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Photoelectric Intensity Measurements of Raman Spectra

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An instrument for the direct photoelectric recording of Raman spectra of liquids is described together with the results obtained for CCl_4, $CHCl_3$, CH_2Cl_2, and C_6H_6. The precision of the results was tested by eight recorded spectrograms of $CHCl_3$. The intensity ratios of anti-Stokes to Stokes lines were found to be in good agreement with theoretical values. Approximate values of the change of the bond polarizability of the $C-Cl$ bond in CCl_4 and the $C-H$ bond in C_6H_6 caused by valence vibrations are calculated from the intensity data.

INTRODUCTION

QUANTITATIVE data on the relative intensities and polarization states of Raman lines are scanty and for the most part unsatisfactory in accuracy because of experimental difficulties and the inadequate theoretical treatment. Since the classical work of Placzek little progress was made in the field until recently, when Wolkenstein,[1] advanced for the calculation of intensities and polarization states for vibrational lines a semi-empirical theory which has yielded values in fair agreement with experimental results. Additional experimental data of improved accuracy are, however, essential to progress in this field.

The use of the photo-multiplier tube in the measurement of Raman line intensities and depolarization factors was introduced by Rank and his associates.[2-4] All previous experiments, except one with a photon counter,[5] employed a photographic photometric technique which is tedious and not very accurate because of the logarithmic character of emulsion response, fluctuations in background on the densitometric tracing caused by the granularity of the emulsion, fluctuations of the standard light source during emulsion calibration exposures, and local variations of the sensitivity and the degree of development of the photographic plate. Accord-

ing to Reitz,[6] the precision attained by the photographic method in careful experiments on Raman spectra is about ±14 percent. The experimental problem can be greatly simplified by the application of the photoelectric technique provided due care is taken to reduce fluctuations in the dark current to insignificance. The use of the photo-multiplier tube[7] is required by the extremely low level of light intensity encountered in Raman work; the linearity of its response is well established, particularly at low levels of illumination, and the only calibration required is its spectral sensitivity. The present work is a preliminary report on relative intensity measurements on the Raman spectra of CCl_4, $CHCl_3$, CH_2Cl_2, and C_6H_6 with a nine-stage photo-multiplier and d.c. amplifier system.

EXPERIMENTAL DETAILS

Photo-Multiplier and Power Supply

An RCA 1P21 photo-multiplier tube with base removed was mounted inside a glass jar fitted with a side arm carrying a glass window, in front of which was mounted a fixed slit of width 0.1 mm. Some dehydrite was placed inside the jar to minimize surface leakage. At room temperature the tube was found to have a dark current of the order of 10^{-8} ampere at an accelerating voltage of 110 volts on the dynodes; since the dark current is due mainly to thermionic emission, cooling with solid carbon dioxide was resorted to with a resultant reduction in dark current to 10^{-11} ampere. The mean fluctuation observed in the dark current was ±5 percent

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with peak fluctuations amounting to ±20 percent. A heating coil was provided near the end of the side arm to prevent condensation of moisture on the window.

Since the secondary emission phenomenon depends mainly on the energy of the primary electrons, the output dark current and the over-all amplification vary markedly with the accelerating voltage on the dynodes as shown in Fig. 1. It is apparent that the voltage supply must be held constant within 0.2 percent or better if 1 percent accuracy in the intensity measurement is to be possible. A special power supply was constructed for this purpose using the degenerative regulator circuit shown in Fig. 2. The output voltage was found to be constant within 0.1 percent for line voltage fluctuations from 100 to 120 volts, and the voltage supplied to the dynodes may be continuously varied by adjustment of R_{12}.

d.c. Amplifier and Recording Device

Since the lowest current to be measured was of the order of 10^{-11} ampere, a d.c. amplifier employing standard radio tubes was adequate. Two RCA-38 tubes operating at reduced filament temperature were used in the balanced circuit shown in Fig. 3. The bias of the active tube was

FIG. 1. Relative amplification and dark current at various accelerating voltages on dynodes.
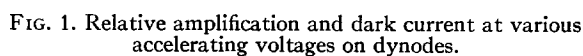
set at −1.20 volt, where the grid current is less than 4×10^{-12} ampere, and the bias of the balancing tube was adjusted so that a change in plate voltage supply from 20 to 30 volts would not produce a disturbance in the plate current balance greater than 0.1 microampere. Degeneration was employed to improve linearity of response. The output of the amplifier was fed
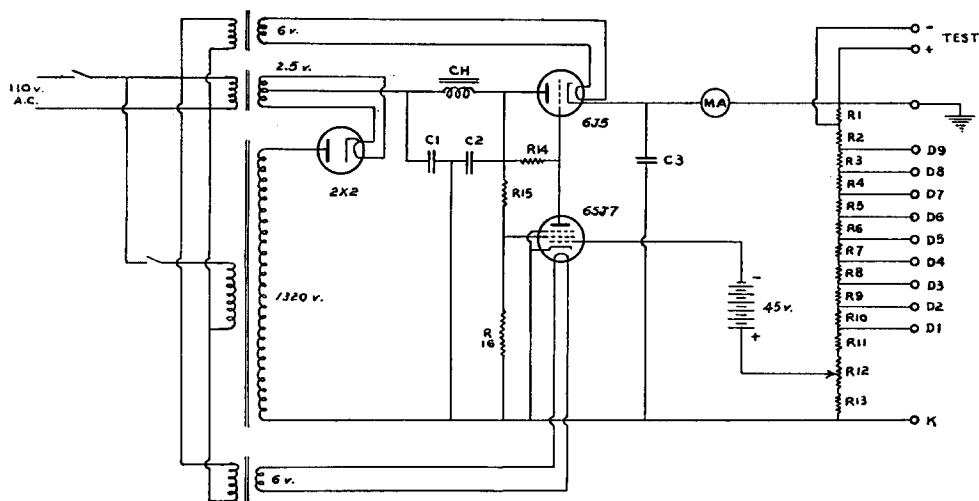
FIG. 2. Circuit of the photo-multiplier power supply.

R1	250 ohm	R14	0.5 megohm
R2	30000 ohm	R15	5.0 megohm
R3–R10	25000 ohm	R16	0.1 megohm
R11	7000 ohm	C1–C3	2 mf 2000 v
R12	10000 ohm	CH	300 H, 7.5-ma choke
R13	8000 ohm	MA	0–10-ma meter
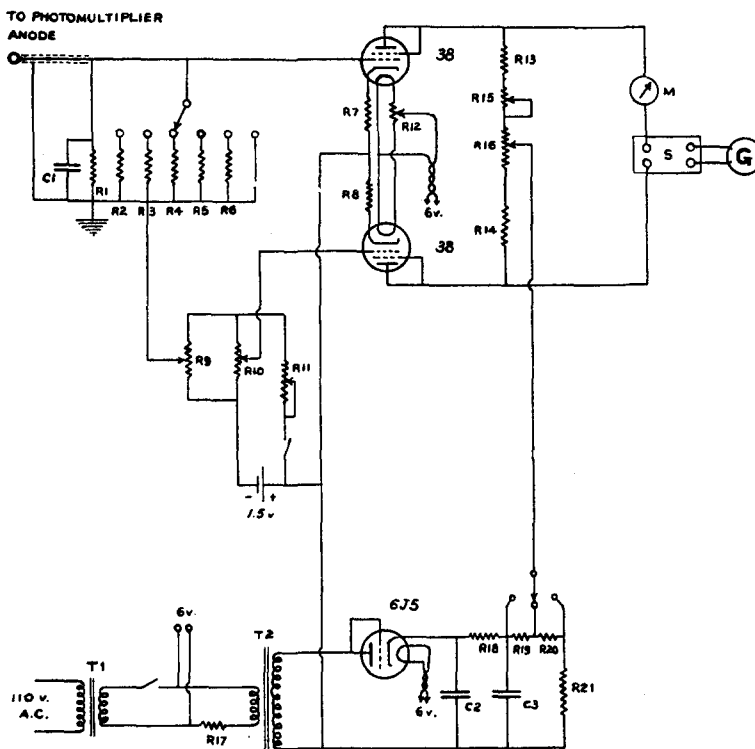
FIG. 3. Circuit for the d.c. amplifier.

R1	100 megohm	R17	5 ohm
R2	10 megohm	R18	5000 ohm
R3	1 megohm	R19, R20	1500 ohm
R4	0.5 megohm	R21	8000 ohm
R5	0.1 megohm	C1	.01 mf
R6	50000 ohm	C2, C3	24 mf, 150 v
R7, R8	1000 ohm	T1	6-v constant voltage transformer
R9–R11	800 ohm	T2	6-v filament transformer
R12	10 ohm	M	0–50 microammeter
R13, R14	50000 ohm	S	10000-ohm universal shunt
R15	400 ohm	G	recording galvanometer
R16	10000 ohm		

through a 0–50 microammeter for direct indication to a short period galvanometer used at reduced sensitivity. Deflections of the galvanometer light beam at a distance of one meter were recorded photographically, and the complete system was calibrated against input voltages supplied by a potentiometer circuit. The response was found to be linear within one percent.

The output current from the photo-multiplier was fed into the amplifier by coaxial cable; the tubes and the input circuit were shielded in a desiccated metal box. Six input resistors were provided for varying the gain of the amplifier, which is 10^4 at 100 megohm input resistance, and were selected to make convenient the change from measurement of intensity of Raman to Rayleigh scattering. A 0.01 mf shunt capacitor was introduced to integrate out the high frequency fluctuations in the photo-multiplier tube anode current. The amplifier was found to be very stable with practically no drift after a warm-up period of about 20 minutes.

Experimental Lay-Out

The Hg λ4358A line from six G.E. H-2 mercury vapor lamps was employed for excitation. The filter solution and spectrograph used have been described previously.[8] An entrance slit of width 0.1 mm was employed. The refrigerated photo-multiplier tube was mounted on a carriage constructed by Mr. L. K. Henke, laboratory chief mechanician, and scanned the focal plane of the camera lens at a speed of 1

[8] J. Y. Chien, J. Am. Chem. Soc. 69, 20 (1947).

mm/min. The recording photographic plate or paper was moved at the rate of 5 mm/min. When the position of the exciting line was reached, as indicated by the microammeter, the gain of the amplifier was reduced manually to a lower range. The gain of the photo-multiplier was adjusted for each sample under investigation by selecting the proper accelerating voltage on the dynodes so that strong Raman lines gave a deflection of ca 100 mm on the recording plate. An accelerating voltage of 115 volts per stage or lower is preferable as it results in lower dark current and less fluctuations.

EXPERIMENTAL RESULTS

Several recorded Raman spectrograms of CCl_4, $CHCl_3$, CH_2Cl_2, and C_6H_6 were made as shown in Fig. 4, and the average results for peak
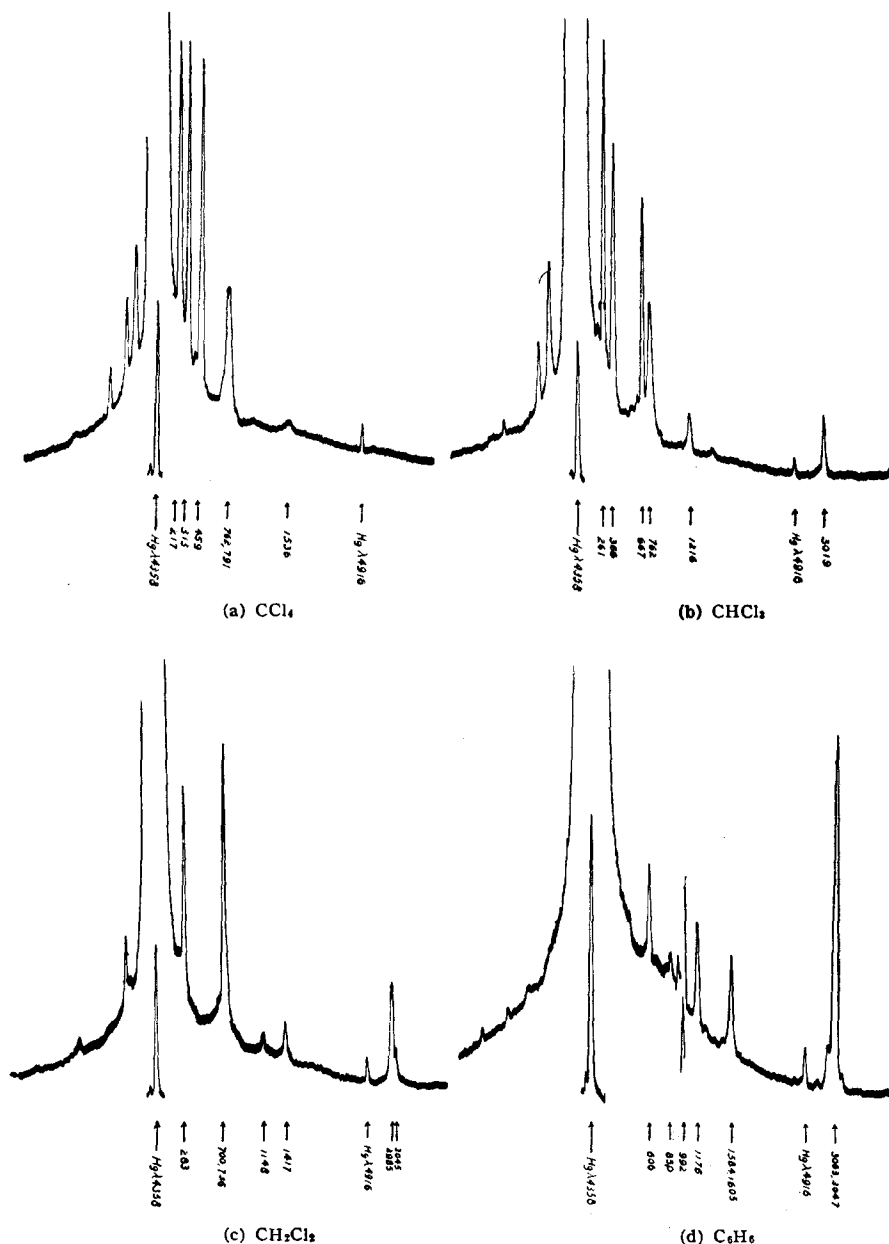

FIG. 4. Recorded Raman spectrograms of CCl_4, $CHCl_3$, CH_2Cl_2, and C_6H_6.

TABLE I. Relative peak intensities of the Raman lines.

(a) CCl₄ (average of 3 runs)

$\Delta\bar{\nu}$	I	Carrelli and Went	Dhar	A. V. Rao	Reitz	Kowalewska	B. P. Rao	Venkateswarlu	Wolkenstein (calc.)
1536	0.4						} 1:7.7	0.9	
791 } 762	4.1	3.8	4.0	3.2	2.5			3.7	2.3
459	10.0	10.0	10.0	10.9	10.0	10.0	10.0	10.0	10.0
313	9.3	13.8	11.3	14.3	9.3	12.9	9.0	8.1	9.2
217	8.2	11.2	6.3	11.9	8.5	10.3	8.0	6.8	13.2
0	1550	620	3330	3960			5000		
−217	3.2								
−313	2.4								
−459	1.2								

(b) CHCl₃ (8 runs)

$\Delta\bar{\nu}$	I	Dhar	A. V. Rao	Kowalewska	Wolkenstein (calc.)
3019	2.9	—	2.7		2.8
1216	1.4	—	1.2		1.9
762	4.4	3.1	2.0	} (1:1.81)	(25.4)
667	7.5	4.4	8.4		13.5
366	7.5	7.4	7.6	5.5	7.6
261	10.0	10.0	10.0	10.0	10.0
0	2530	1850	4000		
−261	3.3				
−366	1.5				
−667	0.4				
−762	0.2				

(c) CH₂Cl₂ (3 runs)

$\Delta\bar{\nu}$	I	Wagner	Wolkenstein (calc.)
3045	1.8	—	1.0
2985	5.4	3.1	2.5
1417	1.4	0.9	0.8
1148	0.7	0.5	0.6
736	3.3	2.0	2.3
700	10.0	10.0	10.0
283	6.7	6.3	6.3
0	3080		
−283	1.9		
−700	0.5		

(d) C₆H₆ (3 runs)

$\Delta\bar{\nu}$	I	Carrelli and Went	Dhar	A. V. Rao	Angus Ingold Leckie	Kohlrausch	Venkateswarlu
3063	} 6.8	} 6.1	—	} 3.7	7.8	} 6.0	} 8.8
3047					4.4		
1605	} 1.4	} 1.7	} 4.0	} 0.6	1.4	1.2	1.0
1584					1.7	1.4	0.7
1176	1.4	2.2	4.7	1.1	2.0	1.7	1.7
992	10.0	10.0	10.0	10.0	10.0	10.0	10.0
850	0.6	0.9	2.0	0.5	0.9	0.7	0.6
606	1.3	1.2	3.7	1.0	1.8	1.5	1.4
0	2100	920	1050	2380			
−606	0.15						
−992	0.13						

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K. Venkateswarlu, Proc. Ind. Acad. Sci. **A21**, 126 (1945).
M. Wolkenstein and M. Eliashevich, Acta Physicochimica (URSS) **20**, 525 (1945).

TABLE II. Relative intensities of the Raman lines of $CHCl_3$ from eight recorded spectrograms.

$\Delta\bar{\nu}$	No. 1	2	3	4	5	6	7	8	Average	Average deviation		Maximum deviation
3019	29	29	29	29	30	—	—	—	29±0.1	0.2 or	1%	1
1216	15	14	14	14	13	—	12	—	14±0.3	0.7	5	2
762	41	44	44	42	45	—	46	48	44±0.7	1.7	4	4
667	70	71	75	79	76	73	70	78	75±1.1	3.0	4	5
366	71	76	79	78	77	78	68	77	75±1.0	2.7	4	7
261				100					100±	—	—	—
0	235×10²	253	276	271	264	—	240	234	253±6	15	6	19
−261	32	36	—	36	35	28	32	31	33±0.9	2.4	7	5
−366	12	16	—	17	18	15	15	11	15±0.7	1.9	13	4
−667	4	4	—	4	4	—	—	—	4±0	0	0	0
−762	3	2	—	1	2	—	—	—	2±0.3	0.5	25	1

intensities are tabulated in Table I, together with values found in the literature. In each case the intensity of the strongest line was arbitrarily fixed at 10. The frequency values of Kohlrausch[9] are used throughout, and a negative sign indicates an anti-Stokes line. The intensities of Rayleigh scattering are also indicated in the table; they are, however, subject to error as a result of wall reflections and scattering from dust particles. All the intensity values tabulated have been corrected for the spectral response of the photo-cathode according to the data of Dieke and Crosswhite.[10]

The accuracy of the measurement is indicated in Table II from the data of eight runs on $CHCl_3$. The average deviation for a single recording is ±5 percent, disregarding very weak lines. The main source of deviation is believed to be variation of the intensity of the source during the run. Further improvement may be obtained by the use of a stabilized power supply for the mercury vapor lamps.

Three runs on CCl_4 with excitation by Hg λ4047A were carried out; water instead of the regular filter solution was circulated through the filter jacket. The relative intensities found are as follows:

$\Delta\bar{\nu}$	Relative intensity
791,762	3.7
459	10.0
313	8.3
217	8.7

The reason for the alternation in the relative intensities of $\Delta\bar{\nu}$ 217 and 313 lines as compared to those observed by 4358A excitation is not immediately obvious.

The validity of the Placzek relation for the ratio of the intensities of anti-Stokes to Stokes lines

$$\frac{I_{AS}}{I_S} = \left(\frac{\bar{\nu}+\Delta\bar{\nu}}{\bar{\nu}-\Delta\bar{\nu}}\right)^4 \exp\left(-\frac{hc}{kT}\Delta\bar{\nu}\right),$$

when the excitation frequency ν is remote from the absorption frequency of the molecule, has been demonstrated previously[11-13] for several cases. The ratios resulting from the intensity values here presented are given in Table III, and are in excellent agreement with the calculated values. The temperature of the liquid was held at 30°C by the circulating filter solution.

TABLE III. Ratio of the intensities of the anti-Stokes to Stokes lines at 30°C.

Substance	$\Delta\bar{\nu}$	I_{AS}/I_S obs.	calc.
CCl_4	217	0.39	0.385
	313	0.26	0.252
	459	0.12	0.118
$CHCl_3$	261	0.33	0.317
	366	0.20	0.200
	667	0.05	0.053
	762	0.05	0.035
CH_2Cl_2	283	0.28	0.288
	700	0.05	0.046
C_6H_6	606	0.11	0.066
	992	0.01	0.013

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REMARKS

Assuming that the polarizability constants of a molecule can be considered as additive bond properties, as demonstrated by Denbigh[14] and assumed in the theory of Wolkenstein,[1] we can evaluate the change of polarizability at the equilibrium inter-atomic distance of the bond caused by the valence vibration of a symmetrical molecule from the intensity of the Raman line of symmetric vibration relative to that of Rayleigh line by the relation,[15]

$$\alpha_{A-B}'^{2} = \alpha_{A-B}^{2}\left(\frac{\tilde{\nu}}{\tilde{\nu}-\Delta\tilde{\nu}}\right)^{4}\frac{I_{R}}{I_{0}}\frac{\rho RT\beta}{M}\frac{8\pi^{2}\mu\Delta\tilde{\nu}c}{h},$$

where α_{A-B} and α_{A-B}' are the bond polarizability and the change of polarizability $(\partial\alpha/\partial r)_{r_0}$ of the bond $A-B$, respectively, μ is the mass of the atom under symmetric vibration, and I_R/I_0 is the ratio of the intensities of Raman to Rayleigh line. The factor $\rho RT\beta/M$, in which ρ is the density, M the molecular weight, and β the isothermal compressibility of the substance, is introduced to compensate for the change of Rayleigh scattering power from the liquid to the gaseous state.[16] The result of such calculations

for the case of the valence vibrations of the $C-Cl$ bond in CCl_4 and the $C-H$ bond in C_6H_6 is as follows:

Bond	C–Cl in CCl$_4$	C–H in C$_6$H$_6$	
Bond polarizability,[14] α	2.61	0.65	$\times 10^{-24}$ cc
$\alpha' = (\partial\alpha/\partial r)_{r_0}$	1.2	0.14	$\times 10^{-24}$ cc/A
Bond distance,[17] r_0	1.76	1.08	A

The compressibility data of Freyer et al.[18] were used in the calculation.

The lowest primary photo-current from the photo-multiplier cathode measurable by the apparatus here described is limited to ca 10^{-16} ampere by the fluctuations in the dark current. In the measurement of the depolarization factors of Raman lines with a more ideal set-up than one employed by Rank et al.,[3] the light intensity encountered would be several times weaker. A liquid air cooled photo-multiplier tube with an appropriately modified amplifier system is being tried in this laboratory.

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