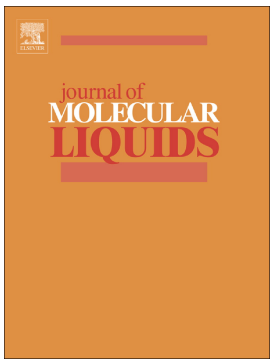

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PII: S0167-7322(18)34089-3
DOI: doi:10.1016/j.molliq.2018.09.092
Reference: MOLLIQ 9698

To appear in: *Journal of Molecular Liquids*

Received date: 7 August 2018
Revised date: 14 September 2018
Accepted date: 18 September 2018

Please cite this article as: Benedito J.C. Cabral , Born-Oppenheimer molecular dynamics, hydrogen bond interactions and magnetic properties of liquid hydrogen cyanide. Molliq (2018), doi:10.1016/j.molliq.2018.09.092

Born-Oppenheimer molecular dynamics, hydrogen bond interactions and magnetic properties of liquid hydrogen cyanide

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Abstract

Magnetic properties are a very sensitive probe of hydrogen bond interactions. In this work, the magnetic shielding constants of liquid hydrogen cyanide (HCN) were investigated through a combined approach, where quantum mechanical calculations are carried out by using configurations generated by Born-Oppenheimer molecular dynamics (BOMD). Following the trends observed in small HCN clusters, the results for liquid HCN show that the magnetic shielding constant $\sigma(^{15}\mathrm{N})$ is increased by 10.5 ± 12 ppm relative to its gas phase value, which is in very good agreement with experiment (10 ppm). The shielding of the N atom in the liquid phase of HCN is in contrast to what is observed in liquid ammonia, where the N atom is deshielded relative to the gas phase. By adopting a natural chemical shielding (NCS) analysis, it is shown that the $\sigma^d(^{15}\mathrm{N})$ diamagnetic shielding constant of HCN is not changed when we move from the gas to the liquid phase. Moreover, the results strongly indicate that the gas-to-liquid chemical shift of the ^{15}N atom is essentially determined by the difference between the nitrogen lone-pair (LP) orbital paramagnetic contribution to $\sigma^p(^{15}\mathrm{N})$. The importance of coupling NCS to BOMD configurations for a better understanding of the relationship between hydrogen bonding and the somewhat anomalous shielding of the ^{15}N atom in liquid HCN is stressed.

Keywords: Born-Oppenheimer molecular dynamics, hydrogen bond interactions, magnetic properties, liquid HCN.