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Heat capacity prediction for polynuclear aromatic solids using vibration spectra

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Abstract

Heat capacity, at constant pressure and volume, are important thermodynamic parameters for solids. C_p is accessible experimentally, from near 0 K to the melting point, while C_V is more accessible by computation. The connection between heat capacity and internal energy and entropy, the generation of solid–fluid phase diagrams and its close relation to molecular structure and atomic scale vibrations are well known. Thus, heat capacity has many direct uses and also has the potential to provide insights into the structure, mean molar mass, and phase behavior of poorly defined aromatic hydrocarbon fractions of industrial interest such as vacuum residues and asphaltenes that are not otherwise available. Infrared, far infrared, Raman and photo acoustic spectra are readily obtained experimentally. However, technical restrictions related to the detection and characterization of such spectra for polynuclear aromatic compounds limit the development of models for predicting heat capacity using experimental vibration spectra. In this paper, two approaches, one relying primarily on experimental spectra, and one based on direct calculation of spectra using density functional theory are presented and their potential for application discussed.

Keywords: Heat capacity; Polynuclear aromatic; Vibration spectra; Prediction; Solids

1. Introduction

Diverse average molecular structures have been proposed for asphaltenes and other ill-defined petroleum fractions obtained in some cases from the same sources and analyzed in a broadly similar manner [1,2]. Proposed average structures range from pendant core models, characterized by a single large central polynuclear aromatic + naphthenic sheet with multiple but short alkane chains connected to it, to archipelago models, characterized by multiple but small polynuclear aromatic + naphthenic sheets interconnected with alkane chains. A central and unresolved question in this literature is which of these two structural models more closely approaches the average structure for these ill-defined petroleum fractions. Further, the phase behavior of these fractions is a key building block for the development of processes for both production and refining. Heat capacity at either constant pressure or volume is a tool for probing molecular structure and phase transitions associated with ill-defined petroleum fractions because of the close relation between molecular structure, vibration spectra, and heat capacity—particularly in the solid state. Preliminary heat capacity measurements for a number of fluids of industrial interest and asymptotic calculations suggest that it should be possible to discriminate between these two proposed molecular prototypes using heat capacity measurements coupled with vibration spectra [3], because one expects the heat capacity of the more flexible “archipelago” molecular prototype to be significantly greater than the heat capacity of the more rigid “pendant core” molecular prototype [1,2]. This interest led us to examine heat capacity prediction methods for polycyclic aromatic hydrocarbon solids as a first step toward developing more generalized models for ill-defined petroleum fractions, such as bitumen, residues, and asphaltenes, which typically possess aromatic carbon contents exceeding 50%. A variety of methods and models are presented in the literature, based on atomic and molecu-

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lar modeling, including basic quantum physical approaches [4–7] and now standard computational routines available in commercial codes such as Gaussian [8]. We are also able to draw upon the vast literature related to the vibrational analysis of polymers (cf. [9]). However, relevant data for polycyclic aromatic hydrocarbons is limited. For example, the gas-phase infrared spectrum for coronene was measured only a few years ago and its Raman spectrum remains incomplete [10].

1.1. Vibrational analysis

Infrared and Raman spectra both reflect atomic and molecular vibrations. Some motions are not infrared active, but may be Raman active. For molecules with a center of symmetry the so-called "*rule of mutual exclusion*" which states that fundamentals appearing in an observed infrared spectrum do not appear in an observed Raman spectrum, and conversely, those appearing in an observed Raman spectrum do not appear in an observed infrared spectrum may be applied. Some vibrations may also be absent from both observed infrared and Raman spectra. It is also generally true that for molecules without a center of symmetry most vibration frequencies are observed in both infrared and Raman spectra [11]. As strong Raman and infrared active vibrations rarely coincide, these spectroscopic techniques can be viewed in general as complementary [12]. Measurement temperature and the physical state of a sample affect the observed spectrum, both in infrared and Raman spectroscopy. While the spectra for a pure solid, liquid and gas are similar, there are frequently fundamental vibrations active in one state but inactive in one or more of the others, especially for large molecules [13]. Further, published data in this field focuses on the "finger print region" used for characterization. Low frequency vibrations, important for heat capacity calculation, are often not measured or reported.

Polynuclear aromatic rich petroleum fractions such as asphaltenes possess reported molecular masses in the range 500–5000 amu and form strongly associated structures with leading dimensions up to over 50 nm. At this point it is not clear whether heat capacity modeling approaches used for polymers are appropriate for this case even though their heat capacities can be correlated using them [3]. Infrared and Raman spectra for typical polymers and their constituent monomers are similar and relatively simple. It has been shown that for a polymer having a repeat unit of n atoms, only $3n$ vibrations, including six vibrations for rotations and translations of the chain as a whole, can arise. Depending on the symmetry properties of the crystal, only part of the $3n$ unit cell vibrations may show some spectral activity [14]. As monomers are well-defined for this case, vibrational spectroscopy in conjunction with accurate quantum mechanical modeling can be used to resolve structural issues, central to the understanding of the properties of polymers [15]. Wunderlich and his colleagues have published extensively on vibrational analysis and the measurement and modeling of the heat capacities of polymers [16–18]. Their results are summarized in the ATHAS databank [19] where they distinguish between skeletal and group vibrations in their correlative models. In addition to the assignment of experimental vibrational frequencies an additional parameter, a measure of the size of vibrating groups, is used to fit experimental heat capacity data. Thus, their method may only be used in the presence of experimental heat capacity data. It is not clear if the mean molar masses and structures of polynuclear aromatic petroleum fractions present in bitumen and crude oil warrant the inclusion of this additional parameter.

1.2. C_V models based on molecular vibration

Heat capacity at constant volume comprises two parts, namely, the energy associated with lattice vibration and the energy associated with atomic vibration, six frequencies and $3n-6$ frequencies, respectively. Each is addressed separately below.

1.2.1. Atomic vibration

Early modeling attempts considered simple monatomic pure materials such as metals. The first significant improvement was the approach proposed by Einstein [20] who considered a lumped model for atomic vibrations. It was a major step forward and in a sense a final step, when Einstein applied the quantum theory of Planck to the motion of atoms in a solid. In Einstein's theory for heat capacity, the motion of atoms is idealized by assuming that a representative atom vibrates in the potential field of all other atoms, taken to be at rest, and that the potential field is isotropic. The energy contribution from each atom can then be written as the energy of three linear harmonic oscillators each associated with the same frequency value [21] and the contribution to the molar heat capacity at constant volume becomes:

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{\exp\left(-\frac{\theta_E}{T}\right)}{\left[1-\exp\left(-\frac{\theta_E}{T}\right)\right]^2} \qquad (1)$$

where $\theta_E = h\nu_E/k$, ν_E is the vibration frequency, k the Boltzmann's constant, h the Planck's constant, and R is the ideal gas constant.

It is further assumed that the energy of these oscillators is governed by the laws of quantum mechanics, i.e.: that they can only vary by amounts which are multiples of $h\nu_E$ [22]. Montroll [23] extended Einstein's equation by considering the inclusion of normal mode frequencies of a crystal with $3n$ degrees of freedom as $\nu_1, \nu_2, \ldots, \nu_{3n}$. C_V then becomes:

$$C_V = R\sum_{i=1}^{3n}\left(\frac{\theta_i}{T}\right)^2 \frac{\exp\left(-\frac{\theta_i}{T}\right)}{\left[1-\exp\left(-\frac{\theta_i}{T}\right)\right]^2} \qquad (2)$$

While Cheban et al. [24] reiterate that the Einstein equation is an excellent base for C_V prediction when a full frequency