

THEORETICAL STUDY OF CS CONTAINING - MOLECULES. II.  
AB INITIO HARTREE FOCK CALCULATIONS FOR THE  
 $CS + HCS^+ \rightarrow (CS)_2H^+$  REACTION

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DEDICATED TO PROFESSOR RAYMOND DAUDEL

**ABSTRACT:** The reaction  $CS ({}^1\Sigma^+) + HCS^+ ({}^1\Sigma^+) \rightarrow (CS)_2H^+$  is analyzed through ab initio calculations at the 4-31G basis set level. The reaction is predicted to be exothermic by 19 Kcal mol<sup>-1</sup>. The equilibrium geometry of the hydrogen-bonded complex  $(CS)_2H^+$  has been established to be of C<sub>∞v</sub> symmetry. The results suggest that  $(SC)_2H^+$  could be an active species in sulphur interstellar chemistry.

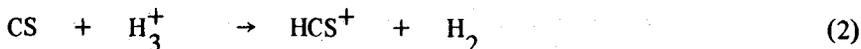
## INTRODUCTION

Theoretical predictions of the structure and stability of hypothetical molecules are certainly necessary in order to assign the astronomical spectral lines and to propose models of interstellar chemistry.

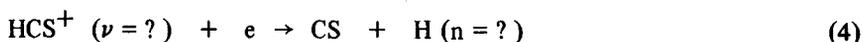
Most light molecular ions can be called nonterrestrial because of their transient chemical stability under laboratory conditions. The thioformyl ion,  $HCS^+$ , is one of such species that was detected spectroscopically in space (1, 2).

Several theoretical models of interstellar sulphur chemistry have been proposed (3-6). The important sources of  $HCS^+$  involve the reactions of CS with non-metallic ions, for example:

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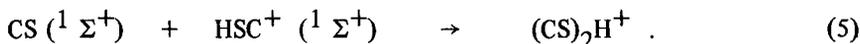


On the other hand,  $\text{HCS}^+$  formed from the above reactions can recombine dissociatively with electrons to recycle CS:



This reaction seems to justify the observed value for the column density ratio  $N(\text{HCS}^+)/N(\text{CS})$  of  $1.3 \cdot 10^{-2}$  (2).

However, the understanding of interstellar sulphur chemistry is rather limited (6), as is based on a small sample of observations. In this sense, it could be of interest to explore theoretically some reactive interactions involving CS or  $\text{HCS}^+$ . For instance, one could ask about the elementary reaction:



To our knowledge, the  $(\text{CS})_2\text{H}^+$  ion has never been observed, and no theoretical work on its physical properties is available.

We have therefore undertaken a detailed investigation of reaction involved in CS chemistry. A previous paper (7) reported a study on the  $2\text{CS} \rightarrow \text{C}_2\text{S}_2$  reaction. The present one deals with ab initio Hartree-Fock (HF) predictions for the clustering reaction (5).

Considering reactions (1) to (4), only reaction (1) has been theoretically examined (8).

## COMPUTATIONAL DETAILS

As in our previous work, calculations were performed with the Monstergauss ab initio program package (9), employing a 4-31G split-valence basis set (10).

Calling  $R(\text{C-C})$  the C-C distance in  $(\text{CS})_2\text{H}^+$ ,  $r_1(\text{C} \dots \text{H})$  the distance between the approaching C atom of CS and the H atom of  $\text{HCS}^+$ , and  $r_2(\text{C-H})$  the C-H distance in  $\text{HCS}^+$ , we computed the total energy as a function of  $R$  and successively minimized the energy with respect to the proton position ( $r_1$ ). The CS bond distance was kept constant during the approach and fixed at the 4-31G value for the  $\text{CS}({}^1\Sigma^+)$  free molecule (7).

The formation of the hydrogen-bonded species  $(CS)_2H^+$  involves a closed-shell reaction and the contribution from electron correlation changes is expected to have no significance.

## RESULTS AND DISCUSSION

The calculated minimum-energy path for the reaction (5) is shown in Figure 1. It can be seen that the  $r_1(C \dots H)$  bond length becomes longer as the  $r_2(C-H)$  distance becomes shorter. The potential minimum is found to have  $C_{\infty V}$  symmetry with bond lengths of  $R = 3.10 \text{ \AA}$ ,  $r_1 = 1.986 \text{ \AA}$  and  $r_2 = 1.114 \text{ \AA}$ . At this equilibrium geometry, the total energy is computed to be  $-869.883043$  hartrees and the binding energy is exothermic by  $19.08 \text{ Kcal mol}^{-1}$ . We predict the formation of the hydrogen-bonded complex  $(CS)_2H^+$  to occur without an activation barrier (Figure 1), however we found a considerable potential barrier for the proton transfer. The calculated potential energy curves are shown in Figure 2. The energy minimum for the symmetric structure  $SCHCS^+$  ( $D_{\infty h}$ ), is obtained at the C-H bond length of  $1.374 \text{ \AA}$  (that is,  $R(C-C) = 2.748 \text{ \AA}$ ).

In Figure 2, it is seen that the adiabatic activation barrier for the proton transfer is calculated as  $5.78 \text{ Kcal mol}^{-1}$ , indicating that the process is not accessible from the vibrational states populated at the low temperature of interstellar clouds as well as room laboratory temperature. Thus, proton resonance could be a laboratory activated event.

In order to check the adequateness of the 4-31G basis set, we have evaluated the activation energy barrier including p polarization functions for H and d polarization functions for C, through a 4-31G\*\* basis set (11), with the 4-31G molecular geometries given in Figure 2. It is found that this basis lowers by  $0.15 \text{ Kcal mol}^{-1}$  the adiabatic barrier height for the proton migration, and thus does not significantly affect our conclusions using the 4-31G basis set. It has been shown that in some sulphur-containing molecules, the 4-31G basis set does work and in other does not work (12). Also, it has been shown (13) that correlation effects on the proton affinity of CS were more than  $6 \text{ Kcal/mol}$  and zero-point energy corrections were more than  $7 \text{ Kcal/mol}$ . Moreover, the CS bond length was found to contract by more than  $0.06 \text{ \AA}$  upon protonation. All these things change the potential energy curve for protonation of CS, and provide elements of doubt about the physical reality of the barrier. Nevertheless, calculations of the  $(OC)_2H^+$  system, with third order Møller-Plesset perturbation theory with a 6-31G\*\* basis set, indicate that the most stable conformation has a  $C_{\infty V}$  structure (14, 15). The second lowest energy conformation has  $D_{\infty h}$  symmetry and, at the 4-31G level of calculation, is about  $4 \text{ Kcal/mol}$  less stable. Inclusion of the electron correlation reduces the barrier to  $1.5 \text{ Kcal/mol}$  (15). Therefore, in our case, the proton transfer barrier is probably overestimated and must be reanalyzed with more extended basis set plus CI.

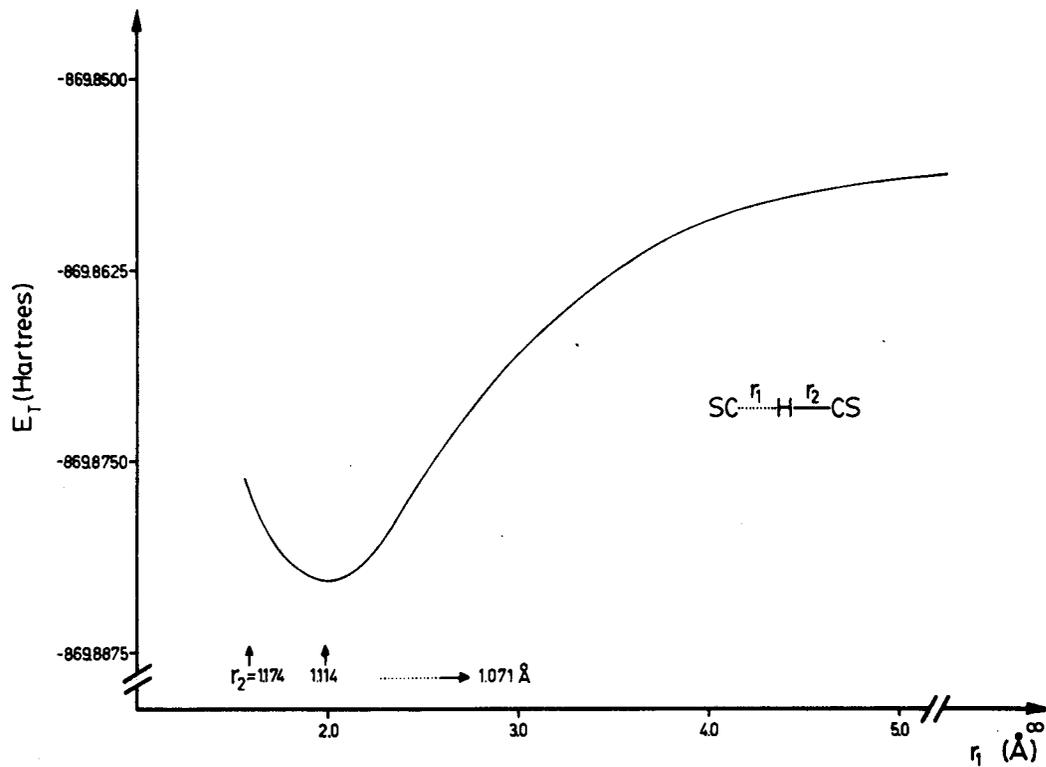


Figure 1. Minimum-energy path for the reaction (5) calculated with a 4-31G basis. At a given R(C-C) distance, the CH bond length ( $r_1$  or  $r_2$ ) is optimized. CS bond lengths are fixed at 1.566 Å, corresponding to that of the  $CS(^1\Sigma^+)$  isolated molecule.

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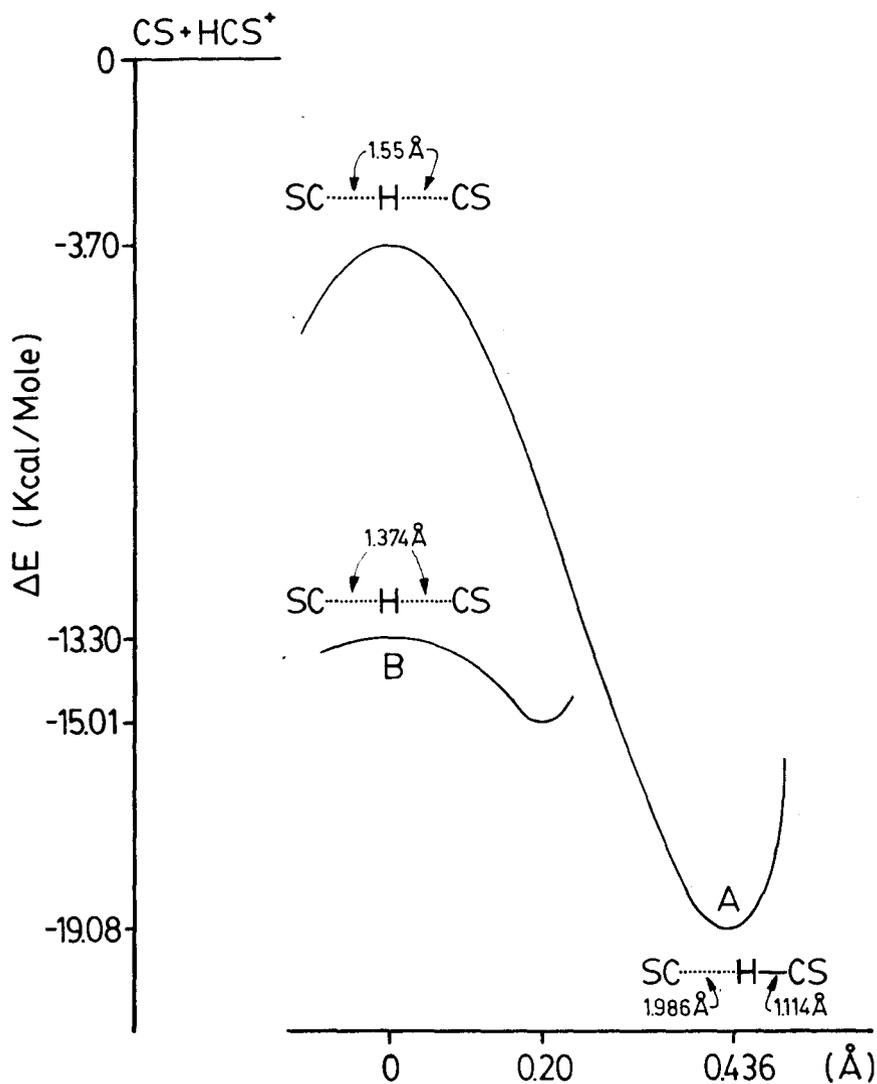


Figure 2. 4-31G potential activation barriers for proton transfer. The energy scale is based on  $E = 0$  Kcal  $\cdot$  mol $^{-1}$  for the  $\text{CS}(^1\Sigma^+)$  and  $\text{HCS}^+(^1\Sigma^+)$  molecules separated to the infinity. A represents the equilibrium unsymmetrical structure, and B the symmetric one. The adiabatic proton transfer involves  $A \rightarrow B$  structure.

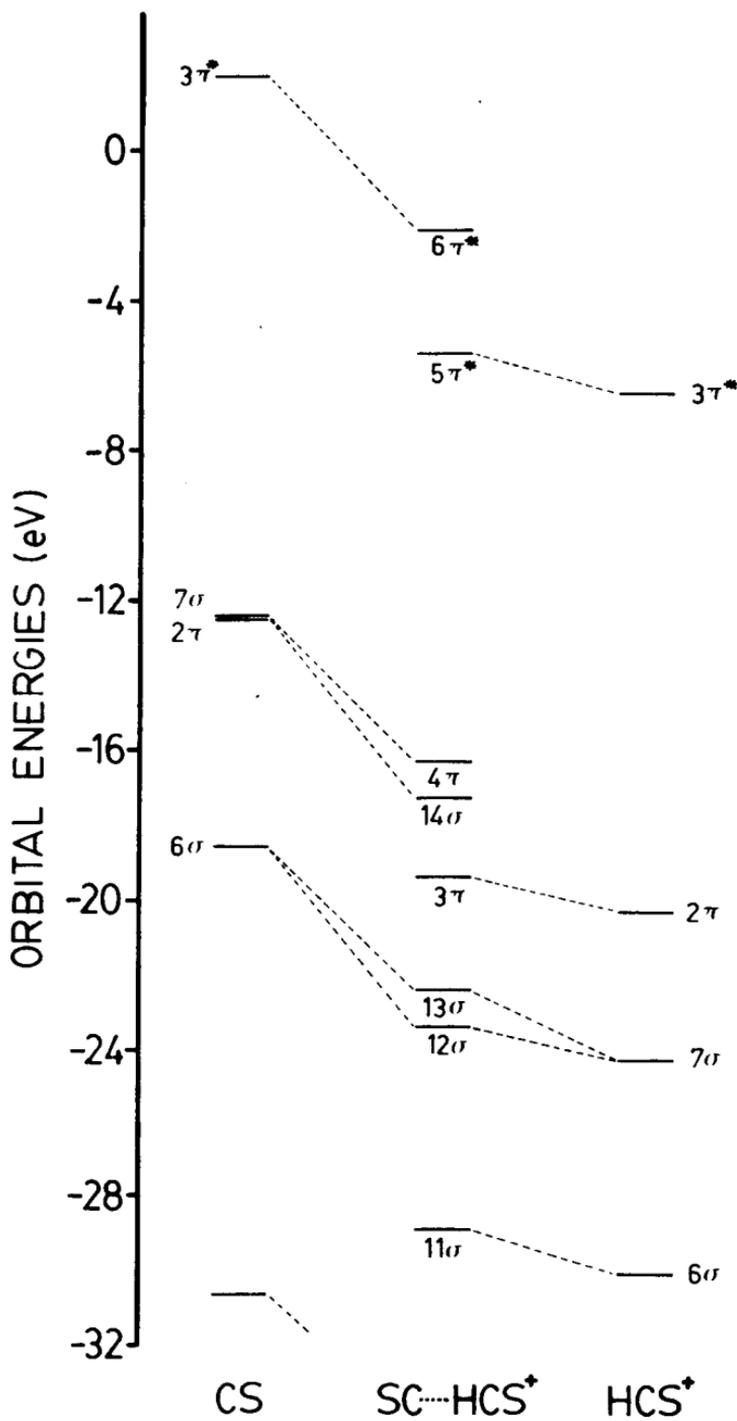
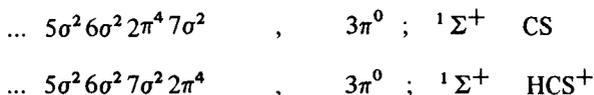


Figure 3. 4-31G orbital energy diagrams.

Considering the individual molecules, the proton affinity of  $\text{CS}(^1\Sigma^+)$  forming  $\text{HCS}^+(^1\Sigma^+)$ , is calculated to be  $188.25 \text{ Kcal/mol}^{-1}$ , which compares well with the value given by a Configuration Interaction calculation of Bruna et al. (8), and with a CI - self consistent electron pair calculation employing a Gaussian basis set of double zeta plus polarization quality (13). Nevertheless, our result is about 13 Kcal/mol higher than the experimental value (16) of 175 Kcal/mol. Other results (13), show that a better description of the proton affinity of CS can be attained with a Gaussian set of double zeta quality ( $174.3 \text{ Kcal/mol}$ ) and a Gaussian set of double zeta plus polarization quality ( $182.5 \text{ Kcal/mol}$ ). Therefore, it can be concluded that our results for CS are within the range of the ones presented in the literature. So far, the  $\text{CSH}^+$  isomer has not been detected, and a competing route  $\text{CS} \dots \text{HCS}$  is not considered here.

In the ground state, CS and  $\text{HCS}^+$  are closed-shell molecules having the following electronic configurations:



It can be seen that the  $7\sigma$  and the  $2\pi$  orbitals of CS are interchanged by protonation. The  $7\sigma$  orbitals is the principal orbital contributing to CH bonding. The orbital energy diagrams for CS and  $\text{HCS}^+$  free molecules and the  $(\text{CS})_2\text{H}^+$  complex are shown in Figure 3. The interpretation of the orbitals of  $(\text{CS})_2\text{H}^+$  turns out to be straightforward. They are localized in the fragments CS or  $\text{HCS}^+$ , with the exception of the  $12\sigma$  and  $13\sigma$  orbitals, which are the only ones really contributing to the hydrogen bonding. In both orbitals, the carbon contributions arise from the  $2s$  and  $2p$  functions, which lead to relatively large CH overlap populations: 0.12 and 0.20 for C ... H and C-H respectively. The C ... H overlap population is a rather large value if one compares with that of 0.33 for C-H in the isolated  $\text{HCS}^+(^1\Sigma^+)$  molecule.

In Table 1, Mulliken atomic charges are presented. We can see that the CS neutral becomes positive by 0.11 e in the  $\text{CS} \dots \text{HCS}$  complex due to a charge transfer via the  $12\sigma$  and  $13\sigma$  orbitals.

**TABLE I**  
4-31G Mulliken net charges

Molecule	Net Charges				
	S	C	H	C'	S'
CS	0.134	- 0.134			
HCS <sup>+</sup>	0.801	- 0.234	0.433		
(S' C' ... H - CS) <sup>+</sup>	0.819	- 0.361	0.433	- 0.396	0.505

Turning now to the question of the proton transfer dynamics, we see that there is a strong penetration through the barrier separating the symmetrical equivalent equilibrium structures, by the delocalized orbitals  $12\sigma$  and  $13\sigma$ . We think that there will be tunneling splitting of the rotational and vibrational levels, however, it could require a very high spectral resolution to detect this level splitting as a result of tunneling. From these general arguments, the spectroscopic characterization of  $(CS)_2H^+$  is that of an unsymmetrical semirigid molecule.

From the data presented here, it can be concluded that the  $(CS)_2H^+$  system may be an active species in the sulphur interstellar chemistry.

#### ACKNOWLEDGEMENTS

This work has received financial support from the University of Chile (DIB) and from Fondo Nacional de Ciencia (Project 1075). We also Thank Mr. Rubén Madrid, Director of the SECI (University of Chile) for providing free computer time. One of us (LMR), acknowledges the hospitality of the Theoretical Chemistry Group of the Faculty of Sciences.

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