From Fig. 1 it appears that our present results [11] fit fairly well the plot of the calculated results by Diness and Roy and only deviate in the composition range 10 to 14% mole. The corresponding excess densities, plotted in Fig. 2, reach a maximum at about 14 mole percent lime. Single results by CARTER and ROTH [5] and by HOFFMANN and FISCHER [9] are also reported in Fig. 2 to support the conclusion that the observed trend is truly representative of a property of the system. Incidentally we remark that the sample used by Carter and Roth was a single crystal specimen.

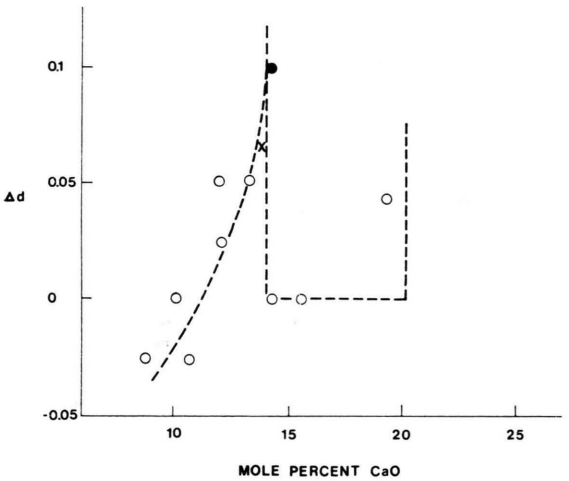

Fig. 2. Plot of the experimental excess density values of lime stabilized zirconia as a function of the lime content. ○ present work, ● Ref. [5], × Ref. [9].

It might be pointed out also that the main difference between our samples and those of Diness and Roy is in the quenching procedure. These authors claim for a quenching rate of 1000 °C sec^{-1}, whereas our samples are furnace cooled (and those of Carter and Roth were quenched at a rate of 200 °C sec^{-1}). The former only can be considered therefore as truly representative of the 1600 °C isotherm, while our samples (and presumably also those of Carter and Roth) reflect the metastabile equilibrium conditions within the broad range of temperatures where ordering processes [5] and subsolidus equilibria are sufficiently fast [12].

According to the phase diagrams reported by GARVIE [2] (who also critically reviewed the earlier results in literature), corresponding to the isotherm of 1600 °C the lower limit of stability of the cubic solid solution is about 10% lime. At lower temperatures a tetragonal solid solution is reported to be stable in equilibrium with the cubic phase, the lower limit of stability of the cubic phase at 1000 °C being about 14% lime. If this would be the case, then the precipitation of the tetragonal phase could account fairly well for the excess density values as well as for the maximum at about 14% lime.

There is, however, the contradictory evidence of the results by DINESS [12], COCCO [13] and BARBARIOL [14], who reported, on the basis of long term annealing experiments, a value for the lower limit of stability of the cubic phase ranging between 10 and 12% lime at temperatures as low as 1000 °C. The latter results, however, do not exclude that another mechanism might be operative, such as superlattice formation [2].

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[12] A. M. DINESS, Thesis, Penn. State University, Dept. Mat. Sci. 1967.

[13] A. COCCO, Chim. Ind. (Milan) **41**, 882 [1959].

[14] I. BARBARIOL, Ann. Chim. (Rome) **55**, 321 [1965].

Calculation of the Proton Chemical Shifts in Strongly Hydrogen Bonded Systems

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The all-electrons semiempirical SCF methods render the study of changes in the electron configuration with hydrogen bonding relatively easy. We wish to show that such methods can give valuable information about the magnetic properties of hydrogen bonded systems.

Proton shielding constants (σ) were calculated for HF, HF_2^- and $H_2F_3^-$ using the well known expression by POPLE [1]

$$\sigma = (e^2/3\,m\,c^2)\sum^{A} P_{\mu\mu}(r^{-1})_{\mu\mu} - 2\,N^{-1}\langle r^{-3}\rangle_A\,\chi_p{}^A - \tfrac{1}{3}\,N^{-1}\sum_{B\neq(A)}\chi_{\alpha\gamma}{}^B\,R_B{}^{-5}(R_B{}^2\,\delta_{\alpha\gamma} - 3\,R_{B\gamma}\,R_{B\alpha}).$$

All matrix elements were calculated with Slater orbitals and with Slater ζ values. The parametrization of the INDO method [2] was that proposed by SICHEL and WHITEHEAD [3] and the basic set consists only of 1s, 2s and 2p atomic orbitals.

Calculated values (Table 1) are separated into diamagnetic (σ_d) and paramagnetic (σ_p) parts. Though

[1] J. A. POPLE, J. Chem. Phys. **37**, 53 [1962].

[2] J. A. POPLE, D. L. BEVERIDE, and P. A. DOBOSH, J. Chem. Phys. **47**, 2026 [1967].

[3] J. M. SICHEL and M. A. WHITEHEAD, Theoret. Chim. Acta **11**, 220 [1968].

	σ_d	σ_p	σ
HF	12.24	−4.84	7.40
HF_2^-	12.02	−2.61	9.41
$H_2F_3^-$	12.07	−2.60	9.47

Table 1. Calculated proton shielding constants (ppm).

only the calculated value of HF can be compared with the measured one we believe that the results characterize the hydrogen bonding in the treated systems. The calculated σ(HF) is much smaller than the experimental one [4] (27.9 ppm) but this is not too surprising because of the use of various approximations inherent in the calculation. Thus only changes of σ using σ(HF) as a standard are meaningful. The diamagnetic part changes only slightly and almost all of the change in σ comes from the paramagnetic part. SCHNEIDER et al. [4] were first to try to explained the change in σ with the occurrence of the hydrogen bond.

We can not separate σ in a manner as they did but it is nevertheless interesting that changes in σ_p show the trend predicted by them.

σ_p can change to a positive value in the linear hydrogen bond systems and such systems were this explanation seems to be the correct one have been in fact observed [5]. Paramagnetic parts in HF_2^- and $H_2F_3^-$ are almost equal. This can be described qualitatively as was done by SCHNEIDER et al.: the anisotropy of the paramagnetic term is removed as a consequence of the non-linearity of $H_2F_3^-$ system. We believe that semiempirical all valence electrons SCF wave functions can describe changes of σ with hydrogen bonding in larger systems and so obtained results are more reliable than results based on models used [6] so far.

[4] W. G. SCHNEIDER, H. J. BERNSTEIN, and J. A. POPLE, J. Chem. Phys. **28**, 601 [1958].
[5] L. W. REEVES and W. G. SCHNEIDER, Can. J. Chem. **35**, 251 [1957].
[6] J. W. EMSLEY, J. FEENEY, and L. H. SUTCLIFFE, High Resolution Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, London 1967, Vol. 1, p. 537.

Abschätzung der Frequenzen des IR-Spektrums des Schwefeldifluorids

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Estimation of the IR-Frequencies of Sulphurdifluoride

The theoretical IR-frequencies of sulphurdifluoride are computed from force constants, which are evaluated by means of molecules with S-F-bonds:
$\nu_1 = 795 \pm 10\ cm^{-1}$, $\nu_2 = 430 \pm 5\ cm^{-1}$, $\nu_3 = 830 \pm 10\ cm^{-1}$.

Bisher sind verschiedene Verfahren zur Darstellung und zum Nachweis von Schwefeldifluorid beschrieben worden. GLEMSER, HEUSSNER und HAAS [1] berichteten, Schwefeldifluorid durch Zersetzung von Dischwefeldifluorid hergestellt zu haben und außerdem ebenso wie PADMA und SATYANARAYANA [2] direkt bei der Silberfluorid-Schwefel-Reaktion. Der Nachweis, der in beiden Fällen durch Elementaranalyse erfolgt ist, ist inzwischen mehrfach angezweifelt worden [3, 4], zumal sich auch die von PADMA und SATYANARAYANA angegebenen chemischen Reaktionen nicht reproduzieren ließen.

Außerdem wurden von SEEL, HEINRICH, GOMBLER und BUDENZ [5] und von WANCZEK [6] massenspektroskopische Nachweise der Existenz dieser instabilen Verbindung geführt. Aber das IR-Spektrum des Schwefeldifluorids ist noch unbekannt. Wohl haben SEEL, BUDENZ und WANCZEK [4] vermutet, daß die im IR-Spektrum des bei der Silberfluorid-Schwefel-Reaktion entstehenden Gasgemisches aus hauptsächlich Schwefeltetrafluorid, Dischwefeldifluorid und 1,2-Difluordisulfan-1,1-difluorid zeitweise auftretende Bande bei 830 cm^{-1} dem Schwefeldifluorid zuzuordnen sei, das mit seinem Dimeren, dem 1,2-Difluordisulfan-1,1-difluorid im Gleichgewicht stehen kann. Daher sind die zu erwartenden IR-Frequenzen des Schwefeldifluorids mit Hilfe der FG-Matrix-Methode nach WILSON, DECIUS und CROSS [7] abgeschätzt worden.

Die Molekülstruktur des Schwefeldifluorids ist aus mikrowellenspektroskopischen Messungen von JOHNSON und POWELL [8] bekannt. Die Daten sind in Tab. 1 aufgeführt. Die zur Berechnung des MVFF (modified valence force field) benötigten Kraftkonstanten f_r (S-F-Bindung), f_α (Winkel-Deformation) und $f_{r\alpha}$ sind graphisch abgeschätzt worden, f_{rr} wurde Null gesetzt. Als Beispiel ist in Abb. 1 die Abschätzung von f_r dargestellt. Die dazu benötigten Daten einiger Moleküle mit S-F-Bindung sind ebenso wie der erhaltene Bereich für die Kraftkonstanten des Schwefeldifluorids in Tab. 1 angegeben.

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[1] O. GLEMSER, W. H. HEUSSNER u. A. HAAS, Naturwiss. **50**, 402 [1963].
[2] D. K. PADMA u. S. R. SATYANARAYANA, J. Inorg. Nucl. Chem. **28**, 2432 [1966].
[3] F. SEEL, Chimia **22**, 79 [1968].
[4] F. SEEL, R. BUDENZ u. K. P. WANCZEK, Chem. Ber., im Druck.
[5] F. SEEL, E. HEINRICH, W. GOMBLER u. R. BUDENZ, Chimia **23**, 73 [1969].
[6] K. P. WANCZEK, Dissertation, Saarbrücken 1970.
[7] E. B. WILSON JR., J. C. DECIUS u. P. C. CROSS, Molecular Vibrations, McGraw-Hill Book Company, London 1955.
[8] D. R. JOHNSON u. F. X. POWELL, Science **164**, 950 [1969].