

Sulfur-33 Magnetic Resonance Spectra of Selected Compounds

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Received March 6, 1972

Abstract: Sulfur-33, because of its low natural abundance, spin of $3/2$, and large quadrupole moment, has been a much neglected nucleus in nmr as well as in other branches of spectroscopy. The use of high rf power levels incident upon the sample, large modulation amplitudes, and signal averaging, however, permits nmr spectra with reasonable signal/noise ratios to be obtained. The present ^{33}S nmr investigation was undertaken to explore the potential of the technique as a structure-determining tool. ^{33}S chemical shifts and spectral line widths are presented for 12 materials. The range of chemical shifts is nearly 600 ppm, whereas spectral line widths vary from ~ 0.2 to 16 G. The organic compounds investigated were carbon disulfide, dimethyl sulfoxide, ethyl disulfide, tetrahydrothiophene, thiophene, and three substituted thiophenes. The inorganic compounds examined included concentrated and dilute (10 *N*) sulfuric acid, aqueous sodium sulfide, and the sulfide anion in cubic zinc sulfide. The highest field resonances were observed for aqueous sodium sulfide and for S^{2-} ; the lowest field resonance was for 10 *N* sulfuric acid. The effects of high symmetry about sulfur and fast chemical exchange on ^{33}S spectral line widths are discussed and illustrated. The ^{33}S nmr results are compared with those of other nuclei in chemically similar compounds.

Sulfur-33, the only reasonably abundant sulfur isotope which possesses a nonzero nuclear magnetic moment, has been a much neglected nucleus in nearly all branches of spectroscopy. Its low natural abundance (0.74%) is obviously a major contributor to this fact. Microwave data have been published for only a few compounds,¹ nuclear quadrupole resonance data are practically nonexistent,² and nmr data are extremely limited.³⁻⁷ Since the spin of ^{33}S is $3/2$, the nucleus possesses a quadrupole moment which also makes it unattractive for high-resolution nmr studies. Nevertheless, ^{33}S nmr is potentially a method for obtaining information about the electronic structures of sulfur-containing molecules and for the determination of sulfur types in molecules or mixtures. Our laboratory has undertaken an investigation of ^{33}S nmr in order to explore these possibilities. Our particular interest is to obtain information concerning the sulfur types in coal as part of a much larger effort to study means of abating sulfur emissions into the atmosphere from the combustion of fossil fuels. From purely chemical and physical points of view, however, answers to several questions concerning ^{33}S nmr are desirable.

(1) Can usable ^{33}S nmr spectra be obtained in reasonable periods of time?

(2) Will quadrupole broadening be so great as to prevent measurements of chemical shifts?

(3) Are spin-spin and spin-lattice relaxation times similar for ^{33}S nuclei in liquids?

(4) Does molecular or crystal symmetry affect ^{33}S line widths in the same manner that they affect resonances of other nuclei with quadrupole moments?

(5) What is the relationship, if any, between ^{33}S nmr data and nmr data for other nuclei, particularly ^{17}O , in the same chemical group?

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The purpose of this paper is to present data which provide at least partial answers to these questions. In addition, the quality of spectra obtained and the chemical shift and line-width data presented may guide others who may attempt to use ^{33}S nmr in their own research studies, e.g., investigation of disulfide linkages in proteins and the effects of substituent groups on the electronic distributions in sulfur-containing heteroaromatic systems.

Experimental Section

^{33}S nmr spectra were obtained using a Varian Associates DP-60 nmr spectrometer operating at 4.33 MHz and equipped with a time-averaging computer and Fieldial scanning unit. Broad-line detection of the dispersion mode was employed in nearly all cases. Compromises had to be made in the choice of many operating parameters, e.g., modulation amplitudes, magnetic field scan rates, spectral time constants, etc., in order to achieve an adequate signal/noise ratio over a reasonable period of time with minimal or easily corrected line distortion. Scan rates used were between 1 and 5 G/min. Actual times of signal averaging ran from 8 min to several days; typical values were 8-12 hr.

Preliminary experiments utilizing a sample of neat carbon disulfide revealed that neither saturation effects nor objectionable spectral line broadening was evident even when using the unattenuated output of the spectrometer's rf unit. In order to increase the rf power level incident upon the sample, an Electronics Navigation Model 310L power amplifier was inserted between the spectrometer's transmitter output and the nmr sample probe. In the case of carbon disulfide, an increase in spectral signal/noise ratio of 2.4 was realized when the H_1 level was slightly less than that which produced noticeable line broadening. This value of H_1 was then maintained throughout the present investigation.

Spectral calibration proved difficult since audio side bands of ^{33}S resonances were not sufficiently intense to be observed. To overcome this difficulty, the magnetic field was increased from the ~ 13.3 kG used to detect ^{33}S to ~ 14.1 kG in order that the much more intense ^{14}N resonance in nitromethane could be observed and modulated with an audio oscillator. The distance between the resulting ^{14}N side bands expressed in units of gauss/chart division was then used to calibrate the ^{33}S spectra. Errors introduced by this method of field calibration could not be determined, but they are expected to be small compared to other experimental uncertainties in the data.

Most of the chemical shifts were determined by the cell substitution technique; in a few cases internal or external carbon disulfide was used. All chemical shifts are reported relative to carbon disulfide which is arbitrarily assigned a chemical shift (δ) of 0. They are reported in units of parts per million (ppm) of magnetic field

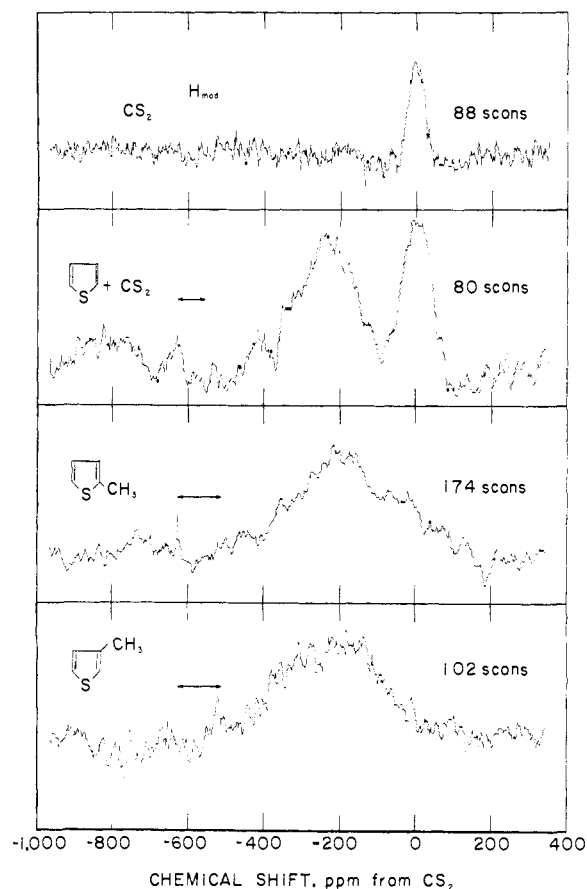


Figure 1. ^{33}S nmr spectra of carbon disulfide and selected thiophenes.

and are most positive for resonances occurring at highest magnetic field.

(References to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.)

Experimental Results

Carbon disulfide and a few thiophenes were the first compounds examined during the present investigation; representative spectra are reproduced in Figure 1. ^{33}S spectral measurements on carbon disulfide have been reported previously; both broad-line^{3,5} and pulse⁷ nmr techniques had been used. The carbon disulfide resonance in a broad-line experiment is easily seen in a single spectrometer scan provided the modulation amplitude employed is about twice the natural line width of the resonance. The spectrum of carbon disulfide shown in Figure 1 was obtained under conditions of low modulation amplitude, low modulation frequency, and very low power level incident upon the sample in order to measure this line width; a considerable period of signal averaging was therefore required.

Eighty scans were required to obtain the spectrum of the thiophene-carbon disulfide solution also shown in Figure 1. This spectrum, when compared with that published earlier of the same solution,⁶ clearly shows the advantages of using the additional rf amplification described in the Experimental Section. The spectrum published in ref 6 required more than 250 scans; that in Figure 1 required only 80 scans and, in addition, was obtained under lower modulation. Signal/noise ratios in the two spectra are comparable.

Also shown in Figure 1 are representative spectra of the two monomethylthiophenes.

Spectra of compounds exhibiting very broad ^{33}S resonances are shown in Figure 2. In most cases, long periods of signal averaging in addition to the use of large modulation amplitudes were required in order to obtain usable spectra. Of the compounds studied thus far, ethyl disulfide exhibited the broadest ^{33}S nmr signal.

Relatively narrow resonances were observed for carbon disulfide, dilute sulfuric acid, and sphalerite powder. Representative spectra of the latter two materials are shown in Figure 3; the observed, but not necessarily the natural, line width in each case was ~ 0.5 G. A second thiophene-carbon disulfide spectrum is included in the figure for comparison purposes. The sphalerite spectrum has an unusual line shape somewhat reminiscent of the esr spectra of F centers induced in alkali halides by irradiation with X-rays.^{8,9} The line shape is a result of rapid passage conditions imposed upon the experiment by the large modulation amplitude and frequency used.

Since it was likely that our limit of resolution was ~ 0.5 G because of the broad-line operating conditions employed, it was decided to try to obtain high-resolution spectra of two of the compounds. In order to do this, the modulation frequency was increased by a factor of 10; thus the actual dispersion mode spectrum rather than its first derivative was obtained. For carbon disulfide, these experiments showed that 0.5 G was the natural line width; for the sphalerite powder, the narrowest resonance observed was ~ 0.2 G.

Chemical shifts and spectral line widths for the compounds investigated are summarized in Table I. The

Table I. ^{33}S Nmr Spectral Data

Compound	n^a	δ , ppm	ΔH , G
Sodium sulfide (aq)	1	261	5
Sphalerite (ZnS) ^b	3	230 ± 6	≤ 0.2
Ethyl disulfide	7	168 ± 88	16
Tetrahydrothiophene	3	89 ± 38	8
Carbon disulfide		0	0.5
3-Bromothiophene	1	-134	5
2-Methylthiophene	2	-178 ± 9	4
3-Methylthiophene	2	-197 ± 26	5
Thiophene (90% in CS_2)	4	-220 ± 6	1.9
Sulfuric acid (concn)	3	-225 ± 32	7
Dimethyl sulfoxide	4	-233 ± 20	8
Sulfuric acid (10 N)	4	-319 ± 5	≤ 0.5

^a Number of individual spectra measured. ^b Spectra of powdered and a large crystalline sample gave identical spectra within experimental error.

line widths given were corrected for the effects of magnetic field modulation using experimental data for carbon disulfide in a plot of the type recommended by Poole.¹⁰

Discussion

^{33}S Resonance in Carbon Disulfide. Of the organic compounds investigated, carbon disulfide gave the narrowest ^{33}S resonance. The line width at half-

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(10) C. P. Poole, Jr., "Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques," Interscience, New York, N. Y., 1967, p 409.

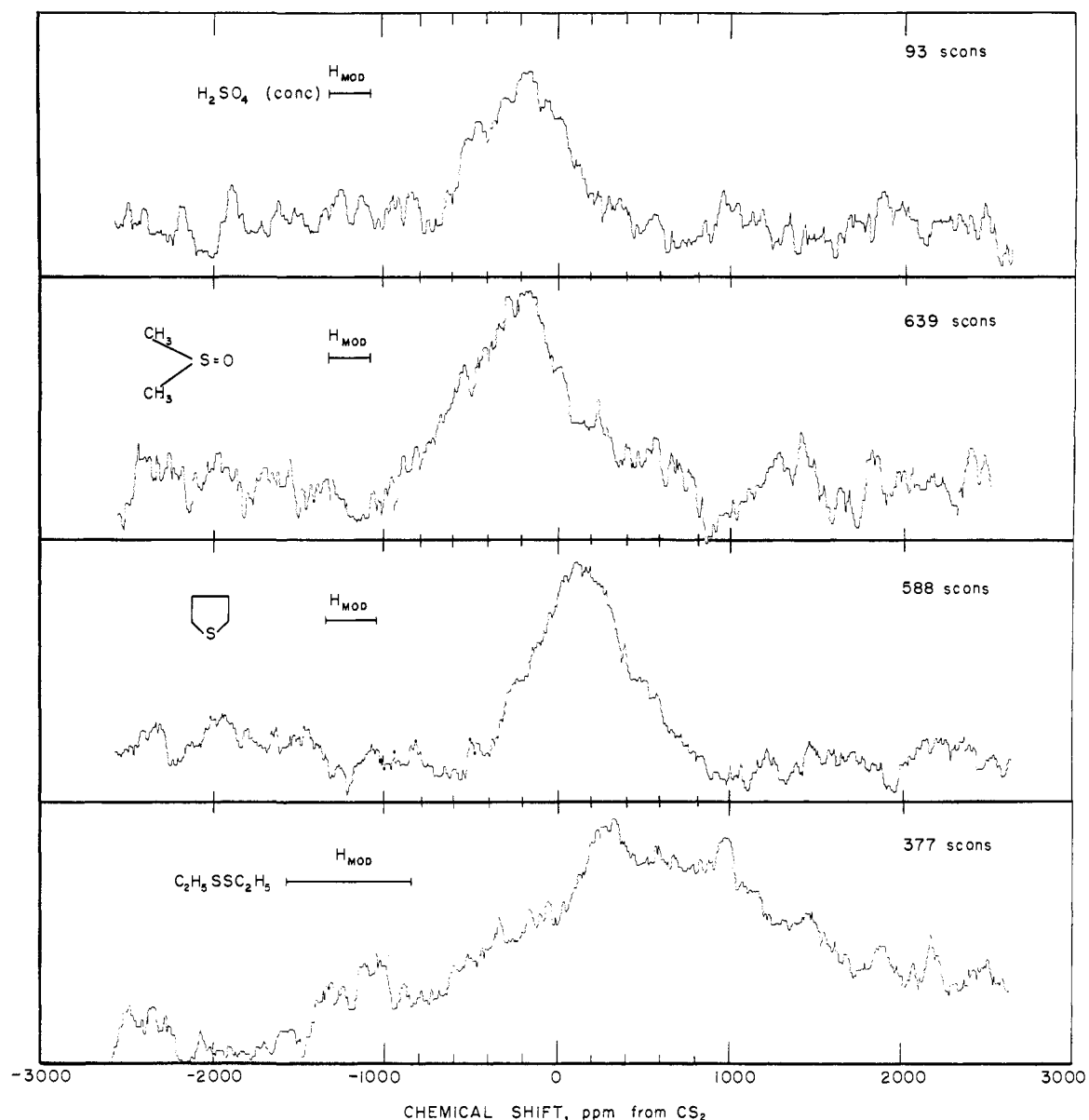


Figure 2. ^{33}S nmr spectra of concentrated sulfuric acid, dimethyl sulfoxide, tetrahydrothiophene, and ethyl disulfide.

intensity is 0.5 G and is essentially that shown in the top spectrum of Figure 1. Karr and Schultz⁵ previously reported a line width of approximately four times this value; overmodulation of their spectrum may have been responsible for the broader line observed. Recently these authors reported the free induction decay curve for carbon disulfide;⁷ their experimental data suggest a line width in close agreement with that measured during the present investigation. The relatively narrow ^{33}S signal and the excellent solvating powers of carbon disulfide make it a useful internal chemical shift standard in those cases where small modulation amplitudes can be used to obtain spectra, *e.g.*, thiophene (top spectrum, Figure 3). Unfortunately the very broad lines observed for most organic compounds require the use of high modulation amplitudes and thus preclude the use of *any* internal chemical shift standard.

The method of Gillen and Noggle,¹¹ when applied to the present data on carbon disulfide, yields a spin-spin relaxation time T_2 of ~ 1 msec which is of the same

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order of magnitude as the 480 μsec measured by Schultz, Karr, and Vickers⁷ at 13.1 MHz using pulse techniques. Schultz, Karr, and Vickers also measured T_1 , the spin-lattice relaxation time; their value of 1.5 msec shows that $T_1 \sim T_2$ at least for ^{33}S nuclei in carbon disulfide. In contrast to the very short ^{33}S nuclear relaxation times which are dominated by electric quadrupole interactions, T_1 for ^{13}C ($I = 1/2$) in carbon disulfide^{12,13} is several orders of magnitude longer than the ^{33}S values. Schmidt and Chan¹⁴ have recently shown that spin-rotation interaction can account for the ^{13}C T_1 in carbon disulfide.

Resonance of ^{33}S in a Symmetrical Electronic Environment. It is well known that relaxation of nuclei having $I > 1/2$ is generally rapid because of electric quadrupole effects; thus nmr resonances of these nuclei are often

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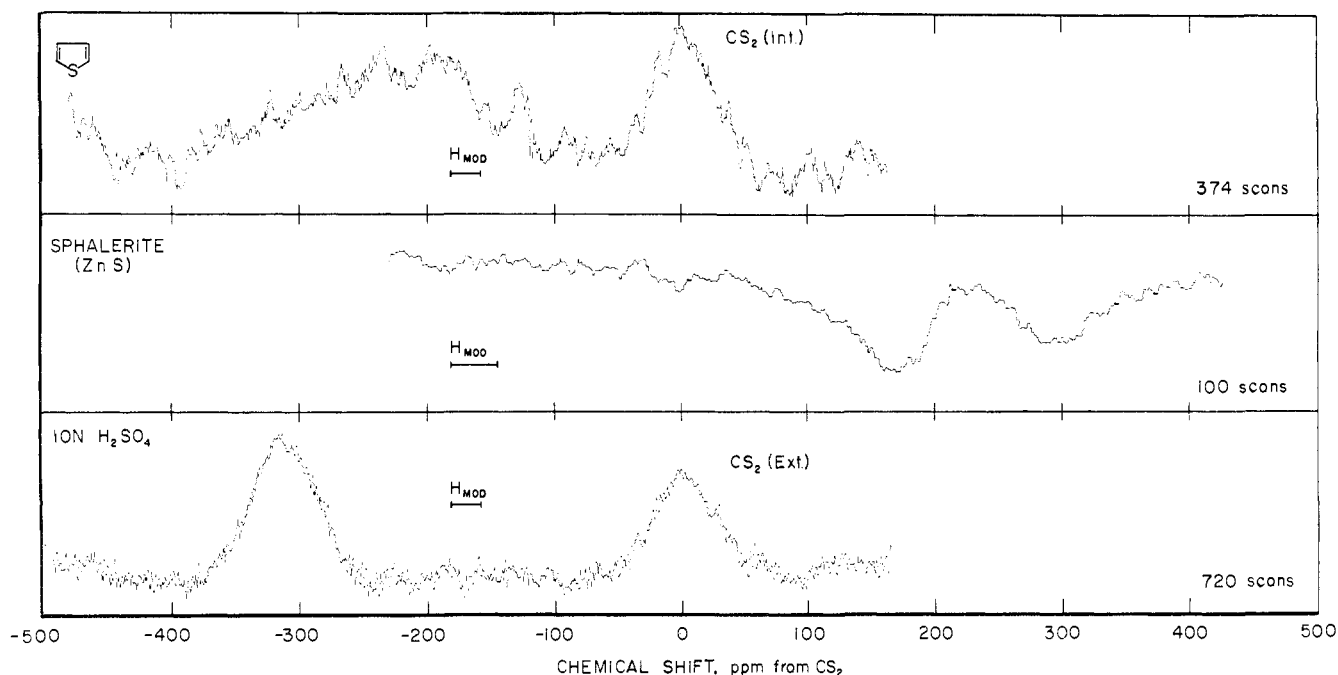


Figure 3. ^{33}S nmr spectra of thiophene, sphalerite powder, and 10 *N* sulfuric acid.

very broad, sometimes to the extent of being undetectable. In those cases where a spherical or near-spherical distribution of nuclear charge prevails, little or no electric field gradient is present at the nucleus and the time required for nuclear relaxation is lengthened; a long T_2 leads to a narrow resonance. The classic example of this phenomena was reported by Ogg and Ray¹⁵ who studied the ^{14}N resonances of ammonium salts; narrow resonances were observed for ^{14}N in tetrahedral environments, *e.g.*, NH_4^+ and $(\text{CH}_3)_4\text{N}^+$, whereas broader ones were exhibited by less symmetric molecules such as $(\text{CH}_3)_2\text{NH}_2^+$.

During the present investigation, ^{33}S spectra were obtained for S^{2-} ions in both powdered and crystalline samples of sphalerite (ZnS); tetrahedral symmetry about the sulfurs prevails in the ion. A spectrum of the powdered material is reproduced in Figure 3; the narrowness of the signal is readily apparent. It should be pointed out that dipole-dipole line broadening in sphalerite is negligible since for all practical purposes the mineral can be considered magnetically dilute; *i.e.*, the only isotope of zinc having nonzero spin is less than 5% naturally abundant. The ^{17}O resonance of O^{2-} in magnesium oxide has also been reported to be relatively narrow.¹⁶

^{33}S Resonance in a System Undergoing Rapid Chemical Exchange. In systems in which nuclei are exchanging sites at a rate greater than the separation in hertz between the signals of the exchanging species, the observed spectrum will be determined by the time-averaged environment of the nuclei. Aqueous solutions of electrolytes yielding hydrogen-containing ions (H_3O^+ , OH^- , HSO_4^- , etc.) were probably the most extensively studied systems, and such investigations were among the earliest applications of nmr.¹⁷ In addition to the

usual proton nmr studies of electrolytic solutions, nmr of other nuclei¹⁸ has also been employed. ^{14}N and ^{36}Cl have proven especially useful in studies of the dissociation of inorganic acids.¹⁸ During the present investigation, concentrated and dilute (10 *N*) samples of sulfuric acid were examined by ^{33}S nmr.

The early Raman spectral studies of Young¹⁹ showed that concentrated sulfuric acid contains predominately H_2SO_4 molecules whereas solutions having concentrations $<14 M$ are essentially devoid of these molecules but contain HSO_4^- with some SO_4^{2-} . For 10 *N* sulfuric acid, Young showed that the ratio of HSO_4^- to SO_4^{2-} was ~ 1.8 . Different ^{33}S nmr chemical shifts would therefore be expected for the two concentrations of sulfuric acid examined; the data of Table I show this difference to be 94 ppm. Because of the broad resonance observed for the concentrated acid, large errors are present in this difference value. A statistical analysis of the data indicated, at least at the 90% confidence level, that the shift in resonance between the two concentrations is indeed real although the actual magnitude of the difference measured is only approximate. This dilution shift to low field is in the same direction as reported for the ^{14}N resonance in nitric acid solutions,¹⁸ but opposite to the shifts of the anion resonances in HX ($\text{X} = \text{halogen}$) acid solutions. It should be noted that in the dissociation of the HX acids, the excess negative charge is localized on the ion whose resonance is being measured whereas in the cases of nitric and sulfuric acids the negative charge is delocalized primarily over the oxygen atoms rather than being localized on the center atom of the ion. The narrowness of the resonance in the dilute sulfuric acid solution is to be expected on the basis of rapid chemical exchange between the various ionic species in the acid. The broadness of the signal for the concentrated acid is not easily understood; the

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very high viscosity of the sample may be a contributing factor.

Aqueous sodium sulfide, another system in which exchange among ionic species is involved, was also examined. The observed line width in this case was considerably larger than that in 10 *N* sulfuric acid indicating a slower exchange rate. Several sulfur-containing species are present in the sodium sulfide solution. It is likely that some of the S²⁻ ions formed by dissociation are hydrolyzed to HS⁻ ions as is indicated by the mild alkalinity of the solution. In addition to these species, hydrogen sulfide (from the hydrolysis of HS⁻) and undissociated sodium sulfide are undoubtedly present.

Other Molecules. Most molecules of interest, however, do not possess the high symmetry of S²⁻ in cubic zinc sulfide nor do they undergo rapid chemical exchange of parts. For these molecules, broader ³³S nmr resonances are to be expected since substantial electric field gradients may be present at the nucleus allowing a highly effective mechanism for nuclear spin relaxation. The spin-lattice relaxation time produced by quadrupole coupling is given by²⁰

$$\frac{1}{T_1} = \frac{3(2I + 3)(1 + \eta^2/3)(e^2qQ/\hbar)^2\tau}{40I^2(2I - 1)}$$

where τ is the correlation time characterizing nuclear reorientations, e^2qQ/\hbar is 2π times the quadrupole coupling constant in hertz, η is the asymmetry factor of the field gradient tensor, and I and Q are the usual nuclear constants. Although Moniz and Gutowsky²¹ and Richards²² have had considerable success in applying this equation to ¹⁴N resonances, the equation is of limited practical value primarily because of the difficulty in evaluating many of the terms. It would be of interest, however, to compare ³³S results with published data on ¹⁷O since both elements are in the same chemical group. Using the known values of I and Q for these two nuclei,²³ assuming that $T_1 = T_2$, and applying the known relationship between spectral line widths and T_2 values,¹¹ one would predict that the line widths of ³³S nmr resonances would be more than 700 times broader than ¹⁷O line widths in completely analogous molecules (obviously such pairs of molecules do not exist, but one could compare data for thiophene and furan, inorganic sulfides and oxides, etc., as approximations). Christ, Diehl, Schneider, and Dahn²⁴ have reported ¹⁷O nmr line widths for a wide variety of compounds and found values ranging from 0.08 to 3.5 G, the average value for 161 different resonances being 0.4 G. Although the ³³S line widths in Table I are generally larger than these, in no case do they differ by a factor near 700. The use of the above equation requires much more information than is commonly available for molecules, e.g., quadrupole coupling constants, asymmetry parameters, and correlation

times. The easiest of these to measure is probably the quadrupole coupling constant; yet a literature search revealed ³³S constants for only seven molecules,¹ none of which were examined by nmr during this investigation.

The broad resonance observed for dimethyl sulfoxide confirms the short free induction decay curve reported previously for this compound.⁷ Unfortunately a T_2 value was not given so only qualitative agreement can be proposed. An unexpected result was the large difference in spectral line width observed for thiophene when either of the chemically nonequivalent hydrogens was replaced with a very weak electron-releasing methyl group. The effect of methyl substitution on the line width was little different from that found in the case of bromothiophene in spite of the very strong electron-attracting properties of the bromo group.

Chemical Shifts. ³³S nmr chemical shifts are given in the literature for very few compounds. Lee⁴ has reported the temperature dependence of the ³³S resonance in paramagnetic MgS, whereas Karr and Schultz⁵ have given shifts for sphalerite, pyrrhotite (Fe_{1-x}S), and elemental sulfur dissolved in carbon disulfide. The present authors have published the spectrum and reported the chemical shift datum for 90% thiophene in carbon disulfide.⁶ As part of the present investigation, we have attempted to reproduce Karr and Schultz's results for sphalerite and for elemental sulfur.

The chemical shift for sphalerite was reported to be +12 G (at 15 kG) from that of carbon disulfide in the paper⁵ by Karr and Schultz; these data yield a δ value of 800 ppm. We have obtained spectra of these authors' original sample in addition to a crystalline sample furnished by another laboratory and determined the chemical shift to be 230 ± 6 ppm (Table I). The signal/noise ratio in our spectra (see Figure 3 for spectrum of powdered sphalerite) was much higher than the 2:1 reported by Karr and Schultz. Using the high rf power levels noted in the Experimental Section, good spectra were obtained after 100 scans were accumulated; the spectrum obtained by Karr and Schultz required 960 scans. Although we can offer no explanation for the chemical shift value reported by these authors, we have no reason to doubt our own more recent data.

Many unsuccessful attempts to observe the resonance of elemental sulfur dissolved in carbon disulfide were also made during this investigation. Even a sample of ³³S enriched sulfur was examined. In no case was a distinct resonance attributable to elemental sulfur observed. Our experience suggests that the ³³S resonance reported by Karr and Schultz for elemental sulfur may have been due to an instrumental artifact.

Although the number of chemical shifts measured during the present work was limited to only 12 materials, two observations were of particular interest. (1) With the exception of aqueous sodium sulfide which contains a variety of sulfur-containing species, the highest field ³³S resonance was observed for the sulfide anion. Completely ionic S²⁻, because of its filled M shell, is spherically symmetric. A high-field resonance is therefore consistent with Ramsey's²⁵ equation for nuclear shielding since in the case of spherical symmetry, the para-

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magnetic contribution to the chemical shift vanishes. (2) The ^{33}S resonance in thiophene is found considerably lower than that of its tetrahydro analog. In general, resonances of aromatic, heteroaromatic, and other unsaturated compounds lie at lower field than their saturated analogs. For example, the ^{17}O resonance in furan is found 260 ppm below that of tetrahydrofuran,²⁴ the ^{13}C resonance in benzene is 101 ppm lower than that of cyclohexane,^{26,27} and the ^{13}C resonances of unsaturated carbons in alkenes are found several tens of parts per million below those of the corresponding alkane carbons.²⁸

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Conclusion

Although we have attempted to provide answers to the questions posed in the introduction, in essence our data offer only clues or partial answers. The broad ^{33}S resonances observed for most of the compounds examined indicate that, in general, measured chemical shifts are of low accuracy and that the possibility of differentiating between sulfur types in mixtures or in natural substances (such as coal) is an extremely remote one unless some means of removing quadrupole broadening is forthcoming or extremely high magnetic fields are employed.

Acknowledgments. The authors are indebted to Drs. F. R. Brown and R. G. Lett for stimulating discussions and thank one of the referees for his very helpful comments.

Spectroscopy of Phenylcyclopropanes and Phenylethanes. Unusual Emissions from Phenylcyclopropanes^{1a}

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Abstract: At 77°K, all phenylcyclopropanes show a benzene-like absorption with a 0-0 band at 274–279 nm. The lesser substituted phenylcyclopropanes (mono-, 1,1-di-, and one 1,2-diphenyl) exhibit benzene-like fluorescence but no benzene-like or any other phosphorescence. The higher substituted phenylcyclopropanes (tri- and tetraphenyl) show no benzene-like fluorescence or phosphorescence but do show a short-lived (~7 msec), long wavelength (~580 nm) phosphorescence. The long wavelength phosphorescence is assigned as originating from a radical-like triplet state in which the C-CH₂-C bond angle is large (100–140°) and the cyclopropane bond connecting the carbon atoms to which the phenyl rings are attached is severely stretched. Mechanisms are given for the quenching of the benzene-like fluorescence and phosphorescence including the role of exciton interaction. A mechanism is given to account for the absence of the radical-like phosphorescence in lesser substituted phenylcyclopropanes. Spin-orbit coupling appears to be large between the radical-like singlets and triplets based on the short lifetime of the phosphorescence as well as its relatively high intensity and the apparent absence of a radical-like fluorescence. We believe an important source of the spin-orbit interaction is from first-order coupling involving one-center terms. The presence of the unusually low-energy radical-like triplet appears to be important in the triplet-triplet sensitized cis-trans isomerization of 1,2-diphenylcyclopropane with low-energy sensitizers. In addition either or both of the radical-like triplet and singlet states are the important excited states leading to direct photoisomerization and/or cycloelimination. The emission spectroscopic results of phenylethanes at 77°K are consistent with the existence of exciton interaction.

We have carried out a comprehensive study of the action of light upon some of the phenylcyclopropanes primarily at 77°K where both photochemical change and optical properties were monitored. Due to some unusual emission results and trends, a complementary study of the phenylethanes was also carried out. The lesser phenyl-substituted cyclopropanes exhibited only a benzene-like fluorescence whereas the more highly phenyl-substituted members exhibited only a very long wavelength (540–585 nm) phosphorescence (not benzene-like). Furthermore, this phosphorescence had a short lifetime (~7 msec). It was believed

that exciton effects² might be contributing to the behavioral trend, and a study of the emission properties of the phenylethanes, which were expected to show an exciton effect, was undertaken. Results from the phenylethanes are used to provide a partial basis for interpretation of the results obtained from the phenylcyclopropanes.

Considerable evidence exists verifying thermal ring opening³ of the cyclopropane ring, and the photochemistry of the cyclopropane ring system has been ex-

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