coordinated NH_3 follows the same general pattern. The k_{21} values are more subject to error because they are determined as intercepts, while the k_{12} values are obtained from slopes. If the substitution reaction proceeds by loss of water (or ammonia) to form a five-coordinate transition state, then dien must stabilize the lower coordination state. More highly coordinated ligands such as EDTA or tetren would require greater rearrangement of the bound groups. Rigid chelate rings in the phenanthroline complexes or strained rings in the α,β-DPA complex might account for their effects. The problem of predicting behavior is difficult because of the lack of detailed knowledge of the effect of structure on the reactant, much less the transition state. Structural effects could include the relative positions of different donor groups, chelate ring size, and steric strain in the complexes. Preliminary work with other metal ions indicates that the same ligands have much different effects on different metals. This is to be expected since different coordination positions are preferred by different metals. Much more data are needed before the relationship between ligand structure and the reactivity of the complex can be well characterized.

In summary, the electron-donating ability of the coordinated groups is more important than the over-all charge of the complex, but the structural arrangement of the coordinated ligand appears to be of still greater importance in determining the rate of replacement of bound water.

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Infrared Spectra of and Bonding in Some X–SO_2–Y Gaseous Molecules[1,2]

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Abstract: The infrared spectra in the range 400 to 4000 cm^{-1} of gaseous and condensed dimethyl sulfone, methyl sulfonyl chloride, and methyl sulfonyl fluoride have been obtained and assigned. The spectra are correlated with those of other X–SO_2–Y molecules (X and/or Y being F, OH, Cl, or CH_3, and including sulfuryl halides, sulfonic acids, and sulfuric acid). Linear relations are observed between the average electronegativity of X and Y and (a) the –SO_2 asymmetric, (b) the –SO_2 symmetric, (c) the S–X stretching, (d) the –SO_2 bending, and (e) the –SO_2 rocking frequencies. They are compared in part to similar correlations for chromyl and molybdenyl compounds and are explained in terms of participation of the d orbitals in the bonding. The three vibrations of sulfur dioxide also fit into these correlations. Previously made correlations are modified and used to predict bond distances for, *e.g.*, gaseous H_2SO_4.

Bonding in molecules of the type X–SO_2–Y[2] has been the subject of some interest,[3,4] in particular because of the participation of the 3d orbitals of sulfur in the bonding. The theoretical aspects have been developed and summarized by Jaffé and Orchin.[4] The species to be considered here[2] have X and Y whose main effect should be inductive and hence well suited for a test of the theory. Direct investigation of the electronic spectra of these molecules has proved difficult because no spectra have been observed in the glass or quartz ultraviolet regions.[4]

The –SO_2 stretching frequencies are accessible to observation and have been characterized by Bellamy and Williams[5] as being essentially free from mass and coupling effects. As such, they should provide a useful probe into the bonding of these compounds. Robinson[6] and Gillespie and Robinson[7] have made extensive studies of these compounds, mostly in the condensed phases. They have also made quantitative correlations of the –SO_2 bond angle and of the S–O bond length with the –SO vibration frequencies.

For purposes of investigating the nature of the bonding, elimination of such perturbations as hydrogen bonding, dipole–dipole effects, and other condensed-phase interactions is desirable; gas-phase spectra are indicated. The gas-phase spectra are of added interest because many high-temperature gaseous molecules of the type X–MO_2–Y (M = Cr, Mo, W, U)

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[2] For the purposes of this paper, X and/or Y include F, OH, Cl, and CH_3. The compounds included, therefore, are the sulfuryl halides, sulfonic acids, sulfuric acid, sulfonyl halides, and dimethyl sulfone.

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[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 17.

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are now known. Extension of the correlations for the sulfur molecules to them would be valuable and would be facilitated if the relative effects of the *n*d and (*n* − 1)d orbitals could be sorted out.

The number of compounds for which such gas-phase data are available has been greatly enlarged lately. These data show that in the gas phase -OH does indeed act like a halogen with an electronegativity of 3.4[8,9] and that a linear correlation of $-SO_2$ stretching frequencies with the electronegativity of X and Y could be established. For the molecules CH_3–SO_2–F,[10] CH_3–SO_2–Cl,[10] and CH_3–SO_2–CH_3,[7,11] only condensed-phase spectra were available. Large deviations from the correlation were observed and seemed to be caused by gas–liquid (or solid) frequency shifts.

The purpose of the present paper is to report the determination of the gas-phase spectra of CH_3SO_2–F, –Cl, and $-CH_3$ and remeasurement of their condensed phase spectra. The vibration frequency *vs.* electronegativity correlations are extended to include the S–X stretching and the $-SO_2$ bending and rocking frequencies. Sulfur dioxide is included in the correlations.

Experimental Section

CH_3SO_2Cl and CH_3SO_2F were products of City Chemical Corp. (New York, N. Y.). $CH_3SO_2CH_3$ was a product of Matheson Coleman and Bell (Cincinnati, Ohio).

The apparatus was that used previously[8] and consisted of a Beckman IR-9 spectrometer (4000–400 cm^{-1}), modified to accept a 1-m over-all length gas diffusion barrier Pyrex cell, with vacuum connections and AgCl windows.

The CH_3SO_2Cl spectrum was run at room temperature; that of CH_3SO_2F was run at about 0°; the $CH_3SO_2CH_3$ vapor spectrum was run at about 250°.

Data and Results

The vapor spectra are shown in Figure 1. In Table I are presented the frequencies of the absorption bands in the region 400–4000 cm^{-1} and the assignments for the gaseous and condensed phase spectra.

$CH_3SO_2CH_3$. The assignment of the bands belonging to dimethyl sulfone has been made on the basis of a tetrahedral skeletal configuration of C_{2v} symmetry, as determined by electron diffraction.[12] The skeleton has nine nondegenerate fundamental vibrations of which the torsional is infrared inactive.

The assignments of 469 cm^{-1} to the SO_2 rocking mode and of 496 cm^{-1} to the SO_2 bending mode are based on the absorption bands observed for such related compounds as H_2SO_4,[8] CH_3SO_2Cl,[10] CH_3SO_2F,[10] CH_3SO_3H, FSO_3H, and $ClSO_3H$.[9,11,13–15] The 707- and 748-cm^{-1} bands have been assigned by analogy[16,17] to C–S–C symmetric and asymmetric stretching modes. The CH_3 symmetric and asymmetric stretching bands were observed only for the solid at 2950 and 3050 cm^{-1}.

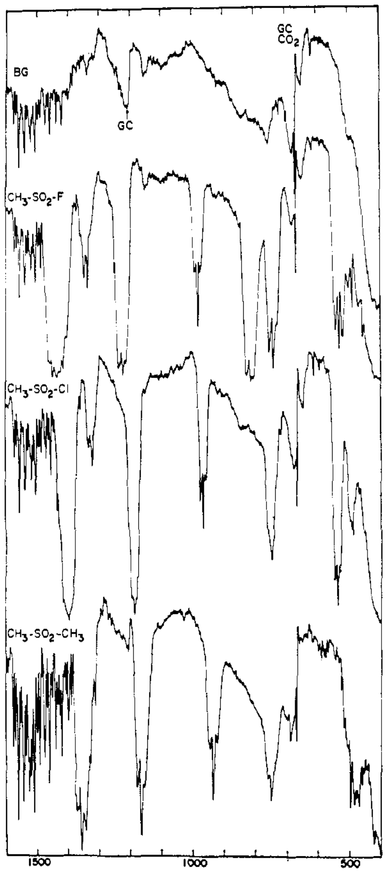

Figure 1. From top to bottom: background and spectra of the vapors above CH_3SO_2F, CH_3SO_2Cl, and $CH_3SO_2CH_3$ in the region between 400 and 1600 cm^{-1}, at about 0, 20, and 250°, respectively. GC at 670 and 1200 cm^{-1} indicates grating changes.

Only small shifts were observed between the solid and the gaseous spectra, except for the CH_3 wagging and S–C_2 asymmetric stretching bands. The former was less in the gas phase by about 20 cm^{-1} and the latter less by about 28 cm^{-1}. No new bands were observed in the gas phase.

CH_3SO_2Cl and CH_3SO_2F. Our assignment of the bands for these two compounds is in agreement with that given by Ham and Hambly,[10] except for the SO_2 symmetric stretching and the S–F stretching modes. It is evident from Table I and Figure 1 that for all the three compounds two strong bands appear at 1160–1225 and at 1350–1450 cm^{-1}. For each compound they are separated by about 200 cm^{-1}. This separation increases going from $CH_3SO_2CH_3$ to CH_3SO_2F in agreement with conclusions reached by Robinson[6] for the SO_2 stretches of related compounds. The assignment in Table I is made accordingly. By analogy,[3,13,14,18] the S–F stretching frequency should be the band at 813 cm^{-1} in the work of Ham and Hambly, and that at 817 cm^{-1} in the present paper.

No substantial shifts have been observed between the gaseous and liquid spectra of CH_3SO_2Cl and CH_3SO_2F, except for the S–F stretch and the SO_2 asymmetric stretch in CH_3SO_2Cl which are shifted by about 20 cm^{-1}. All our bands in the liquid phase, however, appear at frequencies about 10–20 cm^{-1} higher than those given

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Table I. Vibrational Spectra of Gaseous and Condensed $CH_3SO_2CH_3$, CH_3SO_2Cl, and CH_3SO_2F[a]

ν (intensity) for gas phase, cm^{-1}				ν (intensity) for condensed phase, cm^{-1}		
$CH_3SO_2CH_3$ (C_{2v})	CH_3SO_2Cl (C_s)	CH_3SO_2F (C_s)	Assignments[b]	$CH_3SO_2CH_3$	CH_3SO_2Cl	CH_3SO_2F
		450P				
		460Q (w)	S–F wag, a′			468 (w)
		470R				
	487P	481P				
469 (m)	495Q (m)	492Q (m)	SO_2 rock, b_2, a″	475 (ms)	500 (m)	500 (m)
	502R	503R				
485P	536P	522P				
496Q (s)	543Q (s)	534Q (s)	SO_2 bend, a_1, a′	510 (ms)	548 (s)	543 (s)
507R	552 R	547R				
707[c] (w)		731P		705[c] (w)		
	752 (s)	742Q (vs)	S–C str, $^{b_1}_{a_1}$, a′		760 (m)	753 (m)
748[c] (s)		753R		776[c] (m)		
		807P				
		817Q (vs)	S–F str, a′			838 (s)
		828R				
923P	960P	975P				
935Q	969Q (s)	981Q (s)	CH_3 wag, a′	955 (m)	978 (m)	998 (m)
947R	979R	992R				
1152P	1185P	1213P				
1162Q (vs)	1192Q (vs)	1225Q (vs)	SO_2 sym str, a_1, a′	1165 (s)	1185 (s)	1233 (s)
1174R	1200R	1239R				
	1325 1336 (m)	1338 1350 (m)	CH_3 sym bend, a′	1328 (s)	1332 (w)	1358
		1407P		1417 (m)		
		1417Q (vs)	CH_3 sym bend, a″			
		1428R		1432 (m)		
1340P		1440P				
1355Q (vs)	1404 (vs)	1451Q (vs)	SO_2 asym str, b_2, a″	1343 (s)	1386 (s)	1443 (s)
1369R		1460R				
			CH_3 sym str	2950 (w)	2970 (w)	2990 (w)
			CH_3 asym str	3050 (w)	3060 (w)	3070 (w)

[a] sym, symmetric; str, stretch; m, medium; s, strong; v, very; w, weak. [b] The symmetry species are for C_s if only one is given. Otherwise, the first is for C_{2v}. [c] The S–C symmetric stretch of dimethyl sulfone is assigned to the lower frequency band.

by Ham and Hambly. This difference is attributed to the difference in the instruments used.

Two maxima, probably belonging to a doublet, are observed in the gas phase for the CH_3 symmetric bend of the two halides. The CH_3 asymmetric bend in the chloride is overlapped by the SO_2 asymmetric stretching band; it is readily observed in the fluoride because of the shift in the SO_2 asymmetric stretch.

Disussion

Some of the vibration frequencies now available[8,9,19–22] for the gaseous $X\text{–}SO_2\text{–}Y$ molecules are summarized in Figure 2a and b, where they are plotted as a function of the average electronegativity[23,24] of X and Y. The uppermost two lines are for the asymmetric and symmetric $-SO_2$ stretching frequencies. All of the points, including those for compounds containing OH groups as well as the present data, now fall quite closely on a straight line. These vibrations are largely free from mass and coupling effects.[5,25] The systematic change in frequency is most likely due to an inductive effect.

According to the discussion of Jaffé and Orchin,[4] as the positive charge on the S atom is increased, the sulfur 3d orbitals are contracted and can enter more effectively into bonding. Two of these orbitals are of the proper symmetry to receive π electrons from the oxygen. Accordingly, the increase in frequency observed in going from dimethyl sulfone to sulfuryl fluoride probably is due in large part to an increase in pπ–dπ bonding.

The three remaining 3d orbitals, called t_2, are of the correct symmetry to participate in σ bonding. Such participation can account for the systematic changes in the S–X stretching frequencies.

For the $-SO_2$ bending and rocking frequencies, as expected, the scatter is larger. The trend of the frequencies, however, is consistent with the tightening of bonding shown by the stretching modes.

In contrast to sulfur, chromium and molybdenum have $(n - 1)$d orbitals partially filled and readily available for bonding. As was the case for the phosphoryl and vanadyl stretching frequencies,[9] the chromyl and molybdenyl frequencies should be less sensitive to change in X. That this is the case is shown by the data[18,26–32] in Table II.

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Table II. Comparison of -MO_2 Frequencies[a,b] (cm^{-1}) with Variation of X in X-MO_2-X

X	M S	 Cr	 Mo
F	1385	1011	. . .
Cl	1320	989	984
Br	. . .	. . .	975
CH_3	1261[c]	. . .	. . .
Oxide, MO_2	1257		

[a] Average of symmetric and asymmetric stretching frequencies. [b] From ref 18, 26–32. [c] Present work.

In Figure 2, the stretching and bending vibration frequencies for gaseous sulfur dioxide[29] are indicated by filled circles. These are located at electronegativity 2.6, which is that of the free sulfur atom. As far as the vibration frequencies are concerned, sulfur dioxide acts very much like an X-SO_2-Y molecule with X and Y groups that neither donate nor withdraw electrons from the central sulfur atom. Similar behavior was observed for gaseous PO with respect to XYZP=O.[9]

From these observations and the data in Table II, the stretching frequencies for gaseous chromium and molybdenum dioxides are both predicted to lie at about 975 cm^{-1}. Furthermore, any theoretical considerations of X-MO_2-Y should attempt to include the dioxides as members of the series.

Correlations of bond length, bond angle, and force constant with the weighted average SO frequency have been given in Figures 1–3 of the paper by Gillespie and Robinson.[7] Any shifts in frequency due to phase change or hydrogen bonding should be compensated by changes in geometry so that these correlations should hold also for the gaseous molecules studied here. It has been noted,[8] however, that when H is replaced by D in the S-O-H group, there is a negligible change in the frequency of the band assigned to the S-O stretch. This vibration thus seems to be best described as a S-O(H) rather than S-(OH) stretch; the points at lowest frequency in Figures 1 and 3 of ref 7 should therefore be lowered to 939 and 895 cm^{-1} (rather than 968 and 923 cm^{-1}). This change leads to a more reasonable predicted value of 1.58 A for the S-O(H) bond distance in gaseous H_2SO_4.

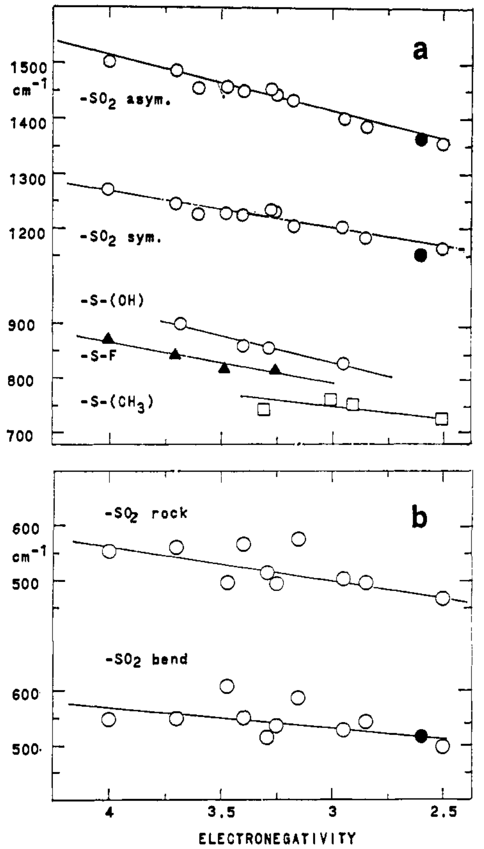

Figure 2. (a) Correlations of ν_{SO_2} asymmetric stretch, ν_{SO_2} symmetric stretch, ν_{S-OH}, ν_{S-F}, and ν_{S-CH_3} of some gaseous X-SO_2-Y molecules with the mean electronegativity[24,25] of X and Y. The solid circles are for the sulfur dioxide vibrations. (b) Correlations of ν_{SO_2} rocking and ν_{SO_2} bending of some gaseous X-SO_2-Y molecules with the mean electronegativity of X and Y. The solid circle is for the sulfur dioxide bending vibration (data from ref 8, 9, 19–22).

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