Effects of anharmonicity and electronic coupling on photoinduced electron transfer in mixed valence compounds

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We develop a semigroup model of electron transfer (ET) dynamics in mixed valence compounds. This model is useful for investigating the effects of anharmonicity in inner sphere nuclear modes, as well as the dependence of the electronic dynamics on the nature of the electronic coupling. Two effective "subsystem" nuclear vibrations are treated explicitly in the model, to account for the rapid electronic energy gap fluctuations induced by the inner sphere vibrations. The essentially Markovian effects of the remaining "bath" modes are approximated by semigroups. We find that including the anharmonicity in inner sphere vibrations leads to a very small increase in the rate of ET. This effect is due to the change in reactant and product vibronic states when anharmonicity is included, as well as the rapid electronic dephasing induced by the bath. An assumption of strong electronic coupling is found to be sufficient to explain experimentally observed ET rates, but the possible role of conical intersections in ultrafast ET reactions is also noted. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519258]

I. INTRODUCTION

Electron transfer (ET) reactions are of widespread interest.^{1–9} Such reactions are central to many biological processes,⁹ and are also of interest to the growing community interested in molecular electronics.^{10,11} Traditional theoretical descriptions of ET in condensed phases have focused on systems either in the high temperature limit, where nuclei can be treated classically, or in the low temperature and small electronic coupling limit, in which case nuclear modes are approximately harmonic and Fermi's Golden rule is valid.^{1,8} Exact, fully quantum mechanical description of complex systems in more general temperature and coupling regimes is not computationally feasible, and as a result, many studies of these regimes have utilized semiclassical approximations.^{12–14}

An alternative and complementary approach is provided by the semigroup methodology,^{15,16} which does not require semiclassical approximations. In this approach, important "subsystem" degrees of freedom are treated fully quantum mechanically, while Markovian effects of the remaining nuclear modes on the reduced density matrix are incorporated based on the Lindblad equation.¹⁷ The semigroup approach can be used to explore a wide range of temperatures, and can serve as a test of the validity of semiclassical approximations which can otherwise only be tested against exact calculations for more simplified model ET reactions.¹²

The semigroup approach is also particularly well suited to investigating effects of anharmonic modes on ET in mixed valence compounds such as $(NH_3)_5 RuNCRu(CN)_5^{-16,18-20}$.

This is in part because the subsystem propagation is readily carried out numerically for nonharmonic surfaces which are not convenient to work with analytically. But equally important is the fact that traditional rate expressions, based on the assumptions of small and constant electronic coupling or the assumption of nuclear thermal equilibrium,¹ cannot be relied upon in the case of ultrafast photoinduced ET between metal centers.^{16,18,20,21} Spatial dependence of the electronic coupling, such as a form for the electronic coupling that gives rise to a conical intersection,^{22–24} can play a role in the rate of an ultrafast ET reaction, and it can also affect the impact of anharmonicity on the reaction dynamics. The semigroup method is ideal for exploring a wide range of electronic coupling strengths and spatial dependence, and is also capable of describing deviations from nuclear thermal equilibrium.¹⁶

The remainder of this paper is organized as follows: In Sec. II, we develop a semigroup model for intramolecular ET in mixed valence compounds. In Secs. III and IV, we discuss parametrization of this model to describe $(NH_3)_5RuNCRu(CN)_5^-$. In Sec. V, we discuss calculations which elucidate the role of anharmonicity and electronic coupling. In Sec. VI, we comment on the possible role of conical intersections in ultrafast ET reactions. In Sec. VII, we present our conclusions.

II. SEMIGROUP MODEL OF ET IN MIXED VALENCE COMPOUNDS

The Hamiltonian governing ET in compounds such as $(NH_3)_5RuNCRu(CN)_5^-$ can be written as

$$\hat{H} = J(|A\rangle\langle D| + |D\rangle\langle A|) + |D\rangle H_D\langle D| + |A\rangle H_A\langle A|, \quad (1)$$

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where $|D\rangle$ denotes the initial ("donor") electronic state, $|A\rangle$ denotes the final ("acceptor") electronic state, J is the electronic coupling, and H_D and H_A are the nuclear Hamiltonians on the electronic surfaces $|D\rangle$ and $|A\rangle$, respectively. The nuclear Hamiltonians H_D and H_A differ in three principal ways: the covalent radii of the metal ions change with electronic state, there is an energy gap between equilibrium nuclear configurations on the two electronic surfaces, and the solvent ("outer sphere") nuclear modes react to the electronic state.^{25,26} As such, the difference between equilibrium inner sphere nuclear configurations, on the two electronic surfaces, is dominated in the case of $(NH_3)_5 RuNCRu(CN)_5^-$ by the displacement of the Ru–N and Ru–C bonds.

To conveniently model ET in mixed valence compounds such as $(NH_3)_5RuNCRu(CN)_5^-$, we make two principal approximations. First, we suppose that the solvent and most inner sphere nuclear modes may be approximated as a Markovian bath, which is to say that their effects can be described by semigroups.¹⁶ Second, we suppose that the reaction is very similar to that between $Ru^{II}(NH_3)_6^{+2}$ and $Ru^{III}(CN)_6^{-3}$, except that the NC bridge fixes the metalmetal distance and affects the electronic coupling strength between electronic states. Accordingly, to model the non-Markovian contributions to the electronic energy gap modulation, we treat only two nuclear modes explicitly and fully quantum mechanically, and we model these two modes after the "breathing" modes that are dominant in the "absence" of the bridge.^{25,26} In one of these modes, the Ru-N bonds stretch, and in the other the Ru-C bonds stretch, with frequencies and anharmonicities comparable to those of the symmetric stretching modes in $Ru^{II}(NH_3)_6^{+2}$ and $Ru^{II}(CN)_6^{-4}$, respectively. The effects of the remaining modes are approximated by semigroups. We note that two previous theoretical studies of ET in mixed valence compounds have considered only a single non-Markovian nuclear mode.^{16,27}

It is useful to define a subsystem Hamiltonian, which differs from Eq. (1) in that the terms describing energy change due to motion in the bath (or approximately Markovian degrees of freedom) are removed. This system Hamiltonian then takes the form

$$\widehat{H}_{S} = J(|A\rangle\langle D| + |D\rangle\langle A|) - |A\rangle \hbar \omega_{DA}\langle A| + |D\rangle$$
$$\times \left(\sum_{i=1,2} H_{D,i}\right) \langle D| + |A\rangle \left(\sum_{i=1,2} H_{A,i}\right) \langle A|, \qquad (2)$$

where the first (coupling) term is the same as in Eq. (1), $\hbar \omega_{DA}$ is the effective electronic energy gap between equilibrium nuclear configurations on the two surfaces, and the nuclear Hamiltonians contain only the two required nuclear modes and are equal to zero at the equilibrium configuration. We have chosen the zero of energy as that of the equilibrium nuclear configuration on the $|D\rangle$ electronic state.

The corresponding reduced density matrix, which describes the subsystem and is sufficient to characterize the ET dynamics, evolves according to¹⁶

$$d\rho/dt = -(i/\hbar)[\hat{H}_s,\rho] + L_D\rho, \qquad (3)$$

where L_D describes relaxation and dephasing due to the bath modes. Herein, we take L_D to be of essentially the same form as described in Ref. 16. For reasons discussed in the following, we choose to work in the energy $(\widehat{H}_S - J[|A\rangle \times \langle D| + |D\rangle \langle A|])$ representation. Then L_D contains a number of terms, the first of which describes electronic dephasing, and is of the form

$$(\partial \rho / \partial t)_{\rm ed} = -\gamma_e \sum_{|Ai\rangle, |Dj\rangle} (|Ai\rangle \langle Dj| \rho_{Ai,Dj} + |Dj\rangle \langle Ai| \rho_{Dj,Ai}),$$
(4)

where γ_e and $\rho_{Ai,Dj}$ are, respectively, the electronic dephasing rate and a density matrix element, and summation takes place over pairs of vibrational states *i* and *j* on different electronic surfaces.

Additionally, L_D contains one term for each pair of vibrational states $|i\rangle$ and $|j\rangle$ on the same electronic surface, describing nuclear relaxation and associated dephasing between the pair of vibrational states.¹⁶ Here, for convenience, we take a simple approximate form for the nuclear relaxation which simplifies interpretation of our results. This limiting form is valid when differences in relaxation rates for different pairs of vibrational states are neglected, and the distribution of nuclear states is not too far from equilibrium.

$$(\partial \rho / \partial t)_{\rm nr} = \sum_{|Xi\rangle, |Xj\rangle} (|Xi\rangle \langle Xj|) \gamma_r (P_X \rho_{Xi, Xj}^{\rm eq} - \rho_{Xi, Xj}), \quad (5)$$

where γ_r denotes the nuclear relaxation rate, P_X denotes the electronic population on electronic state $|X\rangle$, and $\rho_{Xi,Xj}^{eq}$ is the equilibrium (thermal) value of the density matrix element if $P_X = 1$.

The validity of a semigroup description of the bath is corroborated by a recent study employing the surrogate Hamiltonian method to examine ultrafast charge transfer in condensed phase environments.²⁸ The surrogate Hamiltonian method does not assume that the bath is Markovian. Rather, the bath is approximated by a finite number of representative bath modes, which are treated fully quantum mechanically as two-level systems. In cases where the bath induces significant nuclear relaxation in the subsystem, deviation from the exponential decay characteristic of Markovian dynamics is small.

III. NUCLEAR HAMILTONIAN PARAMETERS

In this section, we discuss parametrization of the nuclear Hamiltonians $H_{D,i}$ and $H_{A,i}$ in Eq. (2) for the case of $(NH_3)_5RuNCRu(CN)_5^-$. Electronic structure calculations performed using the commercial package JAGUAR²⁹ were used for the parametrization. As discussed in Sec. II, we approximate the frequencies and anharmonicities of the subsystem (non-Markovian) inner sphere modes by those of the symmetric breathing modes of $Ru^{II}(NH_3)_6^{+2}$ and $Ru^{II}(CN)_6^{-4}$.

To determine the curvature of the electronic surfaces, geometry optimization of the metal complexes $\text{Ru}^{\text{II}}(\text{NH}_3)_6^{+2}$ and $\text{Ru}^{\text{II}}(\text{CN})_6^{-4}$ was performed, and then configurational energies were calculated at the DFT level using the B3LYP functional and LACVP basis, as a function of Ru–N and Ru–C bond length, respectively, for a fully symmetrical a_{1g} normal (breathing) mode. Calculations were performed over

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a 0.4 Å range of bond lengths centered on the value of the length for which the energy was lowest, and ligand geometries were kept constant. A least-squares fit of the data to a Morse potential was then performed for each metal complex, where the Morse potential is of the form³⁰

$$H = D [e^{-\alpha(r-r_0)} - 1]^2, \tag{6}$$

where r_0 is the equilibrium bond length, and D and α determine the surface curvature.

For the case of $\text{Ru}^{\text{II}}(\text{NH}_3)_6^{+2}$, the values of *D* and α were determined to be 0.3625 E_H and 0.8987 a_0^{-1} (r_0 was found to be 4.1753 a_0 , as compared to the experimental value²⁵ of 4.0517 a_0). The nuclear energy eigenvalues were determined by Chebyshev propagation with the relaxation operator e^{-Ht} (see Refs. 31 and 32), and the energy difference between lowest nuclear states found to be 387 cm⁻¹, compared to a value of 350 cm⁻¹ obtained spectroscopically.²⁵

The effective mass for the $Ru^{II}(NH_3)_6^{+2}$ breathing mode was taken to be six times the mass of NH₃, in which case the appropriate normal coordinate is the Ru-N bond length. For this effective mass, the coordinate describing the $Ru^{II}(CN)_{6}^{-2}$ breathing mode should be the Ru-C bond length times the factor $(m_{\rm CN}/m_{\rm NH_2})^{1/2}$. Other than the energy gap $\hbar \omega_{DA}$, the two electronic surfaces [modeled, as noted previously, after $Ru^{II}(NH_3)_6^{+2} + Ru^{III}(CN)_6^{-4}$] were taken to differ only by displacement of the equilibrium bond lengths. The experimentally indicated displacement of the $Ru^{II}(NH_3)_6^+$ surface relative to the $\operatorname{Ru}^{III}(\operatorname{NH}_3)_6^{+3}$ surface is 0.0756 $a_0^{,25}$ We assume a comparable change in covalent radius for the $Ru^{II}(CN)_6^{-4}$ breathing mode, such that the displacement in the nearly normal scaled coordinate is about $(0.0756a_0)(m_{\rm CN}/m_{\rm NH_2})^{1/2}$ $\approx 0.0935a_0$. For the $\operatorname{Ru}^{II}(\operatorname{CN})_6^{-4}$ mode, *D* in Eq. (4) was determined to be 0.2545 E_H , = 1.0833 $a_0^{-1} (m_{\text{NH}_3}/m_{\text{CN}})^{1/2} = 0.8760 a_0^{-1}$. while α

IV. ELECTRONIC COUPLING

We do not employ the usual approximation^{2,3} that the electronic coupling is entirely constant as a function of the nuclear coordinates. In fact, for the parameters we employed, this assumption leads to an unphysical "antiZeno" effect,³³ where non-negligible ET occurs from the bottom of the lower electronic surface to the upper electronic surface. A preferable approach is to represent the electronic coupling as a product

$$J(r) = J_{\max}F(r), \tag{7}$$

where J_{max} is the coupling strength at the "transition state," which is to say the lowest-energy point where the diabatic electronic surfaces intersect, and F(r) is a cutoff function of the distance from the transition state. The function F(r) is taken to be equal to 1 within a specified distance r_c of the transition state, and falls off continuously as $e^{-a^2(r-r_c)^2}$ beyond that cutoff distance. Herein, r_c is generally taken to be the distance from the transition state to the minimum of the higher electronic surface, so that the same function J(r) can reasonably be used with and without the harmonic approximation to the surfaces, and the difference reflects the role of anharmonicity, as independent as possible from the form of

electronic coupling. For the cases we investigated, the ET rate was not very sensitive to the value of *a*; herein we use $a = 1/(0.1r_c)$. While we find that the assumed functional form for the coupling is general enough to fit experimental results, an important direction for future study is to determine the actual electronic coupling strength as a function of configuration for this system, including the possible existence and relevance of a conical intersection.^{22–24}

V. CALCULATIONS

A. General considerations

Nuclear energy eigenstates and eigenvalues on each electronic surface were determined using Chebyshev propagation of the relaxation operator e^{-Ht} .^{31,32} Propagation of the density matrix under the influence of semigroups can be carried out using either a Newton method³¹ or split propagation.³⁴ We found that for the current problem, propagation of the density matrix in the energy eigenstate representation is very efficient, since sufficient accuracy is retained if one considers only the lowest 200 energy eigenstates on each electronic surface. Because the two-mode problem would require a two-dimensional grid in nuclear configuration space, more than 200 grid points would probably be required for accurate propagation in the position representation.

As in Ref. 16, for simplicity we model the photoinitiation of the reaction by taking the initial nuclear state on the electronic surface $|D\rangle$ to be equal to the lowest vibrational energy eigenstate on the electronic surface $|A\rangle$. Propagation then proceeds as described in Ref. 16.

B. The Ru–C bond stretching mode

First, the displacement in the mode describing stretching of the Ru–N bonds was neglected. This mode then played essentially no role, and the dynamics reflected only the effect of the mode describing stretching of the Ru–C bonds. For compounds such as $(NH_3)_5RuNCRu(CN)_5^-$, reaction is known to occur in the inverted regime,^{18,20} and including only one mode affects the energy gap required for the reaction to occur in this regime. Here, for convenience, we consider the energy gap $\hbar \omega_{DA} = 0.0045E_H$, in which case the two electronic surfaces take the form shown in Fig. 1. This energy gap is large enough for anharmonic effects to be appreciable, but small enough to be computationally convenient (a large number of nuclear energy eigenstates is not required for accurate propagation).

In addition to the two anharmonic electronic surfaces shown in Fig. 1, approximate harmonic electronic surfaces (based on Taylor expansion about the equilibrium nuclear configuration) are also shown, as a function of the Ru–C bond stretching coordinate. Including anharmonicity shifts the location of the curve crossing point outward, to a point where the bond is more strongly stretched, and increases the energy of the curve crossing point. Also, the difference in the slopes of the electronic surfaces near the intersection is reduced when anharmonicity is included.

The time-dependent population of the excited-state surface is shown in Fig. 2, with and without including electronic



Lockwood, Ratner, and Kosloff



FIG. 1. The excited and ground diabatic electronic surfaces are shown, as a function of the Ru–C bond stretching coordinate. The solid lines indicate the surfaces when anharmonicity is included. The dashed lines indicate the harmonic approximation to the surfaces, based on Taylor expansion about the equilibrium geometries on each surface. For the approximate harmonic surfaces, the curves cross where the bond displacement and the configurational energy are lower. Additionally, the difference in the slopes of the electronic surfaces near the intersection is increased when the harmonic approximation is made.

dephasing, for both the exact surface and the approximate (harmonic) surface. The electronic coupling strength was arbitrarily chosen to be $0.2 \hbar \omega$, where ω is the angular oscillator frequency 318 cm⁻¹ of the Ru–C stretching mode, while the electronic dephasing time was taken to be 20 fs (consistent with experiment¹⁸). While the two-dimensional electronic coupling function described in Sec. IV does de-



FIG. 2. The excited state population, as a function of time, is shown for the case where electronic dephasing is neglected (solid lines) or included (dashed lines). Bold lines or dashes denote the case where anharmonicity is included, while light lines or dashes denote the case where the harmonic approximation to the surfaces is used. The electronic dephasing rate is 1/(20 fs).

FIG. 3. The excited state population, as a function of time, is shown for the approximate harmonic surfaces, and compared to the case where anharmonicity is included. The electronic dephasing time is 20 fs, and the nuclear relaxation time is 200 fs. Neglecting anharmonicity leads to a small increase in electron transfer rate.

pend on the Ru–N bond stretching coordinate, test simulations indicate that neglecting this dependence does not significantly affect the behaviors discussed in this section. As such, the dynamics reflects only the nature of the Ru–C bond stretching mode.

When electronic dephasing is neglected, the dynamics is visibly affected by the presence of anharmonicity, as shown in Fig. 2. But including the electronic dephasing gives rise to irreversible dynamical behavior, where an asymptotic population value is approached, and also results in a less dramatic effect of anharmonicity. This is in part because at the significant electronic dephasing rate of 1/(20 fs), electronic dephasing reduces the initial ET rate (for both the harmonic and anharmonic cases) and diminishes the short-time population oscillations.

Inclusion of nuclear relaxation is required in order to obtain the correct asymptotic value of the population at long times.¹⁶ In Fig. 3, we show the results when nuclear relaxation, at a rate 1/(200 fs), is included. In addition to altering the asymptotic population limit, including nuclear relaxation also leads to decay of the short-time oscillations in population, as a transition occurs from nonequilibrium dynamical nuclear motion to a thermally relaxed distribution of nuclear configurations. A short-time rate increase with anharmonicity is evident in Fig. 3, despite the higher reaction barrier present when anharmonicity is included (illustrated in Fig. 1). Furthermore, oscillations in the change in excited state population with anharmonicity are negligible at long times, making a comparison of rates meaningful. The small but evident rate increase with anharmonicity can be attributed to three aspects of our model, discussed in the following: the reactant and product vibronic states are affected by anharmonicity, spectral broadening preserves the effect of the short time dynamics at longer times, and the electronic coupling is



FIG. 4. A comparison is made between cases where electronic dephasing ("ed") is included or neglected, and anharmonicity is also either included or neglected. When included, the electronic dephasing time is 20 fs. In all cases, the nuclear relaxation time is 200 fs. The lowest ET rate is obtained when the harmonic approximation is made and electronic dephasing is included. Including anharmonicity increases the rate slightly. Neglecting electronic dephasing significantly increases the rate, but in this case the effect of anharmonicity at short times is not necessarily preserved at long times.

taken to be negligible at sufficient distance from the crossing point of the diabatic electronic surfaces.

The importance of the first factor, the change in vibronic states with anharmonicity, is evident in the short-times dynamics shown in Fig. 2, for the case where bath effects are neglected. The initial population transfer rate is seen to be greater when anharmonicity is included. This effect remains when an initial thermal distribution of reactant vibronic states is used, rather than the initial photoinduced wave packet. However, the wave packet dynamics enhances the effect of anharmonicity since the wave packet momentum is lower in the region where the electronic surface curves cross, leading to an increase in the time spent in this region. Including anharmonicity increases the reactant nuclear density in the curve crossing region, as well as the product vibronic density of states near the energy of this curve crossing region. These effects are consistent with the increase in ET rate.

However, in the absence of the significant effective spectral broadening introduced by the electronic dephasing semigroup, the effect of anharmonicity on the ET rate can be restricted to short times. This is evident in our model when the pure electronic dephasing semigroup is not included, such that the dephasing rate is significantly reduced (although some dephasing remains since the nuclear relaxation semigroup is included). As illustrated in Fig. 4, the ET rate at short times is still affected in this case by anharmonicity, but the effect is temporary. Only at higher electronic dephasing rates do off-resonant electronic transitions make a significant contribution, resulting in less marked population oscillations at short times. With increasing electronic dephasing, it becomes more important that the nuclear density in the coupling region increases with anharmonicity, and less important where the electronic surfaces cross. As a result, the effect of anharmonicity on the initial ET rate is preserved at longer times as well.

It is interesting to note the dual role of increasing electronic dephasing. On the one hand, for high electronic dephasing rates, the overall ET rate decreases with increasing dephasing (consistent with the so-called "Zeno" effect), while on the other hand, the relative importance of offresonant electronic transitions *increases* with increased electronic dephasing, consistent with the so-called "anti-Zeno" effect³³ and effective spectral broadening. The latter effect leads to lower-amplitude oscillations in the excited state population with time, and preserves the short-time effect of anharmonicity at longer times.

The effect of anharmonicity cannot be considered without considering the spatial dependence of the electronic coupling. In fact, for sufficiently large cutoff distances r_c , we find that anharmonicity reduces rather than increases the ET rate. This is a consequence of the significant role of offresonant electronic transitions in the presence of strong electronic dephasing. It should be noted that there are other parameters that also impact the effect of anharmonicity on the rates. In particular, if an electronic energy gap of $\hbar \omega_{DA} = 0$ is used, no significant difference in the dynamics between the harmonic and anharmonic cases is observed, even if the effect of the bath is ignored, underscoring the fact that the importance of anharmonicity increases with the electronic energy gap in the inverted regime. It is also worth noting the difference in the mass and frequency of the subsystem nuclear mode compared to Ref. 16 (a mode with an effective mass of 200 000 m_{ρ} and frequency 110 cm⁻¹ should be used with the parameters in Ref. 16 to reproduce the harmonic oscillator results therein). The high frequency and low effective mass for the mode described here apparently decrease the effect of the anharmonicity-induced barrier height change (illustrated in Fig. 1) on the observed dynamics.

It is interesting to note that a turnover¹⁶ in the ET rate is observed with increasing anharmonicity. As shown in Fig. 5, for high anharmonicity, the ET rate begins to decrease with increasing anharmonicity. In this regime, the rate decrease with anharmonicity can be attributed to the curve crossing point becoming less energetically accessible, consistent with conventional electron transfer models.¹ As such, the anharmonicity in mixed valence compounds can be characterized as low, in the sense that the energetic accessibility of the "transition state" is not significantly affected by anharmonicity.

C. Two nuclear modes and electronic coupling strength

We now turn to the case where displacement of the second (NH₃) mode with an electronic state change is also included. For convenience, we took the electronic energy gap to be $\hbar \omega_{DA} = 0.0075 E_H$. This increased value keeps the reaction in the inverted regime, now that a second mode is included in the subsystem. This energy gap is on the order of, but smaller than, the value suggested by the experimental excitation energy,¹⁸ and is chosen because it is more conve-



FIG. 5. The excited state population as a function of time is shown, for different values of the Morse potential dissociation energy D/D_0 , where D_0 is the correct (fit) value for the system. The correct level of anharmonicity [corresponding to $a = (D/D_0)^{-1} = 1$] leads to a small increase in electron transfer rate over the harmonic case (a=0). A turnover occurs at higher degrees of anharmonicity, after which increasing anharmonicity decreases the electron transfer rate, consistent with decreasing energetic accessibility of the point where the electronic surfaces cross. In all cases, the value of α in Eq. (6) is selected so that the leading (harmonic) term in the potential energy is unaffected, and the magnitude of the higher (anharmonic) terms increase with decreasing *D*. The electronic dephasing time is 20 fs and the nuclear relaxation time is 200 fs.

nient to work with computationally (fewer nuclear energy eigenstates need to be included).

The resulting surfaces are shown in Fig. 6, for the case where the harmonic approximation is invoked, while Fig. 7



FIG. 6. The excited and ground electronic surfaces are shown, as a function of the Ru–C and Ru–N bond stretching coordinates, with a harmonic approximation based on Taylor expansion about the equilibrium nuclear configurations. The surfaces cross along a line of points, forming a seam.



FIG. 7. The excited and ground electronic surfaces are shown, as a function of the Ru–C and Ru–N bond stretching coordinates, with anharmonicity in the Ru–C bond stretch included. There is a small but visible effect of anharmonicity on the location of the points where the surfaces cross.

shows the case where the anharmonicity in the CN mode is included. Anharmonicity has a small but apparent effect on the location of the seam where the curves cross. The dynamics when anharmonicity is included are illustrated in Fig. 8, for the case where electronic dephasing and nuclear relaxation are neglected, the case where only electronic dephasing is included, and the case where both electronic dephasing



FIG. 8. The excited state population as a function of time is shown for the case where both subsystem modes are included. When the effects of both non-Markovian intramolecular modes are included, the effect of the bath on the dynamics is less dramatic. A comparison is made between the case where both electronic dephasing ("ed") and nuclear relaxation ("nr") are neglected, the case where only electronic dephasing is included, and the case where both electronic dephasing and nuclear relaxation are included. The electronic dephasing time is 20 fs. The nuclear relaxation time is 200 fs for the two modes.



FIG. 9. Excited electronic state population relaxation is shown, for various electronic coupling strengths J_{max} . In the legend, nJ denotes an electronic coupling strength which is *n* times the default value, $0.2\hbar \omega$, where ω is the angular oscillator frequency 318 cm⁻¹ discussed in Sec. V B. The electronic dephasing and nuclear relaxation times are, respectively, 20 and 200 fs.

and nuclear relaxation are included. Evidently, for this case of two modes, the closed system behavior at short times is more akin to the irreversible dynamics observed in the presence of the bath, although the long time asymptotic behavior will differ. Also, we note that neglecting anharmonicity leads to a small decrease in ET rate, as is the case for a single nuclear mode.

We followed the analysis described in Ref. 18 of the short-time oscillations in excited state population. In particular, the long-time population relaxation was fit to an exponential function, and then the time-dependent difference between the population and exponential function was Fourier transformed. Predictably, the resulting spectrum consisted primarily of the two subsystem vibration frequencies. Comparison with the results in Ref. 18 indicates that the presence of the solvent and the bridge between ruthenium ions does perturb the short-time coherent vibrational motion. However, frequencies described therein are on the order of the two frequencies appearing in our model.

The effect of varying the electronic coupling strength is illustrated in Fig. 9. For high J_{max} , there is an initial fast ET followed by slower thermal transfer. This is consistent with the interpretation that the extremely fast ET rates in mixed valence compounds are due in part to the fact that the electronic tunneling motion is faster than nuclear relaxation.²¹ Also, for the parameters studied here, turnover behavior¹⁶ with increasing J_{max} is slow to set in. So an assumption of large electronic coupling is sufficient to explain experimental ET rates, without assuming a functional form for *J* that leads to conical intersection.

VI. CONICAL INTERSECTION

In some cases, introducing certain spatial dependence for the electronic coupling, such as forms for the electronic coupling that give rise to conical intersections,^{22–24} can lead to more rapid electron transfer, without requiring an increase in the electronic coupling strength at the conventional "transition state." To create a conical intersection, the abovedescribed function J(r) should be multiplied by a function which is antisymmetric about the line passing through the minimum energy configuration on each surface. Effects of using linear functions of various slope are currently being investigated.

VII. CONCLUSIONS

We have developed a semigroup model of electron transfer dynamics in mixed valence compounds, which elucidates the effects of anharmonicity in inner sphere nuclear modes, as well as the dependence of the electronic dynamics on the nature of the electronic coupling. We find that including the anharmonicity in inner sphere vibrations leads to a very small increase in the ET rate, due in part to the change in reactant and product vibronic states when anharmonicity is included. However, this effect of anharmonicity is dependent on the nature of the electronic coupling, and also is only preserved at long times if the significant spectral broadening induced by the bath is included.

As a result of the significant spectral broadening, offresonant electronic transitions make a significant contribution, resulting in reduction of the short-time oscillations in excited state population. Correspondingly, the importance of the point where the electronic surfaces cross is decreased, and consequently the short-time effect of anharmonicity on the excited state population is preserved at long times. We find that electronic dephasing plays a dual role in the ET dynamics: it induces the spectral broadening which increases the relative importance of off-resonant electronic transitions, consistent with the so-called "anti-Zeno" effect,³³ but also decreases the overall ET rate when electronic dephasing is rapid, consistent with the so-called "Zeno" effect.

The significant "anti-Zeno" effects observed at high electronic dephasing rates make the position dependence of the electronic coupling particularly important. We have considered primarily a coupling function which is constant in the vicinity of the minimum energy configuration where the diabatic electronic surfaces cross, but small near the equilibrium nuclear configurations. For this electronic coupling function, neglecting anharmonicity leads to a small decrease in the ET rate. However, the effect of anharmonicity cannot be resolved independently from consideration of the nature of electronic coupling and dephasing. It is also noteworthy that the presence of the second nuclear mode increases the effective electronic dephasing rate, so that ratelike behavior is observed at lower bath-induced contributions to the electronic dephasing rate.

The degree of anharmonicity in inner sphere modes of mixed valence compounds is small, in the sense that the energetic accessibility of the point where the diabatic electronic surfaces cross is not significantly affected by anharmonicity. At higher anharmonicity, we find that the location of the "transition state" where electronic surfaces cross does play a central role, as it does in conventional electron transfer theories which consider only classical nuclear configurations.¹ But for the small anharmonicity in mixed

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valence compounds, the details of vibronic states play a more significant role in the explanation of anharmonic effects than does the place where the curves cross. In general, we find only very small effects on the ET process due to the anharmonicity in the mixed valence model.

For high electronic coupling strengths, an initial fast ET rate is observed, followed by slower thermal transfer. Also, turnover behavior with electronic coupling is slow to set in with increasing coupling strength. As a result, an assumption of significant electronic coupling is found to be sufficient to explain experimental ET rates, without requiring a nuclear configuration-dependent electronic coupling that leads to conical intersection.

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