

Theoretical Analysis of CO₂ Addition to Ion-Bombarded Porous Silica

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The CO₂ insertion into argon-bombarded porous SiO₂ is studied theoretically via *ab initio* molecular dynamics. The results of this analysis are consistent with CO₂ addition to the SiO₂ skeleton at the diradical silicon defects produced by the bombardment. Molecular dynamics suggests that the addition is initiated with the formation of carboxylate and evolves to ester-like centers.

1. Introduction

The study of the chemical reactivity of porous solids after ion bombardment is very recent.¹ Probably because the native radiation-damage defects (namely, the E' center² and the silicon-link vacancy³) are otherwise practically impossible to synthesize, neither the reaction pathways with gas-phase molecules nor the final products can easily be predicted. The E' center observed in bulk SiO₂ after irradiation is in a triplet state and is usually specified by an index giving the total spin, E'₁. Parallel spins, which prevent recombination in bulk phase, are however not necessary to prevent recombination in a dispersed matrix. In the absence of any other information on spins, we shall adopt the symbol E'.

In ref 1 the infrared (IR) spectra of ion-bombarded porous silica exposed to a CO₂ atmosphere were determined for the sample in as-implanted conditions, after heating at 500 °C, and after exposure to wet air: Figure 1a compares the spectrum of the as-prepared sample with the one after high-temperature annealing (each of these spectra is actually obtained by subtraction of a reference spectrum determined on an unbombarded sample). The comparison shows that the formed species are remarkably stable with respect to temperature and thus suggests that the species are inserted via Si–C bonds rather than Si–O–C bridges (which is known to undergo pyrolysis at around 400 °C⁴). Figure 1b shows that after exposure to wet air at room temperature the complex spectrum of Figure 1a disappears and a peak arises which can be reasonably attributed to a carboxylic acid group, COOH.

The combination of these facts with reported attributions⁵ led the collaboration of ref 1 to ascribe the sharp peak at 1515 cm⁻¹ to the antisymmetric O–O stretching mode of the carboxylate ion, COO⁻, the peak at 1595 cm⁻¹ to carboxylate ions coordinated to a cation or to hydrogen (via hydrogen bonding), and the peak at 1710 cm⁻¹ to a carbonyl C=O local mode. These attributions must be considered as putative, since no CO₂ adducts to (–O)₃Si•Si(O⁻)₃ were actually known. Because of this state of affairs, *ab initio* quantum mechanical calculations can be performed on the hypothesized species in order to validate the correctness of the above attributions and ascertain the stability range.

The *ab initio* quantum mechanical analysis, however, cannot provide an indication about the detailed dynamics of CO₂

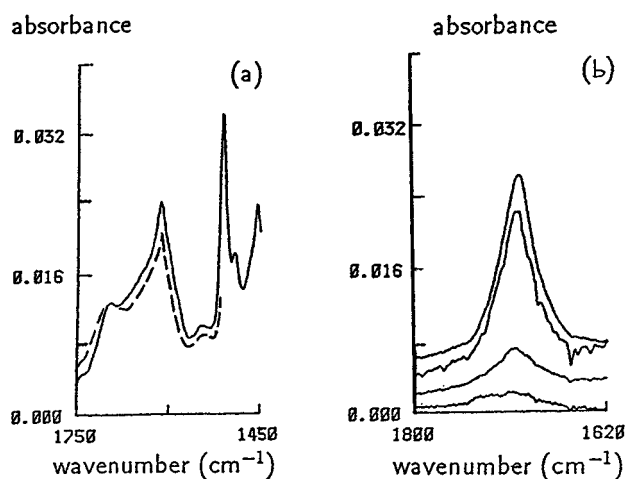


Figure 1. Infrared spectra of (a) as-prepared ion-bombarded porous silica exposed to CO₂ during the bombardment and after heat treatment at 500 °C and (b) after exposure to wet air.

addition, and questions such as “which among the possible adducts are really formed?” or “does the reaction occur via gas-phase collisions or via physisorbed CO₂?” remain unanswered. In this work we try to give preliminary answers to such questions by simulating the reaction of CO₂ with the E' center via *ab initio* molecular dynamics to search for insertion modes in the picosecond time scale.

2. The Theoretical Framework *ab Initio* Molecular Dynamics

The quantum description of chemical reactivity, with the complex problem of crossing of electronic levels and the need for describing nonstationary states, is only the beginning. Although methods based either on the density functional technique or on the Hartree–Fock one are known,^{6–10} there is not a general easy-to-use tool for this.

The feasibility of *ab initio* molecular dynamics calculation, *i.e.* of the numerical integration of the Newton equations of motion for a number of atoms with forces derived at each step from the instantaneous electronic configuration computed by means of the density functional approximation, was first demonstrated by Car and Parrinello.¹¹ Although the Car–Parrinello method provides information on the dynamics of interacting species, its applications to chemical reactivity have however been rare and usually limited to situations close to equilibrium.^{12,13}

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In the following, *ab initio* molecular dynamics is used to simulate the reaction between CO₂ and the E'' center. A number of trajectories is calculated in order to describe the possible products of this reaction.

The E'' center in the stationary state is simulated by two close radicals (HO)₃Si•Si(OH)₃. The adducts formed during the reaction with CO₂ are determined via *ab initio* molecular dynamics with the Car–Parrinello method. All calculations are run on IBM RISC 6000/950 with 200-Mbyte random-access-memory.

In the calculations only valence electrons are treated explicitly. The interaction between the valence electrons and the core electrons plus nuclei is described by means of pseudopotentials; fully nonlocal pseudopotentials of the Bachelet–Hamann–Schluter type¹⁴ are employed for silicon, carbon, and oxygen.

Since the reaction is thought to occur through the interaction of a silicon diradical with an otherwise inert CO₂, the considered model system is formed by a CO₂ molecule in the vicinity of two (HO)₃Si• radicals. These radicals are taken at a distance of 3.14 Å (the Si–Si distance in silicates), and the three OH groups are constructed in a staggered configuration to avoid agostic interactions; the CO₂ molecule is linear, and the C–O distance is 1.19 Å. The considered model has a size approximately 9 Å and is placed in a cubic box with an edge of 30 Å. Periodic boundary conditions are imposed.

The dynamics in each trajectory is preceded by an equilibration and an energy minimization based on conjugate gradients. Each trajectory is followed over a time span ranging from 200 to 400 fs, each step being 0.09 fs long. No restraint on the temperature is placed.

In a few cases the masses of silicon and hydrogen atoms are fictitiously increased to 128 and 200 amu, respectively, in order to take into account the restraint on mobility and velocities due to the solid state environment. Four different initial configurations are considered, differing in the distance and orientation of CO₂ with respect to the silicon centers. The evolution of the system in time is monitored in terms of total potential energy *V* and geometrical parameters.

The employed software package, AIMD (*Ab-Initio* Molecular Dynamics), was developed by IBM. For the purpose of visualization the MSI software tools, in particular the visualizer and the analysis module of DISCOVER,¹⁵ are used by means of an *ad hoc* interface.

3. Dynamics in the Picosecond Time Scale

This section is devoted to search via *ab initio* molecular dynamics the possible adducts that are formed in the picosecond time scale.

3.1. Relaxation of the Silicon-Diradical Center. In the first considered case the starting configuration of the CO₂ molecule is rather far from the two silicon atoms. Two simulations, with real and augmented masses, have been simulated with trajectories lasting 400 and 200 fs, respectively.

Figure 2 reports the potential energy *V* (curve 1) and the silicon–silicon distance *r* (curve 2) against the time *t*. During the run CO₂ escapes from the radical centers and the two silicon atoms monotonically approach to a minimum distance, as it is expected for the silicon–silicon bond to be formed. The energy on the average decreases until a minimum is reached. The nuclear configuration of the minimum is reported in the sketch of Figure 2. In the simulation starting with the same atomic configuration and the silicon and hydrogen mass fictitiously augmented, the amplitude of energy oscillations is reduced as expected. Such large oscillations are due to the fact that the initial potential energy is very high and dramatic energy

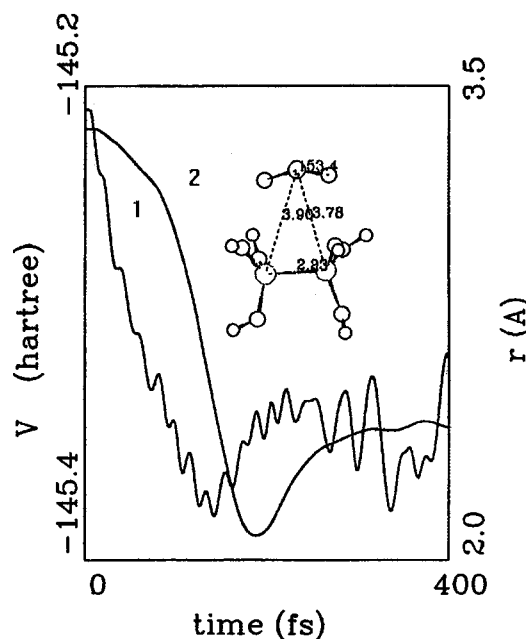


Figure 2. Time evolution of the total potential energy *V* (curve 1) and silicon–silicon distance *r* (curve 2) for a path leading to the formation of a Si–Si bond. The sketch gives the structure of the minimum energy adduct.

exchanges among different (translational, electronic, etc.) degrees of freedom take place. We observe also that when the minimum is reached, the Si–Si distance oscillates between 2.1 and 2.4 Å and the minimum energy is reached twice during the oscillations. The above path can be described as follows: (HO)₃Si•Si(OH)₃ → (HO)₃Si–Si(OH)₃.

Of course, a Si–Si bond can spontaneously be formed only if the energy gained in this process (about 3 eV) exceeds the energy required to strain the SiO₂ skeleton.

In the above situations there is no CO₂ insertion in between silicon atoms. A different reactivity is expected to be observed when the CO₂ initial configurations are such that the van der Waals radii of its constituent atoms overlap appreciably with those of silicon, thus simulating energetic interactions of collisions.

3.2. The Formation of Carboxylate and Ester-like Groups.

In the considered cases the CO₂ in the E'' center (with both real and augmented masses) is assumed to have starting configurations with one of the oxygens pointing toward one of the silicon atoms at a distance that is close to a bonding distance, this way forcing the formation of a Si–O–C=O• adduct. On the contrary, during the two trajectories, lasting 170 fs for real and 400 fs for augmented masses, the system evolves in a way to remove the bumping of the oxygen and the CO₂ bends and flips, while the C–O bonds elongate almost symmetrically until an energy minimum is reached. The resulting configuration can be described as a carboxylate group bound to a silicon. After the CO₂ insertion, the system evolves, overcoming an energy barrier of 5–6 eV, to a configuration that can be described as an ester-like configuration. This configuration is the most stable one and is the absolute minimum of the trajectory and is the same in structure and energy between the two simulations.

Figure 3 reports the results for the run carried out for the system with true mass values, starting from the same initial configuration as for augmented masses: curve 1 gives the potential *V* and curve 2 the Si–Si distance *r*.

The formation of a carboxylate (Figure 3, sketch a) is reported and a subsequent evolution of the system to an ester-like configuration (Figure 3, sketch b) over a total duration of 170

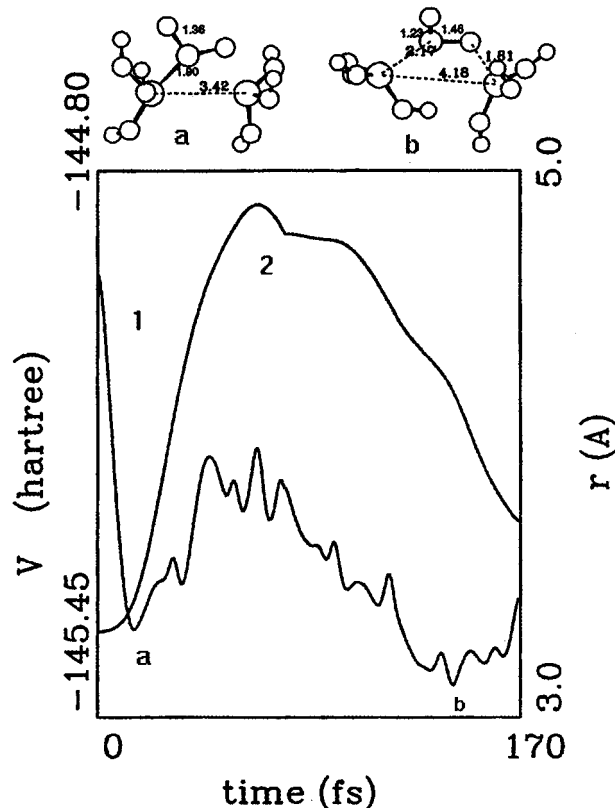


Figure 3. Time evolution of the total potential energy (curve 1) and silicon-silicon distance (curve 2) for a path showing the insertion of CO₂ via the formation first of a carboxylate group and eventually of an ester-like group. Sketches a and b give the structure of the two described adducts.

fs. The Si-Si distance goes from 3.3 Å to almost 5.0 Å and then lowers to 4.18 Å at the minimum energy.

3.3. Insertion with the Formation of Two Siloxyl Radicals. When the CO₂ molecule is symmetrically put in the E'' center with the two oxygens bumping against two oxygen atoms of the silanol groups, a potential energy minimum is observed after 50 fs (Figure 4, sketch a). The configuration can be described as the formation of two single bonds between the carbon and the two silicon atoms, with the O-C-O angle close to 90°, a C-O distance of 1.4 Å, and a Si-Si distance of 3.22 Å.

Since a single bond is formed with each oxygen atom, they are expected to have a radical character, thus forming the following species: (HO)₃Si-(O*)C(O*)-Si(OH)₃.

This first stabilization is followed by an increase in potential energy and the increase of the C-Si distance, of the O-C-O angle to 147–148°, and of the Si-Si distance up to 4.0 Å (Figure 4, sketch 2). In the last part of the run the Si-Si distance lowers to 3.5 Å. As in the other cases, curve 1 reports *V* and curve 2 *r* against time *t*.

4. Discussion

Molecular dynamics suggests that CO₂ addition to the E'' center may result in one or the other of the following adducts: -COO⁻, -C(O)O-. Assuming that the minima identified considering only a few paths are representative of true minima, and taking the energy of reactants as reference level, the above adducts have the enthalpies listed in Table 1. Such energies could be affected by steric hindrance connected to the relaxation of the environment. Oxygen bonding to silicon was never found to initiate the process in any of the simulations.

This conclusion is in apparent contrast with the fact that CO₂ is chemisorbed on (-O)₃Si* radicals with the formation of a

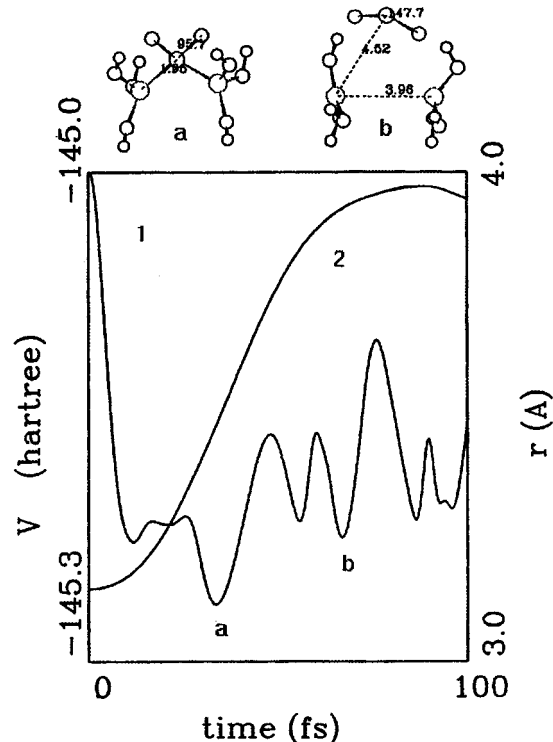


Figure 4. Time evolution of the total potential energy (curve 1) and silicon-silicon distance (curve 2) for a path showing the insertion of CO₂ via the formation of two Si-C bonds. Sketches a and b give the structure of the two adducts described in the text.

TABLE 1: Approximated Formation Enthalpy of the Adducts Predicted by *ab Initio* Molecular Dynamics

adduct	formation enthalpy (eV)
(HO) ₃ Si-(O*)C(O*)-Si(OH) ₃	2–3
(HO) ₃ Si*Si(OH) ₃ + CO ₂	0
(HO) ₃ Si-COO ⁻ + Si(OH) ₃	-0.5
(HO) ₃ Si-C(O)O-Si(OH) ₃	-(3–4)

stable ≡Si-O-C*≡O radical. The first evidence for this radical was given by Radtsig et al.,¹⁶ who showed that isolated (-O)₃Si* radicals, prepared by fracture of SiO₂ in a helium atmosphere and only later exposed to CO₂, react forming another radical, whose electronic configuration is the same as that of the center produced by the reaction of CO with (-O)₃SiO*. Radtsig and co-workers did not find any evidence for a radical center of the formula ≡Si-C(O)-O*.

One sensible interpretation of the two contradicting observations is that because of the CO₂ tendency toward electrophilic attack at carbon to metals of the main groups,¹⁸ the initial adduct is reasonably expected to be ≡Si-C(O)O*.

This state is however metastable and decays fast to other, more stable, configurations. In the absence of another isolated Si radical in its vicinity, the radical resulting from the initial attack isomerizes to the Radtsig radical: ≡Si-C(O)O* → Si-O-C*≡O.

In the presence of another ≡Si* radical, as in E'', at a distance which allows the formation of an ester-like bridge, the initial adduct reacts via the formation of a covalent adduct: ≡Si-C(O)O* + Si* → ≡Si-C(O)O-Si≡.

In the presence of another ≡Si* radical at a distance so short as not to allow a covalent insertion, the initial adduct reacts via electron transfer from ≡Si* to ≡Si-C(O)O*: ≡Si-C(O)O* + *Si≡ → ≡Si-C(O)O⁻ + ⁺Si≡.

This process, in fact, is expected to be either spontaneous or slightly endothermic, the driving force being the electron affinity of ≡Si-C(O)O* (around 4 eV) minus the ionization energy of

$\equiv\text{Si}^\bullet$ (around 6 eV) plus the electrostatic energy (the higher the electrostatic energy, the lower the Si–Si distance).

At last we note that the absence of adducts in which carbon has a tetrahedral configuration is understood by observing that the formation of $(-\text{O})_3\text{Si}-(\text{O}^\bullet)\text{C}(\text{O}^\bullet)-\text{Si}(\text{O}^-)_3$ is a highly endothermic process.

In conclusion, we have identified via *ab initio* molecular dynamics the initial stages of CO_2 addition to the E'' center and shown that the detailed reaction mechanisms cannot be simply understood in terms thermodynamic considerations.

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