of perhaps 3×10^{-2} second can be studied. Another usually more important limitation is the minimum concentration of A which can be detected. Assuming this to be 10^{-6} *M*, reactions with half-lives of 7×10^{-2} second or more can be studied. We are using the method to study some rapid rates involving the reactions of complex ions.

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Dipole Moment Variations in the Hydrogen Halide Molecules[1]

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A two-electron approximation similar to Robinson's method[2] has been applied to the hydrogen halide molecules to determine the sign of $\partial\mu/\partial r$, whose magnitude can be obtained from infrared intensity or dispersion measurements. Using a linear combination of normalized covalent and ionic functions, respectively, of Heitler–London type and Weinbaum type, an equation for μ is obtained in terms of hydrogen-like atomic orbitals and an arbitrary coefficient of the ionic function, λ. 1s and pure p_z orbitals are used, respectively, for hydrogen and halide atoms. Differentiation of this equation with respect to internuclear distance, assuming λ to be a constant, allows one to calculate $\partial\mu/\partial r$. The values of the integrals involved and the parameters necessary are given in Table I. The origin of the coördinate system is chosen at the center of the internuclear distance with the positive *z*-axis going through the hydrogen atom. Effective nuclear charges of the halide atoms were taken from the work of Pauling and Sherman.[3]

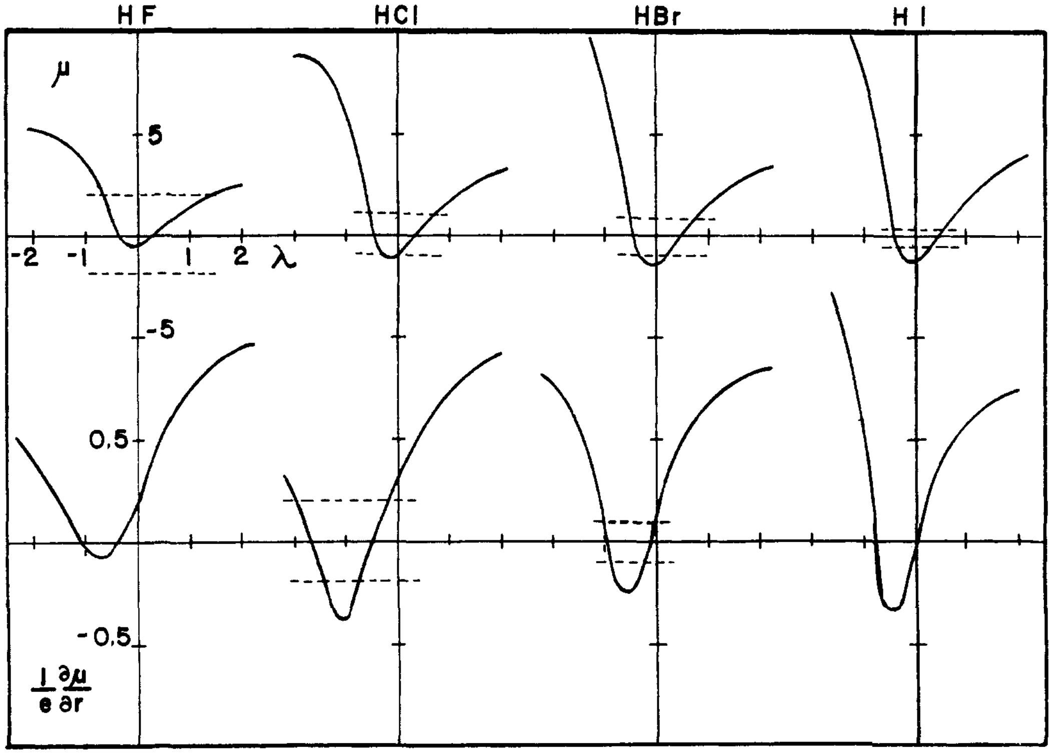

Fig. 1.—Variations of μ and $(1/e)(\partial\mu/\partial r)$ with respect to λ for the hydrogen halide molecules.

TABLE I

VALUE OF INTEGRALS AND PARAMETERS

	r(Å.)	$\Delta = \int sp_z\, d\tau$	$\chi^a = \int sp_z\, z d\tau$	$\partial\Delta/\partial r^a$	$\partial\chi/\partial r$
HF	0.9171	0.3296	0.2667	−0.1167	−0.2514
HCl	1.275	.4852	.4939	− .1204	− .2874
HBr	1.414	.4922	.6988	− .0008040	− .1858
HI	1.604	.4294	.7728	+ .07104	− .04989

[a] In atomic units, $a_0 = 0.5282$ Å.

Results and Discussion.—In Fig. 1 μ and $(1/e)$ $(\partial\mu/\partial r)$ are plotted as functions of λ for the compounds. The observed μ and $(1/e)$ $(\partial\mu/\partial r)$ are indicated by the horizontal dashed lines. No reliable intensities are known for HF or HI. However, $|\partial\mu/\partial r|$ for HI is probably less than that for HBr.[4] Both positive and negative possibilities of the experimental values are shown.

The λ values determined from the observed μ are used to establish the sign of $\partial\mu/\partial r$. The case of μ negative can be ruled out by Robinson's argument; namely, one obtains increasing λ for the sequence HCl and HI implying increasing ionicity in this direction. Furthermore, $|\partial\mu/\partial r|$ increases in the same direction contrary to the observed trend. For positive μ, if λ is negative $|\partial\mu/\partial r|$ again increases in the wrong direction. Moreover, the ionic characters one obtains from these λ values are too large. For positive λ one obtains $\partial\mu/\partial r$ and ionic character

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[1] Presented at the Northwest Regional A.C.S. Meeting, Washington State College, Pullman, Wash., June 12, 1953.

[2] D. Z. Robinson, *J. Chem. Phys.*, **17**, 1022 (1949).

[3] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

[4] E. Bartholomé, *Z. physik. Chem.*, **B23**, 131 (1933).

defined as $\lambda^2[1 + \lambda^2 + 4\lambda\Delta(2 + 2\Delta^2)^{-1/2}]^{-1}$ given in Table II.

TABLE II

	λ	Ionic character, %	$(1/e)(\partial\mu/\partial r)$
HF	1.325	44.7	0.8686
HCl	0.7319	22.0	.6750
HBr	.7169	21.3	.6002
HI	.5868	17.2	.4307

Both the ionic character and $\partial\mu/\partial r$ decrease in the same direction. The magnitudes of the ionic characters are not too unreasonable. The $\partial\mu/\partial r$ values are larger than the experimental values, but one notes qualitative agreement. The values for HCl and HBr are of the same order of magnitude and the HI value is less than either of the former. The ratio of the values from HCl to HI is about 1:0.9:0.6 while the experimental ratio is about 1:0.6:0.4.

In view of the approximation used and the qualitative agreement obtained, one may conclude that the sign of the experimental $\partial\mu/\partial r$ is positive. This choice of sign is in agreement with the results of Smith and Eyring,[5] but not with those of Hammer and Rollefson,[6] Warhurst[7] or Bell and Coop.[8,9]

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(5) R. P. Smith and H. Eyring, THIS JOURNAL, **73**, 5512 (1951).

(6) C. F. Hammer and R. Rollefson, "Symposium on Molecular Structure and Spectroscopy," Ohio State University, Columbus, Ohio, June 12, 1951.

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(8) R. P. Bell and I. E. Coop, *ibid.*, **34**, 209 (1938).

(9) NOTE ADDED IN PROOF.—Herman, Silverman and Wallis, Am. Phys. Soc. meeting, New York, Jan. 28, 1954, have concluded, from a study of infrared vibration-rotation line intensities in HCl, that μ and $\partial\mu/\partial r$ have the same sign.

The Absorption Spectrum of Cs_2CoCl_4 at Liquid Nitrogen Temperatures

BY LEONARD I. KATZIN

RECEIVED FEBRUARY 8, 1954

In continuation of earlier reported work on reflection spectra,[1] it has been possible to obtain absorption spectra for Cs_2CoCl_4 in the solid state, both at room temperature and at liquid nitrogen temperatures, under transmission conditions of good resolution. This makes it possible better to compare the spectrum of the $CoCl_4^=$ group, which has been crystallographically identified in the solid material,[2] and the spectrum of what has always been assumed to be this group, found in appropriate "blue" Co(II) solutions. The previous attempts to obtain similar spectra of solids containing the cobaltous halide complex grouping[3] have not been such as to allow any detailed description of the spectrum to be made.

Experimental

A recrystallized, dry sample of Cs_2CoCl_4, prepared originally by crystallization from water of a $CsCl-CoCl_2$ mixture,[1] was finely ground, and a small portion was reground with a large amount of KBr. A portion of this mixture was further diluted with KBr, and transparent discs of the two mixtures were prepared by published techniques.[4-6] For observation, the discs were mounted in a special evacuated cell which allowed refrigeration with liquid nitrogen.[7] Observations were made, both at room temperature and at liquid nitrogen temperature, with the aid of the Cary recording spectrophotometer. Observations were made at room temperature alone of solutions of cobaltous chloride in concentrated HCl, for comparison with the absorption of the solid preparations. The results are shown in Figs. 1–3.

Grateful acknowledgement is made of the loan of apparatus and of assistance in preparation of the solid samples by Dieter Gruen, and of assistance in obtaining the traces by Peter Pringsheim and James C. Hindman.

Discussion

In Fig. 1 are shown three curves for different concentrations of cobaltous chloride in concentrated HCl. The relative intensities of the strong absorption around 690 mμ and of the weaker peaks below 610 mμ are seen by comparing the heights of the 533 mμ absorption in the three curves. The fourth curve, to show the difference of the "red" absorption, is for cobaltous nitrate in water. The essential features of the chloride absorption do not differ significantly from similar figures which have been published by earlier workers.[8-10]

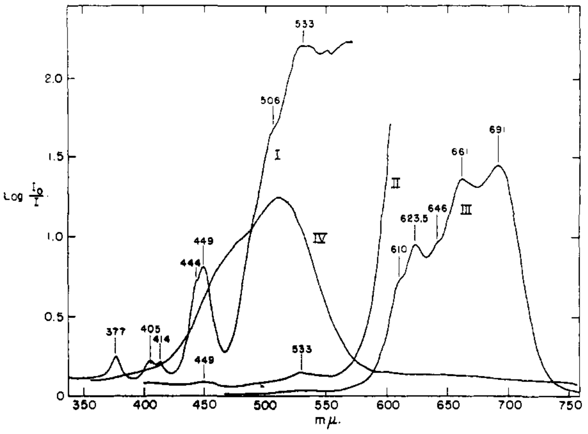

Fig. 1.—Absorption spectra of cobalt solutions. Curves I, II, III, successively lower concentrations of cobaltous chloride in concentrated HCl. Curve IV, cobaltous nitrate in water, to show characteristic difference of "red" cobalt absorption.

The solid preparations of Cs_2CoCl_4 at liquid nitrogen temperatures show peaks greatly sharpened, and slightly shifted to lower wave lengths, compared to the same material at room temperature (not shown). Resolution of groups of peaks, such as the one around 450 mμ, is thereby greatly improved. The most definite difference from the spectrum of the HCl solution is in the relative heights of the components of the main absorption peak between 600 and 700 mμ. Though the effect

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(2) Stanley Siegel, private communication.

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