Theoretical Investigation of the Reactivity of Copper Atoms with Carbon Disulfide

Yana Dobrogorskaya,[†,‡] Joëlle Mascetti,[†] Imre Pápai,[§] Alexander Nemukhin,[‡] and Yacine Hannachi*,[†]

Laboratoire de Physico-Chimie Moléculaire (UMR 5803 CNRS), Université Bordeaux I, 351,
cours de la Libération, F-33405 Talence cedex, France, Chemistry Department, Moscow State University,
Moscow, 119899 Russia, and Theoretical Chemistry Department, Institute of Chemistry,
Chemical Research Center of HAS, Pusztaszeri út 59-67, H-1025 Budapest, Hungary

Received: December 17, 2002; In Final Form: February 10, 2003

The mechanism of the Cu + CS_2 reaction has been investigated using density functional and coupled cluster calculations. The lowest energy route on the potential energy surface corresponds to the insertion product SCuCS via the formation of intermediate coordination complexes: η^1_S and η^2_{CS}, which all lie below the energy of the reactants. Another path corresponding to the formation of a cyclic C_{2v} compound η^2_{SS} leads to the same insertion product, but it involves a higher energy barrier (34.7 kcal/mol vs 26.9 kcal/mol with respect to the reactants at the CCSD(T) level). The dissociation of the insertion product SCuCS into the CuS and CS fragments is found to be endothermic by 43 kcal/mol (CCSD(T) level). Our results are related to experimental data obtained in low-temperature rare gas matrixes and in the gas phase.

1. Introduction

The chemistry of transition metal atoms with heterocumulene molecules, such as CO_2, CS_2, and OCS, which are potential sources of C_1 chemistry (the chemistry of catalyzed formation of compounds containing one carbon atom, such as methane or methanol), plays an important role in different areas of chemistry and biology.[1] Besides CO_2 chemistry, considerable attention has been focused on sulfur-containing transition metal complexes as model compounds of active sites of enzymes and catalytic metal surfaces[2] in order to resolve problems, such as catalyst poisoning, hydrodesulfurization, or synthesis of novel electronic materials.[3] The first reaction of a copper complex with CS_2 was reported in 1931,[4] but the beginning of the CS_2 chemistry actually dates back to 1966, when Baird and Wilkinson[5] synthesized *trans*-$RhCl(CS)(PPh_3)_2$ and $Pt(PPh_3)_2(CS_2)$ from phosphine complexes and CS_2. Since then, CS_2 has been proved to be a very reactive molecule toward transition metals and to undergo a great variety of reactions, such as coordination, insertion, dimerization, or disproportionation.[1,6−8] However, fundamental studies of the basic properties of transition metal sulfides and of binary complexes of CS_2 have been developed slowly.

The first matrix isolation spectroscopic study on $Ni(CS_2)_n$ complexes, with $n = 1-3$, appeared in 1977.[9] Later, Andrews et al. studied reactions of laser-ablated atoms reactions with CS_2 by matrix isolation infrared spectroscopy and DFT calculations and results have been reported on boron,[10] on cobalt, nickel, and copper,[11] and on vanadium.[12] In the case of copper, the carbon-bonded η^1_C and the cyclic η^2_{SS} complexes were formed on annealing the argon matrix, whereas the inserted SCuCS molecule was formed on photolysis, but $(Cu-SCS)^+$ cations were also produced. Very recently, guided ion beam mass spectrometry studies appeared in the literature on the reactions of first-row transition metal with the sulfur-transfer reagents CS_2 and OCS (refs 13 and 14 and references therein). The cross sections for CuS^+ and $CuCS^+$ formation were consistent with initial activation of the neutral reactants by insertion of the metal ion into the CS bond to form the $S-Cu^+-CS$ intermediate. Some theoretical work was also completed on related metal sulfides.[15]

Work in our research group is focused on the reactivity of transition metal atoms with CO_2, CS_2, and OCS, both experimentally, by matrix isolation infrared spectroscopy, and theoretically, through DFT and ab initio methods.[16−19] In light of our previous theoretical comparative study on vanadium insertion into CO_2, CS_2, and OCS,[18] our main goal is to complete the study of the reactions of the 3d transition metal series with heterocumulenes and elucidate their insertion processes into the CX bonds (X = O and S). This study was performed to explore the reactivity of copper atoms with CS_2 and to characterize the products and intermediates. We present the different possible routes from the Cu + CS_2 entrance channel, the relative stabilities of the adducts and insertion products and the reaction barriers between the intermediates. Our results are compared to experimental data from matrix isolation and gas-phase experiments.

2. Computational Details

The ground state of the Cu atom has a $4s^13d^{10}$ electronic configuration. Because the unpaired electron is on s type orbital, when interacting with CS_2 ($^1\Sigma^+{}_g$) a closed-shell molecule, this leads to an $^2A'$ electronic state of C_s symmetry. In our work, we have explored the potential energy of the $^2A'$ state in detail. The species on the $^2A''$ surface, which does not correlate to ground-state reactants, have also been considered but were always found much higher in energy (more than 30 kcal/mol) than the corresponding species on the $^2A'$ surface, and they will not be discussed in the present paper.

The stationary points on the potential energy surface (PES) were located using the B3LYP method of density functional theory.[20−22] For carbon and sulfur we used the 6-311+G(2d) basis set,[23] whereas for Cu, we used the (14,9,5)/[8,5,3] all-

---

* Corresponding author. E-mail: y.hannachi@lpcm.u-bordeaux1.fr.
[†] Université Bordeaux I.
[‡] Moscow State University.
[§] HAS, Budapest.

10.1021/jp027744e CCC: $25.00

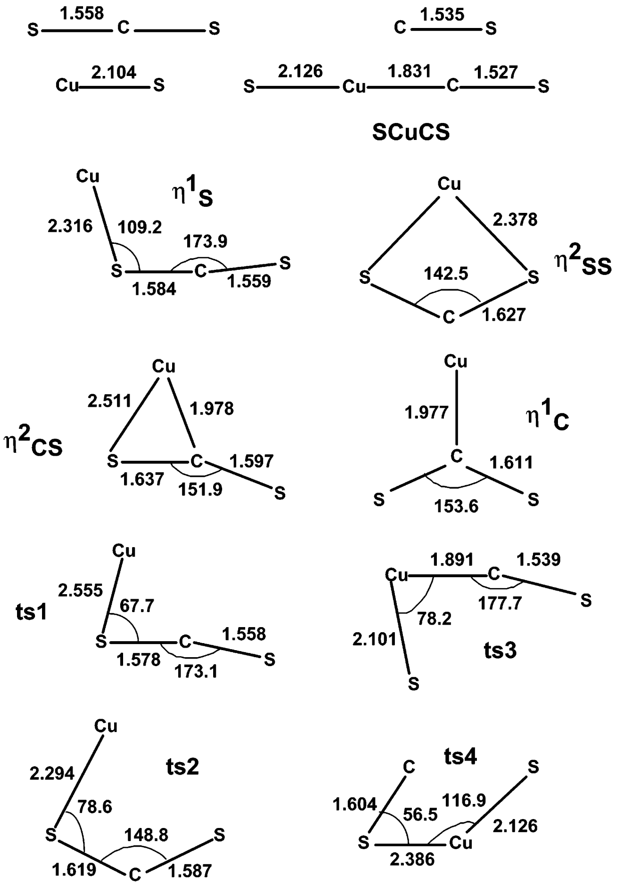

Figure 1. Optimized geometries of the various stationary points located on the Cu + CS_2 $^2A'$ potential energy surface (distances in angstroms, angles in degrees).

electron basis set of Schäfer, Horn, and Ahlrichs (SHA).[24] This later basis set was supplemented with two polarization p functions[25] and a diffuse d function.[26] The harmonic vibration frequencies have been calculated at the same level in order to characterize the stationary points as minima or transition states (TS), to estimate the zero-point energy correction (ZPE) and to generate the force constants needed for intrinsic reaction coordinate (IRC) analysis. The IRC procedure[27] was used to follow the minimum energy path from a transition state to the corresponding local minimum with a step size of 0.1 amu$^{1/2}$ bohr.

For each stationary point, we carried out single-point CCSD(T) energy calculations[28,29] using the standard 6-311+G(3df) basis set.[30] The CCSD(T) energies were corrected for ZPE contributions as obtained from B3LYP calculations. The correlation treatment in the coupled cluster calculations involved all valence electrons. Stability tests were always carried out in order to ensure that the lowest energy solution in the SCF procedure has been found. The metal−ligand binding energies were calculated relative to that of the ground-state reactants. The atomic populations (atomic charges, electron configuration, etc) were derived from natural bond orbital (NBO) analysis[31] carried out for the relevant structures at the B3LYP level. All calculations have been performed using the Gaussian98 program.[32]

3. Results and Discussion

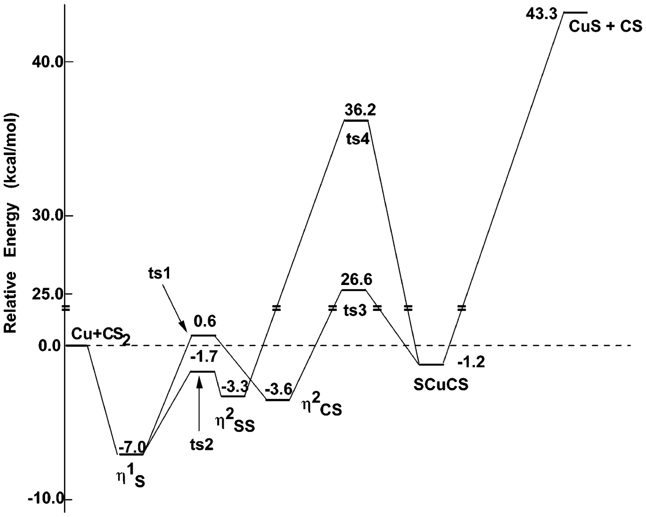

Figure 2. Schematic reaction path of copper atoms with CS_2 at B3LYP level of calculations.

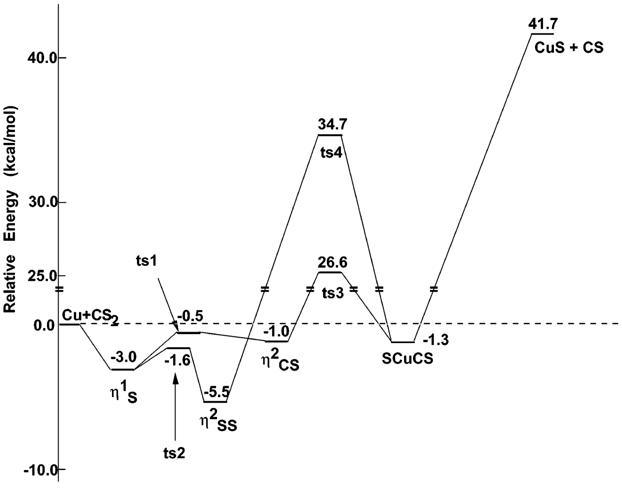

Figure 3. Schematic reaction path of copper atoms with CS_2 at CCSD(T) level of calculations.

TABLE 1: Total Energies (au), ZPE, and Relative Energies (kcal/mol) of the Different Stationary Points Calculated in the Reaction Cu + CS_2 → CuS + CS

	B3LYP/6-311+G(2d)+SHA			CCSD(T)/6-311+G(3df)	
element or molecule	total energy	ZPE	relative energy	total energy	relative energy
Cu	−1640.48929			−1639.30360	
CS_2 ($D_{\infty h}$)	−834.55764	4.28		−833.49857	
Cu + CS_2	−2475.04693	4.28	0	−2472.80217	0
$\eta^1{}_S$ (C_s)	−2475.05826	4.39	−7.0	−2472.80709	−3.0
$\eta^2{}_{SS}$ (C_{2v})	−2475.05169	3.96	−3.3	−2472.81039	−5.5
$\eta^2{}_{CS}$ (C_s)	−2475.05255	4.17	−3.6	−2472.80357	−1.0
SCuCS ($C_{\infty v}$)	−2475.04859	4.10	−1.2	−2472.80401	−1.3
CS	−436.25274	1.85		−435.68793	
CuS	−2038.72230	0.57		−2037.04488	
CuS + CS	−2474.97506	2.42	43.3	−2472.73281	41.7
$\eta^1{}_C$ (C_{2v})	−2475.05215	4.08	−3.5	−2472.80172	0.1
ts1	−2475.04525	3.81	0.6	−2472.80220	−0.5
ts2	−2475.04913	3.93	−1.7	−2472.80415	−1.6
ts3	−2475.00313	3.35	26.6	−2472.75788	26.9
ts4	−2474.98712	2.92	36.2	−2472.74467	34.7

The optimized stationary points are shown in Figure 1. Figures 2 and 3 report the schematic reaction mechanism computed at the B3LYP and CCSD(T) levels. The total energies, zero-point energy corrections (ZPE), relative energies of the reactants, products, intermediate species, and transition structures are collected in Table 1, and the corresponding harmonic vibrational frequencies and infrared intensities are listed in Table 2.

TABLE 2: Calculated Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of the Different Species Identified on the Potential Energy Surface of the Cu + CS_2 → CuS + CS Reaction

species	frequency (IR intensity)
$\eta^1{}_S$ (C_s)	65(0), 208(1), 333(94), 375(0), 624(53), 1467(539)
$\eta^2{}_{SS}$ (C_{2v})	149(0), 186(0), 260(0), 367(77), 636(118), 1172(318)
$\eta^2{}_{CS}$ (C_s)	73(4), 205(8), 344(11), 427(105), 607(275), 1264(395)
SCuCS ($C_{\infty v}$)	58(1), 61(1), 290(6), 313(15), 322(2), 437(3), 1389(613)
CuS	397(4)
CS	1297(87)
CS_2 ($D_{\infty h}$)	398(3), 398(3), 667(0), 1531(689)
$\eta^1{}_C$ (C_{2v})	50i(2), 187(13), 354(10), 434(118), 612(268), 1267(370)
ts1	383i(242), 86(2), 113(14), 370(2), 629(18), 1470(432)
ts2	93i(2), 223(6), 294(0), 319(212), 624(148), 1288(326)
ts3	365i(66), 141(5), 185(6), 311(1), 395(15), 1307(432)
ts4	198i(20), 67(2), 190(1), 375(18), 390(11), 1022(281)

a. Assessment of the Computational Methods. The experimental bond strength in the copper sulfide molecule, which has a $^2\Pi$ ground state, is 64.6 kcal/mol.[33] On the basis of the experimental heats of formation of the copper (80.7 kcal/mol) and sulfur atoms (66.2 kcal/mol),[34] ΔH_f for CuS is 82.3 kcal/mol. With this value and experimental ΔH_f for Cu, CS_2 (28.0 kcal/mol), and CS (67.0 kcal/mol),[34] the Cu + CS_2 → CuS + CS reaction is found to be endothermic by 40.6 kcal/mol. The calculated value depends on how the thermochemistry for the Cu + S → CuS and CS_2 → CS + S reactions is reproduced. For the first reaction, the B3LYP and CCSD(T) values are −62.0 and −59.6 kcal/mol, respectively, which are close to the theoretical values obtained by Bauschlicher and Maître (in the range of 57.4−61.6 kcal/mol)[15] but underestimate the experimental value by 2.6 and 5 kcal/mol, respectively. The calculated reaction energies for CS_2 → CS + S are 105.3 (B3LYP) and 101.3 (CCSD(T)) kcal/mol and compare well with the experimental value of 105.2 kcal/mol. The combination of the thermochemistry of the two above reactions gives the reaction energy for Cu + CS_2 → CS + CuS. The B3LYP method gives 43.3 kcal/mol while CCSD(T) is in a slightly better agreement with a value of 41.7 kcal/mol, but this is due to a better cancellation of errors. The predicted energies can be considered satisfactory taking into account that the experimental CuS bond strength is not very accurately known.

The calculated CS bond lengths in the diatomic molecule and in CS_2 are quite close to the experimental values. The bond lengths obtained at the B3LYP level are 1.535 and 1.558 Å, respectively, which are in line with the corresponding experimental values (1.535 and 1.556 Å).[32,35] The nice agreement also holds for the calculated vibrational frequencies. The calculated (experimental) values are 1297 (1295 cm^{-1}) for CS and 1531, 667, and 398 (1535, 658, and 397 cm^{-1}) for CS_2.[33,36] The situation is a bit less favorable for the CuS molecule. The calculated bond length and harmonic vibrational frequency are 2.103 Å and 397 cm^{-1}, which should be compared to the experimental values of 2.051 Å and 415 cm^{-1}.[33]

Although the harmonic vibrational frequencies and structural parameters of the above species are well reproduced at the B3LYP level, we expect the CCSD(T) method to provide more reliable relative energies for the titled reaction (see also ref 19).

b. Minima. Among the different possible coordination modes,[1,37] three minima, namely, the $\eta^1{}_S$ (C_s, $^2A'$), $\eta^2{}_{CS}$ (C_s, $^2A'$), and $\eta^2{}_{SS}$ (C_{2v}, $^2A_1$), have been located on the Cu + CS_2 potential energy surface (see Figure 1). The $\eta^1{}_C$ (C_{2v}, $^2A_1$) structure is a first-order saddle point corresponding to the CS bond exchange in the $\eta^2{}_{CS}$ complex. The CS insertion product SCuCS ($C_{\infty v}$, $^2\Pi$) has also been located on the PES.

The most stable species at the B3LYP level is the $\eta^1{}_S$ complex, bound by 7.0 kcal/mol with respect to the reactants (see Table 1). The next most stable species is the $\eta^2{}_{CS}$ complex, which is, however, very close in energy to the $\eta^2{}_{SS}$ compound. Theses species lie 3.7 and 3.4 kcal/mol higher in energy than the $\eta^1{}_S$ complex. The SCuCS insertion product is 5.8 kcal/mol less stable than the $\eta^1{}_S$ complex. The picture is somewhat changed at the CCSD(T) level which gives the $\eta^2{}_{SS}$ complex as the lowest energy isomer, bound by 5.5 kcal/mol with respect to the ground-state reactants. The next most stable species is the $\eta^1{}_S$ complex lying 2.5 kcal/mol higher in energy. The SCuCS insertion product and the $\eta^2{}_{CS}$ complex are 4.2 and 4.5 kcal/mol higher in energy than the absolute minimum. The $\eta^2{}_{CS}$ complex is a very “fluxional” molecule since the barrier for the CS bond exchange through the $\eta^1{}_C$ complex is only 0.1 (1.1) kcal/mol at the B3LYP (CCSD(T)) level. This is in line with the very low computed vibrational frequency (73 cm^{-1}, corresponding to the SCCu bending motion, see Table 2).

c. Reaction Mechanism. At the initial step of the reaction, the copper atom binds to the sulfur atom of carbon disulfide molecule without any entrance barrier (see Figures 2 and 3). The $\eta^1{}_S$ complex is more stable by 7 kcal/mol (B3LYP) and 3 kcal/mol (CCSD(T)) than the ground state of the reactants, and has a planar geometry. The CuS bond length in this complex is 2.316 Å, about 0.3 Å larger than in CuS diatomic, which is essentially a single bond.[15] The NBO analysis shows that, in comparison with separate reactants, the atomic charge on Cu atom increases up to +0.16*e*, whereas the atomic charge on S atom, to which Cu is attached, decreases to −0.06*e* (it is −0.20*e* in free CS_2). The electronic configuration of Cu atom in the $\eta^1{}_S$ complex is 4s(0.89)3d(9.93), which means that the electronic configuration of this complex correlates directly to that of ground-state reactants. From the $\eta^1{}_S$ complex, there are two possible ways for the insertion of Cu atoms into the CS bond of CS_2. The first one goes through the formation of the $\eta^2{}_{CS}$ complex, whereas the second one proceeds through a $\eta^2{}_{SS}$ coordination compound.

In the case of $\eta^2{}_{CS}$ complex formation, the system has to overpass a barrier of 7.6 kcal/mol at the B3LYP level, which is reduced to 2.5 kcal/mol with the coupled cluster method. The reaction goes through the transition state called ts1 (see Figures 1-3). In the $\eta^2{}_{CS}$ compound, the CuS and CuC bond distances are 2.51 and 1.98 Å, respectively. The NBO charge on the Cu atom increases to about +0.5*e*. The charge transfer mainly comes from the 4s orbital, as the Cu electronic configuration is 4s(0.65)3d(9.83). The barrier height on the second route is smaller: it is equal to 5.3 kcal/mol at the B3LYP level and only 1.4 kcal/mol at the CCSD(T) level. The transition state (ts2) for this path lies 1.7 (1.6) kcal/mol below the reactants at the B3LYP (CCSD(T)) level. The NBO charge on the Cu atom in the $\eta^2{}_{SS}$ species is also about +0.5*e*, and the Cu electronic configuration is 4s(0.52)3d(9.83).

Further transformation of the $\eta^2{}_{CS}$ complex to SCuCS goes through the transition state called ts3 with an energy barrier of 30.2 (B3LYP) and 27.6 kcal/mol (CCSD(T)). A similar picture is found for the $\eta^2{}_{SS}$ complex, but with a much larger energy barrier. The transition state ts4 lies above the $\eta^2{}_{SS}$ complex by 39.5 and 40.2 kcal/mol at B3LYP and CCSD(T) levels, respectively. In the insertion product, the Cu charge is almost +0.7*e*. This species can be considered as a strongly bounded complex between CuS, a fairly polar molecule, and CS which is sensibly polarized. The dissociation of the insertion product SCuCS into CuS + CS is barrierless. As it can be easily seen in Figures 2 and 3, the products CuS + CS are 44.5 and 43.0

higher than SCuCS at the B3LYP and CCSD(T) levels, respectively.

In our previous study on the Sc + CO2 reaction, the transition states connecting the η^2_{OO} and the η^2_{CO} complexes as well as the one connecting the η^2_{OO} complex and the products (ScO + CO) were located.[19] All our attempts to locate the transition state connecting η^2_{SS} to η^2_{CS} converged either to ts1 or to ts2. The direct dissociation of the η^2_{SS} to CS + CuS transition state could not be located either. This is also the case of the direct S atom abstraction reaction. We checked the possibility of the formation of a η^2_{CS} complex through a direct side on attack of the Cu atom. Constrained geometry optimization with fixed Cu−X distances (X is a midpoint of one CS bond) went to the η^1_S complex leading to the conclusion that an entrance channel to the η^2_{CS} complex does not exist.

d. Alternative Exit Channels. Experimental studies on the gas-phase reactions of Cu^+ with CS_2 reveal the importance of the $(CuS)^+$ + CS and S + $[Cu,C,S]^{+}$[14] (the square brackets means that the connectivity of the Cu, C, and S atoms was not defined but that the signal was assigned to the copper thiocarbonyl cation on the basis of energetic bases). Although we are concerned with neutral species in this work, we also investigate other channels beside the CuS + CS exit channel. In principle, the insertion product SCuCS could lead to S + CuCS or to SCuC + S by the cleavage of the terminal bonds. Our calculations indicate that the $Cu + CS_2 \rightarrow S(^3P) + CuCS\ (^2A')$ is endothermic by 78.1 and 81.4 kcal/mol at the B3LYP and CCSD(T) levels, and the $Cu + CS_2 \rightarrow S(^3P) + SCuC\ (^2\Sigma)$ reaction is even more endothermic (160.4 and 163.1 kcal/mol at the B3LYP and CCSD(T) levels, respectively).[38] In addition, The $Cu + CS_2 \rightarrow S_2\ (^3\Sigma^-_g) + CuC\ (^4\Sigma^-)$ is found to be endothermic by 122.9 (B3LYP) and 124.0 kcal/mol (CCSD(T), whereas the energy of the $Cu + CS_2 \rightarrow C\ (^3P) + CuS_2\ (^2A_2)$ reaction is about 10 kcal/mol higher (136.0 kcal/mol at the B3LYP and 133.2 kcal/mol at the CCSD(T) level). From these results one can clearly conclude that the CuS + CS is the least endothermic exit channel for the title reaction in the gas phase.

e. Comparison with Experiment. In addition to their experimental study, Zhou and Andrews performed DFT calculations on different possible products in the Cu + CS_2 reaction.[11] The calculations used B3LYP and BP86 functionals together with the 6-311+G* basis set for C and S and the Wachters and Hay for copper atom. In the case of neutral species, four stationary points have been located. The η^1_S ($^2A'$), the η^2_{SS} ($^2A_1$), and the η^1_C ($^2A_1$) complexes and the insertion product SCuCS ($^2\Pi$). In agreement with our results, the η^1_C complex was found to be a first-order saddle point. However, the η^2_{CS} complex was not located.

The IR bands observed in argon matrix by Zhou and Andrews are reported in Table 3, along with the proposed assignment. The identification of the reaction products is rather difficult since only one IR absorption, for a given species, is observed. In all cases, this absorption corresponds to the CS stretching vibration. In Table 3, the vibrational frequencies are gathered into 4 groups. The first one corresponds to the insertion product, for which an excellent agreement is obtained. The second group, in the 1140−1190 cm^{-1} range, seems to correspond to the η^2_{CS} and η^1_C complexes. The 1142.4 cm^{-1} band has been tentatively assigned to the η^1_C complex.[11] The calculated isotopic shifts fit reasonably well the observed ones; however, this species is predicted to be a first-order saddle point. One cannot exclude that in the argon matrix the η^1_C species is a local minimum. However, some set of observed IR absorption has to be assigned to the η^2_{CS} complex since it is predicted to be more stable and with comparable calculated dipole moment (2.2 D for η^2_{CS} and 2.0 D for the η^1_C at the B3LYP level). The band observed at 1187.4 cm^{-1} with a 36.1 cm^{-1} (^{13}C) shift and 7.1 cm^{-1} (^{34}S) shift has not been assigned. The observed isotopic shift fits well the calculated ones for the η^2_{CS} complex (41, 7 cm^{-1}), and thus we propose to assign the 1187.4 cm^{-1} to the η^2_{CS} complex. The absorption band at 1133 cm^{-1}, also not assigned, has isotopic shifts close to that of a η^2_{SS} complex. This species might be due to an additional Cu atom on a η^2_{SS} complex bonded either on the Cu or the C side of the complex. The last group of bands in Table 3 corresponds to the η^2_{SS} complex.

TABLE 3: Comparison of Calculated and Observed Vibrational Frequencies and ^{13}C and ^{34}S Isotopic Frequency Shifts (cm^{-1}) for Different Species

assignment (obsd, ref 11)	ν (obsd)	ν(calcd) (this work)	$\Delta\nu$ (obsd)	$\Delta\nu$ (calcd)	assignment (this work)
SCuCS	1385.5	1389	42.1, 8.5	43, 9	SCuCS
SCuCS site	1375.5		41.8, 8.5		
?	1187.4	1264	36.1, 7.1	41, 7	η^2_{CS}
η^1_C	1142.4	1267	34.8, 4	41, 7	η^1_C?[a]
?	1133.9		32.8, 4.3		
η^2_{SS}	1081.9	1172	33.6, 5.8	37, 6	η^2_{SS}
η^2_{SS} site	1079.7		33.8, 5.9		

[a] This species is predicted to be a first-order saddle point (see Table 2); however, one cannot exclude the possibility that it corresponds to a local minimum in the argon matrix.

It is worth noting that the agreement between theory and experiment is less satisfactory for the coordination species as opposed to the insertion product. This suggests that a specific interaction with the host matrix might occur in the case of the coordination complexes. Alternatively, this can be due to the participation of a second Cu atom in the bonding pattern. The Cu dimer is strongly bonded (46.4 kcal/mol)[33] as compared to other first-row transition metal dimers. The η^1_S complex which has a strong calculated IR absorption at 1467 cm^{-1} has not been observed in argon but its cationic form the $(Cu{-}SCS)^+$ species, with a higher CS stretch is observed. As noted by Zhou and Andrews,[11] higher level of calculation might be required in order to reproduce all the observed IR bands.

The fact that the coordination complexes are formed on annealing (without or with anegligible activation energy) is corroborated by our calculations. The insertion product is only observed after photolysis with a concomitant disappearance of the coordination complexes. This result is also in good agreement with our theoretical study since the insertion product formation needs to overcome an energy barrier of at least 26 kcal/mol with respect to the ground-state reactants.

4. Conclusion

The reaction of copper atoms with CS_2 is studied using B3LYP and CCSD(T) calculations. Our results indicate that the formation of the insertion product SCuCS is slightly exothermic. There is no energy barrier at the entrance channel and the first step of the reaction is the formation of an "end-on" complex η^1_S. From this point, two routes are possible to reach the insertion product. The first one goes through the formation of a "side-on" complex η^2_{CS}, with a barrier of 26.9 kcal/mol whereas the second one goes through the formation of a four-membered ring η^2_{SS} complex, with a higher energy barrier 34.7 kcal/mol, with respect to ground-state reactants at the CCSD(T) level. It is interesting to note that the coordination complexes were actually observed in argon matrix after deposition, whereas the insertion reaction was obtained only after photolysis in line with our theoretical results. The decomposition of SCuCS into CuS and CS is found endothermic by 43 kcal/mol at CCSD(T) level. Further work is in progress on the reactions of copper atoms with OCS and CO_2 molecules.

Acknowledgment. This work has been partly supported by a Hungarian-French joint research program (Balaton 2000/00851QL). J.M. acknowledges the allocation of computer time by CNRS through IDRIS (project 11441). Y.D. thanks INTAS program (project 00-00911) for allowing her a visit to Bordeaux (January-March 2002).

References and Notes

(1) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.
(2) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205.
(3) Spiro, C. L.; Banholzer, W. F.; McAtee, D. S. *Thin Solid Films* **1992**, *220*, 122.
(4) Duncan, W. E.; Ott, E.; Reid, E. E. *Ind. Eng. Chem*. **1931**, *23*, 381.
(5) Baird, M. C.; Wilkinson, G. *Chem. Comm*. **1966**, 267 and 514.
(6) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem*. **1974**, *66*, 161.
(7) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Chem. Commun*. **1983**, 545.
(8) Broadhurst, P. V.; Leadbeater, N. E.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans*. **1997**, 4579.
(9) Huber, H.; Ozin, G. A.; Power, W. J. *Inorg. Chem*. **1977**, *16*, 2234.
(10) Hassanzadeh, P.; Andrews, L.; Davy, R. D. *J. Phys. Chem*. **1993**, *97*, 7412.
(11) Zhou, M.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 4394.
(12) Liang, B.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 3738.
(13) Rue, C.; Armentrout, P. B.; Kretzschmar, I.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **2001**, *105*, 8456.
(14) Rue, C.; Armentrout, P. B.; Kretzschmar, I.; Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **2002**, *106*, 9788.
(15) Bauschlicher, C. W., Jr.; Maître, P. *Theor. Chim. Acta* **1995**, *90*, 189.
(16) Galan, F.; Fouassier, M.; Tranquille, M.; Mascetti, J.; Pápai, I. *J. Phys. Chem.* **1997**, *101*, 2626.
(17) Mascetti, J.; Fournier, R.; Pápai, I. *J. Phys. Chem. A* **1997**, *101*, 4465.
(18) Pápai, I.; Hannachi, Y.; Gwizdala, S.; Mascetti, J. *J. Phys. Chem. A* **2002**, *106*, 4181.
(19) Pápai, I.; Schubert, G.; Hannachi, Y.; Mascetti, J. *J. Phys. Chem. A* **2002**, *106*, 9551.
(20) Beck, A. D.*J. Chem. Phys.* **1993**, *98*, 5648.
(21) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(22) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Fritsch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(23) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650; Fritsch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.
(24) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
(25) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *66*, 43.
(26) Hay, P. J. *J. Phys. Chem.* **1977**, *66*, 43.
(27) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.
(28) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys*. **1982**, *76*, 1910.
(29) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
(30) see ref 32.
(31) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(33) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
(34) NIST Chemistry Webbook, NIST standard Reference Data Base Number 69; February 2000 release (http://webbook.nist.gov/chemistry/).
(35) Suzuki, I. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1685.
(36) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1994.
(37) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063. Mascetti, J.; Gallan, F.; Pápai, I. *Coord. Chem. Rev.* **1999**, *190−192*, 557.
(38) Significant spin contamination is observed for SCuC ($^2\Sigma$) species: $\langle S_2 \rangle = 2.01$ at the B3LYP level and 2.72 for the UHF reference wave function used for the CCSD(T) calculation.