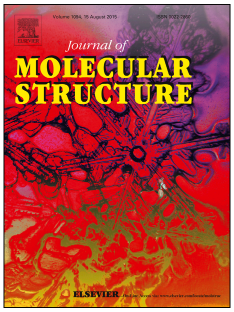

Franck Condon spectra of the 2-tolunitrile dimer and the binary 2-tolunitrile water cluster in the gas phase

Felix Gmerek, Benjamin Stuhlmann, Elvedina Pehlivanovic, Michael Schmitt

PII: S0022-2860(17)30546-X
DOI: 10.1016/j.molstruc.2017.04.092
Reference: MOLSTR 23715

To appear in: *Journal of Molecular Structure*

Received Date: 23 March 2017
Revised Date: 22 April 2017
Accepted Date: 24 April 2017

Please cite this article as: F. Gmerek, B. Stuhlmann, E. Pehlivanovic, M. Schmitt, Franck Condon spectra of the 2-tolunitrile dimer and the binary 2-tolunitrile water cluster in the gas phase, *Journal of Molecular Structure* (2017), doi: 10.1016/j.molstruc.2017.04.092.

Franck Condon Spectra of the 2-Tolunitrile Dimer and the Binary 2-Tolunitrile Water Cluster in the Gas Phase

Felix Gmerek, Benjamin Stuhlmann, Elvedina Pehlivanovic, and Michael Schmitt*

Heinrich-Heine-Universität, Institut für Physikalische Chemie I,
D-40225 Düsseldorf, Germany

Abstract

We present fluorescence emission spectra of the 2-tolunitrile dimer and the 2-tolunitrile water cluster through various vibronic bands in the electronically excited state. From the transition dipole moments in the individual monomers, the 2-TN dimer has shown to form J-aggregates, which is why the one-photon allowed transition is the S_1 state in this cluster in contrast to other symmetric dimers, which tend to form H-aggregates. The changes of the molecular structures upon electronic excitation have been determined from a fit of the intensities in various fluorescence emission spectra. The excited state structure of the 2-TN dimer has been found to be asymmetric, in contrast to the ground state structure. Thus, emission takes place from one of the locally excited monomer moieties in the 2-tolunitrile dimer.

Keywords: Franck-Condon analysis, 2-tolunitrile dimer, water cluster, structure, excitonic splitting

1 Introduction

The 2-tolunitrile (2-TN) dimer belongs to the same class of centrosymmetric homodimers, as the benzonitrile dimer[1–4], the benzoic acid dimer,[5–7], the 2-cyanophenol dimer,[8] the 3-cyanophenol dimer,[9] the azaindole dimer,[10] and the pyridone dimer.[11,12] The question arises, if the electronic excitation in theses homodimers is localized in one of the two equivalent chromophores or if it is delocalized over both chromophores. In a recent comprehensive study, Ottiger *et al.*[13] investigated the exciton (Davydov) splitting in these dimers both experimentally, as well as theoretically using a quenching model that reduces the calculated electronic exciton splitting by a factor which they showed to be the product of excited-state vibrational displacements in the monomer. Clearly, their results point to a delocalized excitation with weak to intermediate coupling. Kopec *et al.*[14] recently showed that the quenched excitonic splitting can be interpreted as nonadiabatic tunneling splitting related to a lower adiabatic double-minimum potential energy surface (PES), but nonadiabatically coupled to the higher PES. One of the delocalized and symmetry-adapted adiabatically split levels in the double-minimum PES has the symmetry of the S_1 state, the other of the S_2-state. It has to be noted, that the aforementioned dimers form H-aggregates[15] with nearly parallel (or antiparallel) transition dipole moment orientations. However, recently a symmetric homodimer, which forms J-aggregates[16] in a molecular beam, the m-cyanophenol dimer, has been investigated.[17]

---

*corresponding author.
Fax: 49 211 8115195; Tel: 49 0211 81 12100; E-mail: mschmitt@uni-duesseldorf.de