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## Effect of temperature on rate of a spin-forbidden transition in uracil and thymine

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**Abstract:** The intersystem crossing rates of uracil and thymine molecules in interaction with a heat bath were studied by means of *ab initio* methods. The rates were calculated employing the time-dependent approach based on the correlation function. The normal modes of the singlet and triplet electronic states were related by the Duschinsky transformation. The correlation function was calculated using the Condon approximation for the spin-orbit matrix element and harmonic approximation for the nuclear motion. The excess vibrational energy in the initial singlet excited electronic state decreased the rate of triplet formation in uracil and thymine. This decrease was more pronounced for uracil. In addition, it was found that the change of the adiabatic energy gap could significantly modify the rate of triplet formation.

**Keywords:** excited states; intersystem crossing; correlation function.

### INTRODUCTION

The ozone layer above the Earth ground protects living beings by absorbing harmful UV radiation below 290 nm. The UV radiation from 290 to 320 nm is partially absorbed while the UV radiation from 320 to 380 nm is not absorbed. The main cellular targets of UV radiation are nucleic acids.<sup>1</sup> Sequences containing two or several pyrimidine bases are hotspots prone to the formation of photolesions. These photolesions can change the genotype of cells and remove the normal capacity to inhibit cell growth. The most frequent photochemical reaction of nucleic acids is intrastrand pyrimidine dimerization. Although time-resolved infrared experiments<sup>2</sup> showed that the main dimerization product is formed in less than 1 ps in a sequence of thymine bases, indicating an ultrafast photochemical reaction on the singlet excited electronic potential surface, the triplet state mechanism is not necessarily excluded.<sup>3</sup> Essentially, in order to decrease the

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yield of the dimerization, it is necessary that the excited state populations relax ultrafast to the ground electronic state. Nevertheless, it was shown that in the pyrimidine bases uracil, thymine and related compounds, a long-lived dark electronic state is formed to a minor extent.<sup>4–8</sup> The electronic structure of this long-lived state has been the subject of long and controversial debates. Recent theoretical work<sup>9</sup> and supersonic jet experiments<sup>8</sup> showed that this dark state is the lowest triplet state.

In previous studies,<sup>9–14</sup> the formation of the triplet state in the pyrimidine bases uracil, thymine and their derivatives were investigated. It was found that the lowest triplet state ( $^3\pi\pi^*$ ) in uracil and thymine is formed *via* the lowest singlet excited state ( $^1n\pi^*$ ). Two mechanisms were proposed for triplet formation upon initial excitation to the second excited singlet state ( $^1\pi\pi^*$ ):<sup>9</sup> a) an internal conversion (IC) to the first excited singlet state ( $^1n\pi^*$ ) followed by intersystem crossing (ISC) to the lowest triplet state ( $^3\pi\pi^*$ ) and b) an ISC transition from the initially populated singlet ( $^1\pi\pi^*$ ) state to the second triplet state ( $^3n\pi^*$ ) followed by IC to the lower triplet ( $^3\pi\pi^*$ ) state. Due to the fast depletion of the initial  $^1\pi\pi^*$  state to the ground and  $^1n\pi^*$  state, it was suggested that lowest triplet state is populated by the ISC process from the  $^1n\pi^*$  state. In all studies<sup>9–14</sup> that were performed, the ISC process was initiated from the lowest vibrational level of the singlet electronic state. These cases corresponded to vibrationally cooled molecules. In this study, the way in which excess vibrational energy, due to interaction of uracil and thymine with a heat bath, modifies triplet formation is investigated. The heat bath was a solvent. In order to calculate the ISC rates, the time-correlation function method is employed.

The paper is organized as follows: in the next section, we present the computational details and a brief explanation of how ISC rates can be calculated when a molecule has excess of vibrational energy due to interaction with a heat bath are given. The complete explanation will be given elsewhere.<sup>15</sup> In the subsequent section, this method is applied to uracil and thymine and the results discussed. Finally, conclusions are given.

#### THEORETICAL METHODS AND COMPUTATIONAL DETAILS

Pure spin Born–Oppenheimer states  $|S_\alpha, \{v_{aj}\}\rangle$  and  $|T_b^\alpha, \{v_{bk}\}\rangle$  were employed for the calculation of the ISC rate. Here,  $S_\alpha$  is a singlet electronic state and  $T_b^\alpha$  is an  $\alpha$  fine-structure component of a triplet electronic state.  $\{v_{aj}\}$  and  $\{v_{bk}\}$  are vibrational states related to the  $S_\alpha$  and  $T_b^\alpha$  states. In this work, the potential surfaces were approximated by a harmonic potential. The normal modes of the triplet  $\{Q_{T_i}\}$  and singlet  $\{Q_{S_i}\}$  electronic states are related by the Duschinsky Transformation:<sup>16</sup>

$$Q_{T_i} = \sum_j J_{ij} Q_{S_j} + D_i \quad (1)$$

where  $J$  is the Duschinsky rotation matrix and  $D$  is the displacement vector.

If initially a molecule is in a thermal equilibrium with the heat bath, then the ISC rate constant is given as an ensemble average:

$$k = \sum_j p(E_{aj})k(j \rightarrow k) \quad (2)$$

where  $P(E_{aj}) = \exp(E_{aj}/k_B T)/Z$  is a canonical ensemble probability of the occupation of the initial vibronic level with an energy  $E_{aj}$ ,  $Z$  is the canonical partition function,  $T$  is the temperature of the thermal bath,  $k_B$  is the Boltzmann Constant and  $k(j \rightarrow k)$  is the ISC rate from the vibronic level with energy  $E_{aj}$  to the vibronic level with energy  $E_{bk}$ .

Assuming the Condon Approximation for the spin-orbit matrix elements, the ISC rate is given by:

$$k = \frac{2\pi}{Z} \left| \langle S_a | \hat{H}_{SO} | T_b^\alpha \rangle \right|^2 \sum_{k,j} e^{-E_{aj}/k_B T} \left| \langle \{v_{aj}\} | \{v_{bk}\} \rangle \right|^2 \delta(E_{aj} - E_{bk}) \quad (3)$$

Transforming this expression to the Heisenberg Picture, one obtains an expression that contains the correlation function. Then, the ISC rate is calculated as the integral of the correlation function:

$$k = \frac{1}{Z} \left| \langle S_a | \hat{H}_{SO} | T_b^\alpha \rangle \right|^2 \int_{-\infty}^{\infty} F(t) dt \quad (4)$$

where the correlation function is:

$$F(t) = \sqrt{\frac{\det(S_T^{-1} S_S^{-1} \Omega_S \Omega_T)}{\det(J^T \Omega_T B_T J + \Omega_S B_S) \det(J^T \Omega_T B_T^{-1} J + \Omega_S B_S^{-1})}} \times \exp\{D^T [\Omega_T B_T J (J^T \Omega_T B_T J + \Omega_S B_S)^{-1} J \Omega_T B_T - \Omega_T B_T] D\} e^{it\Delta E} \quad (5)$$

$\Delta E$  is the singlet-triplet adiabatic energy gap and the matrices  $S_S$ ,  $B_S$ ,  $S_T$  and  $B_T$  are diagonal matrices with the elements:  $\sinh((1/k_B T - it)\omega_{S_i})$ ,  $\tanh(\omega_{S_i}/(2(1/k_B T - it)))$ ,  $\sinh(it\omega_{T_i})$  and  $\tanh(\omega_{T_i}it/2)$ , respectively,  $\omega_i$  is the normal mode frequency, indexes  $S$  and  $T$  label the normal modes of the singlet and triplet electronic states,  $t$  is time and the superscript  $T$  indicates the transposition of the matrix.

The geometries of the  $S_1(n\pi^*)$  and  $T_1(\pi\pi^*)$  states of uracil and thymine obtained with the CC2/cc-pVDZ level of theory<sup>9</sup> were used. The normal mode displacements of the  $T_1$  state relative to the  $S_1$  states of uracil and thymine in dimensionless harmonic oscillator coordinates are presented in Fig. 1. There are several low-frequency modes that are highly displaced in both uracil and thymine. In addition, the C<sub>4</sub>-C<sub>5</sub> bond stretching has a very large displacement (2.84 in uracil and 2.85 in thymine). The Duschinsky matrices for the transition between the  $S_1$  and  $T_1$  states of uracil and thymine are presented in Fig. 2. Almost all modes are mixed. The mixing 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 the low-frequency modes. The adiabatic energy gap between  $S_1$  and  $T_1$  electronic states of uracil and thymine, obtained at CC2/cc-pVDZ level, are 5150 and 6652 cm<sup>-1</sup>, respectively.<sup>9</sup> The adiabatic energy gap and displacement of the normal modes are decisive parameters that contribute to the calculation of the ISC rates. 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<sup>-2</sup> for uracil and 2319 cm<sup>-2</sup> for thymine.<sup>9</sup> All ISC rates that will be presented in this work are the sum of the three ISC rates from the  $S_1$  state to the three fine-structure components of the  $T_1$

state. All normal modes were included in the calculations. The correlation function was calculated for the first 10 fs using 1000 points.

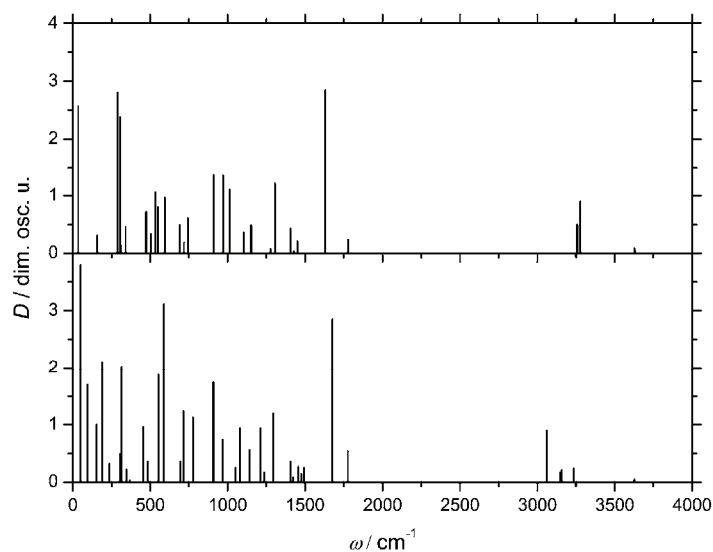


Fig. 1. Displacements of the  $T_1$  normal modes relative to the  $S_1$  normal modes in dimensionless harmonic oscillator coordinates for uracil (upper) and thymine (lower).

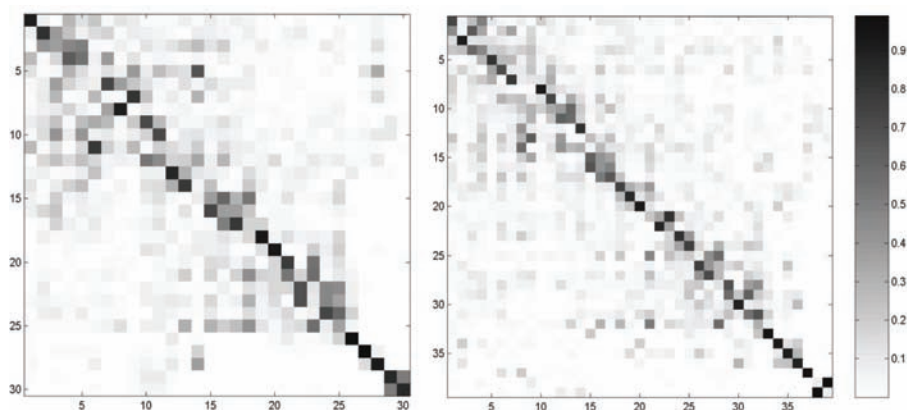


Fig. 2. Duschinsky matrix related to the transition between the  $S_1$  and  $T_1$  states of uracil (left) and thymine (right). In order to visualize the normal mode mixing, absolute values of the matrix elements are shown.

## RESULTS AND DISCUSSION

If an electronic transition in a molecule is slower than the vibrational relaxation, then the normal modes of the electronic state will equilibrate with a heat

bath. This means that the heat bath will determine the average vibrational energy of the electronic state. Since the Boltzmann constant is  $k_B \approx 0.7 \text{ cm}^{-1} \text{ K}^{-1}$ , only the normal modes with the frequencies less than  $\approx 250 \text{ cm}^{-1}$  are more than singly occupied at 300 K. At higher temperatures, 400 and 600 K, this frequency is shifted to  $\approx 300$  and  $500 \text{ cm}^{-1}$ , respectively. This means that the heat bath can excite only low-frequency modes that include a pyrimidization of the ring atoms, an in-plane bending of the C=O bonds and a rotation and bending of the methyl group in thymine. Hence, these modes will have an excess of vibrational energy compared to the high-frequency modes. On the other hand, these modes significantly contribute to the ISC rate because they make a vibronic quasi-continuum in the triplet state.

The correlation functions for uracil and thymine calculated for different temperatures are presented in Fig. 3. In both molecules, the correlation functions decay to zero in approximately 5 fs. These fast decays are related to the large displacements of the normal modes. Since this is a multimode case with Duschinsky rotation, the normal modes with small displacements can also contribute to the correlation function. The correlation functions of thymine decay faster than the correlation function of uracil. This means that in thymine, the vibrational wavepacket on the triplet potential surface leaves the Franck–Condon zone faster than

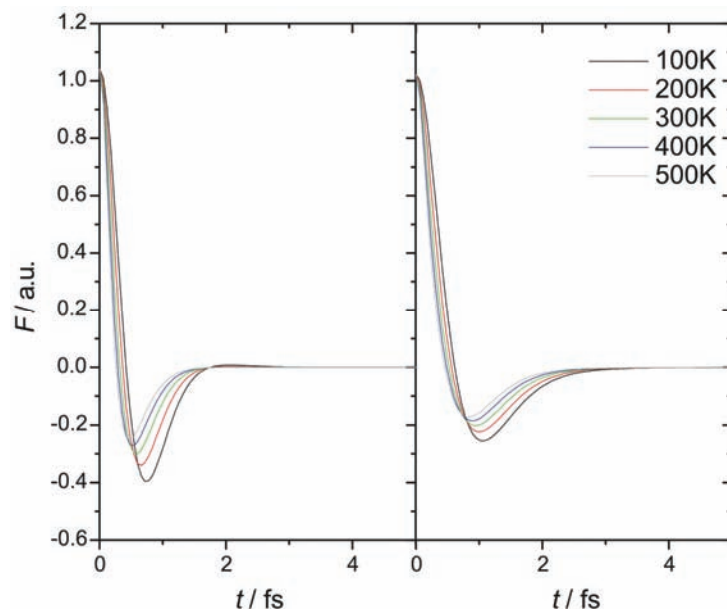


Fig. 3. Time dependence of the correlation function  $F$  for uracil (left) and thymine (right) for various temperatures. The adiabatic energy gap was  $5150 \text{ cm}^{-1}$  for uracil and  $6652 \text{ cm}^{-1}$  for thymine.

in uracil. In addition, the amplitude of the first oscillation is larger for thymine than for uracil. This amplitude for both correlation functions increases with increasing temperature. The same trend is valid for the decay of the first oscillation of the correlation function.

The correlation function at  $t = 0$  should be exactly one but it is slightly higher for uracil and thymine. This is because the determinant of the Duschinsky matrices for uracil and thymine are 0.98 and 0.96, and not 1.00. Therefore, the normal modes of the triplet electronic state are not completely represented by the normal modes of the singlet electronic state without including rotations. This phenomenon is called the axis-switching effect.<sup>17,18</sup> Sando *et al.*<sup>19</sup> showed that the contribution of the nonlinear effect is in principal small for non-radiative transitions.

The ISC rate from the lowest vibrational level of the singlet electronic state (the  $T = 0$  case) for uracil and thymine are  $1.5 \times 10^{10}$  and  $2.5 \times 10^9$ .<sup>13,14</sup> The ISC rates for uracil and thymine as a function of temperature are presented in Fig. 4. In accordance with the correlation function behavior, the rates decrease with increasing temperature. This means that the excess of vibrational energy in the  $S_1$  state decreases the ISC rate for the formation of the triplet state. The explanation for this could be that the excited vibrational levels in the  $S_1$  state have smaller

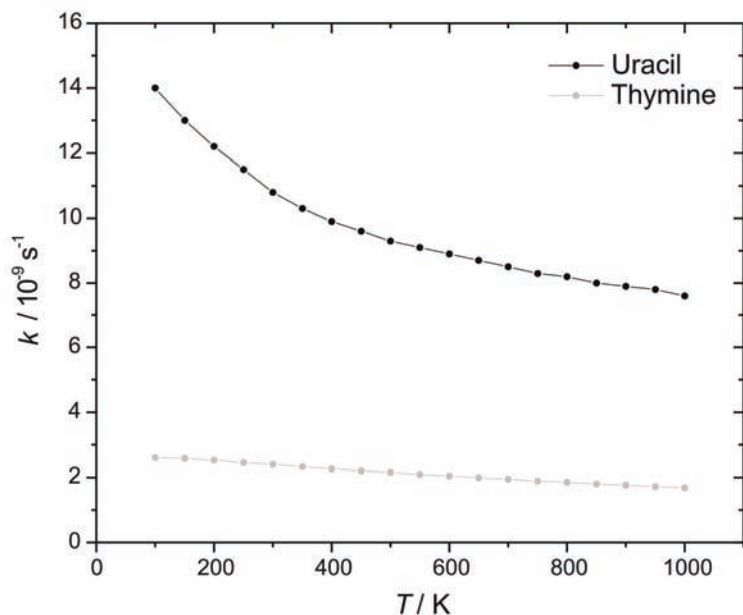


Fig. 4. Temperature dependence of the intersystem crossing rates for uracil and thymine. The adiabatic energy gap was  $5150 \text{ cm}^{-1}$  for uracil and  $6652 \text{ cm}^{-1}$  for thymine.

Franck–Condon integrals with the triplet vibrational level than the lowest vibrational state of the singlet state. The temperature dependence of the rate is more pronounced for uracil than for thymine. In the interval from 100 to 400 K, the rate decrease 30 % for uracil and 10 % for thymine. According to the energy gap law,<sup>20</sup> 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. Thymine has a smaller singlet–triplet energy gap than uracil but the ISC rate is smaller. This is due to the large Duschinsky mixing. In this case, the energy gap law ceases to be valid.

A solvent can modify the adiabatic energy gap and it is of interest to see how the ISC rate depends on the adiabatic energy gap. The ISC rates of uracil and thymine as a function of the adiabatic energy gap calculated at 300 K are presented in Fig. 5. Up to 5000  $\text{cm}^{-1}$ , the rates increase exponentially. For uracil, it changes two orders of magnitude while for thymine one order of magnitude. Hydration blue shifts the  $S_1(^1n\pi^*)$  state by  $\approx 4000 \text{ cm}^{-1}$  and the  $^3\pi\pi^*$  state by  $\approx 800 \text{ cm}^{-1}$ .<sup>10</sup> Hence, singlet–triplet energy gap is then increased by  $\approx 3200 \text{ cm}^{-1}$ . This would increase the ISC rate by an order of magnitude for uracil.

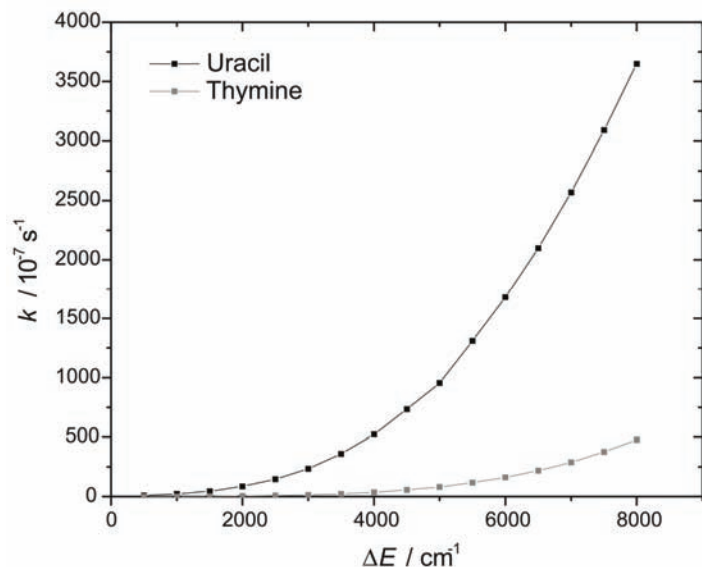


Fig. 5. The dependence of the intersystem crossing rates on the adiabatic energy gap for uracil and thymine. The temperature was 300 K.

#### CONCLUSIONS

The rate of formation of the lowest triplet state in uracil and thymine when the molecule has an excess vibrational energy due to interaction with a heat bath

was studied. In a previous paper on the spin-forbidden transitions in uracil, thymine and their methylated compounds,<sup>9</sup> two mechanisms for triplet formation were suggested, *i.e.*, a) a non-radiative transition from the intermediate  $^1n\pi^*$  state to the lowest triplet state and b) a transition from the initially populated  $^1\pi\pi^*$  state to the second triplet state  $^3n\pi^*$  followed by internal conversion to the lower triplet  $^3\pi\pi^*$  state. In this work, the first mechanism was considered.

The intersystem crossing rates were calculated using the correlation function and canonical ensemble formalism. The normal modes of the triplet and singlet states were related by the Duschinsky transformation. The excess of the vibrational energy was controlled by the temperature of a heat bath. The correlation functions for both molecules decay in 5 fs. The correlation functions of thymine decay faster than the correlation functions of uracil. It was found that excess vibrational energy decreased the rate of triplet formation in uracil and thymine. This dependence was more pronounced for uracil. In addition, the rate of the triplet formation was more susceptible to changes in the adiabatic energy in uracil than in thymine.

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## ИЗВОД

## УТИЦАЈ ТЕМПЕРАТУРЕ НА КОНСТАНТУ БРЗИНЕ СПИНСКИ ЗАБРАЊЕНОГ ПРЕЛАЗА У УРАЦИЛУ И ТИМИНУ

МИХАЈЛО ЕТИНСКИ

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У раду су помоћу *ab initio* метода проучаване константе брзине интерсистемских прелаза у урацилу и тимину који интерагују са топлотним купатилом. Константе брзине су израчунате користећи временски зависна прилаз заснован на корелационој функцији. Нормални модови синглетног и триплетног електронског стања су повезани трансформацијом Душинског. Корелациона функција је израчуната користећи Кондонову апроксимацију за спин–орбитни матрични елемент и хармонијску апроксимацију за нуклеарно кретање. Вишак вибрационе енергије у почетном синглетном електронском стању смањује константу брзине настајања триплетног стања у урацилу и тимину. То смањење је израженије за урацил. Такође, нађено је да промена разлике адијабатских енергија електронски стања може значајно да утиче на брзину настајања триплетног стања.

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