

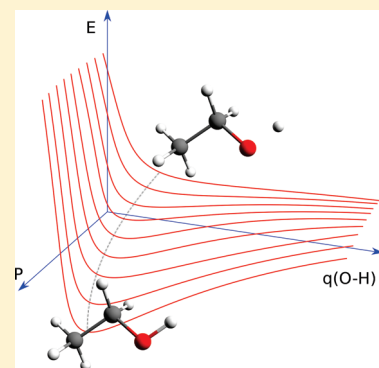
# Changing the Dissociative Character of the Lowest Excited State of Ethanol by Pressure

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**ABSTRACT:** Syntheses based on physical methods, such as pressure and light, are extremely attractive to prepare novel materials from pure molecular systems in condensed phases. The structural and electronic modifications induced by selective optical excitation can trigger unexpected chemical reactions by exploiting the high density conditions realized at high pressure. The identification of the microscopic mechanisms regulating this reactivity, mandatory to design synthetic environments appealing for practical applications, requires a careful characterization of both structural and electronic properties as a function of pressure. Here, we report a spectroscopic study, by FTIR and Raman techniques, of the ambient temperature photoinduced reactivity of liquid C<sub>2</sub>H<sub>5</sub>OD up to 1 GPa. The results have been interpreted by comparison with those relative to the fully hydrogenated isotopomer. The dissociation along the O–H (D) coordinate is the primary reactive channel, but the different reactivity of the two isotopomers with rising pressure highlights a dramatic pressure effect on the energy surface of the first electronic excited state. Dissociation along the O–H (D) coordinate becomes the reaction rate-limiting step due to an increase with pressure of the binding character along this coordinate.



## 1. INTRODUCTION

The effect of pressure on the electronic excited states of molecular compounds is an almost unexplored field in spite of the fundamental role played by these states in determining the chemical stability at high pressure.<sup>1,2</sup> Once the pressure is suitably increased, an intriguing chemistry is indeed revealed in almost all the unsaturated molecules, from the simplest systems such as N<sub>2</sub><sup>3</sup> and CO<sub>2</sub>,<sup>4</sup> to several model hydrocarbons.<sup>2</sup> The high-pressure reactivity results from a complex interplay of several factors ruled by the molar volume reduction, which results in increased intermolecular interactions. From an electronic point of view, the strengthening of these interactions promotes a progressive overlap of molecular orbitals of adjacent molecules, leading to electronic delocalization. At high pressure this can result, especially in  $\pi$ -bonded systems, in a reduction of the energy gap between ground and excited electronic states. In addition, the energy surfaces of the excited states can undergo different modifications along specific configuration coordinates because of their different compressibility.<sup>5</sup> Both contributions can therefore significantly lower the thermal barrier between ground and excited states eventually leading to a mixing of these states, an occurrence invoked in some cases to explain the reactive processes. From a more general point of view, the modifications of the electronic properties due to pressure can also generate aggressive monomeric or dimeric species able to trigger a reaction with the neighboring molecules.<sup>6,7</sup> These species can also be selectively generated by optical population of low energy electronic excited states with the remarkable effect of consistently lowering the threshold pressure for the reaction.<sup>8</sup> The efficiency of this approach has been demonstrated by many examples in which two-photon (TP)

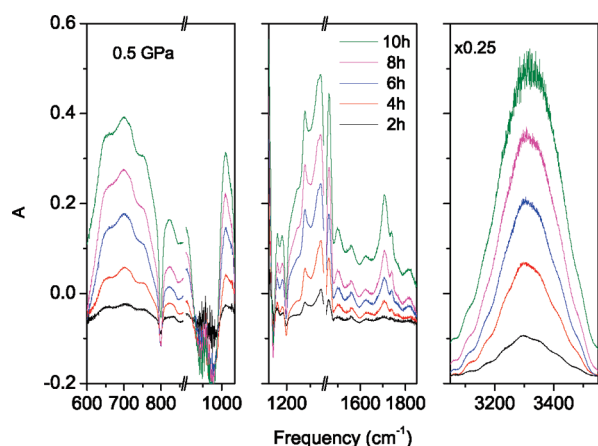
excitation, despite the extremely low absorption cross section, has been successfully employed for this purpose. The excitation through TP absorption processes has the twofold advantage of producing a low concentration of excited molecules, and consequently of reactive centers, and of employing visible or near-UV light instead of vacuum UV (VUV) photons, an important feature for practical applications of this method and for exploiting the diamond anvil cell (DAC) technique due to the absorption of diamond anvils.

Due to the dissociative nature of the lowest electronic excited singlet state, TP absorption of near-UV radiation (350 nm) has been recently employed to create radicals in the simplest R–OH systems. These radicals have been shown to trigger a complex reactivity both in pure alcohols and in water mixtures exploiting the high density conditions attainable at high pressure. Reactions have been reported at a few kilobars once the water molecules were dissociated both in fluid mixtures and in clathrate hydrates of model diatomic molecules such as N<sub>2</sub>, CO,<sup>9</sup> and of some simple hydrocarbons.<sup>10</sup> A remarkable reactivity has also been observed in the liquid phase of the two pure simplest alcohols, ethanol,<sup>11</sup> and methanol,<sup>12</sup> likely because of the presence of the alkyl residues. In these cases, the reaction follows the photoinduced dissociation along both the O–H and C–O coordinates, with the former being far more important as deduced by the reaction products identified. In both alcohols, the reaction products, their relative amount, and the change of the kinetic

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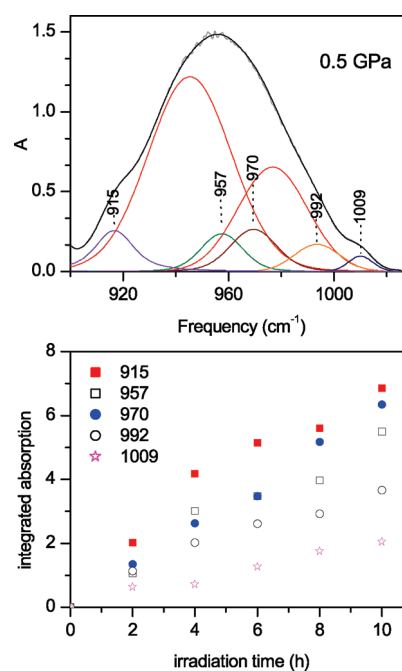


**Figure 1.** Selected spectral regions of FTIR difference absorption spectra measured at ambient temperature as a function of the irradiation time at 0.5 GPa.

behavior clearly indicate a reactivity tuned by pressure. Nevertheless, the interpretation of the different features cannot be performed only on a density increase basis. Density indeed affects the free mean path of the radicals and their rearrangement, as invoked to explain the formation of specific compounds, such as 2,3-butanediol and ethyleneglycol in the ethanol and methanol cases, respectively, but nothing is known about the effect of the increasing density on the efficiency of the dissociative processes at least in the pressure range of the present experiment. Recently, in a comparative study of  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$ , one of the hypotheses formulated to explain the abrupt reactivity depletion for pressures higher than 1 GPa was the reduced efficiency of the dissociation along the O–H coordinate with increasing pressure.<sup>12</sup> Here we report a spectroscopic study of the high-pressure reactivity of ethanol-OD (EtOD) induced at ambient temperature by TP absorption of near UV radiation (350 nm). The comparison with the reactivity of the fully hydrogenated isotopomer in the same pressure, temperature, and irradiation conditions allows the identification of a remarkable effect of pressure on the lowest singlet electronic energy surface, which makes the dissociation the rate-limiting step of the reaction.

## 2. EXPERIMENTAL SECTION

A membrane diamond anvil cell (MDAC) equipped with IIA type diamonds was employed to contain and pressurize liquid EtOD by Sigma Aldrich (99.5% D). Stainless steel gaskets were employed to laterally contain the samples whose initial dimensions were about 50  $\mu\text{m}$  thick and 150  $\mu\text{m}$  in diameter. A small ruby chip was loaded together with the sample for pressure calibration by the ruby fluorescence method. Reactivity was induced by using the UV multiline emission (peaked at 350 nm) of a cw Ar ion laser. The laser beam was focused onto the cell homogeneously illuminating the entire sample. The incident power was set to have 265 mW effectively reaching the sample. Raman spectra were measured in a back scattering geometry by using 50 mW of the 647.1 nm line of a  $\text{Kr}^+$  laser. The different regions of the sample could be probed with a spatial resolution of about 5  $\mu\text{m}$ . The scattered light was dispersed by a single stage monochromator (900 grooves/mm) and analyzed by a CCD detector with a resulting instrumental resolution of 0.7  $\text{cm}^{-1}$ . FTIR absorption measurements were performed with a Bruker-IFS 120



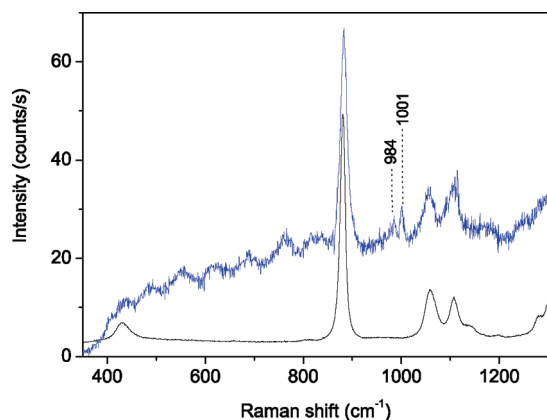
**Figure 2.** Spectral analysis of the absorption bands of the products in the photoinduced reaction of EtOD at 0.5 GPa. Upper panel: spectral decomposition between 900 and 1030  $\text{cm}^{-1}$  after 10 h irradiation. The two stronger absorption bands are due to the reactant, whereas the other five weaker bands are due to the reaction products. Lower panel: evolution with the irradiation time of the integrated area of the products bands.

HR spectrometer modified for high-pressure measurements.<sup>13,14</sup> The instrumental resolution was 1  $\text{cm}^{-1}$ .

## 3. RESULTS

The photoinduced reactivity of pure liquid EtOD was studied at two different pressures: 0.5 and 1.0 GPa. Freshly loaded samples were compressed to the desired pressure, and both IR and Raman spectra were registered before irradiating the sample. No changes were observed in the FTIR spectra in the absence of irradiation in agreement with the stability of fluid EtOD at these pressure conditions. Several irradiation cycles, each one lasting 2 h, were performed. After each of them, FTIR and Raman spectra were measured. The spectral changes due to the appearance of the products bands could not be easily identified in the FTIR spectra due to the strong absorption bands of ethanol. In the attempt to gain evidence for the products absorptions, we calculated the difference spectra by subtracting from the spectrum recorded after each irradiation cycle the spectrum measured at the same pressure before irradiating the sample. In Figure 1 the difference spectra measured in the 0.5 GPa experiment are reported. Here, all the main absorptions, except those around 1700  $\text{cm}^{-1}$ , are ascribable to fully hydrogenated ethanol (EtOH).<sup>11</sup> The strongest product band is that at about 3300  $\text{cm}^{-1}$  due to the OH stretching mode. The formation of EtOH is clear evidence of the dissociation along the O–D coordinate, identified as the primary dissociation channel in the gaseous ethanol, following excitation at 193.3 nm,<sup>15,16</sup> and recently confirmed also in the compressed fluid by TP excitation at 350 nm.<sup>11</sup>

In order to identify the possible formation of other reaction products, we analyzed the spectral region between 900 and 1030  $\text{cm}^{-1}$ . Here, the presence of two bands of EtOD (negative

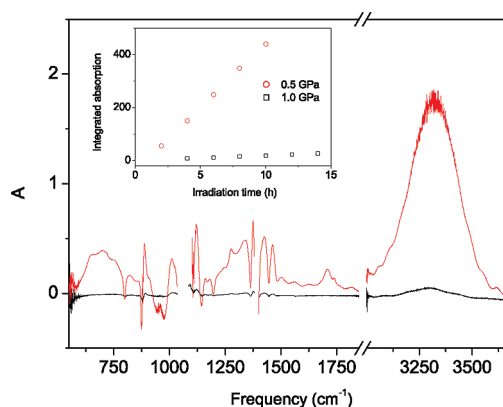


**Figure 3.** Raman spectra of EtOD measured at 0.5 GPa before (lower trace) and after 10 h irradiation (upper trace) with 265 mW of the 350 nm multiline Ar<sup>+</sup> emission. The strong fluorescence background in the irradiated sample prevents the obtainment of a better signal-to-noise ratio.

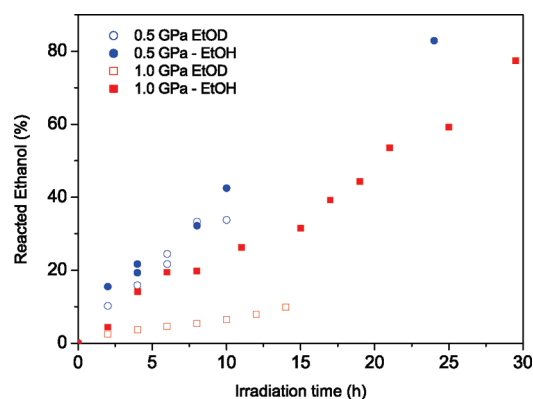
peaks in the left panel of Figure 1) prevented the employment of the difference spectra for this purpose, but the modification of the absorption profile with the irradiation time suggested the growth of bands other than those of fully hydrogenated ethanol. In the high pressure photoinduced reaction of EtOH, the more characteristic bands of the products were indeed found in this spectral region.<sup>11</sup> We reproduced all the absorption patterns using Voigt profiles (Figure 2). The frequencies and the shape (line width and Gaussian/Lorentzian character) of the two EtOD bands were fixed to the values obtained by the fit performed on the spectrum measured before irradiation. All the measurements were indeed performed at the same  $P, T$  conditions. The intensity decrease of the two EtOD bands with irradiation was checked to scale analogously to another band of the reactant, the  $\nu_{19}$  bending mode at  $800\text{ cm}^{-1}$  (negative peak in the left panel of Figure 1), which is isolated, thus providing a reliable determination of the amount of reacted EtOD. Following this procedure, we identified five product bands not ascribable to hydrogenated ethanol (at 915, 957, 970, 992, and  $1009\text{ cm}^{-1}$ ) also determining their intensification with the irradiation time (Figure 2). All these bands can be assigned to the same products identified in fully hydrogenated ethanol reaction.<sup>11</sup> Specifically, the bands at 915, 970, and  $992\text{ cm}^{-1}$  belong to 2-butanol, that at  $957\text{ cm}^{-1}$  belongs to 1,1-diethoxyethane, and the band at  $1009\text{ cm}^{-1}$  belongs to 2,3-butanediol (see ref 11 and references therein). The amount of the three products increases linearly with the irradiation time.

By comparison with the results obtained in fully hydrogenated ethanol we can qualitatively recognize a comparable reactivity in the two systems, being the only remarkable difference the fluorescence of the sample observed during the registration of the Raman spectra (Figure 3), which was not reported in the fully hydrogenated case.<sup>11</sup> Fluorescence from the reacted sample was instead reported in the methanol case, and it was ascribed to the formation of unsaturated compounds deriving from the dissociation along the C–OH coordinate.<sup>12</sup> The occurrence of the C–O bond splitting also in the EtOD case is supported by the observation of two Raman bands (Figure 3), the only ones detected, at 985 and  $1001\text{ cm}^{-1}$ , and assigned to ethane and ethane-d1, respectively.<sup>17</sup>

In the experiment performed at 1.0 GPa, irradiation cycles of the same power and duration as those performed in EtOH



**Figure 4.** Comparison between the difference spectra measured in EtOD at 0.5 (upper trace) and 1.0 (lower trace) GPa after 10 h of irradiation. The time evolution of the integrated absorption of the OH stretching band ( $\sim 3300\text{ cm}^{-1}$ ) at the two pressures is also reported in the inset.



**Figure 5.** Comparison of the amount of EtOH and EtOD transformed in the photoinduced reactions at 0.5 and 1.0 GPa. The percent of transformed ethanol, calculated as described in the text, is reported for both isotopomers and both pressures as a function of irradiation time.

surprisingly induced a barely observable reactivity in deuterated ethanol. In fact, despite a reduction with increasing pressure, the reactivity is always remarkable in fluid EtOH above 0.5 GPa;<sup>11</sup> on the contrary, none of the product bands reported at 0.5 GPa were detected in the IR (2-butanol, 1,1-diethoxyethane, and 2,3-butanediol) and in the Raman (ethane) spectra of irradiated EtOD. Even the IR band relative to the OH stretching mode was only barely visible at 1.0 GPa after 10 h of irradiation (Figure 4), indicating a remarkable depletion of any reactive process. As a further confirmation, the fluorescence characterizing the Raman spectra of the irradiated sample at 0.5 GPa (Figure 3) was also completely missing in the samples irradiated at 1.0 GPa. The different reactivity at the two pressures could be quantified by analyzing the consumption rate of the reactant. In Figure 5 we have plotted the amount of reacted ethanol as a function of irradiation time  $t$ . The percent of transformed ethanol was calculated by using the integrated absorption  $A$  of the band relative to the  $\nu_{19}$  bending mode,<sup>18</sup> at 800 and  $806\text{ cm}^{-1}$  (0.5 GPa values) in EtOD and EtOH, respectively, according to the expression  $(A_0 - A_t)/A_0$ . Both bands are well isolated and not overlapped to product bands. The two data sets are comparable at 0.5 GPa, but a strong reduction of the conversion rate in going from EtOH to

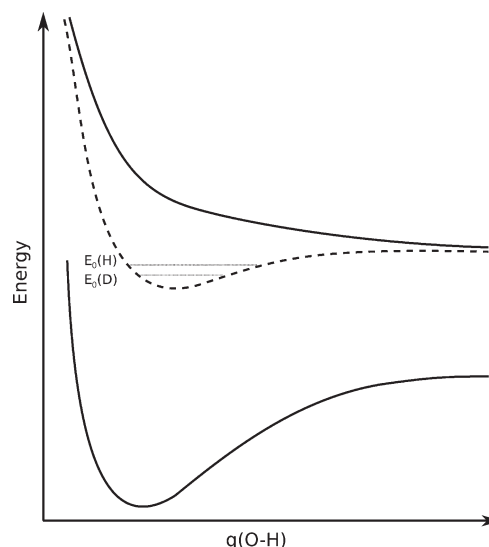


EtOD is evident at 1.0 GPa. In fact, despite a general reduction of the transformation rate with increasing pressure, in the case of EtOH, the consumption rate at 1.0 GPa is about 70% of that at 0.5 GPa, whereas in EtOD it is only  $\sim 13\%$ . The remarkable depletion of the EtOD reactivity on rising pressure was also evidenced by the reduction of the amount of EtOH produced, as observed by monitoring the time evolution of the integrated absorption relative to the OH stretching mode (inset in Figure 4). The amount of this specie is indeed reduced by a factor 23 on going from 0.5 to 1.0 GPa. These data sharply indicate that the reduced reactivity of ethanol with increasing pressure should be mostly related to the dissociation efficiency along the O–H coordinate, the only one involved in the isotopic substitution.

#### 4. DISCUSSION

The reactivity induced in compressed liquid ethanol by irradiating the sample with near-UV light (350 nm) is caused by the population, through a TP absorption process, of the lowest singlet excited state corresponding to the  $n \rightarrow \sigma^*$  Rydberg transition.<sup>19,20</sup> At ambient conditions, the onset of this transition occurs at about 6.9 eV (180 nm), being the absorption band peaked at 8.38 eV (148 nm).<sup>21</sup> The electronic properties of ethanol and methanol exhibit striking similarities.<sup>15,16</sup> This is particularly relevant in view of the extensive experimental and theoretical studies performed on methanol, indicating for the lowest singlet excited state a dissociative character along the  $\text{CH}_3\text{O}-\text{H}$  coordinate and a weakly bonding character along the  $\text{CH}_3-\text{OH}$  one.<sup>22</sup> Analogously, photodissociation studies of ethanol at 193.3 nm have shown the ethoxy radical to be the primary product in the gas phase.<sup>16</sup> Also the photoinduced reactivity of ethanol up to 1.5 GPa has been recently rationalized through these two dissociation mechanisms giving rise to the ethoxy ( $\text{CO}-\text{H}$  cleavage) and ethyl radicals ( $\text{C}-\text{OH}$  cleavage),<sup>11</sup> being the split along the O–H coordinate confirmed to be by far the primary dissociation channel also in the liquid phase. From the ethoxy radical are indeed obtained 2-butanol, 2,3-butanediol, and 1,1-diethoxyethane, whereas ethane is generated by the dissociation along the C–O coordinate.<sup>11</sup> The same reaction mechanisms have been also invoked to explain the high-pressure photoinduced reactivity of methanol,<sup>12</sup> although two features differentiate the reactivity in ethanol and methanol. Methanol is less reactive than ethanol; in addition, the products obtained from methanol are stable on further irradiation, whereas those produced in the ethanol reaction decompose, especially for irradiation exceeding 20 h.

The comparative study of the EtOH and EtOD isotopomers can provide fundamental information about the mechanisms ruling the reactivity of the simplest R–OH systems and how they are affected by pressure. The photodissociation along the O–H coordinate has been indeed demonstrated to be the main source of reactive species, therefore the deuterium substitution can provide, through the kinetic isotope effect (KIE), information about the involvement of the dissociation along the O–H bond in the rate-limiting step of the reaction. No effects on the dynamics of the electronic excited states are expected as a consequence of the isotopic substitution. At 0.5 GPa, the substantial identical reactive behavior of EtOH and EtOD indicates that the rate-limiting step of the reaction has to be searched in the reactive steps following the dissociation, such as the diffusion controlling the reaction between the ethoxy radical and the ethanol molecules, as well as the radical rearrangements required for the



**Figure 6.** Schematic representation of the pressure effect on the potential energy surface of the lowest excited state along the O–H coordinate. Solid line: ambient pressure; dashed line: suggested high pressure modification. The zero point energy for the hydrogenated and deuterated ethanol are also reported.

formation of 2-butanol and 2,3-butanediol.<sup>11</sup> On the contrary, at 1.0 GPa the reactivity in EtOH is reduced approximately by a factor 1.4 with respect to 0.5 GPa, whereas in EtOD none of the reaction products identified at 0.5 GPa could be detected, being the only indications of the occurrence of a chemical change in the sample the reactant decrease and the formation of a very small amount of hydrogenated ethanol. The reduction of approximately a factor 5–6 in the consumption rate of the reactant at 1.0 GPa in going from hydrogenated to deuterated ethanol represents a quite typical value for a primary kinetic isotopic effect, that is, the isotopic substitution occurs in the chemical bond, which breaks in the rate-limiting step of the reaction. This indicates that the O–H bond breaking becomes the rate-limiting step of the reaction with rising pressure. The reactivity decrease on compression immediately suggests a density effect possibly related to the spatial diffusion limited rate regime (strong friction).<sup>23</sup> Despite the huge difference between the pressure regimes of the reaction under study and the examples reported in the literature,<sup>24–26</sup> we cannot exclude the strong friction tail of a Kramers turnover curve; nevertheless we are still unable to explain on this basis the differences observed in the two ethanol isotopomers. On the contrary, a significant modification by pressure of the bonding character of the excited energy surface, at least along the O–H coordinate, agrees well with the experimental data. A graphic representation of this change, including the effect of isotopic substitution, is reported in Figure 6. The presence of deuterium, which lowers the vibrational energy content, allows the formation of the minimum along the O–H coordinate to be appreciated. This obviously also holds for the other channel, because the profile of the excited state along the C–O coordinate has been calculated to be weakly bonding in methanol already at ambient pressure and also neglecting any deepening of the energy minimum with pressure, the reduction of the vibrational energy content due to the deuteration is expected to also depress this channel.

In conclusion, through a comparative study of the photoinduced reactivity as a function of pressure of two different ethanol

isotopomers, EtOH and EtOD, we evidenced a strong pressure effect on the lowest electronic excited singlet state of ethanol. The dissociative character of this state along the O–H coordinate, characterizing the complex photochemistry in the gas phase and in the compressed liquid phase as well, is remarkably reduced on increasing pressure. Taking advantage of the hydroxyl deuteration, we revealed that the O–H split becomes the rate-limiting step at high pressure, thus indicating the capability of pressure to create and deepen a minimum on the excited surface. This study shows for the first time how remarkable the effect of pressure on the electronic excited states can be, which includes implications on the mechanisms regulating the high pressure reactivity. The results reported here could hopefully stimulate both experimental and theoretical efforts in this direction. Spectroscopic studies probing the fast dynamics of phenomena occurring in compressed molecular systems and computational characterization of the electronic states as a function of pressure are indeed completely missing at the moment. Both approaches could instead provide a valuable insight on the modification of the electronic properties under compression, whose knowledge is mandatory to understand the high pressure reactivity of molecular systems.

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