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IR-Spectroscopic Evidence for NaSiO and KSiO in Solid Argon

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ABSTRACT

Condensation of SiO with sodium or potassium, respectively, leads to the formation of $Na^+(SiO)^-$ and $K^+(SiO)^-$. The SiO force constant is reduced to 6.15 mdyn/Å and 6.30 mdyn/Å with respect to uncoordinated SiO (f = 9.0 mdyn/Å). From these results a similar type of bonding can be concluded for the charge transfer complexes $Ag^+(SiO)^-$ and $Ag^+(SiS)^-$ published recently.

INTRODUCTION

Recently the IR spectra detected after the reactions of silver atoms with SiO [1] as well as with SiS [2] in solid argon have been interpreted as the formation of the charge transfer complexes $Ag^+(SiO)^-$ and $Ag^+(SiS)^-$, respectively. On the basis of ab initio calculations different authors suggested the energetically most stable isomer to be a weakly bound linear Ag—O—Si complex with an Ag—O distance of 239 pm [3], 251 pm [4], and 300 pm [2]. Tse [3] found another energy minimum for a bent structure with r(Ag—O) = 244.6 pm. However, these calculations cannot explain the great red shift of the SiO stretching vibration with respect to uncoordinated SiO.

In comparison to silver, a more pronounced charge transfer to SiO is expected in reactions with alkali metals. This model is proved in the following article.

EXPERIMENTAL

To perform a matrix reaction with two different high temperature species with different volatility, two separated furnaces were required, one furnace at 1300°C ($Si_f + 1/2O_{2g} \rightarrow SiO_g$) and a second one at 100°C (K) and 120°C (Na), respectively. Under these conditions, SiO/Na/Ar ratios of 1:1:200 were obtained.

The IR spectra were recorded on a Bruker IFS 66v FTIR spectrometer with the aid of a reflection unit.

RESULTS

After co-condensation of SiO with alkali metals and an excess of argon, the bands assigned to pure SiO at 1226 cm^{-1} and different amounts of $(SiO)_2$ at 803 cm^{-1} and 767 cm^{-1} and $(SiO)_3$ at 973 cm^{-1} were observed.

If sodium was vaporized simultaneously with SiO, additional bands were detected at 1013.9 cm^{-1} (site 1) and 1012.0 cm^{-1} (site 2), which can only be attributed to a matrix reaction product between SiO and Na (Fig. 1). In experiments with $Si^{18}O$ we measured new absorptions at 977.7 cm^{-1} (site 1) and 975.3 cm^{-1} (site 2). Deposition of a mixture of $Si^{16}O$ and $Si^{18}O$ did not result in any new absorption. After photolysis or annealing of the matrix, only dimerization or trimerization of SiO was observed.

The band at 1013.9 cm^{-1} must be assigned to an uncoupled SiO stretching vibration because of its isotopic splitting (Tab. 1). With the aid of a simple frequency calculation the SiO force constant was calculated to be 6.15 mdyn/Å.

The observed frequency shift from 1226 cm^{-1} in uncoordinated SiO to 1013.9 cm^{-1} in NaSiO is in line with that calculated for SiO (1411 cm^{-1})

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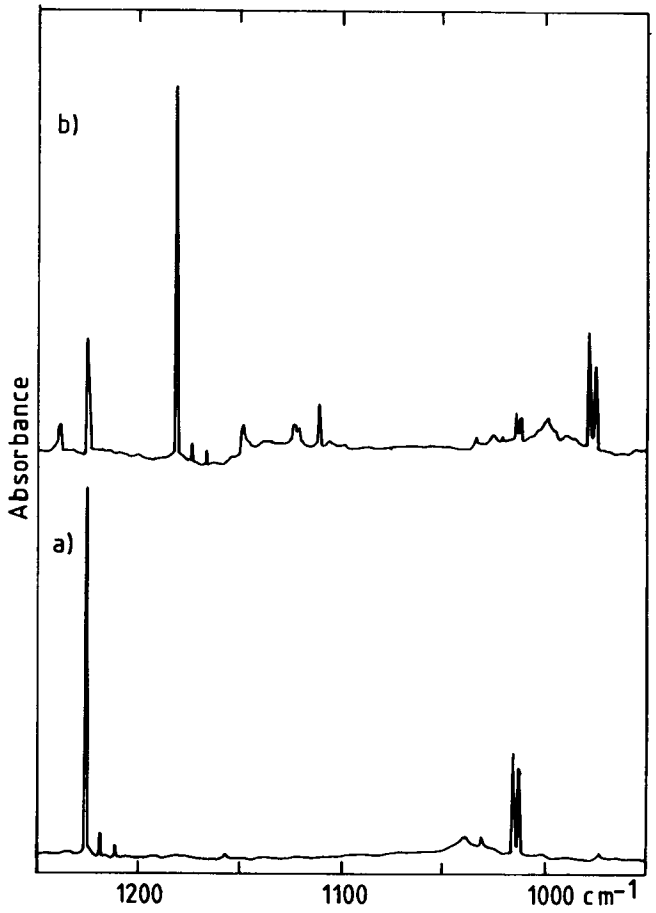

FIGURE 1 Matrix IR spectrum after co-condensation of sodium atoms with $Si^{16}O$ (a) and $Si^{18}O$ (b).

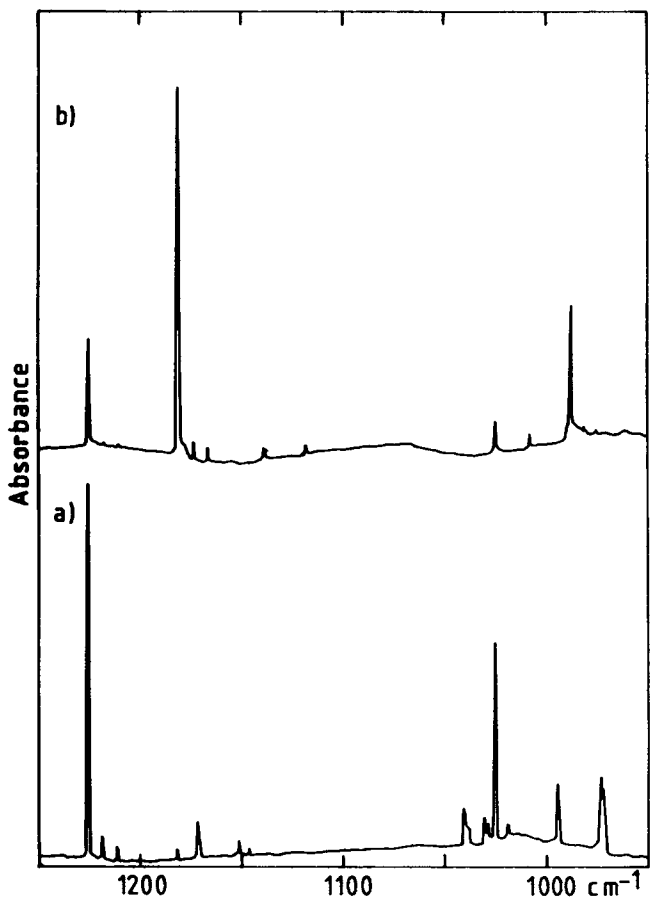

FIGURE 2 Matrix IR spectrum after co-condensation of potassium atoms with $Si^{16}O$ (a) and $Si^{18}O$ (b).

and SiO^- (1214 cm^{-1}) (SCF calculation [2]). Therefore we interpret the reaction product between Na and SiO to be the charge transfer species $Na^+(SiO)^-$.

The formation of species containing more than one metal atom can be excluded, because in this case lower SiO frequencies are expected [5]. A second reason why such reaction products have been excluded is that similar results emerge in experiments of alkali metal atoms with O_2 [6], F_2, Cl_2, Br_2, and I_2 [7].

After co-condensation of potassium with SiO similar results were obtained. One new band at 1025 cm^{-1} is attributable to an SiO stretching vibration because of its $^{16}O/^{18}O$ and $^{28}Si/^{29}Si$ isotopic shifts (Fig. 2, Tab. 1). The value of the SiO force constant has been determined to 6.30 mdyn/Å. Additionally we detected new absorptions at 992.7 cm^{-1} (^{16}O) and 937.7 (^{18}O) cm^{-1}, which have also been observed after a matrix reaction between potassium atoms and molecular oxygen; they are attributed to $K^+O_4^-$ [6]. In contrast to

TABLE 1 Experimental[a] and Calculated Frequencies (cm^{-1}) of $Na^+(SiO)^-$ and $K^+(SiO)^-$

	NaSiO Site 1		*NaSiO Site 2*		*KSiO*	
	Exp.	*Calc.*	*Exp.*	*Calc.*	*Exp.*	*Calc.*
$f(SiO)$ / (mdyn Å^{-1})	6.17		6.14		6.30	
$\nu(^{28}Si^{16}O)$	1013.9	1013.9	1012.0	1012.0	1025.0	1025.0
$\nu(^{28}Si^{18}O)$	977.4	977.4	975.2	975.6	987.7	988.1
$\nu(^{29}Si^{16}O)$					1018.7	1018.6
$\nu(^{29}Si^{18}O)$					981.2	981.4

[a] Corrected for anharmonicities [8].

earlier observations, KO_2 was not observed in our experiments [6].

DISCUSSION

The experiments described here have been performed to confirm the formation of the SiO anion as originally proposed for $Ag^+(SiO)^-$.

On comparison of the SiO stretching motion in AgSiO with those in $Na^+(SiO)^-$ and $K^+(SiO)^-$ an important decrease of ν(SiO) was observed. This was in line with a significant decrease in ionization energies of the metals involved (Ag (7.57 eV), Na (5.14 eV), K (4.34 eV)).

The results can be compared with those for the X_2^- anions (X = F, Cl, Br, I) obtained in several matrix Raman studies after reactions of alkali metal atoms with different halogens X_2 [7]. The slight blue shift in the sequence Na to K as cation (unexpected because of the small decrease in the first ionization energies) is explained with greater polarization effects in the case of potassium. The same situation may be true for the experiments utilizing the system SiO/Na/K.

CONCLUSION

The data presented show that bonding in NaSiO and KSiO has to be described by the formulation $Na^+(SiO)^-$ and $K^+(SiO)^-$, respectively. These results show that bonding in AgSiX (X = O, S) species are in principle of the same type. Because of the high ionization potential of silver, charge transfer is of course smaller.

Because bonding in AgSiO obviously is different from that of CO in transition metal complexes, we will continue our work to find an analogous M—SiO complex that is stabilized by σ donation and π back bonding [9].

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REFERENCES

[1] T. Mehner, H. Schnöckel, M. J. Almond, A. J. Downs, *J. Chem. Soc., Chem. Commun.*, 1988, 177.
[2] R. Köppe, H. Schnöckel, C. Jouany, F. X. Gadea, J. C. Barthelat, *Heteroatom Chem., 209.*
[3] J. S. Tse, *J. Chem. Soc., Chem. Comm.*, 1990, 1179.
[4] G. E. Quelch, R. S. Grev, H. F. Schaefer, III, *J. Chem. Soc., Chem. Comm.*, 1989, 1498.
[5] Based on ab initio SCF and frequency calculations for Na_2SiO the following ground state is expected: E_{tot} = −687.428165 a.u., Na (SiO) Na (C_{2v}), r(Na—Si) = 271.7 pm, r(Na—O) = 215.8 pm, r(Si—O) = 161.6 pm, E(tot) = atomic charges: Na, +0.57; Si, −0.08; O, −1.05; ν(SiO) = 919 cm^{-1}). R. Köppe, H. Schnöckel, unpublished results.
[6] L. Andrews, *J. Chem. Phys., 54*, 1971, 4935. L. Andrews, *J. Phys. Chem., 73*, 1969, 3922.
[7] C. A. Wight, B. S. Ault, L. Andrews, *Inorg. Chem., 15*, 1976, 2147.
[8] H. J. Becher, *Fortschritte der chemischen Forschung, Vol. 10*, Springer, Berlin, 1968.
[9] T. Mehner, R. Köppe, H. Schnöckel, *Angew. Chem., 104*, 1992, 653.