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# Defining the temperature of an isolated molecule

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The microcanonical temperature of an isolated molecule is derived in terms of Boltzmann and Gibbs volume entropies within the quantum harmonic vibrational and equivalent degenerated model approximations. The effects of the entropy functional choice and various approximations are examined. The difference between Boltzmann and Gibbs volume temperatures is negligible for molecules bigger than ten atoms. However, it is significant for smaller systems, opening a way to probe them experimentally. A simple, analytical expression of the temperature as a function of the vibrational energy is provided, allowing predictions with a  $\pm 3\%$  margin of error compared to the exact harmonic estimate. The microcanonical temperature is discussed and exemplified with polycyclic aromatic hydrocarbon molecules and other molecules of astrophysical interest.

## I. INTRODUCTION

Any excess of vibrational energy in a molecule above its zero-point level may induce physical-chemical reactions such as isomerization, dissociation, or rearrangement. The role of such vibrational energy excess is particularly relevant when a light-excited molecule transfers the photon energy to the ground state without emitting radiation. The classic example is the vision mechanism, where a complex sequence of events is triggered in the rhodopsin protein after the retinal chromophore converts the photon energy into vibrational energy.<sup>1</sup>

We often say that a molecule with large vibrational energy is hot. However, if we ask what the molecule's temperature is, the question sounds odd. The fundamental thermochemistry of a canonical harmonic system tells that the environmental temperature determines the vibrational excess through

$$E(T_e) = E_{ZP} + \sum_k \frac{h\nu_k}{e^{h\nu_k/k_B T_e} - 1}, \quad (1)$$

where  $E_{ZP}$  is the vibrational zero-point energy,  $T_e$  is the environmental temperature,  $k_B$  is the Boltzmann constant,  $h$  is the Planck constant, and the sum runs over the vibrational degrees  $k$  with harmonic frequency  $\nu_k$ . Nevertheless, an isolated molecule cannot count on the environment to thermalize. The vibrational energy excess will be trapped there until it is irradiated or induces a chemical reaction.

A hot, isolated molecule is a microcanonical system with constant total energy, and, different from the canonical

problem, we want to determine  $T_m(E)$ , the microcanonical temperature as a function of the energy. Defining the temperature of such an isolated molecule could be worth doing,<sup>2</sup> especially if we aim at describing large systems. Indeed, the temperature of isolated molecules and small finite systems has been under scrutiny for decades in diverse fields. It is needed for computing unimolecular reaction rates,<sup>2-4</sup> sampling initial conditions for dynamics,<sup>5</sup> studying fragmentation and radiative cooling of electrostatically trapped ions,<sup>6-8</sup> determining thermionic electron emission of clusters beams,<sup>9</sup> characterizing phase transitions in clusters,<sup>10</sup> or assigning molecular species in the interstellar medium.<sup>11-13</sup> Defining such a temperature may be helpful even for understanding the photophysics of chromophores in vacuum-like hydrophobic cavities of proteins.<sup>14</sup>

The microcanonical temperature can be used similarly to the canonical temperature to predict the vibrational population distribution when the molecule has an energy excess above its zero-point level. We will naturally use the microcanonical temperature for isolated molecules in a vacuum. We may also use it for assessing situations where the reaction time (for luminescence, isomerization, dissociation, ionization) is much shorter than the collisional time but longer than the vibrational equilibration time. For example, a photoexcited molecule equilibrates vibrationally in the first excited state within a few picoseconds. If it is in a vacuum or within a collisionless regime, its vibrational states are populated according to the microcanonical temperature corresponding to the energy excess. Thus, if we want to

know whether the molecule will fluoresce before it does an intersystem crossing, we should consider that these processes' rates are functions of the microcanonical temperature (as opposed to rates computed at 0 K or at the canonical temperature).

The temperature of isolated systems has been addressed pragmatically using phenomenological approaches for applied purposes. Berry and Smirnov,<sup>10</sup> for instance, started from a reasonable estimate for the heat capacity of isolated clusters to derive their temperature. Another common approach has been to derive the canonical temperature for a canonical ensemble with kinetic averages equivalent to those of the microcanonical system.<sup>3</sup> Andersen *et al.*<sup>15</sup> followed this way to propose a high-energy approximation for the molecular temperature. D'Hendecourt *et al.*<sup>11</sup> estimated the properties of molecules in the interstellar medium from the observed temperature, also using an equivalent-canonical approach. To the best of my knowledge, none of these phenomenological-based works rest on a solid statistical basis and are valid over a broad energy domain.

On the other hand, more statistical-mechanics-oriented works have provided much knowledge on small, isolated systems. We know, for instance, that the microcanonical temperature can be defined independently of the probe,<sup>16</sup> the type of fluctuation we may expect, including the dependence on different entropy definitions,<sup>17-20</sup> and how to count microstates of finite coupled systems.<sup>21-25</sup> Nevertheless, these works usually do not allow for an everyday estimate of the temperature in applied cases of interest.

This paper aims to bridge this gap between theory and applications by deriving a microcanonical temperature for an isolated molecule that can be routinely used in diverse applied fields, has an extended validity domain, and is based on solid statistical mechanics grounds.

## II. THEORETICAL MODEL

To define the microcanonical temperature of an isolated molecule, we must go back to the principles of statistical thermodynamics. For a system with total energy  $E$ , the temperature is defined as

$$T = \left( \frac{\partial S}{\partial E} \right)^{-1}, \quad (2)$$

where  $S(E)$  is the entropy, which is a function of the number of microstates at energy  $E$ . Later, we will discuss what functional of  $E$  is the most adequate when dealing with a small system far from the thermodynamical equilibrium.

If we approximate our isolated molecule by an ensemble of  $N$  quantum harmonic oscillators, the total molecular energy is

$$E_{\xi} = E_{ZP} + \sum_k n_k h\nu_k, \quad (3)$$

where  $n_k$  is the number of quanta deposited in vibrational mode  $k$ , and  $\xi$  denotes a particular ensemble  $\{n_k\}$ . Thus, to know the number of microstates, we must determine the number of solutions of Eq. (3). This means the number of ways we can distribute different values of  $n_k$  among the vibrational modes, keeping  $E$  constant. Despite the simplicity of this formulation, it is a formidably tricky problem to solve analytically.

Fortunately, as I will also show later (Section II.E.3), we can get an approximated solution for the number of microstates by supposing the ensemble of vibrational frequencies  $\{\nu_k\}$  can be replaced by a single average frequency  $\bar{\nu}$ . The degenerated problem, which simplifies to

$$E_M = \left( \frac{N}{2} + M \right) h\bar{\nu}, \quad (4)$$

where  $M = \sum_k n_k$ , is a very well-known statistical-mechanics textbook example.<sup>26, 27</sup>

### A. Modeling an isolated molecule

For modeling the molecule, we assume (1) that it is rigid enough, so its vibrational modes are harmonic; (2) there are no external fields; and (3) it populates only a single electronic state.

The first assumption implies that we will not describe anharmonic modes, like intramolecular hydrogen bonds or internal rotations (like those methyl groups are prone to). We can consider an isolated molecule as an ensemble of weakly coupled quantum harmonic oscillators. By "weakly coupled," I mean that energy can flow between vibrational modes, but the vibrational energy is still approximately given by Eq. (3). This energy flow is crucial for the molecule to ensure that all microstates sharing the same energy are equally probable. For instance, suppose the molecule has  $\nu_1 = 300 \text{ cm}^{-1}$  and  $\nu_2 = 600 \text{ cm}^{-1}$ . A

microstate with  $n_1 = 2$  and  $n_2 = 0$  should be as likely to occur as another one with  $n_1 = 0$  and  $n_2 = 1$  (assuming that  $n_k$  for  $k > 2$  is the same in both microstates). Although a weak coupling is assumed, it is never explicitly considered here.

The second assumption implies that we will also not discuss the temperature associated with the energy allocated in the translational and rotational modes. Note, however, that these components are relevant when probing the isolated molecule.<sup>28</sup> The third assumption means that we will not deal with the sudden vibrational energy change observed during internal conversion.

### B. Reviewing the statistical mechanics' concepts

Before proceeding with the discussion, it is worth revisiting some fundamental concepts from statistical mechanics.<sup>18</sup> The basic quantities we need are the density of states

$$\omega(E) = \text{Tr}[\delta(E - H)], \quad (5)$$

and the integrated density of states

$$\Omega(E) = \text{Tr}[\Theta(E - H)]. \quad (6)$$

In these equations,  $E$  is the energy of a system with a Hamiltonian  $H$ . In Eq. (5),  $\delta$  is the Dirac function and, in Eq. (6),  $\Theta$  is the unit-step function. The trace  $\text{Tr}$  denotes the integral over the Hilbert space.

The entropy can be defined in different ways. For regular systems in the thermodynamic limit ( $N \rightarrow \infty$ ), they all tend to converge to the same result. Nevertheless, when dealing with an isolated molecule, the number  $N$  of degrees of freedom is small, and we cannot assume such equivalence. Among several possibilities, we will discuss two entropy formulations, the Boltzmann entropy<sup>29</sup>

$$S_B(E) = k_B \ln[\varepsilon \omega(E)], \quad (7)$$

and the Gibbs volume entropy<sup>18, 29, 30</sup>

$$S_G(E) = k_B \ln[\Omega(E)]. \quad (8)$$

In Eq. (7),  $\varepsilon$  is a small energy constant.

With either entropy formulation, the microcanonical temperature can be calculated with Eq. (2) and the heat capacity with

$$C = \left( \frac{\partial T}{\partial E} \right)^{-1}. \quad (9)$$

### C. Counting microstates

We can directly count the microstates contributing to either  $\varepsilon\omega(E_\varepsilon)$  or  $\Omega(E_\varepsilon)$ , compute the entropy, and evaluate the derivative in Eq. (2) numerically to get the Boltzmann ( $T_B^{(n)}$ ) and the Gibbs volume ( $T_G^{(n)}$ ) temperatures. The superscript ( $n$ ) denotes the numerical approach to distinguish from other strategies discussed below. To apply the numerical procedure, we note that the molecular energy given by Eq. (3) changes by no less than the energy of the slowest normal mode  $\nu_1$ . Thus, the number of microstates with energy between  $E_k = E_{ZP} + kh\nu_1$  and  $E_k + h\nu_1$  ( $k = 0, 1, 2, \dots$ ) is  $h\nu_1\omega(E_k) = \sum_{n_1} \dots \sum_{n_N} E_{n_1, \dots, n_N} \eta(E_k)$ , (10)

where

$$\eta(E_k) = \begin{cases} 1 & \text{if } E_k \leq E_{n_1, \dots, n_N} < E_k + h\nu_1, \\ 0 & \text{otherwise.} \end{cases} \quad (11)$$

The integrated density of states is

$$\Omega(E_k) = \sum_{j=0}^k h\nu_1 \omega(E_j). \quad (12)$$

For more advanced strategies to count microstates considering coupled anharmonic modes, see Refs.<sup>21, 23</sup> and references therein.

### D. Solving the degenerated problem

As mentioned, the degenerated problem is used below (Section II.E) as an approximation for the molecular problem. Besides that, it is also helpful to check some basic hypotheses and approximations underlying the temperature definition, namely,

- the equivalence between Gibbs volume and Boltzmann entropy,
- the extension of discrete into continuous variable needed to compute derivatives,
- the effect of Stirling's approximation, which is commonly used to simplify the results of the microstates' counting, and
- the impact of the  $N \gg 2$  approximation, also commonly applied to simplify the results.

In Subsections II.D.1 and II.D.2, we will discuss the solution of the degenerated problem in the Boltzmann and Gibbs volume formulations. Although the solution in the Boltzmann formulation is well known,<sup>26, 27</sup> I am not aware of any demonstration using the Gibbs volume formulation

so far. Subsection II.D.3 compares both results and shows how the Boltzmann temperature tends to Gibbs volume temperature for large  $N$ .

### 1. The Boltzmann formulation

The number of microstates satisfying Eq. (4) is the number of ways of allocating  $M = E_M / h\bar{\nu} - N/2$  quanta in  $N$  vibrational modes. Thus, the number of microstates between  $E$  and  $E + h\bar{\nu}$  is the number of multisets of length  $M$  on  $N$  elements,

$$\varepsilon\omega(E_M) = \binom{N}{M} = \binom{M+N-1}{M} = \frac{(M+N-1)!}{(N-1)!M!}, \quad (13)$$

where  $\binom{m}{n}$  and  $\binom{m}{n}$  denote the number of multisets and the binomial coefficient, respectively. The dependence on  $E_M$  is implicit in  $M$ . Taking  $\varepsilon = h\bar{\nu}$  in Eq. (7) allows directly computing the Boltzmann entropy as

$$S_B(E_M) = k_B \ln \left[ \frac{(M+N-1)!}{(N-1)!M!} \right]. \quad (14)$$

The extension of this equation from a discrete to a continuous variable ( $E_M \rightarrow E$ ) allows using Eq. (2) to get

$$T_B^{(e)} = \left( \Psi \left( \frac{E}{h\bar{\nu}} + \frac{N}{2} \right) - \Psi \left( \frac{E}{h\bar{\nu}} - \frac{N}{2} + 1 \right) \right)^{-1} \frac{h\bar{\nu}}{k_B}, \quad (15)$$

where  $\Psi$  is the digamma function defined as

$$\Psi(x) = \frac{d}{dx} \ln[\Gamma(x)] \quad (16)$$

and  $\Gamma$  is the gamma function. The superscript  $(e)$  indicates this is an extended-to-continuous approximation.

Alternatively, we can employ Stirling's approximation  $\ln(n!) \approx n \ln(n) - n$  in Eq. (14). Then, with Eq. (2), we get

$$T_B^{(s)} = \left( \ln \left[ \frac{(2E + (N-2)h\bar{\nu})}{(2E - Nh\bar{\nu})} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B}, \quad (17)$$

where the superscript  $(s)$  indicates Stirling's approximation. Finally, for large systems, we have  $N \gg 2$ , and we get

$$T_B^{(l)} = \left( \ln \left[ \frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B}. \quad (18)$$

Schwabl<sup>31</sup> offers an alternative approach to computing  $T_B$ . Instead of using combinatorial to estimate  $\varepsilon\omega(E)$ , he rewrites this quantity in terms of the Fourier transform of the Dirac function in Eq. (5). The resulting integral is

evaluated via the Laplace method, which requires  $N \rightarrow \infty$ . This approximation once more yields  $T_B^{(l)}$ .

The heat capacity is obtained by replacing  $T_B$  into Eq. (9). With  $T_B^{(s)}$ , we have

$$C_B^{(s)} = \frac{k_B}{4(N-1)} \left( \left( \frac{2E}{h\bar{\nu}} \right)^2 - \frac{2E}{h\bar{\nu}} - N(N-2) \right) \times \ln \left( \frac{2E + (N-2)h\bar{\nu}}{2E - Nh\bar{\nu}} \right)^2, \quad (19)$$

while  $T_B^{(l)}$  gives

$$C_B^{(l)} = \frac{Nk_B}{4} \left( \left( \frac{2E}{Nh\bar{\nu}} \right)^2 - 1 \right) \ln \left( \frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right)^2. \quad (20)$$

### 2. The Gibbs volume formulation

To solve the degenerated problem in the Gibbs volume formulation, we proceed along the same lines as in Section II.D.1 but employing the integrated density of states in Eq. (6). For the quantum harmonic oscillator, this quantity is the number of microstates with energy between 0 and  $E$ ,

$$\Omega(E_M) = \sum_{K=0}^M \binom{N}{K} = \sum_{K=0}^M \binom{K+N-1}{K} = \binom{M+N}{M} = \frac{(M+N)!}{N!M!}, \quad (21)$$

where the sum runs over the density of states defined in Eq. (13) and is evaluated using the hockey-stick identity.<sup>32</sup> Thus, the Gibbs volume entropy is

$$S_G(E_M) = k_B \ln \left[ \frac{(M+N)!}{N!M!} \right]. \quad (22)$$

Replacing it in Eq. (2) gives the extended-to-continuous ( $E_M \rightarrow E$ ) approximation for the microcanonical temperature

$$T_G^{(e)} = \left( \Psi \left( \frac{E}{h\bar{\nu}} + \frac{N}{2} + 1 \right) - \Psi \left( \frac{E}{h\bar{\nu}} - \frac{N}{2} + 1 \right) \right)^{-1} \frac{h\bar{\nu}}{k_B}. \quad (23)$$

Alternatively, with Stirling's approximation in Eq. (22), we have

$$T_G^{(s)} = \left( \ln \left[ \frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B}, \quad (24)$$

which is identical to  $T_B^{(l)}$  in Eq. (18) (we will explore this fact in Section II.D.3). Because of this equality, the heat capacity  $C_G^{(s)}$  is also given by Eq. (20).

### 3. Comparing Boltzmann and Gibbs volume formulations

Let us now compare the previous results for the degenerated problem for a particular example of a system composed of six quantum harmonic oscillators, all with frequency  $1015 \text{ cm}^{-1}$ . Its number of states  $\varepsilon\omega(E)$  and the integrated density of states  $\Omega(E)$  are plotted in Figure 1-top. Both  $\varepsilon\omega(E)$  and  $\Omega(E)$  grow monotonically. The energy resolution is determined by  $\varepsilon$ , which is  $h\bar{\nu}$  for the degenerated problem. We may expect vibrational energy excess of about 2–4 eV for typical photoexcited systems. These values are much bigger than the vibrational frequency (0.13 eV in our example). Thus, we can compute the temperature by numerical differentiation of the entropy [Eq. (2)], using either  $\varepsilon\omega(E)$  to get  $T_B^{(n)}$  or  $\Omega(E)$  to get  $T_G^{(n)}$ .

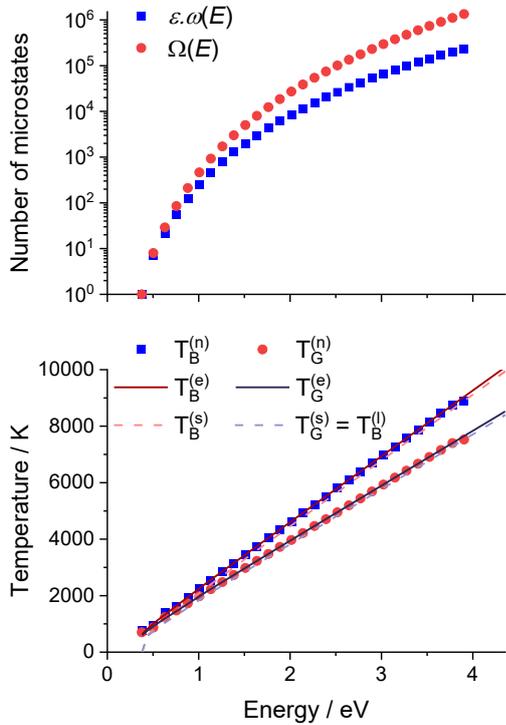


Figure 1. Top: Number of states  $\varepsilon\omega(E)$  and the integrated density of states  $\Omega(E)$  as a function of energy  $E$  for a system composed of  $N=6$  degenerated quantum harmonic oscillators of frequency  $\bar{\nu}=1015 \text{ cm}^{-1}$ . Bottom: Temperature for the same degenerated system computed with different models.

The diverse temperature models are illustrated in the bottom panel of Figure 1. The difference between the temperatures computed with the Boltzmann and Gibbs volume formulations is striking. Although they are similar at low energies, Boltzmann temperature grows much

faster, and the difference between the two formulations at 4 eV amounts to about 1400 K. This divergence between Boltzmann and Gibbs volume temperatures is caused by the small size of our model,  $N=6$ , corresponding to a four-atoms molecule. The difference reduces quickly for bigger systems. For a molecule with 15 atoms ( $N=39$ ), the temperature difference at 4 eV is only 15 K. Indeed, in the thermodynamic limit ( $N \rightarrow \infty$ ), Boltzmann and Gibbs volume temperatures tend to the same values,<sup>17</sup> as we can see comparing Eqs. (18) and (24).

We also can see in Figure 1-bottom that the extended-to-continuous approximations  $T_B^{(e)}$  and  $T_G^{(e)}$  using the gamma function are spot-on. Stirling's approximation in  $T_B^{(s)}$  and  $T_G^{(s)}$  slightly degrades the result, but its main problem is at the very low energies near the zero-point level. As long we are not dealing with this region, we may favor Stirling's approximation given the algebraic simplicity of  $T_B^{(s)}$  and  $T_G^{(s)}$ .

In the Boltzmann formulation, it is usual to assume that  $N \gg 2$ , yielding  $T_B^{(l)}$  in Eq. (18). Although this approximation is fully justified for large systems, it has a major conceptual implication: it shifts the system from a Boltzmann to a Gibbs volume description, as made evident by Eqs. (18) and (24), where we can see that  $T_B^{(l)} = T_G^{(s)}$ .

Several authors,<sup>26, 33, 34</sup> starting from the Boltzmann formulation, already apply the large  $N$  approximation at the level of the number of microstates [Eq. (13)]. Because this approximation reduces Eq. (13) to Eq. (21), they inadvertently work in the Gibbs volume formulation.

#### E. The temperature of an isolated molecule

##### 1. Defining the average frequency

My hypothesis to compute the temperature of an isolated molecule is that there is an average frequency  $\bar{\nu}$  for the  $N$ -degenerated problem that is a good approximation for the isolated molecule, composed of  $N$  different frequencies. I tested two possibilities for the *equivalent degenerated model* (EDM),  $\bar{\nu}$  given as the arithmetic mean

$$\bar{\nu}_A = \frac{1}{N} \sum_k \nu_k = \frac{2E_{ZP}}{N}, \quad (25)$$

and the harmonic mean

$$\bar{\nu}_H = \left( \frac{1}{N} \sum_k \frac{1}{\nu_k} \right)^{-1}. \quad (26)$$

The rationale for adopting  $\bar{\nu}_A$  is the direct analogy to the solution of the degenerated problem. Note, for instance, that Eq. (24) can be rewritten as

$$T_G^{(s)} = \left( \ln \left[ \frac{E + E_{ZP}}{E - E_{ZP}} \right] \right)^{-1} \frac{2E_{ZP}}{Nk_B}. \quad (27)$$

Thus, it is natural to search for an approximated solution to the non-degenerated problem with the same functional form. On the other hand, for a given  $E$ , there are many more microstates involving changes in the number of quanta in the low-frequency than in the high-frequency modes. Thus, it may be helpful to weigh the average frequency toward the low-frequency modes. If we take as weight the maximum number of quanta we can add to a specific vibrational mode,  $n_k^{\max} = E / h\nu_k$  corresponding to the microstate  $(0, \dots, n_k^{\max}, \dots, 0)$ , we get

$$\frac{\sum_k n_k^{\max} \nu_k}{\sum_k n_k^{\max}} = \bar{\nu}_H, \quad (28)$$

providing a rationale for adopting the harmonic mean of the frequencies.

On comparing these two possibilities, we will see in Sections II.E.2 and II.E.3 that the arithmetic mean does better than the harmonic mean.

## 2. Test case: The temperature of $H_2O_2$

Let us now work out a specific example of a small, isolated molecule,  $H_2O_2$ , for which we can count the microstates and compute the temperature numerically.  $H_2O_2$  has four atoms and  $N = 6$  vibrational modes with harmonic frequencies 346, 956, 1330, 1469, 3704, and 3709  $\text{cm}^{-1}$  (computed with the geometry, frequency, noncovalent, extended tight-binding (GFN1-xTB) method<sup>35</sup>). The arithmetic mean frequency is  $\bar{\nu}_A = 1919 \text{ cm}^{-1}$ , and its harmonic mean frequency is  $\bar{\nu}_H = 1015 \text{ cm}^{-1}$ . Up to 4 eV, it has 169,501 microstates, distributed as a function of  $E$  as shown in Figure 2-top. The number of states  $\varepsilon\omega(E)$  is computed with an energy resolution of  $\varepsilon = h\nu_1$  (346  $\text{cm}^{-1}$ ).

The Boltzmann and Gibbs volume temperatures of the isolated  $H_2O_2$  computed by numerical differentiation of the entropy [Eq. (2)] are shown as dots in Figure 2, middle and bottom. The approximated results using the arithmetic mean frequency in the six-degenerated problem are shown in the middle and the harmonic mean in the bottom figure. For a vibrational energy excess of 3.9 eV, the Boltzmann temperature reaches about 9013 K and the Gibbs volume,

7482 K. (Remember, these temperatures do not consider the anharmonicities of  $H_2O_2$ .)

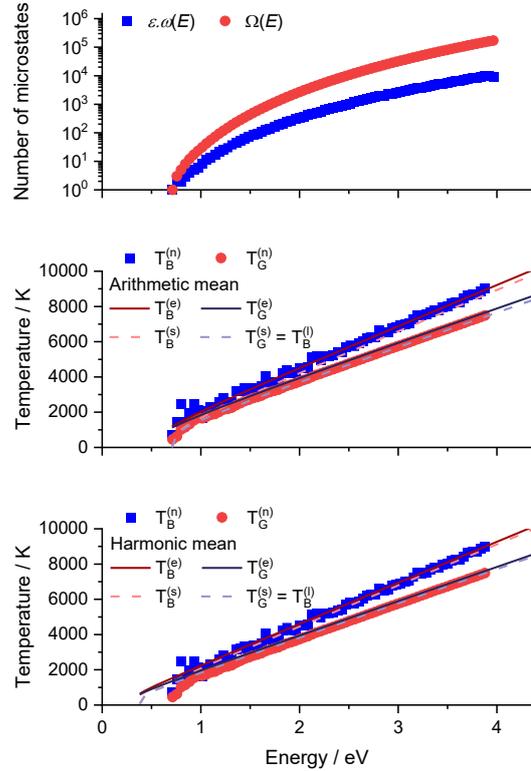


Figure 2. Top: Number of states  $\varepsilon\omega(E)$  and the integrated density of states  $\Omega(E)$  as a function of energy  $E$  for  $H_2O_2$ . Middle: Temperature of the isolated  $H_2O_2$  (dots). The lines are the temperatures for the  $N = 6$  equivalent degenerated model (EDM) with the arithmetic mean frequency of  $H_2O_2$ ,  $\bar{\nu} = 1919 \text{ cm}^{-1}$ . Bottom: Temperature of the isolated  $H_2O_2$  (dots). The lines are the temperatures for the  $N = 6$  EDM with the harmonic mean frequency of  $H_2O_2$ ,  $\bar{\nu} = 1015 \text{ cm}^{-1}$ .

The growth of the number of states  $\varepsilon\omega(E)$  with  $E$ , although monotonic, shows significant fluctuations, especially in the low-energy region. Consequently, the numerically-computed Boltzmann temperature ( $T_B^{(n)}$  in Figure 2) also fluctuates around the six-degenerated mean value. The integrated density of states  $\Omega(E)$  washes out most of these fluctuations and yields a much smoother Gibbs volume temperature function ( $T_G^{(n)}$ ).

All approximated results are excellent in the region above 1 eV. The agreement deteriorates in the low-energy region near the zero-point energy. The exception is Stirling's approximation with arithmetic mean frequency, which also describes the low energy well. The extended-to-continuous approximation does not hold the correct

behavior at low energies, delivering too high-temperature predictions.

### 3. Model validation

The equivalent degenerated model with arithmetic mean frequency gave an excellent approximation for the temperature of the isolated  $\text{H}_2\text{O}_2$ . Nevertheless, is this a general result or just a coincidence? To check this point, I have computed the Gibbs volume temperature for 30 arbitrary systems (10 with  $N = 6$ , 10 with  $N = 7$ , and 10 with  $N = 8$ ) with frequencies randomly distributed between 300 and 3000  $\text{cm}^{-1}$ . The systems with  $N$  equal 7 and 8 do not correspond to molecules because  $N$  must be  $3N_{at} - 6$ . Nevertheless, they are useful to assess the errors. The systems with  $N = 8$  have about  $10^9$  microstates up to 4 eV [see Eq. (21)]. For each energy value, the relative error

$$\delta T = \left| \frac{T_{B/G}^{(n)} - T_{B/G}^{(s)}(\bar{\nu}_{H/A})}{T_{B/G}^{(n)}} \right| \quad (29)$$

between the numerical  $T_B^{(n)}$  and  $T_G^{(n)}$  temperatures and the temperatures of the equivalent degenerated model using Stirling's approximation was evaluated. These errors are shown in Figure 3 for temperatures computed with arithmetic mean frequencies.

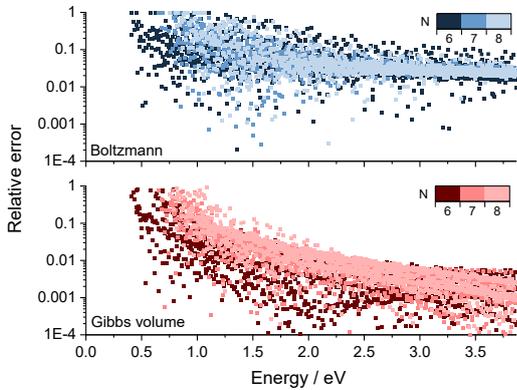


Figure 3. Relative error  $\delta T$  between the numerical temperature and Stirling's approximated temperature of the equivalent degenerated model with arithmetic mean frequencies computed for 30 random systems with  $N = 6, 7$ , and 8. Top: Boltzmann; bottom: Gibbs volume.

Most of the error is in the low-energy region, and they are independent of the system size. The mean relative errors in Table 1 confirm this picture.  $T_G^{(s)}$  with arithmetic mean frequency has a mean relative error of 3% no matter  $N$ . The mean relative error of  $T_B^{(s)}$  also with arithmetic mean frequency is a bit bigger, 8%. The mean relative errors with harmonic means are always larger than those

with arithmetic mean. They are also dependent on the system size, reducing for bigger  $N$ . It is not shown in the table, but most of the error when using the harmonic mean frequency is in the low-energy region. Given the better performance of  $\bar{\nu}_A$  over  $\bar{\nu}_H$ , only the former will be used in Section III.

The better performance of the arithmetic over the harmonic mean is fortunate. It implies that low frequencies, commonly associated with anharmonic modes, are not more relevant than high frequencies in temperature determination.

Table 1. Mean relative error  $\langle \delta T \rangle$  between numerical and EDM approximated temperatures for Gibbs volume (G) and Boltzmann (B) formulations with harmonic (H) and arithmetic (A) mean frequencies.

	$N=6$	$N=7$	$N=8$
$\langle \delta T_{GH} \rangle$	0.24	0.14	0.16
$\langle \delta T_{GA} \rangle$	0.03	0.03	0.03
$\langle \delta T_{BH} \rangle$	0.29	0.16	0.11
$\langle \delta T_{BA} \rangle$	0.08	0.08	0.08

The microcanonical temperature is not an injective function of the energy.<sup>18</sup> This means we may have the same temperature for different energies. Therefore, for an energy  $E$ , the comparison between a temperature based on a continuous energy variable and that based on a discrete energy variable should be made considering the local mean value of the latter around  $E$ . Using the mean relative error as the margin of error is an effective way of considering the mean value of the discrete function.

## III. DISCUSSION

### F. Leading terms in the molecular temperature

The asymptotic expansion of  $T_G^{(s)}$  [Eq. (24)] at  $E \rightarrow \infty$  gives

$$T_G^{(a)} = \frac{E}{Nk_B} - \frac{Nh^2\bar{\nu}^2}{12k_BE} + O\left(\frac{1}{E^3}\right). \quad (30)$$

The leading term is linear in  $E$  and does not depend on the particularities of the molecule, only on its size through  $N$ .

In cluster studies, it is common to estimate the microcanonical temperature using the phenomenological formula<sup>10, 36</sup>

$$T_{cluster} \approx \frac{2\langle E_{kin} \rangle}{Nk_B}, \quad (31)$$

where  $\langle E_{kin} \rangle$  is the mean kinetic energy of the cluster. For a harmonic system,  $2\langle E_{kin} \rangle = E$  and, therefore, Eq. (31) corresponds to the leading term in the Gibbs volume temperature expansion, Eq. (30).

If, instead of the Gibbs volume, we start from the Boltzmann temperature  $T_B^{(s)}$  (Eq. (17)), the asymptotic expansion at  $E \rightarrow \infty$  gives

$$T_B^{(a)} = \frac{E - \frac{1}{2}h\bar{\nu}}{(N-1)k_B} - \frac{(N-1)h^2\bar{\nu}^2}{12k_BE} + O\left(\frac{1}{E^2}\right). \quad (32)$$

As expected,  $T_B^{(a)} \rightarrow T_G^{(a)}$  when  $N \rightarrow \infty$ . However, for small systems, the leading term depends on the molecular properties through  $\bar{\nu}$ . Moreover, the  $(N-1)$  term in the denominator causes  $T_B^{(a)}$  grows faster than  $T_G^{(a)}$  with the energy.

Andersen *et al.*<sup>15</sup> derived the microcanonical temperature of a small isolated system starting from the Boltzmann entropy and searching for the average energy of a canonical system equilibrated at the microcanonical temperature. Their result for an ensemble of  $N$  (non-degenerated) quantum harmonic oscillators in the high-temperature limit is

$$T_{ABH} = \frac{E}{(N-1)k_B}. \quad (33)$$

Considering that in this limit  $E \gg h\bar{\nu}$ , their formula matches the leading order of the  $T_B^{(s)}$  expansion in Eq. (32).

A common assumption in phenomenological models is that the heat capacity (Eq. (9)) of the isolated molecule does not depend on the temperature, so a simple linear relation  $E = CT + E_0$  holds between energy and temperature.<sup>2, 8</sup> According to Eq. (30), such a hypothesis is satisfied for a molecule with  $N$  vibrational degrees if

$$E \gg \frac{Nh\bar{\nu}}{2\sqrt{3}} = \frac{E_{ZP}}{\sqrt{3}}. \quad (34)$$

Note that the radiative cooling should bring the molecule to the nonlinear region even if this relation is initially satisfied.

### G. Effect of the harmonic approximation

The isolated molecule model developed here is purely based on a harmonic approximation. Because the density of microstates as a function of the energy of a fully coupled anharmonic system grows faster than that of a harmonic system,<sup>23</sup> the harmonic microcanonical temperature should

be an upper limit for the exact temperature. (Remember, the temperature is the inverse of the derivative of the density of states.) However, how far off the harmonic temperature is? I will not fully address this question here, but I will show two examples to provide insights into the errors we may expect when using the models derived in this paper.

Aieta *et al.* reported in Ref.<sup>21</sup> the integrated density of microstates  $\Omega(E)$  at energy  $E$  for fully coupled anharmonic systems, computed with the Wang–Landau Monte Carlo method using the Paradensum algorithm.<sup>25</sup> Among the systems they tested, hydrocarboxyl radical (HOCO) and anthracene are particularly interesting because they correspond to two molecular limits: the first is small and flexible, while the second is large and rigid. The anharmonic temperature of these two molecules, computed by numerical differentiation of  $\Omega(E)$  [see Eqs. (2) and (8)], is shown in Figure 4. These temperatures can be directly compared to the Gibbs volume harmonic temperatures  $T_G^{(s)}$ , which are also shown in the figure. They were computed with the same harmonic frequencies used in Ref.<sup>21</sup>.

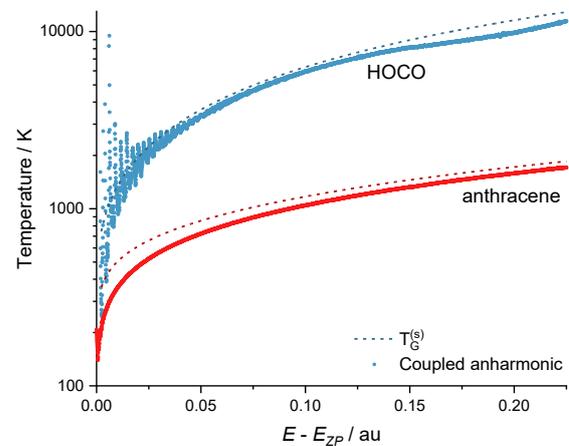


Figure 4. Microcanonical temperature of HOCO (blue) and anthracene (red) computed with the harmonic model using Eq. (24) ( $T_G^{(s)}$ , solid line) and with a fully coupled anharmonic model (dots). The fully coupled anharmonic model is calculated by numerical differentiation of the integrated density of states reported in Ref.<sup>21</sup> (see text).

As expected, the harmonic temperatures are higher than the anharmonic ones. Both approximations agree qualitatively, but the numerical differences are not negligible. For anthracene, the anharmonic temperature is about 150 K smaller than the harmonic one over the entire

domain. For HOCO, the anharmonic temperature is about 300 K lower than the harmonic one for intermediary excitation energies between 0.05 and 0.1 au (1.36 – 2.72 eV). For lower energies, the comparison is unclear due to the strong oscillations in the anharmonic result. The anharmonic temperature is much smaller than the harmonic one at higher energies. The relative error reaches 20% at 0.2 au. This deviation may indicate the limitations of the harmonic approximation for small, flexible systems.

Assuming that the harmonic microcanonical temperature is an upper bound for the exact microcanonical temperature is reasonable for molecules, where the anharmonic modes fully couple. This hypothesis, however, may fail in systems with internal rotations and decoupled modes. For instance, Belega *et al.*<sup>36</sup> proposed that the microcanonical temperature of molecular clusters could be estimated by replacing  $N$  in Eq. (31) with an effective  $N_{\text{eff}}$  factor computed from the reduced averaged kinetic energy in each mode. Their approach applied to the water pentamer yielded a temperature increase of up to 100 K compared to the harmonic approximation.

#### H. Experimental comparison between Boltzmann and Gibbs volume

Currently, there is an ongoing debate on which function is the correct way of computing the entropy for an isolated system. While Hilbert, Hänggi, and Dunkel<sup>18, 29</sup> claimed that, among several entropy models, only Gibbs volume fulfills all three laws of thermodynamics simultaneously, Swendsen and Wang<sup>19</sup> argued that Gibbs volume fails to satisfy the postulates of thermodynamics and make incorrect predictions for systems with nonmonotonic energy densities. (See Ref.<sup>37</sup> for an account of this debate.)

Although this discussion goes beyond the scope of this paper, the present results create a way for experimentally testing which entropy, Boltzmann or Gibbs volume, delivers the best theoretical prediction. We could think of a setup where a small, isolated molecular ion is photoexcited in an electrostatic ion trap.<sup>4, 6, 38</sup> The laser pulse duration should be such as it allows thermal equilibration before radiative decay starts but without losing too much energy resolution. Then, monitoring its radiative cooling would inform on its peak temperature (before any cooling). As discussed in Section II.E.2, for a four-atom molecule with a few eV of energy excess, the

difference between Boltzmann and Gibbs volume temperatures should be significant enough to cause different color emissions.

Alternative experimental setups to test both entropy formulations have also been proposed by Ferrari,<sup>17</sup> in terms of either a non-interacting gas with a two-level internal spectrum or an Ising model of interacting spins.

#### I. Temperature of isolated molecules of applied interest

The temperatures  $T_B^{(s)}$  and  $T_G^{(s)}$  as a function of the excitation energy  $\Delta E = E - E_{ZP}$  are shown in Figure 5-top for a few molecules. All harmonic frequencies were computed at the GFN1-xTB level.<sup>35</sup> These molecules are all systems of astrochemical interest. The difference between Boltzmann and Gibbs volume temperatures is negligible for any system above 24 vibrational degrees (10 atoms). For isolated C<sub>60</sub> at 808 K, Deng and Echt<sup>39</sup> measured its heat capacity as  $12.6 \pm 1.4$  meV/K. According to Eq. (20) and using  $\bar{\nu} = 922$  cm<sup>-1</sup>, this temperature corresponds to  $E = 14.7$  eV, yielding a theoretical estimate of  $C_G^{(s)} = 12.0$  meV/K [Eq. (20)], in excellent agreement with the experiment. Note that this result is smaller than the high-energy limit,  $Nk_B = 15.0$  meV/K ( $N = 174$ ), due to the nonlinear dependence of the temperature on the energy.

If no chemical process occurs, the hot, isolated molecule is expected to cool down due to blackbody radiation.<sup>6-8</sup> Since the seminal papers by Sellgren<sup>40</sup> and Leger and Puget,<sup>12</sup> some specific near-infrared (IR) spectral features of interstellar dust have been assigned to polycyclic aromatic hydrocarbons (PAHs).<sup>41</sup> These earlier works raised the hypothesis that those IR features arise from small, 5–10 Å molecules instantaneously heated to about 1000 K by UV radiation. Working on observational data, Leger *et al.*<sup>11, 12</sup> estimated a color temperature of 600 K, corresponding to a peak temperature of  $950 \pm 150$  K. Then, using the Einstein heat capacity model and assuming 6-eV photoexcitation, they predicted that the IR features should be due to carbon species with about 60 atoms.

We can revisit this assignment by using the microcanonical temperature derived here. Let us assume a peak temperature of  $T = 950 \pm 150$  K and that the arithmetic mean frequency is  $\bar{\nu} = 1100 \pm 100$  cm<sup>-1</sup>. Let us also allow a broader variation in the UV excitation,  $\Delta E_{UV} = 5 \pm 1$  eV. Using Eq. (24), the number of atoms is

$$N_{at} = \frac{\Delta E_{UV}}{3h\bar{\nu}} \left( \exp\left(\frac{h\bar{\nu}}{k_B T}\right) - 1 \right) + 2. \quad (35)$$

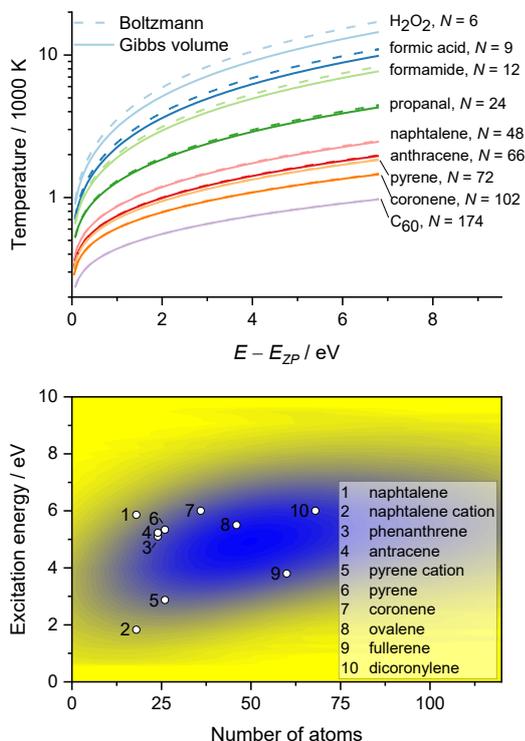


Figure 5. Top: Gibbs volume  $T_G^{(s)}$  (solid lines) and Boltzmann  $T_B^{(s)}$  (dashed lines) temperatures for a few molecules (arithmetic mean frequency).  $N$  is the number of vibrational modes. Bottom: Density map of possible molecular systems with temperature  $950 \pm 150$  K, UV excitation  $5 \pm 1$  eV, and arithmetic mean frequency  $1100 \pm 100$   $\text{cm}^{-1}$ . The density grows from yellow to blue. The dots illustrate the absorption peak of a few PAH molecules with excitation energies taken from the literature: anthracene,<sup>42</sup> naphthalene (neutral and cation), phenanthrene, pyrene (neutral and cation),<sup>43</sup> coronene, dicoronylene, ovalene,<sup>44</sup> and fullerene.<sup>45</sup>

Letting all three parameters vary according to a random normal distribution with standard deviation given by the error bars, we arrive at  $N_{at} = 61 \pm 38$  for  $10^6$  random systems. This mean number of atoms agrees with the previous calculations. Nevertheless, as we can see in the density plot at the bottom of Figure 5, it also indicates that a large variety of possible molecular systems falls within the parameter constraints. The figure also shows a few PAH molecules ranging from small to large sizes. Except for naphthalene neutral and cation, they all fall in the high-density region, as we would expect from PAH mixtures that should occur in the interstellar media.<sup>44, 46</sup> This analysis considers only molecules returning ground state

via radiationless pathways. If they fluoresce, the peak temperature after re-equilibration in the ground state should correspond to a vibrational excess discounting the energy of the emitted photon.

#### IV. CONCLUSIONS

This paper explores the microcanonical temperature of an isolated molecule. The molecule is treated as an ensemble of quantum harmonic oscillators, and the temperature is derived in the frame of Boltzmann and Gibbs volume entropies. Although the direct solution to the problem seems not to be accessible analytically, we discuss how approximations based on an equivalent degenerated model using average frequencies can adequately describe the molecular temperature. The discussion tracks the effect of several hypotheses and approximations on the results, including the entropy functional, the type of average frequency, the extension of discrete into continuous variables, the use of Stirling's approximation, the assumption of a large number of degrees of freedom  $N$ , and the expansion in the leading orders. Table 2 summarizes the several expressions discussed in the text.

The comparison between Boltzmann and Gibbs volume approaches shows that the temperatures converge to the same values for large  $N$ . The difference is already negligible for a ten-atom molecule. However, for smaller molecules, the difference is significant, and it should be possible to probe it experimentally. In particular, we discuss how a common numerical approximation corresponds, in fact, to a shift from the Boltzmann into the Gibbs volume formulation.

We also see how the microcanonical temperature relates to previous phenomenological approaches. For a large vibrational energy excess, the common assumption of a linear relationship between temperature and energy (constant heat capacity) is valid. Nevertheless, dissociative and radiative cooling should bring the system to nonlinear regions.

For practical purposes, for a molecule with more than ten atoms, I recommend using  $T_G^{(s)}$  (the Gibbs volume temperature with Stirling's approximation) or equivalently  $T_B^{(l)}$  (the Boltzmann temperature for large  $N$ ) and arithmetic mean of frequencies. For smaller molecules, the temperature can be computed with either  $T_G^{(s)}$  or  $T_B^{(s)}$ . At this point, it is unclear which one delivers the correct answer.

Table 2. Summary of the microcanonical temperatures derived under different approximations from Boltzmann and Gibbs volume entropies for a degenerated set of  $N$  quantum harmonic oscillators with frequency  $\bar{\nu}$ . For the non-degenerated problem,  $\bar{\nu}$  is the arithmetic mean frequency of the spectrum.  $\Psi$  is the digamma function. For an isolated molecule well-represented by harmonic vibrational modes,  $T_G^{(s)}$  delivers a good approximation for the microcanonical temperature within an error of 3% compared to the exact harmonic estimate.

	Boltzmann	Gibbs volume
Numerical counting	$T_B^{(n)} = \left(\frac{\Delta S_B}{\Delta E}\right)^{-1}$	$T_G^{(n)} = \left(\frac{\Delta S_G}{\Delta E}\right)^{-1}$
Extension of $E_M$ to continuous $E$	$T_B^{(e)} = \left(\Psi\left(\frac{E}{h\bar{\nu}} + \frac{N}{2}\right) - \Psi\left(\frac{E}{h\bar{\nu}} - \frac{N}{2} + 1\right)\right)^{-1} \frac{h\bar{\nu}}{k_B}$	$T_G^{(e)} = \left(\Psi\left(\frac{E}{h\bar{\nu}} + \frac{N}{2} + 1\right) - \Psi\left(\frac{E}{h\bar{\nu}} - \frac{N}{2} + 1\right)\right)^{-1} \frac{h\bar{\nu}}{k_B}$
Stirling's approximation	$T_B^{(s)} = \left(\ln\left[\frac{(2E + (N-2)h\bar{\nu})}{(2E - Nh\bar{\nu})}\right]\right)^{-1} \frac{h\bar{\nu}}{k_B}$	$T_G^{(s)} = \left(\ln\left[\frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}}\right]\right)^{-1} \frac{h\bar{\nu}}{k_B}$
Large $N$ approximation	$T_B^{(l)} = \left(\ln\left[\frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}}\right]\right)^{-1} \frac{h\bar{\nu}}{k_B}$	
Asymptotic expansion at $E \rightarrow \infty$	$T_B^{(a)} = \frac{E - \frac{1}{2}h\bar{\nu}}{(N-1)k_B} - \frac{(N-1)h^2\bar{\nu}^2}{12k_B E} + O\left(\frac{1}{E^2}\right)$	$T_G^{(a)} = \frac{E}{Nk_B} - \frac{Nh^2\bar{\nu}^2}{12k_B E} + O\left(\frac{1}{E^3}\right)$
Constant heat capacity	$T_B^{(c)} = \frac{E - \frac{1}{2}h\bar{\nu}}{(N-1)k_B}$	$T_G^{(c)} = \frac{E}{Nk_B}$

We should also bear in mind that the microcanonical temperature models discussed here are strictly valid for molecules that are not subjected to external fields, populate a single electronic state, and whose vibrational modes can be well-represented by a harmonic approximation. There are two advantages of working within these boundaries. First, they provide simple analytical expressions that allow a straightforward temperature estimation beyond the classical regime. Second, they enable the development of a conceptual understanding that is sometimes hidden when applying advanced numerical approaches. Nonetheless, the present modeling should be extended beyond these approximations in the future. The primary goal should be to tackle anharmonic effects to increase the prediction accuracy.

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## REFERENCES

- S. Gozem, H. L. Luk, I. Schapiro, and M. Olivucci, *Chem. Rev.* **117** (2017) 13502.  
<https://doi.org/10.1021/acs.chemrev.7b00177>
- K. Hansen, *Chem. Phys. Lett.* **620** (2015) 43.  
<https://doi.org/10.1016/j.cplett.2014.12.016>
- C. E. Klots, *J. Chem. Phys.* **90** (1989) 4470.  
<https://doi.org/10.1063/1.456633>
- K. Hansen, *Mass Spectrom. Rev.* **40** (2021) 725.  
<https://doi.org/10.1002/mas.21630>
- R. Crespo-Otero, and M. Barbatti, *Chem. Rev.* **118** (2018) 7026.  
<https://doi.org/10.1021/acs.chemrev.7b00577>
- Y. Toker, O. Aviv, M. Eritt, M. L. Rappaport, O. Heber, D. Schwalm, and D. Zajfman, *Phys. Rev. A* **76** (2007) 053201.  
<https://doi.org/10.1103/PhysRevA.76.053201>
- H. Zettergren, A. Domaracka, T. Schlathölter, P. Bolognesi, S. Díaz-Tendero, M. Łabuda, S. Tosić, S. Maclot, P. Johnsson, A. Steber, D. Tikhonov, M. C. Castrovilli, L. Avaldi, S. Bari, A. R. Milosavljević, A. Palacios, S. Faraji, D. G. Piekarski, P. Rousseau, D.

- Ascenzi, C. Romanzin, E. Erdmann, M. Alcamí, J. Kopyra, P. Limão-Vieira, J. Kočišek, J. Fedor, S. Albertini, M. Gatchell, H. Cederquist, H. T. Schmidt, E. Gruber, L. H. Andersen, O. Heber, Y. Toker, K. Hansen, J. A. Noble, C. Jouvét, C. Kjær, S. B. Nielsen, E. Carrascosa, J. Bull, A. Candian, and A. Pettrignani, *Eur. Phys. J. D* **75** (2021) 152.  
<https://doi.org/10.1140/epjd/s10053-021-00155-y>
- <sup>8</sup> E. Kolodney, B. Tsipinyuk, and A. Budrevich, *J. Chem. Phys.* **102** (1995) 9263.  
<https://doi.org/10.1063/1.469235>
- <sup>9</sup> B. A. Collings, A. H. Amrein, D. M. Rayner, and P. A. Hackett, *J. Chem. Phys.* **99** (1993) 4174.  
<https://doi.org/10.1063/1.466114>
- <sup>10</sup> R. S. Berry, and B. M. Smirnov, *Phys.-Uspekhi* **52** (2009) 137.  
<https://doi.org/103367/UFNe0179200902b0147>
- <sup>11</sup> L. D'Hendecourt, A. Léger, P. Boissel, and F. Désert, in *Proceedings of the 135th Symposium of the International Astronomical Union*, edited by L. J. Allamandola, and A. G. G. M. Tielens (Springer, 1989), pp. 207.  
<https://ui.adsabs.harvard.edu/abs/1989IAUS..135..207D>
- <sup>12</sup> A. Leger, and J. L. Puget, *Astron. Astrophys.* **500** (1984) 279.  
<https://ui.adsabs.harvard.edu/abs/1984A&A...137L...5L>
- <sup>13</sup> C. Leidlmaier, P. Bartl, H. Schöbel, S. Denifl, M. Probst, P. Scheier, and O. Echt, *Astrophys. J.* **738** (2011) L4.  
<https://doi.org/10.1088/2041-8205/738/1/L4>
- <sup>14</sup> L. H. Andersen, and A. V. Bochenkova, *Eur. Phys. J. D* **51** (2009) 5.  
<https://doi.org/10.1140/epjd/e2008-00144-9>
- <sup>15</sup> J. U. Andersen, E. Bonderup, and K. Hansen, *J. Chem. Phys.* **114** (2001) 6518.  
<https://doi.org/10.1063/1.1357794>
- <sup>16</sup> J. Wang, and W.-g. Wang, *Phys. Rev. E* **96** (2017) 032207.  
<https://doi.org/10.1103/PhysRevE.96.032207>
- <sup>17</sup> L. Ferrari, *Eur. Phys. J. Plus* **132** (2017) 487.  
<https://doi.org/10.1140/epjp/i2017-11756-5>
- <sup>18</sup> S. Hilbert, P. Hänggi, and J. Dunkel, *Phys. Rev. E* **90** (2014) 062116.  
<https://doi.org/10.1103/PhysRevE.90.062116>
- <sup>19</sup> R. H. Swendsen, and J.-S. Wang, *Phys. Rev. E* **92** (2015) 020103.  
<https://doi.org/10.1103/PhysRevE.92.020103>
- <sup>20</sup> R. Franzosi, *J. Stat. Mech.* **2019** (2019) 083204.  
<https://doi.org/10.1088/1742-5468/ab3116>
- <sup>21</sup> C. Aieta, F. Gabas, and M. Ceotto, *J. Phys. Chem. A* **120** (2016) 4853.  
<https://doi.org/10.1021/acs.jpca.5b12364>
- <sup>22</sup> G. Mandelli, C. Aieta, and M. Ceotto, *J. Chem. Theory Comput.* **18** (2022) 623.  
<https://doi.org/10.1021/acs.jctc.1c01143>
- <sup>23</sup> T. L. Nguyen, and J. R. Barker, *J. Phys. Chem. A* **114** (2010) 3718.  
<https://doi.org/10.1021/jp100132s>
- <sup>24</sup> M. Basire, P. Parneix, and F. Calvo, *J. Chem. Phys.* **129** (2008) 081101.  
<https://doi.org/10.1063/1.2965905>
- <sup>25</sup> F. Wang, and D. P. Landau, *Phys. Rev. Lett.* **86** (2001) 2050.  
<https://doi.org/10.1103/PhysRevLett.86.2050>
- <sup>26</sup> H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley & Sons, 1985),
- <sup>27</sup> J. E. Mayer, and M. G. Mayer, *Statistical Mechanics* (John Wiley Sons, Inc., 1966),
- <sup>28</sup> T. M. Fuchs, F. Rivic, and R. Schäfer, *Phys. Rev. A* **104** (2021) 012820.  
<https://doi.org/10.1103/PhysRevA.104.012820>
- <sup>29</sup> J. Dunkel, and S. Hilbert, *Nature Physics* **10** (2014) 67.  
<https://doi.org/10.1038/nphys2815>
- <sup>30</sup> J. W. Gibbs, *Elementary Principles in Statistical Mechanics (Chapter XIV)* (Scribner's sons, 1902),
- <sup>31</sup> F. Schwabl, *Statistical mechanics* (Springer Science & Business Media, 2006),
- <sup>32</sup> C. H. Jones, *Fibonacci Q.* **34** (1996) 280.  
<https://www.fq.math.ca/34-3.html>
- <sup>33</sup> P. G. Nelson, *Foundations of Chemistry* **21** (2019) 325.  
<https://doi.org/10.1007/s10698-019-09337-4>

<sup>34</sup> D. V. Schroeder, *An introduction to thermal physics* (Addison Wesley Longman, 2000),

<sup>35</sup> S. Grimme, C. Bannwarth, and P. Shushkov, J. Chem. Theory Comput. **13** (2017) 1989.

<https://doi.org/10.1021/acs.jctc.7b00118>

<sup>36</sup> E. D. Belega, E. A. Cheremukhin, P. V. Elyutin, and D. N. Trubnikov, Chem. Phys. Lett. **496** (2010) 167.

<https://doi.org/10.1016/j.cplett.2010.07.022>

<sup>37</sup> R. H. Swendsen, Rep. Prog. Phys. **81** (2018) 072001.

<https://doi.org/10.1088/1361-6633/aac18c>

<sup>38</sup> S. Martin, J. Bernard, R. Brédy, B. Concina, C. Joblin, M. Ji, C. Ortega, and L. Chen, Phys. Rev. Lett. **110** (2013) 063003.

<https://doi.org/10.1103/PhysRevLett.110.063003>

<sup>39</sup> R. Deng, and O. Echt, J. Phys. Chem. C **119** (2015) 11233.

<https://doi.org/10.1021/jp512276e>

<sup>40</sup> K. Sellgren, Astrophys. J. **277** (1984) 623.

<https://doi.org/10.1086/161733>

<sup>41</sup> M. S. Murga, M. S. Kirsanova, D. S. Wiebe, and P. A. Boley, Mon. Not. R. Astron. Soc. **509** (2021) 800.

<https://doi.org/10.1093/mnras/stab3061>

<sup>42</sup> A. Thöny, and M. J. Rossi, J. Photochem. Photobiol. A **104** (1997) 25.

[https://doi.org/10.1016/S1010-6030\(96\)04575-3](https://doi.org/10.1016/S1010-6030(96)04575-3)

<sup>43</sup> T. M. Halasinski, F. Salama, and L. J. Allamandola, Astrophys. J. **628** (2005) 555.

<https://doi.org/10.1086/430631>

<sup>44</sup> G. Mallocci, G. Mulas, and C. Joblin, Astron. Astrophys. **426** (2004) 105.

<https://doi.org/10.1051/0004-6361:20040541>

<sup>45</sup> B. B. Brady, and E. J. Beiting, J. Chem. Phys. **97** (1992) 3855.

<https://doi.org/10.1063/1.462967>

<sup>46</sup> M. Steglich, C. Jäger, G. Rouillé, F. Huisken, H. Mutschke, and T. Henning, Astrophys. J. **712** (2010) L16.

<https://doi.org/10.1088/2041-8205/712/1/L16>