

Theoretical infrared spectra of MAON molecules

SeyedAbdolreza Sadjadi, Sun Kwok and Yong Zhang

Laboratory for Space Research, Faculty of Science, The University of Hong Kong, Hong Kong, China

E-mail: ssadjadi@hku.hk, sunkwok@hku.hk, zhangy96@hku.hk

Abstract. Techniques of computational quantum chemistry (CQC) are used to explore the vibrational modes of complex organic molecules with mixed aromatic and aliphatic structures.

1. Introduction

Although the family of unidentified infrared emission (UIE) bands at $3.3\ \mu\text{m}$, $6.2\ \mu\text{m}$, $7.7\ \mu\text{m}$, $8.6\ \mu\text{m}$, $11.3\ \mu\text{m}$ and $12.7\ \mu\text{m}$ is commonly attributed to polycyclic aromatic hydrocarbon (PAH) molecules [1], there are other proposals suggesting the UIE bands originate from more complex organic compounds such as hydrogenated PAH [2, 3], hydrogenated amorphous carbon [4], soot and carbon nanoparticles [5], QQC [6], coal [7], oil fragments [8, 9], or mixed aromatic aliphatic organic nanoparticles (MAON) [10, 11].

The infrared spectra of complex amorphous hydrocarbons are poorly known theoretically as the vibrationally modes of large molecules have never been computed by chemists. The introduction of the Gaussian functions by Boys [12] to overcome the difficulty of evaluation of integrals and the new formulations by Roothaan [13] opened the path to solve the Schrödinger equation for molecular systems. The reformulation of the mathematical framework into computer languages marked the first ab initio molecular quantum mechanics computer program in 1968 [14]. These pioneering works have led to a new discipline of computational quantum chemistry (CQC). With the availability of such modern powerful tools, it is now possible to explore the vibrational properties of large organic compounds. In this paper, we show briefly how CQC could help in the interpretation of astronomical IR spectra.

2. Infrared spectra of MAON

MAON's have mixed sp^2/sp^3 hybridizations and consist of isolated islands of benzene rings connected via the saturated hydrocarbon chains. An example of a MAON molecule $\text{C}_{155}\text{H}_{240}$ is shown in Figure 1. The molecular structure is assigned by applying the model(s) of chemical bond to the molecular geometry (defined by the list of Cartesian coordination of nuclei) [17]. The outcome of CQC calculations is the molecular geometry.

We applied the B3LYP/PC1 theoretical level implemented in PQS package [18] to calculate the local minimum geometry of $\text{C}_{155}\text{H}_{240}$, as well as the wavelength of $3N - 6$ numbers of fundamental IR normal modes and their corresponding intensities. The blackbody thermal excitation model is then applied to these calculated data to simulate the IR emission spectra [19]. The calculated spectrum of this molecule is shown in Figure 2.



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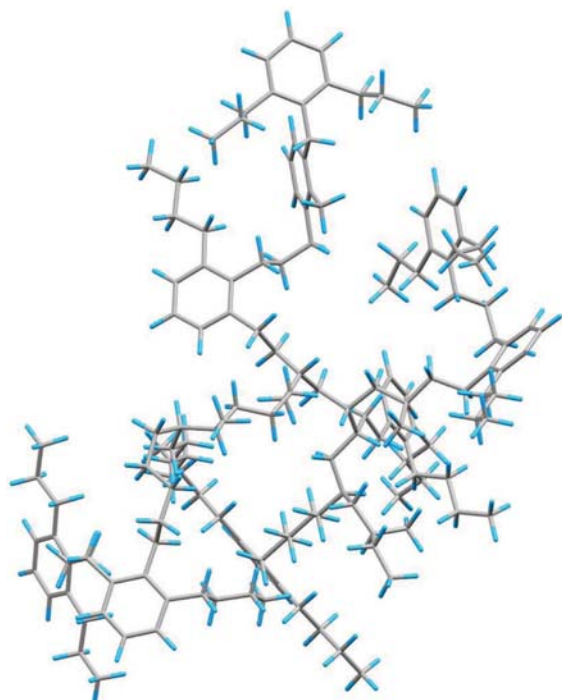


Figure 1. Structure of an example MAON molecule $C_{155}H_{240}$. The C atoms are shown in grey and H atoms in blue.

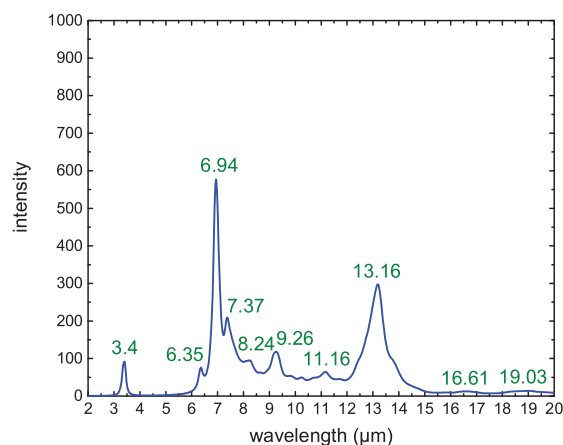


Figure 2. Theoretical spectra of the MAON molecule $C_{155}H_{240}$. Some of the peaks cannot be assigned to a single vibrational mode but are the result of coupled stretching and bending modes.

3. Vibrational analysis of MAON molecules

Unlike pre-quantum mechanical vibration models, there is no pre-defined modes of vibrations in CQC calculations. The molecular vibrational energy levels and intensities are calculated from the pure or mixed second derivatives of molecular energy. Since molecular energy is a hypersurface with $3N$ dimension (N is the number of atoms), the mathematical procedure is performed via special approximation called normal mode vibrational analysis. Besides the energy levels and intensities of vibrations, displacement vectors for all atoms in each normal mode are produced. When these vectors are animated alongside the molecular structure in graphical interface programs such as CHEMCRAFT [20] and GABEDIT [21], the three dimensional picture of molecular vibration can be observed. We can see which atoms, bonds or functional groups are participating in vibrations and how they vibrate.

In addition to visual examination of the movement of the displacement vectors, we have also developed a tool VIBANALYSIS [19] to quantify the contribution of each vibrational mode to a specific band. By such analysis, we can group the participant atoms into aliphatic and aromatic and calculate their contributions quantitatively.

4. The IR signatures of MAONs

The result of an analysis the vibrational bands of our sample MAON molecule is shown in Table 1. We can see that some vibrational modes are simple, e.g., the $3.4\ \mu\text{m}$ band is due to sp^3 C–H stretching modes. However, some vibrational bands are coupled modes, e.g., the $6.35\ \mu\text{m}$ band has major contributions from aromatic C–C stretching and C–H in-plane-bending (86%) coupled with 14% of aliphatic methylene twisting modes. The strongest band at $6.94\ \mu\text{m}$ (Fig.2) has 85% contributions from sp^3 H–C–H scissoring mode. The second strongest band at 13.16

Table 1. Identification of the Vibartional Motions of Emission Bands of C₁₅₅H₂₄₀.

Bands (μm)	Vibrations	Ali/Ar ^a
3.4	methylene asymmetric C–H stretching	100/0
6.35	benzene C–C stretching + benzene C–H INP bending + methylene twisting	14/86
6.94	methyl and methylene scissoring+ benzene C–H INP bending	85/25
7.37	methyl umbrella motion+ methylene wagging	100/0.0
8.24	methyl deformation+ methylene wagging and twisting + benzene C–H INP bending+ benzene ring INP deformation	60/40
9.26	aliphatic chain vibration (methylene wagging + methyl deformation)+ benzene C–H INP bending	96/4
11.16	benzene C–H OOP + methylene wagging+ methyl deformation	85/15
13.16	benzene C–H OOP + methylene rocking	25/75
16.61	benzene ring OOP deformation+ aliphatic chains deformation	76/24
19.03	benzene ring OOP deformation + aliphatic chains deformation	68/32

^aAliphatic/Aromatic characters in precentage.

μm has 75% contribution from aromatic C–H out-of-plane bending mode. Deformation motions occur at longer wavelengths, e.g., in the 8.24, 9.26, 11.16, 16.61 and 19.03 μm bands. As shown in Figure 2, the intensities of such bands are significantly lower than other bands and they are broad and thus it may play role in the formation of plateaus in the astronomical emission spectra.

We have generated 40 MAON molecules with different molecular formulas, geometries and structures and calculated their vibrational spectra. Figure 3 shows that these molecules have similar IR signatures up to 10 μm and but different IR signatures beyond this region. This suggests the spectra with $\lambda < 10 \mu\text{m}$) are mostly determined by the chemical bonds within

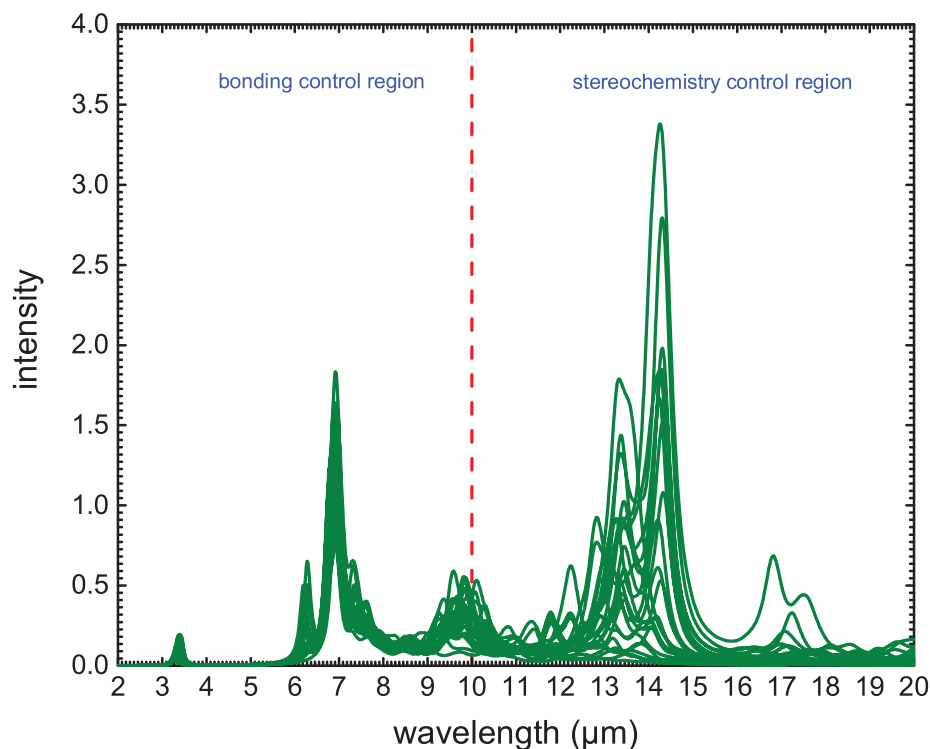


Figure 3. The IR spectra of 40 different types of MAON molecules.

the structure and the bands at $\lambda > 10 \mu\text{m}$ are affected by molecular size and 3D structure (stereochemistry). The convergence of vibrational bands into certain specific wavelength bands gives us hope that the UIE bands can be naturally explained by the MAON structures.

5. Conclusion

Simple PAH molecules have very different individual spectral behavior in the infrared and the fitting of observed UIE spectra requires artificial combinations of PAH mixtures with many free parameters [22]. Preliminary results of infrared spectra of MAON molecules calculated with CQC presented here suggest that the spectra of MAON show consistent qualitative behavior. Further work on a larger group of MAON molecules is needed to confirm this.

Acknowledgments

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6. References

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