

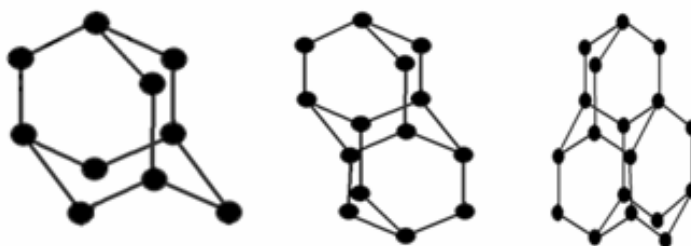
THEORETICAL STUDY ON ^1H , ^{13}C NMR SHIELDING, VIBRATIONAL ASSIGNMENT OF THREE DIAMANTOIDS (ADAMANTANE, DIAMANTANE, TRIAMANTANE)

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In this study, the infrared and Raman spectra of Adamantane were examined using the Gaussian 09 quantum chemistry package.¹ A detailed quantum chemical study will aid in making definitive assignments to the fundamental normal modes of Adamantane and in clarifying the considerable amount of experimental data available for this important molecule. Again, the addition of another unit has reduced the symmetry of the molecule. From Adamantane to diamantane this had little effect, as in both only some limited symmetries were Raman active. This increase in molecule size and decrease in symmetry means we now have 20 intense CH stretch vibrations in the same 100 cm^{-1} (wavenumber) region, which produces a very poorly resolved experimental signal. The calculated spectrum for triamantane still has the same discrepancies as the Adamantane and diamantane calculations, but there is also disagreement in the intensity of vibrations in the region around ~ 1300 and $\sim 1100\text{ cm}^{-1}$ (wavenumber). The addition of another Adamantane unit produces triamantane which has 120 vibrational modes, $35\text{A}_1 + 25\text{A}_2 + 29\text{B}_1 + 31\text{B}_2$. In triamantane, the symmetry has decreased to C_{2v} , so all modes are now Raman active, producing 120 possible signals in it. Also in this study ^1H and ^{13}C NMR chemical shifts were calculated. Comparison of experimental and calculated values indicates that the calculation is done accurately.



INTRODUCTION

Diamantoid 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 ($\text{C}_{10}\text{H}_{16}$) is made up of the central cage of a single diamond unit cell and it was first synthesized by carbocation equilibration in 1957 by von Rague Schleyer.² Adamantane belongs to the most interesting structures produced by nature (See Fig. 1). It possesses a cage-link skeleton which is a unique, rigid, but strain-free ring system composed of three fused chair cyclohexane rings.

The carbon skeleton with its T_d symmetry also represents a fragment of the diamond network.



Fig. 1 – Adamantane.

Since the discovery of Adamantane from petroleum in 1933,³ there has been great interest in

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the properties of this once unique cage-structured molecule. Some years later it was joined by diamantane⁴ (See Fig. 2) to form the two smallest examples of a series of molecules known as “diamond hydrocarbons” or diamondoids.

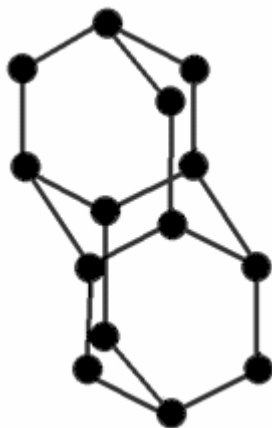


Fig. 2 – Diamantane.

There has been substantial interest in the spectroscopic properties of this class of molecules from an astrophysical view-point. Not only have Nano sized ‘diamond-like’ molecules been found in meteorites,⁵ the occurrence of these compounds as isolated gas phase molecules in the interstellar medium has also been suggested, based on the observation of infrared absorption⁶ and emission^{7,8} bands around 3.5 μm (2880 cm^{-1}) in the spectra of protostars as well as the post-AGB object HR 4049.⁹ This band has been assigned to the tertiary sp^3 carbon (*i.e.*, carbon bound to three carbon atoms) C–H stretching mode,¹⁰ but other explanations have also been put forward.¹¹ The vibrational spectra of Adamantane have been recorded in the literature numerous times under various conditions.^{12,13} Synthetically, chemists managed to reproduce these structures in the laboratory¹⁴ and go two steps further, both producing triamantane¹⁵ (See Fig. 3).

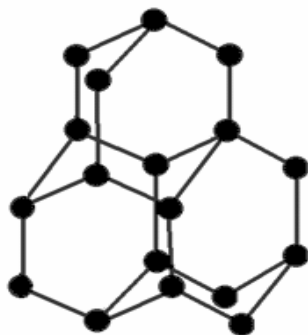


Fig. 3 – Triamantane.

METHOD

Theoretical methods have been applied to predict the vibrational spectra of some of diamondoid molecules. Calculations were performed using either Hartree-Fock theory or the three-parameter hybrid functional of Becke and the correlation functional of Lee, Yang, and Parr_B3LYP. A range of basis sets were used, a selection found as standard in the Gaussian 09¹⁶ software. For small molecules in the gas phase and in solution, *ab initio* quantum chemical calculations can provide results approaching benchmark accuracy and they are used routinely to complement experimental studies. The vibrational frequency of Adamantine was calculated at the Hartree-Fock and DFT (B3LYP) levels of theory using the 6-311+G**basis set. The calculation utilized the T_d symmetry of the Adamantane molecule. Each of vibrational modes was assigned to one of eight types of motion (C-C stretch, C-H stretch, C-C-C bend, CH bend, CH_2 scissors, CH_2 twist, CH_2 wag, and CH_2 rock) by means of visual inspection using the Gaussview program. Also the isotropic ^1H and ^{13}C chemical shifts were calculated. In this study we have optimized geometries of Adamantane and calculated NMR parameter for it.

The assignments were made on the basis of relatively low-level calculations carried out using the Gaussian 09. The experimental Raman spectra were then matched to the overall patterns of the *ab initio* calculation and then modified in the light of the polarization information. In general the calculated frequencies were over-estimated. The small unassigned peak in the Diamantane spectrum between $2250\text{-}2800\text{ cm}^{-1}$ is most probably combination bands. The animation of Diamantane has been produced using the optimized geometry and maximum displacements from the *ab initio* calculation. The individual frames have been calculated using a simple sinusoidal interpolation, and the amplitudes of the vibration have been exaggerated in order to make them visible on the screen.

RESULTS AND DISCUSSION

In this section the results of the calculations for three diamondoids are presented and discussed separately.

Adamantane:

The tertiary carbon binding (Y) and CH₂ scissoring motions of Adamantane were calculated at B3LYP/6-311+G** and HF/6-311+G**. The vibrations have zero intensity in both IR and Raman spectra. Calculated Frequency and Raman activity (cm⁻¹) were indicated in Table 1. Analogous experimental signal of Adamantane is at 1435 cm⁻¹. On the other hand, a strong Raman band at 1220 cm⁻¹ was assigned as CH₂ twisting (coupled with CH bending) motion and another pretty strong Raman band at 1096 cm⁻¹ was assigned as CH₂ Rocking motion (coupled with CH bending).¹⁷

Also the isotropic chemical shifts δ of ¹³C (with respect to TMS) and ¹H were calculated at the same levels and basis sets. The ¹H and ¹³C NMR spectroscopic parameters of Adamantane are summarized in Table 2.

Diamantane:

The tertiary carbon binding (Y) and CH₂ scissoring motions of Diamantane were calculated at B3LYP/6-311+G** and HF/6-311+G**. These vibrations do not appear in experimental IR and Raman spectra [17]. Calculated Frequency and Raman activities were summarized in Table 3. Analogous experimental signal has appeared at 1433 cm⁻¹ and a strong Raman band at 1233 cm⁻¹ was assigned as CH₂ twisting (coupled with CH bending) motion.

Also the isotropic chemical shifts δ of ¹³C (with respect to TMS) and ¹H were calculated at the same levels and basis sets. The ¹H and ¹³C NMR spectroscopic parameters of Diamantane were indicated in Table 4.

Table 1

IR and Raman Frequencies (cm⁻¹) calculated for Adamantane

Vibration mode	B3LYP/6-311+G**	HF/6-311+G**
IR- tertiary carbon binding	1030	1091
IR- CH ₂ scissoring	1444	1453
Raman- CH ₂ twisting motion	1208	1210
Raman- CH ₂ rocking motion	1088	1091

Table 2

The calculated and experimental chemical shifts of Adamantane are reported in δ (ppm)

	HF/6-311+G**	B3LYP/6-311+G**	Experimental
C (2)	34.6845	42.8466	37.85
C (3)	26.4291	35.7069	24.46
H (2)	1.3525	1.8520	1.873
H (3)	1.2954	1.7936	1.756

Table 3

IR and Raman Frequencies (cm⁻¹) calculated for Diamantane

Vibration mode	B3LYP/6-311+G**	HF/6-311+G**
Tertiary carbon binding (cm ⁻¹)	688	668
Frequency (cm ⁻¹)	1469	1453
Raman	1240	1233

Table 4

The calculated and experimental chemical shifts of Diamantane are reported in δ (ppm)

	HF/6-311+G**	B3LYP/6-311+G**	Experimental
C (2)	34.5746	44.0266	37.70
C (3)	24.8165	33.1114	37.70
H (2)	1.3016	1.7816	1.68 ^(a)
H (3)	1.1307	1.7100	1.68 ^(a)

^(a)The ¹H NMR spectrum of Diamantane shows only a singlet at δ 1.68 (CDCl₃)

Table 5

IR and Raman Frequencies (cm⁻¹) calculated for Triamantane

Vibration mode	B3LYP/6-311+G**	HF/6-311+G**
Frequency (cm ⁻¹)	1468	1462
Raman	1088	1091

Table 6

The calculated and experimental chemical shifts of Triamantane are reported in δ (ppm)

	HF/6-311+G**	B3LYP/6-311+G**	Experimental
C (2)	42.2302	45.9558	46.9
C (3)	31.5446	34.9148	36.27
H (2)	1.3818	1.7275	1.67
H (3)	1.0855	1.3649	1.49

Triamantane:

CH₂ scissoring motions were calculated (scaled frequencies are reported) at B3LYP/6-311+G** and HF/6-311+G** and an analogous experimental signal has appeared at 1436 cm⁻¹. A strong Raman band at 1222 cm⁻¹ was assigned as CH₂ wagging motion (coupled with CH bending and CH₂ twisting) and it was calculated at the same levels and basis sets.¹⁸ Frequency (cm⁻¹) value and Raman value were presented in Table 5.

Also the isotropic chemical shifts δ of ¹³C (with respect to TMS) and ¹H were calculated at B3LYP/6-311+G** and HF/6-311+G**. The ¹H and ¹³C NMR spectroscopic parameters of Triamantane are summarized in Table 6.

CONCLUSIONS

In this research, the IR and Raman frequencies were measured for three diamondoids, Adamantan, Diamantane and Triamantane at the DFT level using B3LYP with 6-311+G**basis set or B3LYP/6-311+G** and Hartree-Fock level with 6-311+G**basis set or HF/6-311+G**. Then the results of these calculations were compared with experimental values. Comparisons show that the calculated values are close to the experimental values and this shows the accuracy of the calculations. On the other hand, if we compare B3LYP/6-311+G** and HF/6-311+G** levels, we shall see that DFT calculations are more accurate than Hartree-Fock calculations.

In addition to the comparisons made, mention of a point is also necessary for Triamantan. Strong Raman band in the 681-1222 cm⁻¹ region may be attributed to breathing (C-C stretching), C-H bending and CH₂ twisting (coupled with CH

bending and CH₂ wagging) and CH₂ twisting (coupled with CH bending) motions.

REFERENCES

- M. J. Frisch, R. Trucks, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson. GAUSSIAN 09W, Revision C. 01(Wallingford, CT: Gaussian Inc.), 2009.
- P. V. R. Schleyer, *J. Am. Chem. Soc.*, **1957**, 79, 3292.
- S. Landa and V. Machacev, *Collect. Czech. Chem. Commun.*, **1933**, 5, 1.
- S. Hola, S. Landa and V. Hanus, *Angew. Chem. Internat. Edt.*, **2008**, 5, 1045.
- E. Anders and E. Zinner, *Meteorites*, **1993**, 28, 490.
- L. J. Allamandola, S. A. Sanford, A. G. G. M. Tielens and T. M. Herbst, *J. Astrophys.*, **1992**, 399, 134.
- O. Guillois, G. Ledoux and C. Renaud, *J. Astrophys.*, **1999**, 521, 133.
- C. Van Kerckhoven, A. G. G. M. Tielens and C. Waelkens, *Astron. Astrophys. J.*, **2002**, 384, 568.
- H. C. Chang, J. C. Lin, J. Y. Wu and K. H. Chen, *J. Phys. Chem.*, **1995**, 99, 11081.
- J. C. Blades, D. C. B. Whitted and R. M. Not, *Astron. Soc.*, **1980**, 191, 701.
- W. A. Schutte, A. G. G. M. Tielens, J. L. Allamandola, M. Cohen and D. H. Wooden, *Astrophys. J.*, **1990**, 360, 577.
- K. M. Gough, J. R. R. Dwyer and C. Dawes, *J. Chem.*, **2000**, 78, 1035.
- R. Rao, T. Sakuntala, S. K. Deb, A. P. Roy, V. Vijaykumar, B. K. Godwal and S. K. Sikka, *J. Chem. Phys.*, **2000**, 112, 112.
- P. R. Von Scheleyer and G. A. Olah, (Eds), "Cage Hydrocarbon", Wiley, New York, 1990, p. 138.
- V. Z. Wiliyama Jr., P. R. Von Scheleyer, G. J. Glecher and L. B. Rodewald, *J. Chem. Am. Soc.*, **1988**, 88, 3862.
- L. Bisticric, L. Pejovb and G. J. Baranovic, *Mol. Stroct - Theochem.*, **2002**, 594, 79.
- D. Y. Julliane, R. S. Peter and Z. L. Kátia, *Ann. Magn. Reson.*, **2008**, 7, 32.
- I. Ravil, R. Khusnutdinov, R. Rinat, T. Mukminov, I. Rishat, A. Aminov, M. Leonard, R. Khalilov, S. Ekaterina, L. B. Mescheryakova, M. Usein, *Tetrahedron Letters*, **2014**, 56.