Photoinduced excited state proton rearrangement of 6-hydroxyquinoline along a hydrogen-bonded acetic acid wire

ARTICLE *in* CHEMICAL PHYSICS LETTERS · MARCH 2007

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2007.01.060

1 AUTHOR:

Mohan Singh Mehata
Delhi Technological University
40 PUBLICATIONS **319** CITATIONS

SEE PROFILE

Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 436 (2007) 357–361
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Photoinduced excited state proton rearrangement of 6-hydroxyquinoline along a hydrogen-bonded acetic acid wire

Mohan Singh Mehata *

Photophysics Laboratory, Department of Physics, DSB Campus, Kumaon University, Nainital 263 002, India

Received 11 October 2006; in final form 22 January 2007
Available online 26 January 2007

Abstract

6-Hydroxyquinoline (6-HQ) in benzene emits normal fluorescence around 357 nm. In the presence of acetic acid (HOAc), it exhibits two more bands at ~419 nm and a large Stokes shifted one at ~583 nm with decreased intensity of the normal fluorescence. It appears to form (1:1) and (1:2) complexes-(1:2) 6-HQ/HOAc undergoes an excited state proton rearrangement (*via HOAc wire*) resulting in keto tautomer (emitting at ~583 nm). This appears to be in line with recent findings where ammonia wires facilitate proton/hydrogen translocation (Science, 302, 1736, 2003). However, (1:1) 6-HQ/HOAc exhibits intermediate emission (~419 nm) presumably due to ESIPT.

1. Introduction

Proton transfer process is an elementary reaction of fundamental importance in chemistry and biology. The importance of studying the effect of various environments in the proton transfer phenomena is naturally an important aspect for a better understanding of the problem. The proton transfer dynamics is determined by the size, structure and the motion of the solvent cluster involved as well as the nature of the protropic groups [1–7].

The elementary processes, i.e., fluorescence quenching, charge transfer, dissociation and recombination of proton, proton hopping and molecular motion (in presence of electric field) are important and challenging in the study of hydroxy- and methoxy-quinolines [7–29]. In this class of molecules, bifunctional 6-hydroxyquinoline (6-HQ) is characterized by a weak acidic hydroxyl functional group and a weak basic imine functional group in the ground state [8,9]. In the electronic excited state, the acidity of hydroxyl and basicity of imine groups are considerable enhanced. It is known that 6-HQ is present as cationic (C), anionic (A) and neutral (N) forms in acidic, alkaline and neutral aqueous solutions due to release of proton to solvent or capture of proton from the solvent molecules (see Scheme 1).

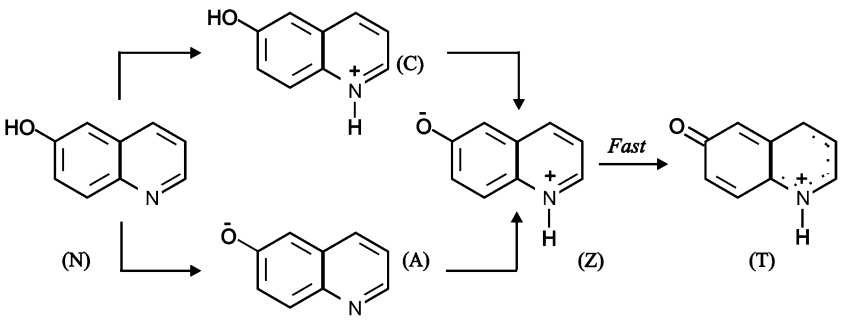
These forms of 6-HQ are differentiated by the position of their lowest energy absorption bands at around 344, 358 and 326 nm, respectively [8–11]. At pH 7, a small amount of tautomeric form of 6-HQ has also been found to coexist with the normal form manifested in the appearance of the 408 nm absorption band [8,9]. These forms were identified as neutral emitting around 380 nm, cationic at ~450 nm, anionic at ~490 nm and tautomer (T) at ~585 nm [8–11].

The effects of solvent viscosity, polarity and dielectric constant on 6-HQ have also been discussed [11]. In alcoholic solvents, the lowest energy absorption maximum of 6-HQ shifts towards red (4 nm) on going from methanol to octanol, whereas the emission maxima remain almost unchanged (~376 nm). Moreover, the solvent viscosity decreases the non-radiative decay rate of the normal fluorescence emission. In ethyl acetate/acetonitrile the emission maximum is blue shifted ($\lambda_{em} \sim 363$ nm) while the absorption does not show any considerable change.

Further, a binary mixture of methanol and water provides a hydrogen-bonded network for –OH and $\geqslant$N functional groups of 6-HQ and this hydrogen bonded complex produces keto tautomer owing to proton rearrangement

* Fax: +91 5942 235576.
E-mail address: msmehata@yahoo.com

0009-2614/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2007.01.060



Scheme 1. Protonation, deprotonation and tautomerization of 6-HQ.

[11]. In the presence of proton accepting guest molecule trimethylamine (TMA), (1:1) 6-HQ:TMA single hydrogen bonded complex is formed in the ground state. This complex undergoes an efficient charge transfer and subsequent proton transfer following photoexcitation resulting contact and solvent separated ion-pairs depending on the solvent environment [11]. In addition to the enol to keto tautomerization, two different forms of 6-HQ depending on the orientation of O–H group, namely cis and trans rotamers have also been suggested with cis as the more stable form [12].

In order to explain keto tautomer emission in a binary mixture of methanol and water, it was suggested that a water cluster is necessary for the enol deprotonation to form a hydrated proton cluster and anion species. Further, a hydrogen bond network is also necessary for the dissociated proton to migrate from a water molecule to another and finally to the nitrogen atom of the imine [10]. In neutral aqueous solution, it was suggested that a release and capture of proton at two functional groups of 6-HQ takes place simultaneously following photoexcitation [9]. Finally, it was assumed that the forward proton transfer process is coupled to intramolecular electron redistribution, yielding a neutral quinonoid configuration, which lowers the probability of the back proton transfer in the excited state (see Scheme 1). In our earlier work [11], we had proposed a scheme for proton transfer in a binary mixture of methanol and water, in which one water molecule and two methanol molecules are necessary to form hydrogen bonded network and hence the keto tautomer results from proton rearrangement. On the other hand, in glycerol, 6-HQ is suggested to be present as keto species in the ground state through a H-bond bridge [14]. It was also suggested that one glycerol molecule (a molecule bigger than methanol, ethylene glycol, etc.) is sufficient to form a H-bond bridge between the two functional groups of 6-HQ [14].

On the other hand, the suitable geometry/relative distance of heterogroups of 7-hydroxyquinoline (7-HQ) allows formation of hydrogen bridged complexes with polyvinyl alcohol, poly(2-hydroxyethyl methacrylate), HOAc as well as with alcohol molecules resulting in an excited state intermolecular proton transfers reaction (ESIPT) [14–21]. In alcoholic solvents, molecular chain is suggested to form such a bridged network with vibrationally assisted triple proton transfer taking place [20]. In a recent report on 7-HQ in reverse micelles [19], it is suggested that in alcoholic solvents a hydrogen bridge is needed for tautomerization of the cis conformer whereas in water protonation/deprotonation is the responsible mechanism. Another molecule 3-hydroxyisoquinoline (3-HIQ) also forms ground state H-bonded complex with HOAc [22]. However, in both the fluorophores single acetic acid molecule is involved in the hydrogen-bonding network resulting in double proton transfer [21,22].

Role of hydrogen-bonded ammonia wires in promoting tautomerization in 7-HQ has been studied by Leutwyler and co-wokers [28–32]. Further, it has been found that addition of water suppresses it [31,32].

In the present study, acetic acid (HOAc) is used as a hydrogen-bonding partner that can form H-bonded complexes with both heterogroups of 6-HQ. It is observed that it exhibits an exceptionally large Stokes shifted and intermediate emission bands besides the normal emission. To explain this large Stokes shifted emission, proton rearrangement in the proposed network scheme has been suggested.

2. Experimental

6-HQ (Aldrich) was recrystallized from ethanol. The purity of 6-HQ was checked from its fluorescence/excitation spectra in different solvents. Acetic acid (HOAc), sulphuric acid (Merck Inc.) and potassium hydroxide (Aldrich) were used as received. All the solvents were used of spectroscopic grade. Double distilled water was used. The concentration of 6-HQ sample used was 10^{-4} M.

Absorption measurements were performed with a Jasco V-550 spectrophotometer and Hitachi U-3500 spectrophotometer. Fluorescence emission and excitation spectra were recorded with a Jasco FP-777 spectrofluorometer and data analyzed by available software.

3. Results and discussion

The absorption and emission spectra of 6-HQ in nonpolar solvent benzene at room temperature are shown in Figs. 1 and 2. In neat benzene, the absorption is structured and shows a maximum centered at around 331 nm (Fig. 1a). The spectrum is virtually same as that of the

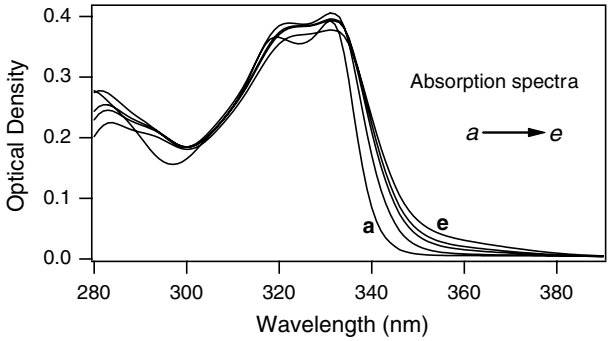


Fig. 1. Absorption spectra of 6-HQ in benzene for various HOAc concentrations (M): 0.0 (a), 0.19 (b), 0.57 (c), 0.86 (d) and 1.24 (e).

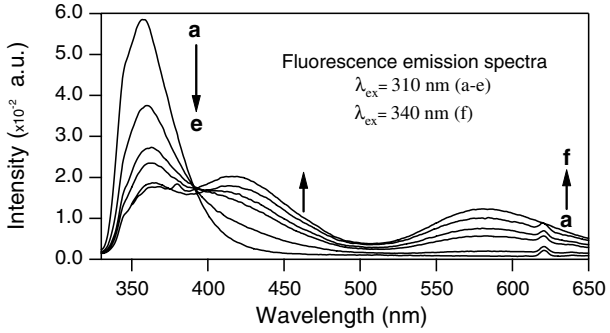


Fig. 2. Fluorescence emission spectra of 6-HQ in benzene for various HOAc concentrations (M): 0.0 (a), 0.19 (b), 0.57 (c), 0.86 (d) and 1.24 (e,f).

dye in other non-polar solvents. The molar absorption coefficient, ε_{max}, at 330 nm is about $\sim$4000 M^{-1} cm^{-1}. In the presence of HOAc, besides the main absorption band, the absorption spectrum shows a shoulder with a long tail extending up to 380 nm. In addition, the absorption spectrum gets broadened (Fig. 1b–e). With increase in HOAc concentration, the spectra show more broadening with the predominant shoulder at around 350 nm.

In neat benzene, 6-HQ shows a single fluorescence emission band with the band maximum at around 357 nm ($\lambda_{ex} = 310$ nm), which is attributed to the normal fluorescence (Fig. 2a). With the addition of HOAc besides the normal emission two new humps in the fluorescence emission spectrum in 390–460 nm and 550–650 nm regions appear. The intensity of these bands gradually increases with increasing the HOAc concentrations and exhibit well resolved bands with Stokes shifts $\sim$6400 and $\sim$13,200 cm^{-1} (emission maxima around 419 and 583 nm, respectively, see Fig. 2). Simultaneously the intensity of normal emission band (357 nm) decreases with increasing the HOAc concentration and finally disappears. The intensity of the 419 nm is relatively higher than that of the 583 nm emission band. Further, with the red edge excitation of the absorption band ($\lambda_{ex} = 340$ nm) both these emission bands become more predominant (Fig. 2f). Note that the positions of 357, 419 and 583 nm emission bands remain same irrespective of HOAc concentrations as well as excitation wavelengths. In addition, a hump around 620 nm in the emission spectra also appears (Fig. 2), which is nothing but the second order of the excitation wavelength ($\lambda_{ex} = 310$ nm). The presence of isoemissive point in the emission spectra at around 390 nm indicates the existence of more than one emitting species.

Fig. 3 shows the fluorescence excitation spectra of 6-HQ in neat benzene as well as in presence of acetic acid. The excitation spectra for the normal emission band (370 nm) in both cases of presence and absence of acetic acid are almost identical to the absorption spectrum (cf. Figs. 1a and 3a,b). However, the excitation spectra for 450 and 580 nm emissions show a red shift with a shoulder and long tail extending up to 380 nm with respect to the 370 nm emission (Fig. 3c,d).

In addition, the absorption and emission spectra in highly aqueous acidic (pH $\sim$ 1) and basic (pH $\sim$ 14) solutions of 6-HQ were also measured (not shown). The emission shows single maximum at around 442 and 484 nm in aqueous acidic and basic solutions, respectively. The spectra are quite similar to that reported earlier [9,23]. With decreasing strengths of acidic and basic solutions, the fluorescence spectra deviate from the single maximum and show dual emissions that should be a signature of deprotonation of cationic and protonation of anionic species [9,10] following photoexcitation (see Scheme 1).

Further, the absorption/emission results were analyzed using Benesi–Hildebrand derivation [33]. The relationship between the initially prepared acetic acid concentration (C_g) and the measured absorption at 350 nm (A_{350}) and fluorescence emission intensity (F_λ) can be expressed as [21,33]

$$\frac{1}{C_g^n} = C_0\varepsilon_{350}K_a\frac{1}{A_{350}} - K_a = \alpha C_0\varepsilon_{350}K_a\frac{1}{F_\lambda} - K_a \qquad (1)$$

where α is the instrumental factor, ε is the molar extinction coefficient, C_0 is the initial concentration of 6-HQ and K_a is the equilibrium constant. The plots of $1/C_g^n$ against $1/A_{350}$ for $n = 1$ and 2 are depicted in Fig. 4. The curve shows clear deviation from linearity at higher concentrations for $n = 1$ whereas for $n = 2$, linear behaviour deviates at low concentrations. The corresponding correlation coefficients are 0.991 and 0.977, respectively. Similarly, the plots $1/C_g^n$ against $1/F_{419}$ and $1/F_{585}$ were examined for $n = 1$

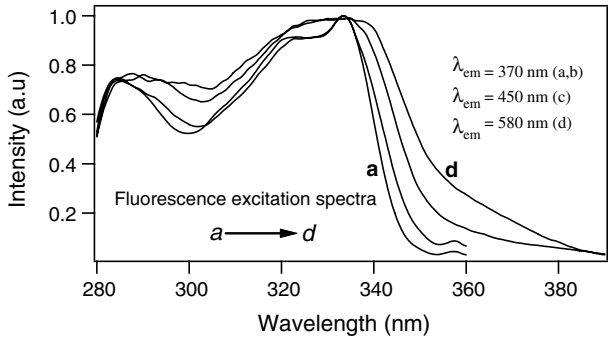


Fig. 3. Normalized fluorescence excitation spectra of 6-HQ in pure benzene (a) and in the presence of 1.24 M HOAc (b–d) for different emission wavelengths.

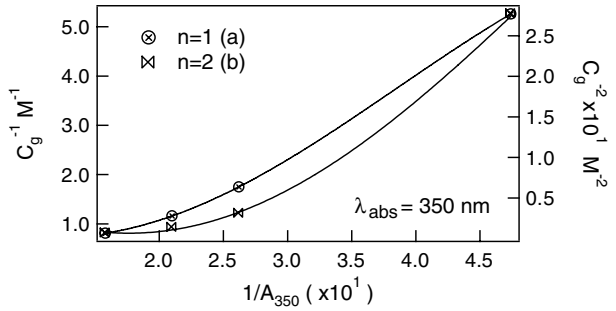


Fig. 4. Plots of reciprocals of molar HOAc concentrations ($1/C_g^n$) versus reciprocal absorbance ($1/A$) at 350 nm for $n = 1$ (a) and $n = 2$ (b).

and 2 (Fig. 5a,b). It is linear for $n = 1$ indicating that the (1:1) complex is dominant. The intercept of the $n = 1$ plot gives a K_a value of 2.0 M^{-1} from absorption and ~4.0 M^{-1} from 419 nm fluorescence band. The small value of K_a indicates that the (1:1) complex is not much strong.

The remarkable changes in absorption as well as in fluorescence excitation spectra of 6-HQ in the presence of HOAc in non-polar solvent benzene clearly indicate the formation of ground state 6-HQ:HOAc complexes. As far as the distance between two functional groups of 6-HQ is considered [12], the length of single molecule of HOAc (even though it possesses both proton accepting as well as proton donating groups) might not be enough to form a H-bonded bridge between the heterogroups of 6-HQ. One molecule of HOAc can form single hydrogen bonded complex either at the –OH group or at the ⩾N group of 6-HQ. Therefore, the formation of excited state photoproduct of 6-HQ involving one molecule of HOAc cannot be expected to explain the presence of 583 nm emission. It

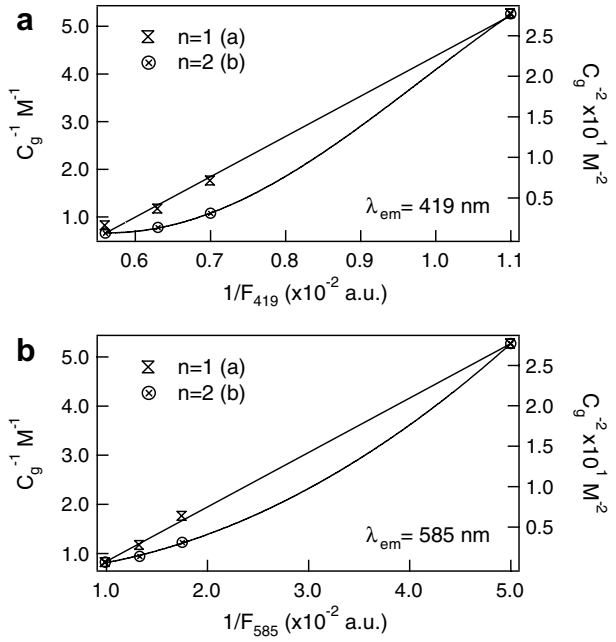


Fig. 5. Plots of reciprocals of molar HOAc concentration ($1/C_g^n$) versus reciprocal fluorescence intensity ($1/F$) at 419 nm (a) and 585 nm (b) for $n = 1$ (a) and $n = 2$ (b).

is worthwhile to mention that unlike the case of 6-HQ, in 3-HIQ a single molecule of HOAc can form conjugated double hydrogen-bonded complex, and undergo an excited state double proton transfer reaction [22]. This possibility is also realized in 7-HQ [14–21] where the distance between two functional groups is relatively less compared to the 6-HQ. In Ref. [21] it was tentatively suggested that the (1:1) 7-HQ(–N–):HOAc(–OH) complex possessing only a single hydrogen bond (unbridged) undergoes an excited state double proton transfer.

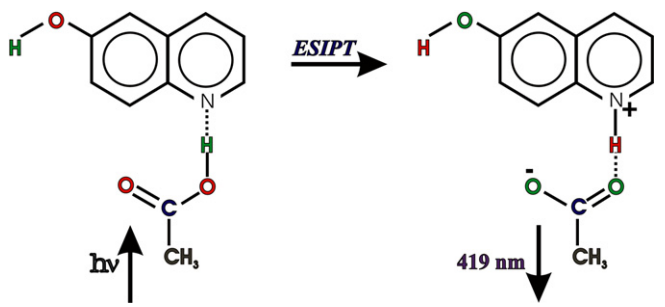
In view of above discussions, it appears that 6-HQ can form two different kinds of hydrogen-bonded complexes with HOAc in the ground state. These complexes are in the (1:1) and (1:2) ratios of 6-HQ and HOAc, respectively. The (1:1) complex can be formed with the ⩾N group of 6-HQ and –OH group of HOAc through a single hydrogen bond (see Scheme 2).

In (1:2) complex, two HOAc molecules may get involved to form a bridged hydrogen bonded network between the –OH and ⩾N functional groups of *cis* 6-HQ (see Scheme 3).

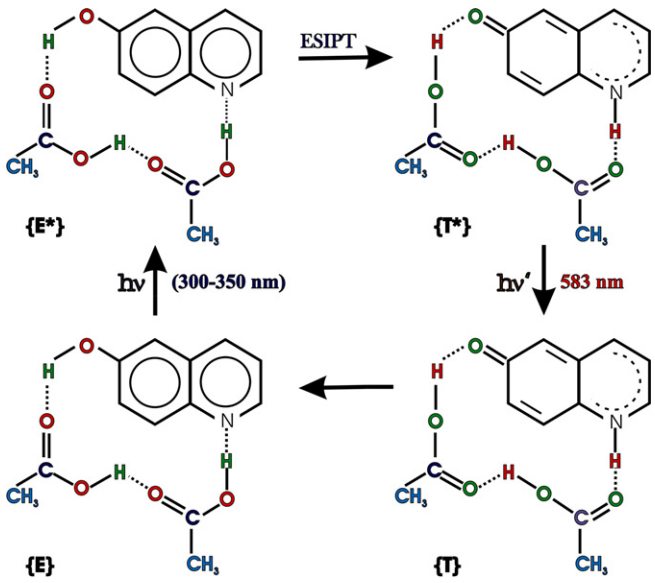
On excitation, the well-bridged hydrogen bonded (1:2) 6-HQ:HOAc complex (E^*) can undergo an excited state multiple proton transfer reaction (proton rearrangement) resulting in keto tautomer (T^*), which emits with a large Stokes shifted fluorescence around 583 nm. The proton transfer reaction takes place from the –OH group to ⩾N functional group of 6-HQ along HOAc wire. The driving force for this process can be found in the simultaneous increase of acidity of –OH and basicity of ⩾N functional groups of 6-HQ because of charge redistribution following photoexcitation.

Besides normal and keto tautomer emissions, the intermediate 419 nm emission band of 6-HQ appears to originate from the (1:1) complex. As discussed [11], 6-HQ forms hydrogen bonded complexes with TMA in the ground state and ion-pairs in the excited state following charge/proton transfer reactions, which emit between 410–440 nm in non-polar (toluene) and polar (acetonitrile) solvents [11]. Moreover, the possibility of emission from cationic or anionic species of 6-HQ can be ruled out as they show considerably red shifted emission. In view of this, the 419 nm emission can ascribe to be originating from the excited state reaction of (1:1) 6-HQ:HOAc complex (see Scheme 2).

Thus, it appears that based on intermolecular H-bonding interactions formation of complex as well as proton



Scheme 2. Excited state reactions of (1:1) 6-HQ:HOAc complex.



Scheme 3. Proton rearrangement in (1:2) 6-HQ:HOAc complex.

rearrangement may be the most likely mechanism for large Stokes shifted tautomeric emission. This is in accordance with the findings of Leutwyler and co-workers [28–32] where hydrogen bridged ammonia wires have been found to facilitate tautomer emission in 7-HQ. Moreover, we would like to point out that we could not clearly decipher the presence of cis/trans isomers in the present work although the (1:2) complex formation is likely to involve the *cis* isomer. In the electroabsorption (Electric field modulation spectroscopy) studies also clear evidence for the presence of more than one form of 6-HQ doped in polymer environment could not be traced [13].

4. Conclusions

The studies of 6-HQ in this preliminary report can be summarized in the following lines. In neat benzene, 6-HQ shows normal fluorescence emission at 357 nm. In the presence of HOAc, in addition to the normal fluorescence, 6-HQ shows two new emission bands at ~419 and ~583 nm. These new bands arise presumably due to the formation of (1:1) and (1:2) 6-HQ:HOAc hydrogen bonded complexes in the ground state. The (1:2) complex may undergo an excited state proton transfer resulting in keto tautomer with a large Stokes shifted emission (~13,200 cm^{-1}) which appears to be in conformity with the concept of promotion of proton/hydrogen transfer in hydrogen-bonded molecular wires [28–32]. However, the intermediate emission (~419 nm) may originate from the ESIPT in the (1:1) complex.

Acknowledgements

Author is indebted to Dr. H.C. Joshi for helpful discussion and critical reading of this manuscript. This work was supported by the Department of Science and Technology, New Delhi under Fast-Track Scheme (Grant No. SR/FTP/PS-35/2004; *Young Scientist fellowship*).

References

[1] N. Agmon, J. Phys. Chem. A 109 (2005) 13.
[2] K.M. Solntsev, D. Huppert, N. Agmon, L.M. Tolbert, J. Phys. Chem. A 104 (2000) 4658.
[3] O. Mohammed, D. Pines, J. Dreyer, E. Pines, E.T.J. Nibbering, Science 310 (2005) 83.
[4] K.M. Solntsev, C.E. Clower, L.M. Tolbert, D. Huppert, J. Am. Chem. Soc. 127 (2005) 8534.
[5] H.C. Joshi, C. Gooijer, G. van der Zwan, J. Phys. Chem. A 106 (2002) 11422.
[6] K.B. Moller, R. Rey, J.T. Haynes, J. Phys. Chem. A 108 (2004) 219.
[7] K.M. Solntsev, E.N. Suillivan, L.M. Tolbert, S. Ashkenazi, P. Leiderman, D. Huppert, J. Am. Chem. Soc. 126 (2004) 12701.
[8] S.F. Mason, J. Philip, B.E. Smith, J. Chem. Soc. A (1968) 3051.
[9] E. Bardez, A. Chatelain, B. Larrey, B. Valeur, J. Phys. Chem. 98 (1994) 2357.
[10] T.G. Kim, Y. Kim, D.-J. Jang, J. Phys. Chem. A 105 (2001) 4328.
[11] M.S. Mehata, H.C. Joshi, H.B. Tripathi, Chem. Phys. Lett. 359 (2002) 314;
M.S. Mehata, H.C. Joshi, H.B. Tripathi, Chem. Phys. Lett. 366 (2002) 628.
[12] A. Bach, J. Hewel, S. Leutwyler, J. Phys. Chem. A 102 (1998) 10476.
[13] M.S. Mehata, T. Iimori, T. Yoshizawa, N. Ohta, J. Phys. Chem. A 110 (2006) 10985.
[14] I.G. Ochoa, P.B. Bisht, F. Sanchez, E. M-Ataz, L. Santos, H.B. Tripathi, A. Douhal, J. Phys. Chem. A 102 (1998) 8871.
[15] A. Douhal, J. Dabrio, R. Sastre, J. Phys. Chem. 100 (1996) 149.
[16] O.-H. Kwon, H. Doo, Y.S. Lee, D.-J. Jang, ChemPhysChem 4 (2003) 1079.
[17] M.S. Mehata, H.C. Joshi, H.B. Tripathi, Spectrochim. Acta A 58 (2002) 1589;
M.S. Mehata, H.C. Joshi, H.B. Tripathi, Spectrochim. Acta A 59 (2003) 559.
[18] S. Kohtani, A. Tagami, R. Nakagaki, Chem. Phys. Lett. 316 (2000) 88.
[19] O.-H. Kwon, T.G. Kim, Y.-S. Lee, D.-J. Jang, J. Phys. Chem. B 110 (2006) 11997.
[20] O.-H. Kwon, Y.-S. Lee, B.K. Yoo, D.-J. Jang, Angew. Chem. Int. Ed. 45 (2006) 415.
[21] P.T. Chou, C.Y. Wei, C.R.C. Wang, F.T. Hung, C.P. Chang, J. Phys. Chem. A 103 (1999) 1939.
[22] C.Y. Wei, W.S. Yu, P.T. Chou, F.T. Hung, T.C. Lin, C.P. Chang, J. Phys. Chem. B 102 (1998) 1053.
[23] M.S. Mehata, Ultrafast Fluorescence Spectroscopy of Some Molecular Systems, Ph.D. Thesis, Kumaon University, Nainital, India, 2002.
[24] O. Poizat, E. Bardez, G. Buntinx, V. Alain, J. Phys. Chem. A 108 (2004) 1873.
[25] E. Bardez, A. Fedorov, M.N. Berberan-Santos, J.M.G. Martinho, J. Phys. Chem. A 103 (1999) 4131.
[26] M.S. Mehata et al., J. Lumin. 93 (2001) 275;
M.S. Mehata et al., J. Lumin. 99 (2002) 47.
[27] H. Yu, O.-H. Kwon, D.-J. Jang, J. Phys. Chem. A 108 (2004) 5932.
[28] C. Tanner, C. Manca, S. Leutwyler, Science 302 (2003) 1736.
[29] C. Tanner, C. Manca, S. Leutwyler, Chimia 58 (2004) 234.
[30] C. Manca, C. Tanner, S. Leutwyler, Chimia 58 (2004) 287.
[31] C. Tanner, M. Thut, A. Steinlin, C. Manca, S. Leutwyler, J. Phys. Chem. A 110 (2006) 1758.
[32] C. Manca, C. Tanner, S. Leutwyler, Int. Rev. Phys. Chem. 24 (2005) 457.
[33] M.L. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.