

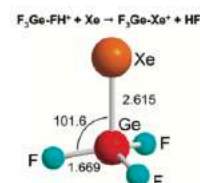
## $F_3Ge-Xe^+$ : A Xenon–Germanium Molecular Species

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**ABSTRACT** Searching for novel compounds of the noble gases still remains a fascinating experimental and theoretical challenge. The trifluorogermoxenon cation  $F_3Ge-Xe^+$ , a stable xenon–germanium molecular species, is obtained in the gas phase by the nucleophilic displacement of HF from protonated  $GeF_4$  by Xe. The alternative isomers  $F_2Ge-Xe-F^+$  and  $FGe-F-Xe-F^+$ , theoretically less stable than  $F_3Ge-Xe^+$  by ca. 80–90 kcal mol<sup>-1</sup>, are not attainable under the employed ion trap mass spectrometric conditions. The observation of  $F_3Ge-Xe^+$  enlarges the evidence concerning the conceivable binding partners of xenon.

**SECTION** Molecular Structure, Quantum Chemistry, General Theory

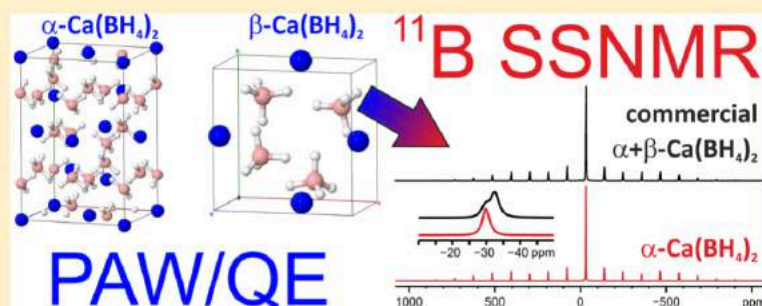


## Coupling Solid-State NMR with GIPAW ab Initio Calculations in Metal Hydrides and Borohydrides

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**S** Supporting Information



**ABSTRACT:** An integrated experimental–theoretical approach for the solid-state NMR investigation of a series of hydrogen-storage materials is illustrated. Seven experimental room-temperature structures of groups I and II metal hydrides and borohydrides, namely, NaH, LiH, NaBH<sub>4</sub>, MgH<sub>2</sub>, CaH<sub>2</sub>, Ca(BH<sub>4</sub>)<sub>2</sub>, and LiBH<sub>4</sub>, were computationally optimized. Periodic lattice calculations were performed by means of the plane-wave method adopting the density functional theory (DFT) generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional as implemented in the Quantum ESPRESSO package. Projector augmented wave (PAW), including the gauge-including projected augmented-wave (GIPAW), methods for solid-state NMR calculations were used adopting both Rappe–Rabe–Kaxiras–Joannopoulos (RRKJ) ultrasoft pseudopotentials and new developed pseudopotentials. Computed GIPAW chemical shifts were critically compared with the experimental ones. A good agreement between experimental and computed multinuclear chemical shifts was obtained.



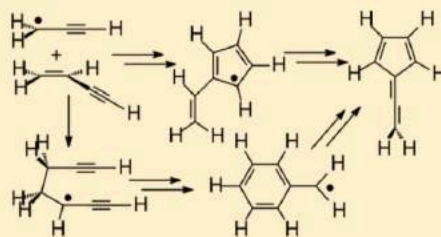
# First Ring Formation by Radical Addition of Propargyl to But-1-ene-3-yne in Combustion. Theoretical Study of the C<sub>7</sub>H<sub>7</sub> Radical System

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## Supporting Information

**ABSTRACT:** Combustive formation of a first carbon ring is an important step in the growth of polycyclic aromatic hydrocarbons (PAHs) and soot platelets. Propargyl radical addition to but-1-ene-3-yne (vinylacetylene) can start this process, possibly forming 5-, 6-, and 7-membered rings. A variety of partially intertwined reaction pathways results from density functional theory (DFT), which indicates three C<sub>7</sub>H<sub>7</sub> radicals, benzyl, troyl, and vinylcyclopentadienyl, as particularly stable. DFT energetics forms a basis for a subsequent Rice–Ramsperger–Kassel–Marcus (RRKM) study at different combustion pressures and temperatures ( $P = 30\text{--}0.01$  atm;  $T = 1200\text{--}2400$  K). RRKM indicates open-chain structures and 5-rings as the most important products. Open-chain structures, whose main contributors are the initial adducts, are favored by lower  $T$  and higher  $P$ , while 5-rings are favored by higher  $T$  and lower  $P$ . The main feature is that the declining yield in open-chain structures with rising  $T$  almost mirrors, at all pressures, the growth with  $T$  exhibited by 5-rings (main contributor: fulvenallene). Thus, the two yield lines for open chains and 5-rings cross at some  $T$ , and their crossing moves toward lower  $T$  values as lower  $P$  values are considered. Because the  $T$  dependence of the yields (slope of the lines) is more pronounced in the  $T$  range close to the line crossing, it also becomes less pronounced at the lowest  $P$  values considered because the crossing region falls at very low  $T$  values. Another constant trait is that 6-rings (mainly benzyl radical) are the third contributor, though they are present at most with a modest maximum yield of 2.4–2.7% in a  $T$  range which moves toward lower  $T$  as  $P$  is reduced.

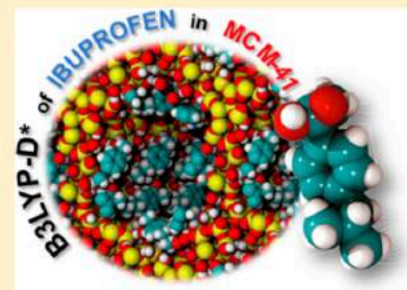


# Large-Scale B3LYP Simulations of Ibuprofen Adsorbed in MCM-41 Mesoporous Silica as Drug Delivery System

Massimo Delle Piane,<sup>†</sup> Marta Corno,<sup>†</sup> Alfonso Pedone,<sup>‡</sup> Roberto Dovesi,<sup>†</sup> and Piero Ugliengo\*<sup>†</sup><sup>†</sup>Department of Chemistry and NIS (Nanostructured Interfaces and Surfaces) Centre, University of Torino, via P. Giuria 7, 10125 Torino, Italy<sup>‡</sup>Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 183, 41100 Modena, Italy

## Supporting Information

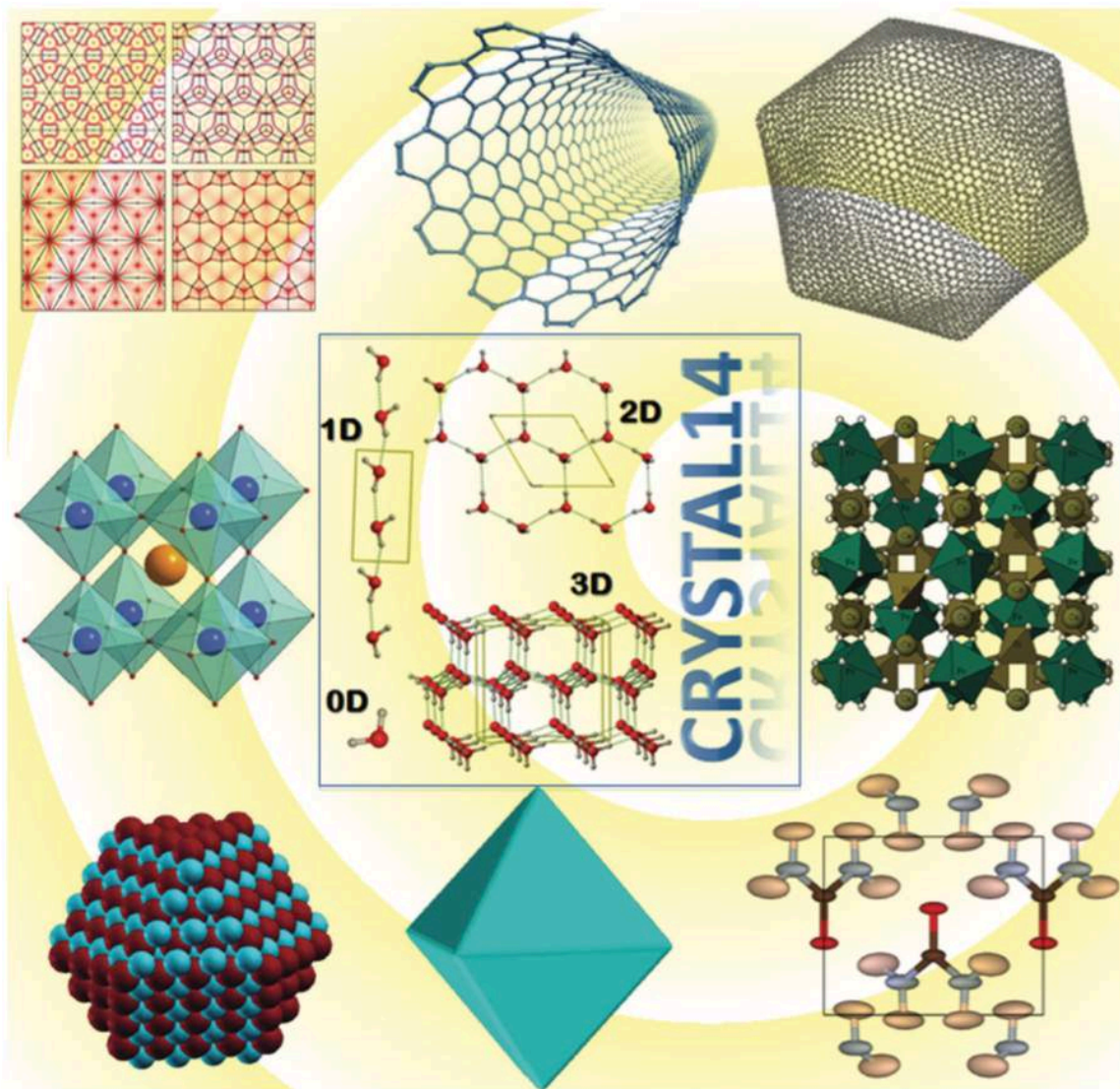
**ABSTRACT:** The atomistic details of the interaction between ibuprofen (one of the most common nonsteroidal anti-inflammatory drugs) and a realistic model of MCM-41 (one of the most studied mesoporous silica materials for drug delivery) were elucidated by quantum mechanical modeling inclusive of London forces. Calculations are based on periodic density functional theory adopting all-electron Gaussian-type basis functions of polarized double- $\zeta$  quality and the B3LYP hybrid functional. By docking the drug on different sites of the MCM-41 pore walls, we have sampled different local features of the potential energy surface of the drug–silica system, both for low and high loadings (one and seven drug molecules per unit cell, respectively). For all cases, ibuprofen adsorption in MCM-41 is exothermic (average  $\Delta H = -99$  kJ·mol<sup>-1</sup>) and exergonic (average  $\Delta G = -33$  kJ·mol<sup>-1</sup>), exclusively when London interactions are taken into account due to their dominant role in dictating all features of this system. The comparison between simulated IR and NMR spectra suggests that static disorder of the adsorbed ibuprofen due to surface sites heterogeneity can also be invoked together with the current interpretation based on a dynamic behavior of the adsorbed ibuprofen to interpret the spectral features. Analysis of H-bond patterns exhibited by the drug interacting with the MCM-41 surface silanol (SiOH) groups revealed the importance of cooperativity in the H-bond strength. The present work shows that large-scale all-electron full quantum mechanical simulations employing accurate hybrid functionals can soon become competitive over modeling studies based on molecular mechanics methods, both in terms of superior accuracy and absence of the problematic parametrization, due to organic/inorganic interface.





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## CRYSTAL14: A Program for the *Ab Initio* Investigation of Crystalline Solids

Roberto Dovesi,<sup>\*,[a]</sup> Roberto Orlando,<sup>[a]</sup> Alessandro Erba,<sup>[a]</sup> Claudio M. Zicovich-Wilson,<sup>[b]</sup> Bartolomeo Civalleri,<sup>[a]</sup> Silvia Casassa,<sup>[a]</sup> Lorenzo Maschio,<sup>[a]</sup> Matteo Ferrabone,<sup>[a]</sup> Marco De La Pierre,<sup>[a]</sup> Philippe D'Arco,<sup>[c,d]</sup> Yves Noël,<sup>[c,d]</sup> Mauro Causà,<sup>[e]</sup> Michel Rérat,<sup>[f]</sup> and Bernard Kirtman<sup>[g]</sup>



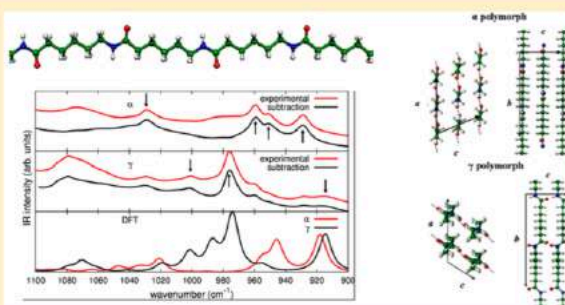
# Ab Initio Calculation of the Crystalline Structure and IR Spectrum of Polymers: Nylon 6 Polymorphs

Claudio Quarti,<sup>†</sup> Alberto Milani,<sup>\*,†</sup> Bartolomeo Civalleri,<sup>‡</sup> Roberto Orlando,<sup>‡</sup> and Chiara Castiglioni<sup>†</sup><sup>†</sup>Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy<sup>‡</sup>Dipartimento di Chimica e Centro di Eccellenza NIS, Università di Torino, Via P. Giuria 7, I-10125 Torino, Italy

## Supporting Information

**ABSTRACT:** State-of-the-art computational methods in solid-state chemistry were applied to predict the structural and spectroscopic properties of the  $\alpha$  and  $\gamma$  crystalline polymorphs of nylon 6. Density functional theory calculations augmented with an empirical dispersion correction (DFT-D) were used for the optimization of the two different crystal structures and of the isolated chains, characterized by a different regular conformation and described as one-dimensional infinite chains. The structural parameters of both crystalline polymorphs were correctly predicted, and new insight into the interplay of conformational effects, hydrogen bonding, and van der Waals interactions in affecting the properties of the crystal structures of polyamides was obtained.

The calculated infrared spectra were compared to experimental data; based on computed vibrational eigenvectors, assignment of the infrared absorptions of the two nylon 6 polymorphs was carried out and critically analyzed in light of previous investigations. On the basis of a comparison of the computed and experimental IR spectra, a set of marker bands was identified and proposed as a tool for detecting and quantifying the presence of a given polymorph in a real sample: several marker bands employed in the past were confirmed, whereas some of the previous assignments are criticized. In addition, some new marker bands are proposed. The results obtained demonstrate that accurate computational techniques are now affordable for polymers characterization, opening the way to several applications of ab initio modeling to the study of many families of polymeric materials.



# Vibrational Properties of MBH<sub>4</sub> and MBF<sub>4</sub> Crystals (M = Li, Na, K): A Combined DFT, Infrared, and Raman Study

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## Supporting Information

**ABSTRACT:** In this work vibrational properties of alkaline-metal borohydrides and of the corresponding tetrafluoroborates are studied by comparing DFT harmonic vibrational IR and Raman spectra of the crystals with the experimental ones, obtained by infrared attenuated total reflection and Raman techniques. The computed internal bending frequencies of the [BX<sub>4</sub>]<sup>-</sup> anions are found to be in good agreement with the experiment, and the computed stretching frequencies of tetrafluoroborates are slightly underestimated. As expected, due to the neglecting of anharmonicity in the DFT spectra, the computed stretching frequencies of borohydrides are overestimated. The peak assignment of the experimental spectra is carried out in terms of factor group theory. For borohydrides, it is mostly in agreement with previously published data but for a peak observed at ca. 1400 cm<sup>-1</sup>. The peak assignment for KBF<sub>4</sub> and LiBF<sub>4</sub> was carried out for the first time in terms of factor group theory. This work is the first step on the way to determining the vibrational properties of the MBH<sub>4</sub> + MBF<sub>4</sub> solid solutions for hydrogen storage materials with enhanced H<sub>2</sub>-release/uptake properties and solid-state electrolytes.

