



Partition function and astronomical observation of interstellar isomers: Is there a link?

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Abstract

The unsuccessful astronomical searches for some important astrophysical and astrobiological molecules have been linked to the large partition function of these molecules. This letter reports an extensive investigation of the relationship between partition function and astronomical observation of interstellar isomers using high level quantum chemical calculations. 120 molecules from 30 different isomeric groups have been considered. Partition function and thermodynamic stabilities are determined for each set of isomeric species. From the results, there is no direct correlation between partition function and astronomical observation of the same isomeric species. Though interstellar formations processes are generally controlled by factors like kinetics, thermodynamics, formation and destruction pathways. However, the observation of the isomers seems to correlate well with thermodynamics. For instance, in all the groups considered, the astronomically detected isomers are the thermodynamically most stable molecules in their respective isomeric groups. The implications of these results in accounting for the limited number of known cyclic interstellar molecules, unsuccessful searches for amino acid and the possible molecules for astronomical observations are discussed.

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1. Introduction

The interstellar medium (ISM) which was seen as an empty vacuum dotted with stars and other celestial bodies by popular opinion in time past is now regarded as the largest chemical reservoir in the universe. This is as a result of the diverse kinds of molecules such as the different carbon chains, highly reactive ions, different organic species, high molecular isomers and the “non-terrestrial” molecules which are very unfamiliar in the terrestrial laboratory; that have been uniquely detected (Herbst, 2001). The advances in the field of astrophysics, astrochemistry and related

fields are the direct results of the improvements in astronomical instruments, spectroscopic tools and the concerted efforts of the laboratory spectroscopists, astrophysicists and the astronomers. The observation of molecular species in the interstellar and circumstellar envelopes has become a reoccurring event as documented in the astrochymist database (http://www.astrochymist.org/astrochymist_ism.html), from the observation of a few diatomic species; CH, CN and CH⁺ in the 1940s, the first alcohols; CH₃OH and CH₃CH₂OH in the 1970s, the observation of the first branched chain molecule in 2014 and to the recent (in 2016) observation of the first interstellar chiral molecule. Till date, about 200 different interstellar and circumstellar molecules have been uniquely detected from different astronomical sources largely through their rotational transition spectra (Etim and Arunan, 2015). There is high hope for

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the observations of more complex molecules in ISM including the “non-terrestrial ones” with the increased advances in these fields.

Of all the known interstellar and circumstellar molecules, only about 10 (including the fullerenes and excluding the unconfirmed claimed observation of 2H-azirine) are cyclic; c-SiC₂, c-SiC₃, c-C₃H, c-C₃H₂, c-H₂C₃O, c-C₂H₄O, benzene, C₆₀, C₇₀ and C₆₀⁺ (Berné et al., 2013 and the references therein). The few number of known cyclic interstellar has resulted in a number of questions. In the searches for interstellar ethylene oxide, Dickens et al. (1997) said “*The question remains of whether cyclic molecules are chemically less abundant than their related linear species in the ISM, or whether their emission in any one transition is weaker because of a larger partition function, so astronomical detections are more difficult*”. Amino acids are important biological molecules. Among these molecules, glycine is the simplest amino acids. Different groups have sought for interstellar glycine from several astronomical sources using different observational facilities with no successful detection of interstellar glycine till date. The difficulties in detecting glycine and other amino acids have been linked to large molecular partition function of these molecules among other factors (Snyder et al., 2005; Jones et al., 2007; Cunningham et al., 2007).

Interstellar isomerism is one of the most pronounced features among interstellar and circumstellar molecules. These isomers are believed to have common precursors for their formation routes and as such have equal chances of been detected in the ISM but this is not the case as some of the isomers are detected while others are not. The aim of this letter is to examine the link between partition and the astronomical detection of isomeric species in ISM. Different isomeric groups with at least one isomer detected from each group are considered. Isomers are considered based on the reason stated above. All the isomeric groups considered here are also subjected to thermodynamic test by determining the accurate enthalpies of formation of each isomeric species and partition function for the same isomeric species. The details of the high level chemical calculations employed in determining the partition function and the enthalpies of formation all the systems considered in this letter are described in the next section.

2. Methodology

The GAUSSIAN 09 suite of programs (Frisch et al., 2009) is employed for all the quantum chemical calculations reported here. The computation of partition function with this program is briefly summarised. The equations used in calculating the different partition functions by the program are described in details by McQuarrie and Simon (2004) and in the white paper on thermochemistry in GAUSSIAN (Ochterski, 2000). For all the systems considered here, the equations are applicable to ideal gases because the particles are assumed to be non-interacting. The error introduced by this assumption depends on the

level of the non-ideality of the system under consideration. This error can easily be mitigated in the present case since the systems under consideration are all isomers with many properties in common. The equation used in computing the translational partition function is given as

$$q_t = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \quad (1)$$

where q_t = translational partition function; m = mass of the molecule; K_B = Boltzmann constant; T = temperature; h = Planck's constant; P = pressure. For the electronic partition function, the usual equation for computing it is given as

$$q_e = w_0 e^{-\epsilon_0/k_B T} + w_1 e^{-\epsilon_1/k_B T} + w_2 e^{-\epsilon_2/k_B T} + \dots \quad (2)$$

where w is the degeneracy of the energy level, and ϵ_n is the energy of the n th level as described in the white paper. The first electronic excitation energy is assumed to be much greater than $K_B T$. Also, the first and higher excited states are assumed to be inaccessible at any temperature. The energy of the ground state is set to zero. Putting these assumptions together, Eq. (2) reduces to

$$q_e = w_0 \quad (3)$$

This equation is simply the electronic spin multiplicity of the molecule under considerations.

Eqs. (4) and (5) are used in computing the rotational partition function for linear molecules and nonlinear polyatomic molecules respectively.

$$q_r = \frac{1}{\sigma_r} \left(\frac{T}{\theta_r} \right) \quad (4)$$

$$q_r = \frac{\pi^{1/2}}{\sigma_r} \left(\frac{T^{3/2}}{(\theta_{r,x} \theta_{r,y} \theta_{r,z})^{1/2}} \right) \quad (5)$$

The parameter σ_r in Eqs. (4) and (5) is called the symmetry number which is the number of indistinguishable orientations of the molecule. The quantity θ_r , $\theta_r(xys)$ is the characteristic temperature for rotation (in the x , y or z plane).

For all the calculations reported here, only equilibrium structures were considered with no imaginary frequency. Hence, the vibrational partition function is computed considering real modes only. The zero-point energy is included in the computing the vibrational partition function; therefore, the first vibrational level is chosen to be the zero of the energy ($V=0$) and the partition function for each vibrational level is given as

$$q_{v,K} = \frac{1}{1 - e^{-\theta_{v,K}/T}} \quad (6)$$

while the overall vibrational partition function is given as

$$q_v = \prod_K^n \frac{1}{1 - e^{-\theta_{v,K}/T}} \quad (7)$$

where K is the index of vibrational modes and $\theta_{v,K}$ is the characteristic temperature for vibration K . Partition function increases with temperature and vice versa. Hence,

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