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Decontamination of DMMP by adsorption on ZnO, A Computational Study

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ABSTRACT

Ab initio calculations at the density functional theory (DFT) and the second-order Møller−Plesset perturbation theory levels with 6-31+G(d), 6-31G(d) basis sets for non-metal atoms and LANL2DZ for metal have been performed for the adsorption of dimethyl methylphosphonate (DMMP) on ZnO by Gaussisn 98 program**.** The calculated rotational constants by B3LYP/6-31G(d) are in more agreement with the experimental values. The type of interaction between the Zn from ZnO and phosphoryl group from DMMP is estimated by AIM analysis. The molecular adsorption occurs by van der waals interaction of $Zn\cdots O{=}P$ With one Hydrogen bonding, between CH_3 groups and oxygen of zinc oxide.

Keywords: DMMP (dimethyl methylphosphonate); ZnO; Decontamination; DFT; MP2; AIM

INTRODUCTION

A. Gas sensors: ZnO

Surface acoustic wave (SAW) sensors are highly sensitive to surface perturbations. Their advantage includes speed, reliability, accuracy, low cost, real time measurement and wireless sensing in inaccessible areas. These sensors are used for detecting chemical warfare agents, explosive vapors, environmental pollutants etc [1].

The sensitive coating deposited on SAW device is generally a limiting element in terms of selectivity, but also strongly in terms of sensor repeatability, reliability and long term stability. In many cases the sensitive coatings are polymers that are generally difficult to deposit homogeneously and efficiently on to the transducer surface. A strict control of the thickness, uniformity, viscosity and film adherence of the coating is necessary in order to obtain reliable performances. Hence metal oxides are preferred over the polymer films. Among various metal oxides (SnO_2, ZnO, WO_3 [2] and TiO_2), ZnO was one of the most widely used gas sensing material [3]. ZnO gas sensors have been fabricated in various forms to detect H_2, NO, NH_3, CH_4, O_2, CO and ethanol [4]. Zinc oxide is a semiconductor with a wide gap energy (3.3eV) and has a wurtzite structure [5], also the melting point of zinc oxide is so high and the surface of

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zinc oxide is Lewis acid and Lewis base, these properties caused to adsorption properties in a wide variety range of phosphorus components [6].

B. Nerve Agents : DMMP

Knowledge eliminate nerve agent pollution, can improve the health of human society, because of hazardous and different mechanism of these materials, researchers are preferring to use stimulant nerve agents and computational methods to investigate their decontamination reaction, instead stimulant nerve agents are less toxic than nerve agents and we can use them for researches purposes, but stimulant nerve agent properties is not look like nerve agent, completely. Sarin is extremely toxic nerve agent, whose exposure may lead to coma, convulsions, loss of consciousness, loss of memory, paralysis, uncontrollable trembling vision problems and death [7].

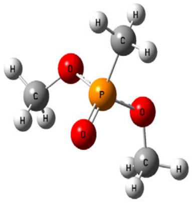

Fig. 1. Molecular structures of DMMP.

Dimethylmethylphosphonate(DMMP) is not classified as a toxic compound, but it can be used as a simulant for sarin training exercises and for calibration of detectors. DMMP is a chemical weapons used in the synthesis of sarin nerve gas. It is a suspected carcinogen [8]. Table 1 shows some properties of DMMP stimulant nerve agent [9].

COMPUTATIONAL METHOD

In this work, we employed MP2 and DFT method with Lee-yang-Parr's correlation Functional (B3LYP) and 6-31+ G(d), 6-31G(d) basis sets for non-metal atoms and LANL2DZ for metal. The scaling of normal-mode frequencies in *ab* initio calculations has been discussed extensively. In the present work, B3LYP values were scaled by a factor of 0.96 [10] and the MP2 values were scaled by factors of 0.94 [11]. The interaction energies of studied adsorption systems were corrected by the Basis Set Superposition Error (BSSE).

All calculations were carried out with the Gaussian 98 program [12] by a CPU corei7 (2G RAM) computer with the windows XP operating system.

Since much of the present work focuses on the infrared (IR) vibrational spectra of adsorbed DMMP, the first task is to show that the properties of the free molecule can be correctly described. One concern lies in determining the influence of the method of calculation and the choice of basis sets on the accuracy of the final results. To this end, two different methods for dealing with electron correlation are considered, namely, second-order Møller-Plesset (MP2) correction to the RHF wavefunction and DFT with the hybrid B3LYP functional. Basis sets of different quality are also evaluated. The experimentally observable properties of interest are the geometry (i.e., bond lengths and angles) or the rotational constants (which are closely related to the geometry) and the vibrational spectra. Rotational constants derived from microwave spectra are the only available data related to molecular geometry [13]. The calculated rotational constants of the DMMP at B3LYP and MP2 are compared with the experimental values, Table 2. The error is defined as (cal-obs/obs) and summed over all three rotational constants.

A quantitative comparison of the bond strength can be given in terms of the bond topological properties. So, the wave functions obtained are evaluated with the program package AIM 2000 [14].

RESULTS AND DISCUSSION

This article reports the development of ZnO coated for the detection of DMMP (Dimethyl methylphosphonate), a stimulant of chemical warfare agant sarin at room temperature.

The calculations include the evaluation of various methods applied, optimized geometries, and charge transfer.

The results for the rotational constants in Table 2 shows an average error of about 6% for B3LYP/6-31G(d) vs 7% for MP2/6-31G(d). The average error for 6-31+G(d) basis set at both levels is more than 6-31G(d). Table 2 shows that the calculated rotational constants by B3LYP/6-31G(d) are in more agreement with the experimental values and with the smallest error with respect to other methods. Therefore, we are focused on the B3LYP/6-31G(d) results for the next calculations.

P=O Interaction with ZnO:

A. IR Analysis

The FT-IR spectroscopy was used by Aurian- Blajeni and Boucher to investigate the adsorption of DMMP on TiO_2, Al_2O_3, MgO, and WO_3. In all cases they observed a decrease in the P=O stretching vibrational frequency, indicated that the surface species is bound through the P=O bond [15].

The harmonic vibrational frequencies of the fully optimized structures were calculated to confirm the stationary point as a local minimum with all positive frequencies, Table 3. The P=O frequency is very sensitive to association effects with the oxygen atom. The environmentally sensitive phosphoryl (P=O) stretching mode of the DMMP molecule is found between 1200 and 1300 cm^{-1} [16-18]. The shift to lower frequency of the P=O stretching mode is consistent with a mechanism involving an interaction between the phosphoric oxygen and Zn. The frequency values show that the molecular adsorption occurs by formation of a Zn…O═P interaction and with one C-H···O bond (H bonding), between CH_3 group and oxygen of zinc oxide.

Table 1. DMMP stimulant nerve agent properties

IUPAC name	phase	Molecular Formula	Molecular Weight	Boiling Point	Melting Point	Vapor Density	Liquid Density	Vapor pressure
(methoxy –methyl phosphoryl) Oxy methane	colorles s liquid at STP	$C_3H_9O_3P$	124.08g/mol	181°C	-50°C	4.2g/ml	1.15g/ml	160 Pa at 25°C

Table 2. Observed and Calculated Rotational Constants (MHz) for DMMP

methods	A	B	C	Sum of errors	Average Error
Experimental[14]	2828.753	1972.329	1614.268	0.000	0.00
B3LYP/6-31+G(d)	2279.758	1886.108	1463.008	0.328	11.04%
MP2/6-31+G(d)	2347.563	1891.209	1581.032	0.340	7.72%
B3LYP/6-31G(d)	2506.271	2068.153	1579.958	0.184	6.12%
MP2/6-31G(d)	2484.934	2119.667	1601.957	0.198	7.11%

Table 3 shows the experimental frequency of DMMP [19] and the frequency shifts at different sites of DMMP after the adsorption on ZnO. The gas-phase value of ν (P=O) is of special interest since it is the mode most affected by adsorption. The frequency shift of phosphoryl group ($\Delta\nu_{(P=O)}$) after the adsorption on ZnO is 154 cm^{-1}, that this is a large change with respect to other frequency shifts. Therefore, the effect of oxygen site of phosphoryl group of DMMP on ZnO is stronger than other sites of DMMP. The type of interaction between the Zn and phosphoryl group is estimated by AIM analysis.

Table 3. Fundamental Frequencies (cm^{-1}) for isolated DMMP and connected to ZnO

Frequencies /cm^{-1}	Experimental^1 DMMP	B3LYP/6-31G(d)		$\Delta\nu^2$
		DMMP	DMMP, ZnO	
ν (P-CH$_3$)	3014	3036	3045	31
ν (O-CH$_3$)	2962	3006	2987	25
ν (O-CH$_3$)	2859	2931	2859	0
ν (O-CH$_3$)	1471	1471	1451	20
ν (P-CH$_3$)	1423	1429	1428	5
ν (P=O)	1276	1277	1122	154
ν (C-O)	1075	1056	1077	2

1.The experimental spectrum was obtained at 8 cm^{-1} resolution at a DMMP pressure of 0.58 Torr in a 30cm gas cell with KBr windows [19]

2.$\Delta\nu = \nu$ (DMMP, ZnO) – ν (DMMP exp.)

B. AIM Analysis

The quantum theory of atoms in molecules (QTAIM) [20] (developed by Professor Richard F.W. Bader and his coworkers), relies on quantum observables such as the electron density ρ(r) and energy densities. A substantial aspect of Bader's theory of atoms in molecules (AIM; Bader, 1994) is the partitioning of a molecule into submolecular or even atomic regions [21, 22]. There is one BCP between each pair of atoms that are bonded, i.e., two atoms linked by a bond path and sharing a common interatomic zero-flux surface. In addition to the set of trajectories which terminate at the BCP and define an interatomic surface, a pair of trajectories originates at the BCP with each member of the pair terminating at one of the nuclei of the chemically bonded atoms. Chemical bonding interactions are characterized and classified according to the properties of the electron and energy densities at the BCP, collectively know as ''bond properties''. The Electron Density at the BCP (ρ_b) has been shown to be strongly correlated with the binding energy for several types of bonding interaction. The ionic bonds, hydrogen bonds and bonds in van der Waals molecules are all closed-shell interactions. In closed shell systems, the electron density at the BCP, ρ_b, is low, i.e. of the order of 10^{-2} au and lower. On the other hand, covalent or polar bonds are shared interactions, typically leading to ρ_b values of the order 10^{-1} au [23, 24]. A quantitative comparison of the covalent bond strength can be given in terms of the bond topological properties.

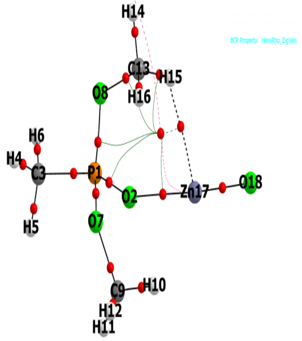

Fig. 2. DMMP connected to ZnO.

Table 4. The Electron Density at the BCP (ρ_b) before and after interactions

ρ_b /au	
Before interaction	After interaction
Zn-O= 0.17068 P_1-O_2= 0.22520 C_{13}-H_{15}= 0.28048 C_{13}-H_{16}= 0.27701	Zn_{17}-O_{18}=0.17236 Zn_{17}-O_2 =0.08736 P_1-O_2= 0.20532 C_{13}-H_{15}=0.28031 C_{13}-H_{16}=0.28072

Table 4 presents the results for the values of the charge density (ρ_b) obtained by the

B3LYP/6-31G(d) method. The value of ρ_b for H_{15} from DMMP structure and Zn_{17} from ZnO molecule is 0.00614 au, of the order 10^{-3}, that the bond character is hydrogen bond interaction (fig 2). The value of ρ_b for connected atoms O_2 –Zn_{17} is 0.08730 au, of the order 10^{-2}, that, this value shows the van der waals interaction between the DMMP and ZnO. The covalent bonds of P_1-O_2 and Zn-O before interaction, leads to ρ_b values of the order 10^{-1} au.

CONCLUSION

We study interaction of DMMP and ZnO by using density functional theory. The calculated rotational constants by B3LYP/6-31G(d) are in more agreement with the experimental values. The favorable adsorption site of DMMP was found at the configuration where the oxygen atom of the P=O point toward the Zn of the ZnO .Our results show that the molecular adsorption occurs by van der waals interaction of $Zn\cdots O{=}P$ and With one C-H···O bond (H bonding), between CH_3 groups and oxygen of zinc oxide.

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