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Previtamin D conformations and the wavelength-dependent photoconversions of previtamin D

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Abstract

Conformational abundances calculated at different levels of theory have been used to derive spectral and photophysical properties of a previtamin D model compound. The individual conformer spectra of absorption are approximated by Gaussian functions using excited state characteristics calculated with the QCFF/sol method. The calculated total UV spectrum for 3-desoxy-previtamin D model compound is found to be in a good agreement with experiment. The ratio of quantum yields for the *cis–trans* and ring-closure photochemical reactions of previtamin D is in excellent agreement with experiment in the long-wavelength spectral region, suggesting that lower-energy excitation photochemistry is conformationally controlled. We postulate that the observed sudden change in the relative efficiency of *cis–trans* vs. ring-closure photoisomerization of previtamin D around 300 nm reflects the opening of new excited state dynamical channel, possibly involving intersystem crossing of the system to excited triplet states.

Keywords: Previtamin D; Conformational control; Density functional calculations; Absorption spectrum modeling; Photoreaction efficiency

1. Introduction

The ultraviolet (UV) part of sunlight which penetrates the earth's atmosphere can cause beneficial and detrimental effects on living organisms [1,22]. The vitally important vitamin D synthesis is induced by natural UV-irradiation in the epidermis [2,23–25]. This reaction sequence involves the photochemical ring-opening of the steroidal precursor 7-dehydrocholesterol (provitamin D) to previtamin D and subsequent thermal rearrangement ([1,7]-hydrogen migration) to the prohormone vitamin D [3,26].

In solutions, the photosynthesis of previtamin D (Fig. 1) is a complex branched network of reversible and irreversible isomerization reactions, with previtamin D occupying the central position. Besides the *cis–trans* isomerization into tachysterol and the naturally occurring ring-closure into lumisterol or provitamin D, there are also irreversible photochemical processes leading to the formation of over-irradiation products, denoted toxisterols (Tox) [4,5].

Provitamin D and its main photoisomers absorb in the same UV-region and, once excited, they all interconvert by photoisomerizations (Fig. 1). In addition previtamin D and tachysterol may undergo irreversible conversions into toxisterols with different efficiencies. This results in complex reaction mixtures whose composition strongly depends on the wavelength of irradiation applied ([6–8,27–36] and references therein) and the reaction medium [4]. For the most part, the wavelength dependence in previtamin D photosynthesis is caused by the different absorbances of the photoisomers involved in the reaction network [6,7,27–33].

There is another, more complicated, wavelength effect in previtamin D photochemistry: a sudden increase in the efficiency of ring-closure reactions relative to *Z*/*E* isomerization at wavelengths between 302 and 305 nm [30–32]. This change in the photoproduct branching ratio appears to be intrinsic to previtamin D itself with the two types of photoreaction simply representing different relaxation channels.

Several models have been put forth recently in an effort to explain the dramatic changes in this branching ratio [7,9,29–33,37]. One of the simplest and most logical explanations involves selective excitation of different conformers possessing different absorption spectra and photoreactivity [10,38,39]. Due to the great flexibility of the previtamin D chromophore [11,12,40] and its non-planar geometry [11–14,40,41], the direct measurement of individual absorption spectra of its conformers is unachievable. Consequently, more sophisticated experimental strategies, such

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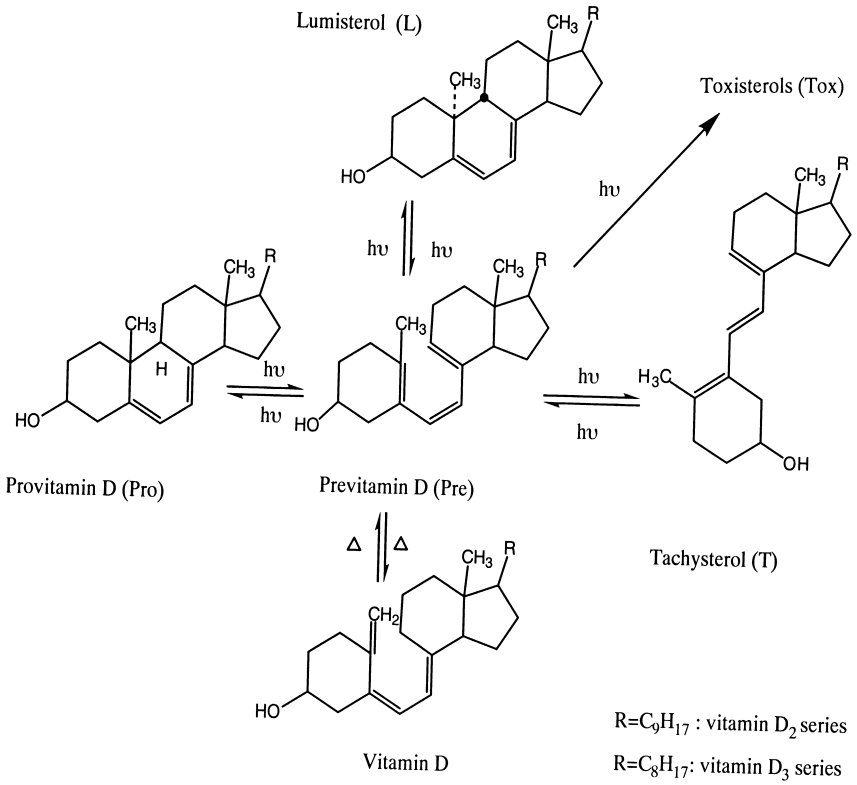

Fig. 1. Reaction scheme for provitamin D photoisomerization.

as low-temperature matrix techniques, along with computational separation of the individual components of the averaged solution spectra have been pursued [30]. No marked difference between the spectra of the *cZc* conformer (the primary one formed after ring-opening from provitamin D) and the extended *tZc* conformers has been found experimentally [15]. Nevertheless, gas-phase semi-empirical calculations [13,14,41] predict a difference in the 0–0 transitions of *cZc* and *tZc* conformers that could explain the origin of the branching ratio wavelength dependence. These calculations suggest that *cZc* conformers can be selectively excited at the very red edge of previtamin D absorption band (which is actually a sum of individual conformer contributions), while the *tZc* conformers remain inactive. In the present work, we examine the notion that the low energy behavior of the wavelength dependence can be attributed to ground state conformational control [10,38,39], a mechanism which has been used successfully to predict the photochemistry of vitamin D and its isomers.

2. Theoretical modeling of the branching ratio for ring-closure vs. *Z*/*E* photoisomerization

In this study, we examine the contribution of previtamin D conformers, *cZc* and *tZc*, to the wavelength dependence of the photoreaction quantum yields. The theoretical approach is similar to one proposed for the photoreactions of conformationally flexible intermediate photoisomers [16,42,43] and modified for the particular case of previtamin D photoisomerizations. Our aim is to obtain an equation for the quantum yield branching ratio of the *cis–trans* vs. ring-closure photoisomerizations. To do this, we will use structural and energetic characteristics of previtamin D conformers obtained from density functional (B3LYP/6-31G(d)), AM1, molecular mechanics MMX, and QCFF semi-empirical computations [12–14,41].

The two-way photochemical reaction model is presented symbolically in Fig. 2. This model has been fully described in Ref. [43] for different degrees of irradiation intensity. In the present study, we focus on the branching ratio of the photoproducts C and D under low-intensity irradiation, given by

$$\frac{f_{\mathrm{C}}}{f_{\mathrm{D}}} = \frac{q_{-}\sigma_2\eta_2}{q_{+}\sigma_3\eta_3} \tag{1}$$

Here $\eta_i \equiv \gamma_i/(k_i+\gamma_i)$ is a characteristic of the excited state, where k_i and γ_i are the rate constants (in s^{-1}) associated with non-reactive and reactive transitions, respectively. The quantities q_- and q_+ refer to the rate constants for the interchange of different conformers. Thus, the ratio q_-/q_+ is determined by the conformational equilibrium in the ground state and can be replaced by the ratio of conformational populations [43]. Finally, σ_i is the absorption cross-section in cm^2. For the case of an intermediate photoproduct whose

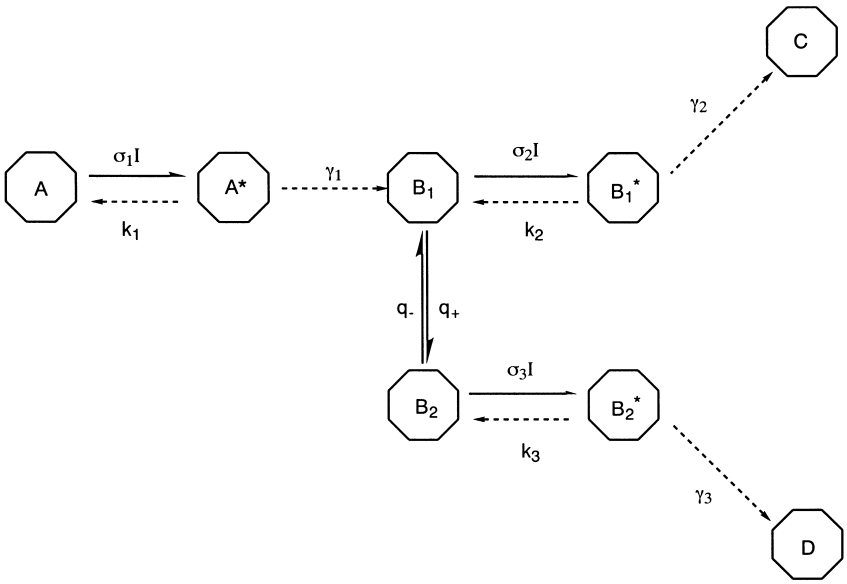

Fig. 2. Model of two-product photolysis reaction involving two conformations of the intermediate isomer. Here, σ_i are the absorption cross-sections (in cm^2) and I is the photon flux (photon $cm^{-2}\,s^{-1}$). The quantities k_i (s^{-1}) and γ_i (s^{-1}) characterize the non-reactive and reactive transitions, respectively.

ground state equilibrium includes several populated conformers, Eq. (1) can be generalized to

$$\frac{f_C}{f_D} = \frac{\sum_i p_i \sigma_i \eta_i}{\sum_j p_j \sigma_j \eta_j} \tag{2}$$

where one set of conformers (i) are precursors of product C whereas another set (j) leads to D.

Previtamin D has at least eight low-energy (within 2 kcal/mol) ground state conformations that differ in their configuration around single bonds (C5–C6 and C7–C8), the sign of their corresponding dihedral angles, and in their A-ring conformations (axial vs. equatorial orientation of 3β-OH) [11–14,40,41]. According to generally accepted assumptions based on conformational control (i.e. the NEER principle [4]) and illustrated in Fig. 3, Eq. (2) can be modified for the specific case of previtamin D photoconversion to

$$\frac{f_{cis\rightarrow trans}}{f_{\text{ring-closure}}} = \frac{\sum_t p_t \sigma_t \eta_t}{\sum_c p_c \sigma_c \eta_c} \tag{3}$$

Here, the indices '*t*' and '*c*' correspond to *tZc* and *cZc* conformers, respectively. The quantity $f_{cis\rightarrow trans}$ is the quantum yield of Pre → T *Z*/*E* isomerization, while $f_{\text{ring-closure}}$ is defined as the sum of Pre → Pro and Pre → L ring-closure quantum yields.

For simplicity, we assume that $\eta_t = \eta_{trans}$, $\eta_c = \eta_{cis}$, are both constant, so that $\eta_{trans}/\eta_{cis} =$ constant. One may then obtain

$$\frac{f_{cis\rightarrow trans}}{f_{\text{ring-closure}}} \propto \frac{\sum_t p_t \sigma_t}{\sum_c p_c \sigma_c} \tag{4}$$

which will be used further when comparing simulation results with the experimental dependence.

3. Computational simulations of the previtamin D UV absorption spectrum

In order to simulate the spectrum of previtamin D using Eq. (4), the conformational distribution, in particular the

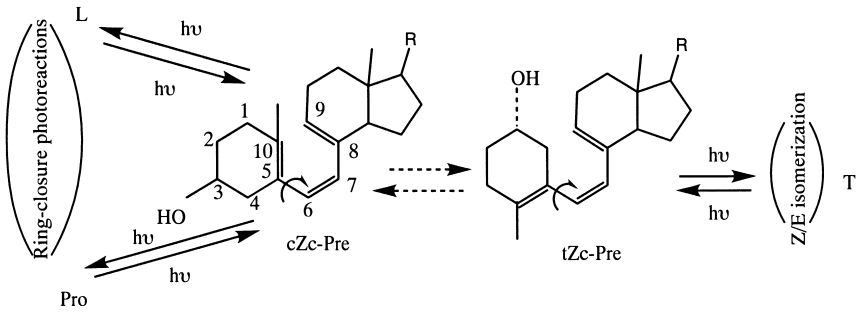

Fig. 3. A simplified two-conformation scheme of previtamin D reversible photoconversions. Here and below, *Z* denotes the *cis* geometry in relation to the C6=C7 double bond. The letters *c* and *t* refer to the *s-cis* and *s-trans* conformations of the C5–C6 and C7–C8 single bonds.

Table 1
The conformational abundance calculated for previtamin D model using different theoretical approaches (Refs. [12–14,40,41])

Geometry	AM1 (%)	MMX-DD (%)	B3LYP/6-31G*		
			I[a] (%)	II[b] (%)	III[c] (%)
3β-OH-equatorial					
(−)*cZ*(−)*c*	14.7	31.0	2.2	3.6	2.9
(+)*cZ*(+)*c*	7.6	8.8	7.5	12.3	11.5
(−)*tZ*(+)*c*	19.8	5.0	18.1	29.9	27.6
(+)*tZ*(−)*c*	17.4	19.4	15.0	24.8	12.4
3β-OH-axial					
(−)*cZ*(−)*c*	6.3	7.7	4.0	2.1	6.1
(+)*cZ*(+)*c*	7.4	7.0	4.2	2.1	4.5
(−)*tZ*(+)*c*	8.9	3.1	12.9	6.6	14.9
(+)*tZ*(−)*c*	17.9	17.9	36.3	18.6	20.3

[a] The conformer percentages based upon their total energies at the B3LYP/6-31G* level of theory.

[b] The conformer percentages based upon the total energies at the B3LYP/6-31G* for 3β-OH-equatorial structures and corrected (+0.7 kcal/mol) total energies of 3β-OH-axial conformations.

[c] The conformer percentages of 3-desoxy-previtamin D model based upon their total energies at the B3LYP/6-31G* level of theory.

cZc and *tZc* rotamer populations, are needed. To this point, there is no definitive experimental knowledge of the ground state conformer populations of previtamin D, so we use the results of different theoretical optimizations summarized in Table 1. In these results, ab initio calculations have been carried out using the Gaussian98 program system [17]. The Becke three-parameter hybrid functional combined with the Lee, Yang and Parr (LYP) correlation functional, B3LYP, was employed in all calculations using density functional theory (DFT) [44–47]. All calculations were performed on the DEC Alpha computer cluster (RISC A21064A) of the University of Vienna Computer Center and on an HP workstation (University of Nevada, Reno).

To account for solvent matrix effects, we have utilized the experimental observation that the equatorial orientation of the hydroxyl group in 3,4-dimethyl-3-cyclohexenol (A-ring model) is favored by 0.7 kcal/mol relative to the axial orientation [18]. This value was added to the relative axial conformer energies, and the column labeled II in Table 1 represents the corresponding populations. Another way to model previtamin D in solvent is given in the column labeled III. This model is a result of B3LYP/6-31G(d) optimizations on a 3-desoxy-previtamin D model which preserves all the geometrical features of previtamin D, but omits intramolecular interactions involving the OH group [41].

To use Eq. (4), one must also know the wavelength-dependent absorption cross-section for each conformer, a non-trivial task for a sterically-hindered conjugated π-system [19,48]. This cross-section is proportional to the oscillator strength and depends on the wavelength of irradiation in the same way as its absorption spectrum

$$\sigma_i \propto f_i R_i(\lambda) \tag{5}$$

where the function $R_i(\lambda)$ characterizes absorption bandshape of the conformer *i*. The absorption of previtamin D is a sum of its individual conformer contributions, weighted by their relative populations, so the total absorption spectrum $S(\lambda)$ can be written as

$$S(\lambda) \propto \sum_i \sigma_i p_i \tag{6}$$

To simulate $R_i(\lambda)$ while avoiding complicated calculations that require detailed information about the ground and excited states, we assume that each conformer has a Gaussian bandshape whose maximum occurs at the Franck–Condon transition wavelength and whose half-width is equal to $\frac{1}{2}(\lambda_{0-0} - \lambda_{FC})$, where λ_{0-0} and λ_{FC} are the wavelengths of the origin 0–0 and vertical Franck–Condon transitions, respectively. This approximation represents a crude means for estimating the width of the absorption profile, likely overestimating the true bandwidth, and it ignores the possibility that the bands may exhibit vibrational structure. Nevertheless, a more sophisticated treatment of the absorption bandshape would require a significant effort to more fully characterize the excited state and is not justified given other approximations that are made in our treatment. The necessary characteristics of the first strongly allowed previtamin D excited state have been calculated previously [13,14,41] and are listed in Table 2.

A simulation of the previtamin D spectrum and the contributions of the *cZc* and *tZc* conformers are presented in Fig. 4a. The overall contribution of the *cZc* conformers is much less than *tZc*, and there is no significant difference in the maxima of their absorptions. Thus, the externally induced changes of the equilibrium between folded (*cZc*) and extended (*tZc*) conformations are expected to be indicated by a change in the intensity of absorption rather than by a spectral shift.

The integrated spectrum of axial conformers has a blue-shifted maximum with respect to the spectrum from the equatorial rotamers (Fig. 4b). This is in agreement with the observed red-shift of the previtamin D absorption band in polar solvents that favor the equatorial conformation [5,11].

Table 2
The excited state characteristics (wavelengths of origin and Franck–Condon transitions and oscillator strengths) of 3-desoxy-previtamin D used for the spectral simulations [14,41]

Conformer	Oscillator strength	λ_{0-0} (nm)	λ_{FC} (nm)
3β-H-equatorial			
(−)*cZ*(−)*c*	0.37	316	248
(+)*cZ*(+)*c*	0.31	321	267
(−)*tZ*(−)*c*	0.42	304	257
(+)*tZ*(−)*c*	0.58	313	267
3β-H-axial			
(−)*cZ*(−)*c*	0.36	317	254
(+)*cZ*(+)*c*	0.32	331	261
(−)*tZ*(+)*c*	0.52	308	257
(+)*tZ*(−)*c*	0.41	304	256

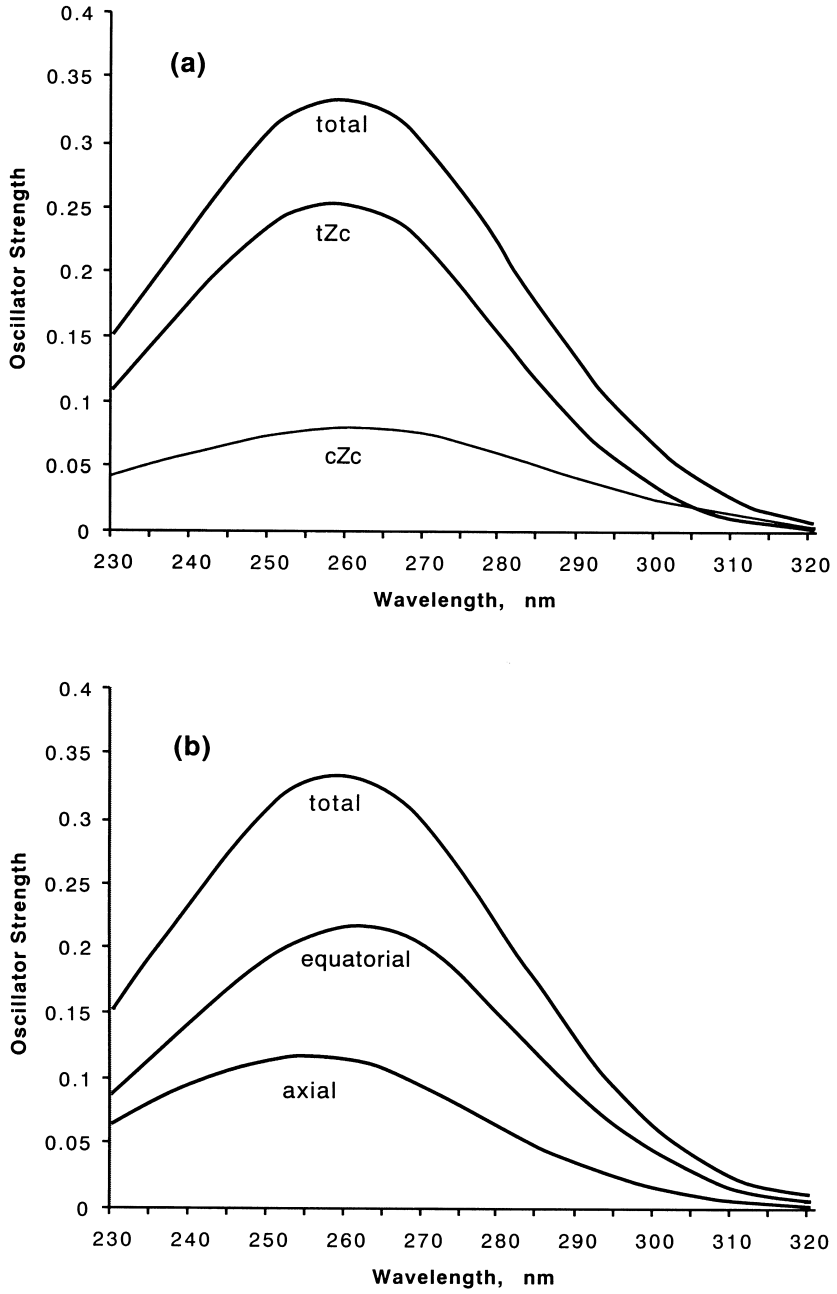

Fig. 4. (a) Calculated absorption spectrum of previtamin D and the contributions from its *cZc* and *tZc* conformers based upon the B3LYP/6-31G(d) conformational populations of 3-desoxy-previtamin D. (b) Calculated absorption spectrum of previtamin D and the contributions of its equatorial and axial conformers based upon the B3LYP/6-31G(d) conformational populations of 3-desoxy-previtamin D.

The results of our spectral simulations compare best with experiment for the 3-desoxy-previtamin D model (see Fig. 5). Other methods/models tend to produce higher values of absorbance. In order to perform this comparison and present both experimental and calculated spectra on the same scale, the experimental oscillator strengths are determined by inverting an expression given by Allinger and Tai [20] for experimental extinction coefficients. We have previously shown that the inverted formula gives a reasonable approximation for the oscillator strengths of previtamin D isomers [14]. In Fig. 6, the wavelength dependence of the *cis–trans*/ring-closure branching ratio, based on calculations using Eq. (4), is compared with the experimentally measured ratio [9,37]. Again, the best agreement is found for the 3-desoxy-previtamin D population (B3LYP/6-31G(d), column labeled III in Table 1) in the long-wavelength region (>302 nm). In the short-wavelength region, the experimental ratio makes an abrupt jump, indicating that *cis–trans* isomerization becomes highly efficient and almost independent of wavelength (between 286 and 296 nm).

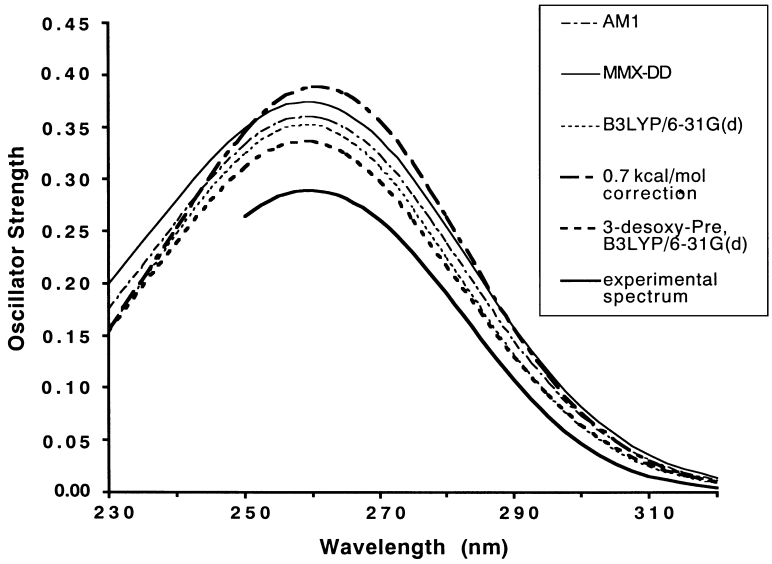

Fig. 5. A comparison of the calculated and experimental absorption spectra of previtamin D.

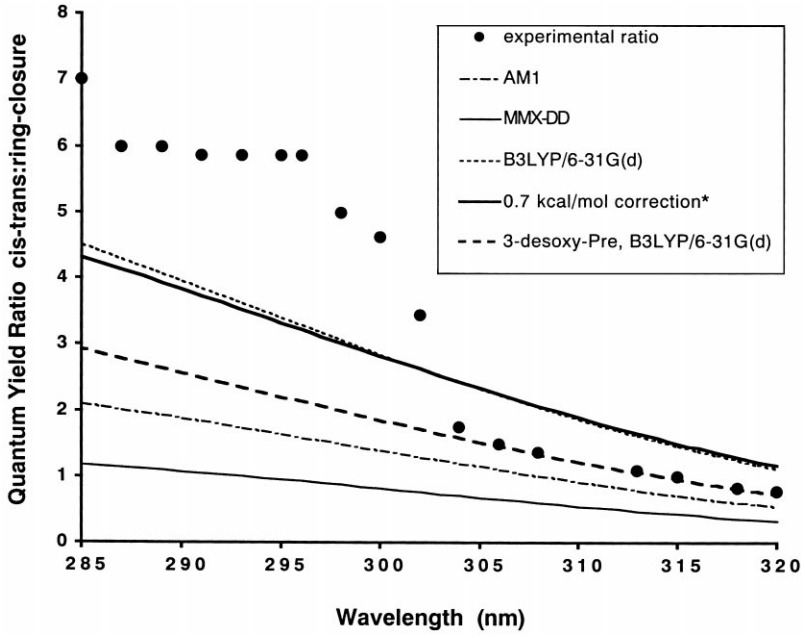

Fig. 6. A comparison of calculated values for $f_{cis \rightarrow trans}/f_{\text{ring-closure}}$ with experimental values for $f_{\text{Pre}\rightarrow\text{T}}/(f_{\text{Pre}\rightarrow\text{Pro}} + f_{\text{Pre}\rightarrow\text{L}})$ (data are taken from Ref. [37]).

Thus, low-energy photons (>302 nm) initiate singlet state photochemistry which is sufficiently well described by a model based upon the conformational control principle. The sudden change in favor of the *cis–trans* photoisomerization at shorter wavelengths suggests the opening of a new reaction pathway for the system. One intriguing possibility is an excited state pathway with a small barrier which starts from *cZc* previtamin D conformations and ends by formation of the *trans*-isomer, tachysterol [21]. This suggestion requires further theoretical and experimental investigation.

4. Conclusions

In this study, we have found that *cZc* conformers have a markedly smaller contribution to the absorption spectrum of previtamin D than *tZc* conformers. Furthermore, an increase in the population of *cZc* conformers should result in an increase in the absorption intensity but would not lead to a marked spectral shift. In the range 303–320 nm, we observe excellent agreement between the theoretical and experimental branching ratios; however, shorter wavelength irradiation

results in a higher branching ratio and different wavelength dependence. This indicates that at wavelengths greater than 303 nm, the reaction follows a classical conformationally controlled model, while the higher-energy photochemistry obeys a different dynamical mechanism. A possible explanation for the shorter wavelength product ratio is the opening of a new excited state channel for *cZc* conformers of previtamin D that enhances *cis–trans* isomerization. Further studies are underway to examine this possibility.

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