Theoretical infrared spectra of MAON molecules

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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 μm, 6.2 μm, 7.7 μm, 8.6 μm, 11.3 μm and 12.7 μm 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 inito 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 sp²/sp³ hybridizations and consist of isolated islands of benzene rings connected via the saturated hydrocarbon chains. An example of a MAON molecule C₁₅₅H₂₄₀ 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 C₁₅₅H₂₄₀, 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.
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 μm band is due to $sp^3$ C–H stretching modes. However, some vibrational bands are coupled modes, e.g., the 6.35 μm 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 μm (Fig.2) has 85% contributions from $sp^3$ H–C–H scissoring mode. The second strongest band at 13.16

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.
Table 1. Identification of the Vibrational Motions of Emission Bands of C_{155}H_{240}.

| Bands (\(\mu\)m) | Vibrations                                                                 | Aliph/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 (methylen 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          |

\(^{a}\)Aliphatic/Aromatic characters in percentage.

\(\mu\)m 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 \(\mu\)m 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 \(\mu\)m and but different IR signatures beyond this region. This suggests the spectra with \(\lambda < 10 \mu\)m) are mostly determined by the chemical bonds within

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**Figure 3.** The IR spectra of 40 different types of MAON molecules.
the structure and the bands at $\lambda > 10 \mu m$ 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.

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6. References

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