Theoretical Study of Aluminum and Gallium Atom Complexes with CO_2, CS_2, and COS

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Various possible structures for neutral ML complexes (M = Al, Ga; L = CO_2, CS_2, and COS) are investigated using density functional methods and the Moller−Plesset perturbation approach. Formation of C_{2v} and C_s species is observed. Obtained vibrational frequencies are compared with experimental data. Differences between CO_2 and CS_2 adducts are discussed. Absence of C_{2v} species for MCS_2 complexes, as seen in experiments, is consistent with calculated relative energies. Erratic behavior of the MP2 method when excluding core electrons from correlation suggests that for gallium 3d semi-core electrons of $GaCO_2$ complex play an important role in complex formation. Very small (ca. −3 kcal/mol) binding energies explain major difficulties in experimental observation of $GaCO_2$ complexes. To investigate this matter further, calculations for experimentally unknown MCOS complexes have been performed.

1. Introduction

The complexation and activation of small molecules by metal centers opens a wide field of new possible reactions. Many transition and alkali metals exhibit, for example, some reactivity toward carbon dioxide.[1−3] In the case of 13 group elements, there exist data on such systems as both aluminum and gallium with carbon monoxide,[4] allene,[5] carbon dioxide,[6−8] carbon disulfide,[7,9] and COS.[9] IR study of $AlCO_2$ in a solid argon matrix[6] reveals a C_{2v}-symmetry molecule with two symmetric metal−oxygen bonds, which under lowering the temperature from 17 to 9 K isomerizes to a lower-energy C_s form with metal − oxygen bonding (tentatively assigned as *trans*-AlOCO). Estimated enthalpy difference between the two forms is 0.4 kcal/mol. In the case of $GaCO_2$ the stability order is reversed[8] and the C_{2v} form is more stable than the C_s form. EPR study of aluminum in a solid CO_2 matrix at 77 K[7] showed no trace of *trans*-AlOCO whereas two forms of C_{2v} symmetry have been found, together with an asymmetric species (C,O-η)-$AlCO_2$. Under these conditions, gallium gives only a trapped atom and an asymmetric structure (C,O-η)-$GaCO_2$. This form is found also for Al and Ga interactions with CS_2, being the only EPR-observed product.[7] No IR spectra have been measured in this study, but LSDA-DFT calculations show existence of three isomers of $GaCO_2$. Gas-phase kinetic measurements[9] prove that an $AlCS_2$ adduct is formed, which is supported by quantum mechanical calculations.

Detailed quantum chemical calculations have been performed for some of M−CO_2 complexes, where M = Na, Li,[10] Pd.[11] There is a report on cationic Al^+CO_2 species.[12] Also $AlCO_2$ has been theoretically investigated both in HF/MP4[13] and DFT-LSDA[14] frameworks. The latter paper describes three possible coordination modes for $AlCO_2$ (that is, C_{2v} with Al−O bonds, *trans*-AlOCO, and (C,O-η)-$AlCO_2$) using Vosko, Wilk, and Nusair local spin density correlation functional.[15] The C,O-η species is found to be the lowest energy form, with C_{2v} structure only 2 kcal/mol higher. These molecules have been assigned as those existing in an argon matrix.[6] On the other hand, MP2 and MP4(SDTQ) calculations[13] predict the C_{2v} species energy to be 2.5 kcal/mol lower in respect to (C,O-η)-$AlCO_2$. Theoretical vibrational frequencies of all the structures are quite similar to each other, which makes it difficult to assign a given experimental IR spectrum to a theoretical one.

The present study has been intended as a systematic treatment of the entire set of ML (M = Al, Ga; L = CO_2, CS_2, COS) complexes, thus being more likely to reveal details of their behavior than isolated computational studies of $AlCO_2$,[13,14] $GaCO_2$,[7] or $AlCS_2$.[9] Furthermore, we try to explain significant differences between $AlCO_2$ and $GaCO_2$ systems as well as between CO_2 and CS_2. Inclusion of COS complexes serves better understanding of binding abilities of this class of molecules. Finally, we try to establish whether considered molecules are reasonably well described by DFT-based methods, which is important when going from 1:1 complexes to more complicated systems, as, for example, clusters.

2. Theoretical Approach

Density functional theory (DFT)[16] is a base for constructing multifarious models of quite good accuracy and reasonable CPU time usage. Hybrids of DFT and HF, as proposed by Becke,[17] are particularly efficient. One of those, Becke's three-parameter hybrid functional[15] coupled with Lee, Yang, and Parr's correlation functional[18] (denoted henceforth B3-LYP), has been selected for this study. As a reference, the Moller−Plesset perturbation method[19] has been used. Triple-ζ split valence 6-311G(d) and 6-311+G(3df) basis sets[20] have been chosen.

Complexes under consideration are ground state doublets of ML stoichiometry, where M = Al, Ga; L = CO_2, CS_2, COS. Throughout the study, we applied the following procedure: starting structures were optimized using unrestricted B3-LYP functional with both 6-311G(d) and 6-311+G(3df) basis sets, and their IR spectra and basis set superposition error (BSSE) corrections were calculated. Resulting structures were then reoptimized at MP2/6-311G(d) level, their harmonic frequencies calculated at the same level, but energies and BSSE corrections obtained with MP2/6-311+G(3df) single-point calculations. All subsequent wave functions were tested for instabilities, of which none were found. For MCO_2 series, additional QCISD(T)/6-

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TABLE 1: Geometrical Parameters Calculated at the MP2/6-311G(d) and B3LYP/6-311G(d) Levels[a]

complex type	MP2-full	B3-LYP[b]	MP2-full	B3-LYP[b]	MP2-full	B3-LYP[b]	MP2-full	B3-LYP[b]
M−(C,X-η)-CX_2	$AlCO_2$		$GaCO_2$		$AlCS_2$		$GaCS_2$	
M−C	2.209	2.215 (2.214)	2.257	2.329 (2.317)	2.174	2.185 (2.184)	2.224	2.298 (2.294)
C−X	1.297	1.290 (1.290)	1.264	1.250 (1.251)	1.664	1.675 (1.663)	1.656	1.661 (1.649)
C−X′	1.189	1.184 (1.181)	1.190	1.185 (1.184)	1.588	1.601 (1.590)	1.593	1.600 (1.589)
M−C−X	58.8	59.2 (58.2)	67.4	67.5 (66.9)	76.5	77.6 (76.9)	79.2	78.7 (78.0)
X−C−X′	138.3	138.4 (137.7)	143.3	144.3 (143.5)	147.7	145.3 (147.2)	148.0	147.9 (150.1)
MX_2C	$AlCO_2$		$GaCO_2$		$AlCS_2$		$GaCS_2$	
M−X	2.039	2.028 (2.003)	2.188	2.227 (2.209)	2.448	2.501 (2.475)	2.546	2.622 (2.600)
C−X	1.258	1.260 (1.260)	1.252	1.247 (1.245)	1.646	1.657 (1.647)	1.645	1.653 (1.641)
M−X-C	85.4	86.6 (86.5)	86.2	86.9 (86.8)	72.0	75.4 (74.8)	73.2	76.3 (75.1)
X−C−X	123.4	121.3 (120.7)	126.3	126.2 (126.0)	132.8	131.4 (132.1)	133.9	133.7 (135.0)
M−S−C−S	0	0	0	0	28.9	20.1 (19.7)	−26.5	−18.7 (−21.0)
trans-MOCX	$AlCO_2$		$GaCO_2$		AlOCS			
M−O	1.772	1.764 (1.753)	*c*	1.893 (1.903)	1.780	1.778 (1.760)		
O−C	1.327	1.315 (1.306)		1.313 (1.305)	1.291	1.279 (1.275)		
C−X′	1.187	1.185 (1.184)		1.187 (1.186)	1.593	1.610 (1.597)		
M−O−C	138.8	163.4 (162.5)		149.5 (141.3)	134.8	135.6 (136.5)		
O−C−X′	130.0	130.3 (130.7)		130.7 (130.8)	148.3	175.2 (174.7)		
M−(C,S-η)-COS	AlCSO		GaCSO					
M−C	2.183	2.201 (2.202)	2.285	2.353 (2.344)				
M−S	2.363	2.399 (2.396)	2.476	2.533 (2.523)				
C−S	1.714	1.735 (1.718)	1.695	1.707 (1.689)				
C−O	1.188	1.180 (1.180)	1.188	1.180 (1.180)				
S−C−O	140.1	138.8 (139.9)	142.6	142.7 (143.9)				
M−C−S	73.6	74.0 (74.2)	75.3	75.4 (75.5)				
M−(C,O-η)-COS	AlCOS		GaCOS					
M−C	2.144	2.192 (2.179)	2.198	2.288 (2.278)				
M−O	1.938	1.952 (1.928)	2.177	2.223 (2.202)				
C−O	1.279	1.267 (1.268)	1.252	1.236 (1.236)				
C−S	1.593	1.606 (1.594)	1.601	1.615 (1.604)				
S−C−O	142.6	142.9 (143.3)	145.7	146.4 (147.0)				
M−C−O	63.2	62.1 (61.5)	72.5	71.2 (70.6)				
MOSC	AlOSC		GaOSC					
M−O	2.064	2.064 (2.023)	*c*	2.396 (2.359)				
M−S	2.450	2.499 (2.503)		2.521 (2.519)				
O−C	1.243	1.238 (1.242)		1.211 (1.212)				
C−S	1.687	1.711 (1.691)		1.740 (1.719)				
O−C−S	126.6	124.7 (125.5)		127.1 (128.1)				
M−O−C	92.7	95.6 (95.6)		91.2 (90.9)				

[a] Bond lengths in Å, angles in degrees. [b] Values given in parentheses correspond to the calculation with the 6-311+G(3df) basis set. [c] There is no minimum on the MP2 PES.

311+G(3df) energy calculations for MP2/6-311G(d)-optimized structures were performed.

All calculations have been performed with the Gaussian94[21] program.

3. Results and Discussion

3.1. General Remarks. Subsequent stages of optimization have shown that B3-LYP/6-311G(d) and B3-LYP/6-311+G-(3df) structures are almost identical, with differences rarely exceeding 0.02 Å and 1°. Energy differences (at the B3-LYP/6-311+G(3df) level) between structures optimized with the smaller and larger basis sets never exceed 0.1 kcal/mol. The MP2/6-311G(d) structures are in almost equally good agreement with their DFT counterparts. Therefore we find the 6-311G(d) basis sufficient for geometry predictions; comparisons of energies require, however, larger basis sets, especially when using MP2 approximation. DFT results are significantly less basis-set dependent. Details of geometrical parameters are given in Table 1.

The calculations have revealed a variety of coordination modes for considered systems. One of the remarkable features of these complexes is that they, in general, gain stability when zero-point vibrational energy correction is taken into consideration. The reason for that is that a carbon dioxide or carbon disulfide molecule "trades" one of the strong C═O bonds for a relatively weak M−O or M−C interaction, and thus zero-point energy correction for the complex is lower than the sum of ZPVEs for substrates.

DFT energies of investigated compounds, given in Table 2, are corrected for BSSE and zero-point vibrational energies. We have calculated BSSE corrections using the counterpoise method[22] with fragment relaxation, as suggested for systems with highly distorted fragments.[23] The BSSE values for MCO_2 and MCS_2 are not greater than 0.83 kcal/mol for the B3-LYP/6-311+G(3df). It was found that zero-point energy and BSSE generally canceled each other out. Unfortunately, MP2/6-311+G(3df) BSSE corrections fall within 2.7 ÷ 5.1 kcal/mol, thus putting in serious doubt reliability of MP2-calculated energies for such systems as $GaCO_2$. For that reason, MP2 BSSE values are given as separate entries in Table 2, instead of being added to MP2 energies.

The results given below are obtained with the B3-LYP/6-311+G(3df) level of theory, and energies given with respect to isolated atoms and CO_2 or CS_2 molecules, unless explicitly stated otherwise. Calculated IR spectra, natural bond orbital (NBO)[24] atomic charges, and spin densities are given in Tables 3 and 4, respectively. Figure 1 describes three distinct models

TABLE 2: Calculated Binding Energies (kcal/mol) of ML Complexes[a]

	calculated binding energies (kcal/mol) of ML complexes					
	Al−(C,O-η)-CO_2	Al−O_2C	*trans*-AlOCO	Ga−(C,O-η)-CO_2	Ga−O_2C	*trans*-GaOCO
B3-LYP/6-311+G(3df)	−13.88 (−0.72/+0.54)	−14.56 (−0.92/+0.55)	−14.85 (−1.09/+0.48)	−3.32 (−0.88/+0.77)	−2.37 (−1.06/+0.81)	+0.13 (−1.39/+0.75)
MP2/6-311+G(3df)	−9.54 (−0.52/+2.73)	−10.23 (+0.00/+2.82)	−10.32 (−0.91/+2.78)	−0.75 (−0.73/+4.18)	−1.15 (−0.96/+4.72)	
QCISD(T)/6-311+G(3df)	−11.64	−12.96	−12.08	−2.12	−3.04	
	Al−(C,S-η)-CS_2	Al−S_2C	Ga−(C,S-η)-CS_2	Ga−S_2C		
B3-LYP/6-311+G(3df)	−25.81 (−0.07/+0.57)	−21.64 (−0.33/+0.48)	−19.96 (−0.22/+0.83)	−15.93 (−0.51/+0.63)		
MP2/6-311+G(3df)	−25.32 (−0.04/+3.05)	−18.72 (−0.04/+3.23)	- 21.00 (+0.06/+4.89)	−15.89 (−0.29/+5.05)		
	Al−(C,S-η)-COS	Al−(C,O-η)-COS	*trans*-AlOCS	AlOSC		
B3-LYP/6-311+G(3df)	−20.03 (−0.42/+0.59)	−14.55 (−0.46/+0.54)	−13.31 (−0.73/+0.53)	−15.93 (−0.80/+0.54)		
MP2/6-311+G(3df)	−17.58 (−0.14/+2.92)	−11.35 (−0.17/+2.81)	−6.80 (−0.51/+2.64)	−12.46 (+0.00/+3.06)		
	Ga−(C,S-η)-COS	Ga−(C,O-η)-COS	GaOSC			
B3-LYP/6-311+G(3df)	−14.19 (−0.48/+0.78)	−5.30 (−0.64/+0.75)	−8.23 (−0.99/+0.70)			
MP2/6-311+G(3df)	−13.45 (−0.32/+4.64)	−3.77 (−0.43/+4.45)	−5.35 (+0.00/+4.25)			

[a] DFT energy values are corrected for ZPE and BSSE (as described in the text), MP2 values are ZPE-corrected. ΔZPE and BSSE values (in that order) are given in parentheses for DFT and MP2 values.

of coordination, named hereafter M(C,O-η)-CO_2, MO_2C, and *trans*-MOCO type.

3.2. $AlCO_2$ Complexes. We have found three minima on the potential energy surface (PES) which correspond to planar structures as is presented in Figure 1 and in Table 1. Calculated binding energies are collected in Table 2. For these complexes the QCISD(T) approach predicts the C_{2v} AlO_2C structure to be the most stable energy minimum, the *trans*-AlOCO to be 0.9 kcal/mol higher, and the Al−(C,O-η)-CO_2 to be 1.3 kcal/mol above minimum (see Table 2). On the other hand, the B3-LYP functional places *trans*-AlOCO as global minimum (−14.85 kcal/mol); the (C,O-η) isomer has the highest energy among minima. This seems to be consistent with solid argon matrix measurements.[6] MP2 sequence is the same as for DFT. However, the MP2 gives only 0.1 kcal/mol difference between AlO_2C and (C,O-η) isomers whereas the B3LYP difference is equal 0.3 kcal/mol and is in good agreement with experimental value of 0.4 kcal/mol received in IR studies in solid argon matrixes.[6]

Absence of *trans*-AlOCO system in EPR measurements at 77K[7] is connected with the fact, that already at ca. 10 K this system isomerizes to give AlO_2C. We explain this as a result of a very flat potential energy surface for Al−O−C bending (note that two first harmonic frequencies for *trans*-AlOCO in Table 3, representing torsional and Al−O−C bending modes, are extremely small and equal 58 and 71 cm^{-1}; the optimized AlOC angle is 139° at MP2 level and 163° for DFT—this discrepancy can be seen as another result of potential energy surface flatness). Thus, even at 77 K vibrational energy prohibits forming of *trans*-AlOCO.

The C═O bond lengths in $AlCO_2$ systems are significantly longer than in CO_2 (1.159 Å). The longest (1.327A in *trans*-AlOCO) is in fact a single C−O bond, as shown by IR measurements.[6] As is presented in Table 2, the CO_2 subunit is highly distorted—the OCO angle varies from 121° in AlO_2C (almost pure sp^2 hybridization) to 138° in Al−(C,O-η)-CO_2, which suggests considerable transfer of electron density. Indeed, as shown by NBO population analysis (Table 4), the aluminum atom has a positive charge of 0.75 ÷ 0.90; therefore, the $AlCO_2$ complexes are radical ion pairs $Al^+CO_2{}^{*-}$. Unpaired spin density tends to move toward the carbon atom, as observed in the EPR experiment.[7] Harmonic vibrational frequencies (Table 3) agree reasonably with experiment[6,8] and confirm existence of at least two isomers of $AlCO_2$. Some of the discrepancies can result from matrix effects. Complexation of an aluminum atom by carbon dioxide lowers frequencies of stretching modes—maximally, in case of AlO_2C, from 2414 to 1491 cm^{-1}; the OCO bending mode frequency rises because of additional metal−oxygen bonds. Again, in the case of the AlO_2C system, with the most distorted OCO angle, this effect is most prominent and frequency of bending mode is shifted from 679 cm^{-1} in an isolated CO_2 molecule to 804 cm^{-1} in the complex.

3.3. $GaCO_2$ Complexes. Structures of these complexes seem very close to their aluminum analogues (see Table 1). However, at the MP2 level no *trans*-GaOCO structure could be found. Experimental evidence shows that in rare gas matrixes GaO_2C is most stable, but *trans*-GaOCO was also observed.[8] At 77 K in CO_2 matrix there is the possibility of Ga−(C,O-η)-CO_2 formation.[7] Our calculations presented in Table 2 show that $GaCO_2$ molecules are much less stable than $AlCO_2$ complexes and the DFT energies are the following: −3.3 kcal/mol for Ga−(C,O-η)-CO_2, −2.4 kcal/mol for GaO_2C, and +0.13 kcal/mol for *trans*-GaOCO (which means that this molecule is energetically disfavored). This is inconsistent with experimental data,

TABLE 3: Calculated (at the B3-LYP/6-311+G(3df) level) vs Experimental IR Spectra of ML Complexes (in cm^{-1}, experimental data in parentheses)

Al−(C,O-η)-CO_2	Al−O_2C	*trans*-AlOCO	Ga−(C,O-η)-CO_2	Ga−O_2C	*trans*-GaOCO
156.1	225.6 (214)[a]	58.3	125.5	122.6	45.6
334.7	321.9	71.0	242.7	266.0	62.7
410.1	354.3 (428)[a]	461.6 (468)[a]	374.5	292.3	344.2 (355)[b]
720.7	803.5 (797)[a]	763.1 (773)[a]	679.1	796.4 (786)[b]	731.6 (707)[b]
1125.7	1306.1 (1266)[a]	1188.7 (1147)[a]	1178.3	1338.1 (1398)[b]	1163.6 (1142)[b]
1893.0	1490.6 (1444)[a]	1843.3 (1780)[a]	1932.0	1585.0 (1535)[b]	1821.7 (1820)[b]
Al−(C,S-η)-CS_2	Al−S_2C	Ga−(C,S-η)-CS_2	Ga−S_2C		
150.5	209.1	104.0	137.4		
306.1	214.1	221.7	176.1		
315.5	252.6	310.1	208.0		
350.2	345.5	352.5	352.0		
636.6	710.1	640.7	708.1		
1247.3	1091.0	1271.3	1114.6		
Al−(C,S-η)-COS	Al−(C,O-η)-COS	*trans*-AlOCS	AlOSC	Ga−(C,S-η)-COS	Ga−(C,O-η)-COS
202.7	148.2	70.1	180.8	138.4	92.9
275.6	302.1	93.7	183.8	225.0	245.8
362.0	371.1	378.7	313.1	353.4	328.0
456.8	536.6	596.5	541.2	480.4	499.7
639.9	880.3	954.0	787.6	681.5	836.6
1831.0	1500.6	1455.7	1492.4	1845.0	1606.1
	CO_2	CS_2	COS		
bend	678.9 (667)[c]	409.2 (397)[c]	531.0 (520)[c]		
stretch sym.	1373.8 (1333)[c]	678.0 (658)[c]	880.1 (859)[c]		
stretch asym.	2413.8 (2349)[c]	1558.4 (1535)[c]	2117.2 (2062)[c]		

[a] Ref 6. [b] Ref 8. [c] Ref 26.

TABLE 4. Net Atomic Charges and Unpaired Spin Populations (in parentheses) of ML Complexes Calculated at B3-LYP/6-311+G(3df) Level with NBO[a]

	CO_2	CS_2	COS				
C	1.010	−0.422	0.416				
O	−0.505		−0.441				
S		0.211	0.025				
	Al−(C,O-η)-CO_2	Al−O_2C	*trans*-AlOCO	Ga−(C,O-η)-CO_2	Ga−O_2C	*trans*-GaOCO	
Al, Ga	0.755 (0.184)	0.900 (0.167)	0.858 (0.031)	0.627 (0.279)	0.804 (0.126)	0.848 (0.018)	
C	0.597 (0.453)	0.715 (0.607)	0.739 (0.680)	0.631 (0.385)	0.735 (0.668)	0.698 (0.674)	
O	−0.860 (0.125)	−0.807 (0.113)	−1.062 (0.090)	−0.739 (0.133)	−0.770 (0.103)	−0.997 (0.112)	
O′	−0.492 (0.238)	−0.807 (0.113)	−0.534 (0.199)	−0.519 (0.203)	−0.770 (0.103)	−0.549 (0.196)	
	Al−(C,S-η)-CS_2	Al−S_2C	Ga−(C,S-η)-CS_2	Ga−S_2C			
Al, Ga	0.675 (0.129)	0.633 (0.131)	0.627 (0.146)	0.597 (0.097)			
C	−0.825 (0.314)	−0.499 (0.540)	−0.774 (0.323)	−0.474 (0.589)			
S	−0.071 (0.102)	−0.067 (0.165)	−0.040 (0.119)	−0.062 (0.157)			
S′	0.221 (0.455)	−0.067 (0.165)	0.188 (0.412)	−0.062 (0.157)			
	Al−(C,S-η)-COS	Al−(C,O-η)-COS	*trans*-AlOCS	AlOSC	Ga−(C,S-η)-COS	Ga−(C,O-η)-COS	GaOSC
Al, Ga	0.631 (0.192)	0.780 (0.152)	0.831 (0.053)	0.767 (0.109)	0.565 (0.208)	0.682 (0.227)	0.692 (0.073)
C	0.059 (0.362)	−0.080 (0.387)	0.193 (0.621)	0.238 (0.582)	0.103 (0.374)	−0.036 (0.337)	0.284 (0.617)
O	−0.452 (0.287)	−0.794 (0.109)	−1.013 (0.081)	−0.759 (0.124)	−0.470 (0.266)	−0.677 (0.131)	−0.650 (0.158)
S	−0.238 (0.159)	0.094 (0.352)	−0.012 (0.245)	−0.245 (0.185)	−0.199 (0.152)	0.031 (0.305)	−0.325 (0.152)

[a] Note that “primed” oxygen (sulfur) atoms are those farther from the metal.

but these are affected by matrix effects. QCISD(T) energy values obtained for MP2 structures are similar to DFT values, but at this level of theory the GaO_2C structure is the global minimum (−3.0 kcal/mol) on the PES. This is also true for MP2 calculations. However, estimated BSSE for MP2 is ca. four times greater than an interaction energy. If BSSE corrections were added to MP2 energy values, the energetic sequence would have been reversed. MP2 BSSE values are also much more basis-set dependent than DFT BSSE. Moreover, exclusion of core electrons from correlation treatment gives erroneous values of energy (over +70 kcal/mol above the reactants—gallium atom and carbon dioxide molecule). Substantial improvement was obtained by retaining gallium 3d semi-core electrons in correlation calculations. Values reported in Table 2 were obtained with full-electron MP2 correction scheme.

These facts suggest that gallium−CO_2 complex formation involves serious changes in gallium electron core. Failure of MP2 and the prohibitive cost of QCISD calculations show that DFT is the most promising method for this class of compounds. The $GaCO_2$ system is an interesting example of the importance of including 3d gallium electrons in correlation calculations.[25] Inclusion of gallium d electrons in antibonding orbitals is evident from careful examination of the Kohn−Sham determinant and from electron density plots. This antibonding effect is probably responsible for serious loss of stability in comparison with $AlCO_2$ complexes.

As noted in Table 3, calculated harmonic frequencies agree well with IR spectra obtained from matrix isolation studies.[8] In particular, the calculated *trans*-GaOCO IR spectrum agrees better with an experimental one, than (C,O-η) isomer spectrum does (e.g., OCO asym. stretch mode—expt 1820 vs calcd 1822 cm^{-1} for *trans*-GaOCO and 1932 cm^{-1} for the (C,O-η) isomer). Both mentioned isomers have C_s symmetry, and it is otherwise difficult to distinguish between them as in the $AlCO_2$ case, *trans*-

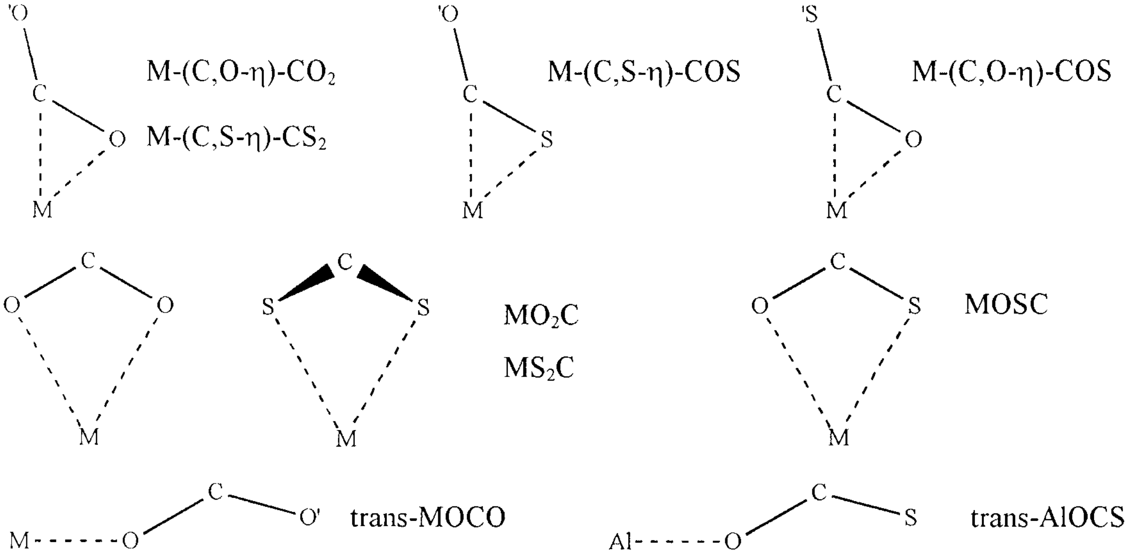

Figure 1. Types of coordination for ML (M = Al, Ga; L = CO_2, CS_2, COS) complexes.

GaOCO is loosely bound and Ga−O−C bending mode frequency lies below 100 cm^{-1}.

As shown by NBO population analysis (Table 4), in any of the $GaCO_2$ molecules the gallium atom is less positively charged than in the respective $AlCO_2$ analogue. Nevertheless, this positive charge ranges from 0.63 to 0.85; $GaCO_2$ molecules are also radical ion pairs. Spin populations on carbon atom are similar for structures observed in rare gas matrixes, and almost twice lower for gallium−carbon coordination present in EPR measurements[7] as molecules with small Ga and ^{13}C hyperfine interactions.

3.4. $AlCS_2$ and $GaCS_2$ Complexes. This class of complexes is almost unexplored in experimental and theoretical studies. EPR data[7] suggest the presence of complexes with metal−carbon bonds; gas-phase kinetic measurements and G2 method calculations[9] show existence of $AlCS_2$ adducts and claim Al−(C,S-η)-CS_2 to be the observed species. Our calculations reveal the following two types of coordination: M−(C,S-η)-CS_2 and MS_2C. Absence of *trans*-MSCS is explained below.

DFT and MP2 energies are in very good agreement with G2 method results.[9] M−(C,S-η)-CS_2 is indeed global minimum on the PES (−25.8 kcal/mol for aluminum vs the G2 value equal −26.4 kcal/mol[9] and −19.96 kcal/mol for gallium species). Its structural details are similar to those of M−(C,O-η)-CO_2. The CS_2 subunit is less deviated from linearity than CO_2 (SCS angle is 147−150°). More importantly, atomic charges are distributed in another way than for MCO_2 molecules. The metal atom is still positively charged (0.68 − aluminum, 0.62 − gallium), but the electron is transferred rather to carbon than sulfur atoms. The latter remain almost neutral, in contrast to negatively charged oxygen atoms in MCO_2 systems. This is to be expected because of the very small electronegativity difference between carbon and sulfur. Also spin density is distributed more evenly over all the CS_2 subunit, with a tendency to remain at the end farthest to metal atom. This would undoubtedly result in smaller ^{13}C EPR hyperfine interactions than for M−(C,O-η)-CO_2.

The most surprising results were obtained for MS_2C coordination type. Both aluminum and gallium MS_2C complexes are 4 kcal/mol higher than respective (C,S-η)-CS_2 structures, and it can explain the absence of MS_2C molecules in EPR measurements at 77 K.[7] The most important feature of these molecules is their nonplanarity (MSCS dihedral angle is ca. 20°). Planar C_{2v} structures of MS_2C turn out to be transition states. However, they lie just 0.47 kcal/mol for AlS_2C and 0.17 kcal/mol for GaS_2C above nonplanar structures. It is therefore expected that interconversion between "left-hand" and "right-hand" conformers of the MS_2C molecule occurs very quickly, so that in this case experiment may also show planar symmetry. The planar transition state has a structure almost identical to that of the nonplanar molecule, with slightly (0.01A) elongated metal−sulfur distance. Note that, as for the (C,S-η) structure, also MS_2C molecules are less deviated from linearity than MO_2C analogues. The SCS angle is equal to 132 ÷ 135°, whereas the OCO angle in MO_2C is 121 ÷ 126°.

The charge distribution for MS_2C, as presented in Table 4, differs from that found in MO_2C case. The metal atom is less positive (0.63 − Al, 0.60 − Ga). The carbon atom has a negative charge of 0.47 ÷ 0.50. Sulfur atoms are almost neutral (−0.06). Electrostatic attraction of metal and carbon atoms may explain nonplanarity of considered molecules—in M−(C,S-η)-CS_2 isomers the carbon atom is already near the metal and there is no possibility of nonplanar distortion. A hypothetical *trans*-MSCS molecule would collapse to the (C,S-η) isomer to increase the interaction, and this process was observed during geometry optimization.

Unpaired spin density of the MS_2C molecule is located mainly on the carbon atom. This isomer, as opposed to (C,S-η)-CS_2, should exhibit a high ^{13}C hyperfine coupling constant in EPR experiments.

3.5. MCOS Complexes. These molecules are experimentally unknown. Kinetic measurements of Al + COS reaction[9] show no trace of AlCOS (contrary to G2 calculations of the same paper, where Al−(C,S-η)-COS is found to be a stable structure 19.6 kcal/mol below the reactants). Our calculations show four possible structures for AlCOS and three for GaCOS. Notably, the B3LYP energy for Al−(C,S-η)-COS is −20.0 kcal/mol, very close to that of the expensive G2 method. This type of coordination is a global minimum on the PES both for Al and Ga series of complexes. Less stable are, in order of increasing energy, MOSC, M−(C,O-η)-COS, and *trans*-AlOCS (nonexistent for Ga). Again, gallium complexes are less stable than their aluminum analogues. We attribute this fact to involvement of gallium 3d electrons in antibonding orbitals, as in the case of $GaCO_2$.

The carbon atom of the COS molecule can coordinate to the metal giving both (C,S-η) and (C,O-η) species. It is evident from Table 2 that the (C,S-η) type is more stable and this effect is more pronounced in the case of GaCOS complexes. For example, the difference between (C,S-η) and (C,O-η) species for gallium systems is 8.9 kcal/mol, whereas for aluminum complexes it is only 5.5 kcal/mol. Our work shows that gallium prefers coordination to sulfur more than an aluminum atom does. It is consistent with increasing softness when going from Al to Ga and from O to S.

The second most stable minimum is the MOSC species, analogous to MO_2C and MS_2C. In contrast to MS_2C, it is planar, and, in agreement with our discussion of the MS_2C case, the carbon atom is positively charged, thus no electrostatic stabilization is to be gained by distorting the C_{2v} structure. The OCS angle (126 ÷ 128°) is greater than the OCO in MO_2C and smaller than the SCS in MS_2C.

In all of the MCOS molecules, there is significant charge transfer from metal to COS. Positive charges of Al vary from 0.63 to 0.83; Ga atom charges are systematically lower and vary from 0.57 to 0.69. Negative charge is located mainly on the most electronegative atom (oxygen). Spin population on the metal atom is rather small. For carbon-coordinated (C,S-η) and (C,O-η) systems the spin density is distributed primarily on carbon and O or S atoms lying farther from the metal. In the case of MOSC and *trans*-AlOCS species, the spin density is located mainly on carbon atom, what should result in considerably greater ^{13}C EPR hyperfine interactions.

4. Conclusion

In this work we have shown that B3-LYP hybrid density functional performance for investigated compounds is significantly better than that of MP2 perturbation results. The latter was found to give erroneous results when neglecting core electron correlation in $GaCO_2$ complexes. DFT results are in very good agreement with QCISD(T) and G2 calculations. The predictive potential of DFT is shown by good agreement of calculated harmonic frequencies with experimental IR spectra of $AlCO_2$ and $GaCO_2$.

The difference between CO_2 and CS_2 complexes can be explained in terms of carbon atom charge—positive in oxygen proximity and negative (or neutral) in sulfur environment. Resulting electrostatic attraction between carbon atom and positively charged metal atom causes the MS_2C-type molecules to become nonplanar.

Gallium complexes are generally weaker than aluminum species, especially for CO_2 complexes. This seems to be an effect of 3d gallium electrons participating in antibonding orbitals. These electrons must therefore be included in correlation calculations.

Generally, a B3-LYP functional performs very well. DFT seems to be a reasonable starting point for investigating aluminum and gallium complexes with CO_2 and similar molecules before applying much more time-expensive methods such as CC or QCISD. It is more so when one wants to model cluster systems such as, for example, for $Al(CO_2)_n$ ($n = 2 \div 4$), for which the cost of QCISD calculations can be prohibitive. Fortunately, even without considering matrix effects, our DFT results agree well with available experimental data and may serve as a theoretical reference for further investigation of MCOS and MCS_2 complexes.

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