

# About diverse behavior of the molecular electric properties upon spatial confinement



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This paper is dedicated to Prof. Juliusz Sworakowski, who has inspired much of our work, to celebrate his 50 years of scientific research.

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## ABSTRACT

We report on the influence of spatial restriction on the static electric properties of two  $\pi$ -electron molecules, namely carbonyl sulfide and chloroacetylene. A two-dimensional harmonic oscillator potential has been applied in order to mimic the effect of orbital compression. All components of the studied tensorial quantities were obtained using the finite-field method. Among others, the nonmonotonic changes of the first hyperpolarizability, observed for the spatially limited OCS molecule, are described for the first time in the literature. Moreover, it has been found that upon embedding in cylindrical confining potential behavior of dipole moment is different for each of the investigated molecular systems. In order to explain the obtained diverse trends, the Hirshfeld technique as well as the concept of hyperpolarizability density has been adopted.

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## 1. Introduction

One of the important directions in the contemporary theoretical chemistry is to understand the changes of fundamental properties of atoms, molecules and other quantum systems upon external spatial confinement. In the first approximation, the quantum-mechanical description of one- and many electron systems in the confining environments is connected with solving the Schrödinger equation with the Hamiltonian in the following form [1–5]:

$$H = H^0 + V_c(\vec{r}), \quad (1)$$

where  $H^0$  is the Hamiltonian of an isolated molecular system and  $V_c(\vec{r})$  is an N-electron confining potential defined as a sum of the one-electron contributions:

$$V_c(\vec{r}) = \sum_{i=1}^N V_c(\vec{r}_i), \quad \text{where } \vec{r}_i = (x_i, y_i, z_i). \quad (2)$$

It should be noticed that different model confining potentials have been already introduced in many theoretical works to simulate the effect of spatial restriction and high pressure on the one- and many electron atoms and molecules [1–3,5–14]. Among

them one can specify the impenetrable and penetrable spherical cavities defined by a given radius of confinement, spherical and cylindrical harmonic oscillator potentials, Morse potential etc. Applying those potentials allows to include mainly the short range repulsive forces, in the description of physics and chemistry of confining spaces [1,15,16]. Nowadays, based on the many valuable scientific studies, it is possible to formulate some important conclusions related to the electronic structure of atoms and molecules embedded into different confining environments, represented by model potentials [1,2,6,12,14,16–27]:

- (a) The total energy of the spatially limited atoms and molecules has been found to increase together with the increasing confinement strength. Upon the critical confinement the electrons of molecular systems are bonded by the potential rather than the nuclei (process of the autoionization of atoms by pressure).
- (b) The bond distances in rigid molecules are shortened upon spatial confinement in comparison to molecules in vacuum. The spatial restriction influence on the shape of the potential energy curves is larger for the excited states rather than for the ground states.
- (c) The presence of spatial confinement leads to the separation of HOMO–LUMO energy gap of both atoms and molecules. As a result, one can observe an increase of the global hardness which defines molecular systems' reactivity.

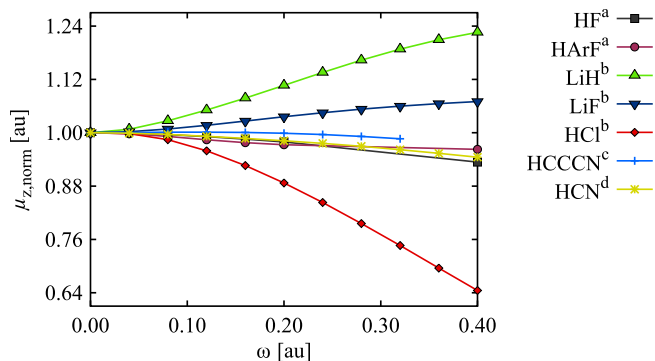
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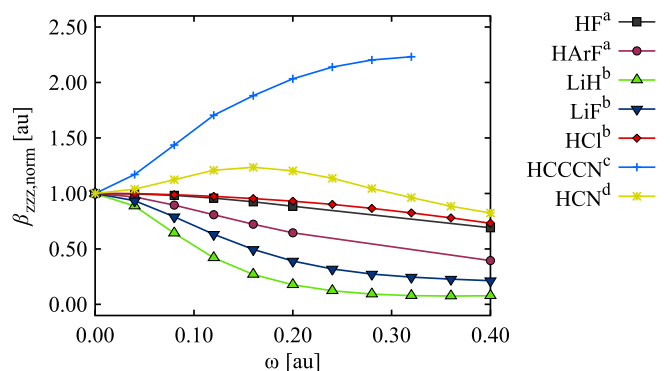
(d) For different types of molecules the increasing confinement strength causes the blue-shift of the vibronic bands.

It should be noted that described changes in the electronic structure of molecular systems under the spatial restriction (orbital compression) will also affect their electric properties. This follows from the perturbation theory, in which the linear and non-linear electric properties are quantitatively defined by the spectroscopic parameters of molecular systems (transition energies and matrix elements of transition dipole moments) [28]. Indeed, numerous results presented in the literature demonstrate that the effective linear polarizability ( $\alpha$ ) as well as second hyperpolarizability ( $\gamma$ ) of atoms, anions, and molecules is significantly reduced in the spatial confinement described by model potentials [1,4,8,9,11,17,29–44]. On the other hand, the behavior of the molecular dipole moment ( $\mu$ ) strongly depends on topology of the confining environment [10,13,18,19,45–47]. For instance, embedding the LiH molecule in different confining spaces of cylindrical symmetry causes an increase of the  $\mu$  value together with the increasing confinement strength [18,45–47]. In turn, for the spherical confinement an opposite tendency appears [13,46]. In the case of molecular first hyperpolarizability ( $\beta$ ), a decrease of its value under the spatial restriction is usually observed [13,19,45,46]. So far, only one exception to this typical picture of  $\beta$  changes can be found in the literature. This refers to the HCCCN molecule, for which the monotonic increase of  $\beta$  value is demonstrated in the cylindrical confinement, represented by the two-dimensional harmonic potential as well as nanotube-like helium clusters [16,48]. In order to clarify the behavior of dipole moment and first hyperpolarizability under the spatial confinement sample results for several molecular species, obtained in our research group, are illustrated in Figs. 1 and 2.

Recently, we have also found that the first hyperpolarizability of the HCN molecule exhibits a nonmonotonic behavior as a function of the confinement strength. For this molecule the spatial restriction initially causes an increase of  $\beta$  followed by the reduction of its value with the increasing confinement strength (cf. Fig. 2). This observation became a starting point to extend our investigations for other molecular systems containing in their structure double and triple bonds. From our systematic research we have selected two molecules, namely carbonyl sulfide (OCS) and chloroacetylene (CICCH), for which different trends in the behavior of dipole moment and first hyperpolarizability in the spatial confinement have been found. Therefore, the main subject of this contribution is to analyze changes in the static linear and nonlinear electric properties of these two molecular systems. Additionally, the Hirshfeld technique [49–52] has been



**Fig. 1.** The normalized dipole moment ( $\mu_{z,\text{norm}}$ ) obtained for different molecules under the spatial confinement: <sup>a</sup>Ref. [19], <sup>b</sup>Ref. [47], <sup>c</sup>Ref. [16], <sup>d</sup>unpublished results (CCSD(T)/aug-cc-pVTZ). For each molecule the  $\mu_{z,\text{norm}}$  quantity was calculated as  $\mu_{z,\text{norm}} = \mu_{z,\omega} / \mu_{z,\omega=0.0}$ . All results refer to molecules embedded in the cylindrical harmonic confining potential.



**Fig. 2.** The normalized first hyperpolarizability ( $\beta_{zzz,\text{norm}}$ ) value obtained for different molecules under the spatial confinement: <sup>a</sup>Ref. [19], <sup>b</sup>Ref. [47], <sup>c</sup>Ref. [16], <sup>d</sup>unpublished results (CCSD(T)/aug-cc-pVTZ). For each molecule the  $\beta_{zzz,\text{norm}}$  quantity was calculated as  $\beta_{zzz,\text{norm}} = \beta_{zzz,\omega} / \beta_{zzz,\omega=0.0}$ . All results refer to molecules embedded in the cylindrical harmonic confining potential.

used in order to explain different trends of changes in the dipole moment, noted for the spatially limited OCS and CICCH molecules. Moreover, as an attempt to understand the origin of diverse behavior of  $\beta$  observed for the investigated systems the concept of hyperpolarizability density, originally proposed by Nakano et al., has been adopted [53,54]. At this stage, it is also worth mentioning that the electronic structure, vibrational as well as electric properties of OCS and CICCH, under usual external conditions, were all studied in the several theoretical and experimental works in the past [52,55–62]. Furthermore, the results of *ab initio* computations obtained for the dipole moment and (hyper)polarizabilities of these molecules have been reported by Maroulis and co-workers [63,64]. Some interesting observations might be also found in the recent study of Jellali et al., in which the high pressure infrared absorption spectra of carbonyl sulfide were determined [65]. The performed measurements are of particular importance for the astrochemical and astrophysical applications, as the OCS molecule is the main reservoir of sulfur in the troposphere of Earth [66] and the second sulfur-containing species in the atmosphere of Venus [67].

## 2. Methodology

In the present contribution the influence of spatial confinement on the electric properties of  $\pi$ -electron molecules, represented by carbonyl sulfide and chloroacetylene, was analyzed. Similarly as in the case of our earlier studies [16,19,45,47,68,69], the two-dimensional harmonic oscillator potential in the form:

$$V_c(\vec{r}_i) = \frac{1}{2} \omega^2 \vec{r}_i^2 = \frac{1}{2} \omega^2 (x_i^2 + y_i^2) \quad (3)$$

was applied to mimic the effect of orbital compression. Such a model potential, which corresponds to the cylindrical confinement, has been previously used in the literature with regard to different aspects of spatial restriction phenomena [1,2,14,16,18,19,39,45,47,68–71]. In the above equation  $\omega$  denotes the quadratic force constant, which allows to control the smoothly varying strength of spatial restriction. It is worth to mention that according to the approach proposed by Zaleśny and co-workers, the effect of spatial restriction modeled within harmonic oscillator potential, might be connected with the valence repulsion between interacting molecular systems [16]. In the scope of this study the  $\omega$  values in the range of 0.0–0.7 au were considered. The geometries of investigated molecules were fully optimized for each quadratic force constant, employing the Broyden–Fletcher–Goldfarb–Shanno method [72]. In doing so, the CCSD approach in connection with Dunning's

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