



Photoexcitation effect on the adsorption of hazardous gases on silica surface



Yonggang Yang^a, Donglin Li^a, Chaozheng Li^a, Yufang Liu^{a,*}, Kai Jiang^b

^a College of Physics and Materials Science, Henan Normal University, Xinxiang 453007, China

^b School of Environment, Henan Normal University, Xinxiang 453007, China

HIGHLIGHTS

- A sample of photoexcitation effect on adsorption of adsorbent is proposed.
- Adsorption relies not on hydrogen bond but charge transfer after photoexcitation.
- Photoexcitation effect is presented as a new standard for detection of adsorbent.

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ABSTRACT

There is very little scientific understanding of photoexcitation effect on the adsorption properties of adsorbent. The adsorption of four hazardous gases (SARIN (propan-2-ylmethylphospho-nofluoridate), methyl dichlorophosphate (MDCP), trimethyl phosphate (TMP) and hydrogen sulfide (H₂S)) on silica surface is taken as target sample in this work. The adsorption energy order (MDCP < SARIN < TMP) in the ground state is consistent with the strength order of intermolecular hydrogen bond (inter-HB) between hydroxyl group of silica surface and hazardous gas, and the desorption order of the three gases in previous reports. However, with the adsorption energy increase of MDCP and the decrease of SARIN and TMP, this order changes remarkably to SARIN < TMP < MDCP after photoexcitation to excited state by absorbing shortwave ultraviolet irradiation. This change is opposite to the inter-HB weakening of MDCP in the first excited (S₁) state and the strengthening of TMP and SARIN in the second excited (S₂) state. This opposite change is caused by formation of intermolecular charge transfer state of MDCP and local excitation of SARIN and TMP. The H₂S is dissociated after photoexcitation to the S₁ state. This work presents photoexcitation as a new standard for the design and detection of adsorption properties of adsorbent for its striking effect on adsorption behaviors.

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1. Introduction

Many technologies have been developed to detect chemical warfare agents (CWAs) and decompose them into nontoxic substances, because of their severe environment contamination and highly deleterious effects on humans [1–4]. Among these CWAs, the nerve agents, such as SARIN and soman, have attracted much concern due to high lethality and have become one of the greatest threats in modern world for the possible use in warfare or terrorist attacks [1,3,5,6]. Surface chemistry of CWAs simulants on environmental materials has become a demanding scientific problem, and is also critical to the rational design of adsorbents and decontamination strategies [1,7–11]. Researchers have designed many

simulants of target nerve agents without extreme toxicity, which cannot fully mimic real environmental fate [9,10]. Theoretical approach can eliminate nerves agents' hazards and bring fundamental insight into wide range of conditions, and thus has become a forceful tool for investigating nerves agents–environmental surface interaction [10].

As one of the most abundant materials in environment, the amorphous silica has been utilized as excellent surrogate and test system for exploring nerve agent gas–surface intermolecular interactions [1,8,12–17]. It has been widely used as adsorbent and catalyst support for its relatively high surface area and unique surface properties [18]. The hydroxylation of silica surface is of critical importance and major concern in the design of a decontamination system because of its controllability [1,11,19–27]. Adsorption of gas-phase molecules to silica surface has been the subject of research in many branches of science [19–28]. The adsorption of silica is known to depend largely on the surface hydroxyl (silanol)

* Corresponding author.

E-mail address: liyufang2005@126.com (Y. Liu).

groups by forming strong hydrogen bonds primarily between surface silanol groups and the oxygen atom of the P=O moiety in the adsorbate [12,28,29].

Many researches have been conducted to better understand the adsorption of nerve agents to silica and design more effective sensing methods [27,30]. Organophosphorous (OP) compounds mimic the structure and surface chemistry of nerve agents with low toxicity [28]. Wilmsmeyer and coworkers have demonstrated that the simulants (methyl dichlorophosphate (MDCP), dimethyl chlorophosphate (DMCP), trimethyl phosphate (TMP), dimethyl methylphosphonate (DMMP) and diisopropyl methylphosphonate (DIMP)) are adsorbed on silica surface through intermolecular hydrogen bond between P=O group and the surface hydroxyl, which is confirmed by their infrared spectroscopy [12,23,31,32]. The strength order of the adsorption follows the trend MDCP < DMCP < TMP < DMMP < DIMP. MDCP, DMMP and TMP are desorbed from silica at 150 °C, 300 °C and at 400 °C respectively [12,23,31]. Temperature is an important factor in affecting adsorption properties of these organophosphorous gases to silica [33]. Moreover, it is demonstrated that the adsorption of DMMP on silica surface depends largely on the hydroxyl coverage of the silica surface [1].

Besides temperature and hydroxyl coverage, photoexcitation effect on the adsorption behaviors of adsorbent has not been extensively studied to our best knowledge. Under normal conditions, silica and its adsorbed complexes are located at ground state, which indicates the lowest energy state and the zero-point energy of the system [34–36]. The ground state of these molecular systems tends to be stable unless the molecular system absorbs energy which is equal to the difference between the ground state and higher state (called excited state). The excited state is a quantum state of the system with higher energy than the ground state [36,37]. These excitation energies are often obtained from irradiation of different wave band, laser, heat and other energy sources. This transition progress occurs with the molecular orbital transition, charge distribution and geometric change, which will induce different changes of adsorption/desorption behaviors. In this work, photoexcitation effect on the adsorption behaviors of four hazardous gases on silica surface will be discussed in detail.

Adsorbent will be excited to the first excited (S_1) state or higher state (S_n , $n \geq 2$) after absorbing transition energy from ultraviolet (UV) light or other energy sources, which will induce different adsorption behaviors, such as adsorption strengthening, desorption or dissociation. Adsorption in the ground state plays a crucial role in the adsorption strength for the adsorbent with large transition energy. The analysis of transition energy and photoexcitation effect will become an important environment effect on adsorption properties of adsorbent. Many works have been reported on study the adsorption of mimetic organophosphonates to silica in the ground state [9–12,22–24,8,31,38–41]. In this work, the adsorption of four hazardous gases to silica before and after photoexcitation is provided as target sample. Samples of nerve agents' simulants (MDCP, TMP), SARIN and hydrogen sulfide are chosen to study their adsorption properties and dynamics behaviors on silica surface in the ground state and excited state. Hydrogen sulfide (H_2S), a toxic gas in the industrial gases, can cause irritation to human health and acidic rains [41–43]. This study will take photoexcitation effect as a new standard for the design and detection of adsorption properties of adsorbent, which will provide comprehensive explanation on adsorption behaviors together with temperature and other environment effects.

2. Theoretical methods

The geometric structures, electronic and infrared spectra of the four complexes are calculated using Gaussian 09 program

suite [44]. Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation functional (B3-LYP functional), in combination with 6-31G* basis set, is used in both the Density functional theoretical (DFT) and TDDFT methods [45,46]. The entire local minimums are confirmed by the absence of any imaginary frequency in vibrational analysis calculations. The wave function analysis is performed by the Multiwfn program in order to obtain the information about reduced density gradient (RDG), electrostatic potential value, electron-hole, the bonding energy, and the Lorentz oscillator [47].

3. Results and discussion

The adsorption of organophosphorous compounds (MDCP, SARIN, TMP) and hydrogen sulfide to silica surface is governed by the intermolecular hydrogen bond interaction. Excited state hydrogen bonding dynamics have been demonstrated to be a reliable tool for studying intermolecular interaction and their dynamic behaviors [48–53]. For convenience, hydrogen bonded complexes for MDCP, SARIN, TMP and H_2S with silica surface are denoted as their monomers. In this work, the adsorption change of MDCP, SARIN, TMP and H_2S on silica surface in excited state are investigated by focusing on the adsorption energy change and dynamics behaviors of intermolecular hydrogen bonding before and after photoexcitation.

3.1. Optimized geometric structures in the ground state and the excited state

The bond lengths and angles of the four complexes in ground and excited states are denoted in For MDCP in Fig. 1A and B, the bond length of P=O...H-O is calculated to be 1.813 Å in the ground state, which lengthens to 1.855 Å after photoexcitation to the excited S_1 state. The bond lengths of P=O and O-H, which are involved in the formation of P=O...H-O, respectively lengthen about 0.105 Å and shorten about 0.002 Å in the S_1 state. The angle OHO changes little from ground state (163°) to the S_1 state (165°), implying a slight change in hydrogen bond interaction sites of P=O...H-O. These changes indicate that the intermolecular hydrogen bond P=O...H-O is weakened when excited to the S_1 state, indicating that the adsorption strength of MDCP on silica surface is weakened compared to that in the ground state. We focus on the second excited (S_2) states of SARIN and TMP because of their small transition probability in the S_1 states. For SARIN in Fig. 1C and D, the bond length of P=O...H-O decreases from 1.741 Å in the ground state to 1.477 Å in the excited S_2 state. The bond length change of P=O...H-O of TMP is similar to that of SARIN, decreasing from 1.716 Å in the ground state to 1.477 Å in the S_2 state. The changes of SARIN and TMP indicate that the intermolecular hydrogen bonds are both strengthened compared to the ground state, implying that the adsorption of SARIN and TMP are both strengthened in the S_2 state compared to ground state. The bond lengths of intermolecular hydrogen bonds of MDCP, SARIN and TMP are consistent with the theoretical results obtained by Troya [28]. In Fig. 1G and H, the silica with two silanol groups is hydrogen bonded with hydrogen sulfide by two O-H...S intermolecular hydrogen bonds, denoted as O₁-H₁...S and O₂-H₂...S. It is observed that the bond lengths of O₁-H₁...S and O₂-H₂...S are 2.602 Å and 2.574 Å respectively, which change to 2.580 Å and 2.603 Å when excited to the S_2 state. This change indicates that intermolecular hydrogen bond O₁-H₁...S is strengthened and O₂-H₂...S is weakened in the S_2 state compared to that in the ground state. The angle O₁H₁S changes little, while the angle O₂H₂S decreases largely from 166° in the ground state to 79° in the excited S_2 state. It is interesting to observe that one of the S-H bonds is cleaved in the S_2 state, indicating dissociation of H_2S after photoexcitation. The bond length and

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