ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/230286404

Theoretical Study of Solvent Influence on the Electronic Absorption and Emission Spectra of Kynurenine

ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · JANUARY 2010

Impact Factor: 1.43 · DOI: 10.1002/qua.22929

CITATIONS
3

READS
8

2 AUTHORS, INCLUDING:

Petr Sherin
International Tomographic Center

21 PUBLICATIONS **179** CITATIONS

SEE PROFILE

Available from: Petr Sherin
Retrieved on: 25 January 2016

Theoretical Study of Solvent Influence on the Electronic Absorption and Emission Spectra of Kynurenine

ENRICO BENASSI,[1,2] PETER S. SHERIN[3]

[1]*Centro S3, CNR Istituto di Nanoscienze, via Giuseppe Campi 213/a, 41125 Modena, Italy*

[2]*School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta, GA 30332-0400*

[3]*International Tomography Center SB RAS, Institutskaya str. 3a, 630090 Novosibirsk, Russia*

Received 19 April 2010; accepted 4 August 2010
Published online 30 November 2010 in Wiley Online Library (wileyonlinelibrary.com).
DOI 10.1002/qua.22929

ABSTRACT: Neutral/zwitterionic form equilibrium, excited state wave functions, absorption and emission spectra of kynurenine (KN) in various solvents (water, methanol, ethanol, and dimethylsulfoxide) have been studied theoretically. The ground electronic state geometries have been optimized by density functional theory methods; the geometries of the first two singlets excited electronic states have been optimized using the CASSCF technique. The influence of the solvent was taken into account by the calculation of the solvation free energies using the Polarizable Continuum Model (PCM). The spectra of electronic absorption and fluorescence emission have been calculated by the CS-INDO S-CI and SDT-CI methods [Momicchioli, Baraldi, and Bruni, Chem Phys, 1983, 82, 229]. The calculated data reproduce the experimental positions of maxima and the solvent-induced shifts of the absorption and emission bands well. The energy gap between the two lowest excited states of KN increases from aprotic to protic solvents. This fact suggests that the "proximity effect" cannot be responsible for the ultrafast decay of KN fluorescence in protic solvents. ©2010 Wiley Periodicals, Inc. Int J Quantum Chem 111: 3799–3804, 2011

Correspondence to: E. Benassi; e-mail: enrico.benassi@unimore.it, ebenassi3@mail.gatech.edu or P. S. Sherin; e-mail: sherin@tomo.nsc.ru

Contract grant sponsor: FASI State Contracts.
Contract grant numbers: 02.512.11.2278, 02.740.11.0262, P708.
Contract grant sponsor: Russian Foundation for Basic Research.
Contract grant numbers: 08-03-00539, 09-04-12135.
Contract grant sponsor: Division of Chemistry and Material Science, Russian Academy of Sciences.

Additional Supporting Information may be found in the online version of this article.

© 2010 Wiley Periodicals, Inc.

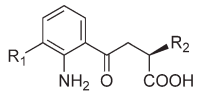
Key words: kynurenine; absorption and emission spectra; proximity effect; DFT calculations; PCM model; CS-INDO/CI

1. Introduction

The lens of mammal eye contains low molecular weight compounds, which operate as ultraviolet (UV) filters. These molecules that are typically metabolic products of tryptophan have kynurenine (KN) as prototype; the most abundant UV filters are 3-hydroxykynurenine O-β-D-glucoside, 4-(2-amino-3-hydroxyphenyl)-4-oxobutanoic acid O-β-D-glucoside, KN, and 3-hydroxykynurenine (see Chart 1). Showing strong absorbance between 300 and 400 nm, they protect the eye tissues (lens and retina) from the harmful sun irradiation. This behavior is due to a fast deactivation of the excited states: these molecules exhibit short fluorescence lifetimes and low fluorescence quantum yields [1], low triplet yields [2, 3], a high photochemical stability [3, 4], and insignificant yields of reactive oxygen species under aerobic photolysis [5]. Until this moment, the mechanism of the effective deactivation is still unclear [1, 2, 5].

Recently, the initial photoprocesses occurring in KN molecule under UV excitation have been investigated on the sub-picosecond time scale by one of us [6]. It has been found that in aqueous solutions KN exhibits very short fluorescence lifetime of about 30 ps. The latter increases by one order of magnitude in alcohols and exceeds 1 ns in aprotic solvents such as dimethylsulfoxide and dimethylformamide. Internal conversion (IC; here this term means all nonradiative decay channels with the exception of the intersystem crossing) is shown to be the main deactivation channel of the lowest singlet excited state of KN [6]. It has been proposed that the vibronic coupling between close-lying n,π^* and π,π^* excited states may be responsible for the fast radiationless $S_1 \rightarrow S_0$ transition (so-called proximity effect) [7]. Lim and coworkers [7] have shown that an out-of-plane bending mode that adiabatically couples the close-lying n,π^* and π,π^* states acts as an efficient accepting mode for the radiationless transition. As a result, the fast conversion of electronic energy of the upper electronic states to vibrational energies of the lower electronic state takes place. The energy gap between n,π^* and π,π^* states drives the rate of IC, because a smaller gap corresponds to a faster conversion. Chemical substitutions and the nature of solvent may change the energy gap and, as a result, the lifetime of the excited states. According to the "proximity effect" model, the observed increase of IC rate with hydrogen-bonding ability of the solvent [6] should be attributed to the following scheme of KN excited states: the n,π^* state is the lowest excited state and n,π^*–π,π^* energy gap decreases from aprotic to protic solvent.

Here, we present the study of the solvent influence on the structure and energy of KN excited states. The main goals of this work are (i) to examine the solvent dependence of the energy gap between two lowest singlet excited states and (ii) to clarify the role of "proximity effect" in the fast deactivation of KN excited states.



	R_1	R_2
kynurenine (KN)	H	NH_2
3-hydroxykynurenine (3OHKN)	OH	NH_2
3-hydroxykynurenine *O*-β-$_D$-glucoside (3OHKG)	OGlu	NH_2
4-(2-amino-3-hydroxyphenyl)-4-oxobutanoic acid *O*-β-$_D$-glucoside (AHBG)	OGlu	H

CHART 1.

2. Computational Details

The geometry of electronic ground state of various KN forms in the gas phase were optimized at the density functional theory (DFT) B3LYP/6-311++G(d,p) level of theory. All stationary points were confirmed to be true minima on their respective potential energy surfaces by analytical computation of the second derivatives of the energy. The corresponding thermal corrections at $T = 298.15$ K and $p = 1.00$ atm were calculated to obtain the enthalpy and Gibbs free energy values.

To take the solvation effects into account, the geometries of various KN forms were reoptimized at DFT level employing the Polarizable Continuum Model (PCM) approach in the Klamt and coworkers' [8] form of conductor-like screening model, considering dimethylsulfoxide (DMSO), ethanol, methanol, and water as solvents.

Note that KN has several conformers. Geometries of all these conformers were optimized and their spectra were calculated as described below. However, the calculated spectra of various

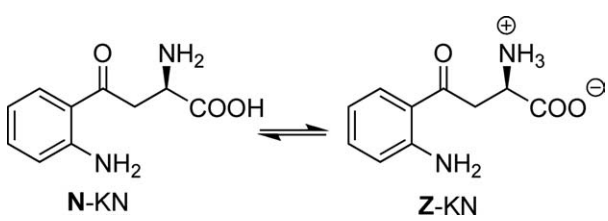
conformers turned out to be nearly identical. Therefore, only properties of the lowest energy species are discussed in this article.

The B3LYP/6-311++G(d,p) optimized geometries were used for the further single point calculations of the electronic absorption spectra. The absorption bands corresponding to the vertical excitations $S_0 \rightarrow S_n$ ($n = 1, 2, 3, 4, 5$) were calculated by the CS-INDO/CI method [9] using Ohno and Klopman [10] and Mataga and Nishimoto [11] parameterizations for integrals. The configuration interaction calculations were carried out both in the singly excited (S-CI) and in involving multiple excitations (SDT-CI) schemes. The molecular orbital (MO) active space in the CI calculations included 15 occupied MOs and 15 virtual MOs. The full MO calculations were also performed. In the SDT-CI calculations, about 1,000 configurations were considered. The Miertus and coworkers method [12] was used in the CS-INDO/CI calculations to take solvation into account.

The calculations of the emission fluorescence spectra $S_{n'} \rightarrow S_0$ ($n' = 1, 2$) required the geometry optimization of the excited states. This procedure was performed at the CASSCF (12,10)/6-311++G(d,p) level of theory [13]. On the basis of the analysis of the wave functions, the different active spaces were defined for the two excited states of interest. The CASSCF optimized geometries of the first two singlet excited states were used for the CS-INDO/CI single point calculations. All quantum chemical calculations were performed using the Gaussian03 suite of programs [14].

3. Results and Discussion

As mentioned in the Introduction, our main goal was to examine the solvent influence on the structure and energy of KN excited states. The KN, a typical α-amino acid, might in principle exists in two forms: neutral (N-KN) and zwitterionic (Z-KN, Scheme 1). The neutral–zwitterionic equilibrium depends strongly on the phase and on the solvent nature. It is natural that the ionic form in the gas phase is significantly less thermodynamically favorable than the neutral species. Similarly, it might be expected that in the condensed phase the zwitterion is more preferable.



SCHEME 1.

TABLE I

The relative Gibbs free energies of neutral and zwitterionic forms of KN in gas phase and in different solvents at room temperature. The neutral form was chosen as a reference compound for the calculations of the relative thermodynamic properties.

	ΔG^0 (kcal/mol)
Gas phase	(25.3)
Dimethylsulfoxide	−1.5
Ethanol	−2.5
Methanol	−2.8
Water	−3.7

The values in parentheses were obtained at the HF level of theory.

The calculations confirm this suggestion: we were even not able to optimize the zwitterionic form at the DFT B3LYP level, all the attempts led to the neutral KN form. However, we did localize the zwitterionic structure at the HF level of theory. This form was found to lie ~25 kcal/mol higher [in the $\Delta(\Delta H^0)$ scale] than the neutral one. Solvation profoundly stabilizes the highly polar zwitterion, and it becomes more preferable species in all solvents examined. The relative Gibbs free energies of two KN forms in various solvents, calculated using the PCM approach, are given in Table I. As the neutral isomer turned out to be thermodynamically unfavourable in all solvents, we studied in detail only properties of the zwitterionic form.

The DFT B3LYP optimized geometry of Z-KN in ethanol is shown in Figure 1; it did not vary much with the solvent. The wave functions of Z-KN singlet excited states S_n ($n = 1, 2, 3, 4, 5$) were calculated by CS-INDO S-CI (singly excited scheme) and SDT-CI (multiple excitations scheme) methods using the DFT optimized geometries of KN in the selected solvents (Supporting Information Table S1). A comparison between S-CI and SDT-CI calculations shows a modest influence of

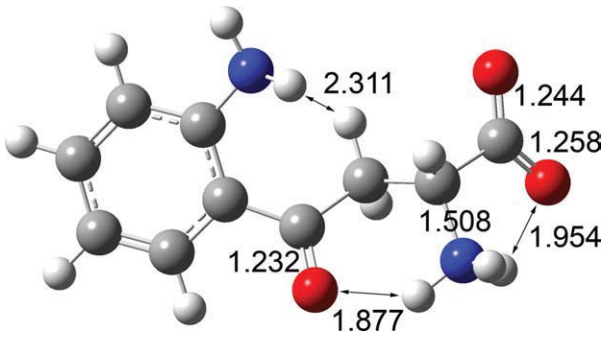


FIGURE 1. DFT optimized geometry of Z-KN in ethanol solution (the PCM model was used). Some interatomic distances are in Ångstrøms; atom labels: white (H), gray (C), blue (N), and red (O). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyexcited configurations on the wave functions. Comparing the S-CI and the SDT-CI calculations, the inversion of some states should be noted: in particular, the first two excited states are always exchanged with exception of the water solution.

Within the framework of the S-CI model, which give a better description of experimental absorption and fluorescence emission spectra (see below), the first excited state wave function is characterized by a combination of several excited determinants, principally single-excited ones; the main contribution corresponds to a $n \rightarrow \pi^*$ transition. At the same time, the second excited state wave function corresponds essentially to a $\pi \rightarrow \pi^*$ transition, which shows a remarkable charge transfer character, from aniline moiety to the carbonilic group. In contrast, the third transition—independently on solvent—has a character of the local excitation on the oxygen of carbonyl group. The other transitions vary a lot as a function of solvent. In the case of DMSO, the inversion of S_4 and S_5 is observed in addition to the inversion of S_1 and S_2. For ethanol and methanol, the picture is quite similar. In the case of water, a lot of modifications have been noticed in the four excited state wave functions. In comparison to previous cases, the charge transfer configurations play more important role.

The optimized geometries of the first two excited states obtained at the CASSCF level slightly differ from the ground state one. In particular, the C—N and C—O bond lengths increase by ~0.25–0.30 Å, whereas the benzene ring and the hydrocarbon chain do not undergo any remarkable changes. For the S_1 state, the angles are changed in the direction that causes N—O to be larger (nitrogen of aniline group and oxygen of carbonyl group), although both the atoms stay on the plane of the ring. On the contrary, in the case of the S_2 state, these two atoms deviate from the benzene plane. Anyway, all these modifications are quite modest.

Figure 2 shows experimental [6] and calculated (the CS-INDO S-CI method) absorption and emission spectra of KN in the selected solvents (see also Supporting Information Table S2). It is seen from Figure 2 that both energies and oscillator strengths of the calculated transitions reproduce the experimental data well. A blue shift of $S_0 \rightarrow S_1$ and $S_{1'} \rightarrow S_0$ transitions (mainly $n\pi^*$) and a red shift of $S_0 \rightarrow S_2$ and $S_{2'} \rightarrow S_0$ transitions (mainly $\pi\pi^*$) from DMSO to water perfectly agrees with a well-known fact that the H-bonding leads to the destabilization of $n\pi^*$ state and the stabilization of $\pi\pi^*$ state [15]. As a consequence, the obtained results reproduce the marked red shift of KN

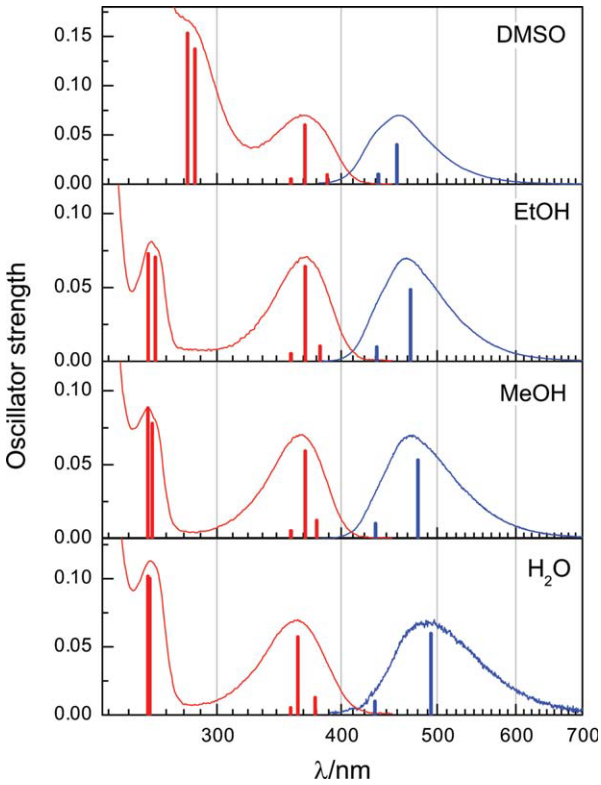


FIGURE 2. Experimental [6] and calculated absorption (red) and fluorescence emission (blue) spectra of Z-KN in various solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II

The experimental Stokes shifts $\Delta\nu$[6], energy differences between the calculated transitions (first $\Delta E_{S_0\to S_1} - \Delta E_{S_{1'}\to S_0}$ and second $\Delta E_{S_0\to S_2} - \Delta E_{S_{2'}\to S_0}$ transitions), and the energy gaps between the lowest excited states, ΔE_{pe}, for KN in various solvents

	$\Delta\nu$/cm (eV)	$(\Delta E_{S_0\to S_1} - \Delta E_{S_{1'}\to S_0})$/eV	$(\Delta E_{S_0\to S_2} - \Delta E_{S_{2'}\to S_0})$/eV	ΔE_{pe}/eV
Dimethylsulfoxide	5300 (0.66)	0.36	0.65	−0.12
Ethanol	5700 (0.71)	0.40	0.73	−0.22
Methanol	5900 (0.74)	0.42	0.77	−0.27
Water	7700 (0.96)	0.43	0.91	−0.35

fluorescence well from DMSO to water [6]. The $S_{2'} \to S_0$ ($\pi\pi^*$) transition exhibits the lowest transition energies for all solvents used, that, according to the Kasha's rule, point out the $\pi\pi^*$ state as the lowest excited state of KN.

The Stokes shifts (i.e., the gap between the maxima of the first absorption and fluorescence bands) [6] of the experimentally observed absorption and emission bands and the calculated first and second transitions are listed in Table II. A good agreement between experimental and calculated data can also be seen: the values of Stokes shifts increase from DMSO to water. It is also worth mentioning that the Stokes shifts of the second transition correlate well with the experimental ones [6]; this indicates a small contribution of $n\pi^*$ state in the main KN absorption band. The value of the energy gap between two lowest excited states $S_{2'}$ and $S_{1'}$ ($\Delta E_{pe} = \Delta E_{S_{2'}\to S_0} - \Delta E_{S_{1'}\to S_0}$) also increases from aprotic to protic solutions (Table II).

Our results show that the $\pi\pi^*$ state is the lowest excited state of KN and the energy gap between $n\pi^*$ and $\pi\pi^*$ states increases from DMSO to water. These results contradict the suggestions based on the "proximity effect" model [7]. In terms of this model, the increase of IC rate from aprotic to protic solution should lead to the inverted picture: the $n\pi^*$ state should be the lowest excited state and the energy gap $n\pi^*$–$\pi\pi^*$ should decrease from aprotic to protic medium. Thus, the "proximity effect" cannot be used to explain the significant decrease of S_1 state lifetime of KN in protic solvents. The experimental data show that the IC acceleration in protic solvents is presumably caused by intermolecular hydrogen bonding interactions between chromophoric (aminoacetophenone) moiety of the KN and solvent molecules. Indeed, more work is necessary to clarify the influence of these intermolecular interactions on KN photophysics.

4. Conclusions

The calculated and experimental absorption and emission spectra of KN exhibit very good agreement for all solvents studied. The energy gap between two lowest excited states increases on varying the nature of solvent (from aprotic to protic). This evidence declines the "proximity effect" to be responsible for the fast radiationless decay of KN excited state in protic solvents.

ACKNOWLEDGMENTS

The authors are grateful to the Georgia Institute of Technology for computational facilities and to Dr. Vitaly Kiselev (Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk) for fruitful discussion and critical remarks.

References

1. Dillon, J.; Wang, R. H.; Atherton, S. J. Photochem Photobiol 1990, 52, 849.
2. Tsentalovich, Yu. P.; Snytnikova, O. A.; Sherin, P. S.; Forbes, M. D. E. J Phys Chem A 2005, 109, 3565.
3. Sherin, P. S.; Tsentalovich, Yu. P.; Snytnikova, O. A.; Sagdeev, R. Z. J Photochem Photobiol B 2008, 93, 127.
4. Tsentalovich, Yu. P.; Snytnikova, O. A.; Forbes, M. D. E.; Chernyak, E. I.; Morozov, S. V. Exp Eye Res 2006, 83, 1439.
5. Krishna, C. M.; Uppuluri, S.; Riesz, P.; Zigler, J. S.; Balasubramanian, D. Photochem Photobiol 1991, 54, 51.
6. Sherin, P. S.; Grilj, J.; Tsentalovich, Yu. P.; Vauthey, E. J Phys Chem B 2009, 113, 4953.
7. (a) Lim, E. C. J Phys Chem 1986, 90, 6770; (b) Wassam, W. A.; Lim, E. C. J Chem Phys 1978, 68, 433; (c) Lai, T.-I.; Lim, B. T.; Lim, E. C. J Am Chem Soc 1982, 104, 7631; (d) Lai, T.-I.; Lim, E. C. J Am Chem Soc 1985, 107, 1134.
8. Eckert, F.; Klamt, A. AIChE J 2002, 48, 369.
9. Momicchioli, F.; Baraldi, I.; Bruni, M. C. Chem Phys 1983, 82, 229.

10. (a) Ohno, K. Theor Chim Acta 1964, 2, 219; (b) Klopman, G. J Am Chem Soc 1964, 86, 4550.
11. (a) Mataga, N.; Nishimoto, K. Z Phys Chem 1957, 12, 335; (b) Mataga, N.; Nishimoto, K. Z Phys Chem 1957, 13, 140.
12. (a) Miertus, S.; Kysel, O. Chem Phys 1977, 21, 27; (b) Costanciel, R.; Tapia, O. Theor Chim Acta 1978, 48, 383; (c) Miertus, S.; Kysel, O. Chem Phys Lett 1979, 65, 395; (d) Tomasi, J.; Persico, M. Chem Rev 1994, 94, 3027.
13. (a) Hegarty, D.; Robb, M. A. Mol Phys 1979, 38, 1795; (b) Eade, R. H. E.; Robb, M. A. Chem Phys Lett 1981, 83, 362; (c) Schlegel, H. B.; Robb, M. A. Chem Phys Lett 1982, 93, 214; (d) Bernardi, F.; Bottini, A.; McDougall, J. J. W.; Robb, M. A.; Schlegel, H. B. Far Symp Chem Soc 1984, 19, 137; (e) Frisch, M. J.; Ragazos, I. N.; Robb, M. A.; Schlegel, H. B. Chem Phys Lett 1992, 189, 524; (f) Yamamoto, N.; Vreven, T.; Robb, M. A.; Frisch, M. J.; Schlegel, H. B. Chem Phys Lett 1996, 250, 373.
14. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J.A. Gaussian 03; Gaussian Inc.: Pittsburgh, PA, 2003.
15. Kasha, M. Light and Life; Johns Hopkins Press: Baltimore, MD, 1961.