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Ab initio study of the Rehbinder effect

Part I *Mechanical strength of the chemical bond in various approximations*

V. S. YUSHCHENKO[‡], E. D. SHCHUKIN[§]
Institute for Physical Chemistry of the Russian Academy of Sciences, Moscow 117915, Russia
M. HOTOKKA
Department of Physical Chemistry, Åbo Akademi University, SF-20500 Åbo, Finland

Ab initio calculations of the interatomic force as a function of the nuclear separation in the SiO molecule were performed using various theoretical models in order to find the simplest method suitable for a quantum chemical study of the mechanism of the Rehbinder effect in relatively large model systems. The polarization functions in the basis set were found to be essential. The results obtained by using the 3-21G* and 6-31G* basis sets did not differ significantly. The Møller-Plesset perturbation theory was tested up to the fourth order with single, double, triple and quadruple replacements. Limited configuration interaction calculations including the single and double replacements were also performed. Both correlated methods were found to be unsuitable for the present calculations, because a proper description of the deformed bonds requires a significant amount of excited open-shell configurations.

1. Introduction

The Rehbinder effect [1–3], i.e. the reduction of the mechanical strength and plasticity of solid materials when in contact with certain liquids or gases, can be caused by a variety of surface phenomena. One of the most obvious and "direct" reasons is the weakening of the interatomic bonds in the surface layer of the solid due to interaction with the active species. Modern quantum mechanical methods and computer technology allow a direct evaluation of the mechanical strength of chemical bonds in simple systems (see [4–6] for recent reviews on applications of quantum mechanical modelling in material science).

The computational resources set limits to the objects and methods of quantum chemical investigations in material science. One always faces a compromise between (1) rigorous and exact calculations on very small systems that are far from any real solid material on the one hand, and (2) rough calculations on large enough systems to be relevant from an experimental point of view, on the other. The effect of the various approximations may be difficult to estimate in the latter case, in particular when the influence of intermolecular interactions is studied. We prefer the model systems that reflect the main features of solid and fluid phases and an *ab initio* approach because it involves the fewest assumptions and because the effect of each approximation can be tested separately by using suitable small molecules. This approach forces us to use the simplest theoretical model sufficient at least for semi-quantitative description of the effect under investigation. Therefore, it is necessary to learn which theoretical model is the most suitable for this study.

Metallic solids are difficult to study by using conventional quantum chemical methods because the interatomic interactions are completely non-local. In solids with covalent (or predominantly covalent) bonds the properties of the interactions are, to a large extent, determined by the interacting atoms and their nearest neighbours. In our previous work [7, 8] the weakening of the carbon–carbon bond (the most widespread one in organic nature) was considered. In the present work we studied the most abundant bond type in inorganic nature – the SiO bond. It determines the strength of silica and various minerals. The Rehbinder effect in such systems is well known and widely studied experimentally (see [9–12] for recent reviews). One of the primary substances that cause the reduction of the mechanical strength of such materials is water. A detailed discussion on the mechanisms of the Rehbinder effect in the silica/water system will be presented in the next paper of the current series. However, it can be noted here that a recent quantum chemical study of this phenomenon [13], including calculation of the energy difference between (Si–O–Si) + H_2O and 2(Si–OH), did not result in any definite conclusions,

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[‡] Also: Department of Physical Chemistry, Åbo Akademi University, SF-20500 Åbo, Finland.

[§] Also: Department of Materials Science and Engineering,The Johns Hopkins University, Baltimore, MD 21218, USA.

but Catlow *et al.* [13] consider the hypothesis that water facilitates the rupture of the Si–O to be encouraging.

The main purpose of the present study was to calculate and compare the forces that resist the mechanical rupture of the Si–O bond in the presence and absence of a water molecule. The brittle character of the fracture of silica implies that this process is mainly determined by the applied force, the thermal fluctuations playing a minor role. The smallest system that can reasonably be expected to reproduce the properties of silica in water is $Si_2O_7H_6$ and H_2O which has the central Si–O–Si fragment and the correct nearest neighbours. This is quite a sizable problem for *ab initio* calculations. Therefore, a comparison of the theoretical models, which is the subject of the present paper, was performed on the SiO molecule. The double bond of this model molecule is admittedly quite different from the single Si–O bond in silica, but the unsaturated nature of the model molecules makes the test even more rigorous.

The SiO molecule has been studied extensively by using *ab initio* methods from 1972 [14] to the present time [15], but most of the papers deal with the equilibrium or near-equilibrium geometry. They report accurate calculations of other properties than those studied in the present work using advanced but time-consuming methods and can therefore be used here for comparison only.

2. Methods

The calculations were performed mainly on a VAX-6510 computer using the GAUSSIAN-86 program [16]. The restricted Hartree–Fock (RHF) calculations were done using the 3-21G, 3-21G*, and 6-31G* basis sets. The Møller–Plesset perturbation theory [17, 18] is a popular and convenient method to include the electron correlation effects in the calculation in an approximate fashion. It was tested at various levels of approximation from the second-order (MP2) and third-order (MP3) theory to fourth-order (MP4) approximation with all double and quadruple (MP4DQ), single, double and quadruple (MP4SDQ) and single, double, triple and quadruple (MP4SDTQ) substitutions. The configuration interaction method [19] with all single and double substitutions from the Hartree–Fock reference state (CISD) was also tested. It is a more advanced but, on the other hand, very time-consuming quantum chemical method for including the electron correlation effects. Both the MP and CI calculations were performed using the 6-31G* basis set.

The multiconfiguration self-consistent field method (MC–SCF) is a useful tool for studying systems where chemical bonds are broken. The potential energy curves were calculated by using the 6-31G* basis set and a rather limited active subspace consisting of the bonding and antibonding σ and π orbitals. All substitutions were allowed within the active subspace resulting in a complete active space (CAS) wavefunction. The GAMESS program [20] was used.

The theoretical method and the basis set needed to obtain sufficiently accurate results vary depending on the properties to be calculated. The criterion for selecting the method of choice in the present work is its ability to predict the interatomic forces and the mechanical strength of the bonds which are obtained as the maximum interatomic force during the rupture. The range of bond distances to be studied is also determined by this goal: the maximum force needs to be found. In the present work a much wider range of deformations extending to an almost completely dissociated molecule was studied.

3. Results and discussion

Results for the equilibrium state are listed in Table I. For the RHF and MP4 calculations our results agree with the previous calculations using the same basis set [21] but using the MP2 and MP3 approximations we obtain lower energies than Snyder and Raghavachari [21]. The potential energy and interatomic force curves are shown in Figs 1 and 2, respectively. The results from calculations using various orders of MP theory are given in Figs 3 and 4. The potential energy curves obtained using the MC–SCF method are in

TABLE I Parameters of the equilibrium structures of the SiO molecule obtained using different theoretical models

Theoretical model	R_0 (nm)	Energy (Hartree)
RHF/3-21G	0.153 63	– 361.845 86
RHF/3-21G*	0.149 56	– 361.942 12
RHF/6-31G*	0.148 70	– 363.778 84
MP2/6-31G*	0.154 23	– 364.059 41
MP3/6-31G*	0.151 02	– 364.037 50
MP4DQ/6-61G*	0.152 14	– 364.045 23
MP4SDQ/6-31G*	0.153 84	– 364.054 36
MP4SDTQ/6-31G*	0.156 93	– 364.064 49
CISD/6-31G*	0.151 60	– 364.029 12
MC–SCF/6-31G*	0.153 50	– 363.905 32
MC–SCF/6-311G**	0.152 16	– 363.958 88
Experiment	0.150 97	–

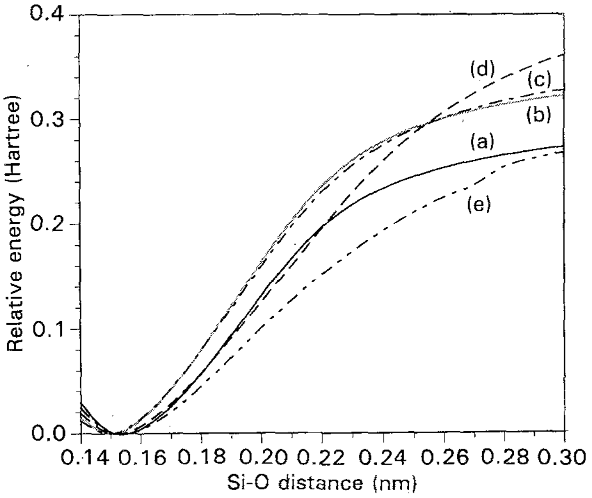

Figure 1 Potential curves obtained in (a) RHF/3-21G, (b) RHF/3-21G*, (c) RHF/6-31G*, (d) CISD, and (e) MC–SCF calculations.

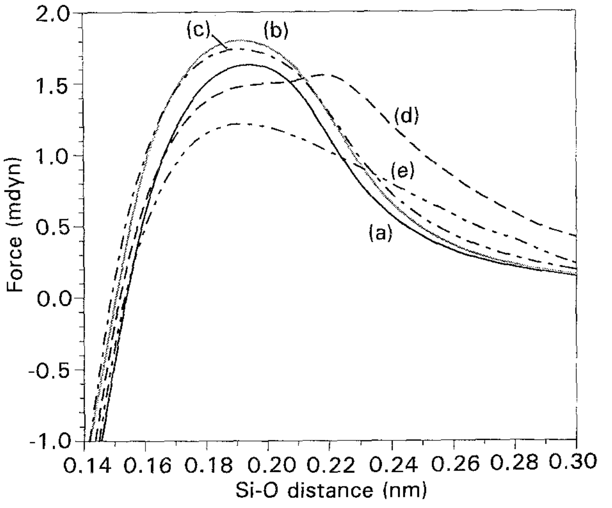

Figure 2 Force curves for the same theoretical models as in Fig. 1.

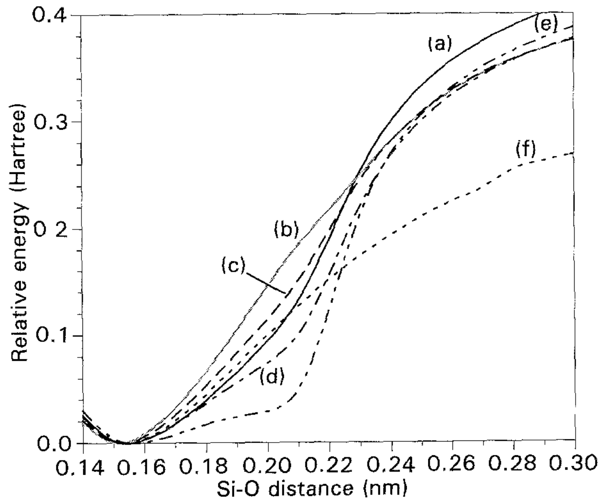

Figure 3 Potential curves in Møller–Plesset perturbation theory using the (a) MP2, (b) MP3, (c) MP4DQ, (d) MP4SDQ, and (e) MP4SDTQ approximations. Results of MC–SCF calculations are also shown for comparison.

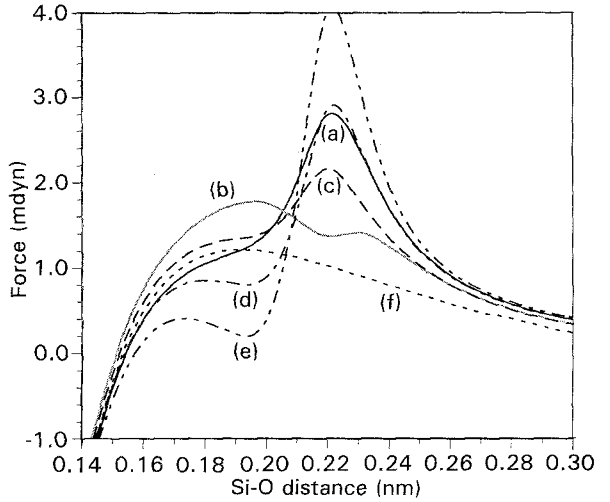

Figure 4 Force curves for the same theoretical models as in Fig. 3.

good agreement with the SCF and CI results of Langhoff and Arnold [22].

The restricted Hartree-Fock calculations are known to provide an accurate force field for molecules with an Si–O bond [23, 24] provided that *d*-type polarization functions are included in the basis sets, in particular for atoms bearing lone-pair electrons [25]. Therefore, RHF calculations using the 3-21G, 3-21G*, and 6-31G* basis sets were performed in order to elucidate the role of the basis set in the calculation of the interatomic force in a stretched bond.

A comparison of the results obtained using the 3-21G and 3-21G* basis sets confirms the significance of the polarization functions [25] in calculations of the interatomic force. Both the calculated strength of the bond and the critical elongation are clearly affected by the inclusion of the *d*-functions in the basis set. When the more flexible 6-31G* basis set is used, the total energies are obviously lower but the force curve remains virtually unchanged as compared to the 3-21G* calculations. Only around the extremum is there a visible difference. The strength of the bond and the force constant are slightly overestimated in all RHF calculations as compared to the more advanced models. It is a known feature of the Hartree–Fock model that it gives too-rigid bonds [26]. The vibrational frequencies calculated by using the RHF method are usually scaled by a factor of about 0.9 in order to achieve agreement with experiment. An interesting peculiarity of the present calculations is that improvements of the basis set at the RHF level of approximation shift the results away from those obtained by using more advanced and precise methods. The 3-21G basis set gives the best agreement with the CISD and MC–SCF force curves, in particular at small deformations of the bond.

Because the fracture of the solid in the active environment involves a simultaneous rupture of the bonds in the solid and formation of bonds with the molecules of the active medium, it is important for the analysis of the Rehbinder effect to have a good quality description at large interatomic distances. The Hartree–Fock calculations underestimate these interactions and in this region a more complete basis set gives better results. In general, taking into account the limited computer resources and the size of the target system, the 3-21G* basis set is considered to be a good compromise.

The Mulliken overlap populations, charges of atoms and the dipole moments calculated by using the 3-21G* and 6-31G* basis sets, are shown in Fig. 5. Both basis sets give almost the same total overlap populations. However, there are marked differences in the calculated charges and dipole moments, especially at the distorted geometries, the larger basis set giving the worst results. It is interesting to note that the ratio of the dipole moment to the Mulliken gross population, which is a measure of the distance between the effective charges, increases more rapidly than the separation of the nuclei.

It is important to include electron correlation for a strained chemical bond and for interactions between molecules. A popular and convenient method to incorporate these effects into an *ab initio* MO calculation is the Møller–Plesset perturbation theory. It has been shown to give reliable results for many chemical systems [24], but for some systems its convergence is

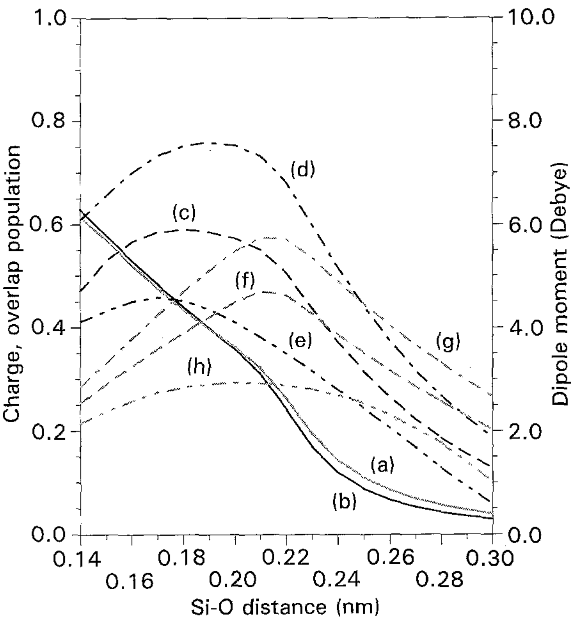

Figure 5 Changes in (a, b) the overlap populations, (c–e) atomic charges, and (f–h) dipole moments with bond deformation by using the (b, c, f) RHF/3-21G*, (a, d, g) RHF/6-31G* and, in the latter two cases, the (e, h) MC-SCF/6-31G* model.

poor. This problem was mentioned by Snyder and Raghavachari [21] in connection with their calculations on the SiO molecule. It was also forcefully pointed out in an article by Nobes *et al.* [27] titled "A dramatic failure of Møller-Plesset perturbation theory". It was therefore interesting to elucidate this problem in the force calculations on the stretched SiO bond.

The results of our MP calculations are presented in Figs 3 and 4. A comparison of the curves shows clearly that the convergence failed at this level of approximation. The origin of such a poor convergence turns out to be the failure of the Møller–Plesset perturbation theory to treat satisfactorily certain low-lying doubly-excited determinants [28–30]. Indeed, the MC–SCF calculations show that CI expansion for the deformed molecule contains significant contributions from excited open-shell states.

The configuration interaction approach usually gives more precise and reliable data than the MP approximation, as shown by a comparison of the two methods for SiO and other 22 electron diatomics [15]. Calculations at the CI level require much more computer time than the RHF or MP calculations and initially we intended to use them for evaluating the quality of the more approximate methods. Yet, although the potential energy curve obtained by using the CISD method is, indeed, close to the MC–SCF one, in the force curve there is a spurious second maximum that has no physical meaning.

Our conclusion is that the RHF approximation can be used to calculate the interatomic forces during a bond rupture. The choice of basis set does not affect the force curves at semi-quantitative level. The electron correlation methods should be used with care, although a proper description of the dissociation process requires excited states that are neglected in the RHF model.

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