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Ab Initio Computation of the Duschinsky Mixing of Vibrations and Nonlinear Effects

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We present an analysis of the Duschinsky effect and its application to real molecules. We discuss the many subtle aspects of applying the theory to calculations and give examples of a nonlinear normal coordinate transformation. We show how to judge if nonlinear effects are small enough to be neglected through use of the zero-order axis-switching approximation, which allows calculation of Franck−Condon factors (FCF). However, even with the zero-order axis-switching approximation, nonorthogonality can occur in the Duschinsky matrix, and this must be corrected to allow proper FCF calculations. We have calculated the Duschinsky effect for two systems that form the anion in an electron-transfer ion pair, $V(CO)_6^-$ and $Co(CO)_4^-$. The formation of the D_{3d} neutral vanadium species is accompanied by a small geometric distortion and small Duschinsky effect, despite the change in point group from O_h. We discuss how to perform the calculations to properly represent degenerate vibrations and how to test if the linear approximation is adequate. The tetrahedral cobalt anion undergoes a much larger geometrical distortion, which results in a larger Duschinsky effect, upon formation of the nearly C_{3v} neutral species. The analysis of the cobalt system, with a C_1 symmetry for the neutral, demonstrates the methods required when there is no simplification from symmetry. These two examples show the validity of the zero-order axis-switching approximation. The cobalt complex has much larger reorganization energy and a much greater dependence of reorganization energy on the choice of reference state, as expected when the Duschinsky effect is larger. We briefly outline the method of applying these computations to electron-transfer rate calculations.

Introduction

When a molecule undergoes an electronic transition, the change in electronic state is usually accompanied by a change in the normal modes of vibration. This phenomenon was first considered in 1937 by Duschinsky,[1] and is therefore given the name the Duschinsky effect. The result is that normal modes of one state are no longer orthogonal to the normal modes of the other state. A result is that the overlap integrals of the vibrational wave functions, or Franck−Condon factors (FCF), are no longer separable into products of one-dimensional FCF calculations, and one must use multidimensional FCF. We have recently shown that the additional complexity of multidimensional FCF can lead to large effects on electron-transfer rates.[2] Therefore, a treatment of the Duschinsky effect is required that demonstrates how to compute the Duschinsky effect for complex molecules. Furthermore, there are many subtle points in using and interpreting the theory that are illustrated through specific calculations on complex molecules involved in electron transfer within ion pairs.

For complex molecules, it is difficult to generalize the relationship between the two sets of normal modes involved in a transition. Duschinsky proposed that the two sets of normal modes were related by a linear transformation. This is analogous to a simple multidimensional rotation and translation and leads to the following,[1,3−5]

$$Q' = JQ + K \tag{1}$$

$$J = L'^T L \tag{2}$$

$$K = L'^T m^{1/2}(x^0 - x^{0\prime}) \tag{3}$$

$$\xi = LQ \tag{4}$$

$$\xi = m^{1/2}(x - x^0) = m^{1/2}\rho \tag{5}$$

where x is the vector of Cartesian coordinates, $m^{1/2}$ is a diagonal matrix with each atom's mass appearing three times, x^0 is the vector of equilibrium coordinates, ρ is the Cartesian displacement coordinate vector, ξ is the mass weighted Cartesian displacements coordinates, L is the normal coordinate matrix, Q are normal coordinates, K is the normal coordinate displacement vector, and J is the Duschinsky matrix. Also, primed terms refer to the initial state and unprimed terms refer to the final state. The matrix L transforms the mass-weighted Cartesian displacement coordinates, ξ, into normal coordinates, Q. K gives the displacements between the equilibrium structures of the two states in terms of initial state normal coordinates. The two states must be oriented so that they have the largest number of symmetry elements in common with the center of mass at the origin; however, this condition is not sufficient to prevent potential nonlinear effects from axis-switching that must occur between the two states.

Axis-Switching Effects

Nonlinear Effects. Many authors have developed methods to calculate multidimensional FCF.[3,6−10] All of this work has assumed a linear transformation between sets of normal coordinates, as was suggested by Duschinsky. However, Duschinsky's analysis ignored complications arising from the separation of vibrations, translations, and rotations. These complications were resolved for a single state by Eckart[11] at around the same

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time as Duschinsky's work. Later, Hougen and Watson[12] showed that in order to satisfy the Eckart conditions for both states, axis-switching effects need to be taken into account. This results in eq 6, which ensures that the rotational and translational coordinates of both states are equal to zero. Basically, this means that the coordinate system must rotate upon a change in electronic state in order to satisfy these conditions. These axis-switching effects can lead to experimentally observable phenomena. Experimental observation of nominally forbidden rotational lines in the gas-phase spectrum of acetylene has been explained by including axis-switching effects.[12] The axis-switching also makes the transformation nonlinear since the axis-switching matrix depends on the instantaneous coordinates, which are continuously changing as the molecule vibrates. With axis-switching taken into account, eqs 2 and 3 become eqs 7 and 8.[5]

$$x^0 + \rho = B(x^{0\prime} + \rho') \tag{6}$$

$$J = L'^T B^{-1} L \tag{7}$$

$$K = L'^T m^{1/2}(B^{-1}x^0 - x^{0\prime}) \tag{8}$$

$$\sum_{i=1}^{N} m_i \begin{pmatrix} x^{0\prime}_{3i-2} \\ x^{0\prime}_{3i-1} \\ x^{0\prime}_{3i} \end{pmatrix} \times \left(T^{-1} \begin{pmatrix} \rho_{3i-2} + x^0_{3i-2} \\ \rho_{3i-1} + x^0_{3i-1} \\ \rho_{3i} + x^0_{3i} \end{pmatrix} \right) = 0 \tag{9}$$

Here, B is a 3N × 3N block diagonal matrix with the 3 × 3 Hougen and Watson axis-switching matrix, T, appearing along the diagonal. T is given by eq 9 and the sum is over each atom.[5,12] The axis-switching matrix, T, depends on the instantaneous coordinates and gives rise to the nonlinearity. Fortunately, the axis-switching effects, and the resulting complications, occur only for certain vibrational modes, namely modes that are of the same symmetry as a rotation.[4]

The following discussion assumes that the point group is based on only the symmetry elements that are common to both states, with a relative axis orientation having the maximum number of symmetry elements in common. The symmetry may be lower than that of either state by itself. For example, the ground state of ethylene is planar D_{2h}, and the excited state is thought to have one CH_2 group rotated by 90° with D_{2d} symmetry. To achieve the proper relative axis orientation, one state must be rotated by 45°, resulting in a common D_2 point group.

Axis-switching effects occur only for displacements along modes of the same symmetry as a rotation. Axis-switching effects occur because the motions caused by displacements along vibrational normal modes of one state cannot be described by displacements along a linear combination of only vibrational normal modes of the other state. To properly describe these motions we must include rotational coordinates.[4,5] Molecules of high enough symmetry (common point group of two states not C_1, C_s, C_i, C_n, C_{nh}, or S_n) exhibit these effects only for certain nontotally symmetric modes. For axis-switching effects to occur for displaced totally symmetric modes, the common point group of the molecule must have rotations that belong to the totally symmetric representation. From inspection of point group tables, this is true only for low symmetry (C_1, C_s, C_i, C_n, C_{nh}, and S_n) point groups. Since there can be no displacements along nontotally symmetric modes between the equilibrium structures of the two states, the overall axis-switching effects are expected to be smaller in the higher symmetry cases.

Zero-Order Axis-Switching Approximation. The transformation between sets of normal coordinates can be made linear. This is accomplished with the zero-order axis-switching approximation. This approximation is accomplished by replacing eq 9 with eq 10.[12]

$$\sum_{i=1}^{N} m_i \begin{pmatrix} x^{0\prime}_{3i-2} \\ x^{0\prime}_{3i-1} \\ x^{0\prime}_{3i} \end{pmatrix} \times \left((T^0)^{-1} \begin{pmatrix} \mathbf{x}^0_{3i-2} \\ x^0_{3i-1} \\ x^0_{3i} \end{pmatrix} \right) = 0 \tag{10}$$

Equation 10 is the result of ignoring the displacements in eq 9. This results in an approximate linear transformation and allows the use of standard equations for Franck−Condon factors. One problem is that there are eight possible solutions to eq 9.[7] Of the eight, four can be ruled out because T^0 is a rotation matrix, so the determinant must be equal to +1. Of the four remaining solutions, the proper choice is obvious from the relative orientation of the two states after rotation. Solving eq 10 for the proper solution can be difficult. Fortunately, a closed form solution has been derived which easily gives all eight solutions.[7] The first step is to form the following 3 × 3 matrix.

$$C_{\alpha\beta} = \sum_{i=1}^{N} m_i[(x_i^0)_\alpha (x_i^{0\prime})_\beta] \tag{11}$$

In eq 11, α and β denote x, y, and z. For planar molecules, C_{zz} is set equal to unity. Diagonalization of the product $C^T C$ results in a matrix, R, with eigenvectors as columns, and the corresponding diagonal matrix of eigenvalues, λ. An additional matrix Λ, which has +1 or −1 along the diagonal, is needed. The equation for T^0 is

$$T^0 = R\Lambda\lambda^{1/2}R^T C^{-1} \tag{12}$$

with the eight solutions arising from the eight possibilities for Λ. Again, four solutions are ruled out because the determinant of T^0 must be +1. Of the remaining four, the correct choice is made by converting to B^0 and applying the rotation to $x^{0\prime}$ and comparing the orientation to x^0, or equivalently rotating x^0 by $(B^0)^{-1}$ and comparing to $x^{0\prime}$. The choice that results in structures with corresponding atoms in closest proximity is correct. In addition, Ozkan describes a method that works if only a 2-dimensional rotation is needed for the axis rotation.[4]

For the high symmetry point groups (not C_1, C_s, C_i, C_n, C_{nh}, or S_n), zero-order axis-switching is not required if the two states of the molecule are oriented in such a way that they have the highest number of common symmetry elements.[4] However, if the states are not aligned in such a manner, zero-order axis-switching is necessary to align the states in the proper manner. In the low symmetry point groups (C_1, C_s, C_i, C_n, C_{nh}, and S_n), the zero-order axis-switching always must be included to properly orient the equilibrium structures of the two states relative to each other. In this case, a maximum coincidence of common symmetry elements still does not ensure that the Eckart conditions are satisfied at equilibrium in both coordinate systems. The application of a zero-order axis-switching method still leaves nonlinear effects in some vibrations, and we discuss this in the following paragraph.

Since molecules are always vibrating and the instantaneous coordinates changing, even in the ground vibrational state, the zero-order approximation should lead to errors in FCF. Generally, in electron transfer rate calculations and absorption and emission spectrum calculations, totally symmetric modes are of much more importance than nontotally symmetric modes.

This is due to the lack of displacements along nontotally symmetric modes. For the high symmetry cases, no axis-switching effects occur along the totally symmetric modes, so the ignored nonlinearities occur only along nondisplaced, nontotally symmetric modes. Since the important region for FCF along nondisplaced modes is small, consisting only of the width of the wave function, small nonlinear axis-switching effects will occur and their neglect should be an acceptable approximation. In the low symmetry cases, axis-switching and the accompanying nonlinearities do occur for displaced totally symmetric modes. Since there are displacements along these modes, the important region for FCF calculation is much larger, suggesting larger errors involved in ignoring the nonlinear aspect of the transformation.

However, even in the low symmetry case, the zero-order axis-switching approximation has been suggested to be a fairly good approximation as long as displacements are small.[4,12] This suggests that using a linear transformation, which is necessary to use published methods for FCF calculations, might be a good approximation for either totally symmetric or nontotally symmetric modes. A convenient method of computing multidimensional FCF has been developed that uses recursion relations.[13]

Nonorthogonality of the Duschinsky Matrix. There is an additional problem when we consider modes with the same symmetry as a rotation. Since the vibrations of one state cannot be properly described as a linear combination of vibrations of the other state, the Duschinsky matrix is not orthogonal and has a determinant that is not equal to one.[4] This results in a violation of the sum rule for FCF. The squares of the FCF of a vibrational level of one electronic state with all of the vibrational levels of another electronic state should sum to unity, but do not when the determinant of J is not unity. The sum rule violation will obviously lead to errors in absolute rate calculations, with calculated rates being too large. Errors will also occur in absorption and emission spectra, even if in arbitrary units, because the relative errors are not the same for each FCF calculated. However, this might be overcome in an approximate way through a renormalization of the Duschinsky matrix, although we have not tested this idea.

It must be noted that the preceding analysis was performed using Cartesian coordinates. A similar analysis exists in the literature using internal coordinates.[4] However, this results in more complex equations and requires the determination of the internal coordinates as a function of Cartesian coordinates, which is not a trivial matter with a unique correspondence.

Parameters from Ab Initio Calculations

We have used a specific quantum chemistry package, Gaussian,[14] although the general method should be similar for any quantum chemistry package. First, a geometry optimization and a vibrational normal mode calculation must be performed for both states of interest. Since the normal modes are given in the standard orientation, this same orientation must be used for the atomic coordinates. Since the standard orientation is not in center of mass coordinates, but instead is in center of nuclear charge coordinates, the atomic coordinates must be translated into center of mass coordinates unless the symmetry is high enough that this is already the case. This has no effect on the normal modes. In eq 2, the normal mode matrix, L, is given in mass-weighted coordinates, while Gaussian outputs give normal modes in coordinates that are not mass weighted. To convert the normal modes to the correct type of coordinates, multiplication of the matrix $m^{1/2}$ of eq 5 and the Gaussian normal coordinate matrix must be performed. Then, each column of this matrix must be renormalized to give an orthogonal normal mode matrix where $L^{T}L = 1$. This factor is called the reduced mass in Gaussian.

It is essential to orient the two states with the maximum number of common symmetry elements. A relative orientation change may be necessary because each state can be in a different standard orientation. To ensure that the relative orientation is correct, calculation of T^0 can be performed as a test. If the resulting T^0 is the unit matrix, the states are properly oriented and eqs 2 and 3 can be used to calculate J and K. If T^0 is not the unit matrix, then conversion to B^0 is needed and eqs 7 and 8 must be used to find J and K. Complications may arise from degenerate modes when the degeneracy in a high symmetry state is broken in a lower symmetry state. An example of this will be discussed in the next section. We emphasize that B^0 must always be calculated for low symmetry (C_1, C_s, C_i, C_n, C_{nh}, and S_n) point groups.

Example Calculations for Electron Transfer

Two examples involving a state change from an anion to a radical were selected for study because these represent the anion half of an electron-transfer ion pair system.[15,16] The two states are both lowest energy states, so that standard ab initio methods can give excellent results. We expected the anion to undergo a geometrical distortion and change in symmetry upon formation of the neutral radical species, resulting in substantial Duschinsky effects. The cation half of the ion pair complex has less geometric reorganization so that we emphasize the anion component in order to reduce the computational effort. In addition, the calculations remain transferable since a variety of cations can be used to form the ion pair.[15]

$V(CO)_6$. The first example is $V(CO)_6{}^{-1/0}$. This serves as the anion in the ion pair $Co(Cp)_2{}^+|V(CO)_6{}^-$, which undergoes photoinduced electron transfer to form a radical pair which then undergoes a spontaneous reverse electron-transfer back to the ion pair. An interesting feature of this system is that experiments have shown different electron-transfer rates as a function of vibrational level in the $V(CO)_6$ radical.[16,17] B3LYP calculations were performed with the 6-311G basis set for vanadium and 6-311G(d,p) basis sets for carbon and oxygen. The calculations result in an octahedral geometry for the anion and D_{3d} geometry for the neutral species. The resulting atomic coordinates are given in Table 1. For the neutral species, the C−V−C angles are 93.8° and 86.2°, compared to 90° in the O_h anion. In addition, normal mode calculations were performed at the optimized geometry of each state. The symmetries and frequencies of the resulting vibrations are given in Table 2. In both cases, the standard orientation was in center of mass coordinates due to the symmetry of the molecule, so it was unnecessary to translate the coordinates. From inspection of the coordinates of the two species, it can be seen that the two states are oriented differently and do not have the maximum number of symmetry elements in common. This is due to the way Gaussian chooses the standard orientation for O_h and D_{3d} symmetries. To correct this, B^0 was calculated from eq 12.

In the octahedral anion, the vibrational calculation results in two A_{1g}, four E_g, three T_{1g}, six T_{2g}, twelve T_{1u}, and six T_{2u} vibrational normal modes. When treated in D_{3d} symmetry, the triply degenerate modes become A and E modes. For example, T_{1u} becomes E_u and A_{2u}. The calculated O_h mode correlates to four A_{1g}, one A_{2g}, ten E_g, two A_{1u}, four A_{2u}, and twelve E_u modes in D_{3d} symmetry, as is also calculated for the D_{3d} neutral species. The application of eqs 7 and 8 results in a Duschinsky matrix, J, and a displacement vector, K. The displacement

TABLE 1: Standard Orientation Atomic Coordinates (in angstroms) for $V(CO)_6$, $V(CO)_6^-$ in O_h Symmetry, and $V(CO)_6^-$ in D_{3d} Symmetry

	D_{3d} $V(CO)_6$			O_h $V(CO)_6^-$			D_{3d} $V(CO)_6^-$		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
V	0	0	0	0	0	0	0	0	0
C	0	1.701632	1.086112	0	0	1.970822	0	1.609178	1.137843
C	0	−1.701632	−1.086112	0	0	−1.970822	0	−1.609178	−1.137843
C	−1.473657	−0.850816	1.086112	0	1.970822	0	−1.393589	−0.804589	1.137843
C	1.473657	0.850816	−1.086112	0	−1.970822	0	1.393589	0.804589	−1.137843
C	−1.473657	0.850816	−1.086112	1.970822	0	0	−1.393589	0.804589	−1.137843
C	1.473657	−0.850816	1.086112	−1.970822	0	0	1.393589	−0.804589	1.137843
O	0	2.669554	1.690295	0	0	3.128572	0	2.554477	1.80627
O	0	−2.669554	−1.690295	0	0	−3.128572	0	−2.554477	−1.80627
O	−2.311902	−1.334777	1.690295	0	3.128572	0	−2.212242	−1.277238	1.80627
O	2.311902	1.334777	−1.690295	0	−3.128572	0	2.212242	1.277238	−1.80627
O	2.311902	−1.334777	1.690295	−3.128572	0	0	2.212242	−1.277238	1.80627
O	−2.311902	1.334777	−1.690295	3.128572	0	0	−2.212242	1.277238	−1.80627

TABLE 2: Calculated Vibrational Frequencies, Symmetries, and Displacements for the $V(CO)_6/V(CO)_6^-$ System

	D_{3d} $V(CO)_6$				O_h $V(CO)_6^-$				D_{3d} $V(CO)_6^-$			
	ν (cm^{-1})		K^a	λ_i (cm^{-1})^b	ν (cm^{-1})		K^a	λ_i (cm^{-1})^b	ν (cm^{-1})		K^a	λ_i (cm^{-1})^b
ν_1	54.46	E_u	0	0	54.42	T_{2u}	0	0	52.22	A_{1u}	0	0
ν_2	54.46	E_u	0	0	54.42	T_{2u}	0	0	52.37	E_u	0	0
ν_3	66.2	A_{1u}	0	0	54.42	T_{2u}	0	0	52.37	E_u	0	0
ν_4	82.07	E_g	0	0	89.29	T_{2g}	−1.012	121	88.59	A_{1g}	1.752	357
ν_5	82.07	E_g	0	0	89.29	T_{2g}	0.56	37	88.62	E_g	0	0
ν_6	83.54	A_{1g}	1.733	311	89.29	T_{2g}	1.317	205	88.62	E_g	0	0
ν_7	89.95	A_{2u}	0	0	96.55	T_{1u}	0	0	96.03	A_{2u}	0	0
ν_8	96.22	E_u	0	0	96.55	T_{1u}	0	0	96.08	E_u	0	0
ν_9	96.22	E_u	0	0	96.55	T_{1u}	0	0	96.08	E_u	0	0
ν_{10}	312.84	E_g	0	0	364.69	T_{1g}	0	0	363.95	E_g	0	0
ν_{11}	312.84	E_g	0	0	364.69	T_{1g}	0	0	363.95	E_g	0	0
ν_{12}	326.22	E_g	0	0	364.69	T_{1g}	0	0	363.96	A_{2g}	0	0
ν_{13}	326.22	E_g	0	0	382.27	A_{1g}	−0.45	438	382.27	A_{1g}	0.45	438
ν_{14}	336.81	A_{2g}	0	0	389.91	E_g	0	0	389.74	E_g	0	0
ν_{15}	348.67	A_{1g}	−0.5465	538	389.91	E_g	0	0	389.74	E_g	0	0
ν_{16}	399.91	A_{2u}	0	0	462.52	T_{1u}	0	0	462.34	A_{2u}	0	0
ν_{17}	402.33	E_u	0	0	462.52	T_{1u}	0	0	462.36	E_u	0	0
ν_{18}	402.33	E_u	0	0	462.52	T_{1u}	0	0	462.36	E_u	0	0
ν_{19}	456.01	E_u	0	0	518.23	T_{2u}	0	0	517.13	A_{1u}	0	0
ν_{20}	456.01	E_u	0	0	518.23	T_{2u}	0	0	517.24	E_u	0	0
ν_{21}	456.07	A_{1g}	0.24	178	518.23	T_{2u}	0	0	517.24	E_u	0	0
ν_{22}	471.76	E_g	0	0	522.63	T_{1u}	−0.222	200	521.86	A_{1g}	−0.281	319
ν_{23}	471.76	E_g	0	0	522.63	T_{1u}	0.062	16	521.86	E_g	0	0
ν_{24}	511.54	A_{1u}	0	0	522.63	T_{1u}	0.163	108	521.86	E_g	0	0
ν_{25}	543.27	A_{2u}	0	0	678.06	T_{1u}	0	0	677.69	A_{2u}	0	0
ν_{26}	622.14	E_u	0	0	678.06	T_{1u}	0	0	677.76	E_u	0	0
ν_{27}	622.14	E_u	0	0	678.06	T_{1u}	0	0	677.76	E_u	0	0
ν_{28}	2045.3	E_g	0	0	1954.81	T_{1u}	0	0	1954.77	A_{2u}	0	0
ν_{29}	2045.3	E_g	0	0	1954.81	T_{1u}	0	0	1954.77	E_u	0	0
ν_{30}	2066.03	E_u	0	0	1954.81	T_{1u}	0	0	1954.71	E_u	0	0
ν_{31}	2066.03	E_u	0	0	1974.09	E_g	0	0	1974.04	E_g	0	0
ν_{32}	2068.98	A_{2u}	0	0	1974.09	E_g	0	0	1974.04	E_g	0	0
ν_{33}	2169.92	A_{1g}	0.1075	807	2084.04	A_{1g}	0.133	1142	2084.04	A_{1g}	−0.133	1142
	$\lambda_v = \Sigma\lambda_i = 1834$ cm^{-1}				$\lambda_v = \Sigma\lambda_i = 2257$ cm^{-1}				$\lambda_v = \Sigma\lambda_i = 2266$ cm^{-1}			

[a] *K* calculated assuming given state is the initial state in units of amu$^{1/2}$ Å. [b] Reorganization energies calculated in coordinate system of the respective state.

vector, *K*, gives displacements in initial state normal coordinates. Since the two sets of normal coordinates are not the same, *K* depends on which state is assumed to be the initial state. We calculated *K* for both states being the initial state, and the results are given in Table 2. The resulting vibrational reorganization energies,[18] an important factor in ET, are also given in Table 2. The different displacement vectors lead to reorganization energies that depend on the set of normal coordinates. The total vibrational reorganization energy is 1834 cm^{-1} in the normal coordinates of the radical and 2257 cm^{-1} in the normal coordinates of the anion. As we discuss in a related manuscript,[2] the normal definition of reorganization energy presumes the absence of the Duschinsky effect, and the value depends on the reference coordinates. The absolute values are not as large as in our next example since the geometry change is small.

One property of the Duschinsky matrix is that modes of different symmetries cannot mix. An additional fact is that only totally symmetric modes may have displacements. This means that only four modes should have nonzero values in *K*, and these same modes should form a 4 × 4 block of *J*, since there are four totally symmetric modes when treated in D_{3d} symmetry. The four A_{1g} modes of the neutral species should mix with the

TABLE 3: Duschinsky Matrix for the $V(CO)_6/V(CO)_6^-$ System (assuming neutral species is initial state)[a]

(a) A_{1g} Block

	Q_4	Q_{13}	Q_{22}	Q_{33}
Q'_6	−0.9987	0.0475	0.0044	0.0204
Q'_{15}	−0.0471	−0.9975	0.0521	0.0064
Q'_{21}	−0.0057	−0.0515	−0.9972	0.054
Q'_{33}	−0.021	−0.0082	−0.0535	−0.9983

(b) E_g Block

	Q_4	Q_5	Q_{10}	Q_{11}	Q_{14}	Q_{15}	Q_{23}	Q_{24}	Q_{31}	Q_{32}
Q'_4	−0.0004	−0.9969	0	−0.0061	−0.0002	0.0687	0	−0.0131	0.0052	0
Q'_5	−0.9969	0.0004	−0.0061	0	0.0687	0.0001	−0.0131	0	0	−0.0052
Q'_{10}	0	−0.0675	−0.0002	0.3963	0.0021	−0.9035	−0.0001	0.1345	0.0482	0
Q'_{11}	0.0675	0	−0.3963	−0.0002	0.9036	0.0021	−0.1345	−0.0001	0	0.0482
Q'_{12}	0.0225	0	0.9132	0.0004	0.4043	0.0009	0.0275	0	0	−0.0354
Q'_{13}	0	0.0225	−0.0004	0.9132	−0.0009	0.4043	0	0.0275	0.0353	0
Q'_{22}	−0.0045	0	−0.0812	−0.0001	0.1137	0.0003	0.9897	0.0009	0	−0.0322
Q'_{23}	0	−0.0045	0.0001	−0.0812	−0.0003	0.1137	−0.001	0.9897	0.0322	0
Q'_{28}	0	0.0081	0	−0.0488	−0.0001	0.0249	0	−0.0393	0.9976	0
Q'_{29}	0.0081	0	−0.0488	0	0.0249	0.0001	−0.0393	0	0	−0.9976

[a] Values less than 10^{-4} ignored. Q represent anion modes, and Q' represent neutral modes.

two A_{1g} modes of the anion along with two of the T_{2g} modes ($T_{2g} \rightarrow A_{1g}$ and E_g). However, this is not the case. The A_{1g} modes of the neutral species mix with eight modes of the anion, the two A_{1g} modes, and all six of the T_{2g} modes. Similar results are seen for the other sets of triply degenerate anion modes. Also, if the anion is treated as the initial state, K shows displacements in eight modes, the two A_{1g} and six T_{2g} modes, as shown in Table 2.

This problem results from an implicit arbitrariness in choosing degenerate normal modes. The convention that Gaussian follows results in three degenerate modes, described as T_{2g} modes, that do not correspond to one A_{1g} and two E_g modes in D_{3d} symmetry. This can be seen by the fact each T_{2g} mode of the anion mixes with both E_g and A_{1g} modes of the radical instead of only one symmetry type and how all T_{2g} modes show a displacement instead of only one of each degenerate set. Our way of getting around this problem was to slightly distort the anion into D_{3d} symmetry. By changing x and y coordinates by 10^{-5} angstroms in the correct direction, the total energy and vibrational frequencies were very slightly shifted, but the normal modes were treated as in D_{3d} symmetry. The new standard orientation resulted in structures that had the maximum number of symmetry elements in common, making B^0 unnecessary. Also, J properly separated into symmetry blocks, and K gave only four displaced modes, as shown in Table 2. The resulting vibrational reorganization energy changes slightly from the octahedral case, from 2257 to 2266 cm^{-1}. The determinant of J is 0.997, very close to unity, with the discrepancy occurring in the E_g block, which is the symmetry for rotations around x and y. The 1×1 A_{2g} block is within 10^{-5} of negative one, orthogonal within our numerical accuracy (ignoring the arbitrary sign), even though A_{2g} is the symmetry of the third rotation around z. This means that the A_{2g} mode of anionic and neutral species are nearly identical, as revealed by inspection of the normal mode output, and negligible axis-switching effects should occur for this mode. The A_{1g} block of J, shown in Table 3, reveals that very little mixing occurs in the totally symmetric modes. This also is true for most other symmetries that are not shown. This is not surprising since the geometry change in this case is not large, suggesting the electron density and therefore the force constants do not change much. However, the E_g block does show a moderate amount of mixing. Care must be taken since mixing of degenerate modes is not physically meaningful due to the arbitrariness in choice and order of degenerate normal modes. Each set of two degenerate modes must be considered together and mixing among the set ignored. The E_g block of the Duschinsky matrix, shown in Table 3, reveals that the third and fourth E_g modes (ν_{10} and ν_{11} of both species) are well mixed with the fifth and sixth E_g modes (ν_{12} and ν_{13} of the neutral species and ν_{14} and ν_{15} of the anion). As an example, we will discuss the degenerate pair of radical normal modes Q'_{10} and Q'_{11}, which has significant contributions from two sets of degenerate anion normal modes. The Q'_{10}/Q'_{11} pair has contributions of 0.3963 and 0.0002 from the Q_{10}/Q_{11} pair and 0.9036 and 0.0021 from the Q_{14}/Q_{15} pair. It must be emphasized that the entire 2×2 block must be considered when determining the amount of mixing and not the individual elements when doubly degenerate modes are considered.

The equations for J and K are based on eq 6, where x^0 are equilibrium coordinate vectors and ρ are displacement vectors. The nonlinearity results from the displacement dependence of B in this equation, which is ignored to get a linear transformation. One way to test the validity of the linear approximation is to test eq 6 with displacements along various normal modes while ignoring the coordinate dependence of B, which is the unit matrix in this case. Equation 6 should fail for displacements in the A_{2g} and E_g modes, since these have the same symmetry as a rotation, but should remain valid for the other modes. Rearranging eq 6 to equal zero, the root-mean-squared of the difference of each Cartesian coordinate from zero is used as a measure of validity. Some results are given in Figure 1, where normal mode displacements of 1 to 2 are typically large values. As expected, eq 6 fails for displacements in the E_g and A_{2g} modes, but the disagreements are small, with rms disagreements of less than 10^{-3} Å for reasonable normal mode displacements, suggesting that the linear approximation is a good one. This is consistent with the closeness of the determinant of the Duschinsky matrix to unity. However, for correct FCF, one must have a determinant equal to unity, so problems may still arise if the E_g modes are taken into account without some sort of renormalization of the E_g block.

$Co(CO)_4$. The other example is $Co(CO)_4^{-1/0}$, which forms a similar ion pair, $Co(Cp)_2^+|Co(CO)_4^-$, that undergoes similar ET reactivity.[19] Again, B3LYP calculations were performed with the 6-311G basis set for cobalt and 6-311G(d,p) basis sets for carbon and oxygen. In this case, the calculations result in a

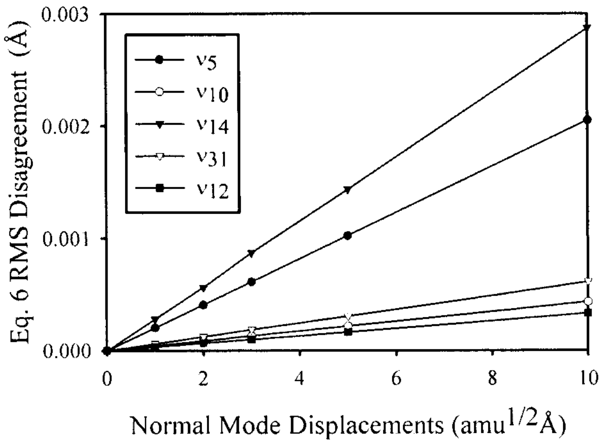

Figure 1. Root-mean-square (rms) disagreement of each Cartesian coordinate in eq 6 for displacements along several E_g and A_{2g} normal modes for the $V(CO)_6$ system. The coordinate dependence of B is ignored.

TABLE 4: Standard Orientation Atomic Coordinates (in angstroms) for $Co(CO)_4$ and $Co(CO)_4^-$

	$Co(CO)_4$			$Co(CO)_4^-$		
	x	*y*	*z*	*x*	*y*	*z*
Co	0.000004	−0.000318	−0.212456	0	0	0
C	−0.000015	−0.000402	1.628417	1.01298	1.01298	1.01298
C	−1.555843	−0.897775	−0.516878	−1.01298	−1.01298	1.01298
C	0.000098	1.795842	−0.516414	−1.01298	1.01298	−1.01298
C	1.555765	−0.897933	−0.516847	1.01298	−1.01298	−1.01298
O	−0.000042	−0.000817	2.766589	1.683685	1.683685	1.683685
O	−2.530524	−1.459219	−0.703171	−1.683685	−1.683685	1.683685
O	0.000157	2.920787	−0.701967	−1.683685	1.683685	−1.683685
O	2.530393	−1.459475	−0.70312	1.683685	−1.683685	−1.683685

tetrahedral geometry for the anion. For the neutral species, a C_1 geometry results. The atomic coordinates are given in Table 4, and the frequencies and symmetries of the vibrations are given in Table 5. Although this neutral geometry is very close to C_{3v}, all attempts to find an optimized structure with higher than C_1 symmetry failed. The C−Co−C angles are about 99.6° and 117.3°, compared to the T_d value of 109.5°. The low C_1 symmetry is unfortunate since the lack of symmetry in the neutral species does not allow the breaking of the Duschinsky matrix into symmetry blocks, greatly complicating the analysis. However, this allows study of a case where zero-order axis-switching is necessary and nonlinear effects occur for all modes, including displaced modes.

The result for calculation of T^0 from eq 12 is shown in Table 6. T^0 was converted to B^0, and eqs 7 and 8 were used to calculate *J* and *K*. The result for *K* is given in Table 5 along with the corresponding vibrational reorganization energies, which total to 4925 cm^{-1} in the normal coordinates of the radical and 6183 cm^{-1} in the normal coordinates of the anion. These values are much larger than for $V(CO)_6$ and their dependence on coordinate is much greater due to the larger Duschinsky mixing. Two portions of the Duschinsky matrix representing modes 1 to 8 and 10 to 21 are given in Table 7. The analysis is much more difficult because *J* does not form symmetry blocks; however, it is obvious from inspection of *J* that there is much more normal mode mixing in this case than in the vanadium case. This is expected since there is a much larger geometry change for $Co(CO)_4$ than $V(CO)_6$. For example, ν_{13} and ν_{14} of the neutral species include significant contributions from modes 10 to 17 of the anion. Also, ν_{15} of the neutral species contains contributions from several anion modes, including the high frequency ν_{21}. Many of the diagonal elements are near 0.5, signifying a significant contribution from other modes. The large Duschinsky effect suggests that ion pairs involving $Co(CO)_4$ are examples of systems where including the Duschinsky effect in calculated electron-transfer rates may be important. In another manuscript[2] we have developed a general model for the Duschinsky effect in electron transfer that shows large rate enhancement for inverted region electron transfer.

TABLE 5: Calculated Vibrational Frequencies, Symmetries, and Displacements for the $Co(CO)_4$/$Co(CO)_4^-$ System

	$Co(CO)_4$			$Co(CO)_4^-$			
	ν (cm^{-1})	K^a	λ_i (cm^{-1})^b	ν (cm^{-1})		K^a	λ_i (cm^{-1})^b
ν_1	59.75	−0.0055	0	72.37	E	−0.0036	0
ν_2	59.87	−0.0148	0	72.37	E	0.0036	0
ν_3	80.74	−0.0544	0	85.65	T_2	−1.6548	298
ν_4	80.9	−0.0455	0	85.65	T_2	−1.5274	254
ν_5	85.05	2.7752	826	85.65	T_2	−1.8185	360
ν_6	267.94	0.0006	0	315.59	T_1	−0.001	0
ν_7	268.1	0.004	0	315.59	T_1	0	0
ν_8	287.31	0.0009	0	315.59	T_1	0.001	0
ν_9	394.65	0.6389	943	477.58	A_1	−0.325	357
ν_{10}	394.92	−0.3739	323	538.3	E	0.0002	0
ν_{11}	396.38	−0.0354	3	538.3	E	−0.0001	0
ν_{12}	431.85	−0.3364	313	544.66	T_2	0.2149	203
ν_{13}	469.78	−0.0029	0	544.66	T_2	0.2161	205
ν_{14}	469.86	−0.0155	1	544.66	T_2	0.1842	149
ν_{15}	477.27	−0.7805	2058	574.75	T_2	−0.483	1143
ν_{16}	482.5	−0.0511	9	574.75	T_2	−0.1594	124
ν_{17}	483.15	0.0079	0	574.75	T_2	−0.2756	372
ν_{18}	2095.16	0.0001	0	1967.67	T_2	0.0269	42
ν_{19}	2095.22	0.0001	0	1967.67	T_2	0.0266	41
ν_{20}	2106.64	−0.028	52	1967.67	T_2	0.0264	40
ν_{21}	2179.74	−0.0751	397	2070.03	A_1	0.2021	2595
	$\lambda_v = \Sigma\lambda_i = 4925$ cm^{-1}			$\lambda_v = \Sigma\lambda_i = 6183$ cm^{-1}			

[a] *K* calculated assuming given state is the initial state in units of $amu^{1/2}$ Å. [b] Reorganization energies calculated in coordinate system of the respective state.

TABLE 6: Calculated T^0 for the $Co(CO)_4$/$Co(CO)_4^-$ System (assuming neutral species is initial state)

x	*y*	*z*
0.70708	−0.40846	0.57723
0.00003	0.81632	0.5776
−0.70713	−0.40839	0.57722

The determinant of *J* is 0.983, close to unity, but not as close as the previous example. This suggests that the vibrational normal modes of the anion are not as well represented by combinations of vibrational normal modes of the other state without including rotations, leading to larger axis-switching effects. In fact, since the neutral species has no symmetry, axis-switching effects need to be taken into account for every mode. B^0, the zero-order axis-switching matrix, is correct only at the equilibrium geometry of either state, but any displacements from equilibrium will cause eq 6 to fail. Some results, including the smallest and largest failures, are given in Figure 2. Larger disagreements are seen for certain modes of $Co(CO)_4$ than for either the A_{2g} or E_g modes of $V(CO)_6$, as would be expected based on the determinant of *J*. Errors in calculated FCF are expected not only due to the value of the determinant but also due to the nonlinear effects that are ignored in the zero-order axis-switching approximation. The vibrational wave functions have width, so for correct FCF the coordinate dependence of *B* must be known and the nonlinear effects would have to be included in the FCF, which is not currently possible. However, the coordinate dependence of *B* should not be large in the region important for FCF calculations, which is between the equilibrium geometry of the two states, and the failure of eq 6 is small for

TABLE 7: Portions of the Duschinsky Matrix for the $Co(CO)_4$/$Co(CO)_4^-$ System (assuming neutral species is initial state)[a]

(a) Modes 1 to 8

	Q_1	Q_2	Q_3	Q_4	Q_5	Q_6	Q_7	Q_8
Q'_1	−0.8718	0.2352	−0.0029	−0.3173	0.2684	−0.0169	−0.0082	0.0092
Q'_2	0.2319	0.8724	0.3391	−0.1522	−0.1877	−0.0003	0.0139	0.0134
Q'_3	−0.3548	−0.2201	0.5297	0.223	−0.6994	0	0.0013	0.0004
Q'_4	0.216	−0.3488	0.5013	−0.7443	0.1424	−0.0008	−0.0001	0.0005
Q'_5	−0.0026	−0.0062	0.5779	0.5053	0.6007	−0.0008	0.0004	0.0009
Q'_6	0.0047	0.0019	0.0025	0.0021	−0.0035	−0.5742	−0.7422	−0.2076
Q'_7	−0.004	0.0046	0.0035	−0.003	0.001	0.5414	−0.2045	−0.7669
Q'_8	0.0003	0.0003	0.0008	0.0002	−0.0006	0.5707	−0.5975	0.5632

(b) Modes 10 to 21

	Q_{10}	Q_{11}	Q_{12}	Q_{13}	Q_{14}	Q_{15}	Q_{16}	Q_{17}	Q_{18}	Q_{19}	Q_{20}	Q_{21}
Q'_{10}	0.7027	−0.1212	0.2332	−0.3425	−0.1425	−0.1267	−0.161	0.0466	−0.0191	−0.0493	0.0651	0.0213
Q'_{11}	−0.166	−0.8045	0.0861	0.2358	−0.4089	0.094	−0.1121	−0.1229	−0.075	0.0575	0.0182	0.0027
Q'_{12}	0.0048	−0.0013	0.3489	0.3512	0.3008	0.6006	0.2005	0.3421	0.0162	0.0159	0.0163	0.008
Q'_{13}	0.1853	0.3655	−0.0129	0.5642	−0.641	−0.1577	0.0954	0.217	−0.0138	0.0146	−0.001	−0.0005
Q'_{14}	−0.3643	0.1887	0.6916	−0.3708	−0.3384	−0.0231	0.2504	−0.1285	−0.0094	−0.0081	0.015	−0.0031
Q'_{15}	−0.015	0.0004	0.4459	0.4562	0.3927	−0.5318	−0.2358	−0.2699	−0.037	−0.0363	−0.0374	−0.1304
Q'_{16}	0.2544	−0.1474	−0.1043	0.0999	0.0987	−0.1085	0.8399	−0.3916	−0.0048	−0.004	0.0016	−0.0085
Q'_{17}	−0.1478	−0.2547	0.0049	−0.1205	0.1203	−0.5035	0.2788	0.7355	−0.0025	0.0036	0	0.0013
Q'_{18}	−0.0275	−0.1057	0.0093	0.032	−0.0482	0.0065	−0.0066	−0.0082	0.7541	−0.6147	−0.1395	−0.0003
Q'_{19}	0.1064	−0.028	0.0455	−0.0336	−0.0134	−0.0011	−0.0097	0.0072	0.2731	0.5147	−0.7915	0.0002
Q'_{20}	0.0003	−0.0006	−0.0196	−0.0195	−0.0169	0.0493	0.0163	0.028	−0.5761	−0.5764	−0.5735	0.0278
Q'_{21}	−0.0003	0.0002	0.0689	0.0689	0.0588	−0.065	−0.0216	−0.037	0.0097	0.0093	0.0097	0.9876

[a] Values less than 10^{-4} ignored. Q represent anion modes, and Q' represent neutral modes.

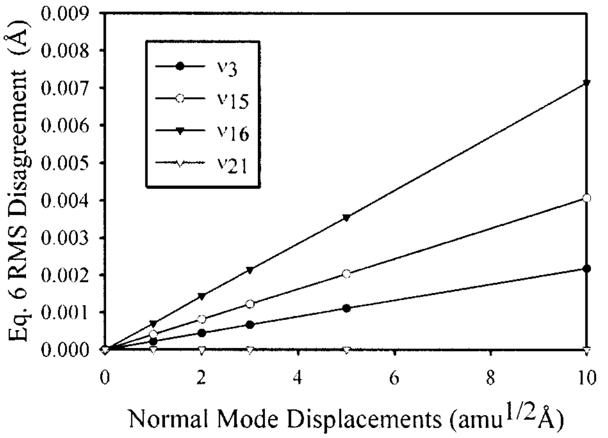

Figure 2. Root-mean-square disagreement (rms) of each Cartesian coordinate in eq 6 for displacements along several normal modes for the $Co(CO)_4$ system. The coordinate dependence of B is ignored.

reasonable displacements. In addition, the greatest failure of eq 6 occurs for modes with displacements near zero, which have the smallest importance for FCF calculations. In light of this, the zero-order approximation does appear to be a good approximation and is the best currently available.

Application to Electron-Transfer Rate Calculations

The goal of this paper has been to demonstrate how complications arise in applying the Duschinsky effect to specific molecules. All phenomena involving radiative or nonradiative transitions can be impacted by the Duschinsky effect, and it has been generally ignored in electron-transfer models. There have been many studies including the Duschinsky effect in absorption[20−27] and resonance Raman[28−30] spectral simulation. However, very few studies of rate processes[17,31−33] have included the Duschinsky effect, and none are systematic. In a related paper,[2] we have performed the first systematic study that demonstrates the major importance of the Duschinksy effect to ET rates in the inverted region. Those results were not molecule specific, so further application to real systems requires the methods of this paper.

For electron-transfer rate calculations, a basic sum over states Fermi's golden rule implementation can be used. This results in eq 13.[34,35]

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} H_{\mathrm{ab}}^2 (4\pi\lambda_{\mathrm{s}} k_{\mathrm{B}} T)^{-1/2} \times \sum_{\mathrm{i}} P(\epsilon_{\mathrm{i}}) \sum_{\mathrm{f}} \langle \chi_{\mathrm{i}} | \chi_{\mathrm{f}} \rangle^2 \exp\left[\frac{-(-E_{00} + \epsilon_{\mathrm{f}} - \epsilon_{\mathrm{i}} + \lambda_{\mathrm{s}})^2}{4\lambda_{\mathrm{s}} k_{\mathrm{B}} T}\right] \quad (13)$$

In eq 13, i is the initial (excited) state, f is the final (ground) state, H_{ab} is the electronic coupling of the two states, λ_{s} is the solvent reorganization energy, E_{00} is the free energy difference, χ is the vibrational wave function, $P(\epsilon_{\mathrm{i}})$ is the distribution of initial vibrational states. Equations 14 and 15 can be used for absorption and emission spectra respectively, with the identities of the initial and final states reversed for absorption versus emission spectra.[35]

$$A(\omega) \propto \omega \sum_{\mathrm{i}} P(\epsilon_{\mathrm{i}}) \sum_{\mathrm{f}} \langle \chi_{\mathrm{i}} | \chi_{\mathrm{f}} \rangle^2 \exp\left[\frac{-(\omega - E_{00} - \epsilon_{\mathrm{f}} + \epsilon_{\mathrm{i}} - \lambda_{\mathrm{s}})^2}{4\lambda_{\mathrm{s}} k_{\mathrm{B}} T}\right] \quad (14)$$

$$E(\omega) \propto \omega^3 \sum_{\mathrm{i}} P(\epsilon_{\mathrm{i}}) \sum_{\mathrm{f}} \langle \chi_{\mathrm{i}} | \chi_{\mathrm{f}} \rangle^2 \exp\left[\frac{-(\omega - E_{00} + \epsilon_{\mathrm{f}} - \epsilon_{\mathrm{i}} + \lambda_{\mathrm{s}})^2}{4\lambda_{\mathrm{s}} k_{\mathrm{B}} T}\right] \quad (15)$$

Equations 13−15 can be used in conjunction with any of the previously published methods[3,6−10] for calculating multidimensional FCF.

Conclusion

We have presented an analysis of complexities that can occur when applying the Duschinsky effect to real molecules. There are subtle nonlinear transformation issues that can arise for transitions between two states, and these are discussed in general terms and for specific molecular examples. These nonlinear effects cannot be taken into account in FCF calculations; however, we have shown these to be small enough to be neglected through use of the zero-order axis-switching approximation. In addition, we identified a problem that arises from nonorthogonality of the Duschinsky matrix, and a correction method must still be tested before exact results can be obtained from FCF calculations. The Duschinsky effect has been calculated for two molecules involved in electron-transfer reactions of ion pairs. The anion part of the pairs, $V(CO)_6^-$ and $Co(CO)_4^-$, and their respective neutral species, have been included in the calculations. The vanadium species undergoes a geometry change from an octahedral anion to a D_{3d} neutral species. However, the accompanying geometrical changes are small and result in small Duschinsky effects. The calculation illustrated how to perform the computations to allow correct description of degenerate normal modes and how to describe mixing among degenerate modes. In addition, a method of testing the linear approximation was developed that shows its validity for this molecule. On the other hand, the cobalt species undergoes a much greater geometrical distortion from the tetrahedral anion into a nearly C_{3v} neutral species of C_1 symmetry. This results in a much larger Duschinsky effect, and the lack of symmetry in the neutral species greatly complicates the analysis of the Duschinsky matrix since it does not break into symmetry blocks. The cobalt molecule is a case where zero-order axis-switching is necessary, and nonlinear effects occur for all modes, including displaced modes. The absolute reorganization energy and coordinate dependence of the reorganization energy were much larger for this molecule. We briefly outlined methods of applying such computations to electron-transfer rates that can be generalized to many rate processes.

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