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Synthesis of Diatomic Radicals*

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FREE diatomic radicals, studied for many years by the methods of optical spectroscopy, have mostly resisted similar attempts to observe their microwave spectra. What we have lacked has been a systematic method of producing and maintaining cool, reasonably dense, gases of their simple but extremely reactive molecules. In this letter we wish to report the discovery of such a method, and to give some preliminary results obtained with it. Among these results are microwave spectra which, to our knowledge, are the first discrete spectra of any kind recorded for the molecules SeH and TeH.

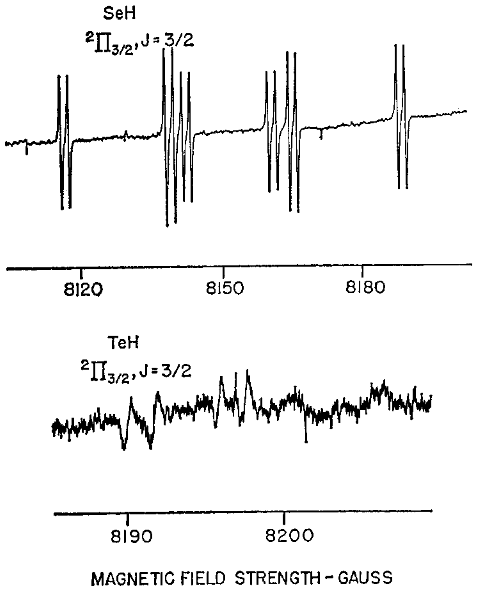

FIG. 1. Paramagnetic resonance spectra of free SeH and TeH radicals, recorded at 9215 Mc/sec with a superheterodyne reflection-type spectrometer. Only the four strongest lines of the TeH spectrum are shown.

These two new spectra, shown in Fig. 1, were observed when the products of an electrical discharge in hydrogen gas were conducted through a microwave-absorption cell whose walls had been coated with elemental selenium in the one case, elemental tellurium in the other. Similar trials with a sulfur-lined absorption cell generated the microwave spectrum of SH[1,2] when the inlet gas was hydrogen and of SO[1] when the inlet gas was oxygen. This sort of chemical procedure is, of course, not new but has been used for decades as a means of studying reactions between atoms and solids.[3] What is now evident, however, is that these reactions can evolve diatomic radicals in large numbers, sufficient for microwave-absorption spectroscopy and, perhaps, optical absorption spectroscopy as well. In Table I are listed the maximum partial pressures of radicals mentioned above, as determined by comparing microwave-absorption intensities with those of the stable radical NO at a known pressure. Poor knowledge of electric dipole moments limits the reliability of partial pressures determined in this way, and the absolute values given in Table I are probably correct only in order of magnitude.

TABLE I. Partial pressures of synthesized radicals, estimated from microwave absorption intensities. Total pressure in all cases is approximately 100 μ Hg.

Radical	Relative microwave absorption intensity	Permanent electric dipole moment (10^{-8} esu)	Partial pressure (μ Hg)
SO	1550	1.4[a]	50
SH	240	0.3[b]	10
SeH	60	0.2[b]	5
TeH	3	0.1[b]	1

[a] D. R. Lide, Jr. (private communication).

[b] Crude estimates based on electronegativities [L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed. p. 98].

Paramagnetic resonance was used as the detection method, rather than conventional microwave absorption, both because of the superior sensitivity that can be realized with a fixed-frequency spectrometer and because the locations of paramagnetic resonance spectra can be predicted more accurately from existing optical data. This predictability of the spectra lightens the task of detecting and identifying new radicals although, conversely, it limits the amount of information on molecular structure that is obtainable from the spectra. For radicals in $^2\Pi$ states the molecular g-factor Λ-type doubling, and hyperfine structure can be found by direct measurement of line positions, while the fine structure and rotational constants can be estimated from second-order shifts of the lines. Preliminary values of these quantities for SeH and TeH are given in Table II. The results for TeH are tentative, since several of the lines in this very weak spectrum have not been de-

TABLE II. Molecular constants of the $^2\Pi_{3/2}$, $J=\frac{3}{2}$ ground states of SeH and TeH, derived from paramagnetic resonance spectra.

Molecular constant[a]	SeH	TeH
Molecular g factor, $\bar{g}_J$	0.80800 ± 0.00010	0.80366 ± 0.00020
Λ-type doubling frequency, ν_Λ	(14.4 ± 0.1) Mc/sec	(6.6 ± 0.2) Mc/sec
Hyperfine structure coupling constant, A_1	(1.9 ± 0.1) Mc/sec	(1.8 ± 0.2) Mc/sec
Rotational constant, B_0	(7.98 ± 0.08) cm^{-1}	(5.56 ± 0.15) cm^{-1}
Spin–orbit constant, A_0	$-(1600\pm50)$ cm^{-1}	$-(2250\pm200)$ cm^{-1}

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

tected with certainty as yet. For SO, which has a $^3\Sigma$ ground state, the paramagnetic resonance spectrum is complicated by severe magnetic uncoupling effects, and no analysis has been attempted. Conventional microwave absorption measurements, which should yield better structural information on these radicals, are underway in this laboratory, as are also searches for paramagnetic resonance spectra of other diatomic radicals, employing various gas–solid combinations. Radicals which have been searched for without success, in room-temperature experiments, include SeO, NS, SCl, PO, CH, SiH, and SiCl.

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[1] SH also can be produced by adding hydrogen sulfide gas to the products of an electric discharge in hydrogen or water vapor [C. C. McDonald, J. Chem. Phys. **39,** 2587 (1963)], but the present method yields concentrations larger by as much as an order of magnitude. Since the gas-phase reaction also, under certain conditions, deposits solid sulfur, it may be that the essential mechanism of SH production is the same in both cases.

[2] H. E. Radford and M. Linzer, Phys. Rev. Letters **10,** 443 (1963).

[3] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1953).

Polarization of Laser Light Scattered by Gases

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Accurate determination of the polarization of light scattered by gases requires a parallel, monochromatic beam of light of the maximum intensity. We use a continuous He–Ne gas laser ($\lambda=6328$ Å), placing the gas sample *inside* the resonant cavity, where a very high intensity is available (equivalent to a beam of approximately 100 mW). Figure 1 represents the apparatus. The resonant cavity is defined by the two mirrors, between which the standing wave of linearly polarized light is set up, the plane of polarization being determined by the orientation of the Brewster angle windows on the discharge tube (containing the He–Ne mixture) and the scattering cell. The windows are optically contacted onto the cell, which is made of silica, painted black on the outside. The discharge tube is activated by a rf oscillator, using external electrodes.

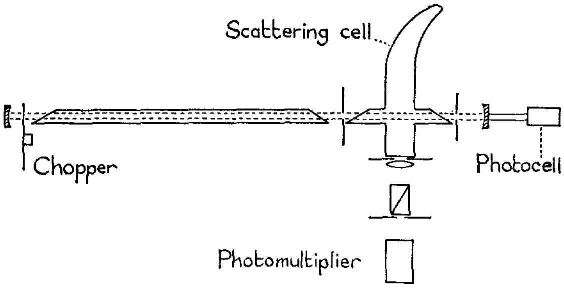

Fig. 1. Laser and scattering cell. The Brewster angle windows are shown twisted through 90°.

Table I. Depolarization ratios ρ_0 at 1 atm and 20°C, and polarizabilities for $\lambda=6328$ Å.

	$10^2\cdot\rho_0$	α (Å^3)	$(\alpha_{\parallel}-\alpha_\perp)$ (Å^3)
Ar	0.041 ± 0.005	1.663	0
Xe	0.043 ± 0.001	4.112	0
SF$_6$	0.045 ± 0.001	4.52	<0.02
H$_2$	0.93 ± 0.05	0.823	0.310 ± 0.007
N$_2$	1.05 ± 0.01	1.767	0.706 ± 0.004
O$_2$	3.09 ± 0.02	1.598	1.111 ± 0.004
CO$_2$	4.13 ± 0.02	2.635	2.133 ± 0.005

Light scattered in a direction normal to the plane of polarization is collected by a lens and passed through the Glan–Thompson analyzer. The intensities polarized parallel and perpendicular to the electric vector of the laser beam are measured successively, both with the cell filled with gas ($I_{||}$, $I_\perp$), and evacuated ($I_{||}^0$, $I_\perp^0$); the depolarization ratio $\rho_0=(I_\perp-I_\perp^0)/(I_{||}-I_{||}^0)$. The lens, having a stop in its focal plane, only accepts light diverging from the lens axis by less than $2\frac{1}{2}°$. Stray light from the side walls of the cell is rejected, giving a low background ($I_\perp^0/I_\perp=0.02$ for 1 atm of CO$_2$). Better collimation of scattered light is unnecessary with a polarized primary beam.

The light is detected by a red-sensitive photomultiplier (EMI 9558A) as an alternating signal (the laser is chopped at 325 cps), amplified and balanced against a reference signal derived from a photocell monitoring the main beam. A phase-sensitive device is used as null detector.

Gas samples are taken from commercial cylinders and freed from dust by passage through a sintered glass filter, of average pore size 2 μ.

The scattered light includes Raman lines as well as the Rayleigh line. The classical formula relating the molecular anisotropy κ to ρ_0,

$$\kappa^2=(\alpha_{||}-\alpha_\perp)^2/9\alpha^2=5\rho_0/(3-4\rho_0),$$

refers to the depolarization of the Rayleigh and pure rotational Raman lines taken together. Inclusion of the vibrational spectrum causes a small error; use of an interference filter to select the Rayleigh line affects the strongly polarized rotational lines and so causes a larger error.

ρ_0 for Ar and Xe should be zero at 1 atm; the observed depolarization (see Table I), attributed to apparatus defects, constitutes a zero error. The figure for SF$_6$ refers to the Rayleigh line, the Raman vibrational lines being excluded by an interference filter whose passband has a half-width of 200 cm^{-1}. There are no rotational lines.