlet or the triplet well. If  $E$  is greater than  $V(\Phi)$  at the crossing, but less than the maximum in  $V_S$  or  $V_T$ , the motion is still basically oscillatory, but each time the system passes through the crossing there is a possibility of a spin change. If  $E$  is greater than the maxima of  $V_S$  and  $V_T$ , the motion is rotatory, but again with a probability of a spin change at each crossing. Thus there is a resemblance to curve crossings arising in atomic collisions associated with reactions such as a charge neutralization reaction



or its reverse. In the above collision the system passes through the crossing point *twice* (once going in to a turning point and once going back out), so that if  $P$  is the probability per crossing of no change in electronic state, and  $1 - P$  is the probability per crossing of a change, then the probability of the reaction is  $2P(1 - P)$  and that of no reaction is  $P^2 + (1 - P)^2$ . Since there is some energy of interaction  $E_{12}$  between the two states at the crossing, the true adiabatic curves do not cross, so that the term *adiabatic* refers to the passage in which there is a change in electronic state, and the term *nonadiabatic* to the passage in which there is *not* a change.

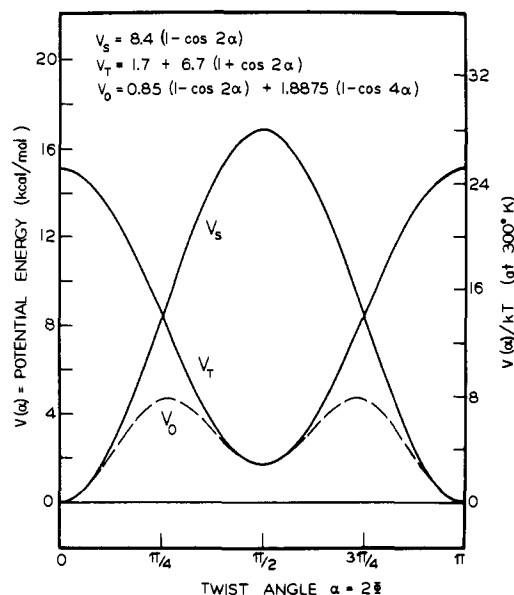


Figure 1. Plots of  $V_S$ ,  $V_T$ , and  $V_0$  from eq 1, 2, and 5, respectively, vs. twist angle  $\alpha = 2\Phi$ , using parameters obtained by setting  $V_0$  or  $V_T$  at  $\alpha = \pi/2$  equal to the planar-tetrahedral energy difference  $\Delta H^\circ$  for Ni(dpp)Cl<sub>2</sub> (ref 2) and  $V_S$  or  $V_T$  at  $\alpha = \pi/4$  equal to the activation energy  $\Delta H_t^\ddagger$  for this complex.

In the familiar Landau-Zener description<sup>3-10</sup> of these transitions, the nonadiabatic probability  $P$  is given by

$$P(v) = \exp[-2\pi E_{12}^2/\hbar v(x_0)|s_1 - s_2|] \quad (9)$$

where  $E_{12}$  is the interaction energy at the crossing coordinate  $x_0$ ,  $v(x_0)$  is the magnitude of the velocity at the crossing,  $|s_1 - s_2|$  is the magnitude of the difference in slopes of the curves  $V_1$  and  $V_2$  at the crossing, and  $\hbar$  is Planck's constant divided by  $2\pi$ . The velocity  $v(x_0)$  is given by

$$v(x_0) = \{2[E - V(x_0)]/m\}^{1/2} \quad (10)$$

where  $E$  is the total energy in the reaction coordinate,  $V(x_0)$  is the potential energy at the crossing of the unperturbed curves, and  $m$  is the reduced mass. Later we shall replace the symbol  $V(x_0)$  by  $E^\ddagger$  to denote its role as the activation energy. Using  $V_S(\alpha)$  from eq 1 and  $V_T(\alpha)$  from eq 2 as  $V_1$  and  $V_2$ , respectively,

$$|s_1 - s_2| = 2(a + c) \sin(2\alpha_0) \quad (11)$$

where  $\alpha_0$  corresponds to the intersection and is given by eq 3. For the special case  $b = a - c$  which we used in fitting eq 1 and 2 to eq 5,  $\alpha_0 = \pi/4$ , so that  $|s_1 - s_2| = 2(a + c)$ . Thus for the first and second parametrizations described in section I using Ni(dpp)Cl<sub>2</sub> data,  $|s_1 - s_2|$  equals 30.2 and 60.2 kcal mol<sup>-1</sup> rad<sup>-1</sup>, respectively. We shall use these values in obtaining rough estimates of eq 9.

The approximations inherent in the Landau-Zener model have been discussed by many authors,<sup>3-10</sup> with particular emphasis on its accuracy for very small values of  $v(x_0)$ . Coulson and Zalewski<sup>6</sup> have shown that the limits within which the original Landau-Zener formula (eq 9) is valid are seldom found in actual practice. They give a more generally valid expression involving an integral of the interaction energy  $E_{12}(R)$  over the entire range of the appropriate nuclear coordinate  $R$ . However, as a rough guide to the reaction probability we use the simple form given in eq 9. This assumption seems justifiable as a first step since we do not require the detailed information given by the reaction probability as a function of energy (or velocity), but instead need only the Boltzmann averaged reaction probability. This averaging is described below and in the Appendix.

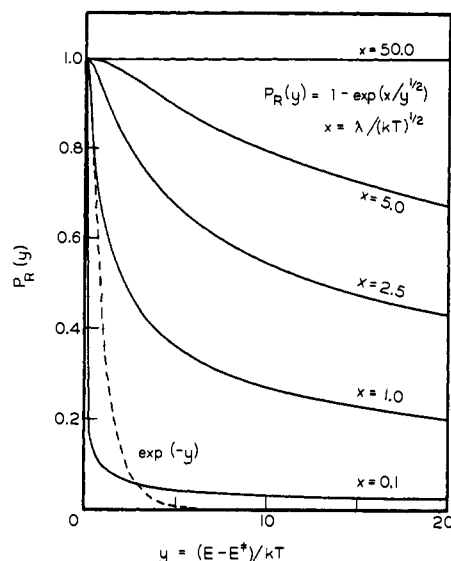


Figure 2. Plot of the Landau-Zener reaction probability of eq A 1 vs. reduced energy  $y$  of eq 13 for various values of the reduced parameter  $x$  of eq 12. Also shown (dashed curve) is a Boltzmann factor in the reduced energy  $y$ , with the multiplicative factor  $\exp(-V^\ddagger/kT)$  omitted so that the Boltzmann factor is unity for  $y = 0$ .

Whereas in a reaction such as eq 8 there are just two crossings per collision, the cyclic nature of the twisting coordinate  $\Phi$  causes the Ni(II) complex to pass repeatedly through crossing points. Thus even if the thermally averaged adiabatic transition probability  $1 - P(T)$  is very small for a single crossing, the probability per unit time might be large given a high frequency of crossings. This is the result which we wish to demonstrate in this section.

We now define dimensionless variables

$$x = (2m)^{1/2} \pi E_{12}^2 / \hbar |s_1 - s_2| (kT)^{1/2} \quad (12)$$

and

$$y = [E - V(x_0)]/kT = [E - E^\ddagger]/kT \quad (13)$$

in which  $E^\ddagger = V(x_0)$  is the activation energy, so that eq 9 may be written in the reduced form

$$P(y) = \exp(x/y^{1/2}) \quad (14)$$

The Boltzmann constant  $k$  used in eq 12 and 13, as well as in many subsequent equations, will be understood to be replaced by the gas constant  $R$  when energies are used in kcal/mol. Note that  $T$  does *not* appear in eq 9; its inclusion in eq 12 and 13 is for later convenience in thermal averaging. We now denote eq 14 as  $P_{NR}(y)$ , the probability of *no* reaction per crossing, and the complementary probability  $1 - P_{NR}$  as  $P_R$ , the probability of reaction per crossing. Figure 2 shows  $P_R(y)$  vs.  $y$  for various values of  $x$  ranging from 0.1 to 50.0. At  $y = 0$ , which is the reaction threshold,  $P_R = 0$  and  $dP_R/dy = 1$ , although this limiting slope is not obvious in Figure 2 for the smaller  $x$  values. Also shown in Figure 2 is a Boltzmann factor  $\exp(-y)$ ; we note for  $x > 1$  that  $P_R$  is essentially unity for energies many  $kT$  above threshold, while for  $x < 1$ ,  $P_R$  falls rapidly with increasing energy as compared to the Boltzmann factor. Thus unless  $E_{12}$  or  $m$  is very small, or  $|s_1 - s_2|$  is very large,  $P_R$  is in effect a unit step function in the energy above threshold.

In the Appendix we discuss the thermal averaging of  $P_R(y)$  leading to

$$P_R(T) = \exp(-E^\ddagger/kT) [1 - \phi_0(x)] \quad (15)$$

where  $\phi_0(x)$  is given by

$$\phi_0(x) = \int_0^\infty \exp(-y) \exp(-x/y^{1/2}) dy \quad (16)$$

We show there for  $x \gg 1$  that  $P_R(T)$  reduces to  $\exp(-E^\ddagger/kT)$ .

Writing  $P_{NR}(T)$  as  $1 - \epsilon$ , where  $\epsilon = \exp(-E^\ddagger/kT)$ , or more properly  $\exp(-E^\ddagger/kT)$  times  $1 - \phi_0(x)$ , we now seek the number  $n$  of thermally averaged approaches to a crossing such that there is a probability of  $1/2$  of the given spin state *not* changing. That is, we find  $n$  such that

$$P_{NR}^n = (1 - \epsilon)^n = 1/2 \quad (17)$$

For  $E^\ddagger = 8.4$  kcal/mol,  $T = 300$  K, and  $x \approx 30$ , such that  $1 - \phi_0(x) \approx 1$ ,  $\epsilon = 7.6 \times 10^{-7}$ , giving  $n = \ln 2/\epsilon = 9.1 \times 10^5 \approx 10^6$ . Thus  $n$  approaches in  $\tau$  s corresponds to a spin half-life  $\tau_{1/2}$  of  $\tau$  s. If we set  $\tau \lesssim 10^{-6}$  s, based on the *upper* limit from NMR data for typical Ni(II) complexes, we obtain a *lower* limit of  $\sim 10^{12}$  approaches per second necessary to yield the desired half-life. Even ignoring degeneracy factors, which can range up to 9 depending upon the number of components of a  ${}^3T_1$  term that connect to a spin-singlet, this number of approaches per second is readily obtainable given a hindered torsional frequency in the variable  $\Phi$  of at least  $10^{12} \text{ s}^{-1}$ . A harmonic fit to the curves  $V_S(\Phi)$  and  $V_T(\Phi)$  in section II yields, for a reduced mass of  $3.7 \times 10^{-38} \text{ g cm}^2/\text{rad}^2$  (see Appendix), frequencies of approximately  $1.2 \times 10^{12} \text{ s}^{-1}$ . Since there are four approaches to a crossings per cycle, the number of approaches per period is  $4gv$ , where  $g$  is a degeneracy factor. Thus a value of  $4gv$  at least equal to  $10^{12} \text{ s}^{-1}$  is readily attainable! It should be noted that the activation energy is a crucial *input* parameter to this spin-survival lifetime calculation, and not a *result*. Further, the *reversibility* of the spin-isomerization is not relevant here; that is, it does not matter, for purposes of *this* question, that a spin-singlet that converts to a spin-triplet might quickly return to a spin-singlet. Reversibility, however, will play a crucial role in the more sophisticated kinetic analysis of the next section.

#### IV. Dynamical Systems Theory and Chemical Relaxation

A formalism useful in considering the kinetics of the equilibration of planar-tetrahedral Ni(II) complexes is dynamical systems theory (DST),<sup>11</sup> which is the study of sets of coupled differential equations and is concerned largely with the existence, uniqueness, and stability of steady-state and periodic solutions of these sets of equations. We shall be concerned only with the simplest of these sets of differential equations, namely, those corresponding to closed systems and whose equations are first order and linear with constant coefficients. A system is said to be closed if there are neither sources nor sinks for any state. We have recently outlined<sup>12</sup> the convenient matrix formulation<sup>13-15</sup> of such first-order systems and presented a number of properties of the solutions of the rate equations. A brief summary of DST is given here as an introduction to its applications to the present problem.

Consider a closed system consisting of  $n$  states labeled  $1, \dots, n$ . Let  $x_i(t)$  be the fractional concentration of species in state  $i$  at time  $t$ . These concentrations satisfy  $x_i(t) \geq 0$  for all  $i$  and  $t$ , and are normalized such that

$$\sum_i x_i(t) = 1 \text{ for all } t \quad (18)$$

Also let  $w_{ij}$  be the first-order rate constant for the transition from state  $i$  to state  $j$ , with  $w_{ij} \geq 0$  for all  $i$  and  $j$ . The  $w$ 's may be interpreted as thermally averaged rate constants  $k(T)$  or as energy-dependent rate constants  $k(E)$  such as given by the product of a Landau-Zener reaction probability  $P_R(E)$  and a frequency of approach to a crossing. The time evolution of

each  $x_i(t)$  can then be represented by a master equation,

$$\dot{x}_i(t) = \sum_j (w_{ji}x_j(t) - w_{ij}x_i(t)) \quad (19)$$

The set of  $n$  such equations can be placed into matrix form,

$$\dot{\mathbf{X}}(t) = \mathbf{A}\mathbf{X}(t) \quad (20)$$

where  $\dot{\mathbf{X}}(t)$  and  $\mathbf{X}(t)$  are  $n$ -dimensional column vectors whose elements are  $\dot{x}_i(t)$  and  $x_i(t)$ , respectively, and  $\mathbf{A}$  is an  $n \times n$  matrix whose elements are

$$a_{ij} = w_{ji} \text{ for } i \neq j, \text{ and} \quad (21)$$

$$a_{ii} = -\sum_{k \neq i} w_{ik}$$

If  $\mathbf{A}$  can be diagonalized, the solution of eq 19 corresponding to the  $j$ th eigenvalue  $\alpha_j$  of  $\mathbf{A}$  is

$$x_i^{(j)}(t) = v_{ij} \exp(\alpha_j t) \quad (22)$$

where  $v_{ij}$  is the  $i$ th element of the eigenvector corresponding to the  $j$ th eigenvalue. The general solutions of eq 19 are linear combinations of the  $x_i^{(j)}(t)$ .

$$x_i(t) = \sum_j b_j v_{ij} \exp(\alpha_j t) \quad (23)$$

The coefficients  $b_j$  are determined by the initial conditions  $x_i(0)$ ,

$$x_i(0) = \sum_j b_j v_{ij} \quad (24)$$

or, in matrix notation,

$$\mathbf{X}(0) = \mathbf{V}\mathbf{B} \quad (25)$$

where the elements of the  $n$ -dimensional column vectors  $\mathbf{X}(0)$  and  $\mathbf{B}$  are  $x_i(0)$  and  $b_i$ , respectively, and the elements of the  $n \times n$  matrix  $\mathbf{V}$  are  $v_{ij}$ . Thus,

$$\mathbf{B} = \mathbf{V}^{-1}\mathbf{X}(0) \quad (26)$$

where  $\mathbf{V}^{-1}$  is the inverse of  $\mathbf{V}$ , and

$$\mathbf{X}(t) = \mathbf{V}\mathbf{Y}(t) \quad (27)$$

where  $\mathbf{Y}(t)$  is a column vector whose elements are  $b_i \exp(\alpha_i t)$ . Note that  $\mathbf{Y}(0) = \mathbf{B}$ .

The eigenvalues of  $\mathbf{A}$  are in general complex, but their real parts are always nonpositive.<sup>14</sup> If a system obeys detailed balance then its eigenvalues have zero imaginary parts and are thus real.<sup>14</sup> An equilibrium solution (eq 22) of eq 19 is one whose eigenvalue is zero. In general,  $\mathbf{A}$  has exactly  $n - m$  zero eigenvalues where  $m$  is the rank of  $\mathbf{A}$ . It has been shown<sup>14</sup> that  $\det \mathbf{A} = 0$ , and thus at least one equilibrium solution always exists. State  $i$  is said to communicate with state  $j$  if a system prepared in state  $i$  has a nonzero  $x_j(t)$  at later times; that is, if  $w_{ij} \neq 0$  or if there exists a sequence of states  $k, l, l+1, \dots, m-1, m$  such that  $w_{ik}w_{kl}w_{l,l+1} \dots w_{m-1,m}w_{mj} \neq 0$ . If all states communicate with all other states, then the system is called strongly connected<sup>16</sup> and only one equilibrium solution exists.<sup>17</sup> This will be the case for all of the systems we now consider.

While we can easily solve the preceding equations for arbitrary sets of rate constants, a greater insight results from considering certain special cases which also can serve as idealized models for the interconversion of structures of Ni(II) complexes. If a system consists of set  $\mathbf{A}$  of  $m$  states and a set  $\mathbf{B}$  of  $n$  states, and if each of the  $m$  states has forward and reverse rate constants  $w_f$  and  $w_r$ , respectively, to and from each of the  $n$  states, and if all  $w$ 's are zero *within* each set, then we

have shown<sup>12</sup> that the  $m + n$  eigenvalues are a unique  $\alpha = 0$ , a set  $\alpha = -nw_f$  with degeneracy  $m - 1$ , a set  $\alpha = -mw_r$  with degeneracy  $n - 1$ , and a unique  $\alpha = -(mw_r + nw_f)$ . For  $m = n = 1$ , the only nonzero eigenvalue is the familiar  $\alpha = -(w_f + w_r)$  decay constant for a nonequilibrium distribution in a two-state system. For  $m = 1$ , but  $n$  variable, as in application to a spin-singlet interacting with  $n$  components of a  $^3T_1$  term of a tetrahedral Ni(II) complex, the nonzero eigenvalues are a set  $\alpha = -w_r$  with degeneracy  $n - 1$  and the unique  $\alpha = -(nw_f + w_r)$ . The values  $-w_r$  correspond to the relatively slow decay modes in which a nonequilibrium distribution *within* the set  $\mathbf{B}$  of  $n$  states equilibrates via the unique state in set  $\mathbf{A}$  subject to the constraint that  $\dot{x}_1 = 0$ , that is, that the concentration in the unique state (the singlet) remains constant at its equilibrium value of  $w_r/(nw_f + w_r)$ . The more negative eigenvalue  $\alpha = -(nw_f + w_r)$  corresponds to the relatively fast mode in which an imbalance of the set  $\mathbf{A}$  concentration relative to the set  $\mathbf{B}$  concentration decays with time, subject to the constraint that each state in set  $\mathbf{B}$  has the same displacement from equilibrium. As given by eq 22-27, an arbitrary set of concentrations is a linear combination of all  $m + n$  modes, and thus the system does not in general have a simple exponential time evolution. It should be added that we have also extended<sup>12</sup> the treatment to include nonzero  $w$ 's *within* each set. The intraset relaxation modes are no longer necessarily slower than the intersets modes, but the eigenvalues for the intersets modes are independent of the values of the intraset rate constants.<sup>18</sup>

The application of the above results to the Ni(II) complexes follows by the identification of each  $w$  as the product of a thermally averaged Landau-Zener transition probability as given by eq 15 and a frequency  $\nu$  to be specified later. Thus  $w_f = \nu \exp(-E^\ddagger/RT) \simeq (7.6 \times 10^{-7})\nu$  for  $E^\ddagger = 8.4$  kcal/mol and  $T = 300$  K, and  $w_r = \nu \exp[(-E^\ddagger + \Delta E)/RT] \simeq (1.3 \times 10^{-5})\nu$  for  $\Delta E = 1.7$  kcal/mol. While these  $w$ 's must satisfy  $\Delta E = -RT \ln(w_f/w_r)$ , they do not reproduce the Ni(dpp)Cl<sub>2</sub> equilibrium constant<sup>2</sup> of 0.75 unless  $n$  is set equal to  $\exp(\Delta S/R)$ , a value in the range 9-14 using  $\Delta S = 4.8 \pm 0.5$  eu. The simplifying assumption is made here that  $w_f$ , and similarly  $w_r$ , is the same for each member of the triplet set  $\mathbf{B}$ . That is, we are ignoring the fact that different components of the triplet not only intersect the singlet at different energies, but also that they are characterized by different spin-orbit couplings to the singlet and by different  $|s_1 - s_2|$  values as appear in eq 9. Given these assumptions as defining an *average* interaction, the most negative decay constant  $\alpha = -(nw_f + w_r)$  becomes  $(-1.53 \times 10^{-5})\nu$  for  $n = 3$ , the number of triplet levels connecting to the singlet in  $D_2$  symmetry.<sup>1</sup> For motion along intersecting curves such as in Figure 1 there are *four* approaches per period of quasi-harmonic motion in a sinusoidal well. Thus the effective frequency of encounter  $\nu$  is four times the torsional vibrational frequency. If the latter is  $1.2 \times 10^{12} \text{ s}^{-1}$  (see section III), then  $\alpha = -7.3 \times 10^7 \text{ s}^{-1}$  for the intersets mode and  $-6.2 \times 10^7 \text{ s}^{-1}$  for each of the intraset modes. These values are comparable because  $w_f < w_r$  in this case. The assumption of quasi-harmonic motion is not a bad approximation for energies below the maxima in the unperturbed potential energy curves, and admits the further simplification that since the frequency of harmonic motion is independent of energy, the frequency of traversals of the avoided crossing points is also independent of energy. Thus it was valid to interpret the  $w$ 's as thermally averaged rate constants. In general, however, the proper procedure would be to solve for the decay modes as a function of energy and *then* carry out a thermal averaging. While the preceding decay constants are obtained from a highly idealized model, they do indicate that decay constants of the order of  $-10^7 \text{ s}^{-1}$  may be accounted for using reasonable parameters. More importantly, the model portrays relationships between features of the potential energy surfaces and kinetic parameters.

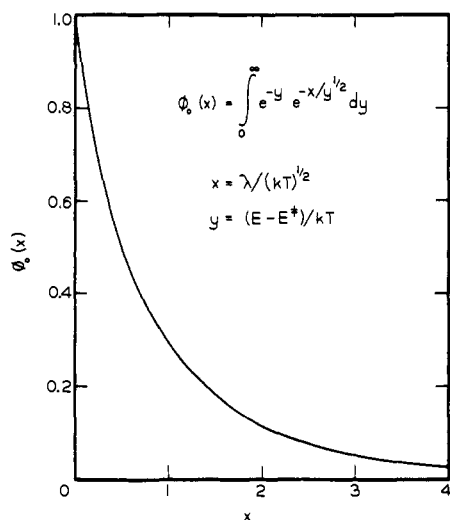


Figure 3. Plot of the integral  $\phi_0(x)$  of eq A4 vs.  $x$ .

## V. Summary

In the second article of this series we have described the kinetics of the equilibration of planar spin-singlet and tetrahedral spin-triplet species of Ni(II) complexes using two different but related theoretical approaches. First, simplified potential energy curves in a twisting coordinate were used together with the Landau-Zener for transitions at curve crossings to estimate the number of thermally averaged approaches to a crossing needed per second in order for the half-life of a given spin species not to exceed approximately  $10^{-6}$  s. The resulting value of  $\sim 10^{12}$  is compatible with estimated torsional frequencies. Second, the general method of analyzing kinetic networks known as dynamical systems theory was outlined and applied to the description of chemical relaxation such as occurs in experiments<sup>2</sup> where the thermal equilibrium between the species is disturbed. A number of model kinetic systems were considered which have the cyclic symmetry characteristic of the interconversion of the structures of Ni(II) complexes along non-bond-tupturing bending and twisting coordinates. Eigenvalues (decay constants) and eigenvectors for displacements from equilibrium were presented for these systems and used to describe different types of possible relaxation processes.

In conclusion we have shown that the observed rapid rates of interconversion of planar spin-singlet and tetrahedral spin-triplet species of Ni(II) complexes are compatible with the assumption of a "curve crossing" process involving thermally averaged Landau-Zener transition probabilities. One major reason that the interconversion is often so rapid despite the small value of the thermally averaged spin-change probability per approach to a curve crossing is that the crossing occurs in a torsional vibrational coordinate, so that the number of "encounters" per second is proportional to the vibrational frequency. In short, the system is "trapped" in a cyclic coordinate and cannot avoid frequent crossings except in the limit of the thermal energy being extremely small compared to the activation energy (say  $20kT \ll E^\ddagger$ ). It should be noted that we have not attempted to elucidate the electronic factors determining the activation energy for a given complex, but instead have presented an analysis of the interconversion process in which the activation energy is a parameter. Similar analyses should be possible for other spin equilibration reactions, such as that between singlet and quintet states of six-coordinate Fe(II).

A subsequent article in this series will present a number of refinements of the theoretical analysis. These include the use of more realistic potential energy functions, the extension of the Landau-Zener treatment to include both spherical polar

angles  $\theta$  and  $\Phi$  simultaneously (both Teller<sup>19</sup> and Nikitin<sup>7b</sup> have discussed Landau-Zener transition probabilities in a two-dimensional Cartesian space), and the extension to strong-coupled noncrossing curves<sup>20</sup> using the recent methods of Dinterman and Delos.<sup>21</sup>

**Acknowledgment.** The authors wish to thank The University of Michigan Computing Center for use of the Amdahl 470V/6 computer.

## Appendix. Thermal Averaging of Landau-Zener Transition Probability

In section III we considered the Landau-Zener probability of reaction at a curve crossing in the form

$$P_R(y) = 0 \quad \text{for } y < 0 \quad (\text{A1})$$

$$P_R(y) = 1 - \exp(-x/y^{1/2}) \quad \text{for } y \geq 0$$

The variables  $x$  and  $y$  are given in dimensionless reduced form in eq 12 and 13, respectively. We now define a thermally averaged reaction probability  $P_R(T)$  as

$$P_R(T) = \frac{\int_0^\infty \exp(-E/kT) P_R(E) dE}{\int_0^\infty \exp(-E/kT) dE} \quad (\text{A2})$$

which reduces to

$$P_R(T) = \exp(-E^\ddagger/kT) [1 - \phi_0(x)] \quad (\text{A3})$$

in which

$$\phi_0(x) \equiv \int_0^\infty \exp(-y) \exp(-x/y^{1/2}) dy \quad (\text{A4})$$

Essentially identical thermal averagings have been given before,<sup>7b,10a,22</sup> but we wish to have the results expressed in our notation. Expression A3 is for the process state 1  $\rightarrow$  state 2; for the reverse process, replace  $E^\ddagger$  in the experimental pre-factor by  $E^\ddagger - \Delta E$ , where  $\Delta E \equiv E_2 - E_1$ . Thus the ratio of forward to reverse reaction probabilities is  $\exp(-\Delta E/kT)$ , a familiar result for nondegenerate states.

The integral  $\phi_0(x)$  in eq A3 and A4 arises in various thermal averagings including the description of thermal neutron scattering. A power series expansion useful for  $x < 1$  was given by Zahn<sup>23</sup> and an asymptotic solution useful for large  $x$  was given by Laporte.<sup>24</sup> Corrections and extensions of the asymptotic solution have been noted by Torrey<sup>25</sup> and by Abramowitz.<sup>26</sup> We have written a FORTRAN program to evaluate  $\phi_0(x)$  to at least seven significant figure accuracy for arbitrary values of  $x$ . Figure 3 shows  $\phi_0(x)$  for  $x$  values up to 4, at which point the function has fallen from its value of unity at  $x = 0$  to 0.023 86.

For a rough estimate for  $x$  appropriate to a complex such as Ni(dpp)Cl<sub>2</sub>, we took  $E_{12} = \zeta(3d) = 1.86$  kcal/mol = 649 cm<sup>-1</sup>,  $m$  = reduced motion of inertia =  $3.7 \times 10^{-38}$  g cm<sup>2</sup>/rad<sup>2</sup> (based on rotation of Cl<sub>2</sub> only, with bond length of 2.51 Å and a Cl-Ni-Cl bond angle of 90°),  $|s_1 - s_2| = 30.2$  kcal mol<sup>-1</sup> rad<sup>-1</sup> (see section III) and  $T = 300$  K, yielding  $x = 31.6$  and  $\phi_0(x) = 3.27 \times 10^{-8}$ . For neighboring values of  $x = 30$  and 35,  $\phi_0(x) = 6.142 \times 10^{-8}$  and  $8.954 \times 10^{-9}$ , respectively. If the larger value of  $|s_1 - s_2| = 60.2$  kcal/mol is used instead,  $x = 15.8$  and  $\phi_0(x) = 2.925 \times 10^{-5}$ . Thus  $\phi_0(x) \ll 1$ , reducing  $P_R(T)$  to

$$P_R(T) = \exp(-E^\ddagger/kT)$$

Note that  $x$  varies only as  $m^{1/2}$ , so that the value of  $m$  used is not critical as long as it is not too small. For bisbidentate complexes  $m$ , and hence  $x$ , would be larger than the values given above, so that  $\phi_0(x)$  would be even less important when

compared to unity. While  $E_{12}$  does enter  $x$  quadratically, the exact value used is not very important unless it is small enough to give  $x$  less than, say, unity. The insensitivity of  $1 - \phi_0(x)$  to variation in  $x$  when  $x \gg 1$  is simply the result of the rapid fall-off of the Boltzmann factor  $\exp(-y)$  as compared to  $P_R(y)$ . This behavior was shown in Figure 2 and discussed in section III.

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## Resonance Raman Spectra of Cobalt(II)-Imidazole Complexes: Analogues of the Binding Site of Cobalt-Substituted Zinc Proteins

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**Abstract:** Raman spectra, excited in the visible and near-ultraviolet (363.8 nm) regions, are reported for imidazole (ImH) and its  $N_1$  and  $C_2$  deuterated derivatives, and for several cobalt(II) complexes, chosen as analogues for the coordination group of zinc (cobalt) proteins  $\text{Co}(\text{ImH})_4^{2+}$ ,  $\text{Co}(\text{ImH})_2\text{Cl}_2$ ,  $\text{Co}(\text{Im})_4^{2-}$ ,  $\text{Co}(\text{his})_2$ , and  $\text{Co}(\text{his})_2^{2-}$  (his = histidinate), as well as  $N_1$ -methyl,  $C_2$ -methyl, and  $N_1$  and  $C_2$  deuterated analogues. Excitation in the visible absorption band enhances cobalt-ligand modes of the tetrahedral complexes. The intensity patterns suggest a vibronic mixing mechanism with charge-transfer upper states. The cobalt-imidazole frequencies suggest unusual strength for the Co-ImH bond in  $\text{Co}(\text{ImH})_4^{2+}$ , perhaps reflecting hydrogen bonding to the solvent. Imidazole ring modes are reassigned on the basis of corrected deuteration data. Frequency shifts on binding to  $\text{Co}^{2+}$  are unremarkable. However, the most intense band, at  $1255 \text{ cm}^{-1}$ , shifts significantly upon  $N_1$  deuteration when complexed but not when free, and may therefore serve as a marker for cobalt-bound imidazole in proteins. The complexed ring modes are not enhanced in the visible but show significant enhancement in the near UV.

Zinc is a relatively abundant element in biological organisms, and plays an essential role in a large number of enzymatic reactions.<sup>1</sup> The structure of the zinc binding site has been elucidated for a growing list of proteins by x-ray crystallography. The structural aspects of catalysis are of great current interest for these enzymes. Zinc(II) being a  $d^{10}$  ion provides few spectroscopic signatures for the monitoring of structure. It can be substituted with cobalt(II) ( $d^7$ ), however, with retention of at least partial enzymatic activity.<sup>2</sup> The resulting cobalt enzymes give characteristic visible (ligand-field) absorption spectra.

Resonance Raman spectroscopy affords a selective probe of chromophore structure. Vibrations which are coupled to the resonant electronic transition are subject to enhancement of their Raman intensity. The frequencies and intensities of the Raman bands are sensitive to structural changes occurring at the chromophore. In principle, resonance Raman spectra of cobalt-substituted enzymes could provide a vibrational sig-

nature of the active site. The experiment was tried by Loehr and co-workers,<sup>3</sup> without positive results, but their available laser wavelengths were far from resonance. In view of recent reports of substantial Raman enhancement of cobalt-ligand stretching modes in resonance with the visible absorption bands of tetrahedral cobalt(II) complexes,<sup>4</sup> the cobalt enzymes bear reexamination.

The most common zinc active-site ligand is imidazole. Three imidazoles are bound to zinc in carbonic anhydrase,<sup>5</sup> two in carboxypeptidase<sup>6</sup> and thermolysin,<sup>7</sup> and one in liver alcohol dehydrogenase.<sup>8</sup> It is therefore of importance to define the Raman characteristics of cobalt(II) imidazole complexes. Yoshida et al. have published a Raman study of such complexes,<sup>3</sup> which was, however, limited to the high-frequency ligand modes, and to excitation with blue and green laser lines. In the present work we have focused on resonance effects observable in the red and the near-ultraviolet regions of the spectrum. The former provides selective enhancement of co-