Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics 330 (2006) 360–364
Chemical Physics
www.elsevier.com/locate/chemphys

A compact model system for electron–phonon calculations in discotic materials

Olga Kruglova [a], Fokko M. Mulder [a], Arek Kotlewski [b], Stephen J. Picken [b], Stewart Parker [c], Mark R. Johnson [d], Gordon J. Kearley [a,*]

[a] Department of Radiation, Radionuclides and Reactors, Faculty of Applied Sciences, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands
[b] Department of Nanostructured Materials, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
[c] CCLRC, The ISIS Facility, Rutherford Appleton Laboratory, Chilton, OX11 0QX, UK
[d] Institut Laue-Langevin (ILL), BP 156, 38042 Grenoble, Cedex 9, France

Received 6 June 2006; accepted 5 September 2006
Available online 14 September 2006

Abstract

Electron–phonon coupling underlies the unwanted rapid relaxation of electrically excited states in potential organic solar-cell materials. A compact model for the vibrational dynamics of 2,3,6,7,10,11-hexakishexyloxytriphenylene (HAT6) is derived from the combined use of inelastic neutron scattering (INS) spectroscopy and first-principles calculations. Because this model reproduces the essential features of the vibrational dynamics and electronic structure on the aromatic core of HAT6 it can be used as a basis for future calculations of the relaxation mechanisms of the electronically excited states.

Keywords: Inelastic neutron scattering; Vibrational spectroscopy; Organic solar cells; Ab-initio calculations

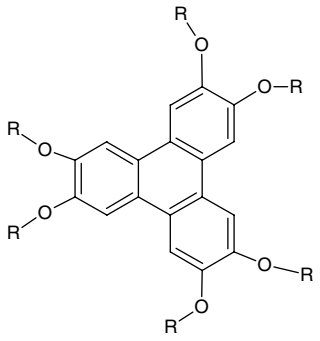
1. Introduction

Discotic molecules can self assemble into columns that are of interest due to the conductivity afforded by the overlap of π-systems on neighbouring molecules. The stack of organic disks functions not only as a hole conductor, but also as a light absorbing dye giving the possibility of novel types of self-assembling photo-voltaic cells [1]. In the present work we are interested in model systems based on well-known symmetrical hexaether derivatives of triphenylene (Fig. 1). The aromatic core is surrounded with six alkoxy tails that are required for columnar liquid crystal phase formation. The optimum side-chain length that gives the broadest mesophases range is found between five and seven carbons in the alkyl tail. Further increase or decrease of the tail length is reduces the temperature range of Col_h mesophases formation. For that reason 2,3,6,7,10,11-hexakishexyloxytriphenylene (HAT6) is the most studied member from the whole homologous series.

Slow whole-body motions of the disks on the pico- and nano-second timescale perturb the charge-transfer between neighbouring molecules, and there have been a number of recent publications on this issue [2–7]. In the present study however, we are concerned with the faster vibrational motions of the triphenylene core that are responsible for the relaxation of the electronically excited states created by absorbed photons. The study of these excited states is rather difficult for two reasons. First, although density functional theory (DFT) calculations are routinely used to establish the vibrational modes of modestly sized molecule systems, such calculations in the electronically excited states are not straightforward. This difficulty can be at least partially overcome by using large aromatic systems in which the distortion of the nuclear structure in the electronically excited states tends to be spread over the whole

* Corresponding author. Fax: +31 152788303.
E-mail address: g.j.kearley@tnw.tudelft.nl (G.J. Kearley).

0301-0104/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2006.09.006



HAT6: R=-C_6H_{13}
HAT6D: R=-C_6D_{13}
HAT3: R=-C_3H_7
HAT3D: R=-C_3D_7
HAT1: R=-CH_3
HAT1D: R=-CD_3
HHT: R=-H
HHT-D R=-D

Fig. 1. Structures of investigated triphenylene derivatives.

molecule, leading to only slight changes in the vibrational eigenvectors. That is, the normal modes of vibration in the electronically excited will be rather similar to those in the ground-state. Second, even in the electronic ground-state accurate electronic structure calculations for discotic systems are somewhat time consuming, and in order to proceed, we need to establish the smallest model that accurately reproduces the vibrational dynamics of the aromatic cores.

Even in the solid-state the tail conformation is uncertain and the longer timescale dynamics in the liquid–crystalline columnar Col_h phase are rather complex. These effects are difficult to model at the DFT level and again, it would be convenient to establish that whilst the tails are required for the structure, they can actually be ignored in the study of the core vibrations. Excluding the tails may not be as obvious as it first appears since we know that on the picosecond timescale the dynamics of the cores and tails are strongly coupled [6,7]. Further, interdigitation of the tails between disks on neighbouring columns could bring the terminal methyl group of on molecule into close proximity of a core of a different molecule.

In order to establish the minimum model we need to measure the vibrations of the cores in the presence of the tails, and establish the sensitivity of the core vibrations to tail length. This can be conveniently achieved using INS, which reports mainly on H-atom motion, see for examples Ref. [8] and references therein. By deuteration of the alkoxy tails, we see mainly the vibrational dynamics of the H-atoms that are attached directly to the cores, and any spectral changes arising from alteration of the tail length reflect sensitivity to tail length and/or tail conformation. By comparing the measured INS spectra with those from DFT calculations we can establish the validity of the DFT method in these systems, and the relative importance of intermolecular interactions in the vibrational dynamics of the aromatic cores. It turns out that a single isolated disk with rather short-tails has almost the same vibrational dynamics in the core as that measured for a discotic molecule with tails that are 6C-atoms long in the bulk material. Nevertheless, there is some spectral sensitivity to the conformation of the alkoxy group itself, and this can be reproduced by DFT calculations on a single molecule.

2. Results and discussion

2.1. Observed INS spectra, sensitivity of core modes to tail length

Discotic systems are of technological interest in their columnar phases, which are normally stable over a fairly narrow temperature range around room temperature. At lower temperatures the order increases and the molecules tend to adopt a herringbone arrangement with stronger intermolecular interactions. Our INS spectra were recorded at 20 K in order to avoid the broadening effect of the Debye–Waller factor, and consequently, our spectra will reflect the stronger intermolecular interactions of the more crystalline phase, rather than those of the columnar phase. Since we will show that an isolated molecule approach is satisfactory even in the presence of these stronger interactions, it is clear that the details of the crystal structure are not relevant to the present study.

INS spectroscopy was chosen for two reasons. First because it is fairly straightforward to calculate the intensities, and secondly because the incoherent scattering of the D-nucleus (and almost all other nuclei) is many times lower than that of the H-nucleus. Measured INS spectra of three triphenylene derivatives HAT1D, HAT3D and HAT6D, are illustrated in Fig. 2, the integers referring to the number of carbon atoms in the alkoxy tails, and the "D" being used to denote that the H-atoms of the tails were deuterated. It is immediately apparent that the spectra of the homologues are remarkably similar. These spectra arise from the 6H-atoms that are directly connected to the aromatic rings, and we can see that to a very good approximation the vibrational dynamics of the triphenylene cores are independent of the aliphatic tails. Examples of the vibrational displacements of the cores are illustrated in Fig. 3, where the participation of the H-atoms connected to the cores can be seen. The most significant difference is upward shift of the strong peak at around 850 cm^{-1} in HAT3D compared with HAT1D and HAT6D, which we will discuss later. Other small differences at higher energies almost certainly arise

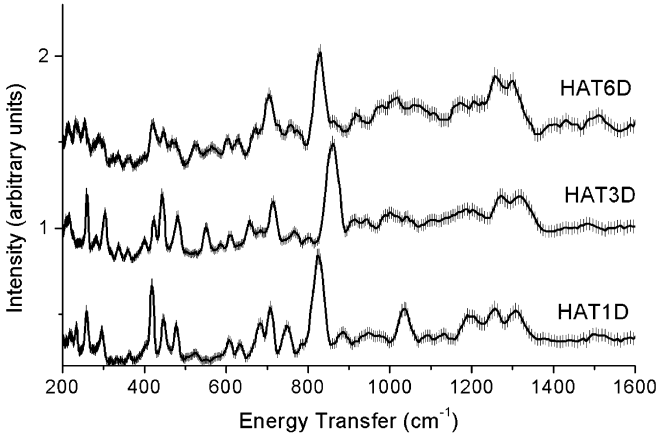


Fig. 2. Observed INS spectra of HAT6D, HAT3D and HAT1D.