**Table II.** Predicted Chemical Shifts, $\tau$, Based on Local Anisotropy Effects[a]

| | $\Delta\tau$, ppm | $\tau_{\text{calcd}}$ | $\tau_{\text{obsd}}$ |
|---|---|---|---|
| Bisdehydro[12]annulene (I) | −1.48 | 2.92 | −0.9 |
| Bisdehydro[16]annulene (II) | −1.51 | 2.89 | 2.25 |
| Tetradehydro[24]annulene (III) | −0.57 | 3.83 | 1.80 |
| Cyclododecatrienetriyne (IV) | +1.24 | 5.64 | 5.55 |

[a] Using $-19.4 \times 10^{-6}$ cm$^3$/mole for $\Delta\chi$.

this circumstance, the value calculated for the downfield shift, $\Delta\tau$, would be halved and the lack of agreement between the predicted chemical shift and that observed (Table II) would be more pronounced. It is not clear why tetradehydro[24]annulene (III) apparently does not interconvert between equivalent conformers, if indeed the molecule has the structure assigned to it. Dreiding molecular models of II and III indicate that rotation of the *trans* bonds ought to occur with approximately equal facility. However, the nmr spectrum of III shows an absorption at low field, $\tau$ 1.80, with an intensity that accounts for only *ca.* half of the *trans* double bond hydrogens.

The four compounds that have been discussed thus far have all contained triple bonds. We attach no significance to this circumstance. It is simply that of the data available at this time in the literature, these cases seem to exhibit shifts which lie outside the normal range of values for olefinic hydrogens and cannot be readily explained on grounds other than a paramagnetic ring current. Two other annulenes, 16 and 24 (see Table I), we suggest display nmr spectra that may be the results of averaging processes (probably *via* bond rotations and bond isomerizations) which cause the hydrogens to become magnetically equivalent. If so, it could turn out that nmr spectra taken at relatively low temperatures would show distinct absorptions due to inner and outer ring hydrogens similar to the [14]- and [18]annulenes, but with the chemical shifts of the corresponding hydrogens shifted in opposite directions.[17]

[17] NOTE ADDED IN PROOF. For a recent report concerning bond isomerization and variable temperature nmr spectra of [16]annulene, see G. Schröder and J. F. M. Oth, *Tetrahedron Letters*, **34**, 4083 (1966).

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# Infrared Spectra of Methane-, Fluoro-, and Chlorosulfonic Acids

**Scaria M. Chackalackal and Fred E. Stafford**

*Contribution from the Department of Chemistry and The Materials Research Center, Northwestern University, Evanston, Illinois 60201.* *Received April 27, 1966*

**Abstract:** The infrared spectra in the region 4000–400 cm$^{-1}$ of methane-, fluoro-, and chlorosulfonic acids were obtained. A gas-diffusion barrier cell prevented reaction with the cell windows. Superheating of the vapors permitted spectra of the monomers to be clearly identified. Shifts in bands due to breaking up of hydrogen bonding prove to be a powerful means of making or confirming band assignments. The systematic variations in band frequencies due either to the liquid–monomer transition or to the variation of X (F, OH, Cl, $CH_3$) in X–$SO_2$–OH are discussed.

The infrared spectra of fluoro- and chlorosulfonic acids in the solid and liquid states, and also in the gaseous state, at temperatures up to 60° were obtained and examined by Savoie and Giguère.[1] Gerding and Maarsen[2] have reported the infrared spectrum of liquid methanesulfonic acid, but they believed that the spectrum was impure because of the attack by the acid on the rock salt plates. In addition, several workers made Raman studies on the liquid acids.[3–7]

Savoie and Giguère[1] observed that good portions of fluoro- and chlorosulfonic acids remain dimerized in the vapor state even near 60°. In our studies with sulfuric and deuteriosulfuric acids,[8] which gave sufficient vapors only above 170° for making measurements, there was no evidence of association in the vapor.

The reported frequency shifts of some of the bands of the fluoro- and chlorosulfonic acids[1] for the transition from liquid to the monomeric vapor state are not comparable to the shifts observed for sulfuric acid.[8] Some shifts, particularly for the –$SO_2$ stretches of fluoro- and chlorosulfonic acids not only are smaller, but even are of the opposite sign. In this paper we will try to find an explanation for this discrepancy. The results so obtained will be compared with those presently obtained for methanesulfonic acid.

## Experimental Section

The apparatus for taking the spectra in the region 400–4000 cm$^{-1}$ is described elsewhere.[8] The cell described there, which will be called cell A in this paper, is suitable only for the study of nearly saturated vapors over liquids or solids. For the purpose of superheating the vapor, the liquid or solid sample was heated in a side arm attached to the center of the cell, and the vapor evolved was superheated in the cell itself. Gas windows also were provided. In cell B the gas windows were just outside the furnace, and in cell C they were near the ends, close to the AgCl windows. During the runs, argon at 1 atm flowed through the gas windows. The power of the superheating technique to aid in assigning bands will be shown particularly by the discussion of the S–F and S–O(H) stretches of fluorosulfonic acid.

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[1] R. Savoie and P. A. Giguère, *Can. J. Chem.*, **42**, 277 (1964).

[2] H. Gerding and J. W. Maarsen, *Rec. Trav. Chim.*, **77**, 374 (1958).

[3] A. Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 2384 (1956).

[4] I. Sandemann, *J. Chem. Soc.*, 1135 (1953).

[5] R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 644 (1962).

[6] R. Vogel-Högler, *Acta Phys. Austriaca*, **1**, 323 (1948).

[7] A. Simon, H. Kriegsmann, and H. Dutz, *Chem. Ber.*, **89**, 2378 (1956).

[8] S. M. Chackalackal and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 723 (1966).

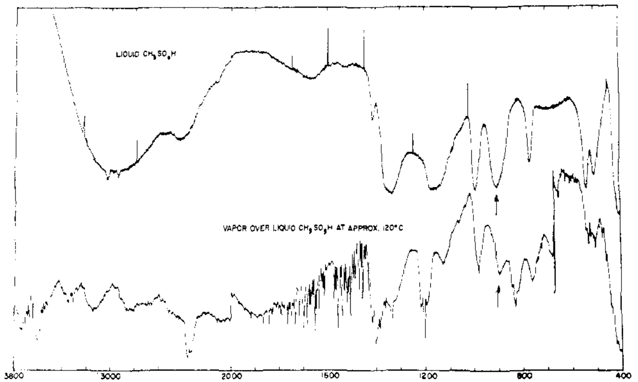

Figure 1. Light absorption (going down) *vs.* wavenumber between 3800 and 400 $cm^{-1}$: A (top), liquid methanesulfonic acid between silver chloride plates, double beam; B (bottom), vapor at nominal temperature of 120°, single beam. The arrows indicate the S–O(H) stretch of the associated molecule; *cf.* Figure 2. In all of the single-beam spectra, there are discontinuities at 670, 1200, and 2000 $cm^{-1}$ because of grating changes. The $CO_2$ bands are seen at 670 and ~2355 $cm^{-1}$, and the water band is seen at 1300–1900 $cm^{-1}$.

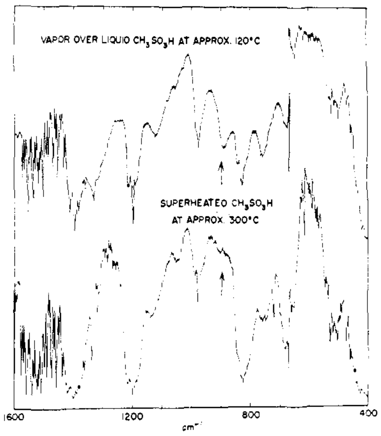

Figure 2. Comparison of the spectra of saturated (B), and superheated (C, bottom) methanesulfonic acid vapors. The arrows indicate the disappearance of the S–O(H) stretching band for the associated molecule. See also Figure 1. The frequency range in this case is 1600–400 $cm^{-1}$.

In cell A, saturated vapors over the following samples were studied: (1) a sulfonic acid alone, (2) a 1:1 mixture of sulfonic acid and concentrated sulfuric acid, and (3) a 1:1 mixture of the sulfonic acid and concentrated deuteriosulfuric acid. The last sample gave vapors containing deuterated sulfonic acid.

The spectrum of liquid methanesulfonic acid was obtained by holding a thin film of the acid between AgCl windows. The spectrum was taken using the normal double-beam mode of operation of the Beckman IR-9 spectrometer. The spectra of the vapors were taken in the single-beam mode.

Methanesulfonic acid was a product of Eastman Organic Chemicals. Fluorosulfonic acid, Allied Chemical, technical quality, was redistilled before use. Chlorosulfonic acid was a Matheson Coleman and Bell, practical quality, product.

## Results and Discussion

**Methanesulfonic Acid.** In Figures 1 and 2, spectra A, B, and C give, respectively, the spectrum of liquid methanesulfonic acid, of its saturated vapor at ~120° (using cell A), and of the superheated vapor at ~300° (using cell B). Table I summarizes the Raman bands reported in the literature, the infrared spectra of the liquid and of the vapor, and the assignments of the bands to the normal modes of vibration (for the structures of the molecules and the assignments of the bands, see ref 5).

The assignments of S–O wag, $SO_2$ rock, $SO_2$ bend, and C–S stretch were made previously, mostly on the basis of Raman polarization studies; we agree with them. Gerding and Maarsen[2] observed a broad band for the liquid acid at 718 $cm^{-1}$ and assigned it to the S–O(H) stretch. The comparable band in our spectrum A is the very broad weak band at 680 $cm^{-1}$. This could very well be the -OH wag, which is raised to this high frequency by hydrogen bonding.

The region 800–1000 $cm^{-1}$ furnishes some interesting information. In spectrum A, there are two bands and in spectrum B there are three bands in the same region. Of these, the bands at 988 in the liquid and 980 $cm^{-1}$ in the vapor are identified as the $CH_3$ wag, by comparison with the bands observed in the same region for methylsulfonyl chloride, methylsulfonyl fluoride, and dimethylsulfone.[9] Another band that should be expected in this region is the S–O(H) stretch. (Work with sulfuric acid[5] showed that this frequency did not shift upon deuteration; hence the best description is S–O(H) rather than S–(OH).) The band at 900 $cm^{-1}$ in spectrum A is easily assigned to this mode of vibration. In spectrum B, one of the bands is very close to the above band while the other is about 60 $cm^{-1}$ away. Considering the average shift of more than 80 $cm^{-1}$ for the S–O(H) stretching modes in sulfuric acid when it passed from the liquid to the monomeric vapor state,[8] we tentatively assigned the band at 829 $cm^{-1}$ to the S–O(H) stretch of the free molecule. The closeness of the other band to the S–O(H) stretch of the liquid acid indicated that it could be due to the S–O(H) stretch of the associated molecule. Spectrum C of the superheated vapor was therefore obtained; it gave no sign of the band at 891 $cm^{-1}$, confirming the assignment.

In spectrum A, there are three bands in the region 1100–1500 $cm^{-1}$. Of these, the sharp band of medium intensity at 1418 $cm^{-1}$, which is partly eclipsed in spectra B and C, is the asymmetric $CH_3$ bend. The broadness of the other two bands suggests that they may be due to more than one mode of vibration. In spectrum B, in the same region there are four bands. Of these strong bands, those at 1203 and 1403 $cm^{-1}$ are definitely the symmetric and asymmetric $SO_2$ stretching vibrations of the monomer. The other two bands could be ascribed to the same modes of the associated molecule. But the persistence of the band at 1122 $cm^{-1}$ in the spectrum of the superheated vapor shows that it is a different mode of vibration. By comparison with the S–O–H bending frequencies in sulfuric and other sulfonic acids,[1,8] and the observation that they do not shift markedly upon hydrogen bonding, it is assigned to the S–O–H bend even though this band in spectrum B is clearly reinforced by the $SO_2$ symmetric stretching band of the associated species. The S–O–D bending vibration was not observed, and is believed to be masked by the S–C and S–O–(H,D) bands. In methylsulfonyl fluoride and methylsulfonyl chloride,[9] $CH_3$ symmetric deformations are observed at 1341 and 1324 $cm^{-1}$, respectively. The $CH_3$ symmetric deformation in methanesulfonic acid could be expected between their two frequencies. The band at 1338 $cm^{-1}$

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(9) N. S. Ham and A. N. Hambly, *Australian J. Chem.*, **6**, 33 (1953); M. Spoliti, S. M. Chackalackal, and F. E. Stafford, to be submitted for publication.

Table I.[a] Vibrational Spectra of Methanesulfonic Acid ($cm^{-1}$)

| Raman[b] liquid | Infrared liquid | Infrared vapor | Species | Approximate description |
|---|---|---|---|---|
| 338 | | | a′ | S–C wag |
| 420 | | | a ′ | Torsion |
| 480 | 480 w | 473 w | a′ | S–O wag |
| 506 | 501 ms | 494 | | |
| | | 502 m | a′′ | $SO_2$ rock |
| | | 507 | | |
| | | 519 | | |
| 535 | 534 s | 528 | a′ | $SO_2$ bend |
| | | 536 | | |
| | 670 ± 10 w, b | | a′′ | OH wag (?) (assoc) |
| | | ~748 | a′ | S–C stretch (free) |
| 772 | 767 ms | 760 s | a′ | S–C stretch (assoc) |
| | | 817 | | |
| | | 829 | a′ | S–O(H) str (monomeric) |
| | | 842 | | |
| 904 | 900 vs | 891 s | a′ | S–O(H) str (assoc) |
| 985 | 988 s | 972 | | |
| | | 980 s | a′ | $CH_3$ wag |
| | | 988 | | |
| 1122 | 1140/1150 | 1122 m | a′ | S–O–H bend |
| 1174 | 1174 vs | | a′ | $SO_2$ sym str (assoc) |
| | | 1193 | | |
| | | 1203 s | a′ | $SO_2$ sym str (monomer) |
| | | 1215 | | |
| 1265[c] | 1338 | 1338 m | a′ | $CH_3$ sym bend |
| 1350 | 1350 s | | a′′ | $SO_2$ asym str (assoc) |
| | | 1403 ± 5 s | a′′ | $SO_2$ asym str (monomer) |
| 1420 | 1418 m | 1418 m | a′ | $CH_3$ asym bend |
| | 1670 mb | | | Combination band |
| | 2434 mb | | | "Satellite" band |
| | | 2656 | | |
| | | 2667 ms | a′ | OD str (monomer) |
| | | 2677 | | |
| 2945 | 2945 w, sh. | | a′ | CH sym str |
| | 2977 s, vb | | a′ | –OH str (assoc) |
| 3032 | 3036 w, sh | | a′′ | CH asym str |
| | | 3600 | | |
| | | 3610 ± 2 | a′ | –OH str (monomer) |
| | | 3623 | | |

[a] w = weak, m = medium, ms = medium strong, s = strong, v = very, b = broad, vb = very broad, sh = sharp. Unless otherwise indicated, no shifts in frequency could be observed between free and associated gaseous molecules. [b] Gillespie and Robinson.[5] [c] A band is observed in the Raman spectrum at 1368 $cm^{-1}$ for methanesulfonate ion. The analogous line is possibly masked by the $SO_2$ symmetric stretch of the acid.[5]

could very well be due to the $CH_3$ symmetric deformation, even though its intensity seems to have been accentuated by the $SO_2$ asymmetric stretching band of the associated molecules.

The broad band at 1670 appears to be similar to the broad bands observed for phosphorus acids in the same region. This is believed to be a combination band. The band at 2434 $cm^{-1}$ has been described as a satellite band, whose origin has been variously explained.[10]

In spectrum A, the broad band centered at 2977 $cm^{-1}$ is due to the stretching vibration of the hydrogen bonded –OH. In spectrum B the medium strong, sharp band with PQR branches at ~3610 $cm^{-1}$ is due to the –OH stretching vibration of the free molecule. For the vapor over a mixture of the acid with $D_2SO_4$, an additional band with the same characteristics was observed at 2667 $cm^{-1}$. This is assigned to the OD stretch.

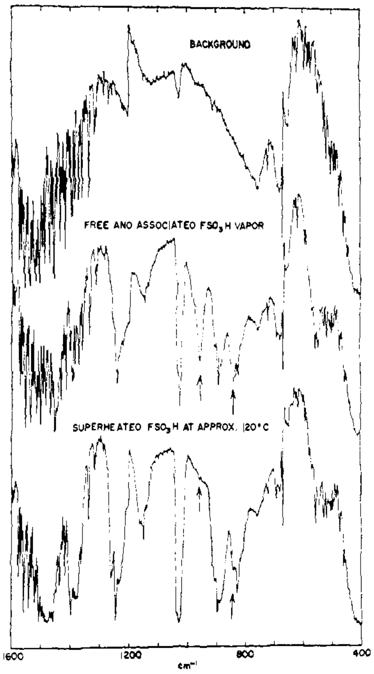

Figure 3. Spectra of partially (D, middle) and extensively (E, bottom) superheated fluorosulfonic acid vapors from 1600 to 400 $cm^{-1}$. The arrows show the S–OH (957 $cm^{-1}$) and S–F (847 $cm^{-1}$) stretching bands for the associated molecules. Both bands disappear when the vapor is superheated in the cell with gas windows. The magnitudes of the shifts from associated to free molecules unambiguously indicate which band is due to S–F and which to S–O(H) stretching. This is a powerful means of making band assignments.

**Fluorosulfonic Acid.** The discussion of fluoro- and chlorosulfonic acids in this paper will be limited to areas where our findings do not agree with those of Savoie and Giguère.[1]

Figure 3 gives the spectra of fluorosulfonic acid. The spectrum D, which was obtained by using cell C, is that of the vapor containing both associated and monomeric species.

In the 800–1000-$cm^{-1}$ region of spectrum D, there are four bands. For the purpose of getting the spectrum of the free molecules alone, the spectrum of superheated fluorosulfonic acid was obtained with cell B. In spectrum E which was thus obtained, and as shown in Table III, there are only two bands in this region, one at 897 $cm^{-1}$ and the other a quadruplet, with its strong Q branch split to 827/830 $cm^{-1}$. One of these is the S–O(H) stretch and the other the S–F stretch of the free molecule. If one assumes that the band at 957 $cm^{-1}$ in spectrum A is the S–O(H) stretch of the associated molecule, there is no difficulty in identifying the band at 897 $cm^{-1}$ as the S–O(H) stretch of the free molecule; to assign the band at 827/830 $cm^{-1}$ as the S–O(H) stretch of the free molecule would require a shift of about 130 $cm^{-1}$ for the liquid–monomer vapor transition. Such a shift would be even higher than that observed for sulfuric acid for the same transition. On the other hand, if the 847-$cm^{-1}$ band is the S–O(H) stretch of the associated molecule, the shift from 844 to 827–830 $cm^{-1}$ would be comparatively far too small. The logical assignment is given in Table II.

A shift of 60 $cm^{-1}$ for the S–OH stretch in fluorosulfonic acid when the hydrogen bond is broken is comparable to the shifts of its other stretching vibrations

[10] See, *e.g.*, A. E. Chapman and L. E. Thirlwell, *Spectrochim. Acta*, 20, 937 (1964).

**Table II.** Bands Observed for Fluorosulfonic Acid Vapor in the Region 800–1000 Cm$^{-1}$ and Their Assignments

| Ref 1 Frequency maxima of bands, cm$^{-1}$ | Present work: Frequency maxima of bands, cm$^{-1}$ | Present work: Assignment |
|---|---|---|
| 812 | 816 | S–F stretch free mol.[a] |
| 823 | 827 | |
| 827 | 830 | |
| | 841 | |
| 844 | 847 | S–F stretch, assoc mol. |
| 887 | 887 | S–OH stretch, free mol.[a] |
| 896 | 896 | |
| 906 | 906 | |
| 958 | 957 | S–O(H) stretch, assoc mol. |

[a] From Figure 3E.

and also to the shifts of S–O(H) stretching vibrations of sulfuric and other sulfonic acids. This assignment agrees with the linear plot of S–O(H) stretching frequency *vs.* the electronegativity of X in X–SO$_2$–OH that was made in ref 8.

The above assignment leads to a significant conclusion. The shift in the S–F stretch to lower frequency as the acid passes from the associated to monomeric state indicates that the fluorine atom is not directly involved in the hydrogen-bond formation.

The spectrum has fairly strong bands of SO$_3$ in it. This is in disagreement with the observation of Ruff[11] that the acid is very stable even at 900°.

**Chlorosulfonic Acid.** Chlorosulfonic acid turned out to be the most elusive of the three compounds for high-temperature infrared studies. The spectrum obtained by superheating its vapor did not give evidence for the presence of even traces of chlorosulfonic acid. In fact, chlorosulfonic acid that was distilled at 1 atm at 152° gave an almost identical spectrum. The product of distillation under reduced pressures (at 50° at ~10 mm) showed the presence of compounds other than chlorosulfonic acid in the vapor. We did not try to identify the compounds so formed, but even at temperatures as low as 40° the acid in the vapor state is dissociated into SO$_3$ and HCl. Ryadneva and Lenskii[12] noticed the presence of S$_2$O$_5$Cl$_2$ and SO$_2$Cl$_2$ below 85° and found that relative amounts varied considerably under varying conditions.

As a consequence, we rely on the spectra of saturated vapors, which has the major drawback that the increase of temperature can increase the intensity of the bands of both the associated and monomeric species at the same time. However, close study of the several spectra obtained at different temperatures from 0 to 120° leads to the following observations.

The band at 497 cm$^{-1}$, which was assigned by Savoie and Giguère to the –SO$_2$ bending mode, seems to be the SO$_3$ asymmetric deformation mode ($\nu_2$)[8,13] of sulfur trioxide. The S–O–H bend of the associated species was observed at 1158 cm$^{-1}$, but we have not been able to identify the S–O–H bend of the monomeric species. The weak band observed around ~1230 by Savoie and Giguère[1] was observed by us also. This band is almost certainly the SO$_2$ symmetric stretch of the monomer. We believe that the band observed at 1395/1380 cm$^{-1}$ is actually the SO$_3$ asymmetric stretch of sulfur trioxide. This and the band at 497 cm$^{-1}$, however, are present in the spectra of liquid and solid HSO$_3$Cl. The band at 1410 cm$^{-1}$, which we too observed, is the SO$_2$ asymmetric stretch of the associated molecule. We observed also a band of weak to medium intensity at 1455 ± 5 cm$^{-1}$, and this we assign to the SO$_2$ asymmetric stretch of the free molecule.

For the mixture of D$_2$SO$_4$ and chlorosulfonic acid, a band at 2658 cm$^{-1}$ was observed. It was not possible to resolve its PQR branches.

Accordingly, the monomer–liquid frequency shifts given in Table VI of ref 8 should be corrected to read: Cl–SO$_2$–OH: +478 (OH; str); +45 (SO$_2$, asym); +20 (SO$_2$, sym); −66 (S–O(H)).

**Comparison.** Table III gives the bands between 400 and 4000 cm$^{-1}$ of the monomeric species of fluoro-, chloro-, and methanesulfonic acids and of sulfuric acid. With the exception of chlorosulfonic acid, for which there are also larger uncertainties in the data, certain trends are observed in the stretching frequencies. As the electronegativity of X in X–SO$_2$–OH is increased, the OH stretching frequency seems to decrease slightly; the S–O(H) and the two –SO$_2$ frequencies increase.

**Table III.** Vibrational Frequencies (cm$^{-1}$) of the Monomeric[a] Fluoro-, Chloro-, and Methanesulfonic Acids and of Sulfuric Acid

| F–SO$_2$–OH | HO–SO$_2$–OH | Cl–SO$_2$–OH | CH$_3$–SO$_2$–OH | Description |
|---|---|---|---|---|
| | | | 473 | S–O wag |
| 556<br>545 | 550 | 513 | 528 | SO$_2$ bend |
| 568<br>556 | 568 | | 501 | SO$_2$ rock |
| 827<br>830 | | 614 | 760 | S–X str (X = F, Cl, C) |
| 896 | 834/883 | 852 | 829 | S–O(H) str |
| 1150 | 1138<br>1159 | | 1122 | S–O–H bend |
| 1243 | 1223 | 1235 ± 5 | 1203 | SO$_2$ sym str |
| 1480<br>1491 | 1450 | 1455 ± 5 | 1403 | SO$_2$ asym str |
| 2661 | 2663 | 2658 | 2667 | –OD str |
| 3605 | 3610 | 3587<br>3569 | 3610 | –OH str |

[a] CH vibrations not included; some values are taken from ref 1 For triplets only the Q branch is given.

Studies with superheated vapors of fluorosulfonic acid at ~120° (Figure 2, spectrum E) showed no evidence of association between molecules in the vapor state. Chlorosulfonic acid was more strongly hydrogen bonded. For methanesulfonic acid, association disappeared at about 140°. In agreement with the observations of Biscarini, *et al.*,[14] the less electronegative substituent on the sulfur permits the sulfuryl oxygens to become more basic and leads to stronger hydrogen bonding. Since methanesulfonic acid is therefore expected to form the strongest hydrogen bonds of the

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(11) O. Ruff, *Chem. Ber.*, **47**, 656 (1914).

(12) L. P. Ryadneva and A. S. Lenskii, *J. Appl. Chem. USSR*, **36**, 2340 (1963).

(13) R. W. Lovejoy, J. H. Colwell, D. F. Eggers, Jr., and G. D. Halsey, Jr., *J. Chem. Phys.*, **36**, 612 (1962).

(14) P. Biscarini, G. Galloni, and S. Ghersetti, *Spectrochim. Acta*, **20**, 267 (1964).

four acids, it is reasonable that it was not possible to observe any association for $H_2SO_4$ in the vapor state at the higher temperature used.

Attention is called to Table VI in ref 8 as corrected here for $ClSO_3H$, where shifts in the stretching frequencies of sulfuric and sulfonic acids with the change of phase from liquid to the monomolecular state are compared. The present study confirms the conclusion arrived at in that paper and explains the discrepancies noted there.

**Acknowledgments.** We thank Professor Paul A. Giguère for helpful comments. Robert J. Loyd, Department Instrument Engineer, designed the external light source and chopper system. Terry V. Iorns built the furnace assembly. Alan G. Marshall helped in some phases of the work.

This work was supported in part by the Northwestern University Materials Research Center, and principally by the U. S. Army Research Office, Durham. Acquisition of the infrared spectrometer was made possible by a National Science Foundation facilities grant. The work was presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Paper 145V.

# Infrared Spectra of Some Gaseous Molybdenum Oxides and Oxyhalides

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*Contribution from the Department of Chemistry and The Materials Research Center, Northwestern University, Evanston, Illinois 60201.* *Received April 27, 1966*

**Abstract:** A special high-temperature, gas-diffusion barrier cell has been used to examine the spectra from 4000 to 400 cm$^{-1}$ of some involatile molybdenum compounds. For $MoO_2Cl_2$ the symmetric and asymmetric $Mo{=}O$ stretches are at 972 and 990 cm$^{-1}$, and for $MoO_2Br_2$ at 969 and 991/999 cm$^{-1}$. An Mo–Cl stretch was observed at 450 cm$^{-1}$. For the vapors above $MoO_3(s)$, bands were observed at 969 and 815 cm$^{-1}$. For $MoOCl_4$, a band at 1015 cm$^{-1}$ is assigned to the $Mo{=}O$ stretch. Predictions are made for $H_2MoO_4$ and $H_2CrO_4$. Heating $MoO_3(s)$ plus HCl gives rise to the $MoO_2Cl_2(g)$ bands.

The existence of several gaseous molybdenum oxides and oxyhalides, including $(MoO_3)_n$, $MoO_2Cl_2$, $MoO_2Br_2$, $MoOCl_4$, and $MoO(OH)_2Cl_2$ has been reported.[1] There has been some spectrometric work on the solid compounds, but none to our knowledge on the vapor phase infrared spectra. The latter would be of particular interest in evaluating the systematics of the structure and the thermodynamic properties of various high-temperature systems.

Berkowitz, Inghram, and Chupka[2] report a mass spectrometric investigation of the vapors from $MoO_3$ in a molybdenum Knudsen cell at 525° and found that the most abundant species was $Mo_3O_9$, with lesser amounts of $Mo_4O_{12}$ and $Mo_5O_{15}$ and only a slight trace of $MoO_3$ and $Mo_2O_6$. Owing to the surprising stability of the polymeric species at high temperature, they postulated a puckered, hexagonal ring structure. The same structure is reported for the similar trioxane vapor,[3] and for the analogous $(SO_3)_3$[4,5] and $(SeO_3)_n$.[6]

The formation of solid $MoO_2Cl_2$ by direct reaction of $MoO_2$ with $Cl_2$ has been reported.[7,8] Sutton reports[9] early electron diffraction work indicating that $MoO_2Cl_2$ (g) has a tetrahedral configuration.

The increased volatility of molybdenum and its oxides in the presence of water vapor at high temperature has been reported[10–12] and is explained by the formation of $H_2MoO_4$. It is likely that this molecule is analogous to $H_2SO_4$ and fits into a series $MoO_2X_2$ with X = F, OH, Cl, Br.

$MoOCl_4$ has been prepared[13,14] in various ways, including a high-yield method[14] involving direct oxidation of $MoCl_5$ at 215°. The analogous $SOF_4(g)$ is well characterized spectroscopically and structurally.[15–17] On the other hand, there seems to be a great deal of ambiguity concerning the presumably analogous gaseous $MoO(OH)_2Cl_2$.[7,8,18,19] Reaction of

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[1] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962; S. A. Shchukarev and A. V. Suvorov, *Russ. J. Inorg. Chem.*, **6**, 763 (1961); I. A. Glukhov and L. A. Tikhomirov, *Dokl. Akad. Nauk Tadzh. SSR*, **3**, 15 (1960).

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