

Gas-phase Electron Resonance Spectra of SF, SeF, SeO ($^3\Sigma$ and $^1\Delta$) and IO

By A. CARRINGTON,* G. N. CURRIE, P. N. DYER, D. H. LEVY, and T. A. MILLER

(Department of Theoretical Chemistry, University of Cambridge)

WE report the detection of the gas-phase electron resonance spectra of SF, SeF, SeO ($^3\Sigma$ and $^1\Delta$), and IO. Using techniques which have been described elsewhere,¹ we have studied reactions between atoms and secondary gases, the mixing occurring inside the electron resonance microwave cavity.

SF, SeF, and IO have $^2\Pi_{3/2}$ ground states and we

detect the spectra of molecules in the lowest rotational level, with $J = 3/2$. SF and SeF were obtained by reaction of fluorine atoms (produced by passing CF_4 through a microwave discharge²) with OCS and OCSe respectively. Both spectra consist of six lines occurring between 7500 and 8500 gauss (microwave frequency ~ 8700 Mc./sec.), which arise from the second-order Zeeman splitting and

the ^{19}F hyperfine interaction (nuclear spin $\frac{1}{2}$). The spectrum of IO was observed by reaction of oxygen atoms with CF_3I , and consists of eighteen lines, arising from the second-order Zeeman splitting and nuclear hyperfine splitting from ^{127}I (nuclear spin $5/2$). Analysis of these three spectra yields the rotational constants B_0 (and hence the bond lengths); we are also able to observe Stark splittings in the spectra³ and hence the electric dipole moments will be measurable. In each case we obtain the magnetic hyperfine component along the internuclear axis,⁴ and for IO the ^{127}I electric quadrupole coupling constant is also determined. The radicals SF and SeF do not

constant. In the case of SeO in its $^3\Sigma$ ground state we observe a group of four lines arising from the Zeeman components of the $J = 1, K = 2 \longleftrightarrow J = 1, K = 1$ transition.

All of the spectra described in this note, except that of $^3\Sigma\text{-SeO}$, show a first-order Stark effect and were detected using a microwave cavity which employs 100 kc./sec. Stark modulation.^{3,5} $^3\Sigma\text{-SeO}$ has only a second-order Stark effect and was therefore detected using a 100 kc./sec. Zeeman-modulated cavity.⁶

The Table presents a brief summary of the gaseous free-radicals which have so far been detected by electron resonance.

TABLE

Summary of gaseous free-radicals whose electron resonance spectra have been detected.

Radical	Electronic state	Method	Reference
OH	$^2\Pi_{3/2}$	H_2O discharge	7
	$^2\Pi_{1/2}$	H_2O discharge	8
SH	$^2\Pi_{3/2}$	H_2O discharge + H_2S	9, 10
SeH	$^2\Pi_{3/2}$	Se(solid) + H	10
TeH	$^2\Pi_{3/2}$	Te(solid) + H	10
SO	$^3\Sigma$	SO_2 discharge; $\text{OCS} + \text{O}$	11, 12
	$^1\Delta$	$\text{OCS} + \text{O} + ^1\Delta\text{-O}_2$	13
ClO	$^2\Pi_{3/2}$	Cl_2/O_2 discharge	1, 4
BrO	$^2\Pi_{3/2}$	$\text{Br}_2 + \text{O}$	1, 14
IO	$^2\Pi_{3/2}$	$\text{CF}_3\text{I} + \text{O}$	this work
NS	$^2\Pi_{3/2}$	$\text{H}_2\text{S} + \text{N}$	1, 15
SF	$^2\Pi_{3/2}$	$\text{OCS} + \text{F}$	this work
SeF	$^2\Pi_{3/2}$	$\text{OCSe} + \text{F}$	this work
SeO	$^3\Sigma$	$\text{OCSe} + \text{O}$	this work
	$^1\Delta$	$\text{OCSe} + \text{O} + ^1\Delta\text{-O}_2$	this work

appear to have been detected previously by any physical method.

The spectrum of SeO was observed by reaction of OCSe with the products of a microwave discharge in O_2 . Four lines between 9 and 10 kilogauss arise from SeO in its excited $^1\Delta_2$, $J = 2$ state and the separation between them yields the rotational

D. H. L. thanks the NSF for NATO Post-Doctoral Fellowship, T. A. M. thanks the Marshall Commissioners for a Marshall Scholarship, G. N. C. thanks B.P. for a Post-graduate Scholarship and P. N. D. thanks the S.R.C. for a studentship.

(Received, May 22nd, 1967; Com. 507.)

¹ A. Carrington and D. H. Levy, *J. Chem. Phys.*, 1966, **44**, 1298; A. Carrington and D. H. Levy, *J. Phys. Chem.*, 1967, **71**, 2.

² A. Carrington, D. H. Levy, and T. A. Miller, *J. Chem. Phys.*, 1966, **45**, 4093.

³ A. Carrington, D. H. Levy, and T. A. Miller, *J. Chem. Phys.*, 1966, **45**, 3450.

⁴ A. Carrington, P. N. Dyer, and D. H. Levy, *J. Chem. Phys.*, to be published.

⁵ A. Carrington, D. H. Levy, and T. A. Miller, *Rev. Sci. Instr.*, to be published.

⁶ A. Carrington, *Proc. Roy. Soc.*, to be published.

⁷ H. E. Radford, *Phys. Rev.*, 1960, **122**, 114.

⁸ H. E. Radford, *Phys. Rev.*, 1962, **126**, 1035.

⁹ C. C. McDonald, *J. Chem. Phys.*, 1963, **39**, 2587.

¹⁰ H. E. Radford, *J. Chem. Phys.*, 1964, **40**, 2732.

¹¹ J. M. Daniels and P. B. Dorain, *J. Chem. Phys.*, 1964, **40**, 1160; 1966, **45**, 26.

¹² A. Carrington, D. H. Levy, and T. A. Miller, *Proc. Roy. Soc.*, 1967, **A, 298**, 340.

¹³ A. Carrington, D. H. Levy, and T. A. Miller, *Proc. Roy. Soc.*, 1966, **A, 293**, 108.

¹⁴ A. Carrington, P. N. Dyer, and C. H. Levy, *J. Chem. Phys.*, to be published.

¹⁵ A. Carrington, D. H. Levy, and J. C. Robertson, *J. Chem. Phys.*, to be published.