The role of Duschinsky rotation in intersystem crossing: a case study of uracil

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Abstract: The intersystem crossing rate for the transition between the lowest excited singlet and triplet electronic states of uracil was studied by means of *ab initio* methods. The rate was evaluated using the time-dependent approach based on the correlation function and its two approximations: the second-order cumulant expansion and the short-time approximation. The normal modes of the singlet and triplet states are related by the Duschinsky transformation, *i.e.*, by rotation and translation. It was found that for singlet–triplet adiabatic energy gaps below 6000 cm^{-1}, the inclusion of the Duschinsky rotation is necessary for quantitative results. Above energy gaps of 6000 cm^{-1}, the rates obtained with and without the Duschinsky rotation are similar. The cumulant expansion approximates well the correlation function. The short-time approximation, although crude, can be used as the first estimate of the rate.

Keywords: uracil; excited states; intersystem crossing.

INTRODUCTION

Absorption of ultraviolet light creates excited electronic states in molecules. These states will eventually decay to the ground electronic state through radiative or non-radiative processes.[1–3] Non-radiative processes can be observed indirectly as they modify the spectra and rates of photochemical reactions. If a non-radiative transition is between electronic states of the same spin multiplicity, then the process is an internal conversion (IC), otherwise it is an intersystem crossing (ISC). Transitions between states with different spin multiplicities are formally forbidden in non-relativistic quantum theory. In order to treat these transitions, spin–orbit coupling must be taken into account.

Uracil is pyrimidine nucleobasis that is involved in the formation of nucleic acids. Its excited states properties are intriguing because although to a large ex-

tent they are photostable, ultrafast time-resolved experiments showed that electronic relaxation from the initially excited $^1\pi\pi^*$ state proceeds in multiple steps.[4–6] Much is known about the relaxation of the singlet excited states of uracil but knowledge of the dynamics of its triplet states are still limited. Although the triplet state has a low quantum yield, it is of interest when excited-state nucleic acids chemistry is considered. Triplet excited states usually have much longer lifetimes than singlet states and their reactivity is also higher.

Nanosecond pump–probe experiments with low-pressure molecular beams revealed that uracil and its methylated compounds, after initial photoexcitation to the S_2 ($\pi\pi^*$) state, were captured in the dark electronic state that lived several tens to hundreds of nanoseconds.[7–10] Based on quantum-chemical calculations, Marian and coworkers argued that this state is the lowest triplet state T_1 ($^3\pi\pi^*$).[11] They proposed two mechanisms for the formation of the triplet: (a) a non-radiative transition from the intermediate singlet S_1 ($n\pi^*$) state to the lowest triplet state, (b) a transition from the initially populated S_2 state to the second triplet state T_2 ($n\pi^*$) followed by internal conversion to the lowest triplet T_1 state. Due to the experimental findings that there is a fast depletion of the initially excited state to the ground electronic state and the S_1 state, Marian and coworkers suggested that T_1 state is populated by ISC process from the intermediate singlet S_1 state.

In the condensed phase, the S_1 and T_1 states are populated during electronic relaxation from the initially excited S_2 state.[12,14] The quantum yield of the triplet state depends on the solvent and it ranges from 0.02 in water up to 0.54 in ethyl acetate for 1-cyclohexyluracil[12] and 1.00 for 6-azauracil.[13]

The rate of the ISC is determined by the properties of the chromophore, such as spin–orbit and vibronic couplings. For rigid molecules in the body-fixed rotating molecular coordinate system, the electronic potential energy in the vicinity of the minimum can be diagonalized by introducing normal-mode coordinates $\{Q_i\}$. Electronic transitions are usually followed by a change in normal modes. Normal modes of the final state could be displaced and rotated relative to the normal modes of the initial state. The transformation that relates two sets of the normal modes is called the Duschinsky transformation.[15]

Usually, non-totally symmetric modes or modes with very small displacements are ignored in electronic relaxation rate calculations. This is justified when the normal modes of the electronic states are neither mixed nor distorted. In this case, non-totally symmetric modes have zero Franck–Condon (FC) integrals. Even when there is a distortion, it is possible to ignore their contribution to the rate. Sando *et al.*[16] showed that when the Duschinsky rotation is present, non-totally symmetric modes cannot be ignored in the calculation of the electron transfer rate, particularly when their number is large. They argued that in real

molecules, low-frequency modes could mix with high-frequency modes so that their net contribution to the rate increases.

The goal of this work was to establish to what extent the rotation of the normal modes is important for the quantitative evaluation of the $S_1 \rightarrow T_1$ ISC rate in uracil. By comparing the rates obtained with and without the Duschinsky rotation, the importance of the various approximations for the evaluation of the ISC rate will be established.

The paper is organized as follows: in the next section, the manner in which ISC rates can be calculated using the correlation function approach and its approximations is explained. Then, details of the rate calculations are presented. In the subsequent section, this method is applied to the calculation of the intersystem crossing rates for uracil and the results are discussed. Finally, conclusions are given.

The correlation function method

ISC rates are calculated using truncation of the time dependent perturbation expansion, *i.e.*, the Golden rule approximation. This is justified because all atoms in uracil are light so that spin–orbit coupling $\hat{H}_{SO}$ could be treated as a perturbation. As zero-order states, pure spin Born–Oppenheimer states $\left| S_a, \{v_{aj}\} \right\rangle$ and $\left| T_b^\alpha, \{v_{bk}\} \right\rangle$ were used. Here S_a is a singlet electronic state and T_b^α is an α fine-structure component of a triplet electronic state. $\{v_{aj}\}$ and $\{v_{bk}\}$ are vibrational states related to the S_a and T_b^α states. In this work, potential surfaces are approximated by a harmonic potential. The normal modes of the triplet $\{Q_{T_i}\}$ and singlet $\{Q_{S_i}\}$ electronic states are related through the Duschinsky transformation:[15]

$$Q_{T_i} = \sum_j J_{ij} Q_{S_j} + D_i \tag{1}$$

where J is the Duschinsky rotation matrix and D is the displacement vector. The Duschinsky matrix represents to what extent normal modes of the triplet electronic state are mixed based on the normal modes of the singlet electronic state. The displacement vector presents the displacement of the triplet potential surface in respect to that of the singlet.

The rate from the initially populated vibronic state $\left| S_a, \{v_{aj}\} \right\rangle$ to the triplet vibronic states $\left| T_b^\alpha, \{v_{bk}\} \right\rangle$, assuming the statistical limit (high density of the final states), is given by the Golden Rule Formula:

$$k_{ISC} = 2\pi \sum_k \left| \left\langle S_a, \{v_{aj}\} \right| \hat{H}_{SO} \left| T_b^\alpha, \{v_{bk}\} \right\rangle \right|^2 \delta(E_{aj} - E_{bk}) \tag{2}$$

Spin–orbit matrix elements are generally a function of normal mode coordinates. They can be expanded using the Taylor expansion:

$$\left\langle S_{\mathrm{a}},\{v_{\mathrm{aj}}\}\left|\hat{H}_{\mathrm{SO}}\right|T_{\mathrm{b}}^{\alpha},\{v_{\mathrm{bk}}\}\right\rangle = \left\langle v_{\mathrm{aj}}\left|\left\langle S_{\mathrm{a}}\left|\hat{H}_{\mathrm{SO}}\right|T_{\mathrm{b}}^{\alpha}\right\rangle\right|_{Q_0}\left|v_{\mathrm{bk}}\right\rangle + $$

$$+\left\langle v_{\mathrm{aj}}\left|\sum_i \frac{\partial\left\langle S_{\mathrm{a}}\left|\hat{H}_{\mathrm{SO}}\right|T_{\mathrm{b}}^{\alpha}\right\rangle}{\partial Q_{\mathrm{i}}}\right|_{Q_0} Q_{\mathrm{i}}\left|v_{\mathrm{bk}}\right\rangle + \ldots \tag{3}$$

Keeping only the first term represents the Condon approximation and contributes to the direct spin–orbit coupling. The second and higher order terms represent the Herzberg–Teller expansion and they contribute to the vibronic spin–orbit coupling. It is assumed that a spin–orbit matrix element is expanded at an optimized geometry of the initial (singlet) electronic state. In this work, only the direct spin–orbit coupling will be considered. This is justified when the spin––orbit matrix element is large.

Assuming only a direct spin–orbit coupling, the ISC rate from the initial vibronic level, is given by:

$$k_{\mathrm{ISC}} = 2\pi\left|\left\langle S_{\mathrm{a}}\left|\hat{H}_{\mathrm{SO}}\right|T_{\mathrm{b}}^{\alpha}\right\rangle\right|^2 \sum_k \left|\left\langle v_{\mathrm{aj}}\left|v_{\mathrm{bk}}\right\rangle\right|^2 \delta(E_{\mathrm{aj}} - E_{\mathrm{bk}}) \tag{4}$$

In this case, the calculation of the rate is reduced to the calculation of the electronic part $\left|\left\langle S_{\mathrm{a}}\left|\hat{H}_{\mathrm{SO}}\right|T_{\mathrm{b}}^{\alpha}\right\rangle\right|$ and the vibrational part, *i.e.*, the Franck–Condon integrals $\left\langle v_{\mathrm{aj}}\left|v_{\mathrm{bk}}\right\rangle$.

Recently, Marian and coworkers developed a new method for the calculation of ISC rates using a time-dependent approach.[17] It is based on a transformation of expression (4) into the Heisenberg picture. Instead of the evaluation of an enormously large number of the Franck–Condon integrals, the method evaluates the correlation function. The rate is then obtained by performing an integration of the correlation function. If the initial state is the lowest vibronic state of the singlet manifold, then:

$$k_{\mathrm{ISC}}^{\mathrm{corr}} = \left|\left\langle S_{\mathrm{a}}\left|\hat{H}_{\mathrm{SO}}\right|T_{\mathrm{b}}^{\alpha}\right\rangle\right|^2 \int_{-\infty}^{\infty} F_{\mathrm{corr}}(t)\,\mathrm{d}t \tag{5}$$

where

$$F_{\mathrm{corr}}(t) = 2^{N/2}\sqrt{\frac{\det(\mathbf{S}_{\mathrm{T}}^{-1}\boldsymbol{\Omega}_{\mathrm{S}}\boldsymbol{\Omega}_{\mathrm{T}})}{\det(J^{\mathrm{T}}\boldsymbol{\Omega}_{\mathrm{T}}\mathbf{B}_{\mathrm{T}}J + \boldsymbol{\Omega}_{\mathrm{S}})\det(J^{\mathrm{T}}\boldsymbol{\Omega}_{\mathrm{T}}\mathbf{B}_{\mathrm{T}}^{-1}J + \boldsymbol{\Omega}_{\mathrm{S}})}} \times$$

$$\times \exp\{D^{\mathrm{T}}[\boldsymbol{\Omega}_{\mathrm{T}}\mathbf{B}_{\mathrm{T}}J(J^{\mathrm{T}}\boldsymbol{\Omega}_{\mathrm{T}}\mathbf{B}_{\mathrm{T}}J + \boldsymbol{\Omega}_{\mathrm{S}})^{-1}J\boldsymbol{\Omega}_{\mathrm{T}}\mathbf{B}_{\mathrm{T}} - \boldsymbol{\Omega}_{\mathrm{T}}\mathbf{B}_{\mathrm{T}}]D\} \times \tag{6}$$

$$\times \mathrm{e}^{it(\Delta E_{\mathrm{ST}} + 1/2 Tr\boldsymbol{\Omega}_{\mathrm{S}})}$$

and $\boldsymbol{\Omega}$, $\mathbf{S}$ and $\mathbf{B}$ are diagonal matrices with elements $(\boldsymbol{\Omega})_{\mathrm{ii}} = \omega_{\mathrm{i}}$, $(\mathbf{S})_{\mathrm{ii}} = \sinh(i\omega_{\mathrm{i}}t)$, $(\mathbf{B})_{\mathrm{ii}} = \tanh(i\omega_{\mathrm{i}}t/2)$, ω_{i} is a normal mode frequency, indexes S and T label normal modes of the singlet and triplet electronic states, respectively, and superscript T

indicates the transposition of a matrix. ΔE_{ST} is the adiabatic energy between singlet and triplet electronic states.

In order to ease the calculations of the correlation function, two approximations were derived.[17] The first approximation is based on the cumulant expansion. The expression obtained using the second-order cumulant expansion of the correlation function is:

$$k_{ISC}^{cum} = \left| \left\langle S_a \left| \hat{H}_{SO} \right| T_b^\alpha \right\rangle \right|^2 \int_{-\infty}^{\infty} F_{cum}(t)\mathrm{d}t = \left| \left\langle S_a \left| \hat{H}_{SO} \right| T_b^\alpha \right\rangle \right|^2 \int_{-\infty}^{\infty} \exp(-i\kappa_1 - \kappa_2)\mathrm{d}t \quad (7)$$

where the first and the second cumulants are:

$$\kappa_1 = (\frac{1}{4}\sum_i \frac{M_{ii}}{\omega_{S_i}} + C - \Delta E_{ST})t \quad (8)$$

$$\kappa_2 = \frac{1}{8}\sum_{i,j} \frac{M_{ij}^2}{\omega_{S_i}\omega_{S_j}}\left\{ \frac{-it}{\omega_{S_i} + \omega_{S_j}} + \frac{1 - \exp[-it(\omega_{S_i} + \omega_{S_j})]}{(\omega_{S_i} + \omega_{S_j})^2}\right\}$$
$$+ \frac{1}{2}\sum_i \frac{A_i^2}{\omega_{S_i}}[\frac{-it}{\omega_{S_i}} + \frac{1 - \exp(-it\omega_{S_i})}{\omega_{S_i}^2}] \quad (9)$$

Values of the matrix $\mathbf{M}$, vector $\mathbf{A}$ and scalar C are: $\mathbf{M} = \mathbf{J}^T\mathbf{\Omega}_T^2\mathbf{J} - \mathbf{\Omega}_S^2$, $\mathbf{A} = \mathbf{J}^T\mathbf{\Omega}_T^2\mathbf{D}$ and $C = \frac{1}{2}\mathbf{D}^T\mathbf{\Omega}_T^2\mathbf{D}$. There is a particular simple expression for the rate if the first and second cumulants are expanded up to the second order in time.[17] This gives the short-time approximation:

$$k_{ISC}^{ST} = \left| \left\langle S_a \left| \hat{H}_{SO} \right| T_b^\alpha \right\rangle \right|^2 \sqrt{\frac{\pi}{\frac{1}{16}\sum_{i,j} \frac{M_{ij}^2}{\omega_{S_i}\omega_{S_j}} + \frac{1}{4}\sum_i \frac{A_i^2}{\omega_{S_i}}}} \times$$

$$\times \exp(-\frac{(\frac{1}{4}\sum_i \frac{M_{ii}}{\omega_{S_i}} + C - \Delta E_{ST})^2}{\frac{1}{4}\sum_{i,j} \frac{M_{ij}^2}{\omega_{S_i}\omega_{S_j}} + \sum_i \frac{A_i^2}{\omega_{S_i}}}) \quad (11)$$

This expression does not require integration for its evaluation. The first test results showed that both the cumulant and short-time approximation gave results that were similar to the complete correlation function results.[17]

The calculation of the correlation function and its cumulant expansion involves only matrix multiplication, matrix inversion and calculation of a determinant. They have odd imaginary parts and even real parts. Due to this, the evaluation of the rate is reduced to the calculation of the correlation function or its cumulant expansion in a real positive time interval. The input parameters

required for the calculation of the ISC rate are normal mode frequencies of the initial and final states, their displacements, the Duschinsky matrix, the electronic adiabatic energy gap and spin-orbit matrix element.

DETAILS OF THE INTERSYSTEM CROSSING RATE CALCULATIONS

In this work, the electronic structure data obtained in the work of Marian and co-workers[11] for uracil and its methylated compounds was used. They optimized the S_1 ($^1n\pi^*$) and T_1 ($^3\pi\pi^*$) excited states using the coupled-cluster with approximative doubles (CC2) method. This method represents an approximation of the coupled-cluster singles and doubles (CCSD) method, in which the singles equations are retained in the original form and the doubles equations are truncated to first order in the fluctuating potential.[18] The basis set was Dunning's cc-pVDZ basis set (C, N, O, 9s4p1d/3s2p1d; H, 4s1p/2s1p).[19,20] The excited state geometries were optimized without symmetry constraints. The molecular geometry of the S_1 state was planar while the T_1 state was non-planar. Since there is a large difference in the S_1 and T_1 molecular geometries, the parameters from the Duschinsky relation, the displacement and mixing of the normal modes are large. The normal mode frequencies and displacements of the S_1 and T_1 states of uracil are presented in Table I. There are several low-frequency modes that are highly displaced. The Duschinsky matrix for the transition between the S_1 and T_1 states of uracil is shown in Fig. 1. Almost all normal modes of the triplet states have more than one component in the basis of the singlet state normal modes. The mixing of the normal modes is particularly large for the low-frequency modes and the two highest frequency modes that represent N–H oscillation. In addition, some high-frequency modes are mixed with low-frequency modes.

TABLE I. Frequencies of the normal modes of the S_1 ($n\pi^*$) and T_1 ($\pi\pi^*$) electronic states of uracil and displacements of the T_1 normal modes in dimensionless harmonic oscillator coordinates

$S_1\ \omega_i$ / cm^{-1}	$T_1\ \omega_i$ / cm^{-1}	Displacement	$S_1\ \omega_i$ / cm^{-1}	$T_1\ \omega_i$ / cm^{-1}	Displacement
35.53	126.58	–2.57	970.84	959.28	–1.37
157.82	158.63	–0.31	1012.93	1014.62	1.11
287.76	228.99	–2.80	1105.30	1144.59	–0.36
302.49	367.48	–2.38	1150.37	1226.78	0.49
311.36	460.53	–0.13	1276.78	1353.70	–0.08
341.19	480.02	0.46	1306.92	1361.40	–1.23
472.37	497.58	–0.72	1405.45	1378.63	0.43
503.72	530.57	0.33	1427.08	1404.59	0.03
533.69	554.60	1.06	1451.08	1456.93	0.21
550.11	640.72	0.81	1631.67	1609.53	–2.84
593.22	683.30	0.97	1777.20	1769.36	–0.24
690.71	697.63	–0.49	3256.56	3240.67	–0.50
718.40	727.41	–0.18	3276.26	3255.20	0.90
742.69	762.45	–0.61	3626.67	3599.49	0.09
910.20	938.30	–1.38	3630.50	3599.67	–0.04

The adiabatic energy gap between the S_1 and T_1 electronic states of uracil obtained at the CC2/cc-pVDZ level is 5150 cm^{-1}. Spin–orbit matrix elements were calculated[11] using the SPOCK program based on the DFT/MRCI electronic structure method.[21] SPOCK employs a

one-center mean-field approximation of the Breit–Pauli Hamiltonian.[22] SOME were calculated at the S_1 optimized minimum. The sum of the squares of all spin–orbit matrix elements between the S_1 state and all fine-structure components of the T_1 state is 2391 cm^{-2}. All rates that will be presented in this work are the sum of the three rates from the S_1 state and the three fine-structure components of the T_1 state.
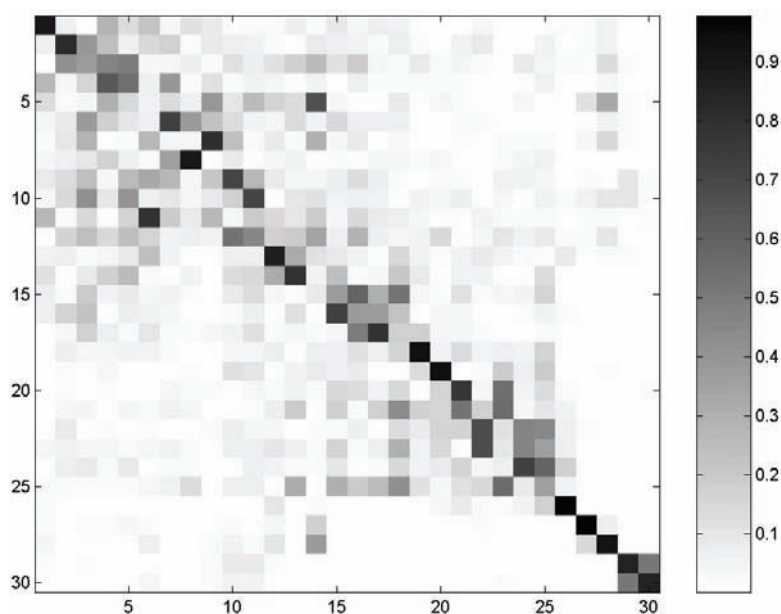

Fig. 1. The Duschinsky matrix related to the transition between the S_1 and T_1 states of uracil. In order to visualize the normal mode mixing, absolute values of the matrix elements are shown.

All normal modes are included in the rate calculations. The correlation function was calculated for the first 10 fs using 100 points. It was found that the rate is very robust to the density of points required for the integration of the correlation function.

RESULTS

The time dependence of the correlation function F_{corr} and its second-order cumulant expansion F_{cum} when the Duschinsky rotation is excluded and included are shown in Figs. 2 and 3, respectively. The adiabatic energy gap for the calculation was 5150 cm^{-1}. The correlation function and its cumulant expansion practically overlap in Fig. 2. The plotted functions perform one oscillation and then decay to zero. After 10 fs, their values are practically zero. The second-order cumulant expansion approximates the correlation function very well. Comparing the correlation function when the Duschinsky rotation is excluded and included, one finds that the amplitude of the correlation function oscillation in the first case is larger than in the second. The rates obtained using the correlation function and its second-order cumulant expansion are 6.66×10^9 and 6.64×10^9 s^{-1}, when the

Duschinsky rotation is excluded and 1.53×10^{10} and 2.60×10^{10} s^{-1}, when the Duschinsky rotation is included. The rates obtained using the short-time approximations are 1.47×10^{10} and 2.73×10^{10}, respectively. There is an order of magnitude higher rate when the Duschinsky rotation is included. Only the short-time approximation gives the same order of magnitude in both cases. In the absence of the Duschinsky rotation, the correlation function method gives the same result as the approximate cumulant expansion, as can be deduced from Fig. 2. This is an encouraging result because it is easier to calculate the cumalant expansion than the correlation function. When the Duschinsky rotation is present, the cumulant approximation gives a slightly higher value than the exact correlation function. Although the short-time approximation is a simple approximation, it gives reasonable results. Marian and coworkers [11] calculated the $S_1 \rightarrow T_1$ ISC rate for uracil using the time-independent method, *i.e.*, they explicitly summed the Franck––Condon factors. As the number of the Franck–Condon factors was enormous, they limited the number of quanta in the triplet state normal modes to five per mode. This limitation decreased the number of the final vibronic levels. Using the same adiabatic energy gap, spin–orbit matrix elements and the Duschinsky rotation, they obtained 0.93×10^{10} s^{-1} for the rate value. This value is the lower limit for the true value due to the limitations concerning the accessible number of the final state vibronic levels. The present rates obtained with the Duschinsky rotation are in accordance with the result obtained by the time-independent method.
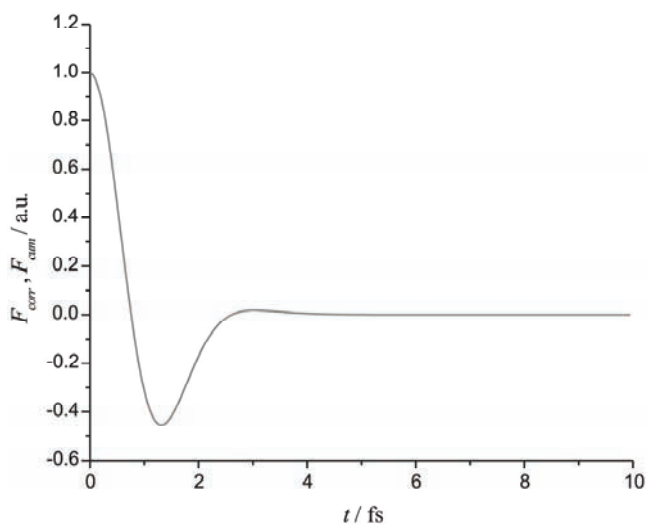

Fig. 2. Time dependence of the correlation function F_{corr} (black) and the second–order cumulant expansion F_{cum} (gray) – overlapped. The Duschinsky rotation was excluded and the adiabatic energy gap was 5150 cm^{-1}.

Solvation can modify adiabatic energy gaps. Etinski and Marian[23] found that hydration could significantly shift electronic excited states. They found that the $S_1(n\pi^*)$ state was blue-shifted by 0.56 eV and that the $S_2(\pi\pi^*)$ state was red-

shifted by 0.19 eV. Due to this, it is of importance to examine in what manner the adiabatic energy gap modifies the ISC rate. The rate constants calculated using the three methods: the correlation function, the second-order cumulant expansion and the short-time approximation for various adiabatic energy gaps are contained in Table II. The rate obtained without the Duschinsky rotation is one to three orders of magnitude smaller than the rate obtained with the Duschinsky rotation for energy gaps below 6000 cm^{-1}. For larger energy gaps, the inclusion of the Duschinsky rotation does not significantly contribute to the rate values. The least sensitive to the adiabatic energy gap change is the short-time approximation. It gives rather good results when the Duschinsky rotation is included.
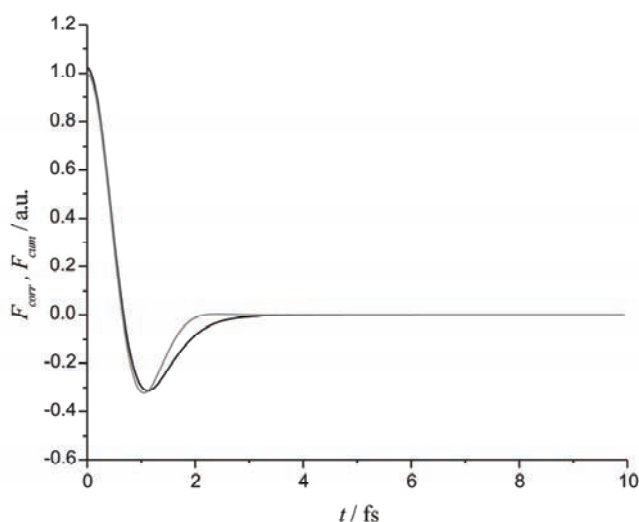

Fig. 3. Time dependence of the correlation function F_{corr} (black) and the second-order cumulant expansion F_{cum} (gray). The Duschinsky rotation was included and the adiabatic energy gap was 5150 cm^{-1}.

TABLE II. The intersystem crossing rates calculated by the three methods: the correlation function (k_{corr}), the second-order cumulant expansion (k_{cum}) and the short-time approximation (k_{st}) for different adiabatic energy gaps

ΔE / cm^{-1}	Without the Duschinsky rotation			With the Duschinsky rotation		
	k_{corr} / 10^8 s^{-1}	k_{cum} / 10^8 s^{-1}	k_{st} / 10^{10} s^{-1}	k_{corr} / 10^9 s^{-1}	k_{cum} / 10^{10} s^{-1}	k_{st} / 10^{10} s^{-1}
1000	0.0483	0.0808	0.124	0.102	0.535	0.716
2000	0.810	0.912	0.241	0.684	0.823	1.02
3000	5.03	5.20	0.449	2.48	1.23	1.43
4000	19.7	19.9	0.799	6.52	1.77	1.96
5000	57.8	57.6	1.36	13.8	2.48	2.62
6000	137	136	2.21	25.2	3.36	3.43
7000	276	275	3.44	40.7	4.44	4.40
8000	487	485	5.11	59.9	5.69	5.53
9000	770	769	7.26	81.6	7.10	6.79
10000	1110	1110	9.86	104	8.61	8.17

According to the simple rule, called the energy gap law,[24] it is generally assumed that the rate of a non-radiative transition between two electronic states becomes larger if the energy difference between the states decreases. This simple rule is limited to non-displaced potential energy surfaces. In the present case, where the potential surfaces are strongly displaced, the rate increases with increasing energy gap. When the Duschinsky rotation is excluded in the rate calculation, the increase of the rate is five orders of magnitude for energy gaps from 1000 to 10000 cm^{-1}. On the other hand, it increases only three orders of magnitude when the Duschinsky rotation is present. This is due to fact that the Duschinsky rotation mixes many modes so that the Franck–Condon factors become less sensitive to an energy gap change.

CONCLUSIONS

We have studied The $S_1 \rightarrow T_1$ intersystem crossing rate in uracil was studied using the time-dependent approach. Three different rate equations were used. The first uses an exact correlation function and the second and third are approximations. The first approximation is the second-order cumulant expansion of the correlation function. The second approximation is an expansion of the cumulant formula up to the second order in time. This is the short-time approximation.

Since the normal modes of the singlet and triplet potential energy surfaces are different, the Duschinsky transformation between the normal modes was introduced. It relates the normal modes of the singlet and triplet states by translation and rotation.

It was found that the time-dependent approach gave similar rates as they were obtained using the time-independent approach. Furthermore, the issue of the necessity to include the Duschinsky rotation of the normal modes was examined. It was found that for adiabatic energy gaps larger than 6000 cm^{-1}, there was a good agreement between the rates obtained with and without the Duschinsky rotation. In addition, for these adiabatic energy gaps, the rates obtained using the cumulant expression and the correlation function, when the Duschinsky mixing was excluded, were practically the same. As it is easier to calculate the cumulant expansion than the complete correlation function, this result looks promising for the application of this method to molecules with a large number of normal modes. For energy gaps below 6000 cm^{-1}, it is necessary to include the Duschinsky mixing in order to obtain qualitatively the rate. Although crude, the short-time approximation is easy to calculate and it can serve as a first estimate of the rate.

И З В О Д

УЛОГА РОТАЦИЈЕ ДУШИНСКОГ У ИНТЕРСИСТЕМСКИМ ПРЕЛАЗИМА:
СТУДИЈА О УРАЦИЛУ

МИХАЈЛО ЕТИНСКИ

Факулūеū за физичку хемију, Универзиūеū у Беоīраду, Сūуденūски ūрī 12–16, ū. ūр. 47, 11158 Беоīрад

Константа брзине интерсистемских прелаза између најнижег побуђеног синглетног и триплетног електронског стања урацила је проучавана помоћу *ab initio* метода. Константа брзине је израчуната користећи временски зависан прилаз заснован на корелационој функцији и њеним двема апроксимацијама: кумулантном развоју другог реда и апроксимацији кратког времена. Нормални модови синглетног и триплетног стања су повезани трансформацијом Душинског, тј. помоћу ротације и транслације. Нађено је да је за синглетно–триплетне адијабатске енергетске процепе испод 6000 cm^{-1} укључивање ротације Душинског неопходно за добијање квантитативних резултата. Изнад 6000 cm^{-1}, константе брзине добијене са ротацијом Душинског и без ње су сличне. Кумулатни развој добро апроксимира корелациону функцију. Апроксимација кратког времена, иако груба, може се користити као прва процена константе брзине.

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