DOI: 10.1002/chem.200700118

Methanesulfenyl Fluoride, CH_3SF, a Missing Link in the Family of Sulfenyl Halides: Formation and Characterization through the Matrix Photochemistry of Methyl Thiofluoroformate, $FC(O)SCH_3$

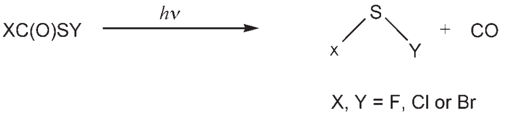
Rosana M. Romano,*[a] Carlos O. Della Védova,[b] and Anthony J. Downs[c]

Abstract: Matrix-isolation experiments have afforded the means of preparing the hitherto unknown sulfur(II) fluoride, methanesulfenyl fluoride, CH_3SF. Broadband UV-visible irradiation of methyl thiofluoroformate, $FC(O)SCH_3$, isolated in a solid Ar matrix results, first, in photoisomerization of the *syn* into the *anti* form of the molecule, and, subsequently, in the elimination of CO with the concomitant formation of CH_3SF. Continued irradiation brings about tautomerization of this product with the detachment and migration of a hydrogen from the methyl group to give the molecular complex $H_2C{=}S{\cdots}HF$. The changes have been monitored and the photoproducts detected and identified by the IR spectra of the matrices, and the conclusions confirmed: 1) with reference to the corresponding behavior of the perdeuterated molecule $FC(O)SCD_3$; 2) by analogy with the properties of related molecules, for example, $ClC(O)SCH_3$, CH_3SCl, and $H_2C{=}S{\cdots}HCl$, and; 3) by comparison with the vibrational properties simulated for the different molecules by ab initio and density functional theory methods.

Keywords: conformational equilibrium · IR spectroscopy · matrix isolation · methanesulfenyl fluoride · photochemistry

Introduction

Few classes of compounds have benefited more from matrix-isolation studies than the sulfur(II) fluorides which are typically labile compounds subject to association and disproportionation under normal conditions.[1] Such studies have been instrumental in the characterization of sulfur difluoride following its formation by the passage of SCl_2 vapor through a heated bed of AgF.[2] The first observation of the mixed fluorides ClSF and BrSF likewise came from UV photolysis of matrix-isolated FC(O)SCl[3] and FC(O)SBr,[4] respectively, resulting in the concomitant extrusion of CO (as in Equation (1)). In this context we became interested in how methanesulfenyl fluoride, CH_3SF, might be produced. To the best of our knowledge, experimental methods had failed to detect this molecule, although it had been the subject of two quantum-chemical studies,[5,6] prompted by the proposal of Baker and Dyke,[5] that it is one of the products formed by the reaction of fluorine atoms with CH_3SSCH_3 which had been monitored by He I photoelectron studies.



(1)

Following the precedents set by ClSF and BrSF, we targeted methyl thiofluoroformate, $FC(O)SCH_3$,[7,8] as a likely matrix precursor to CH_3SF. In this, we were encouraged by recent investigations of matrices doped with the corresponding thiochloroformate, $ClC(O)SCH_3$,[9] UV irradiation of which has been shown to result in CO elimination with the

---

[a] Prof. Dr. R. M. Romano
CEQUINOR (UNLP-CONICET), Departamento de Química
Facultad de Ciencias Exactas
Universidad Nacional de La Plata
47 esq. 115, (1900) La Plata (Argentina)
Fax: (+54) 221-4259485
E-mail: romano@quimica.unlp.edu.ar

[b] C. O. Della Védova
CEQUINOR (UNLP-CONICET) and Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET)
Departamento de Química
Facultad de Ciencias Exactas
Universidad Nacional de La Plata
47 esq. 115, (1900) La Plata (Argentina)

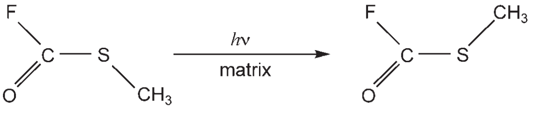
[c] Prof. Dr. A. J. Downs
Inorganic Chemistry Laboratory
University of Oxford
South Parks Road, Oxford, OX1 3QR (UK)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

formation of the known molecule CH_3SCl; the latter is itself photolabile, undergoing a tautomeric change to form the loosely bound molecular complex $H_2C{=}S{\cdots}HCl$. Here, we report the results of experiments in which solid Ar matrices doped with either $FC(O)SCH_3$ or $FC(O)SCD_3$ have been irradiated with UV light. On the evidence of the IR spectra of the matrices, photolytic randomization of the conformers of the molecule is followed by photodecomposition that proceeds in much the same way as for the thiochloroformate. The experiments thus afford the first observation of the sulfenyl fluoride CH_3SF, as well as the complex $H_2C{=}S{\cdots}HF$ to which it is subsequently converted on continued irradiation. The different products have been identified and characterized: 1) by their IR spectra, with particular reference to the effects of deuteration; 2) by quantum-chemical calculations and comparison of the vibrational properties thus forecast with the observed spectra, and; 3) by reference to the vibrational spectra of known cognate molecules.

Results and Discussion

IR spectra of normal and perdeuterated *syn*- and *anti*-$FC(O)SCH_3$: The IR spectrum of methyl thiofluoroformate, $FC(O)SCH_3$, both as a vapor and trapped in a solid Ne or Ar matrix, has already been reported;[8] an assignment of the vibrational modes has been proposed and an approximate force field calculated. The IR spectrum we have now measured for the compound isolated in an Ar matrix is entirely consistent with that described earlier (see Supporting Information). Thus, the four most distinctive absorptions were seen to occur near 1803, 1069, 760, and 645 cm^{-1}, being attributable to the $\nu(CO)$, $\nu(CF)$, $\nu_{as}(CSC)$, and $\rho(CO)$ modes, respectively.[8] Under the improved spectral resolution of the present experiments, however, it was possible also to discern some weak bands that had previously escaped detection. These included a group of absorptions observed in the spectrum recorded immediately after deposition of the matrix that grew on irradiation with broadband UV-visible light from either the Hg–Xe or the D_2 lamp. Comparison with the results of theoretical calculations performed with different methods suggests that these absorptions arise not from the *syn* (**A**) but from the *anti* (**B**) conformer of $FC(O)SCH_3$ (in which the C=O bond is oriented *anti* with respect to the S−CH_3 bond), which has not been identified previously (Scheme 1). The *syn–anti* randomization of matrix-isolated sulfenyl carbonyl compounds under UV-visible irradiation appears to be a general feature of this family of compounds, as reported previously, for example, for ClC(O)SCl,[9,10] ClC(O)SBr,[11] FC(O)SCl,[12] FC(O)SBr,[4] $CH_3C(O)SH$,[13] FC(O)SNSO,[14] and FC(O)SSC(O)F.[15]



Scheme 1. Photochemical interconversion of the *syn* and *anti* forms of $FC(O)SCH_3$ under matrix conditions.

For further evidence, we measured the IR spectrum of perdeuteromethyl thiofluoroformate, $FC(O)SCD_3$, both as a vapor (see Supporting Information) and isolated in an Ar matrix. The results correlate closely with those for the normal compound and are also well reproduced by the theoretical calculations. Hence the equilibrium between the *syn* and *anti* gaseous molecules at ambient temperatures, as well as, the photolytic interconversion of the rotamers in the Ar matrix, was again observable in the spectra recorded for the deuterated compound. Selected portions of the matrix spectra are illustrated in Figures 1 and 2.

The calculated vibrational spectra of the two conformers of $FC(O)SCH_3$ are very similar, presenting only small differences of wavenumber, which are well matched by the experimental findings. The theoretical vibrational wavenumbers calculated with the HF, MP2, and B3LYP approximations and the 6-31+G* basis set are presented as Supporting Information.

Assuming that the IR extinction coefficients of the different fundamental bands are the same for the *syn* and *anti* conformers, we conclude that the vapor of $FC(O)SCH_3$ consists of approximately 98% of the *syn* form (**A**) in equilibrium with 2% of the *anti* form (**B**). This corresponds to a free energy difference $\Delta G^{\ominus}$ of about 2.4 $kcal\,mol^{-1}$, in excellent agreement with the forecasts of theoretical calculations (see Supporting Information).

Photodecomposition of matrix-isolated $FC(O)SCH_3$ and $FC(O)SCD_3$: In a series of experiments, an Ar matrix doped with $FC(O)SCH_3$ or $FC(O)SCD_3$, typically in the proportion of approximately 1:1000, was irradiated with broadband UV-visible light. There was a choice of two sources of photolyzing radiation. The first was a Hg–Xe arc lamp with quartz optics giving radiation spanning the wavelength range $200 \leq \lambda \leq 800$ nm; the second was a D_2 discharge lamp with a LiF window and offering passage in vacuo to radiation with wavelengths in the range $150 \leq \lambda \leq 800$ nm. The advantage of the D_2 lamp was that it has a much higher output of light in the region of 200 nm.[16] In practice, the only difference between the results of the various experiments was that the photochemical changes proceeded significantly faster when the D_2 lamp was used. In no case did photodecomposition of the thiofluoroformate precursor proceed to the extent of more than about 25%, but use of the D_2 lamp achieved a greater build-up of intensity for the product bands in a given time, and so spared the IR transmission of the matrix. This was important in aiding the detection of the intermediate species, which was the main target of the present research.

Formation of CO and OCS: In addition to the changes in the IR spectra caused by interconversion of the different rotamers, several other new bands were observed to grow on irradiation of the matrix. The most distinctive of these was the cluster of absorptions occurring in the region 2135–2150 cm^{-1} readily identifiable with the photoelimination of

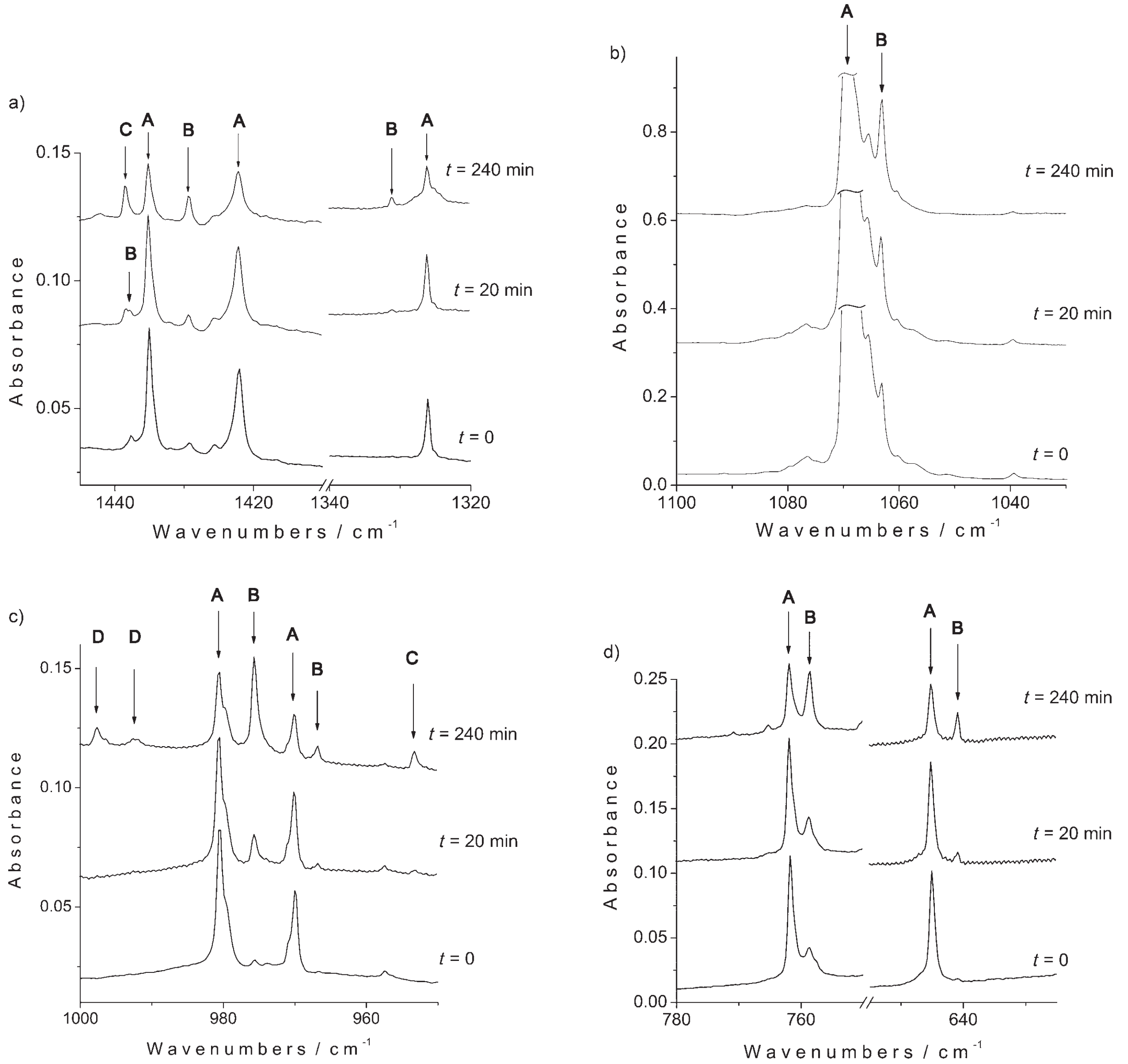


Figure 1. FTIR spectrum for an Ar matrix initially containing $FC(O)SCH_3$ at different irradiation times in the regions: a) 1410–1450 and 1320–1340 cm^{-1}; b) 1030–1100 cm^{-1}; c) 950–1000 cm^{-1}; and d) 750–780 and 625–655 cm^{-1}. **A** and **B** represent *syn*-$FC(O)SCH_3$ and *anti*-$FC(O)SCH_3$, **C** and **D** CH_3SF and the molecular complex $H_2CS\cdots HF$, respectively.

CO.[9,11,17] The sharpest feature, appearing at 2147.9 and 2148.0 cm^{-1} on photolysis of $FC(O)SCH_3$ and $FC(O)SCD_3$, respectively (see Supporting Information), implies some kind of loose complexation of the CO molecule. While free CO isolated in an Ar matrix absorbs at 2138.2 cm^{-1},[17] several loosely bound complexes characterized by a blue shift of the $\nu(CO)$ fundamental have been reported, for example, 2140.7 cm^{-1} for $OC\cdots Cl_2$, 2148.3 cm^{-1} for $OC\cdots BrCl$, 2154.0/2157.0 cm^{-1} for $OC\cdots ICl$, and 2144.2/2145.6 cm^{-1} for $OC\cdots ClI$.[18] A plausible explanation of the present results is that the CO is still held in the same matrix cage as the other fragment of photodissociation, that is, as the loosely bound adduct $OC\cdots CH_3SF$ or $OC\cdots CD_3SF$. The components of the multiplet appearing at lower wavenumber must correspond to more or less weakly complexed CO molecules, with CH_3F as a possible partner.

The evolution of the bands at 2135–2150 cm^{-1} was matched by the appearance and growth of a weaker band occurring at 2058.4 cm^{-1} for $FC(O)SCH_3$, or 2058.1 cm^{-1} for $FC(O)SCD_3$, which is also readily recognized as arising from OCS.[19] As with other carbonyl sulfenyl compounds,[9,11] it appears therefore that the elimination of OCS affords a secondary channel for photodecomposition, presumably proceeding in accordance with Equation (2), although no sig-

$$FC(O)SCH_3 \xrightarrow{h\nu} O{=}C{=}S + CH_3F \qquad (2)$$

nals attributable to CH_3F or CD_3F could be detected, being masked in all probability by stronger absorptions of the largely unchanged thiofluoroformate.

Formation of CH_3SF (C) and $H_2C{=}S\cdots HF$ (D): As the bands associated with CO and OCS developed, so too did other bands that could not be identified with any known molecules. Following our normal practice in charting the photochemistry of matrix-isolated compounds of this sort,[9,11,19] we grouped the new absorptions into different sets according to their behavior as a function of irradiation time (see Figure 3). Two such sets, identified with distinct products **C** and **D**, could thus be recognized: **C** was an intermediate photoproduct that first accumulated and then decayed on continued photolysis, this decay correlated with the emergence and growth of the final product **D**.

With $FC(O)SCH_3$ as the precursor, **C** was characterized by IR bands with the following wavenumbers: 2989, 1438.3,

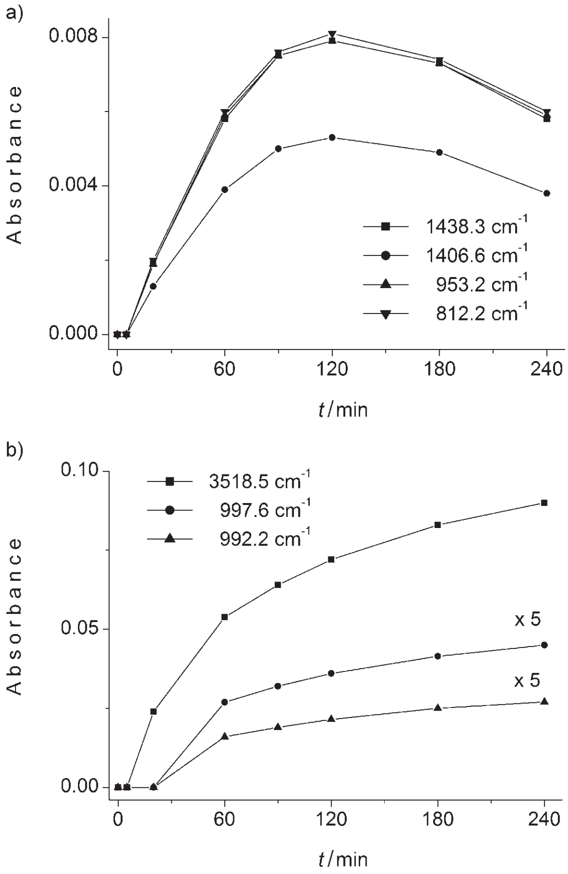


Figure 3. Plots as a function of irradiation time of the intensities of the bands assigned to: a) **C**, CH_3SF and b) **D**, $H_2CS\cdots HF$ in the IR spectrum of an Ar matrix initially containing $FC(O)SCH_3$.

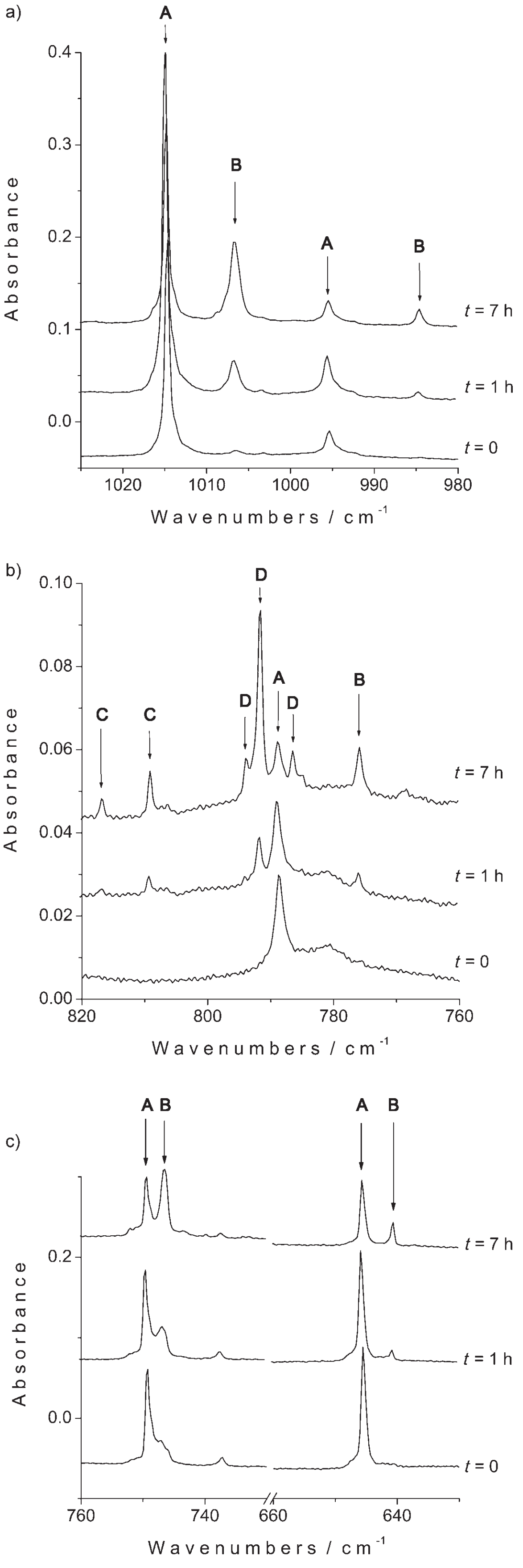


Figure 2. FTIR spectrum for an Ar matrix initially containing $FC(O)SCD_3$ at different irradiation times in the regions: a) 980–1030 cm^{-1}; b) 760–820 cm^{-1}; and c) 630–760 cm^{-1}. **A** and **B** represent *syn*-$FC(O)SCD_3$ and *anti*-$FC(O)SCD_3$, **C** and **D** CD_3SF and the molecular complex $D_2CS\cdots DF$, respectively.

1406.6, 1310.2, 953.2, 939.9, 812.2, and 704.4 cm^{-1}, the most intense features being those at 1438.3, 953.2, and 812.2 cm^{-1} (see Figure 4, for example). With $FC(O)SCD_3$ as the precursor, the corresponding set comprised bands at 1051.5, 1028.6, 999.5, 816.6, 809.0, 768.3, and 666.2 cm^{-1}, that at 809.0 cm^{-1} being more intense than any other by a factor of at least 2.5. Any counterpart to the 2989 cm^{-1} feature of the $FC(O)SCH_3$ product was liable to be masked in the second spectrum by the relatively strong absorptions of CO molecules in one form or another.

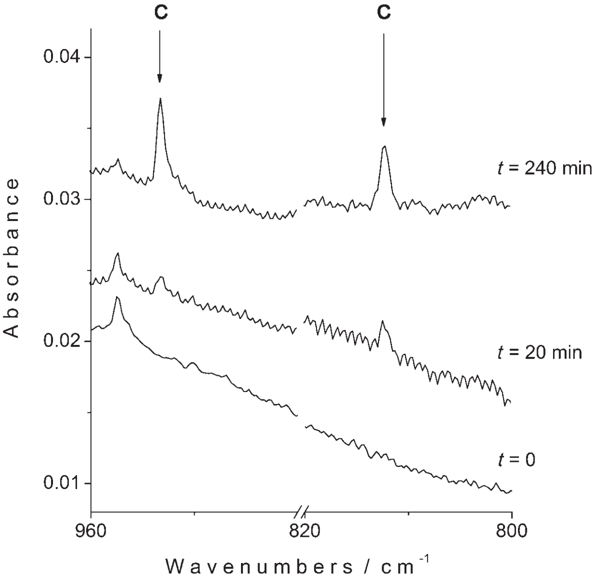


Figure 4. FTIR spectrum in the regions 940–960 and 800–820 cm^{-1} for an Ar matrix initially containing $FC(O)SCH_3$ at different irradiation times. **C** represents the CH_3SF molecule.

Correlation of the spectra of the different isotopomers of **C** produced from $FC(O)SCH_3$ and $FC(O)SCD_3$ indicates the following H:D ratios for the other bands (with wavenumbers in cm^{-1}) displayed by the natural form: 1438.3, 1.3679:1; 1406.6, 1.3675:1; 1310.2, 1.3109:1; 953.2, 1.1673:1; 939.9, 1.2234:1; 812.2, 1.0040:1; 704.4, 1.0573:1. In addition to the band at 2989 cm^{-1} suggesting a ν(CH) mode, there is additional evidence that the bands at 1400–1440, 1310, and 930–960 cm^{-1} that mostly represent $\delta_{as}(CH_3)$, $\delta_s(CH_3)$, and $\rho(CH_3)$ modes, respectively, for a CH_3 group bound to an atom with a relative atomic mass near 30 and subject to nothing higher than a plane of symmetry. The high intensity of the band at 812.2 cm^{-1}, allied to the small-to-modest shifts on deuteration of this and the band at 704.4 cm^{-1} are then consistent with the assignment of the two low-energy bands to what are predominantly ν(SF) and ν(SC) vibrations, respectively. All except the band at 812.2 cm^{-1} have wavenumbers close to those of the analogous modes of matrix-isolated CH_3SCl.[9] Association of the 812.2 cm^{-1} band with a ν(SF) fundamental is supported by the wavenumbers assigned to such modes in related sulfenyl fluorides. Thus, the symmetric and antisymmetric ν(SF) modes of SF_2 isolated in an Ar matrix occur at 832.5/829.5 and 805.0/804.6/802.1 cm^{-1}, respectively.[2,20] For ClSF[3] and BrSF,[4] also isolated in Ar matrixes, ν(SF) is set at 780 and 765 cm^{-1}, respectively, whereas it is reported to occur at 806 cm^{-1} for gaseous CF_3SF or 792 cm^{-1} for the solid compound.[21]

By contrast, the final product **D** was recognizable as being formed from $FC(O)SCH_3$ by absorptions at 3518.5, 2976.8, 997.6, 992.2, 567.8, and 550.6 cm^{-1}; the product from $FC(O)SCD_3$ absorbed at 2597.6/2588.0, 793.7/791.5, 786.3, and 475.5 cm^{-1}. The most distinctive feature in each case is the high wavenumber of the first band (see Figure 5, for example), which, with an H:D ratio of 1.355:1, must surely correspond to the ν(HF) or ν(DF) mode of an HF molecule. The HF (DF) monomer immobilized alone in an Ar matrix

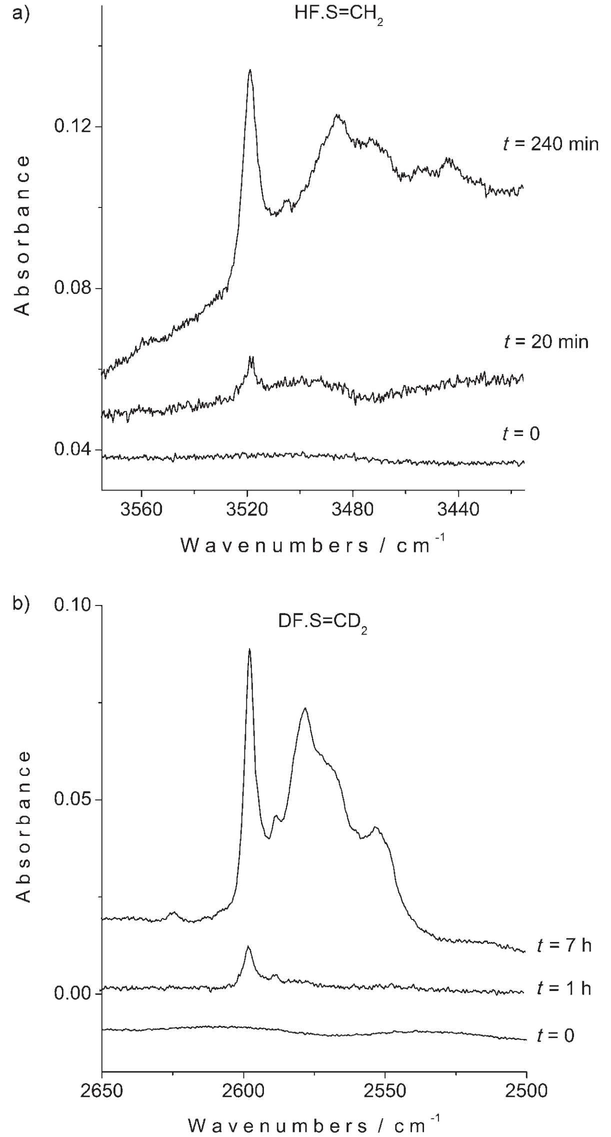


Figure 5. a) FTIR spectrum in the region 3410–3570 cm^{-1} for an Ar matrix initially containing $FC(O)SCH_3$ at different irradiation times; b) FTIR spectrum in the region 2500–2650 cm^{-1} for an Ar matrix initially containing $FC(O)SCD_3$ at different irradiation times.

is characterized by ν(HF) = 3953.8 (2895.8) cm^{-1},[22] and so with a red shift of −435.3 (about −300) cm^{-1}, the high-energy absorption suggests that **D** is a 1:1 hydrogen-bonded complex between HF and a basic molecule formed presumably by elimination of HF from **C**. Because the red shift, $\Delta\nu$(HF), gives a rough measure of the hydrogen bond strength, we must assume that the base is comparable with $H_2C{=}O$ [$\Delta\nu$(HF) = −384 cm^{-1}],[23] H_2O [$\Delta\nu$(HF) = −400 cm^{-1}],[24] $Me_2C{=}CMe_2$ [$\Delta\nu$(HF) = −413 cm^{-1}],[24] $CH_3S^{\bullet}$ [$\Delta\nu$(HF) = −439 cm^{-1}],[25] and CH_3SH [$\Delta\nu$(HF) = −440 cm^{-1}][26] in the strength of its binding to the HF molecule.

Of the remaining bands belonging to the normal version of **D**, that at 2976.8 cm^{-1} presumably arises from a ν(CH) fundamental; any ν(CD) counterpart (expected near 2150 cm^{-1}) in the spectrum of the deuterated version would almost certainly be obscured by the CO absorption in this region. The bands occurring at 997.6 and 992.2 cm^{-1} were observed to undergo significant shifts on deuteration, with H:D ratios of 1.257:1 and 1.262:1, respectively.

Although the spectra were plainly incomplete, providing only a partial characterization of the base molecule partnering the HF, the signals that could be detected all had wavenumbers close to those of prominent features in the spectrum thioformaldehyde, $H_2C{=}S$ or $D_2C{=}S$, isolated either alone,[27] or as the adduct $H_2C{=}S\cdots HCl$[9] in an Ar matrix. The remaining absorptions at 567.8 (that shifted to 475.5 cm^{-1} on deuteration) and 550.6 cm^{-1} were assigned to the in-plane and out-of-plane $FH\cdots S$ deformations, respectively, by comparison with the predictions of theoretical calculations (see below).

Because the initial build-up of **C** parallels the release of CO suggests that **C** is the hitherto elusive compound methanesulfenyl fluoride, CH_3SF. Since **D**, an HF adduct, appears to be the sole product formed on prolonged UV-visible photolysis of **C**, all the evidence available to us favors the formulation $H_2C{=}S\cdots HF$. Strong circumstantial support for these conclusions comes from the results of analogous studies on the matrix-isolated thiochloroformate $ClC(O)SCH_3$.[9] Here, UV-visible photolysis has been shown to result in CO photoelimination with the concomitant formation of the known sulfenyl chloride CH_3SCl; the latter is then subject to photoisomerization to the hydrogen-bonded complex $H_2C{=}S\cdots HCl$.

Characterization of CH_3SF and CD_3SF (C): To check the inferences drawn from the IR spectra, from the experimental circumstances, and from analogies with related studies,[9] we have carried out ab initio (HF and MP2) and density functional theory (DFT/B3LYP) calculations on CH_3SF. These give an equilibrium bent geometry for the molecule with C_s symmetry, the S−F bond being *syn* with respect to one of the C−H bonds of the methyl group. A typical calculation with the MP2/6-311++G** approximation sets the S−F and S−C distances at 1.668 and 1.781 Å, respectively, and the C-S-F angle at 97.5°, which is in good agreement with results previously deduced at the MP2/6-31G(d) level by Baker and Dyke.[5] Out of the twelve IR-active fundamentals, eight have been observed for CH_3SF and seven for CD_3SF, with wavenumbers and isotopic shifts in convincing agreement with those computed by calculation. The relevant details are set out in Table 1 along with the experimental IR wavenumbers reported for the related molecules CH_3SCl and CD_3SCl each trapped in an Ar matrix.[9,28] Additional theoretical vibrational results are presented as Supporting Information.

Table 1. Vibrational wavenumbers [in cm^{-1}] of the IR absorptions assigned to CH_3SF and CD_3SF isolated in solid Ar, together with the results of theoretical calculations and the experimental wavenumbers of matrix-isolated CH_3SCl and CD_3SCl.

CH_3SF		CD_3SF		CH_3SCl	CD_3SCl	Assignment
Ar matrix	MP2/6-31+G*	Ar matrix	MP2/6-31+G*	Ar matrix[a]	Ar matrix[a]	
–	3154 (5)	–	2342 (3)	3009	2259	ν_{as} CH_3
2989 (15)	3132 (10)	–	2319 (4)	2993	2243	ν_{as} CH_3
–	3050 (11)	–	2184 (7)	2927	2135	ν_s CH_3
1438.3 (98)	1503 (19)	1051.5 (7)	1094 (7)	1436	1053	δ_{as} CH_3
1406.6 (66)	1464 (12)	1028.6 (18)	1057 (7)	1406	1026	δ_{as} CH_3
1310.2 (15)	1379 (4)	999.5 (3)	1050 (5)	1315	1008	δ_s CH_3
953.2 (98)	986 (16)	816.6 (22)	802 (28)	964	730	ρ CH_3
939.9 (16)	995 (7)	768.3 (15)	752 (3)	957	762	ρ CH_3
812.2 (100)	744 (100)	809.0 (100)	736 (100)	523	517	ν SF (ν SCl)
704.4 (20)	697 (4)	666.2 (38)	637 (1)	705	651	ν CS
–	280 (5)	–	256 (5)	–	–	δ CSF
–	189 (<1)	–	140 (<1)	–	–	τ

[a] Reference [28].

Although the agreement between the observed and calculated intensity patterns for CH_3SF and CD_3SF leaves something to be desired, this is not altogether surprising for a molecule of low symmetry where few of the vibrations at lower wavenumbers are well described in terms of a single internal coordinate, and for observed spectra that were invariably weak and liable in some cases to be overlaid by the absorptions of other molecules. No account has been taken either of the possibility of weak complexation between CH_3SF or CD_3SF and its CO coproduct much of which is likely to be retained in the matrix cage where it is formed.

Characterization of $H_2C{=}S\cdots HF$ and $D_2C{=}S\cdots DF$ (D): The 1:1 complex between HF and $H_2C{=}S$ that we deduce as being the most likely identity of **D** is not wholly unprecedented. It has been investigated earlier by quantum-chemical calculations involving different HF, post-HF, and DFT methods.[29,30] Although the geometry and bonding properties have been reported on this basis, and a binding energy, ΔE, of 4.5–6.6 kcal mol^{-1} has been deduced, there is no reference to the vibrational properties expected of the molecule. As far as we know, moreover, no experimental evidence of the complex has been presented. Accordingly, we have carried out both ab initio and DFT calculations of our own. Typical of the results are those afforded by B3LYP/6-31+G* methods; these indicate an equilibrium geometry which, like that of $H_2C{=}S\cdots HCl$,[9] is a bent planar one with the HF axis directed toward the S atom and subtending a $C{=}S\cdots H$ angle close to 90°, as shown in Figure 6. Such a structure and its dimensions tally with those deduced in the earlier theoretical studies.[29,30] The vibrational properties computed for the present model, together with the corresponding properties computed on a similar basis for the free subunits $H_2C{=}S$ and HF, the experimental results both for the normal and perdeuterated forms of **D** and for the complex $H_2C{=}S\cdots HCl$, are given as Supporting Information.

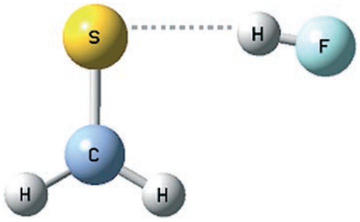


Figure 6. Molecular model of the $H_2CS\cdots HF$ complex optimized with the B3LYP/6-31+G* theoretical model.

Where comparisons can be made, there is good agreement between the theoretical and experimental wavenumbers. Both the direction and magnitude of the wavenumber shifts found experimentally to be induced by complexation are reproduced by the calculations. For example, the experimental (HF) shift of $-435.3\,cm^{-1}$ is matched theoretically by a shift of $-437.9\,cm^{-1}$. Small blue shifts of the fundamentals that could be observed for the $H_2C{=}S$ subunit are also anticipated satisfactorily by the calculations. Low intensity in terms of IR absorption, masking by more intense absorptions of other species, and wavenumbers falling below the minimum threshold of the present measurements are then explanations sufficient to account for the fundamentals of $H_2C{=}S\cdots HF$ and $D_2C{=}S\cdots DF$ that escaped detection. Despite these omissions, though, we have little doubt that **D** has thus been identified correctly.

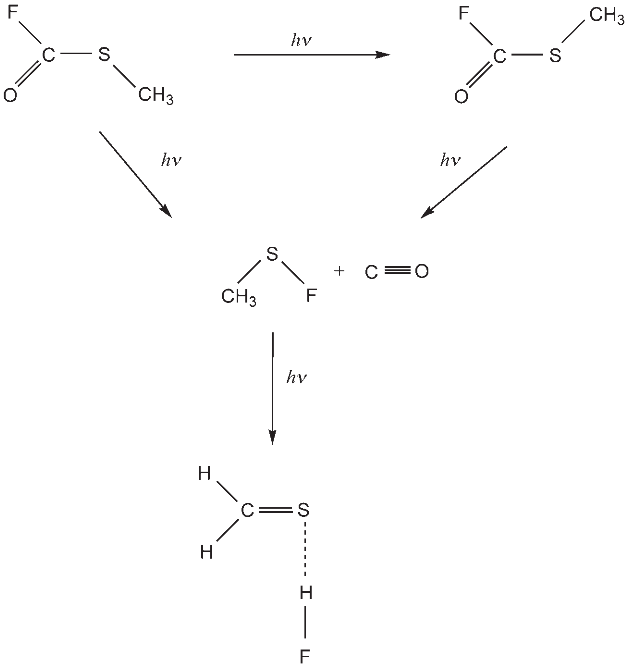
Conclusions

The matrix photochemistry of methyl thiofluoroformate, $FC(O)SCH_3$, follows closely the precedents set by the corresponding thiochloroformate, $ClC(O)SCH_3$.[9] The various reaction channels have been charted by characterization of the photoproducts by their IR spectra and by monitoring the behavior of the IR absorptions as a function of photolysis time. The conclusions have been endorsed by studying the effects of perdeuteration of the parent compound and carrying out quantum chemical calculations on the putative products.

The photolytic interconversion of the two rotamers of $FC(O)SCH_3$ is the first process observed on broadband UV-visible irradiation of the matrix-isolated molecule, behavior made familiar by analogous studies of other sulfenyl carbonyl compounds, for example, $ClC(O)SCH_3$,[9] FC(O)SCl,[12] FC(O)SBr,[4] and ClC(O)SBr.[11] The unambiguous identification of IR absorptions due to the less stable *anti* rotamer allows us to conclude that the vapor is composed of approximately 98% of the *syn* form and 2% of the *anti* form at ambient temperatures, in good agreement with the forecasts of quantum chemical calculations. Both forms of $FC(O)SCH_3$ then photodecompose. The main reaction channel involves the elimination of CO with the formation of the hitherto elusive sulfenyl fluoride CH_3SF, thus emulating similar photochemical processes starting from $ClC(O)SCH_3$,[9] FC(O)SCl,[3] FC(O)SBr,[4] and ClC(O)SBr.[11]

In a final step, continued UV-visible irradiation brings about a tautomeric change in CH_3SF, with detachment of a hydrogen atom from the methyl group to form HF and thioformaldehyde, $H_2C{=}S$, which together form the complex $H_2C{=}S\cdots HF$.

Scheme 2 summarizes these photochemical events. In addition, there are secondary reactions involving, for example, the elimination of OCS, together presumably with CH_3F although this could not be detected, as well as the formation of loosely bound CO complexes.



Scheme 2. Outline of the photochemical reactions of $FC(O)SCH_3$ isolated in a solid Ar matrix.

Experimental and Computational Procedures

$FC(O)SCH_3$ was prepared by the reaction of $ClC(O)SCH_3$ with TlF (both from Aldrich) at ambient temperature,[7] and subsequently purified by repeated trap-to-trap condensation under vacuum. The purity of the compound was checked by reference to the IR spectrum of the vapor and to the ^1H, ^{13}C, and ^{19}F NMR spectra of the liquid.[8] The perdeuterated compound $FC(O)SCD_3$ was prepared for the first time by the corresponding reaction of $ClC(O)SCD_3$[9] with TlF, and also purified by repeated trap-to-trap condensation. The Ar matrix gas was used as supplied (BOC, Research grade).

Gas mixtures of $FC(O)SCH_3$ or $FC(O)SCD_3$ with Ar in the proportion of about 1:1000 were prepared by standard manometric methods. Such a mixture was then deposited on a CsI window cooled to approximately 15 K by means of a Displex closed-cycle refrigerator (Air Products, model CS202) by using the pulsed-deposition technique.[31,32] The IR spectrum of each matrix sample was recorded at a resolution of $0.5\,cm^{-1}$, with 256 scans and an accuracy of $\pm 0.1\,cm^{-1}$, by using a Nicolet Magna-IR 560 FTIR instrument equipped with either an MCTB or a DTGS detector (for the ranges 4000–400 or $600–250\,cm^{-1}$, respectively). Following deposition and IR analysis of the resulting matrix, the sample was exposed to broadband UV-visible radiation ($200 \leq \lambda \leq 800$ nm) from a Spectral Energy Hg-Xe arc lamp operating at 800 W. The output from this lamp was limited by a water filter to absorb IR radiation and so minimize any heating effects. Alternatively, photolysis was effected with the radiation emitted under vacuum through a LiF window ($150 \leq \lambda \leq 800$ nm) by a deuterium lamp integrated into the matrix assembly. In either case, the IR spectrum of the matrix was then recorded at different times of irradiation in order to monitor closely the decay and growth of the various absorptions. Attempts to confine the photolyzing radiation issuing from the Hg-Xe lamp to a narrower range of wavelengths by means of a filter served only to reduce the flux of active radiation and so slow to an unacceptable extent the rates of the photochemical changes.

Computational details: HF, MP2, and density functional theory (B3LYP) calculations with 6-31+G* and 6-311++G** basis sets were performed by using the Gaussian 98 program package[33] under the Linda parallel execution environment by using two coupled personal computers. The geometry optimizations were performed by using standard gradient techniques with simultaneous relaxation of all of the geometric parameters. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found.

Acknowledgements

The authors acknowledge with thanks a British Council-Fundación Antorchas award for British–Argentine cooperation. C.O.D.V. and R.M.R. thank Jesus College Oxford, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 4695), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), and the Facultad de Ciencias Exactas, Universidad Nacional de La Plata for financial support. R.M.R. is also grateful to the Fundación Antorchas and to the Royal Society of Chemistry for a grant for international authors. In addition, A.J.D. is indebted to the EPSRC for support allowing the purchase of equipment.

---

[1] *Sulphur, Gmelin Handbook of Inorganic Chemistry, Suppl. Vol. 2*, Springer, Heidelberg, **1978**, pp. 3–13; N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Elsevier, Oxford, **1997**, pp. 683; N. Wiberg, *Inorganic Chemistry*, Walter de Gruyter, Berlin, **2001**, pp. 523–526.
[2] A. Haas, H. Willner, *Spectrochim. Acta Part A* **1978**, *34*, 541–544.
[3] H. Willner, *Z. Naturforsch. B* **1984**, *39*, 314–316.
[4] C. O. Della Védova, H.-G. Mack, *Inorg. Chem.* **1993**, *32*, 948–950.
[5] J. Baker, J. M. Dyke, *J. Phys. Chem.* **1994**, *98*, 757–764.
[6] Y.-S. Cheung, W.-K. Li, C.-Y. Ng, *J. Phys. Chem.* **1995**, *99*, 5967–5969.
[7] W. Caminati, R. Meyer, *J. Mol. Spectrosc.* **1981**, *90*, 303–314.
[8] C. O. Della Védova, *J. Raman Spectrosc.* **1989**, *20*, 483–488.
[9] R. M. Romano, C. O. Della Védova, A. J. Downs, *J. Phys. Chem. A* **2004**, *108*, 7179–7187.
[10] R. M. Romano, C. O. Della Védova, A. J. Downs, S. Parsons, C. Smith, *New J. Chem.* **2003**, *27*, 514–519.
[11] R. M. Romano, C. O. Della Védova, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2001**, *123*, 5794–5801.
[12] H.-G. Mack, H. Oberhammer, C. O. Della Védova, *J. Phys. Chem.* **1991**, *95*, 4238–4241.
[13] R. M. Romano, C. O. Della Védova, A. J. Downs, *J. Phys. Chem. A* **2002**, *106*, 7235–7244.
[14] H.-G. Mack, H. Oberhammer, C. O. Della Védova, *J. Mol. Struct.* **1992**, *265*, 347–357.
[15] H.-G. Mack, C. O. Della Védova, H. Oberhammer, *J. Phys. Chem.* **1992**, *96*, 9215–9217.
[16] R. Phillips in *Sources and Applications of Ultraviolet Radiation*, Academic Press, London, **1983**; *CRC Handbook of Chemistry and Physics, 85th ed.* (Ed.: D. R. Lide), CRC, Boca Raton, **2004–2005**.
[17] H. Dubost, *Chem. Phys.* **1976**, *12*, 139–151.
[18] R. M. Romano, A. J. Downs, *J. Phys. Chem. A* **2003**, *107*, 5298–5305.
[19] Y. A. Tobón, L. I. Nieto, R. M. Romano, C. O. Della Védova, A. J. Downs, *J. Phys. Chem. A* **2006**, *110*, 2674–2681, and references therein.
[20] P. Hassanzadeh, L. Andrews, *J. Phys. Chem.* **1992**, *96*, 79–84.
[21] W. Gombler, *Z. Anorg. Allg. Chem.* **1978**, *439*, 193–206.
[22] L. Andrews, G. L. Johnson, *J. Phys. Chem.* **1984**, *88*, 425–432.
[23] L. Andrews, G. L. Johnson, *J. Phys. Chem.* **1984**, *88*, 5887–5893.
[24] A. J. Barnes, *J. Mol. Struct.* **1983**, *100*, 259–280; L. Andrews, *J. Mol. Struct.* **1983**, *100*, 281–303.
[25] M. E. Jacox, *Can. J. Chem.* **1983**, *61*, 1036–1043.
[26] L. Andrews, R. T. Arlinghaus, R. D. Hunt, *Inorg. Chem.* **1986**, *25*, 3205–3209.
[27] D. J. Clouthier, D. A. Ramsay, *Annu. Rev. Phys. Chem.* **1983**, *34*, 31–58.
[28] H. Saito, H. Kurabe, E. Suzuki, F. Watari, *Spectrochim. Acta Part A* **1995**, *51*, 2447–2451.
[29] P. Kollman, J. McKelvey, A. Johansson, S. Rothenberg, *J. Am. Chem. Soc.* **1975**, *97*, 955–965.
[30] S. Salai Cheettu Ammal, P. Venuvanalingam, *J. Phys. Chem. A* **2000**, *104*, 10859–10867.
[31] M. J. Almond, A. J. Downs, *Adv. Spectrosc.* **1989**, *17*, 1; I. R. Dunkin in *Matrix-Isolation Techniques: A Practical Approach*, Oxford University Press, New York, **1998**.
[32] R. N. Perutz, J. J. Turner, *J. Chem. Soc. Faraday Trans. 2* **1973**, 452–461.
[33] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

Received: January 24, 2007
Revised: April 3, 2007