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cule is removed as when a symmetrical one is. In other words, in the mixed methanes, the formation of a methylene ion accompanied by an H_2 or T_2 molecule occurs twice as frequently with respect to predicted values as does the formation of a methylene ion accompanied by HT. If the methylene ion is accompanied by atoms to an appreciable extent, then this effect is even more pronounced.

ACKNOWLEDGMENTS

The author would like to express his thanks to Dr. Joseph F. Walling of Arizona State University,[15] a summer Staff Member of this laboratory in 1960, for obtaining many of the spectra and assisting in the early computations, and to Jack R. Brown of this laboratory for assistance with the IBM calculations.

APPENDIX

C. E. Berry has kindly furnished equations and data permitting the calculation of mass discrimination effects in the cycloidal mass spectrometer. Relative to CH_4^+, there is a loss of intensity from discrimination effects of 1.2%, 2.3%, 3.9%, and 5.1% as one progresses from CH_3T^+ to $CH_2T_2^+$, CHT_3^+, and CT_4^+, respectively. When this correction is applied, the relative sensitivities of these five species become 1.000, 0.945, 0.873, 0.971, and 1.000.

There are corresponding small changes in the pattern coefficients most of which are well within the experimental uncertainties of the coefficients themselves and which are, therefore, not reported here.

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EPR Spectra of SH, SD, and SO Radicals in the Gaseous State*

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A 12-line EPR spectrum at a microwave frequency of 8.850 kMc/sec has been observed in the field region from 7400 to 7700 G that is attributed to electric-dipole transitions between Zeeman levels of the $J=\frac{3}{2}$ rotational state of gaseous SH($^2\Pi_{\frac{3}{2}}$). Average Λ splittings and proton hyperfine splittings were 190 G and 5.4 G, respectively. The SH radicals were produced in the spectrometer cavity by adding H_2S at the cavity entrance to a stream of discharge-dissociated H_2O vapor flowing through the cavity. When H_2S was added to a stream of dissociated D_2O, an additional spectrum attributed to SD($^2\Pi_{\frac{3}{2}}$, $J=\frac{3}{2}$) was observed. Another species in these gaseous systems gives rise to a third EPR spectrum that is believed to result from electric-dipole transitions between Zeeman levels of different rotational states of SO($^3\Sigma$).

INTRODUCTION

ELECTRON paramagnetic resonance spectroscopy has considerable potential as a technique for studying mechanisms of gaseous chemical reactions that involve free radicals. Detection and characterization of EPR spectra of gaseous species are essential prerequisites of such chemical studies and have been the objectives of much recent research in EPR spectroscopy of gaseous species. EPR spectra of several gaseous atomic species have been reported but there have been few observations of gaseous diatomic or polyatomic free radicals. Sufficient concentrations of transient paramagnetic molecular species for observation by EPR spectroscopy are not easily attained because of the great reactivities and consequent short lifetimes of such species and because of the distribution of these free radical populations among many rotational states that exhibit individual EPR spectra. Beringer, Rawson and Henry[1] have pointed out that diatomic molecules that exhibit Λ doubling of Zeeman levels[2] and that have large electric dipole moments should be detectable by electric-dipole EPR spectroscopy at considerably smaller concentrations than are required for conventional magnetic-dipole EPR spectroscopy. Recently, Radford[3] has made the first observation by EPR of a transient molecular species in the gas phase in his investigation of the electric-dipole EPR spectra of OH($^2\pi_{\frac{3}{2}}$), OH($^2\pi_{\frac{1}{2}}$) and OD($^2\pi_{\frac{3}{2}}$). We wish to add to the growing catalogue of EPR spectra of gaseous species by reporting here the detection by electric-dipole EPR spectroscopy of gaseous SH($^2\pi_{\frac{3}{2}}$), SD($^2\pi_{\frac{3}{2}}$), and a third species believed to be SO($^3\Sigma$).

EXPERIMENTAL

A Varian V 4500 EPR spectrometer and 12-in. magnet were used for this investigation. The cavity was replaced by a pill-box-shaped cavity that operates in

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* Contribution No. 870.

[1] R. Beringer, E. B. Rawson, and A. F. Henry, Phys. Rev. **94**, 343 (1954).

[2] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, Inc., Princeton, New Jersey, 1950).

[3] H. E. Radford, Phys. Rev. **122**, 114 (1961); **126**, 1035 (1962).

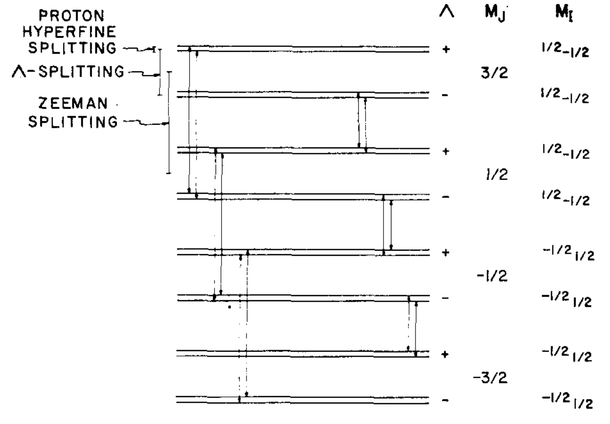

Fig. 1 Schematic representation of expected transitions of SH($^2\Pi_{3/2}$, $J=\frac{3}{2}$)

the TE-011 mode. The cavity was positioned so that both electric and magnetic components of the microwave field were normal to the external magnetic field, and hence both electric-dipole and magnetic-dipole EPR transitions could be detected. The steady magnetic field in the cavity was modulated at 100 kc/sec. Gas was contained in the cavity in a quartz vessel of 35 cc volume. The quartz vessel was provided on either side with quartz tubes (12 mm o.d.) that passed through ports in the cavity walls and provided an inlet and outlet for gas flow through the cavity. These tubes were connected to a conventional high-vacuum apparatus for manipulation of gases at low pressures.

Observable concentrations of gaseous free radicals were obtained in the spectrometer cavity in the following manner. Water vapor was permitted to flow through the cavity at a pressure of 0.4 to 0.6 mm. The H_2O vapor was dissociated in the quartz inlet tube a few inches upstream from the cavity in an electrodeless discharge induced by 2450 Mc/sec radiation from a 125-W Raytheon diathermy power supply. Magnetic dipole EPR spectra of H ($^2S_{1/2}$)[4] and O($^3P_2$ and $^3P_1$)[5] were observed, as well as electric-dipole spectra of OH($^2\Pi_{3/2}$, $J=\frac{3}{2}$ and $J=\frac{5}{2}$).[3] Hydrogen sulphide from a second gas inlet system was then mixed into the dissociated H_2O vapor at the entrance to the cavity. As the H_2O flow was increased, the intensities of the spectra of H, O, and OH decreased, and a new spectrum, attributed to SO, appeared. When the H_2S flow was just sufficient to quench the H spectrum (O and OH having already disappeared), the EPR spectrum of SH was observed. This flow of H_2S caused a pressure increase in the cavity of about 30%, and modest deviations from these flow conditions resulted in the disappearance of the SH spectrum. The spectrum of SO was detectable for a wide range of H_2S/H_2O flow ratios.

The frequency of the cavity microwave field was monitored with a Hewlett–Packard Wavemeter (Model X350A). Field measurements were made with a proton NMR-type gaussmeter (Nuclear Magnetics Corporation precision gaussmeter Model M-2) by placing the probe adjacent to the spectrometer cavity in the magnet gap. Relative intensities of EPR absorption lines were estimated by comparison of the first derivative absorption curves recorded at constant, low power levels taking the intensity of a resonance line as proportional to the product of the square of the separation of the points of maximum slope of the absorption and the maximum amplitude of the derivative curve.

RESULTS AND DISCUSSION

Possible electric-dipole transitions between Λ-doubled Zeeman levels of a polar diatomic molecule in a $^2\Pi_{3/2}$ electronic state have been discussed in detail by Radford.[3] A schematic representation of such transitions for the ground rotational state ($J=\frac{3}{2}$) of SH($^2\Pi_{3/2}$) is presented in Fig. 1 and includes hyperfine splitting by the hydrogen nucleus. The observed EPR spectrum that is attributed to SH($^2\Pi_{3/2}$, $J=\frac{3}{2}$) is shown in Fig. 2. The 12 predicted transitions are observed, and the field positions of the spectral lines are consistent with an average Λ splitting of 190 G and an average proton hyperfine splitting of 5.4 G.

When H_2S was added in the manner described to a stream of discharge-dissociated D_2O, additional spec-

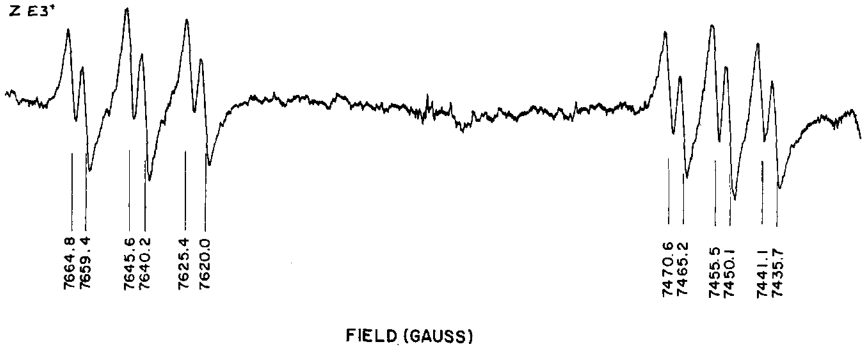

Fig. 2. Electric dipole EPR spectrum of SH($^2\Pi_{3/2}$, $J=\frac{3}{2}$). Microwave frequency = 8.850 kMc/sec.

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[4] R. Beringer and E. B. Rawson, Phys. Rev. **87**, 228 (1952).
[5] E. B. Rawson and R. Beringer, Phys. Rev. **88**, 677 (1952).

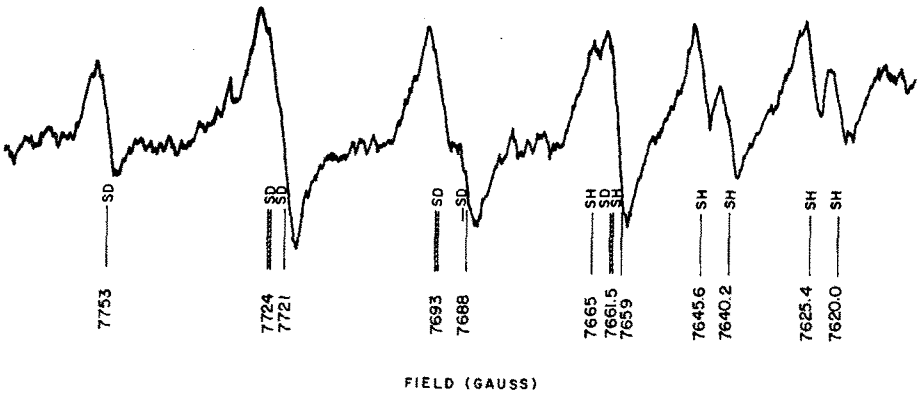

FIG. 3. Electric-dipole EPR spectra of SD($^2\Pi_{3/2}$, $J=\frac{3}{2}$). Microwave frequency=8.850 kMc/sec.

tral lines were detected in the field region of the SH EPR spectrum as shown in Fig. 3. These additional lines are believed to result from electric-dipole transitions of SD($^2\Pi_{3/2}$, $J=\frac{3}{2}$) corresponding to those already described for SH. Intensity relationships and line separations in the spectrum of Fig. 3 indicate that the SD spectrum consists of 6 lines at the positions shown in Fig. 3 that are not completely resolved from each other and from the SH spectrum. In SD, the average Λ splitting has decreased to 28 G with the result that the high- and low-field triplets from Λ-splitting of the three Zeeman transitions are intermingled. The deuterium hyperfine splitting is not resolved.

It seems likely that SH was produced by the reaction

$$H+H_2S\rightarrow H_2+SH,$$

and that SD was produced by

$$D+H_2S\rightarrow HD+SH,$$

$$D+SH\rightarrow SD+H.$$

The production of transient species by such atom–molecule reactions appears to be a promising general technique for preparing detectable concentrations of gaseous free radicals for EPR studies.

The assignment of the third novel EPR spectrum that was observed in these studies to SO($^3\Sigma$) is based on the following observations and deductions. The spectrum consists of four lines—two very strong lines and two weak lines each having intensities of about 5% of the intensity of the nearest strong line. The field positions of these lines at three different microwave frequencies are presented in Table I. Surprisingly, the field positions of the lines increase as the microwave frequency is decreased, whereas field positions corresponding to transitions between Zeeman levels of a rotational state are expected to decrease with decreasing cavity frequency. The intensities of the four lines changed in a similar manner as experimental parameters were varied, and these changes were not similar to changes in the spectra of the other observed species. In assigning these lines, it is noted first that the unknown species must be composed of one or more of the elements, H, O, and S. Furthermore, this relatively strong spectrum probably arises from electric-dipole transitions since the cavity is comparatively insensitive to magnetic dipole transitions. Thus, the spectrum does not result from O_2, S_2, or from atomic species. The unknown species probably does not contain hydrogen since its spectrum was unchanged when D_2O was substituted for H_2O in the discharge gas stream. The remaining possibility among diatomic species is SO($^3\Sigma$). Although electric-dipole transitions are not possible between Zeeman levels of a rotational state of SO($^3\Sigma$), such transitions between Zeeman levels of *different* rotational states are allowed. The energy separations of Zeeman levels of the lower rotational states of SO($^3\Sigma$) have not been evaluated as a function of magnetic field, but examination of the zero-field separation of these rotational levels leads one to the conclusion that transitions between Zeeman levels of neighboring rotational states might well occur at a frequency of 9×10^9 cps in the field range that we have examined. Furthermore, the field positions of these transitions would increase with decreasing microwave frequency as observed. The strong lines are assigned to $S^{32}O^{16}$ and the weak lines are attributed to $S^{34}O^{16}$ since the natural abundances of S^{32} and S^{34} are 95% and 4.2%, respectively. While the assignment of the novel four-line spectrum to SO($^3\Sigma$) seems very reasonable, the possibility that it arises from a polyatomic species has not been eliminated.

TABLE I. Field positions of electric-dipole EPR transitions of SO($^3\Sigma$).

Microwave frequency (cps$\times10^{-9}$)	Positions of strong lines (gauss)		Positions of weak lines (gauss)	
	High field	Low field	High field	Low field
8.850	5833	2783	5148	2456
9.046	5627	2666		
9.680	4896	2263		