Matrix-Isolated van der Waals Complexes Formed between CS₂ and Dihalogen Molecules XY, Where XY = Cl₂, Br₂, BrCl, ICl, or IBr

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Weakly bound 1:1 complexes formed between CS₂ and a dihalogen molecule XY = Cl₂, Br₂, BrCl, ICl, or IBr have each been trapped in an Ar matrix and hence investigated experimentally by their IR spectra as well as theoretically by MP2 and density functional calculations. A planar structure, with an intermolecular angle close to 90°, is expected for such a S=C=S···XY molecular complex. Moreover, for each system involving a heteronuclear dihalogen, two possible complexes exist, viz., S=C=S···XY and S=C=S···YX. The calculated structures, vibrational properties, and binding energetics of the complexes are analyzed, and the NBO formalism is used to interpret their bonding properties. The IR spectra of the complexes thus simulated provided vital guidance for the interpretation of the matrix spectra. For example, complexation was predicted and observed (i) to induce red shifts of the principal absorptions associated with both the CS₂ and XY components and (ii) to result, through the change in symmetry, in activation of some modes that are IR-silent for the free components.

Introduction

Our group in La Plata has been interested in recent years in the matrix isolation of novel species through photochemical reactions.[1−3] For example, (bromocarbonyl)sulfenyl bromide, BrC(O)SBr, was isolated for the first time in an Ar matrix initially doped with Br₂ and OCS following the action of broad-band UV−visible photolysis (eq 1).[1]

$$Br{-}Br + O{=}C{=}S \xrightarrow[\text{matrix}]{h\nu} \qquad (1)$$
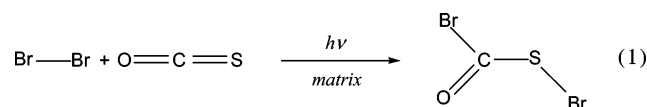
Following the same strategy, iodocarbonylsulfenyl bromide, IC(O)SBr, was formed by the photochemically activated reaction of OCS with ICl.[3] The family of carbonyl dihalide compounds, O=CXY, was likewise successfully completed by the isolation of the last two members, O=CICl and O=CIBr.[2] In this case, an Ar matrix doped with a mixture of CO and the interhalogen molecule IX (with X = Cl or Br) was irradiated with broadband UV−visible light. As reported previously,[4,5] trapping CO and a dihalogen molecule together in an Ar matrix results, prior to photolysis, in the formation of weakly bound CO/XY molecular complexes. Elucidation of the mechanism of the ensuing photochemical reactions is then critically dependent on an understanding of the intermediate role played by such molecular complexes.

Photolytically activated reactions occurring between carbon disulfide, CS₂, and dihalogen molecules XY (where X and Y may be the same or different halogen atoms) isolated together in an Ar matrix have been shown to yield the hitherto unknown halothiocarbonylsulfenyl halides, XC(S)SY.[6] It is in this context

that we became interested in investigating the possible formation of van der Waals complexes between the two species CS₂ and XY, partly because of their likely intermediacy in the photochemical reactions and partly because of an interest in the physical nature of the interactions themselves. As far as we know, no experimental studies of these systems have been reported previously.

Here, we describe, then, the results of experiments in which CS₂ has been isolated together with each of several dihalogens XY, where XY = Cl₂, Br₂, BrCl, ICl, or IBr, in solid Ar matrixes at ca. 15 K. The IR spectra signal the formation of dihalogen complexes which have been identified and characterized by their IR absorptions. The analysis is supported by the results of MP2 and density functional theory (DFT) calculations.

## Experimental and Theoretical Methods

Commercial samples of Cl₂ and Br₂ and also of ICl, IBr, and CS₂ (all from Aldrich) were purified by repeated trap-to-trap condensation in vacuo. BrCl was produced by mixing equimolar amounts of Cl₂ and Br₂, leading to an equilibrium mixture of BrCl, Cl₂, and Br₂.[7] Ar gas (BOC, research grade) was used without further purification.

Gas mixtures of dihalogen or interhalogen molecules (XY), CS₂, and Ar in different proportions were prepared by standard manometric methods. Each such mixture was deposited on a CsI window cooled to ∼15 K by a Displex closed-cycle refrigerator (Air Products, model CS202) using the pulsed deposition technique.[8,9] The IR spectrum of each matrix sample was recorded at a resolution of 0.5 cm⁻¹ and with 256 scans using a Nicolet Magna-IR 560 FTIR instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000−400 cm⁻¹ or 600−250 cm⁻¹, respectively). Following deposition and IR analysis of the resulting matrix, the sample was exposed to broadband UV−visible radiation (200 ≤ λ ≤ 800 nm) from a Spectral Energy Hg−Xe arc lamp operating at 800 W. The

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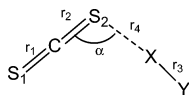
Figure 1. Schematic representation of the geometry of the molecular complex formed between CS_2 and a dihalogen molecule.

output from the lamp was limited by a water filter to absorb infrared radiation and so minimize any heating effects. The IR spectrum of the matrix was then recorded at different times of irradiation. The IR spectra of Ar matrixes doped separately with CS_2, BrCl, and ICl were also studied for the purposes of comparison.

MP2 and density functional theory (B3LYP) calculations were performed with the Gaussian 98 program package[10] under the Linda parallel execution environment using two coupled personal computers. Both 6-31+G* and 6-311+G* basis sets were tried for all the atoms except for iodine, to which a LANL2DZ basis set[11] including an effective core potential (ECP) was applied. The ECP chosen was that proposed by Hay and Wadt[12] which incorporates mass velocity and Darwin relativistic effects. The LANL2DZ basis set corresponds to an effective core potential[13] plus a double-ζ basis for iodine atoms.

On the basis of a simple molecular orbital picture of carbon disulfide, a planar structure, with an intermolecular angle α close to 90°, is expected for a S=C=S···XY molecular complex (X, Y = Cl, Br, or I), as depicted in Figure 1.

Additionally, for each CS_2/XY system involving a *hetero*nuclear dihalogen, two possible complexes exist, viz. S=C=S···XY and S=C=S···YX, depending on the halogen atom coordinated to the CS_2.

Prior to the full geometry optimization of each system, and using the model depicted in Figure 1 as a starting structure, a scan of the interatomic distance between the two subunits was performed in steps of 0.1 Å. Thereafter, and using the minimum of the potential energy curve as the starting value, geometry optimization with simultaneous relaxation of all the geometric parameters was followed by a vibrational frequency calculation to ascertain that the optimized structure corresponded to a genuine minimum.

The binding energies were calculated using the correction proposed by Nagy et al.[14] and expressed by eq 2

$$\Delta E^{corr} = \Delta E - \text{BSSE} - \text{GEOM} \qquad (2)$$

where ΔE^{corr} and ΔE are the corrected and uncorrected binding energies, respectively, BSSE corresponds to the error due to the basis set superposition, and the term GEOM takes into account the geometry differences between free CS_2 and XY monomers and each of the subunits as they occur in the complex dimer. These terms can be calculated through eqs 3–5

$$\Delta E = -[E(\text{AB}) - E^{m,m}(\text{A}) - E^{m,m}(\text{B})] \qquad (3)$$

$$\text{BSSE}_{(d,d-d,m)} = -[E^{d,d}(\text{A}) - E^{d,m}(\text{A}) + E^{d,d}(\text{B}) - E^{d,m}(\text{B})] \qquad (4)$$

$$\text{GEOM}_{(d,m-m,m)} = -[E^{d,m}(\text{A}) - E^{m,m}(\text{A}) + E^{d,m}(\text{B}) - E^{m,m}(\text{B})] \qquad (5)$$

where the superscripts m and d refer to the monomers and dimer, respectively. The first superscript refers to the geometry of the species, and the second one refers to the basis set used to calculate the energy at a geometry defined by the first

superscript. The BSSE terms have been calculated by applying the counterpoise procedure developed by Boys and Benardi.[15]

Results and Discussion

1. Theoretical Calculations. All the calculations performed, using both MP2 and DFT methods with different basis sets, converged to the same qualitative results. We describe here only the DFT results obtained with the B3LYP approximation and 6-31+G* basis sets for all the atoms other than iodine, for which a LANL2DZ basis set was employed.

a. Equilibrium Geometries. With each of the dihalogens Cl_2 and Br_2, CS_2 forms a single 1:1 complex corresponding to a potential energy minimum. With an interhalogen such as BrCl, ICl, or IBr, however, two possible complexes can be identified, namely, the species S=C=S···XY and S=C=S···YX, each also corresponding to a true minimum in the potential energy surface with no imaginary vibrational frequencies. In every case, a planar structure is favored with the XY subunit directed toward one of the sulfur atoms and roughly orthogonal to the axis of the CS_2 subunit (see Figure 1). The calculated geometric parameters for the optimized structures are given in Table 1. As a useful criterion of bonding character of the molecular complexes, the calculated van der Waals penetration distance, d_p, is included in the last column of Table 1. This parameter is defined according to eq 6, where r_{vdW} corresponds to the sum of the van der Waals radii of the relevant atoms and r_{eq} denotes the equilibrium interatomic distance in the complex.[17] It is

$$d_p = r_{vdW} - r_{eq} \qquad (6)$$

accepted that "donor−acceptor" interactions prevail in complexes with $d_p \geq 0.1$ Å.

b. Vibrational Properties. A planar penta-atomic molecular complex is characterized by nine normal modes of vibration. Four of them are associated with the internal vibrations of the linear triatomic CS_2 subunit and one with that of the dihalogen moiety. The four remaining vibrations, involving motions of the CS_2 with respect to the XY subunit, are characterized by wavenumbers well below the low-energy threshold (250 cm^{-1}) of the present IR measurements and will be excluded from further discussion.

The IR spectrum simulated by the B3LYP/6-31+G* approximation for the free CS_2 molecule presents two absorptions at 1549.4 and 403.5 cm^{-1}, the first corresponding to the antisymmetric C=S stretching mode, $\nu_{as}(CS_2)$, and the second to the doubly degenerate bending mode, $\delta(CS_2)$. The symmetric $\nu_s(CS_2)$ fundamental of the $D_{\infty h}$ molecule, predicted at 672.4 cm^{-1}, is IR-silent. Complexation is expected to cause some significant changes in the spectrum in addition to the wavenumber shifts typical of van der Waals complexes. The lowering of symmetry of the CS_2 moiety in the complex (from $D_{\infty h}$ to C_s) produces a modest IR activation of the $\nu_s(CS_2)$ mode, together with a splitting of the bending mode into distinct in-plane and out-of-plane versions. Table 2 lists calculated wavenumbers (B3LYP/6-31+G*) for selected modes of the different molecular complexes, together with the wavenumber shifts of the $\nu_{as}(CS_2)$ and $\nu(XY)$ modes with respect to the free subunits. Red shifts of both these modes are predicted to occur on complexation. With the interhalogen molecules BrCl, ICl, and IBr, the shifts are larger when coordination occurs via the more polarizable (i.e., less electronegative) halogen atom.

c. Binding Energies. The binding energies, ΔE, calculated for the different complexes on the basis of eq 3, are presented in Table 3, which also lists the two terms that contribute to the

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TABLE 1: Geometric Parameters for the Different Complexes Formed between CS_2 and Cl_2, Br_2, BrCl, ICl, or IBr (distances in Å, angles in deg) Calculated Using the B3LYP/6-31+G* Approximation

molecular complex	r_1	$\Delta r_1{}^a$	r_2	$\Delta r_2{}^b$	r_3	$\Delta r_3{}^c$	α	r_4	$d_p{}^d$
S=C=S⋯Cl_2	1.560	-3.0×10^{-4}	1.566	$+3.0 \times 10^{-4}$	2.059	$+1.4 \times 10^{-3}$	100.1	3.283	0.31
S=C=S⋯Br_2	1.557	-6.0×10^{-4}	1.568	$+5.0 \times 10^{-4}$	2.343	$+1.9 \times 10^{-3}$	92.7	3.216	0.46
S=C=S⋯ClBr	1.560	-3.0×10^{-4}	1.566	$+3.0 \times 10^{-4}$	2.190	$+5.5 \times 10^{-4}$	97.6	3.223	0.37
S=C=S⋯BrCl	1.557	-6.0×10^{-4}	1.569	$+6.0 \times 10^{-4}$	2.203	$+1.8 \times 10^{-3}$	95.7	3.158	0.52
S=C=S⋯ClI	1.561	-2.0×10^{-4}	1.564	$+1.0 \times 10^{-4}$	2.445	$+1.5 \times 10^{-3}$	96.3	3.306	0.28
S=C=S⋯ICl	1.556	-7.0×10^{-4}	1.571	$+8.0 \times 10^{-4}$	2.453	$+2.3 \times 10^{-3}$	98.8	3.371	0.42
S=C=S⋯BrI	1.560	-3.0×10^{-4}	1.566	$+3.0 \times 10^{-4}$	2.569	$+1.5 \times 10^{-3}$	103.1	3.363	0.32
S=C=S⋯IBr	1.557	-6.0×10^{-4}	1.569	$+6.0 \times 10^{-4}$	2.569	$+1.5 \times 10^{-3}$	101.3	3.478	0.31

^{a} $\Delta r CS(1) = r CS(1)_{complex} - r CS(1)_{free}$. ^{b} $\Delta r CS(2) = r CS(2)_{complex} - r CS(2)_{free}$. ^{c} $\Delta r XY = r XY_{complex} - r XY_{free}$. ^{d} van der Waals radii from ref 16. See text for definition.

TABLE 2: Wavenumbers (in cm^{-1}) for the Different Complexes Formed between CS_2 and Cl_2, Br_2, BrCl, ICl, or IBr Calculated Using the B3LYP/6-31+G* Approximation

molecular complex	$\nu_{as}(CS_2)$	$\Delta\nu_{as}(CS_2)^a$	$\nu_s(CS_2)^b$	$\delta(CS_2)^c$	$\delta_{oop}(CS_2)^c$	$\nu(XY)$	$\Delta\nu(XY)^d$
S=C=S⋯Cl_2	1545.0	−4.4	671.8	404.6	401.4	481.3	−32.6
S=C=S⋯Br_2	1543.9	−5.5	671.6	402.7	398.8	301.6	−22.0
S=C=S⋯ClBr	1545.9	−3.5	672.4	404.0	401.0	414.7	−17.8
S=C=S⋯BrCl	1542.2	−7.2	671.2	399.1	401.2	402.9	−29.5
S=C=S⋯ClI	1546.9	−2.5	672.8	404.7	403.2	317.8	−20.5
S=C=S⋯ICl	1544.1	−5.3	670.8	408.2	401.0	315.1	−23.3
S=C=S⋯BrI	1546.0	−3.3	672.3	404.3	403.0	235.1	−13.2
S=C=S⋯IBr	1546.7	−2.7	672.0	408.0	402.3	236.5	−11.8

^{a} $\Delta\nu_{as}(CS_2) = \nu_{as}(CS_2)_{complex} - \nu_{as}(CS_2)_{free}$; $\nu_{as}(CS_2)_{free} = 1549.4$ cm^{-1}. ^{b} $\nu(CS_2)_{free} = 672.4$ cm^{-1} (IR-inactive). ^{c} $\delta(CS_2)_{free} = 403.5$ cm^{-1}. ^{d} $\Delta\nu(XY) = \nu(XY)_{complex} - \nu(XY)_{free}$.

TABLE 3: Calculated Uncorrected and Corrected Binding Energies ΔE, BSSE and GEOM Corrections, Net Charge q Transferred, and Orbital Stabilization for the Different Complexes Formed between CS_2 and Cl_2, Br_2, BrCl, ICl, and IBr

molecular complex	ΔE (kcal mol^{-1})	ΔE^{corr} (kcal mol^{-1})	BSSE (kcal mol^{-1})	GEOM (kcal mol^{-1})	q (e)	$\Delta E_{n\sigma*}$ (kcal mol^{-1})
S=C=S⋯Cl_2	+0.53	+0.51	+0.17	−0.15	0.032	−3.45
S=C=S⋯Br_2	+2.43	+0.52	+2.13	−0.22	0.052	−6.25
S=C=S⋯ClBr	+1.98	+0.10	+2.01	−0.13	0.034	−3.72
S=C=S⋯BrCl	+3.87	+1.10	+2.98	−0.21	0.061	−6.71
S=C=S⋯ClI	−3.43	+0.23	−3.52	−0.14	0.035	−2.90
S=C=S⋯ICl	−2.44	+1.47	−3.67	−0.24	0.066	−7.52
S=C=S⋯BrI	−2.92	+0.47	−3.24	−0.15	0.036	−3.78
S=C=S⋯IBr	−2.77	+0.87	−3.47	−0.17	0.046	−5.67

corrected energy, viz. BSSE (eq 4) and GEOM (eq 5). Every one of the eight complexes investigated has a small but positive corrected binding energy falling in the range 0.1−1.5 kcal mol^{-1}. The complexes formed with the homonuclear dihalogen molecules, S=C=S⋯Cl−Cl and S=C=S⋯Br−Br, are predicted to have very similar binding energies on the order of 0.5 kcal mol^{-1}. When CS_2 interacts with a heteronuclear dihalogen, coordination to the less electronegative halogen is plainly preferred on the evidence of the results set out in Table 3. The most strongly bound complexes are S=C=S⋯ICl, S=C=S⋯BrCl, and S=C=S⋯IBr, with stabilization energies with respect to the corresponding isolated monomers of 1.47, 1.10, and 0.87 kcal mol^{-1}, respectively.

d. NBO Analysis. The bonding properties of each of the complexes have been interpreted by a natural bond orbital (NBO) analysis in terms of "donor−acceptor" interactions.[17] Such an analysis of all the dihalogen complexes formed with CS_2 predicts a charge transfer from the CS_2 to the dihalogen subunit. The amount of charge transferred (q) varies from complex to complex, as revealed in Table 3, being greatest for S=C=S⋯ICl, S=C=S⋯BrCl, and S=C=S⋯IBr, with values of ca. $0.066e$, $0.061e$, and $0.046e$, respectively.

The largest contribution to the stabilization energy arises from the interaction of the lone pair of the S with the unfilled σ antibonding orbital of the dihalogen molecule, as depicted in Figure 2 for S=C=S⋯Cl−Cl. This energy lowering could be

expressed by the following second-order equation

$$\Delta E_{n\sigma*}(SCS⋯XY) = -2\frac{\langle n_S| \hat{F} |\sigma^*_{XY}\rangle^2}{\epsilon_{\sigma_{XY^*}} - \epsilon_{n_S}} \tag{7}$$

in which F is the Fock operator and ϵ is the orbital energy. The calculated values for the energy lowering due to this interaction, also included in Table 3, reach a maximum in S=C=S⋯ICl, with a stabilization of 7.52 kcal mol^{-1}.

2. Experimental Findings. *a. $Cl_2/CS_2/Ar$ Mixtures.* Mixtures of Cl_2, CS_2, and Ar in the proportions 2:1:200, 0.5:1:200, and 0.2:1:200 were condensed on the cooled CsI window. The strongest feature of the IR spectrum, measured immediately after
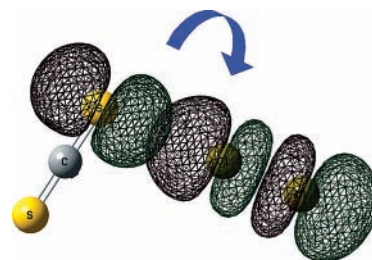
Figure 2. Schematic representation of the interaction between the lone pair of an S atom of CS_2 with the unfilled σ antibonding orbital of the Cl_2 molecule.
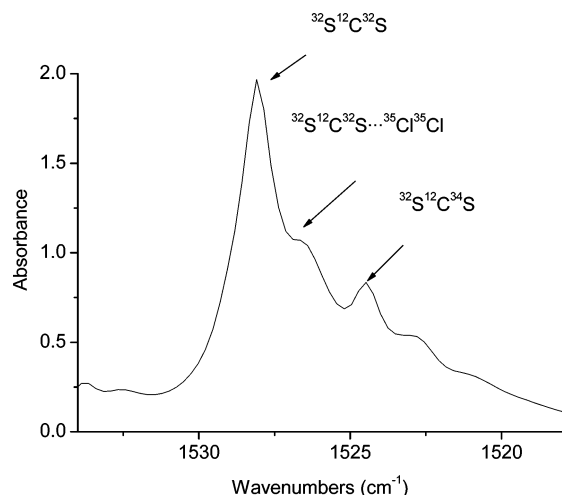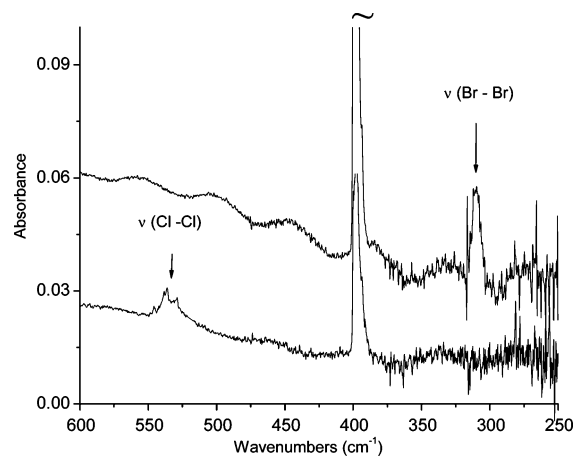
Figure 3. FTIR spectrum in the $\nu_{as}(CS_2)$ spectral region for an Ar matrix formed by co-deposition of a gaseous mixture of Cl_2, CS_2, and Ar (2:1:200).
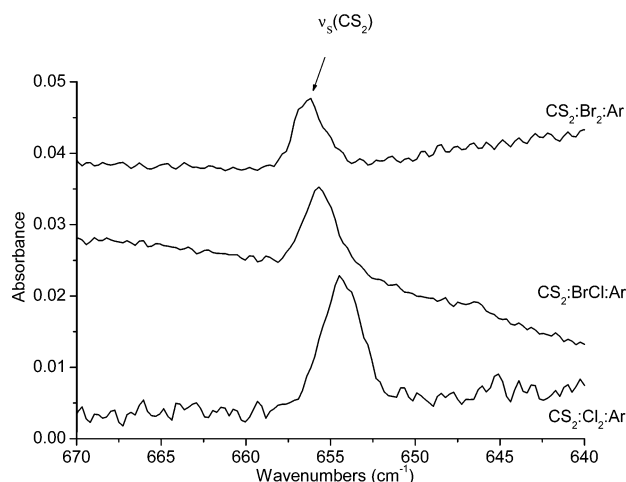
Figure 4. FTIR spectra in the $\nu_s(CS_2)$ spectral region for an Ar matrix formed by co-deposition of a gaseous mixture of XY ($=Cl_2$, BrCl, or Br_2), CS_2, and Ar (2:1:200).

deposition of the matrix, was observed at 1528.1 cm^{-1}, corresponding to the $\nu_{as}(CS_2)$ mode of the free CS_2 molecule, with a weak satellite at 1524.5 cm^{-1} associated with the analogous mode of the $C^{34}S^{32}S$ isotopomer.[18,19] As shown in Figure 3, however, there was an additional shoulder at 1526.6 cm^{-1} observed only when Cl_2 was present. This absorption is then red-shifted by 1.5 cm^{-1} with respect to free CS_2; the same shift was observed for the band due to the complexed $^{13}CS_2$ molecule occurring near 1477 cm^{-1}. The symmetric stretching mode, $\nu_s(CS_2)$, was observed to become IR-active in the complex, appearing as a very weak feature at 654.5 cm^{-1} (see Figure 4). The corresponding wavenumber for free CS_2 isolated in an Ar matrix, as measured by its Raman spectrum, is reported to be 657.7 cm^{-1}.[19] The splitting of the deformation mode of CS_2 induced by complexation was also observable, giving rise to absorptions at 399.9 and 393.7 cm^{-1}, respectively. According to the results of the theoretical calculations, the band shifted to higher wavenumber with respect to free CS_2 can be assigned to the in-plane deformation, while the other, shifted to lower wavenumber, can be assigned to the out-of-plane deformation. The only other features associated with coordinated CS_2 were combination bands observed near 2822 cm^{-1} [$\nu_{as}(CS_2) + 2\nu_s(CS_2)$] and 2176 cm^{-1} [$\nu_{as}(CS_2) + \nu_s(CS_2)$] as very weak absorptions.

Figure 5. FTIR spectra in the region 250−600 cm^{-1} of an Ar matrix formed by co-deposition of a gaseous mixture of Cl_2, CS_2, and Ar (2:1:200) (lower trace) and Br_2, CS_2, and Ar (2:1:200) (upper trace).

TABLE 4: Comparison of the Experimental and Calculated Wavenumbers (in cm^{-1}) for the S=C=S···Cl−Cl Complex

	experimental (Ar matrix)		B3LYP/6-31+G*	
mode	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
$\nu_{as}(CS_2) + 2\nu_s(CS_2)$	2822.2	−3.1		
$\nu_{as}(CS_2) + \nu_s(CS_2)$	2176.3	−1.5		
$\nu_{as}(CS_2)$	1526.6	−1.5	1545.0	−4.4
$\nu_{as}(^{13}CS_2)$	1476.8	−1.5	1494.7	−4.6
$\nu_s(CS_2)$	654.5	−3.2	671.8	−0.6
$\nu(^{35}Cl_2)$	536.2	−12.9	481.3	−32.6
$\nu(Cl_2)$ ($^{35}Cl^{37}Cl$···SCS)	528.9	−12.9	474.9	−32.0
$\nu(Cl_2)$ ($^{37}Cl^{35}Cl$···SCS)			474.5	−32.4
$\nu(^{37}Cl_2)$	521.8	−12.5	468.1	−31.8
$\delta(CS_2)$	399.9	+2.1	404.6	+1.1
$\delta_{oop}(CS_2)$	393.7	−4.1	401.4	−2.1

In addition to the IR bands arising from free and perturbed CS_2, a weak triplet could also be discerned at 536.2/528.9/521.8 cm^{-1}, as illustrated in Figure 5. This can be attributed to the $\nu(ClCl)$ fundamental of perturbed Cl_2 isotopomers in the CS_2···Cl_2 complex. The corresponding wavenumbers for free Cl_2 isolated in a solid Ar matrix, determined from the laser-induced fluorescence and Raman spectra,[20] are reported to be 549.1, 541.8, and 534.3 cm^{-1} for $^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$, respectively. Recently, we reported similar activation of the ν-(ClCl) mode in the OC···Cl_2 molecular complex isolated in an Ar matrix, with the absorptions occurring at 545.0, 537.6, and 530.3 cm^{-1} for the different isotopomers.[4] Table 4 lists the experimental wavenumbers of the absorptions identifiable with the CS_2···Cl_2 complex isolated in an Ar matrix, together with the wavenumber shifts with respect to the free molecules under comparable conditions. The results of the DFT (B3LYP/6-31+G*) calculations are also included for comparison.

b. Br_2/CS_2/Ar Mixtures. Mixtures of Br_2, CS_2, and Ar in the proportions 2:1:200, 1:1:200, 1:0.5:200, and 0.5:0.1:200 were deposited on the cooled CsI window. The IR spectra of the resulting matrixes showed, in addition to the bands corresponding to free CS_2, new bands that could be assigned to either the CS_2 or the Br_2 molecules perturbed by complexation (see Table 5).

The four fundamentals of the perturbed CS_2 could thus be observed. The $\nu_{as}(CS_2)$ fundamental appeared at 1524.5 cm^{-1}, red-shifted by 3.6 cm^{-1} with respect to free CS_2; the absorption near 1475 cm^{-1} corresponding to the mode $\nu_{as}(^{13}CS_2)$ also displayed a similar shift. The $\nu_s(CS_2)$ mode was discernible as

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TABLE 5: Comparison of the Experimental and Calculated Wavenumbers (in cm^{-1}) for the S=C=S···Br$_2$ Complex

| mode	experimental (Ar matrix)		B3LYP/6-31+G*	
	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
$\nu_{as}(CS_2) + 2\,\nu_s(CS_2)$	2820.2	−5.1		
$\nu_{as}(CS_2) + \nu_s(CS_2)$	2173.3	−4.5		
$\nu_{as}(CS_2)$	1524.5	−3.6	1543.9	−5.5
$\nu_{as}(^{13}CS_2)$	1474.8	−3.5	1492.9	−6.4
$\nu_s(CS_2)$	656.2	−1.5	671.6	−0.8
$\delta(CS_2)$	395.9	−1.9	402.7	−0.8
$\delta_{oop}(CS_2)$	393.7	−4.1	398.8	−4.7
$\nu(Br_2)$	310	−6	301.6	−22.0

TABLE 6: Comparison of the Experimental and Calculated Wavenumbers (in cm−^{1}) for the Complexes Formed between CS$_2$ and BrCl

mode	experimental (Ar matrix)		B3LYP/6-31+G*	
	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
	SCS···BrCl			
$\nu_{as}(CS_2) + \nu_s(CS_2)$	2169.0	−8.8		
$\nu_{as}(^{13}CS_2)$	1471.7	−6.6	1491.3	−6.9
$\nu_s(CS_2)$	655.7	−2.0	671.2	−1.2
$\nu(BrCl)$	420	−16	402.9	−29.5
$\delta(CS_2)$	396	−2	401.2	−2.3
$\delta_{oop}(CS_2)$	394	−4	399.1	−4.4
	SCS···ClBr			
$\nu_{as}(^{13}CS_2)$	1473.8	−4.5	1494.8	−3.4

an extremely weak band at 656.2 cm^{-1} (see Figure 4). The two features identified with the in-plane and out-of-plane CS$_2$ deformation modes of S=C=S···Br$_2$ were both observed to be shifted to lower wavenumber with respect to the corresponding degenerate fundamental of free CS$_2$ by 1.9 and 4.1 cm^{-1}, respectively, a result in satisfying agreement with the predictions of the theoretical calculations. Again, two combination modes associated with the perturbed CS$_2$ molecule could be recognized in weak absorptions appearing near 2820 and 2173 cm^{-1}. Another weak band could also be discerned at 310 cm^{-1}, as illustrated in Figure 5. This is most plausibly ascribed to the perturbed Br$_2$ molecule in the S=C=S···Br$_2$ complex. The corresponding wavenumber, reported on the basis of the Raman spectrum of free Br$_2$ isolated in a solid Ar matrix, is 315.6 cm^{-1}.[20] The $\nu(BrBr)$ mode, which is IR-silent in the free molecule, thus becomes weakly active in IR absorption on complexation of the Br$_2$, while appearing to suffer a red shift of ca. 6 cm^{-1}.

c. Cl$_2$/Br$_2$/CS$_2$/Ar Mixtures. Mixtures of Cl$_2$, Br$_2$, CS$_2$, and Ar in the proportions 2:2:1:200 were deposited on the cooled CsI window. A mixture of gaseous Cl$_2$ and Br$_2$ gives rise to an equilibrium between these two species and the interhalogen BrCl.[7] The IR spectra of the matrixes also containing CS$_2$ were dominated by the absorptions of free CS$_2$ and BrCl molecules, but new features attributable to interactions between the different components were also observed. Several bands could readily be recognized as arising from the complexes CS$_2$···Cl$_2$ and CS$_2$···Br$_2$ described in the preceding sections. The remaining bands, listed in Table 6, could be associated with interactions between the CS$_2$ and BrCl molecules.

The theoretical analysis leads us to expect two different van der Waals complexes for the system CS$_2$/BrCl, corresponding to the interaction of one sulfur atom of CS$_2$ with either a chlorine or a bromine atom of the BrCl subunit. The calculations anticipate greater stability for the S=C=S···BrCl complex than for the S=C=S···ClBr one, with an energy advantage of about 1 kcal mol^{-1} on the basis of the B3LYP/6-31+G* approximation. The simulated spectra for these two complexes differ
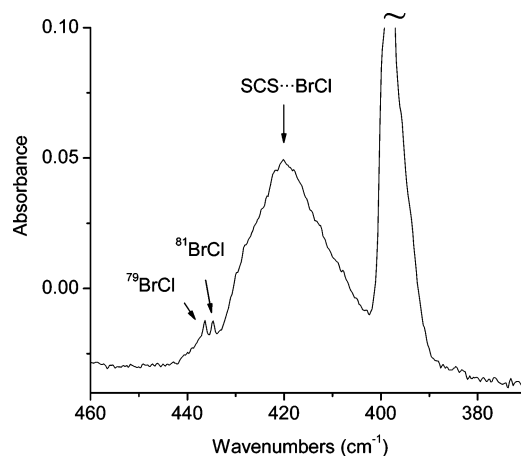

Figure 6. FTIR spectrum in the $\nu(BrCl)$ spectral region for an Ar matrix formed by co-deposition of a gaseous mixture initially composed of Cl$_2$, Br$_2$, CS$_2$, and Ar (2:2:1:200).

basically in the greater red shifts for the $\nu_{as}(CS_2)$ and $\nu(BrCl)$ modes experienced by the S=C=S···BrCl isomer, reflecting its superior stability and the stronger interaction between the two subunits. There is also a difference in the wavenumbers of the deformation modes of the CS$_2$ subunit. Whereas both the in-plane and out-of-plane deformation modes of S=C=S···BrCl are predicted to be red-shifted, the in-plane deformation of S=C=S···ClBr is predicted to be blue-shifted, with the out-of-plane deformation red-shifted with respect to the corresponding mode of free CS$_2$.

Guided by our theoretical results, we have succeeded in assigning the absorptions attributable in practice to interaction between the CS$_2$ and BrCl molecules to the more stable S=C=S···BrCl complex (see Table 6). It was possible to observe only the $\nu_{as}(^{13}CS_2)$ mode of this species (the region centered near 1525 cm^{-1} corresponding to $\nu_{as}(^{12}CS_2)$ fundamentals being too congested to permit meaningful analysis) and the CS$_2$ deformation modes, with results in good agreement with the calculated ones. The $\nu_s(CS_2)$ mode (see Figure 4) and one combination band were also observed.

The same complex could also be identified by a red shift in the absorption associated with the $\nu(BrCl)$ fundamental, as shown in Figure 6. Bands at 436.3 and 434.8 cm^{-1} have been reported[21] for the free isotopomers ^{79}BrCl and ^{81}BrCl as formed by photolysis of ClC(O)SBr isolated in an Ar matrix. Attempts to record the IR spectrum of BrCl isolated in an inert gas matrix have resulted in rather complicated spectra that may be interpreted in terms of different aggregates of the molecules BrCl, Cl$_2$, and Br$_2$.[22] Comparison with our earlier studies[21] suggests that the weak absorptions observed at 436.3 and 434.8 cm^{-1} in the spectrum of a matrix that also included CS$_2$ should be assigned to the uncomplexed BrCl molecules. The relatively strong, broad absorption appearing at 420 cm^{-1}, about 16 cm^{-1} red-shifted with respect to free BrCl, could then be linked to $\nu(BrCl)$ of the S=C=S···BrCl complex.

Exposure of the matrix to broadband UV−visible radiation resulted in the development of a new band in the $\nu_{as}(^{13}CS_2)$ region with a red shift of 4.5 cm^{-1} with respect to free CS$_2$. It is well-established that less stable molecular complexes can be formed by matrix photolysis of more stable species. For example, the less stable CO···Cl$_2$ complex was revealed after irradiation of the more stable OC···Cl$_2$ complex isolated in a noble gas matrix.[4,5] In view of such precedents and of the predictions of our theoretical calculations, we believe that the absorption formed after irradiation of the matrix can be plausibly assigned to the less stable S=C=S···ClBr complex.
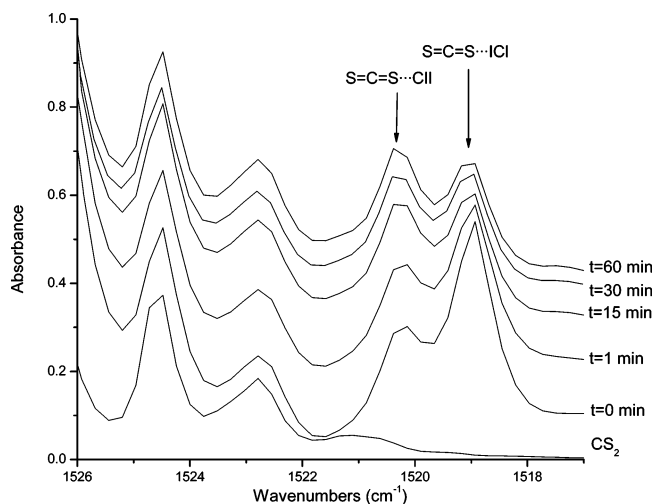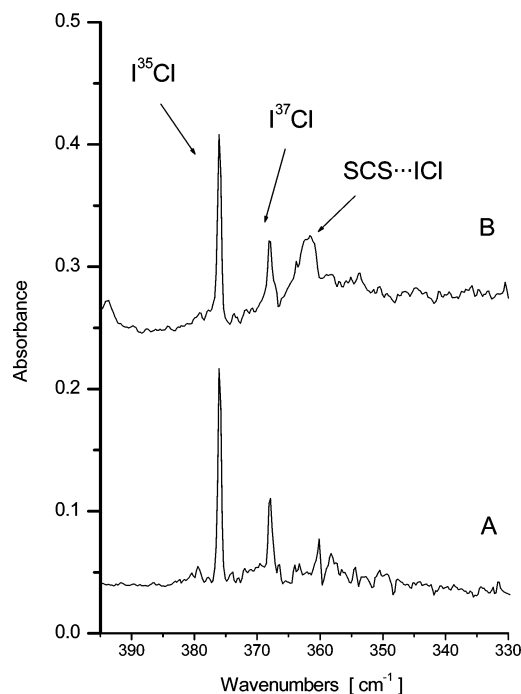
Figure 7. FTIR spectra in the $\nu_{as}(CS_2)$ spectral region for an Ar matrix formed by co-deposition of a gaseous mixture of CS_2 and Ar in the proportions 1:200 (lower trace) and ICl, CS_2, and Ar in the proportions 1:1:200 before photolysis and after photolysis for different times.

TABLE 7: Comparison of the Experimental and Calculated Wavenumbers (in cm^{-1}) for the Complexes Formed between CS_2 and ICl

mode	experimental (Ar matrix)		B3LYP/6-31+G*	
	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
SCS···ICl				
$\nu_{as}(CS_2) + \nu_s(CS_2)$	2167.7	−10.1		
$\nu_{as}(CS_2)$	1519.1	−9.0	1544.1	−5.3
$\nu_{as}(^{13}CS_2)$	1469.6	−8.7	1493.1	−5.1
$\nu_s(CS_2)$	654.6	−3.1	670.8	−1.6
$\delta(CS_2)$	398.9	+1.1	408.2	+4.7
$\delta_{oop}(CS_2)$	394.2	−3.6	401.0	−2.5
$\nu(ICl)$	361.6	−14.4	315.1	−23.3
SCS···ClI				
$\nu_{as}(CS_2)$	1520.4	−7.7	1546.9	−2.5
$\nu_{as}(^{13}CS_2)$	1470.8	−7.5	1495.7	−2.5

d. ICl/CS₂/Ar Mixtures. A gaseous mixture of ICl, CS_2, and Ar in the proportions 1:1:200 was condensed on the cooled CsI window and the matrix subsequently irradiated with broadband UV−visible light ($200 \leq \lambda \leq 800$ nm), first for 1 min and then for 1, 2, and 4 h, respectively. The spectrum of the matrix immediately after deposition showed, in addition to the bands due to free CS_2, new bands in the $\nu_{as}(CS_2)$ region at 1519.1 and 1520.4 cm^{-1}, respectively, as shown in Figure 7. Taking into consideration the relative intensities of these two bands, the relative shifts with respect to $\nu_{as}(CS_2)$ for free CS_2, and their behavior as a function of irradiation time, we propose that the 1519.1 cm^{-1} absorption—the more intense in the spectrum taken immediately after deposition—arises from the complex S=C=S···ICl, which is forecast by our calculations to be more stable than S=C=S···ClI. On the other hand, the band at 1520.4 cm^{-1}, which grew on photolysis, is tentatively assigned to this other complex, S=C=S···ClI. Table 7 compiles the wavenumbers of the absorptions observed in the IR spectra recorded for mixtures of CS_2 and ICl isolated together in a solid Ar matrix. In addition to the $\nu_{as}(^{12}CS_2)$ and $\nu_{as}(^{13}CS_2)$ modes of both complexes, features near 2168, 655, 399, and 394 cm^{-1} could be ascribed to the more stable S=C=S···ICl isomer, being associated with a combination band and the $\nu_s(CS_2)$ and in-plane and out-of-plane $\delta(CS_2)$ fundamentals, respectively.

The absorption corresponding to the $\nu(ICl)$ mode near 370 cm^{-1} also showed a significant red shift on complexation of the ICl. Figure 8A illustrates the IR spectrum of an Ar matrix

Figure 8. FTIR spectra in the $\nu(ICl)$ spectral region for an Ar matrix formed by co-deposition of a gaseous mixture of (A) ICl and Ar (1:200) and (B) ICl, CS_2, and Ar (1:1:200).

TABLE 8: Comparison of the Experimental and Calculated Wavenumbers (in cm^{-1}) for the S=C=S···IBr Complex

mode	experimental (Ar matrix)		B3LYP/6-31+G*	
	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
$\nu_{as}(CS_2) + \nu_s(CS_2)$	2169.1	−8.7		
	2167.3			
	2166.5			
$\nu_{as}(CS_2)$	1519.7	−8.4	1546.7	−2.7
$\nu_{as}(^{13}CS_2)$	1470.2	−8.0	1495.6	−2.6
$\nu_s(CS_2)$	655	−3	672.0	−0.4
$\delta_{oop}(CS_2)$	393.6	+4.2	402.3	+1.2

doped with ICl. The doublet appearing at 376.0/368.0 cm^{-1} corresponds to the isotopomers $I^{35}Cl$ and $I^{37}Cl$, respectively, in agreement with the results of earlier experiments.[23] When ICl was mixed with CS_2 in an Ar matrix, a new broad IR band centered at 361.6 cm^{-1} was observed (see Figure 8B). This is most plausibly assigned to $\nu(ICl)$ of the S=C=S···ICl complex; its broadness may reflect the occupation of different matrix sites or, possibly, overlapping of the corresponding feature of the second isomer, S=C=S···ClI.

e. IBr/CS₂/Ar Mixtures. A gaseous mixture of IBr, CS_2, and Ar in the proportions 1:2:400 was deposited on the cooled CsI window. In addition to the bands corresponding to free CS_2, the spectrum of the resulting matrix exhibited a new band in the $\nu_{as}(CS_2)$ region at 1519.7 cm^{-1} which can be attributed to S=C=S···IBr (see Table 8), predicted by our calculations to be the more stable of the two possible complexes. This absorption was accompanied by the corresponding $\nu_{as}(^{13}CS_2)$ feature at 1470.2 cm^{-1}, the weakly activated $\nu_s(CS_2)$ mode at 655 cm^{-1}, the out-of-plane deformation mode at 393.6 cm^{-1}, and a combination band appearing near 2169 cm^{-1}. No clear absorption could be associated with the $\nu(IBr)$ mode of either free IBr or any complex with CS_2. However, this would be expected to occur near 270 cm^{-1},[24] and therefore close to the low-energy cutoff of the present measurements.

Attempts to observe IR signals that could be associated with the second complex S=C=S···BrI were to no avail. Irradia-

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tion of the matrix with broadband UV−visible light (200 ≤ λ ≤ 800 nm), first for 15 min and then for 4 h, did not produce any new features in the spectral regions where the absorptions of this complex might be expected to occur.

Conclusions

The present studies have afforded the first experimental evidence of the formation of 1:1 van der Waals complexes between CS$_2$ and different dihalogen or interhalogen molecules. For all the systems CS$_2$/XY to be studied, quantum chemical calculations predict that the molecular complex is always more stable than the separated CS$_2$ and XY units. Moreover, when XY corresponds to a heteronuclear dihalogen, two different forms are expected according to whether X or Y makes the connection to CS$_2$, both of them having a positive binding energy. However, as with similar complexes between CO and dihalogens,[4] coordination to the less electronegative halogen is preferred.

Formation of the different van der Waals complexes was monitored experimentally by reference to the FTIR spectra of mixtures of CS$_2$ and XY isolated together in solid argon matrixes. Not only did this confirm the red shifts of most of the absorptions associated with both subunits on complexation, but the activation of some previously IR-silent modes was also verified. Thus, the symmetric stretching mode of CS$_2$ and the stretching modes of the homonuclear dihalogens Cl$_2$ and Br$_2$ were observed weakly in the IR spectra of the relevant complexes, further evidence of the interaction between the CS$_2$ and XY molecules. The degenerate CS$_2$ deformation mode experiences a splitting into an in-plane and out-of-plane vibration, in keeping with the lowering of symmetry (to C_s) brought about by complexation of the CS$_2$ molecule.

The strength of the S=C=S···XY interaction, as measured by the calculated binding energy of 0.5−1.5 kcal mol^{-1}, varies in the order Cl$_2$ ≈ Br$_2$ < IBr < BrCl < ICl when coordination occurs via the less electronegative halogen atom of the heteronuclear dihalogen molecules. This order is roughly mirrored by the wavenumber shift of the antisymmetric stretching mode, $\Delta\nu_{as}$(CS$_2$), induced by complexation of the CS$_2$ subunit, viz. −1.5, −3.6, −8.4, −6.6, and −9.0 cm^{-1} for XY = Cl$_2$, Br$_2$, IBr, BrCl, and ICl, respectively. The corresponding red shifts of the ν(XY) fundamental of the dihalogen subunit vary in practice from ca. −6 cm^{-1} for XY = Br$_2$ to −16.4 cm^{-1} for XY = BrCl. Earlier matrix studies of van der Waals complexes formed by Cl$_2$ have yielded $\Delta\nu$(Cl$_2$) values ranging from −7 cm^{-1} for H$_2$CO···Cl$_2$ to −85 cm^{-1} for C$_2$Me$_4$···Cl$_2$.[25] The measured $\Delta\nu$(Cl$_2$) of −12.9 cm^{-1} we have found for S=C=S···Cl$_2$ thus implies that CS$_2$ is a somewhat stronger base with respect to a dihalogen than either CO (since $\Delta\nu$(Cl$_2$) = −4.1 cm^{-1} for OC···Cl$_2$[4]) or H$_2$CO.[25] By contrast, the lowest binding energies are those calculated for the adducts in which the more electronegative halogen atom of IBr, BrCl, or ICl is linked to CS$_2$. We find limited experimental evidence to suggest the existence of these complexes, most notably in the case of the CS$_2$/ICl system where broadband UV−visible irradiation of the Ar matrix appeared to favor the formation of the less stable S=C=S···ClI complex over its S=C=S···ICl counterpart.

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