Intramolecular anharmonicity in the naphthalene molecule: thermodynamics and spectral effects

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The anharmonicity of the ground electronic state of the naphthalene molecule has been investigated using a tight-binding potential energy surface model. The vibrational density of states is calculated from a mixed classical quantum theoretical approach. The primary assumption of this model is that the evolution of the mean anharmonic quantum energy as a function of temperature follows the classical evolution. From the thermal expansion of the classical free energy obtained using a reversible-scaling method, the mean vibrational frequency has also been determined as a function of temperature.

1. Introduction

In recent years, polycyclic aromatic hydrocarbons (PAH) have been proposed as likely emitting molecules of the unidentified infrared bands from the interstellar medium.[1,2] These IR bands have been observed, with strong emission features, at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm. On the basis of these spectroscopic signatures, the presence of large aromatic molecules has been proposed. However, many questions are not at all elucidated. As examples, the size distribution, the degree of ionization and the stability of such molecules with respect to the UV excitation sources from nearby stars are still open questions. Another important issue is the evolution of the IR active frequencies with vibrational temperature. Indeed when a PAH absorbs a UV stellar photon, the molecule is electronically excited. As internal conversion is a very efficient process in this class of large molecules, the molecular system becomes rapidly highly vibrationally excited in the ground electronic state but stays rotationally and translationally cold. This transient heating mechanism of very small grains has been first proposed by Sellgren.[3]

One major channel for the de-excitation of these highly vibrationally excited molecules is the infrared radiation emission. Many experimentalists are very interested in this problem. High-temperature absorption spectra have already been collected.[4–6] More recently infrared emissions of highly excited PAH molecules following a UV excitation have also been measured.[7–14] Both vibrational shifts and spectral broadenings with respect to temperature have always been observed significantly.

From a theoretical point of view, many workers have brought valuable information on the vibrational frequencies from *ab initio* calculations.[15–17] These calculations are very powerful to give spectroscopic features in the low temperature regime for which the harmonic approximation remains valid. However, they do not provide any information regarding the anharmonicity effects of the potential energy surface on the IR vibrational frequencies. Recently an alternative procedure in which the potential energy surface is built from a tight-binding framework has been developed in our group.[18] The major interest of such a simplified electronic approach is that the IR spectrum for a vibrationally hot molecule can be directly obtained from tight-binding molecular dynamics simulations. Spectroscopic data as a function of vibrational temperature can then be deduced from such these spectra for the neutral molecules as well as for their cations.[19]

In this context the detailed modelling of the emission IR spectra under astrophysically relevant conditions has been the concern of several recent studies.[21–23] In order to simulate the IR emission intensity profile, they essentially need a key thermodynamical function, namely the microcanonical vibrational density of states. Usually the harmonic quantum density of states (HQDOS) is used. However, it is more rigorous to deal with the anharmonic quantum density of states (AQDOS) when the potential energy surface anharmonicity is not negligible.

In this article, after describing the theoretical backgrounds (Section 2), we present the results of our calculations, specifically performed in the case of the naphthalene molecule (Section 3). The values of the AQDOS obtained using the model developed recently by us[24] are given first. We then analyze the temperature effect on the vibrational frequencies using an alternative method based on the calculation of the classical free energy as a function of temperature $F(T)$. The reversible-scaling method, proposed by de Koning *et al.*,[20] is employed for this purpose. The knowledge of $F(T)$ leads to the temperature dependence of the normal mode frequencies. This temperature dependence can be understood as a thermal average of the intramolecular frequencies.

2. Numerical procedure

Before focusing on the theoretical tools necessary for the calculations of the anharmonic quantum density of states and of the evolution of the mean vibrational frequencies as a function of temperature, we first describe the potential energy model from which classical canonical or microcanonical simulations can be easily generated for molecules as large as naphthalene.

2.1. Potential energy surface

The potential energy surface for the ground electronic state of the $C_{n_C}H_{n_H}$ system built using the semi-empirical tight-binding

formalism has been described in detail elsewhere.[18] There has been considerable interest in this model for application to quite large systems in cluster physics and in solid-state physics. By accounting, in a simple way, for the quantum mechanical nature of bonding, the simulation of the dynamics of such these systems is much faster than that of *ab initio* methods. Briefly, the tight-binding Hamiltonian can be written as:

$$H_{\mathrm{TB}} = \sum_i \frac{p_i^2}{2m_i} + \sum_i \sum_{j>i} V_{\mathrm{core}}^{(i,j)}(r_{ij}) + V_{\mathrm{TB}}(\{\boldsymbol{r}\}) \qquad (1)$$

In this expression the first term corresponds to the total kinetic energy of the nuclei and the second, describing short-range repulsions between the core atoms, has been taken simply as a sum of diatomic potentials which have the following analytic form:

$$
\begin{aligned}
V_{\mathrm{core}}^{(i,j)}(r_{ij}) = {} & V_{\mathrm{core}} \left(\frac{r_0}{r_{ij}} \right)^{m_a} \\
& \times \exp \left\{ m_b \left[-\left(\frac{r_{ij}}{r_c} \right)^{m_c} + \left(\frac{r_0}{r_c} \right)^{m_c} \right] \right\}
\end{aligned}
\qquad (2)
$$

The V_{core}, r_0, r_c, m_a, m_b and m_c parameters for each bond type have been reported in the previous paper. Finally, the last term in eqn. (1) corresponds to the electronic tight-binding potential which is defined by:

$$V_{\mathrm{TB}} = \sum_l n_l \langle \Psi_l | h_{\mathrm{TB}} | \Psi_l \rangle + U \sum_l \delta_{n_l,2} \qquad (3)$$

The first contribution to V_{TB} corresponds to the sum of the molecular eigenvalues of all the molecular states $|\psi_l\rangle$. The number of electrons in the lth molecular state is noted n_l. The second contribution in this equation will be discussed hereafter. The Hamiltonian operator h_{TB} is expressed in terms of atomic orbitals as:

$$
\begin{aligned}
h_{\mathrm{TB}} = {} & \sum_{i,\alpha} \varepsilon_\alpha^{(i)} \left| \varphi_\alpha^{(i)} \right\rangle \left\langle \varphi_\alpha^{(i)} \right| \\
& + \sum_{i,\alpha} \sum_{j,\beta} t_{\alpha,\beta}^{(i,j)}(r_{ij}) \left| \varphi_\alpha^{(i)} \right\rangle \left\langle \varphi_\beta^{(j)} \right|
\end{aligned}
\qquad (4)
$$

where $|\varphi_\alpha^{(i)}\rangle$ and $\varepsilon_\alpha^{(i)}$ correspond to the atomic orbital α centered on the lth atom and its eigenvalue (given parametrically in ref. 18), respectively. The elements of the h_{TB} matrix, called the hopping matrix elements, correspond to the interaction between the atomic orbitals. The radical elements $t_{\alpha,\beta}^{(i,j)}(r_{ij})$ are assumed to follow the same radial dependence as the repulsive part of the potential [see eqn. (2)]. The angular part of the hopping matrix elements for the s–p and p–p interactions are calculated following the initial work of Slater.[25]

The eigenstates $|\psi_l\rangle$ and their eigenvalues are obtained by the matrix diagonalization procedure. The matrix dimension depends on the orthogonal atomic orbital basis set. The number of basis functions has to be chosen reasonably low in order to save computing time. In our system of interest, only the occupied valence atomic orbitals are considered (2s and 2p orbitals for carbon and the 1s orbital for hydrogen). Consequently, a $C_{n_C}H_{n_H}$ system involves the construction of an $(N \times N)$ matrix with $N = 4n_C + n_H$.

If the lth molecular state is written as $|\psi_l\rangle = \sum_{a,k} c_{a,k}^{(l)} |\varphi_a^{(k)}\rangle$, the tight-binding potential energy finally reads:

$$V_{\mathrm{TB}} = \sum_l n_l \sum_{i,\alpha} \sum_{j,\beta} c_{i,\alpha}^{(l)*} c_{j,\beta}^{(l)} \left\langle \varphi_\alpha^{(i)} \middle| h_{\mathrm{TB}} \middle| \varphi_\beta^{(j)} \right\rangle + U \sum_l \delta_{n_l,2} \quad (5)$$

The last term in this expression is an empirical way of taking into account the electron–electron interaction. Due to the positive value of U (see ref. 18), the system is less stable when two electrons are located on the same molecular orbital.

From our tight-binding molecular dynamics simulations, computed data on equilibrium geometry and harmonic frequencies have been obtained for naphthalene and compared with both *ab initio* results and data derived from experiment. A detailed discussion of these results can be found in our previous work.[18]

2.2. The anharmonic quantum density of states calculation

We have recently proposed a model for calculating the anharmonic quantum density of states for large systems.[24] We shall give here some streamlines of this model.

Consider a separable Hamiltonian H_0 composed of n harmonic oscillators, the quantum harmonic mean energy ($\langle E^{(\mathrm{h,q})} \rangle$), heat capacity ($C^{(\mathrm{h,q})}$) and partition function ($Q_\beta^{(\mathrm{h,q})}$) can be expressed analytically. These three thermodynamical functions at a given inverse temperature β are totally defined *via* the knowledge of the harmonic normal mode frequencies. It is well known[26] that the HQDOS can be assessed from the three analytic thermodynamical functions abovementioned. Within this theoretical framework, the quantum harmonic density of states, $\Omega^{(\mathrm{h,q})}(E)$, is assumed to follow the analytical form given by:

$$\Omega^{(\mathrm{h,q})}(E) = a(E - b)^c \qquad (6)$$

where a, b and c are *adjustable* parameters which can be determined from $\langle E^{(\mathrm{h,q})} \rangle_\beta$, $C^{(\mathrm{h,q})}$ and $Q_\beta^{(\mathrm{h,q})}$. The function $\Omega^{(\mathrm{h,q})}(E)$ is obviously defined only when the vibrational energy is larger than b. A similar generalised expression of density of states in a semi-empirical approach had been proposed by Whitten and Rabinovitch[27] following the former Marcus and Rice work.[28]

Analytical expressions of the a, b and c parameters can be straightforwardly derived.[26] These three parameters are *temperature dependent* and must therefore be calculated in the temperature range of interest: the estimation of the microcanonical density of states at energy E must be performed *via* the calculation of a, b and c at temperature for which $\langle E^{(\mathrm{h,q})} \rangle_\beta \simeq E$. From this last equality, it is not possible to express analytically the temperature as a function of energy E so that analytical expressions of a, b and c cannot be given explicitly as a function of E. The HQDOS obtained by this method in the case of naphthalene is in very good agreement with that deduced from the exact counting method proposed by Stein and Rabinovitch (see Fig. 1).[29] By extending the model of Borjesson *et al.*[26] to the case of anharmonic systems, it has been shown[24] that the AQDOS can be calculated from three new parameters a', b' and c' associated with the *anharmonic* Hamiltonian.

As was assumed previously,[24] the evolution of the mean anharmonic quantum energy as a function of temperature can
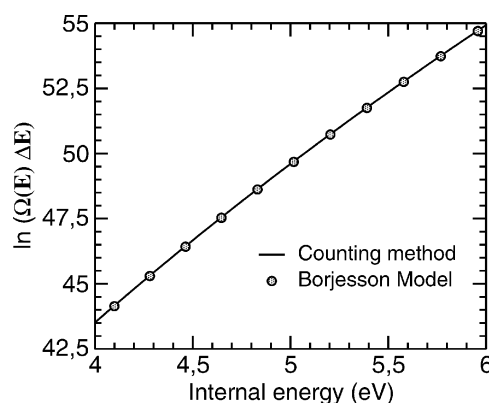
Fig. 1 Logarithm of the harmonic density of states $\Omega(E)$ calculated from the counting method[29] and from the Borjesson model[26] [see eqn. (6)]. The interval energy ΔE has been taken equal to 0.0124 eV.

be described by the following relationship:

$$\langle E^{(a,q)} \rangle_\beta = \langle E^{(h,q)} \rangle_\beta + g(\beta) \langle E^{(h,cl)} \rangle_\beta + (E_{ZPE}^{(a)} - E_{ZPE}^{(h)}) \quad (7)$$

In this expression, $E_{ZPE}^{(h)}$ and $E_{ZPE}^{(a)}$ correspond, respectively, to the zero-point energy in the harmonic and anharmonic cases. The dimensionless classical anharmonic function, $g(\beta)$, is defined by:

$$g(\beta) = \frac{\langle E^{(a,cl)} \rangle_\beta - \langle E^{(h,cl)} \rangle_\beta}{\langle E^{(h,cl)} \rangle_\beta} \quad (8)$$

In our previous paper,[24] it was demonstrated that the c' parameter can be written as:

$$c' = c + n\left(g(\beta) - \beta \frac{dg(\beta)}{d\beta}\right) \quad (9)$$

in which n is the number of degrees of freedom.

The b' parameter can be expressed as a function of the harmonic b parameter by the relation:

$$b' = b + n\frac{dg(\beta)}{d\beta} + (E_{ZPE}^{(a)} - E_{ZPE}^{(h)}) \quad (10)$$

Finally the a' parameter is given by:

$$a' = a\frac{c!}{c'!}\frac{\exp[\beta(b'-b)]}{\beta^{(c'-c)}}\frac{Q_\beta^{(a,q)}}{Q_\beta^{(h,q)}} \quad (11)$$

in which the quantum partition function ratio $Q_\beta^{(a,q)}/Q_\beta^{(h,q)}$ is obtained from:

$$\frac{Q_\beta^{(a,q)}}{Q_\beta^{(h,q)}} = \exp\left[(1-\alpha)\beta E_{ZPE}^{(h)} + n\int_\beta^{\beta_0} \frac{g(x)}{x}dx\right] \quad (12)$$

The α constant, defined by $E_{ZPE}^{(a)} = \alpha E_{ZPE}^{(h)}$, has been estimated using the semi-classical adiabatic-switching method (see further section).

It has been shown[24] that the ratio $Q_\beta^{(a,q)}/Q_\beta^{(h,q)}$ is in fact independent of the choice of β_0 (eqn. (12)), the only condition on β_0 being that $1/\beta_0$ has to be much smaller than the lowest frequency of the molecular system concerned.

We now look more precisely at the analytical expressions for a', b' and c'. It is obvious that only the $g(\beta)$ function and the α parameter are required. The two following sub-sections describe the theoretical methods used to determine numerically their values.

2.3. Canonical Nosé–Hoover simulation

The mean classical energy $\langle E^{(a,cl)} \rangle_\beta$ at a constant temperature β must be calculated on the "real" anharmonic potential energy surface in order to evaluate the function $g(\beta)$ (see eqn. (8)). For this purpose, the Nosé–Hoover algorithm[30] has been employed. It permits the calculation of the energy probability density (and thus its mean value) in the canonical ensemble. In this formalism, the physical system (a sub-system) interacts with a fictitious degree of freedom s which mimics the heat bath (another sub-system). It has to be noted that we have not necessarily employed the Nosé–Hoover chains formalism here[31] due to the large number of degrees of freedom of our molecular system.

According to Nosé,[30] the new Hamiltonian H of the whole system can be written as:

$$H = H_{TB} + nk_BT\ln(s) + \frac{s^2 p_s^2}{2Q} \quad (13)$$

where p_s is the momentum associated to the coordinate s and H_{TB} corresponds to the tight-binding Hamiltonian described previously. An energy flow (governed by the Q parameter) becomes possible between the two sub-systems. This parameter

has to be chosen such that the typical periods of the energy fluctuations are of the same order of magnitude as the typical periods associated to the intramolecular motions. Hamiltonian equations are solved using a fifth-order Adams–Moulton predictor–corrector algorithm. The typical time step for the canonical simulation of the naphthalene molecule was 0.1 fs.

2.4. Adiabatic-switching method

The adiabatic-switching method[32] has been used in order to calculate the α value (see eqn. (12)), which is directly linked to the displacement of the zero-point energy (ZPE) induced by the anharmonicity of the potential energy surface. Within this semi-classical method, the invariance of the vibrational quantum numbers in an adiabatic transformation is used. The adiabatic transformation between the harmonic Hamiltonian H_{harm} and the anharmonic tight-binding Hamiltonian H_{TB} is achieved from $t = 0$ to $t = t_{AS}$ using a time-dependent Hamiltonian $H(t)$:

$$H(t) = f(t) H_{TB} + (1 - f(t)) H_{harm} \quad (14)$$

Following the work of Johnson,[33] the $f(t)$ function has been taken as:

$$f(t) = -\left(\frac{t}{t_{AS}}\right)^4 \times \left[20\left(\frac{t}{t_{AS}}\right)^3 - 70\left(\frac{t}{t_{AS}}\right)^2 + 84\left(\frac{t}{t_{AS}}\right) - 35\right] \quad (15)$$

Consequently the time dependent Hamiltonian is evolving slowly from the separable normal mode harmonic Hamiltonian to the real anharmonic Hamiltonian of the system. For a given set of vibrational quantum numbers in H_{harm}, it is trivial to find initial conditions which satisfy the semi-classical quantization. The Hamiltonian $H(t)$ is then considered and the final energy at the end of the adiabatic procedure will correspond to the ZPE if all the initial quantum numbers are set equal to zero. The typical adiabatic-switching simulation time t_{AS} was taken to be equal to 8 ps.

2.5. Reversible-scaling method

Recently, de Koning et al.[20] have proposed an elegant method, the so-called reversible-scaling, which allows the simulation of the temperature dependence of the classical free energy in an anharmonic system. In this method, the evolution of the free energy between $T_{min} = T_0/\lambda(t = 0)$ and $T_{max} = T_0/\lambda(t_{max})$ (the time-dependent functional form of λ will be given hereafter) is calculated by scaling the potential energy function from $\lambda(t = 0) V_{TB}(r)$ to $\lambda(t_{max}) V_{TB}(r)$ in the canonical ensemble.

It can be found that the free energy $F(T)$ of the system follows the very simple relation:

$$F(T) = \frac{T}{T_0}F(T_0) + \frac{nk_BT}{2}\ln\left(\frac{T}{T_0}\right) + \frac{T}{T_0}\int_0^t \frac{d\lambda}{dt}\bigg|_{t'} V_{TB}(r)dt' \quad (16)$$

where $T = T_0/\lambda(t)$.

The integral $W(t) = \int_0^t d\lambda/dt|_{t'} V_{TB}(r)dt'$ is calculated using a Nosé–Hoover simulation at T_0 yielding a time dependent potential energy. Following the prior paper of de Koning et al.,[20] the time evolution of the λ parameter has been taken as $\lambda(t) = 1 - t/t_0$ from $t = 0$ to t_{max}. This unique canonical simulation allows theoretically the extraction of the free energy between T_0 and $T_0/[1 - (t_{max}/t_0)]$. In all the simulations, t_0 has been taken equal to 20 ps. For the particular case of the naphthalene molecule, the lowest temperature T_0 has been taken as 100 K for which the free energy $F(T_0)$ has been reasonably estimated in the harmonic approximation. The

reversible-scaling method has been applied up to $T_{max} = 4200$ K. Between T_0 and T_{max}, eight temperature intervals have been considered in order to minimize the absolute uncertainty on F, induced by the errors in the calculation of the integral $W(t)$ when the potential energy surface is scaled.

Calvo et al.[34] have shown that it is possible, from the knowledge of $F(T)$, to connect a temperature-dependent effective normal mode frequency $\nu_i(T)$ with the evolution of F as a function of T. The frequency of this ith mode $\nu_i(T)$ has been developed as the thermal expansion:

$$\nu_i(T) = \nu_i^{(h)}\left(1 - \gamma_1 T + \frac{\gamma_2}{2}T^2 - \frac{\gamma_3}{6}T^3\right) \quad (17)$$

In this expression, $\nu_i^{(h)}$ corresponds to the harmonic normal mode frequency of the ith mode. The thermal expansion proposed above is in fact straightforwardly linked to the anharmonic character of the potential energy surface. From the thermal expansion of $\nu_i(T)$, the classical anharmonic partition function can be written as:

$$Q(T) = \frac{1}{\prod_{i=1}^{n} \beta h \nu_i(T)}$$
$$= \frac{(1 - \gamma_1 T + \frac{\gamma_2}{2}T^2 - \frac{\gamma_3}{6}T^3)^{-n}}{\prod_{i=1}^{n} \beta h \nu_i^{(h)}} \quad (18)$$

By definition, the free energy $F(T)$ is:

$$F(T) = -k_B T \ln Q(T) = F^{(h)}(T)$$
$$+ n k_B T \ln\left(1 - \gamma_1 T + \frac{\gamma_2}{2}T^2 - \frac{\gamma_3}{6}T^3\right) \quad (19)$$

in which $F^{(h)}(T) = k_B T \sum_{i=1}^{n} \ln(\beta h \nu_i^{(h)})$ corresponds to the harmonic free energy. The anharmonic free energy, obtained from the reversible-scaling method, can be fitted as:

$$F(T) = F^{(h)}(T) + k_B \sum_{p=1}^{3} \frac{(-1)^p \chi_p}{p!} T^{p+1} \quad (20)$$

Considering eqns. (19) and (20), the relations between the γ_n and the χ_n coefficients can be easily derived:

$$\gamma_1 = \frac{\chi_1}{n}$$
$$\gamma_2 = \frac{1}{n}\left(\chi_2 + \frac{\chi_1^2}{n}\right) \quad (21)$$
$$\gamma_3 = \frac{1}{n}\left(\chi_3 + \frac{3\chi_1\chi_2}{n} + \frac{\chi_1^3}{n^2}\right)$$

3. Results and discussion

3.1. Anharmonic quantum density of states

We now present the results from the calculation of the AQDOS for the naphthalene molecule. Within the potential energy surface calculated from the tight-binding approach, the normal mode frequencies of this molecule have been obtained by diagonalizing the Hessian matrix, evaluated at the equilibrium geometry. The harmonic zero-point energy has been found to be equal to $E_{ZPE}^{(h)} = 4.174$ eV. From the adiabatic-switching method, the anharmonic zero-point energy $E_{ZPE}^{(a)}$ has been deduced to yield an $\alpha = E_{ZPE}^{(a)}/E_{ZPE}^{(h)}$ parameter equal to 0.983.

The method proposed by Borjesson et al.[26] to calculate the harmonic density of states has been applied to the naphthalene molecule. The a, b and c parameters were calculated as a function of temperature. Eqn. (6) was used to calculate the HQDOS which was then compared to the exact counting method proposed by Stein and Rabinovitch.[29] In Fig. 1 these

two curves are shown from 4 to 6 eV to illustrate the excellent agreement between these two methods. The difference for $\ln(\Omega(E)\Delta E)$ between them is always less than 10^{-2}.

As explained in the previous section the calculation of the AQDOS needs for the classical anharmonicity function $g(\beta)$. This function has been estimated at various temperatures using a canonical Nosé–Hoover simulation. In such tight-binding potential energy surface, the $g(\beta)$ function is always positive and smaller than 1. The temperature dependence of the g appears to be approximatively linear with however, around $T = 1200$ K, a slight tendency to increase less rapidly with temperature.

Using the $g(\beta)$ function, the a', b' and c' parameters are calculated from eqns. (9)–(11) and compared to the harmonic a, b and c parameters. Thus the effects of the anharmonicity of the potential energy surface can be analyzed. In Fig. 2, all these parameters have been plotted as a function of temperature both in the harmonic and anharmonic cases.

It appears that $b' < b$ at low temperature, which is the direct consequence of the lower value of the calculated anharmonic zero-point energy $E_{ZPE}^{(a)}$ with respect to the harmonic zero-point energy $E_{ZPE}^{(h)}$. Indeed the major contribution to b' in the low temperature regime is the difference between the zero-point energy in the harmonic and anharmonic cases because $dg(\beta)/d\beta$ is very close to zero in this temperature domain. On the other hand, for temperatures higher than about 1000 K, b' becomes larger than b due to the fact that the evolution of b' is more and more governed by the contribution $ndg(\beta)/d\beta$ which is always negative. Thus, the global tendency is that the b' parameter decreases more rapidly than b as a function of T due to the anharmonicity.

The evolution of the difference between c and c' as a function of temperature can be easily understood by analyzing eqn. (9). At low temperature the functions $g(\beta)$ and $dg(\beta)/d\beta$ tends to zero, thus c' tends to c in this low temperature region. At higher temperature, the shape of the potential energy surface is such that the classical anharmonicity function is always positive and that $dg(\beta)/d\beta < 0$. Consequently c' is always found larger than c because the term $[g(\beta) - \beta dg(\beta)/d\beta]$ is positive.

Finally the evolution of the a and a' parameters are shown in Fig. 2(iii). As the values of these parameters depend on the two other's values, the influence of the anharmonicity of the
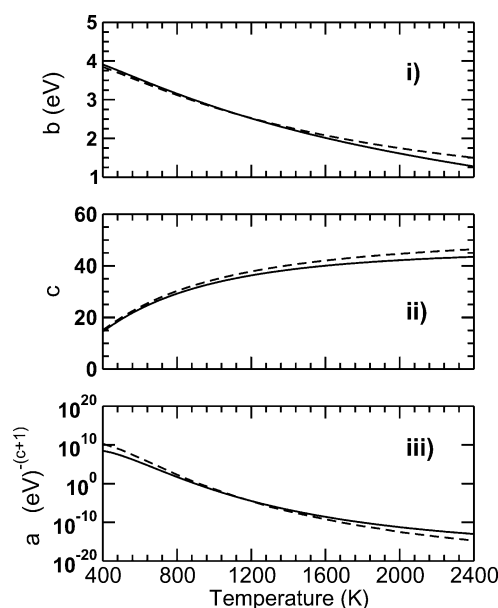

Fig. 2 The density of states parameters as a function of temperature: (i) b and b' (see eqn. (10)); (ii) c and c' (see eqn. (9)); (iii) a and a' (see eqn. (11)). The solid-lines correspond to the harmonic parameters (a, b and c) and the dashed lines to the anharmonic parameters (a', b' and c').
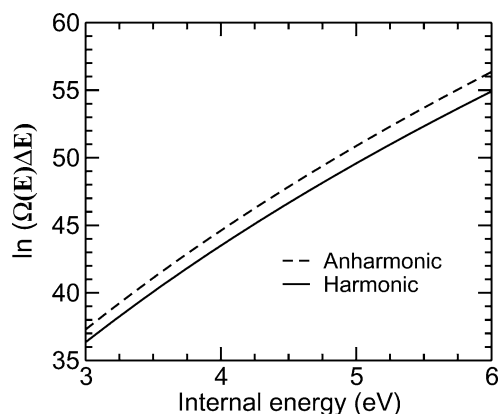
Fig. 3 Logarithm of the harmonic and anharmonic vibrational densities of states as a function of internal energy. The interval energy has been taken equal to $\Delta E = 0.0124$ eV.

potential energy surface on a and a' is not direct. The global result is that a' decreases more rapidly than a as a function of temperature.

The anharmonic quantum density of states has thus been built using the temperature dependence of these three parameters. In Fig. 3, the HQDOS and AQDOS have been plotted up to an internal energy equal to 6 eV. The two curves have not been shown for internal energies lower than 0.2 eV because, in this low energy region, the densities of states are not smooth functions, which is a necessary condition to use this method.

From the analysis of Fig. 3, it is clear that the effect of the anharmonicity on the density of states is quite important. For further study in a statistical description of the fragmentation process of PAH molecules. The anharmonicity of the potential energy surface is expected to play a significant role. It could appear that the harmonic approach is not at all adapted. In such PAH systems, the internal energy necessary to break a C–H bound is typically 4 eV. At this given internal energy, the ratio between HQDOS and AQDOS is equal to 3.065. This ratio becomes equal to 4.221 when the internal energy is raised to 6 eV. The evolution of this ratio may induce important effects on the kinetics and energetics of the fragmentation process.

3.2. Vibrational shift *versus* temperature

Another way to analyze the importance of the anharmonicity in such a molecule is to study the temperature dependence of the IR active bands frequencies. This information can be directly obtained using a tight-binding molecular dynamics simulation at different temperatures.[19] In this paper, we have concentrated ourselves on an alternative statistical reversible-
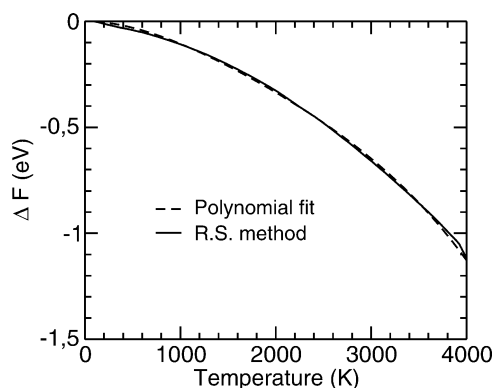

Fig. 4 Evolution of the difference between the anharmonic and harmonic classical free energies ($\Delta F = F^{(a)} - F^{(h)}$) as a function of temperature. The adjustment $\Delta F = -\chi_1 T^2 + 1/2\,\chi_2 T^3 - 1/6\chi_3 T^4$ is also shown (dashed line).
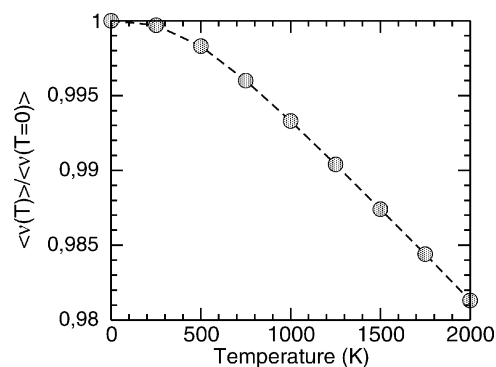

Fig. 5 Plot of the geometric mean frequency $\langle \nu(T) \rangle / \langle \nu(T=0) \rangle$ as a function of temperature.

scaling approach which has been followed to obtain this spectroscopic information.

The reversible–scaling method[20] has been used to give the exact anharmonic free energy. The difference $\Delta F = F^{(a)} - F^{(h)}$ between the anharmonic and harmonic free energies has been plotted in Fig. 4 as a function of temperature. The adjustment of ΔF by eqn. (20) is also shown. The fitting procedure yields the χ_1, χ_2 and χ_3 coefficients and thus the γ_1, γ_2 and γ_3 coefficients can be obtained from eqn. (21). From the formalism proposed by Calvo *et al.*,[34] the geometric mean frequency, noted $\langle \nu(T) \rangle$ ($= [\prod_{i=1}^{n} h\nu_1(T)]^{1/n}$), is calculated as a function of temperature by making the assumption that all the frequencies are anharmonically affected with the same proportion.

In classical and quantum approaches, the mean internal energy evolves differently as a function of temperature. A relationship between "classical" $\beta_{(C)}$ and "quantum" $\beta_{(Q)}$ temperatures can be deduced by equalizing the mean internal energies, *i.e.* $\langle E^{(a,q)} \rangle_{\beta(Q)} = \langle E^{(a,cl)} \rangle_{\beta(C)}$. From this temperature correspondence, the dependence of the mean frequency as a function of the temperature can thus be obtained when we consider the quantum behaviour of the system. The result is shown in Fig. 5. A non-linear behavior appears at high temperatures, which confirms the temperature dependence of the IR active frequencies extracted directly from the tight-binding molecular dynamics simulations.[19] The theoretical result can then be compared with the results of Joblin *et al.*'s experiment[6] on the temperature dependence of the C–H stretching mode (around 3000 cm^{-1}) for the naphthalene molecule. These experimental data, obtained in a relatively small temperature range (between 500 K and 900 K), have been linearly fitted to yield a slope equal to 2.01×10^{-2} cm^{-1} K^{-1}, inducing an experimental red shift of about 8 cm^{-1} in this temperature range. This is quite consistent with our theoretical value equal to 11 cm^{-1} in the same temperature range.

4. Conclusion

We have calculated the anharmonic density of states of the naphthalene molecule using a mixed classical quantum approach. When comparing with the harmonic case, a significant difference appears at high internal energy. Using the de Koning *et al.*'s method, the evolution of the mean vibrational frequency as a function of temperature has straightforwardly been obtained from the thermal evolution of the free energy. It should be noticed that this procedure is an alternative approach to obtaining the temperature dependence of the active infrared bands for large PAH molecules, with respect to a direct determination of the spectra using a tight-binding molecular dynamics simulation.[19]

We are currently characterizing the anharmonic vibrational density of states of some PAH cations such as fluorine$^+$, pyrene$^+$ and coronene$^+$, which will be later used for studies of the fragmentation processes using a statistical approach, namely phase space theory.[35] The influence of the

anharmonicity on the fragmentation rates could thus be evaluated. The method proposed here to incorporate the anharmonicity could then be compared to others methods.[36–39] Another important piece of information which remains to be investigated is the evolution of the mean frequency temperature dependence with increasing the molecular size. Work is currently in progress in these directions.

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