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Journal of Molecular Spectroscopy 238 (2006) 158–167

Journal of
MOLECULAR
SPECTROSCOPY

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Infrared spectroscopic investigation of higher diamondoids

Jos Oomens [a,*], Nick Polfer [a], Olivier Pirali [a], Yuko Ueno [b,c], Roha Maboudian [b], Paul W. May [d], Jacob Filik [d], Jeremy E. Dahl [e], Shenggao Liu [e], Robert M.K. Carlson [e]

[a] FOM Institute for Plasma Physics "Rijnhuizen", Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands
[b] Department of Chemical Engineering, University of California Berkeley, Berkeley, CA 94720, USA
[c] NTT Microsystem Integration Laboratories, Atsugi, Kanagawa 243-0198, Japan
[d] School of Chemistry, University of Bristol, Bristol BS8 1TS, UK
[e] Molecular Diamond Technology, Chevron Technology Ventures, Richmond, CA 94802, USA

Received 11 April 2006
Available online 5 May 2006

Abstract

Attenuated total reflection Fourier transform infrared spectra are recorded for a number of diamond molecules (or higher diamondoids) in the spectral range between 650 and 3000 cm^{-1}. Molecules studied are diamantane, triamantane, [121]tetramantane, [123]tetramantane, [1(2,3)4]pentamantane, [12(3)4]pentamantane, 3-methyl-[1(2,3)4]pentamantane, and [12312]hexamantane (cyclohexamantane). Spectral trends are clearly recognized throughout the spectra revealing the general fingerprint of this class of molecules. In general, the spectra show good agreement with density functional theory calculations at the B3LYP/D95(d,p) level of theory.

Keywords: Diamondoids; Infrared; Spectroscopy

1. Introduction

Diamondoid molecules consist of a diamond-like carbon cage, where all carbon atoms are sp^3 hybridised, and dangling bonds at the edges of the systems are terminated with hydrogen atoms. The smallest member of the family, adamantane ($C_{10}H_{16}$) is made up of the central cage of a single diamond unit cell and was first synthesized by carbocation equilibration in 1957 by von Rague Schleyer [1]. The next members of the family are diamantane and triamantane possessing two and three diamond cages, respectively. For higher diamondoids, starting with tetramantane (four cages), structural isomers can be formed.

Diamondoids show remarkable rigidity, strength, and thermodynamic stability, as well as interesting electronic properties [2], which may be of use in chemical, polymer, and pharmaceutical applications, as well as in nanotechnology.

Moreover, there has been substantial interest in the spectroscopic properties of this class of molecules from an astrophysical view-point. Not only have nanometer-sized 'diamond-like' molecules been found in meteorites [3], the occurrence of these compounds as isolated gas-phase molecules in the interstellar medium, has also been suggested, based on the observation of infrared absorption [4] and emission [5,6] bands around 3.5 μm (2880 cm^{-1}) in the spectra of protostars as well as the post-AGB object HR 4049 [6]. This band has been assigned to the tertiary sp^3 carbon (i.e., carbon bound to three carbon atoms) C–H stretching mode [7], but other explanations have also been put forward [8,9]. Further evidence for the existence of interstellar diamondoid molecules could be obtained by comparing the complete vibrational spectra of such diamondoids with astronomical data [10].

Although the very smallest members of the diamondoid family can now be readily synthesized, this is not the case for species larger than triamantane. Hence, in spite of the wide interest in diamondoids, relatively few studies have been reported on the characterization of these molecules.

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[*] Corresponding author. Fax: +31 30 603 12 04.
E-mail address: joso@huygens.rijnh.nl (J. Oomens).

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doi:10.1016/j.jms.2006.05.001

A recent breakthrough in diamondoid research was the discovery that higher diamondoids can be isolated from petroleum, which was shown for species up to the size undecamantane (11 cages) [11]. As a result, various analytical techniques including GC/MS and NMR have been applied to identify and characterize these novel species [12].

From a spectroscopic point of view, only Raman spectra of a selection of diamondoids with a size ranging from adamantane to [121321]heptamantane have been published very recently [13]. In addition, theoretical methods have been applied to predict the vibrational spectra of some of these molecules. An extensive computational study of adamantane and some of its ionic and dehydrogenated radical species was reported by Yan et al. [14]. For the adamantyl closed-shell cation, an experimental infrared spectrum was also obtained [15]. The Raman spectrum of crystalline cyclohexamantane was interpreted with density functional theory (DFT) calculations by Richardson et al. [16]. An infrared spectroscopic study on deposited diamondoid nanoparticles (5–350 nm in size) focusing on the 3 μm spectral range was successfully interpreted with DFT computations on individual molecular diamondoid structures, giving insight into the size dependence of the spectra [17].

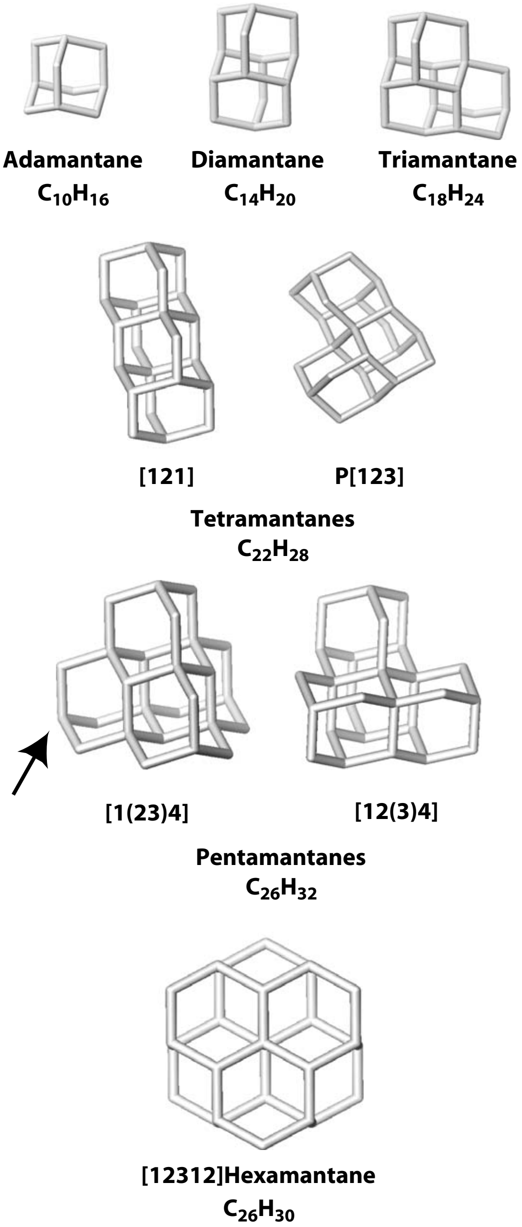

Fig. 1. Higher diamondoid structures considered in this work. Hydrogen atoms have been omitted for clarity; all structures are fully saturated. The smallest member of the family, adamantane, is shown for comparison. The arrow indicates the carbon atom where by the substitution of a hydrogen atom for a methyl group, the 3-methyl-[1(2,3)4]pentamantane is formed.

To our knowledge, no infrared spectra have to date been reported for individual higher diamondoid molecules. Moreover, no direct comparison between theoretical and experimental spectra for these molecules has been reported. In this contribution, we present the first infrared spectra for a number of higher diamondoids, and present an analysis based on DFT computations of the vibrational spectra. The systems studied are diamantane, triamantane, [121]tetramantane, [123]tetramantane, [1(2,3)4]pentamantane, [12(3)4]pentamantane, and [12312]hexamantane (cyclohexamantane), which are shown in Fig. 1. (Note that we follow the nomenclature introduced in ref. [18].) In addition, we present the infrared spectrum for the [1(2,3)4]pentamantane molecule methylated at the position of the arrow in Fig. 1 (3-methyl-[1(2,3)4]pentamantane).

2. Methods

2.1. Experimental

Higher diamondoid species (size going up to undecamantane) have been isolated from petroleum oil by vacuum distillation, high-temperature pyrolytic destruction of non-diamondoid species combined with chromatographic techniques [11]. The size and shape separations are performed using high performance liquid chromatography in ultrahigh purity. The molecules studied here are neutrals, fully sp^3 hybridized molecules with completely hydrogenated surfaces plus one mono-methylated species.

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the diamondoid molecules were recorded with the use of a Thermo Nicolet Avatar 370 FT-IR spectrometer and an ATR accessory with a ZnSe ATR crystal. The spectra of [12(3)4]pentamantane and 3-methyl-[1(2,3)4]pentamantane were recorded in Bristol (UK) at slightly higher resolution, using a Perkin-Elmer 'Spectrum One' FTIR spectrometer. The higher resolution was required to better resolve the bands in the congested spectra of these molecules. All spectra are obtained from pure, powdered diamondoid samples, and measurements were performed at room temperature. The intensity of the ATR absorbance spectra are corrected for the penetration depth of the evanescent wave, which is proportional to the wavelength.

One can notice that two enantiomers (P and M) exist for the molecule [123]tetramantane. Since the light source used