An *Ab initio* Molecular Orbital Study of Silanol–Hydrogen Complexes: A Model for the Interaction of Hydrogen with Silicate Hydroxyl Groups

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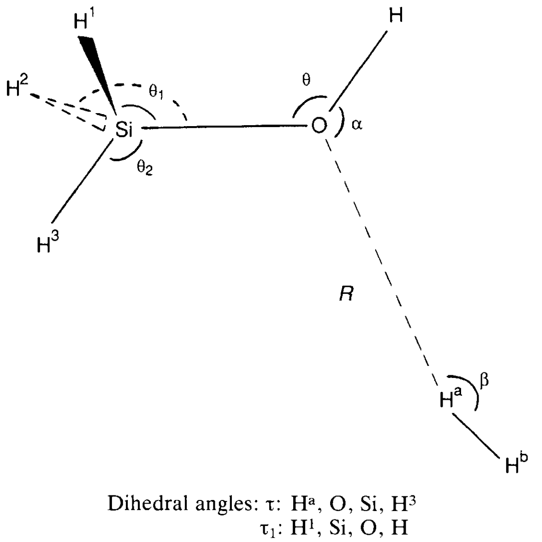
The geometry of the weak van der Waals complex formed between H_2 and silanol is determined by high level *ab initio* molecular orbital methods and is shown to provide a good model for H_2 adsorption complexes on silicates and zeolites.

According to the selection rules the vibrations of the H–H bond in molecular hydrogen do not appear in the IR spectrum. It has been shown however that the adsorption of H_2 onto silicates and zeolites leads to the appearance of the forbidden transition in the IR spectrum.[1–3] The adsorption sites have been identified as corresponding to the acid sites (Brønsted or Lewis) on the corresponding adsorbent and indeed it has been shown that the extent of perturbation of the H–H bond as measured by wavenumber shift and intensity value can be correlated with the acidity of the Brønsted acid site.[3]

The nature of the adsorption complex cannot be determined experimentally and we resort to theoretical modelling of the adsorption site to gain some information in this regard and also to see if the relaxation of the selection rules for the H–H stretching vibration can be predicted. Previous studies[4–6] have shown that the silanol molecule (H_3SiOH) can act as a suitable model for a terminal hydroxyl group in silicates and the interaction of H_2 with the hydroxyl group of this molecule was used to mimic the adsorption complex. The calculations were performed using the Gaussian 88 molecular orbital program running on the Amdahl VP1200 computer at the Manchester Computing Centre.

The size of the system permits the use of high-level post-Hartree–Fock calculations to study the geometrical parameters of the adsorption complex. Several configurations for the complex were studied using HF 3-21G, HF 6-31G**, MP2 6-31G** and CISD 6-31G** levels of theory and a full account of the exploration of the configuration space for the complex will be presented later. The global energy minimum found for the complex is given in Fig. 1 and the optimised



Dihedral angles: τ: H^a, O, Si, H^3
τ_1: H^1, Si, O, H
τ_2: H^2, Si, O, H
τ_3: H^3, Si, O, H

Fig. 1 The global minimum structure on the potential energy surface for the $H_3SiOH \cdots H_2$ complex

Table 1 Fully optimised geometrical parameters; distances in Å, angles in degrees, stabilization energies, in kJ mol^{-1}, for the global minimum energy structure on the potential energy surface for the $H_3SiOH \cdots H_2$ complex

	SCF/6-31G**	CISD/6-31G**
	Intermolecular parameters	
R	2.799	2.618
α	95.47	95.61
β	172.7	172.2
τ	0.0	0.0
	Intramolecular parameters	
Si–O	1.646	1.661
O–H	0.942	0.954
Si–H^1	1.478	1.474
Si–H^2	1.478	1.474
Si–H^3	1.470	1.465
H^a–H^b	0.733	0.735
θ	120.0	117.9
θ_1	111.3	111.7
θ_2	106.9	106.1
τ_1	−60.16	−60.39
τ_2	60.16	60.39
τ_3	180.0	180.0
ΔE	−2.209	−3.226
ΔE^0	4.329	
$\Delta E^{\mathrm{BSSE}a}$	1.541	

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[a] BSSE = basis set superposition error.

Table 2 SCF/6-31G** harmonic frequencies, ω_e in cm^{-1}, IR intensities, A, in km mol^{-1}, and Raman activities, A' in $Å^4$ amu^{-1}, for the ν_{H-H} and ν_{O-H} stretching modes of the global minimum structure and free monomer units; the frequency shifts with respect to the monomer units are in parentheses

	ω_e	A	A'
H_2 molecule			
ν_{H-H}	4636	0	84
H_3SiOH molecule			
ν_{O-H}	4230	117	72
$H_3SiOH \cdots\cdots H_2$ complex			
ν_{H-H}	4622 (−14)	8	128
ν_{O-H}	4228 (−2)	118	70

geometrical parameters are given in Table 1 at HF 6-31G** and CISD 6-31G** levels. A weak van der Waals type interaction complex is predicted to be formed with interaction occurring principally with the oxygen atom of the silanol molecule.

Table 2 summarises the predicted vibrational characteristics of the complex together with the corresponding characteristics of the isolated silanol and hydrogen units. The calculations clearly predict the allowance of the H–H stretching vibration for the interaction complex in agreement with experimental observations. It is also noted that the stretching vibration is predicted to be decreased by 14 cm^{-1} compared with the free hydrogen molecule. Experimental studies also show a decrease, though by a larger value of 20–35 cm^{-1}.

In summary therefore we have demonstrated, using a suitable cluster model, the ability of *ab initio* molecular orbital methods to predict correctly the allowance of IR transitions for hydrogen after adsorption on silicate hydroxyl groups. The local geometry of the adsorption complex indicates that H_2 interaction occurs, principally, with the oxygen atom of the silanol molecule.

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References

1 N. Shepherd and D. Y. C. Yates, *Proc. R. Soc. London, Ser. A*, 1956, **238**, 69.
2 V. B. Kazansky, L. M. Kustov and V. Y. Borovkov, *Zeolites*, 1983, **3**, 77.
3 E. Loeffler, U. Lohse, C. Deuker and V. B. Kazansky, *Zeolites*, 1990, **10**, 266.
4 P. J. O'Malley and J. Dwyer, *J. Chem. Soc., Chem. Commun.*, 1987, 72.
5 P. J. O'Malley and J. Dwyer, *Chem. Phys. Lett.*, 1988, **143**, 97.
6 P. Ugliengo, V. R. Saunders and E. Garrone, *J. Phys. Chem.*, 1989, **93**, 5210.