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The Astrochemistry Implications of Quantum Chemical Normal Modes Vibrational Analysis

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Abstract: Understanding the molecular vibrations underlying each of the unknown infrared emission (UIE) bands (such as those found at 3.3, 3.4, 3.5, 6.2, 6.9, 7.7, 11.3, 15.8, 16.4, 18.9 μm) observed in or towards astronomical objects is a vital link to uncover the molecular identity of their carriers. This is usually done by customary classifications of normal-mode frequencies such as stretching, deformation, rocking, wagging, skeletal mode, etc. A large literature on this subject exists and since 1952 ambiguities in classifications of normal modes via this empirical approach were pointed out by Morino and Kuchitsu. New ways of interpretation and analyzing vibrational spectra were sought within the theoretical framework of quantum chemistry. Many of these methods cannot easily be applied to the large, complex molecular systems which are one of the key research interests of astrochemistry. In considering this demand, a simple and new method of analyzing and classifying the normal mode vibrational motions of molecular systems was introduced. This approach is a fully quantitative method of analysis of normal-mode displacement vector matrices and classification of the characteristic frequencies (fundamentals) underlying the observed IR bands. Outcomes of applying such an approach show some overlap with customary empirical classifications, usually at short wavelengths. It provides a quantitative breakdown of a complex vibration (at longer wavelengths) into the contributed fragments such as their aromatic or aliphatic components. In addition, in molecular systems outside the classical models of chemical bonds and structures where the empirical approach cannot be applied, this quantitative method enables an interpretation of vibrational motion(s) underlying the IR bands. As a result, further modifications in the structures (modeling) and the generation of the IR spectra (simulating) of the UIE carriers, initiated by proposing a PAH model, can be implemented in an efficient way. Here fresh results on the vibrational origin of the spectacular UIE bands based on astrochemistry molecular models, explored through the lens of the quantitative method applied to thousands of different vibrational motion matrices are discussed. These results are important in the context of protoplanetary nebulae and planetary nebulae where various molecular species have been uncovered despite their harsh environments.

Keywords: astrochemistry; planetary nebulae; UIE bands; normal modes; displacement vectors

1. Introduction

Detection in or towards various astronomical objects of broad emission infrared bands at certain wavelengths, i.e., 3.3, 3.4, 3.5, 6.2, 6.9, 7.7, 8.7, 11.3, 15.8, 16.4 & 18.9 μm led to the hypothesis that organic molecules are the carriers of these observed bands. These are a diverse range of organic molecular compounds from polyaromatic hydrocarbons (PAHs) [1,2], hydrogenated PAHs [3], nitrogenated PAHs [4], nanodiamonds [5], oil fragments [6], quenched carbonaceous composites (QCC) [7] and mixed aromatic-aliphatic organic nanoparticles (MAON) [8]. The main purpose of this work is to briefly discuss some new results of our on-going theoretical efforts and to explore the molecular vibrational

origin of these mysterious UIE bands [9] through the lens of each of the proposed astrochemistry models above.

Most of the assignments of molecular vibrational motions and their responsible fragments or bonds are still based on an empirical approach which can potentially lead to incorrect interpretation of the molecular structure(s) of unknown carrier(s) of IR spectra [10–12]. Our theoretical approach aims to provide complementary information to other methods of simulating fundamental, combination, overtone [13–16] and ro-vibrational [17,18] bands of the Infrared spectra so generated.

An example of an astrochemistry application of our methodology is our recent work on the vibrational origins of the 3.28 and 3.3 μm components of the 3.3 μm feature known in the framework of the current PAH model [19]. The customary classification and assignment of the first component at 3.28 μm to the so-called *bay* and the second at 3.3 μm , to the *non-bay* -C-H stretching modes in PAH molecules (for example there are two bay C-H bonds, each from one ring, in the phenanthrene molecule) cannot adequately explain the observed wavelength difference and flux ratio of these two UIE features. This is due to the large and complex coupling between the stretching modes of aromatic -C-H bondings (bay and non-bay) [19].

The primary empirical tool developed for interpreting and simulating the frequency and intensity of molecular fundamental infrared (IR) bands is the model of normal-mode vibration. Reference [10] noted are no rules to exactly define the customary (empirical) classifications of normal-mode frequencies as a result of bond stretching, deformation, rocking, wagging, skeleton mode, etc. The key role of having a well-defined system for assigning and classifying the vibrational motions in the interpretation of observed IR spectra was recently discussed by Tao et al. [20]. Their main argument is that normal modes are delocalized over all constituent atoms of a molecule. Hence, without any definite rules, assigning a vibration to a particular bond(s) or fragment(s) is a difficult and ambiguous task.

Although new mathematical methods to resolve this problem were introduced into quantum chemical models since 1998 [11,12] these are not suitable methods to apply for analysis of vibrational motions of large molecules with complex structures [12], especially the types of molecules of particular interest in astrochemistry. The recent generalized subsystem vibrational analysis, developed by Tao et al. [20] might be a good framework for our purposes but the reliability of this model needs to be confirmed in different classes of molecules. Clearly not all the possible 10^{33} to 10^{180} molecular species within the structural space of organic chemistry can be explored theoretically. Vibrational analysis and interpretation of IR spectra hence plays a key role in choosing the right bondings and fragments to modify in the astrochemistry molecular models and to inform a better understanding of the origin of the mysterious UIE bands.

In this regard, we have developed and introduced a simple approach for vibrational analysis based on displacement vector analysis of normal modes [9]. These are $N \times 3$ matrices, where N is the number of atomic centers with a total number of $3N-6$ normal modes for each molecule. We applied our methods to numerous examples of vibrational motions in simple and complex organic compounds composed of different types of chemical bonds, structures and sizes [9,19,21–23]. Our methodology provides consistent results compared to the more customary (empirical) approach and in a fully quantitative fashion while additionally revealing important details of vibrational motions that are not recovered by the more traditional techniques. Another example is our detailed and comprehensive vibrational motion analysis of the complex correlation of a band's peak wavelength position of the out of plane bending mode vibration of aromatic -C-H bondings (OOPs) with the exposed edges (neighbor -C-H bondings) in the structure of PAH molecules [23]. Such correlation was originally suggested as due to a monotonic increase in wavelength position by increasing the exposed edge [24].

2. Brief Summary of Our Previous Work

Here we present a brief summary of our latest findings and understanding of the types of vibrational motions underlying UIE bands. This is based on our application of displacement vector analysis of vibrational normal modes to thousands of Raman and IR active modes of PAHs [19]

with different aliphatic and olefinic side chains [9,19] and MAON type molecules [21]. In the customary empirical approach, the vibrational origin of an IR band is assigned to the vibration with strongest intensity. Unfortunately, the type of vibration and the responsible fragment(s)/bonds cannot be correctly assigned in this way [10–12,20]. Neglecting the rest of the vibrational motions, including the Raman modes, will lead to incomplete or, in the case of long wavelength bands, an incorrect interpretation of the origin of an IR band. Below is an itemized summary of our current findings. Thereafter our new results are presented for the first time.

- In hydrocarbons within the realm of classical molecular structure only C-H stretching vibrations occur. This holds for any combination of different aromatic (sp^2), olefinic (sp^2) and aliphatic (sp^3) groups within a molecule. Considering the low amplitude motions in our analysis we did not find the signatures of other types of vibrations in this spectral region.
- For the above types of molecules the aromatic (sp^2) C-H vibrations do not show any common wavelength coverage with aliphatic (sp^3) stretching modes (non-overlap wavelength range). The vibrational motions of these two types of C-H bonds are reported to be uncoupled.
- Olefinic (sp^2) C-H stretching shows a common wavelength coverage with aromatic (sp^2) C-H vibrations (overlapped wavelength ranges). However, vibrational motions of these two bond types occur independently without any couplings.
- Olefinic (sp^2) C-H stretching motion couples partly with aliphatic (sp^3) C-H vibrations.
- These vibrational characteristics of olefinic C-H stretching motions can glue the wavelength range of aliphatic (sp^3) and aromatic (sp^2) C-H stretching vibrations. In other words, they can make an indirect coupling between these two uncoupled and non-overlapped vibrational motions. This effect can be considered as one of the origins of the formation of a plateau in this spectral region.
- The symmetric and asymmetric C-H stretching motions of methyl and methylene groups are highly coupled with common wavelength coverage of the resultant features. Thus, vibrational motions of these two functional groups in this wavelength region are difficult to discriminate against under different UIE features.
- In neutral honeycomb PAH molecules, the stretching vibrations of C-H bonds in the bay and non-bay positions show considerable coupling in addition to their common wavelength coverage.

3. New Results from This Work

The results presented here are from new quantum chemical calculations performed within density functional theory using mathematical tools to solve the Schrodinger equation for molecular systems (B3LYP and BHandHLYP functionals, in combination with a PC1 basis set family). This model delivers an average error of 0.12–0.13 μm (within the wavelength range of 2 to 20 μm) in reproducing the fundamental bands of laboratory gas-phase IR spectra for the different classes of organic molecules [9]. The effects of anharmonicity in vibrations and rotational-vibrational couplings on final IR bands wavelength positions are considered by applying the Laury et al. [25] scheme of double-scale factors for harmonic normal-mode calculations.

3.1. The 3 μm Region

Models: PAH, PAHs with Side Groups, Aliphatic Hydrocarbons and MAONs

Although this part of the emission spectra seems to be well explored in terms of the types of vibrational motions in the framework of cited astrochemistry models, plateau formation, the flux ratio of bands used to estimate the aliphatic/aromatic contents of UIE carriers, the long wavelength UIE features (such as the 3.51 μm peak assigned to nano-diamond structures) and the relationship of these features to the other UIEs at different IR wavelengths have remained unsolved issues. A comprehensive vibrational analysis and classification of normal modes will play a key role in addressing these issues. Specifically, we found that by keeping the molecular structure of organic compounds within the

framework of classical Lewis model of bonding and structure the classifications and assignments of normal modes are not simple and definite as implied from the customary (empirical) approach. Perhaps classifications, assignments, and interpretation of vibrational motions underlying IR bands within the empirical approach would be ambiguous for non-classical molecular structures such as an amorphous type complex hydrocarbon molecule shown in Figure 1. Here a modern and advanced molecular chemical bonding and structure theory such as the quantum theory of atoms in molecules should be recalled to assist the interpretation [26–28].

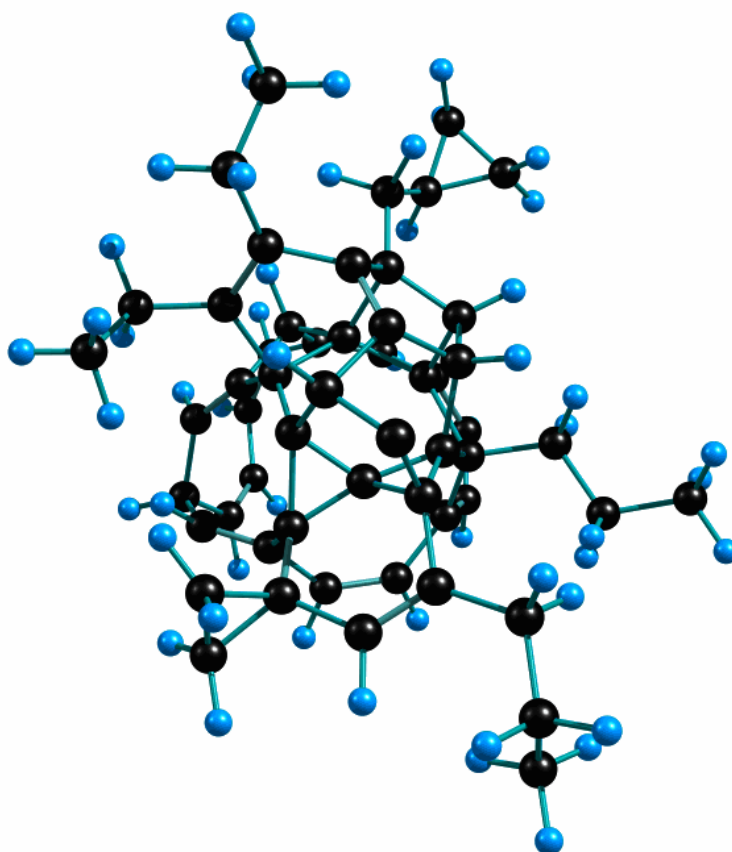


Figure 1. Local minimum geometry of an amorphous type complex hydrocarbon molecule ($C_{55}H_{52}$) at B3LYP/PC1 model. The molecule is composed of non-classical core and classical side groups.

3.2. The 6–10 μm Region

Model Used: PAH

Figure 2 summarizes the results of our new, quantitative vibrational analysis followed by statistical manipulations within the wavelength step size of 0.1 μm , performed on all normal modes of a set of 70 neutral honeycomb PAH molecules with the size of 6 to 136 carbon atoms [19,23]. Based on this new mathematical analysis we find that:

- All normal-mode vibrations (IR and Raman active modes) within this wavelength range occur in the symmetry plane of the PAH molecule. They are all in-plane modes. We did not detect any low amplitude out of plane modes through our quantitative analysis.
- All vibrations are reported as highly coupled modes. This includes the 6.2 μm feature described as an uncoupled C-C stretching band (zone (a) in Figure 2). Only the wavelength range of 8.6 to 8.9 μm is found to contain pure aromatic C-H in-plane bending modes (zone (c) in Figure 2).

These pictures of vibrations, derived and assigned purely from theory, are in very good agreement with the results of experimental spectroscopy reported by Jobelin et al. [29] from IR spectra of

numbers of PAH molecules. *This agreement with experimental work demonstrates the reliability of our quantitative vibrational analysis methodology which is a key point to exploring the origin of UIE bands at longer wavelengths.*

- In Figure 2 we have labeled and described these vibrations as coupled C-C stretching and C-H in-plane modes. These are commonly used labels. These types of motions also occur at longer wavelengths in PAH molecules. We explain later a possible way of discriminating such vibrations and assigning them to intrinsic fragments. It should be mentioned that the comprehensive vibrational analysis of this 6–10 μm region and the 3 μm part of the spectra has led us to suggest that the olefinic carrier of the 6 μm UIE feature observed in the famous protoplanetary red rectangle nebulae HD44179 [22]. This feature was previously assigned to CO molecule.

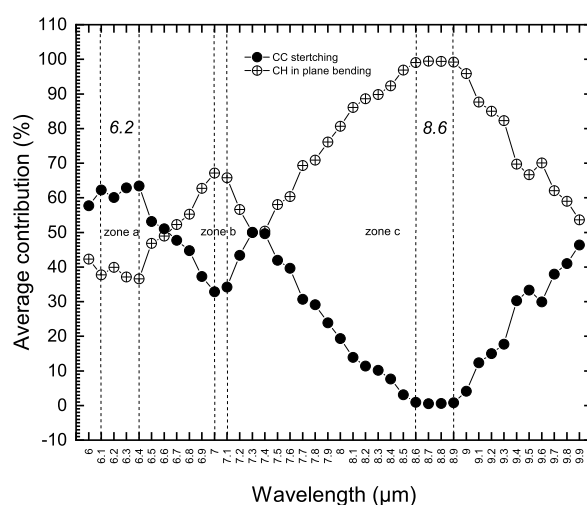


Figure 2. The newly calculated changes in average contributions of aromatic C-C stretching and C-H in-plane bending modes in neutral honeycomb PAH molecules.

3.3. The 11–15 μm Region

Mode Usesl: PAH

For neutral planar honeycomb PAH molecules, this wavelength range contains two major types of motions. They are either in-plane or out of molecular plane vibrations. We did not detect any vibrational motions composed of both types of these vibrations. Each of these two major types of vibrations has their own subdivision vibrations, where the out of plane bending mode of aromatic C-H bondings is one of the well-known categories. The origin of each UIE feature in this wavelength range is complex and cannot be assigned by one label. By filtering all coupled vibrational motions, it is found that the pure uncoupled C-H out of plane bending modes vibrate at different frequencies, independent of their classical exposed edge origin [23].

3.4. Skeletal Modes

Model Used: MAONs

One of the ambiguous concepts in vibrational analysis is the concept of the skeletal mode (or skeleton mode). Usually, this refers to the vibrational motion of a part of the molecules composed of elements heavier than hydrogen, such as the C-C stretching mode in PAH molecules [2]. Such a picture is also satisfied by the other types of vibrational motions over both short and long wavelength ranges in different classes of organic molecules. This concept is becoming more confusing by introducing heteroatoms such as nitrogen, oxygen, sulfur, etc... into the structure of organic molecules.

Here we provide an alternative way to define skeletal mode by considering all atoms not only heavy ones. We chose the MAON model [8], because of its 3D structural diversity. The results of vibrational analysis of 17,257 normal modes (IR and Raman active modes) of 56 MAON type molecules are plotted in Figure 3 from 2 to 30 μm . All MAONs were composed of benzene, methyl, and methylene classical functional groups. The statistical analysis has been carried out within the wavelength interval of 0.1 μm . The simulated IR signature of these MAONs can be found in [21]. Such a statistical plot (Figure 3) can be obtained for any class of organic molecule by applying our methodology [9].

In Figure 3, the smallest number of total atoms that contributes to the vibrations obtained within a 0.1 μm interval is plotted against wavelength. On average this number shows a sudden increase from 14.4 μm towards longer wavelengths. This enables us to split the IR spectra of MAONs into two major regions (Figure 3). We suggest that the long wavelength section is labeled as the skeletal mode section. Here the vibrational motions are delocalized in nature. The short wavelengths section which contains localized vibrations (i.e., a smaller number of atoms are involved) is labeled as bonding modes.

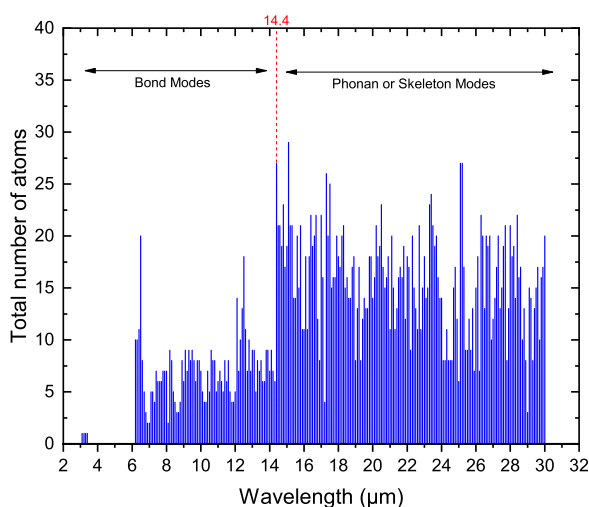


Figure 3. A new plot presented for the first time of statistical analysis done on the results of displacement vector matrix analysis of 17,257 normal modes (all Raman and IR active modes) in 56 different mixed aromatic-aliphatic organic nanoparticles (MAON) type molecules. Statistical analysis performed within the wavelength interval of 0.1 μm from 2 to 30 μm . The abrupt change in the total number of participant atoms occurs at a wavelength of ~ 14.4 μm . Two regimes of vibrational motions are distinguishable as bond(bonding) and skeletal(skeleton) modes in MAON molecules.

4. Conclusions

Despite the harsh conditions, the rich chemistry of proto- and planetary nebulae is seen in their strong UIE bands. Here, new quantitative and comprehensive results of displacement vector analysis of normal modes are reported for PAH molecules in the range of (6–10 μm)—see Figure 2. The C-C stretching, C-H bending coupling diagram (Figure 2), provides theoretical explanations for laboratory experimental observations as well as describing UIE band origin in a quantitative way in light of the PAH model. The analysis of $>17,000$ vibrational normal modes of MAONs with different numbers of atoms and structures within the range of (2–30 μm) are presented for the first time (Figure 3). This shows a boundary at 14.4 μm between two regimes of complex molecular motions and provides clues to the bond(s) and fragment(s) responsible for different IR features. With such valuable quantitative information, modeling the structure of unknown UIE carriers and further computations on their spectroscopic properties are performed effectively. With the correct description of the molecular vibrations underlying the UIE bands, we can get closer to explaining the mechanism of the formation of another spectacular feature of UIE bands, i.e., the plateaus at 8, 12, 17 and 21 μm . It should be emphasized that this type of molecular vibrational motion analysis

is not restricted, like customary empirical approaches, to the molecules with classical bond types, fragments, and functional groups. The complex molecular vibrations in Figure 1 with non-classical bond types and structure (and unlimited numbers of such molecules), can be analyzed. This will push the modeling of UIE carriers to include new species with exotic properties.

Hence, computational quantum chemistry provides vital theoretical resources to discover the molecular carriers of these mysterious bands. This is currently performed by modeling the spectroscopic properties of large numbers of complex organic molecules. The calculated data is then processed via vibrational analysis for interpretation of the origin of UIE features. This provides valuable information linking the spectra to molecular structure. This assists further modifications of the proposed astrochemistry molecular models. Although the link between molecular structure and IR features is a complex relationship and sometimes confusing, our present results of vibrational analysis on thousands of normal modes on different classes of organic molecules can contribute significantly in addressing the vibrational origin of UIE bands and their unknown molecular carriers.

Author Contributions: S.S. undertook all the mathematical modelling based on the existing collaboration and wrote the bulk of the manuscript. Q.A.P. as supervisor provided some oversight, critique, discussion, vetting and re-writing of certain aspects of the paper.

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