ADDITIONS AND CORRECTIONS

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Susan Ng, Soujanya Yarasi, Philip Brost, and Glen R. Loppnow*: Initial Excited-State Structural Dynamics of Thymine Are Coincident with the Expected Photochemical Dynamics

Pages 5130−5135. Recently, we presented the UV resonance Raman cross sections and absorption spectrum of thymine, one of the nucleobases found in DNA.[1] Analysis of this data, and using the previously reported vibrational normal-mode analysis,[2] resulted in a picture of the excited-state structural dynamics for thymine in which the structural distortions occur primarily along the photochemical reaction coordinate.

Attempts to reproduce the simulations with the data presented in the paper led to the realization that their is an inconsistency in the results presented in this paper. Susan Ng (who has been added as an author to the Addition and Correction) realized these inconsistencies. In error in Figure 3 and Tables 1 and 2 of the original article are the reported *total experimental* Raman cross sections (σ_R) and the *differential calculated* Raman cross sections ($d\sigma_R/d\Omega$). The differential and total Raman cross sections are related by

$$\sigma_R(E_L) = \frac{8\pi}{3}\left(\frac{1+2\rho}{1+\rho}\right)\frac{d\sigma_R}{d\Omega} \qquad (1)$$

where E_L is the excitation energy and ρ is the depolarization ratio. Revised Figures 2 and 3 and revised Tables 1 and 2 are given above. While this revision changes the resulting parameters for the excited-state structural dynamics of thymine, it does not change any of the major conclusions of the paper, particularly that the structural dynamics of thymine in the excited state lie along the photochemical reaction coordinate.

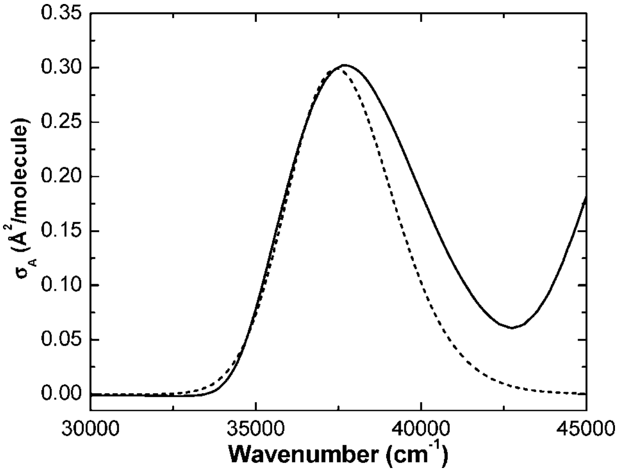

Figure 2. Experimental (solid line) and simulated (dotted line) absorption spectra of thymine. The simulated absorption spectra were calculated by using the parameters of Table 1. Discrepancies at energies greater than 42 000 cm^{-1} are due to higher-energy electronic transitions, which were not modeled here.

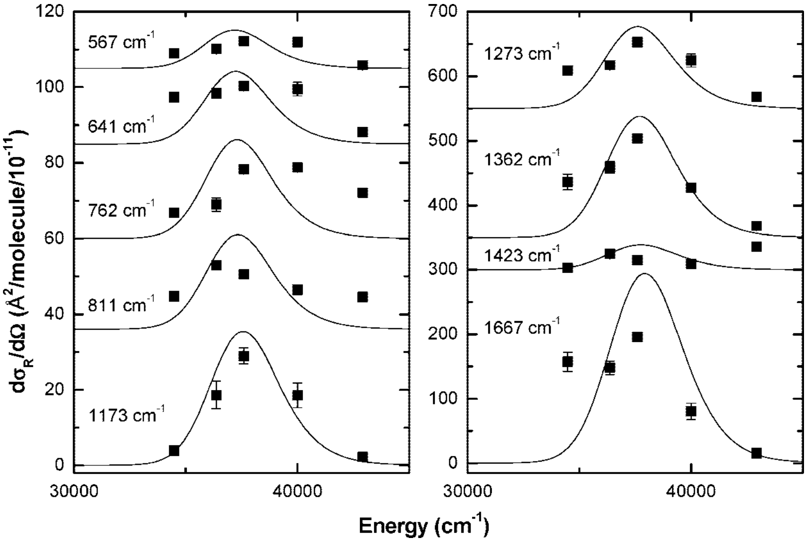

Figure 3. Experimental (points) and calculated (solid line) resonance Raman excitation profiles of thymine. The excitation profiles were calculated by using the parameters of Table 1. The excitation profiles have been offset along the ordinate for greater clarity of presentation. Note the difference in ordinate scales between the left and right panels.

TABLE 1: Harmonic Mode Parameters of Thymine[a]

mode (cm^{-1})	mode assignment[b]	$\lvert\Delta\rvert$
567	$90\ \gamma(N_1H_7) - 6\ \gamma(N_3H_9)$	0.24
641	$28\ \text{be}(C_4O_{10}) - 27\text{be}(C_2O_8) + 14\ \text{be}(C_5C_{11}) + 6\text{ring def } 2$	0.30
762	$60\ \gamma(C_2O_8) - 12\ \text{ring def } 6 + 8\text{ring def } 4 + 6\ \gamma(C_4O_{10}) - 5\ \gamma(N_3H_9)$	0.30
811	$45\ \text{ring def } 1 + 20\nu(C_5C_{11}) - 11\ \nu(N_1C_2)$	0.28
1173	$21\ \nu(C_2N_3) + 20\ \text{be}(C_6H_{12}) - 16\ \text{be}(N_1H_7) - 12\ \nu(N_3C_4) - 11\ \nu(C_6N_1)$	0.24
1237	$29\ \nu(C_5C_{11}) - 21\ \nu(C_6N_1) - 12\ \text{ring def } 1 + 10\ \nu(N_1C_2) - 10\ \nu(C_4C_5) - 8\ \nu(C_2N_3)$	0.44
1362	$42\ \text{be}(C_6H_{12}) + 12\ \nu(C_5C_6) + 9\ \nu(N_1C_2) - 9\ \nu(C_2N_3)$	0.50
1423	$15\ \nu(C_2N_3) - 13\ \nu(C_4C_5) - 11\ CH_3\ \text{umb} + 9\ \text{be}(N_1H_7) - 8\ \nu(N_1C_2) + 7\ \text{be}(C_4O_{10}) + 7\ \text{be}(C_2O_8) - 6\ \text{ring def } 2 - 6\ \text{be}(N_3H_9)$	0.22
1667	$61\ \nu(C_5C_6) - 13\ \text{be}(C_6H_{12}) - 8\ \nu(C_6N_1) - 5\ \nu(C_5C_{11})$	0.55

[a] Frequencies listed are the experimental frequencies reported here. Displacements (Δ) are in units of dimensionless normal coordinates and were obtained by fitting eqs 1 and 2 of ref 1 with the following parameters: temperature $T = 298$ K, Brownian oscillator line shape $\kappa = \Lambda/D = 0.1$, Gaussian homogeneous line width $\Gamma_G = 1700\ \text{cm}^{-1}$, inhomogeneous line width $\Theta = 1075\ \text{cm}^{-1}$, $E_0 = 35650\ \text{cm}^{-1}$, and transition length $M = 0.67$ Å. The estimated errors in the parameters used in the calculation are as follows: zero−zero energy (E_0) ±1%, transition length (M) ±1%, homogeneous line width (Γ) ±5%, inhomogeneous line width (Θ) ±5%, and displacements ±5%. [b] Mode assignments from ref 2. Abbreviations: ν, stretching; def, deformation; γ, wagging; be, bending. Numbers represent the total percentage potential energy distribution (PED) of the listed internal coordinate(s) to the normal mode. Only PEDs greater than 10% have been listed. Positive and negative PEDs represent the phases of the respective internal coordinate contributions.

TABLE 2: Experimental and Calculated Total Resonance Raman Overtone and Combination Band Cross Sections for Thymine[a]

mode (cm^{-1})	$d\sigma_{\text{experimental}}/d\Omega$ (Å^2/molecule-sr × 10^{-10})	$d\sigma_{\text{calculated}}/d\Omega$ (Å^2/molecule-sr × 10^{-10})
2596	2.92 ± 0.12	2.48
2720	2.90 ± 0.10	1.75
2899	4.16 ± 0.98	3.63
3014	5.43 ± 0.90	5.40

[a] The excitation wavelength is 257 nm. Cross sections were calculated with eq 1 of ref 1 by using the parameters of Table 1.

References and Notes

(1) Yarasi, S.; Brost, P.; Loppnow, G. R. *J. Phys. Chem. A* **2007**, *111*, 5130–5135.

(2) Yarasi, S.; Billinghurst, B. E.; Loppnow, G. R. *J. Raman Spectrosc.* **2007**, *38*, 1117–1126.

10.1021/jp806433h