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Abstract

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STUDY OF THE E.P.R. SPECTRUM OF A RAREFIED HYDROGEN SULFIDE FLAME

In recent years several works have appeared on the detection and identification of the radio spectra of short-lived diatomic radicals—both microwave spectra and Stark and Zeeman spectra. The first short-lived diatomic radical whose microwave spectrum ([1]), as well as whose e.p.r. spectra ([2]), were studied in the gas phase is the free hydroxyl OH. Owing to the presence of two closely spaced levels of the Λ doublet (∼ 1660 MHz), it proved possible to observe several series of lines having electric-dipole transitions much more intense than the ordinary lines of the e.p.r. spectrum. A second analogous molecule (ground state $^2\Pi_{3/2}$) proved to be the very short-lived molecule HS. The e.p.r. spectrum of HS was obtained by adding hydrogen sulfide to the discharge products of hydrogen or water vapor directly in the absorbing cell of the resonator ([3], [4]). At the same time, two single lines ([4]) were found in fields of the order of 2500 and 5500 oersteds; these were assigned to transitions between two closely spaced rotational components of the SO molecule, as well as to their satellites $S^{34}O$. The microwave spectrum of SO, due to transitions between rotational levels, was recently obtained by the reaction of atomic oxygen with COS and H_2S ([5]). The energy of the transition between the rotational levels $J = 1$, $K = 1$ and $J = 1$, $K = 2$ is approximately 13,000 MHz, i.e., only somewhat greater than the energy of the 3-centimeter range. Only because of the existence of such a close "K-doubling" was it possible to observe the e.p.r. spectrum of the SO molecule ([4]). Earlier attempts to obtain the microwave spectrum of the SO radical ([6]) in a discharge of sulfur vapors together with sulfur dioxide led to the detection of the rotational spectrum of S_2O. The lowest frequency of a rotational transition of the S_2O molecule is 18,000 MHz, i.e., approximately twice the usual frequency of the e.p.r. method, and if the structure of the S_2O molecule indicated in ([6]) and Zeeman transitions are possible, then only in very large magnetic fields. Another diatomic radical whose microwave spectrum has been studied is the nonparamagnetic molecule CS ([7]) (ground state $^1\Sigma$).

The relatively recent study of flames by radiospectroscopy includes chiefly the e.p.r. method ([8]–[12]). The present work gives a description of the e.p.r. spectrum of atoms and radicals detected in a rarefied hydrogen sulfide flame.

The study of the slow oxidation reaction of hydrogen sulfide ([13]) showed that

during the induction period there is an appreciable accumulation of the SO radical. Directly in a hydrogen sulfide flame, optical absorption spectra of the radicals SO, OH, and S_2 were observed ([14]). In flash photolysis of an $H_2S + O_2$ mixture ([15]) under isothermal conditions (strong dilution with an inert gas), the absorption spectrum of sulfur monoxide was observed, though in the form of its dimer S_2O_2. Under adiabatic conditions the S_2O_2 spectrum was not observed.

A mass-spectroscopic study of the flame near the third limit indicates the existence of S_2O ([16]). The HS radical has not yet been detected directly in the hydrogen sulfide flame. The optical spectrum of HS was observed when H_2S was added to a hydrogen flame with oxygen ([17]). Despite the large number of works devoted to the oxidation of hydrogen sulfide, the mechanism of this reaction cannot at present be regarded as established ([18]). With the advent of the e.p.r. method, broad possibilities opened up for a detailed study of this reaction. First of all, an attempt was made to detect free hydrogen and oxygen atoms in a rarefied flame of mixtures of hydrogen sulfide with oxygen. For this purpose a reactor with an internal diameter of 8 mm was made, whose heater consisted of platinum wires arranged perpendicular to the microwave electric field. The reactor was placed at the center of the resonator, so that in the volume under study mainly the magnetic field was concentrated (a transmission resonator with a wave of type H_{011} was used). At a temperature of 350—450°, pressure $5 \div 15$ mm Hg, and linear velocity $1.5 \div 3$ m/sec, appreciable signals of hydrogen and oxygen atoms were recorded ([19]).

In order to detect spectra of particles possessing electric dipole transitions (OH, HS, and SO), a quartz absorption cell was made which completely filled the resonator. Directly above the resonator a furnace was placed, whose temperature was about 600°. In this case the resonator was heated by hot air to temperatures of the order of 150°. This achieved two aims simultaneously. First, no deposit formed on the walls of the absorption cell, which, without heating the resonator, greatly interfered with the work. Second, it was possible in this way to ignite the mixture, preheated in a narrow reactor ($d = 1$ cm), directly in the resonator cell of diameter 4.4 cm. Initially the flame is ignited in the upper furnace at a pressure of $5 \div 7$ mm Hg, depending on the H_2S/O_2 ratio; then, when the linear velocity is increased and the pressure lowered, the flame moves downward and is ignited inside the resonator.

Under such conditions we succeeded in detecting the hydroxyl signal, due to transitions $J = {}^3/_2(m_J)^+ \leftrightarrow (m_J - 1)^-$ in the form of an unresolved doublet, as well as three single signals in fields of the order: a) 2500 oersted, b) 4300 oersted, c) 5500 oersted, which, in our opinion, should be assigned to SO. The signals are due to electric dipole transitions between rotational levels: $J = 1, K = 1$ and $J = 1, K = 2$ with $\Delta m_J = 0 \pm 1$. Line b) corresponds to the transition with $\Delta m_J = 0$. Lines a) and c) belong to transitions with $\Delta m_J = \pm 1$. It should be noted that the level $J = 1, K = 2$ has a negative g-factor ([20]). Indeed, for the $^3\Sigma$ level of a Hund' s-case-b molecule,

$$g = \frac{J(J+1) + S(S+1) - K(K+1)}{J(J+1)},$$

which gives, for the lower and upper levels, $g_1 = 1$ and $g_2 = -1$, respectively. When the energy in the magnetic field is comparable with the spacing between the nearest levels, linear splitting of the levels occurs only in small fields. In our case this is in fields of not more than a few hundred oersted. An exact calculation in this case is rather complicated ([20]).

It should be noted that line b) lies only a few tens of oersted lower than the line of atomic oxygen. For comparison we observed a carbon monoxide flame with an addition of hydrogen sulfide, in which H and O atoms and the OH radical are readily detected. The intensities of all three lines in the SO spectrum proved to be equal, as they should be for the above-mentioned transitions and a wave of type H_{011}.

Thus, in a hydrogen sulfide flame, appreciable concentrations of atomic hydrogen and oxygen are observed, as well as OH and SO radicals. Of the atoms and radicals participating in the reaction, possible ones are also sulfur atoms, the HS radical, and the S_2O molecule. As already indicated above, the spectrum of S_2O, if it can be observed at all, can only be observed in very large ···

fields ([6]). On our SP-78 magnet, the maximum field attainable at present is 12,000 oersteds.

Under the experimental conditions described earlier, over a fairly wide range of pressures and linear velocities and with the most varied mixture compositions, we were unable to detect the spectrum of the HS radical either under exhaust conditions, when the flame is above the resonator, or under conditions in which the flame is directly in the resonator. In connection with strong pressure broadening, a number of experiments were carried out at pressures somewhat below 1 mm Hg. In addition, we were unable to detect HS in a flame of $2CO+O_2+\alpha H_2S$, in which hydrogen sulfide served as a hydrogen donor, at very small additions. With appreciable additions of hydrogen sulfide, the color of the flame changes and a hydrogen-sulfide flame strongly diluted with CO is obtained. When hydrogen sulfide is added to a hydrogen flame, a decrease in the signals of H, O, and OH is observed, but no new lines appear.

We also made an attempt to detect HS by adding hydrogen sulfide to the products of a hydrogen flame. However, the presence of unburned oxygen led to our obtaining a hydrogen-sulfide flame initiated by H and O atoms and by the OH radical of the hydrogen flame.

In this case it was again possible to observe lines a), b), and c) of the SO radical. Thus, it should be assumed that the concentration of HS must be less than the concentration of OH, and that detection of HS in an H_2S flame requires either increasing the sensitivity of the instrument or increasing the filling factor of the resonator with the electric field. The spectrum of atomic sulfur has so far

not been observed by anyone. It is natural to expect that its spectrum will be identical with the spectrum of atomic oxygen and will lie near line b) of the SO spectrum ([22]). We therefore hope in the near future to check again the line of atomic oxygen, as well as line b) from the observed spectrum. We note here some kinetic regularities in the behavior of OH and SO.

The OH spectrum can be observed only at small linear flow velocities, i.e., when the contact time is large and the induction period has already ended. Under these conditions the SO signal is rather weak. At small contact times, sulfur monoxide is observed, while hydroxyl is absent. The impression is created that at the initial moment there is appreciable accumulation of SO, and only then do chains involving OH develop. All three lines a), b), and c) show noticeable broadening with increasing pressure and at a pressure of 2-3 mm Hg have a width of not less than 10 oersteds; moreover, the greater width of lines a) and b) is apparently associated with the presence of molecular oxygen.

The SO spectrum appears at the ratio $\alpha = H_2S/O_2 = 15\%$ and disappears at $\alpha = 50\%$, reaching a maximum in the region $\alpha = 25\%$. As the temperature of the preheater is raised, the maximum of the SO signal shifts toward larger α.

It should be noted that our qualitative explanation of the three lines of the SO spectrum agrees with the interpretation of the spectrum obtained by Danielson and Dorain ([23]) in the discharge of SO_2 vapors. Work ([23]) became known to us only after this article had been written.

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CITED LITERATURE

[1] G. C. Dausmanis, T. M. Sanders, C. H. Townes, Phys. Rev., **100**, 1735 (1955). [2] H. E. Radford, Nuovo Cimento, **14**, 245 (1959). [3] H. E. Radford, M. Linzer, Phys. Rev. Let., **10**, No. 10, 443 (1963). [4] C. C. McDonald, J. Chem. Phys., **39**, No. 10, 2587 (1963). [5] E. X. Powell, D. R. Lide, J. Chem. Phys., **41**, 1413 (1964). [6] D. J. Meschi, J. Mol. Spectr., **3**, 405 (1959). [7] Roger Kewley, J.

Chem. Phys., **39**, 2856 (1963). **8** V. V. Azatyan, V. N. Panfilov, A. B. Nalbandyan, *Kinetics and Catalysis*, **2**, issue 2, 295 (1961). **9** V. V. Azatyan et al., *DAN*, **141**, 129 (1961). **10** V. N. Balakhnin et al., *DAN*, **154**, 883 (1964). **11** V. N. Balakhnin et al., *DAN*, **154**, 1142 (1964). **12** L. Yu. Rusin, A. M. Chaikin, A. E. Shilov, *Kinetics and Catalysis*, **5**, 1121 (1964). **13** N. M. Emanuel, *ZhFKh*, **14**, 863 (1940). **14** F. Waidau, *Proc. Roy. Soc. London*, **A132**, 320 (1931). **15** R. G. W. Norrisch, A. P. Leelenberg, *Proc. Roy. Soc.*, **A240**, 293 (1957). **16** D. G. H. Marsden, *Canad. J. Chem.*, **41**, No. 10, 2607 (1963). **17** A. G. Gaydon, G. Whittingham, *Proc. Roy. Soc.*, **A189**, 313 (1947). **18** N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Publishing House of

the USSR Academy of Sciences, 1958. **19** G. A. Sachyan, A. B. Nalbandyan, *Izv. AN SSSR, Ser. Khim.*, **7**, 1964, 1341. **20** Ch. Tauss, A. Sh. Shavlov, *Radiospectroscopy*, IL, 1959. **21** M. Tinham, M. N. P. Strandberg, *Phys. Rev.*, **97**, No. 4, 951 (1955). **22** M. E. Radford, V. W. Hughes, *Phys. Rev.*, **114**, 1274 (1959). **23** J. M. Daniels, P. B. Dorain, *J. Chem. Phys.*, **40**, 1160 (1964).

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