AIP Publishing The Journal of Chemical Physics

No Access
Submitted: 18 April 2012
Accepted: 08 July 2012
Published Online: 02 August 2012

Theoretical study of the absorption and nonradiative deactivation of 1-nitronaphthalene in the low-lying singlet and triplet excited states including methanol and ethanol solvent effects

J. Chem. Phys. **137**, 054307 (2012); https://doi.org/10.1063/1.4738757

Yoelvis Orozco-Gonzalez[1,2, a)], Kaline Coutinho[1], Jorge Peon[3], *and* Sylvio Canuto[1, a)]

View Affiliations

ABSTRACT

The photophysics of the 1-nitronaphthalene molecular system, after the absorption transition to the first singlet excited state, is theoretically studied for investigating the ultrafast multiplicity change to the triplet manifold. The consecutive transient absorption spectra experimentally observed in this molecular system are also studied. To identify the electronic states involved in the nonradiative decay, the minimum energy path of the first singlet excited state is obtained using the complete active space self-consistent field//configurational second-order perturbation approach. A near degeneracy region was found between the first singlet and the second triplet excited states with large spin-orbit coupling between them. The intersystem crossing rate was also evaluated. To support the proposed deactivation model the transient absorption spectra observed in the experiments were also considered. For this, computer simulations using sequential quantum mechanic-molecular mechanic methodology was used to consider the solvent effect in the ground and excited states for proper comparison with the experimental results. The absorption transitions from the second triplet excited state in the relaxed geometry permit to describe the transient absorption band experimentally observed around 200 fs after the absorption transition. This indicates that the T_2 electronic state is populated through the intersystem crossing presented here. The two transient absorption bands experimentally observed between 2 and 45

$T_1 \rightarrow T_5$ transitions, supporting that the intermediate triplet state (T_2) decays by internal conversion to T_1.

ACKNOWLEDGMENTS

This work has been partially supported by nBioNet, Instituto Nacional de Ciência e Tecnologia de Fluidos Complexos (INCT-FCx), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfieçoamento de Pessoal de Nivel Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP). We thank the computer center of the University of São Paulo for the use of the MOLCAS program.

REFERENCES

1. B. Rusakowicz and A. C. Testa, Spectrochim. Acta, Part A **27**, 787 (1971). https://doi.org/10.1016/0584-8539(71)80157-5 , Google Scholar, Crossref

2. R. W. Anderson, R. M. Hochstrasser, H. Lutz, and G. W. Scott, Chem. Phys. Lett. **28**, 153 (1974). https://doi.org/10.1016/0009-2614(74)80040-0 , Google Scholar, Crossref

3. K. Hamanoue, S. Hirayama, T. Nakayama, and H. Teranishi, J. Phys. Chem. **84**, 3074 (1980). https://doi.org/10.1021/j100459a015

Google Scholar, Crossref

4. C. Capellos and G. Porter, J. Chem. Soc., Faraday Trans. 2 **70**, 1159 (1974). https://doi.org/10.1039/f29747001159 , Google Scholar, Crossref

5. R. Hurley and A. C. Testa, J. Am. Chem. Soc. **90**, 1949 (1968). https://doi.org/10.1021/ja01010a004 , Google Scholar, Crossref

6. R. Morales-Cueto, M. Esquivelzeta-Rabell, J. S. Zugazagoitia, and J. Peon, J. Phys. Chem. A **111**, 552 (2007). https://doi.org/10.1021/jp065364d , Google Scholar, Crossref

7. Y. He, A. Gahlmann, J. S. Feenstra, S. T. Park, and A. H. Zewail, Chem. Asian. J. **1**, 56 (2006). https://doi.org/10.1002/asia.200600107 , Google Scholar, Crossref

8. K. Hamanoue, T. Nakayama, K. Kajiwara, S. Yamanaka, and K. Ushida, J Chem. Soc., Faraday Trans. **88**, 3145 (1992). https://doi.org/10.1039/ft9928803145 , Google Scholar, Crossref

9. K. Fukuhara, M. Kurihara, and N. Miyata, J. Am. Chem. Soc. **123**, 8662 (2001). https://doi.org/10.1021/ja0109038 , Google Scholar, Crossref

10. J. S. Zugazagoitia, C. X. Almora-Días, and J. Peon, J. Phys. Chem. A **112**, 358 (2008). https://doi.org/10.1021/jp074809a , Google Scholar Crossref ISI

11. J. J. Mikula, R. W. Anderson, L. E. Harris, and E. W. Stuebing, J. Mol. Spectrosc. **42**, 350 (1972). https://doi.org/10.1016/0022-2852(72)90091-4 , Google Scholar, Crossref

12. T. Fournier, S. M. Tavender, A. W. Parker, G. D. Scholes, and D. Phillips, J. Phys. Chem. A **101**, 5320 (1997). https://doi.org/10.1021/jp970470o , Google Scholar, Crossref

13. M. A. El-Sayed, J. Chem. Phys. **38**, 2834 (1963). https://doi.org/10.1063/1.1733610 , Google Scholar, Scitation, ISI

14. J. S. Zugazagoitia, E. Collado-Fregoso, E. F. Plaza-Medina, and J. Peon, J. Phys. Chem. Phys. A **113**, 805 (2009). https://doi.org/10.1021/jp8087397 , Google Scholar, Crossref

15. C. Reichardt, R. A. Vogt, and E. Crespo-Hernandez, J. Chem. Phys. **131**, 224518 (2009). https://doi.org/10.1063/1.3272536 , Google Scholar, Scitation, ISI

16. D. Beljonne, Z. Shuai, G. Pourtois, and J. L. Bredas, J. Phys. Chem. A **105**, 3899 (2001). https://doi.org/10.1021/jp010187w , Google Scholar, Crossref

17. S. P. McGlynn, T. Azuim, and M. Kinoshita, Molecular Spectroscopy of the Triplet State (Prentice-Hall, New York, 1969). Google Scholar

https://doi.org/10.1021/ja00469a003 , Google Scholar, Crossref

19. S. Shaik and N. D. Epiotis, J. Am. Chem. Soc. **102**, 122 (1980). https://doi.org/10.1021/ja00521a022 , Google Scholar, Crossref

20. M. D. Su, J. Phys. Chem. **100**, 4339 (1996). https://doi.org/10.1021/jp950290j , Google Scholar, Crossref

21. W. R. Rocha, K. Coutinho, W. B. Almeida, and S. Canuto, Chem. Phys. Lett. **335**, 127 (2001). https://doi.org/10.1016/S0009-2614(01)00024-0 , Google Scholar, Crossref

22. K. Andersson, P. Å. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992). https://doi.org/10.1063/1.462209 , Google Scholar, Scitation, ISI

23. P. O. Widmark, P. Å. Malmqvist, and B. O. Roos, Theor. Chim. Acta **77**, 291 (1990). https://doi.org/10.1007/BF01120130 , Google Scholar, Crossref

24. P. O. Widmark, B. J. Persson, and B. O. Roos, Theor. Chim. Acta **79**, 419 (1991). https://doi.org/10.1007/BF01112569 , Google Scholar, Crossref

25. M. Merchán, L. Serrano-Andrés, M. P. Fülscher, and B. O. Roos, Recent Advances in Multireference Methods, edited by K. Hirao

26. B. A. Hess, C. M. Marian, U. Wahlgren, and O. Gropen, Chem. Phys. Lett. **251**, 365 (1996). https://doi.org/10.1016/0009-2614(96)00119-4 , Google Scholar, Crossref, ISI

27. P. Å. Malmqvist and B. O. Roos, Chem. Phys. Lett. **155**, 189 (1989). https://doi.org/10.1016/0009-2614(89)85347-3 , Google Scholar, Crossref, ISI

28. J. Tatchen and C. M. Marian, Chem. Phys. Lett. **313**, 351 (1999). https://doi.org/10.1016/S0009-2614(99)00997-5 , Google Scholar, Crossref

29. D. Danovich, C. M. Marian, T. Neuheuser, S. D. Peyerimhoff, and S. Shaik, J. Phys. Chem. A **102**, 5923 (1998). https://doi.org/10.1021/jp980391s , Google Scholar, Crossref

30. M. Merchán, L. Serrano-Andrés, M. A. Robb, and L. Blancafort, J. Am. Chem. Soc. **127**, 1820 (2005). https://doi.org/10.1021/ja044371h , Google Scholar, Crossref, ISI

31. G. Karlström, R. Lindh, P. Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P. O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, and L. Seijo, MOLCAS, version 7.6, a program package for computational chemistry, University of Lund, 2011; Google Scholar
G. Karlström, R. Lindh, P. Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P. O. Widmark, M. Cossi, B. Schimmelpfennig, P.

https://doi.org/10.1016/S0927-0256(03)00109-5 , Google Scholar, Crossref, ISI

32. R. A. Marcus, Rev. Mod. Phys. **65**, 599 (1993). https://doi.org/10.1103/RevModPhys.65.599 , Google Scholar, Crossref, ISI

33. K. V. Mikkelsen and M. A. Ratner, Chem. Rev. **87**, 113 (1987). https://doi.org/10.1021/cr00077a007 , Google Scholar, Crossref

34. V. Balzani, A. Juris, M. Venturi, S. Campagna, and S. Serroni, Chem. Rev. **96**, 759 (1996). https://doi.org/10.1021/cr941154y , Google Scholar, Crossref

35. M. Head-Gordon, R. J. Rico, M. Oumi, and T. J. Lee, Chem. Phys. Lett. **219**, 21 (1994). https://doi.org/10.1016/0009-2614(94)00070-0 , Google Scholar, Crossref, ISI

36. D. E. Woon and T. H. Dunning Jr., J. Chem. Phys. **98**, 1358 (1993). https://doi.org/10.1063/1.464303 , Google Scholar, Scitation, ISI

37. Y. Orozco-Gonzalez, K. Coutinho, and S. Canuto, Chem. Phys. Lett. **499**, 108 (2010). https://doi.org/10.1016/j.cplett.2010.09.033 , Google Scholar, Crossref

38. R. C. Barreto, K. Coutinho, H. C. Georg, and S. Canuto, Phys. Chem. Chem. Phys. **11** 1388 (2009). https://doi.org/10.1039/b816912h ,

39. M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004. Google Scholar

40. H. C. Georg, K. Coutinho, and S. Canuto, Chem. Phys. Lett. **429**, 119 (2006). https://doi.org/10.1016/j.cplett.2006.08.047 , Google Scholar, Crossref

41. T. L. Fonseca, H. C. Georg, K. Coutinho, and S. Canuto, J. Phys. Chem. A **113**, 5112 (2009). https://doi.org/10.1021/jp809694w , Google Scholar, Crossref

42. M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids (Clarendon, Oxford, 1987). Google Scholar

43. K. Coutinho and S. Canuto, DICE, a Monte Carlo program for molecular liquid simulation, University of São Paulo, 2007. Google Scholar

44. W. L. Jorgensen and D. L. Severance, J. Am. Chem. Soc. **112**, 4768 (1990). https://doi.org/10.1021/ja00168a022 , Google Scholar, Crossref, ISI

45. M. L. P. Price, D. Ostrovsky, and W. L. Jorgensen, J. Comput. Chem. **22**, 1340 (2001). https://doi.org/10.1002/jcc.1092 , Google Scholar, Crossref

https://doi.org/10.1021/j100398a015 , Google Scholar, Crossref, ISI

47. M. G. Martin and J. I. Siepmann J. Phys. Chem. B **102**, 2569 (1998). https://doi.org/10.1021/jp972543+ , Google Scholar, Crossref, ISI

48. J. Kongsted, A. Osted, K. V. Mikkelsen, and O. Christiansen, Mol. Phys. **100**, 1813 (2002). https://doi.org/10.1080/00268970110117106 , Google Scholar, Crossref, ISI

49. M. E. Martin, M. L. Sánchez, F. J. Olivares del Valle, and M. A. Aguilar, J. Chem. Phys. **113**, 6308 (2000). https://doi.org/10.1063/1.1308283 , Google Scholar, Scitation

50. E. Cancés, B. Mennucci, and J. Tomasi, J. Chem. Phys. **107**, 3032 (1997). https://doi.org/10.1063/1.474659 , Google Scholar, Scitation , ISI

51. C. M. Breneman and K. B. Wiberg, J. Comput. Chem. **11**, 361 (1990). https://doi.org/10.1002/jcc.540110311 , Google Scholar, Crossref, ISI

52. K. Coutinho, S. Canuto, and M. C. Zerner, J. Chem. Phys. **112**, 9874 (2000). https://doi.org/10.1063/1.481624 , Google Scholar, Scitation

53. K. Coutinho, H. C. Georg, T. L. Fonseca, V. Ludwig, and S. Canuto,

https://doi.org/10.1016/j.cplett.2007.02.012 , Google Scholar, Crossref

54. M. L. Sánchez, M. A. Aguilar, and F. J. Olivares Del Valle, J. Comput. Chem. **18**, 313 (1997); https://doi.org/10.1002/(SICI)1096-987X(199702)18:3<313::AID-JCC2>3.0.CO;2-X , Google Scholar, Crossref
M. L. Sánchez, M. A. Aguilar, and F. J. Olivares Del Valle, J. Mol. Struct.: THEOCHEM **426**, 181 (1998); https://doi.org/10.1016/S0166-1280(97)00319-9 , , Google Scholar, Crossref
see also: A. M. Losa, I. F. Galván, M. E. Martin, and M. A. Aguilar, Solvation Effects on Molecules and Biomolecules, edited by S. Canuto (Springer Science, Berlin, 2008), Chap. 6. , Google Scholar

55. A. B. Zahlan, G. M. Androes, G. M. Hameka, F. M. Heineken, C. A. Hutchison, G. W. Robinson Jr., and J. H. van der Waals, The Triplet State (Cambridge University Press, Cambridge, 1967). Google Scholar

56. S. K. Lower and M. A. El-Sayed, Chem. Rev. **66**, 199 (1966). https://doi.org/10.1021/cr60240a004 , Google Scholar, Crossref, ISI

57. M. A. El-Sayed, J. Chem. Phys. **36**, 573 (1962). https://doi.org/10.1063/1.1732572 , Google Scholar, Scitation

58. J. Quenneville, M. Greenfield, D. S. Moore, S. D. McGrane, and R. J. Scharff, J. Phys. Chem. A **115**, 12286 (2011). https://doi.org/10.1021/jp204104j , Google Scholar, Crossref

59. N. J. Turro, Modern Molecular Photochemistry (University Science Books, Sausalito, CA, 1991). Google Scholar

60. M. Takezaki, N. Hirota, and M. Terazima, J. Chem. Phys. **108**, 4685 (1998). https://doi.org/10.1063/1.475883 , Google Scholar, Scitation, ISI

61. M. Govindarajan and M. Karabacak, Spectrochim. Acta, Part A **85**, 251 (2012). https://doi.org/10.1016/j.saa.2011.10.002 , Google Scholar, Crossref

62. See supplementary material at http://dx.doi.org/10.1063/1.4738757 for full geometry information of the singlet and triplet geometries optimized in this work. Google Scholar