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EPR Spectrum of Gas-Phase Sulfur Atoms*

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GROUND-state S atoms have been detected by means of their paramagnetic resonance spectrum among the products of a reaction of H_2S with discharged wet H_2. To this writer's knowledge, this is the first time that an observation of this spectrum has been reported. The S-atom spectrum is similar to that of O atoms. All of the information required for its analysis may be obtained from the work of Radford and Hughes[1] on the O-atom spectrum.

The atoms were produced in a 1.2-cm-i.d. quartz flow tube which passed through the center of a TE_{011} mode microwave cavity resonant at 9212.37 MHz. With the quartz inserted, the cavity Q was about 5000. A microwave discharge (2450 MHz, 60-W power input) was maintained in flowing wet H_2 50 cm upstream from the cavity center. Water vapor could be added in variable amounts 20 cm upstream from the discharge. Hydrogen sulfide was introduced at a point 5 cm upsteam from the cavity center. Matheson ultra-high-purity-grade H_2 was passed through a liquid-nitrogen trap located upsteam from the water-vapor inlet. The EPR spectrometer was of the superheterodyne type.

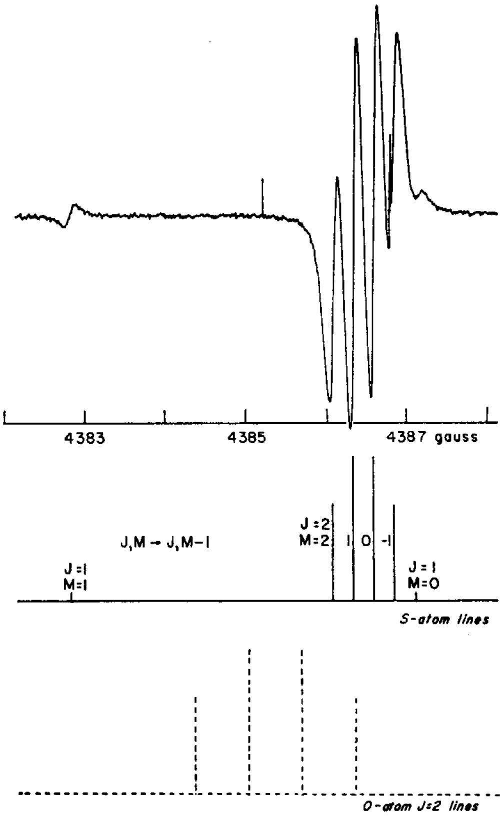

FIG. 1. EPR spectrum of S atoms together with calculated second-order Zeeman splittings. O-atom $J=2$ lines are shown for comparison. Height of calculated lines is proportional to their intensities for a room-temperature Boltzmann electronic-energy distribution. Experimental conditions were: pressure, 0.030 torr; H_2 flow, 2×10^{-6} mole sec^{-1}; H_2O flow, 10×10^{-8} mole sec^{-1}; H_2S flow, 7×10^{-8} mole sec^{-1}; microwave power to cavity, 30 μW; and a spectrometer time constant of 0.3 sec. The separation of the derivative maxima of the resolved line was 0.13 G. The spike in the recorder tracing at 4385.2 G is a field marker, while that at 4386.8 is a noise feature.

The observed spectrum is shown in Fig. 1. Represented here is the spectrum of the isotopes ^{32}S and ^{34}S (95.0% and 4.22% natural abundance, respectively), which have zero nuclear spin. The difference in the spectrum of these isotopes would be too small to be detectable in the present experiment. A search for the spectrum of ^{33}S (0.76% natural abundance and nuclear spin $\frac{3}{2}$) was unsuccessful. The second-order Zeeman patterns, calculated from the known multiplet splittings[2] are also shown in Fig. 1. As well as can be estimated from the incompletely resolved lines, the observed splittings agree with the calculated splittings. Within the experimental uncertainty encountered here, the center of the S-atom $J=2$ second-order Zeeman pattern could be taken to be inversely proportional to the $^3P_2$ g factor, g_2. The pattern center was measured relative to the accurately known[1] line positions of the O-atom spectrum. This spectrum appeared when the H_2S flow was turned off. This technique eliminated the uncertainty involved in trying to measure the field differential (approximately 0.25 G) existing between the center of the cavity and the external proton NMR probe used to measure the field. Only the completely resolved low-field line of the $J=1$ transition was measured relative to the O-atom

TABLE I. Observed atomic g factors g_1 and g_2 for the ${}^3P_1$ and ${}^3P_2$ states, respectively, of S atoms. For comparison, values of g_1 and g_2 for O atoms, measured by Radford and Hughes (see Ref. 1), are also given.

g factor	S atoms	O atoms
g_1	1.501029 ± 0.000042	1.500986 ± 0.000002
g_2	1.500541 ± 0.000024	1.500921 ± 0.000002

lines. The g factor g_1 for the ${}^3P_1$ state was determined from this line position after applying a calculated correction for the second-order Zeeman effect. The principal source of error in g_1 arises from the difficulty in measuring the position of this weak line rather than from the uncertainty in the calculated correction.

The results of the analysis are shown in Table I which also includes for comparison the O-atom g factors from Ref. 1. The error limits given for the S-atom g factors are twice the observed standard deviation of the mean of several measurements. These limits were chosen large to include possible systematic errors arising primarily from the inability to completely resolve the lines. Theoretical calculations[3] of O-atom g factors have shown that deviations from the value $g_1=g_2=1.5011596$ predicted by the Schwinger theory[4] arise primarily from relativistic and diamagnetic effects on the Zeeman Hamiltonian and less importantly through departures from Russell–Saunders coupling. Calculations of this sort would be required to account for the observed S-atom g factors. One interesting aspect of such a calculation would be an explanation of the lack of any significant observed difference in g_1 for O and S atoms.

With O_2 to calibrate the spectrometer sensitivity, an absolute S-atom concentration of 3×10^{13} atom cm^{-3} was estimated for spectra recorded under the conditions indicated in Fig. 1. An increase in the H_2S flow produced an increase in the S-atom signal for H_2S additions up to about 4.5%; a further increase in the H_2S flow caused the signal to decrease rapidly. The EPR spectrum of SH was also observed under these conditions. For this species, the maximum signal occurred at a higher H_2S flow than that which gave the maximum S-atom signal. Upon addition of 4.5% H_2S, the H-atom signal decreased by about $\frac{1}{2}$ from its value observed without addition of H_2S. The system also exhibited similar behavior at the somewhat higher pressure of 0.2 torr. An attempt is being made to determine the mechanism responsible for the S-atom production.

The author wishes to thank Dr. H. E. Radford for a number of helpful discussions.

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Ionization Cross Sections for Neutral–Neutral Collisions Utilizing Asymmetric Charge Transfer*

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A SERIES of papers[1–4] has described the measurements of ionization cross sections σ_- for neutral atoms and molecules colliding with other neutral species at low energies. The technique of obtaining the neutral beam has been that of ionization in an electron-bombardment source, electrostatic acceleration and focusing, and neutralization of the ions by symmetric charge transfer. Essential to this procedure is the determination of the slow ion current formed in the charge-transfer cell and the relationship of the slow current to the neutral beam intensity. This determination, and details of the apparatus, are described by Utterback and Miller.[5] The neutral intensity is believed to be accurate to about 20%, and ionization cross sections determined in this fashion are reproducible to 10% or better.

As long as the charge-transfer cross sections are suf-

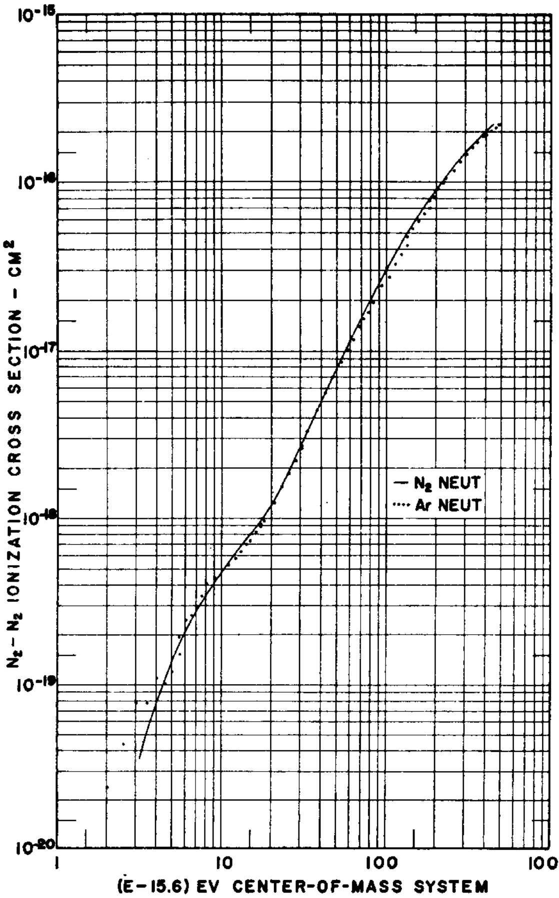

FIG. 1. Effect of asymmetric neutralization on N_2–N_2 ionization measurements.