



Polarizability of isomeric and related interstellar compounds in the aspect of their abundance

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ABSTRACT

Currently, about 100 carbon-containing molecules have been detected in interstellar and circumstellar environments, and this list includes isomeric substances. In most cases, the minimum energy principle is able to explain the ratio of abundances of the isomeric compounds but in some cases is not. Trying to rationalize the questions unsolved within the energetic approach, we have theoretically studied the polarizability of isomeric and related compounds detected or proposed in interstellar conditions. As we found, in general both energy and polarizability provide the consistent estimates for the ratio of the isomers (e.g., for the isomers having generic formulae CHO, CHN, C₃H, C₃H₂, CHNO, C₂H₃N, C₂H₆O, etc.). In the case of the C₄H₃N isomers, the most abundant isomer (cyanoallene) is not the most stable but the least polarizable that is in a good agreement with relevant experimental study. We assume that the efficiency of the use of polarizability is due to its relevance to the molecules' response to the external electric fields, i.e., more polarizable molecules are more responsive, more reactive, and, hence, less abundant. Further, we have analyzed the polarizabilities of polycyclic aromatic hydrocarbons, fullerene hydrides (fulleranes), polyynes, and their derivatives with respect to their possible detection under interstellar conditions.

1. Introduction

Recent advances in the studies on interstellar and circumstellar molecules evidence that they undergo complex and sometime antagonizing chemical transformations, for example, addition *versus* dissociation reactions. In general, reactions of interstellar compounds result in the growing molecular size, and currently, nearly 150 space molecules are known including 110 carbon-containing species, mainly organic (Müller et al., 2005; Ziutys, 2006; Herbst and van Dishoeck, 2009; Ehrenfreund et al., 2011). Numerous questions arise when scrutinized the features of interstellar chemistry such as the questions about the largest achievable molecular size (Cataldo et al., 2012), maximally possible complexity of interstellar molecules (Sabirov, 2016), formation of certain classes of polyaromatic (Snow et al., 1998; Lovas et al., 2005; Peeters et al., 2005; Ehrenfreund et al., 2007; Kwok and Zhang, 2011; Cataldo et al., 2013; Poater et al., 2017), biogenic (Sato et al., 2018) and fullerene compounds (Cataldo et al., 2009; Cami et al., 2010; Iglesias-Groth et al., 2012; Omont, 2016), and isomerism of space molecules (Remijan et al., 2005; Lattelais et al., 2009, 2010a,b; Toulouze et al., 2012; Altnöder et al., 2014; Karton and Talbi, 2014). Indeed, one generic formula usually corresponds to different organic

molecules, which further differ in physical properties and chemical behavior. The predominance of some isomers is relevant to prebiotic chemistry because isomerism drastically affects biological activity of organic compounds. Moreover, the contents of the isomers in natural sources may be relevant to their origins. For example, the distribution of isomeric hydrocarbons in petroleum is statistical and depends on their relative stabilities but one of the isomers dominates if they are resulted from biogenesis (Calvin, 1969). Currently, there is a sufficient number of isomeric species with estimates of their relative abundances in interstellar media and this number is expected to grow further. The available observational data on the isomeric species has been summarized in previous very thorough study (Lattelais et al., 2009) (Table 1).

The minimum energy principle (MEP) is a widely used theoretical approach for detecting favorable and unfavorable isomers (Hoffmann et al., 1997). It postulates that the thermodynamic favorability correlates with the total energy within one isomeric set, i.e., the isomer with minimal total energy is thermodynamically more favorable and expected to be more stable and, hence, more achievable under laboratory conditions or natural environment. This principle is applied to interstellar and circumstellar species in basal works demonstrating its

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Table 1
Abundance ratios of the observed isomeric carbon-containing species (taken from Lattalais et al., 2009)^a.

Most stable isomer (A)	Other isomers (B)	Ratio [A]/[B]	Type of the object ^b
HCO ⁺	HOC ⁺	350–6000	MC
		150–1800	HC
		50–7000	PDR
HCN	HNC	0.6–3	MC
		5–80	HC
		0.5–3000	PDR
		10–200	AGB
		5–15	MC
cyc-C ₃ H ⁺	l-C ₃ H ⁺	2	PDR
		10–70	MC
cyc-C ₃ H ₂ : ⁺	l-C ₃ H ₂ : ⁺	50–150	HC
		30	PDR
		30	AGB
		40–90	MC
		> 1000	HC
CH ₃ CN	CH ₃ NC	50	MC
		> 50	HC
CH ₃ CHO	CH ₂ CNH	~100	HC
	cyc-C ₂ H ₄ O	2–10	HC
	CH ₂ CHOH	2–10	HC
CH ₃ CH ₂ OH	CH ₃ OCH ₃	0.3–3	HC
		20–60	MC
HC ₃ N	HC ₂ NC	20–200	AGB
		160–450	MC
		1000	AGB
HC ₂ CHO	cyc-H ₂ C ₃ O	5	MC
		0.01–0.1	HC
CH ₃ COOH	HCOOCH ₃	~0.05	MC
	CH ₂ OHCHO	~0.05	HC
CH ₃ –CC–CN	CH ₂ =C=CHCN	0.25	MC

^a The valence deficiencies for C₃H and C₃H₂ isomers are shown. Acronyms *l* and *cyc* mean linear and cyclic structures, respectively.

^b Designations of interstellar objects: molecular clouds (MC), hot cores and hot corinos (HC), photodissociation regions (PDR), and asymptotic giant branch stars (AGB).

high descriptive and prognostic strength (Remijan et al., 2005; Lattalais et al., 2009, 2010a,b; Karton and Talbi, 2014). Moreover, Lattalais et al. (2009) conclude that the abundances of the isomers can be at least qualitatively deduced from their relative energies, so the chemical transformations upon their synthesis and destruction have almost no influence on the isomer ratio (Lattalais et al., 2009).

Significantly, the principle is supported by the ratios of the isomer abundances estimated for diverse astronomical objects. However, there are exceptions from the abovementioned regularity, *viz.* the sets corresponding to generic formulae C₄H₃N (methylcyanoacetylene *versus* cyanoallene) and C₂H₄O₂ (acetic acid – methyl formate – glycol aldehyde). These exceptions have been explained with the insufficiency of the measurements (the case of C₄H₃N) or peculiarities of the adsorption of the formed compounds on the grain surfaces (the case of C₂H₄O₂) that lead to underestimation of the abundance of the highly adsorbed isomer (Lattalais et al., 2009).

However, there may be another reason of the mentioned mismatch that relates to the minimum energy principle. It perfectly works only in the case of equilibrium conditions of synthesis of the isomers, homologues, or related compounds. At the same time, it is a question whether the conditions of interstellar and circumstellar media correspond to equilibrium because molecules in these environments interact with diverse radiation fields. Here, fullerenes are the most illustrative example. As is known, C₇₀ is less abundant than C₆₀ both under interstellar and laboratory arc-discharge conditions (Cataldo et al., 2009; Cami et al., 2010; Ōsawa, 2012). At the same time, the C₇₀ fullerene is thermodynamically slightly more stable than C₆₀ in standard conditions (Beckhaus et al., 1994). Therefore, additional factors are invoked to reconcile thermodynamic favorability and observations such as kinetic

stability, entropy, reaction paths *etc.* In this aspect, the relation of the ratios of the isomers to their molecular or physicochemical parameters may be important for understanding of the behavior of organic matter in space. We propose that polarizability is one of such useful properties as it describes molecules' behavior in electric fields (Bonin and Kresin, 1997; Sabirov, 2014a). In weak electric fields (up to 10⁵ V cm⁻¹), polarizability tensor is a coefficient of the linear relation between the dipole moment of the molecule (μ_{ind}) induced by the field and the field strength F :

$$\mu_{\text{ind}} = \alpha F \quad (1)$$

Polarizability defines other important physicochemical parameters and processes including dispersion interactions, refraction, dielectric permittivity, Rayleigh scattering, Kerr electro-optic effects *etc.* (Bonin and Kresin, 1997; Hohm, 2013; Blair and Thakkar, 2014). Moreover, this quantity correlates with the stability of the compounds (Ghanty and Ghosh, 1996; Chattaraj et al., 1999; Doerksen and Thakkar, 1999; Hohm, 2000; Sabirov and Bulgakov, 2011; Sabirov et al., 2012; Thakkar, 2012; Blair and Thakkar, 2013; Sabirov, 2013). Indeed, the minimum polarizability principle is known in several formulations, *e.g.*, as applied to our case, *the most stable isomer has lower mean polarizability*. Note that the application of this principle to isomeric species has a quality of correlation, *i.e.*, the principle may be violated (Thakkar, 2012; Blair and Thakkar, 2013). Additionally, polarizability has been already proved as an important parameter for assessing the interaction of organic matter with elementary particles, *e.g.*, positrons (Danielson et al., 2009; Gribakin and Swann, 2015).

Previously, we have theoretically studied polarizability of fullerene derivatives, aromatic and polycyclic hydrocarbons (Sabirov and Bulgakov, 2011; Sabirov et al., 2012, 2014a,b, 2016; Sabirov, 2013, 2014a,b; Sabirov and Ōsawa, 2015) and found its relations with stability and chemical structure. In the present work, we perform a theoretical study on polarizability of isomeric interstellar molecules toward their stabilities and abundances.

2. Computational details

The PBE/Λ22m density functional theory method (Priroda program) were used for quantum chemical calculations (Perdew et al., 1996; Laikov and Ustynyuk, 2005). The Λ22m basis set includes the contracted Gaussian-type functions (8s,4p)/[3s,2p] for hydrogen and (12s,8p,4d)/[6s,5p,2d] for the second-row elements combined with the uncontracted ones (8s,6p)/[3s,2p] for H and (12s,10p,9d,6f)/[8s,7p,5d,2f] for the second-row elements (Laikov, 2005). The PBE functional with the basis sets of this class reveals high accuracy as applied to calculating physicochemical parameters of complex fullerene and organic compounds, especially their polarizability (See, *e.g.*, Misochko et al., 2007; Sabirov, 2014a).

We were performed the standard DFT-optimization and vibration modes solving for each chemical structure to prove that all the optimized geometries correspond to the minima of the potential energy surfaces. Further, the components of polarizability tensors α were calculated using the finite field approach as the second order derivatives of the total energy E with respect to the homogeneous external electric field F :

$$\alpha_{ij} = -\frac{\partial^2 E}{\partial F_i \partial F_j} \quad (2)$$

Tensors α were calculated in the arbitrary coordinate system and then diagonalized (the eigenvalues of the polarizability tensors of the studied compounds are collected in Supplementary Material). Their eigenvalues α_{ii} define mean polarizability α :

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

The chosen DFT-method provides accurate estimates of mean

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