

钱人元学术论文选集

SELECTED WORKS OF

QIAN RENYUAN

中国科学院化学研究所

INSTITUTE OF CHEMISTRY

THE CHINESE ACADEMY OF SCIENCES

钱人元学术论文选集

SELECTED WORKS OF
QIAN RENYUAN

中国科学院化学研究所

INSTITUTE OF CHEMISTRY

THE CHINESE ACADEMY OF SCIENCES



编 选 说 明

1. 本论文选集分 14 个研究领域汇列。
2. 凡对某一领域的研究成果已有综述性论文发表的以综述性论文列入,不再列入个别论文。
3. 同一论文有中文和外文稿分别发表时以中文稿列入。
4. 在目录中每一篇选列的论文题后括弧中号码表示在本书最后的“钱人元著作题录”中的号码。
5. 本选集中也列入几篇以前未经发表的论文,在目录中文题后以(*)表示,另二篇目录中文题后有(+)的是即将在 Macromol. Symp. (1997)刊出的论文。
6. 每篇选列的论文上均表明了原出版刊物名称、年、页。

钱 人 元 简 历

1917年9月19日生于常熟西乡汤家桥(现属张家港)。1931年孝友中学(初中)毕业,1934年苏州中学(高中)化工科毕业,1939年浙江大学化学系毕业。1944—1947年在美国威斯康辛大学化学系进修。1948年回国后历任厦门大学(1948—49)、浙江大学(1949—51)副教授,1951—56年先后任中国科学院物理化学研究所(上海)、应用化学研究所(长春)、有机化学研究所(上海)研究员。1956年迄今任中国科学院化学研究所(北京)研究员,其间于1977—81年任副所长,1981—85年任所长。中国科学院院士(1980)。中国化学会理事长(1982—86),中国化学会高分子学科委员会主任(1986—94),国际纯粹及应用化学协会(IUPAC)高分子学部第二委员会会员(1985—97),第二委员会IV.2.1工作组东亚研究会议主席(1993—95)。太平洋高分子协会(PPF)理事(1990—94)。第三届全国人民代表大会代表,第五、六、七、八届全国政协委员。

他是我国高分子物理化学与高分子物理学研究教学的创建人之一,四十年来在高聚物分子量测定、高分子溶液性质、高聚物表征和剖析、高聚物加工—结构—性质相互关系等方面的研究作出了许多重要贡献。1956年获中国科学院科学奖金三等奖(高聚物分子量测定),1977年被评为中国科学院先进工作者,1978年获全国科学大会奖(高分子溶液性质),1980年获国家发明三等奖(降低丙纶纺丝温度),1987年获中国石油化工总公司科学技术进步奖一等奖(纺丝用聚丙烯树脂的开发、工业生产和应用),1989年获中国科学院自然科学奖一等奖(高聚物结构性能关系的研究的典型事例—聚丙烯纺丝),1991年被评为中国科学院“七·五”重大科研任务先进工作者(聚酯工程塑料),1992年获中国科学院自然科学奖二等奖(主链液晶高聚物的条带织构形成),1994年被评为中国科学院优秀教师。他领导研究的聚丙烯纺丝降温母粒技术曾获日内瓦第14届创造发明和新技术国际博览会银质奖(1986),布鲁塞尔第35届国际发明博览会麦斯塔特副首相大奖及金牌奖(1986)。

七十年代以来在我国创建有机固体电导的研究,对电荷转移复合物晶体和导电高聚物进行了广泛的研究,特别在有机固体中的载流子迁移性质、聚吡咯的聚合机理、分子链结构与质子化问题等作出了重要贡献。1988年和1995年分别获国家自然科学奖二等奖(1988,有机金属导体;1995,导电聚吡咯的研究),1989年和1993年分别获中国科学院自然科学奖一等奖(1989,导电高聚物;1993,导电聚吡咯的研究)。

八十年代以来开展了高分子凝聚态基本物理问题的研究，得到中国科学院与国家自然科学基金委员会的重大项目支持，1992 年列入国家攀登计划项目，他作为项目首席科学家，带领国内优秀高分子物理学家，对高分子从溶液形成固体的凝聚过程、高分子液晶态、高聚物非晶态的链间凝聚缠结与玻璃化转变、非晶态高聚物不同尺度的取向态、高聚物取向态结晶、高分子的单链玻璃体和单链单晶等高分子凝聚态的一些基本物理问题在分子水平上进行富有创新意义的探讨。

七十年代以来他在高分子和有机固体两个研究领域与国际学术界有非常活跃的学术交流活动，担任过多次国际学术会议的国际顾问委员会成员，应邀做过多次国际学术会议的邀请演讲，多次到美国、日本、德国、意大利、荷兰、瑞典、澳大利亚和朝鲜人民民主主义共和国进行学术访问和讲学，前后做过国际学术会议的学术演讲和国外访问学术演讲共百余次。组织过中-美(1979)、中-日(1981, 1984, 1990)、中-德(1986, 1989)、中-意(1989, 1995)、中-英(1992, 1994)、和中-韩(1993, 1995)高分子双边学术讨论会，中-日(1983, 1986, 1989, 1992)有机固体电导及有关现象双边学术讨论会。

基于他在科研工作中对国家的重大贡献于 1994 年获求是杰出科学家奖。由于他在中日高分子学术交流与合作中所起的重要作用，日本高分子学会于 1995 年授与他第一届国际奖。

1940 年以来他共在国内外学术期刊发表研究论文二百五十多篇，综述和书籍专章四十多篇，专著二册，专利二则。

钱人元学术论文选集目录

编选说明

钱人元简历

论文选录

1. Raman 光谱

Raman spectra of aqueous solutions of potassium thiocyanate (3) 1

硫代氰酸钾溶液的粘度 (26) 4

Photoelectric intensity measurements of Raman spectra (4) 5

2. 化学动力学

Kinetic analysis of irreversible consecutive reactions (7) 12

On the probability formulation of chemical reaction kinetics (6) 18

3. 分子偶极矩

Dielectric-constant measurements by the heterodyne-beat
method (5) 19

羟基硅烷的偶极矩 (37) 23

八甲基环四硅氧烷的构象(*) 29

4,4',6,6'-四苯基-2,2'-二亚噻喃的构型 (172) 31

4. 高分子溶液性质

高分子溶液的第二维利系数 (R16) 35

The second virial coefficients of polymethyl methacrylate mixed
fractions in acetone (27) 42

聚苯乙烯甲苯溶液第二维利系数的分子量依赖性 (102) 51

On the molecular weight dependence of the second virial coefficient
of polystyrene in toluene (130) 59

5. 高聚物的分子量分布

高聚物的分子量分布 (*) 63

Comment on the paper "A proposed method for estimating poly-
mer molecular weight distribution without fractionation" (*) 75

6. 高分子溶液的激基缔合物荧光

Excimer studies of polymer solutions over the entire concentration
range (R39) 77

Fluorescence spectra of polybenzamide in isotropic and nematic

solutions (235)	92
7. 高分子液晶态	
A study of band texture formation of nematic solutions of poly-(1,4-phenylene terephthalamide) in sulfuric acid (218)	100
Band texture formation of sheared polymeric liquid crystalline state (R41)	109
Solidification-induced and shear-induced band texture in thermotropic liquid crystalline polymer films (243)	119
Recent advances in the observation of disclinations of main-chain nematic polymers (R46)	126
8. 高聚物流体的流变性质	
经不同程度降解聚丙烯的熔体流变性质 (131)	149
激光测速法研究高聚物流体在矩形隙缝收缩流中心线的流速分布 (121)	154
Velocity field of convergent flow into a rectangular slit for a polymeric fluid (151)	162
Rheological studies on solutions of poly-p-phenylene terephthalamide in H_2SO_4 (197)	169
9. 高聚物非晶态和结晶	
Crystallization and chain orientation in hot drawn amorphous poly(ethylene terephthalate) films (82)	175
高聚物热释电流的极化温度扫描法 (138)	182
Crystalline morphology of poly(polytetramethylene ether glycol aryl dicarboxylate) (180)	186
Length of chain segment motion needed for crystallization (240)	197
Fourier transform infrared studies of poly(ethylene terephthalate) film in the glass transition region (185)	202
The concept of cohesional entanglement (+)	211
The state of high global chain orientation but nearly random segmental orientation of amorphous polymers (+)	223
10. 高分子的单链凝聚态	
Monte Carlo simulation of a confined random walk chain (156)	231
Single-chain polystyrene glasses (227)	235
Single-chain condensed state of flexible-chain polymers (R49)	239
Molecular dynamics simulation of crystal nucleation behavior of	

a single-chain touching a substrate surface (247)	255
Morphological observations of single-chain glassy polystyrene by means of tapping mode atomic force microscopy (250)	261
11. 高聚物的声发射	
Acoustic emission of polymers (R34)	271
12. 聚丙烯	
Effects of molecular weight distribution on the melt spinning of polypropylene fibers (144)	289
Effect of high molecular mass tail in the mol mass distribution of polypropylene on injection molding (166)	318
Properties of EDAM copolymers as polypropylene resin modifier (242)	323
13. 有机固体的电导和光导	
Studies of organic semiconductors for 40 years (R38)	333
Carrier transport properties of poly(1,6-bis-9-carbazolyl- 2,4-hexadiyne) (184)	350
有机固体中载流子陷阱的表征 (R37)	355
Carrier transport properties of poly(substituted phenylacety- lene)s (216)	365
14. 导电聚吡咯	
Electrochemically prepared polypyrroles from aqueous solutions (160)	370
Electrochemical aspects of polypyrrole (181)	386
The role of H ⁺ ions in the electrochemical polymerization of pyrrole (204)	394
On the molecular chain structure of conducting polypyrrole (R42)	405
Inductance effect in the AC impedance of conducting polypyrrole films (225)	414
钱人元学术著作题录	420

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Raman Spectra of Aqueous Solutions of Potassium Thiocyanate

By JEN-YUAN CHIEN

Introduction

The Raman spectrum of water, the most conspicuous example of molecular association in the liquid state, has been subjected to numerous studies, especially on the modification of the main band between $\Delta\bar{\nu}$ 3200–3600 cm^{-1} at different temperatures,¹ by the effect of solutes² and in the crystalline field.³ The presence of ions usually increases the intensity of Raman scattering, shifts the maxima and alters the relative intensities of band components, and is in general parallel to the effect of increased temperature. These effects have been explained as due to a gradual change of the water structure, pictured either as a change in a quasi-lattice arrangement of water molecules,^{1c} or as a dissociation of water polymers.^{1a} The temperature and solute effects on water structure have also been studied by X-ray diffraction,⁴ infrared absorption spectra,⁵ magnetic susceptibility measurements,⁶ and investigation of the thermodynamic properties of water and aqueous solutions of electrolytes. Recent calorimetric measurements⁷ have shown that the heat of vaporization of water from concentrated potassium thiocyanate solutions at 30° is about 2% lower than that from pure water. This indicates the breaking of hydrogen bonds of liquid water in the ionic field created by the solute. The Raman spectrum of potassium thiocyanate in aqueous

solution has previously been reported,⁸ but since no information on the modification of the Raman band of the water was included the present investigation was carried out.

Experimental Details

The 4358 Å. line of mercury was employed for excitation. Two experimental arrangements were used, one with six G.E. H-2 mercury vapor lamps and a horizontal Raman tube, the other with seven water cooled d. c. mercury arcs and a vertical Raman tube. The arcs⁹ were made of 10-mm. Pyrex tubing, gave an effective arc length of 9", and operated at 5–8 amperes at 80–90 volts. The water-cooled arcs gave lower light output, but relatively less background and yielded cleaner spectra. The filter solution¹⁰ used to isolate the λ 4358 Å. line consisted of 4% *p*-nitrotoluene and 1/10,000 crystal violet R B bluish, (Cassella Color Co.), in 95% ethyl alcohol.

The spectrograph used was a Steinheil type GH, with three glass prisms and $f/3$ 195 mm. f.l. collimator and camera lenses. Spectra were taken on Eastman 103J plates, developed in D19, and then traced by a photoelectric microdensitometer. An iron arc comparison spectrum was taken on each plate and traced alongside the Raman spectrum. Displacements of peaks on the tracing were measured to within 0.03 mm. by means of a special comparator constructed by Mr. L. K. Henke, laboratory chief mechanician, and frequencies were determined by linear interpolation of the wave numbers of the two nearest iron lines. Rayleigh scattering of the mercury λ 4916 or λ 4078 Å. line was used for correction of any lateral displacement between the Raman and comparison spectra occurring either during picture taking or during tracing. All wave numbers were reduced to those in vacuum by means of Kayser's table.¹¹

Solutions were prepared from reagent potassium thiocyanate and conductivity water. Controlled exposures ranging from two minutes to two hours were used, at a

(1) (a) I. R. Rao, *Proc. Roy. Soc. (London)*, **A145**, 489 (1934); (b) M. Magat, *Ann. phys.*, (11) **6**, 108 (1936); (c) P. C. Cross, J. Burnham and P. A. Leighton, *THIS JOURNAL*, **59**, 1134 (1937).

(2) (a) J. H. Hibben, *J. Chem. Phys.*, **5**, 166 (1937); (b) P. A. Leighton and J. Burnham, *THIS JOURNAL*, **59**, 424 (1937); (c) Th. G. Kujumzelis, *Z. Physik*, **110**, 760 (1938).

(3) P. G. N. Nayar, "Raman Jubilee Volume," p. 419 (1938).

(4) (a) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938); (b) G. W. Stewart, *ibid.*, **7**, 869 (1939), **11**, 72 (1943).

(5) E. Ganz, *Ann. Physik*, **28**, 445 (1937).

(6) Cf. N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 166.

(7) J. B. Hunter and H. Bliss, *Ind. Eng. Chem.*, **36**, 950 (1944).

(8) (a) A. Dadiou and K. W. F. Kohlrausch, *Monatsh.*, **55**, 400 (1930). (b) P. Krishnamurti, *Ind. J. Phys.*, **5**, 663 (1930). (c) A. Langseth, J. R. Nielsen and J. U. Sorensen, *Z. physik. Chem.*, **B27**, 102 (1934). (d) J. Goubeau and O. Gott, *Ber.*, **73**, 127 (1940).

(9) The author is indebted to Dr. Paul Bender and Messrs. Philip Lyons and Paul Reinker for the development of the arcs used in this work.

(10) B. Uribe-Vergara, Thesis, University of Wisconsin, 1945.

(11) H. Kayser, "Tabelle der Schwingungszahlen," Edwards Bros., Ann Arbor, Michigan, lithographic reprint. 1944.

slit width of 0.06 mm. (For the iron arc comparison spectra, a slit width of 0.025 mm. was used.)

Results and Discussion

The experimental results are summarized in Table I.

TABLE I

RAMAN FREQUENCIES OF WATER AND POTASSIUM THIOCYANATE SOLUTIONS

Solution	Mole ratio KSCN: H ₂ O	Molality	Temp., °C.	Raman frequencies			
				H ₂ O	(SCN) ⁻		
Pure water		12	1849	3202 (40) ^a	3409 (60)		
Pure water		25	..	3223 (37)	3428 (63)		
Pure water		85	..	3254 (30)	3445 (70)		
1:40	1.4	25	..	3241 (35)	3440 (65)	750	2069
1:15	3.7	25	1645	3260 (32)	3450 (68)	746	2069
1:6	9.3	25	1633	3272 (25)	3460 (75)	751	2069
1:3	18.5	25	..	3260 (19)	3452 (81)	735	2069
1:3	18.5	12	1625	..	3452	745	2067
1:3	18.5	85	1624	..	3472	745	2067

^a The numbers in parentheses indicate the relative intensities of the two components of the main water band.

The frequencies of the band components were determined by graphical resolution of the band, assuming symmetrical configurations, from the tracings shown in Fig. 1. The spectra employed for the frequency determinations were so chosen that the main water band had been satisfactorily exposed, and was of approximately equal density for all the solutions. This permits a more legitimate comparison of both frequency shifts and band shapes for different solutions, as Cross, *et al.*,^{1c} have pointed out that the apparent band maxima shift with length of exposure, especially when overexposed.

The accuracy of the frequencies of the band components is estimated at 10 cm.⁻¹, due to the extreme broadness of the band and the arbitrariness of resolution. The frequencies for the thiocyanate ion, except one, are in good agreement with those given in the literature,⁸ and tabulated in Table II.

TABLE II

RAMAN FREQUENCIES FOR THE THIOCYANATE ION

Observers	Year	Frequencies cm. ⁻¹
Dadieu and Kohlrausch	1930	750 2067
Krishnamurti	1930	747 2050
Langseth, Nielsen and Sorensen	1934	750 796 2066
Goubeau and Gott	1940	747 2066

For the Raman frequencies of liquid water, considerable differences of opinion have been recorded in the literature, especially with regard to frequencies below 1000 cm.⁻¹.¹² In Fig. 1 there is a suggestion of a band in the 130 cm.⁻¹ region, but its origin is questionable since it was not observed with λ Hg 4047 Å. excitation. In the 450 cm.⁻¹ region humps on tracings of highly exposed plates are regularly observed due to scattering in the spectrograph and halation caused by the exciting line. (Even slight halation is enough to

(12) I. R. Rao and P. Koteswaram, *Phil. Mag.*, **25**, 90 (1938).

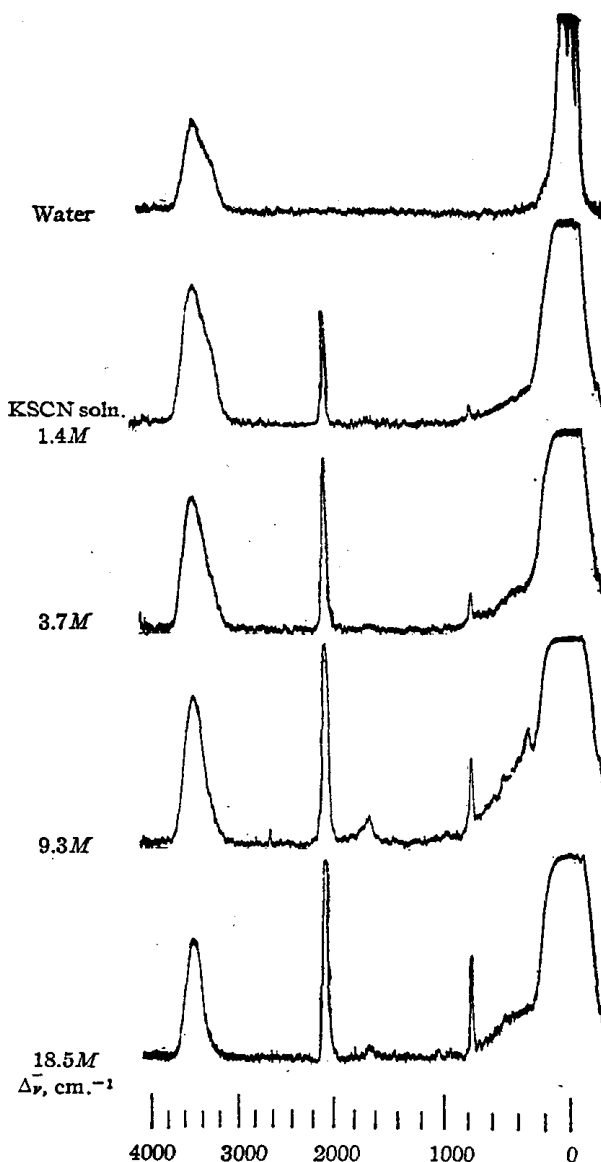


Fig. 1.—Raman spectra of water and aqueous solutions of potassium thiocyanate.

bring out the inevitable continuous background from the light source.) The broad 1650 cm.⁻¹ band is quite definite, while the 3600 cm.⁻¹ component of the main band is not apparent even at 85°.

The presence of the dissolved potassium thiocyanate greatly enhances the intensity of the Raman scattering. The 1650 cm.⁻¹ band is displaced toward lower frequencies with increasing concentration; as reported by Kujumzelis^{2c} it may be as low as 1625 cm.⁻¹ in iodide solutions. The main band is shifted toward higher frequencies with the 3200 cm.⁻¹ component greatly suppressed, so that the band has a sharp and symmetrical appearance for concentrated solutions. The frequency shift of both components shows an increase with increasing salt concentration up to a

concentration of 1:6, and thereafter a slight decrease. Similar behavior has been observed in solutions of zinc chloride^{2b} and hydrogen chloride.¹³

If the relative intensity of the two components of the band can be taken as a measure of the extent of inter-molecular association in water, then water in a 3.7 *M* solution of potassium thiocyanate at 25° has a structural temperature around 60°, and in a 9.3 *M* solution over 100°. This striking effect of potassium ion and thiocyanate ion on the structure of water is in conformity with the low hydration of both ions and the resulting far extending ion-fields, as discussed by Ulich.¹⁴

(13) L. Ochs, J. Guéron and M. Magat, *J. phys. radium*, (8) **1**, 53 (1940).

(14) H. Ulich, *Angew. Chem.*, **49**, 279 (1936).

Acknowledgment.—The author wishes to express his thanks to the China Institute in America, New York, for a scholarship covering the period during which the work here reported was carried out.

Summary

The Raman spectra of aqueous solutions of potassium thiocyanate and of pure water at various concentrations and temperatures have been described. The results show a great increase in the structural temperature of water in potassium thiocyanate solutions caused by the perturbing ionic field created by the solute.

MADISON, WISCONSIN

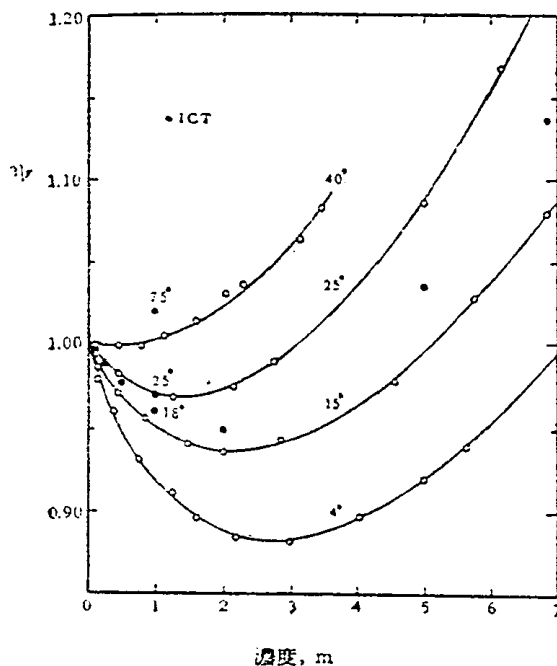
RECEIVED JUNE 29, 1946

硫代氰酸鉀溶液的粘度

近年来从液体结构的观点来研究电解质溶液，日漸引起注意，特别是离子对液态水结构的影响，对水合作用的了解开辟新的途径^[1]。作者之一曾从 KCNS 濃溶液的組合散射光譜^[2]推断此溶液中水的结构接近較高温度純水中的结构，这样可以解釋 30°C 时 KCNS 濃溶液中水的蒸發潜热小于純水約 2% 的實驗事实^[3]。Самойлов^[4] 在研究水合作用时得到的結論，認為水合不能看作离子与水分子的永久性結合，而應該看作离子对它近邻水分子平移运动的活化能和松弛時間的影响所致。减低水分子平移活化能和松弛時間的离子称作“負水合离子”，K⁺ 就属于这一类。

負水合离子首先表現在溶液粘度比純水为小。在比較大的濃度和温度范围内电解质溶液的粘度数据并不多，KCNS 溶液只有 18° 时 0.1—5m 的粘度数据^[5]。因此作者等在 4, 15, 25, 40°C 进行了一直到 10m 溶液的粘度测定，得到下列結果(附圖)：(1) $\eta_r = \eta_{\text{溶液}} / \eta_{\text{純水}}$ 对濃度的錢都有一最小值，温度愈低时愈显著，

到 40° 此粘度降低的效应已接近消失。(2) $\eta_r = 1$ 时的溶液濃度随温度的升高而减小，25° 时在 3m 左右。(3) 在实验范围内 $d\eta_r/dT > 0$ 。(4) 从 $\log \eta - \frac{1}{T}$ 圖得到的 25° 时的流动活化能 3m 溶液与 70° 左右的純水相近，6m 溶液比 100° 时的純水还要小。



这些事实完全与离子对水分子结构改变的想法相符。尤其有趣的是同最近發表的 NaCNS 溶液粘度数据^[6]来对比，后者 $\eta_r > 1$ 而且 η_r 随濃度的增加要快得多(在 7m 时 $\eta_r \approx 2$)，在 7m 以下 $d\eta_r/dT > 0$ ，在 7m 以上 $d\eta_r/dT < 0$ ， $\log \eta - \frac{1}{T}$ 錢比純水的更弯曲，流动活化能比純水大。类似的鉀盐与鈉盐溶液性質的鮮明对比也表現在 KCl 和 NaCl 溶液中水分子的自扩散系数的不同^[7]，前者比純水大，随濃度遞增，后者比純水小，随濃度遞減。这些事实都証实負水合与水合正离子的分界錢确在 K⁺ 和 Na⁺ 之間^[8]。

錢 人 元 李承欣 張天民 三慧才
(中国科学院化学研究所) (山东工学院化工系)

1957 年 6 月 16 日

- [1] П. С. Богоявленский, 在复旦大学演講稿。
- [2] 錢人元, J. Am. Chem. Soc., **69**, 20 (1947).
- [3] J. B. Hunter and H. Bliss, Ind. Eng. Chem., **36**, 950 (1944).
- [4] О. Я. Самойлов, ДАН, **77**, 633 (1951).
- [5] Int. Crit. Tables V, 18, 1928.
- [6] M. L. Miller and M. Doran, J. Phys. Chem., **60**, 186 (1956).
- [7] 王瑞麟 (J. H. Wang), J. Phys. Chem., **58**, 686 (1954).
- [8] О. Я. Самойлов, Изв. АН СССР ОХН, **242** (1953).

Photoelectric Intensity Measurements of Raman Spectra

JEN-YUAN CHIEN AND PAUL BENDER

Department of Physical Chemistry, University of Wisconsin, Madison, Wisconsin

(Received February 17, 1947)

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 tube⁷ 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

¹ M. Wolkenstein and M. Eliashevich, *Acta Physico-chimica (URSS)* 20, 525 (1945).

² D. H. Rank, R. J. Pfister, and P. O. Coleman, *J. Opt. Soc. Am.* 32, 390 (1942).

³ D. H. Rank, R. J. Pfister, and H. H. Grimm, *J. Opt. Soc. Am.* 33, 31 (1943).

⁴ D. H. Rank, and R. V. Wiegand, *J. Opt. Soc. Am.* 36, 325 (1946).

⁵ V. Kudrjawzewa, *Acta Physico-chimica (URSS)* 3, 613 (1935).

⁶ A. W. Reitz, *Zeits. f. physik. Chemie* B38, 275 (1937).

⁷ J. A. Rajchman and R. L. Snyder, *Electronics* 13, 20 (1940).

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 overall 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

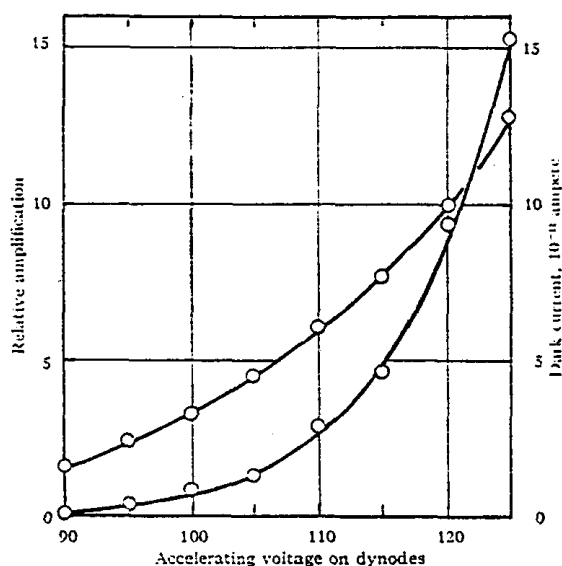


FIG. 1. Relative amplification and dark current at various accelerating voltages on dynodes.

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

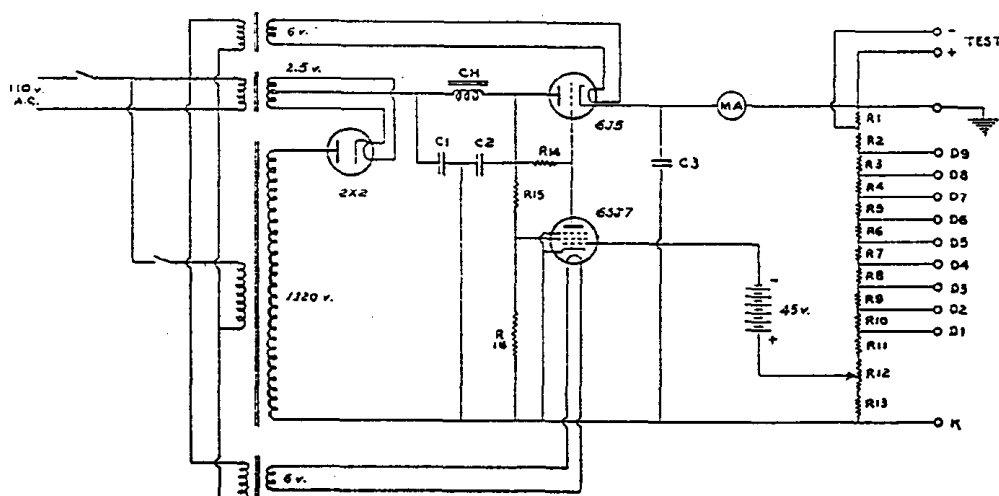


FIG. 2. Circuit of the photo-multiplier power supply.

R_1	250 ohm	R_{14}	0.5 megohm
R_2	30000 ohm	R_{15}	5.0 megohm
R_3-R_{10}	25000 ohm	R_{16}	0.1 megohm
R_{11}	7000 ohm	C_1-C_3	2 mf 2000 v
R_{12}	10000 ohm	CH	300 H, 7.5-ma choke
R_{13}	8000 ohm	MA	0-10-ma meter

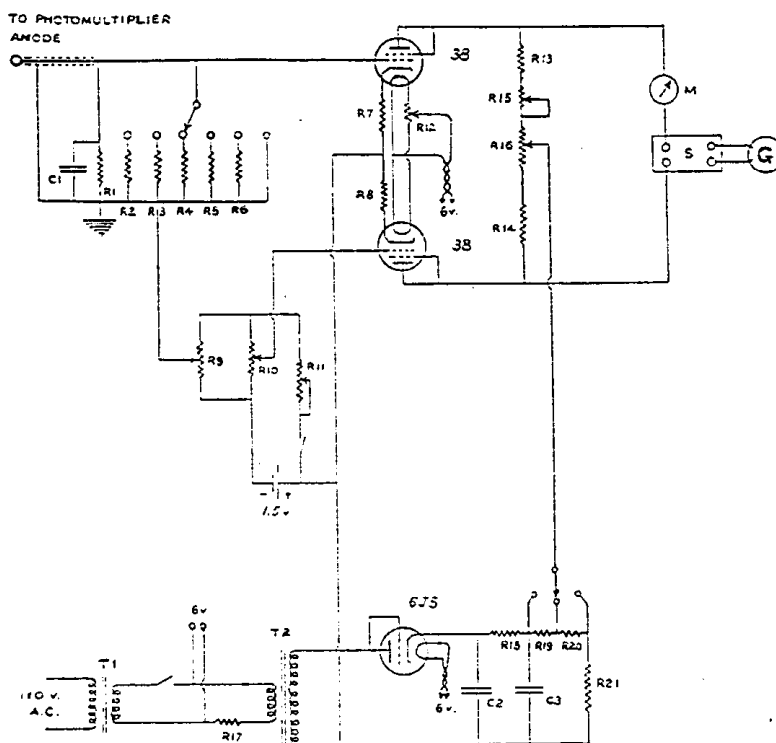


FIG. 3. Circuit for the d.c. amplifier.

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 ml. 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 $\lambda 4358\text{\AA}$ 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 mechanic, 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

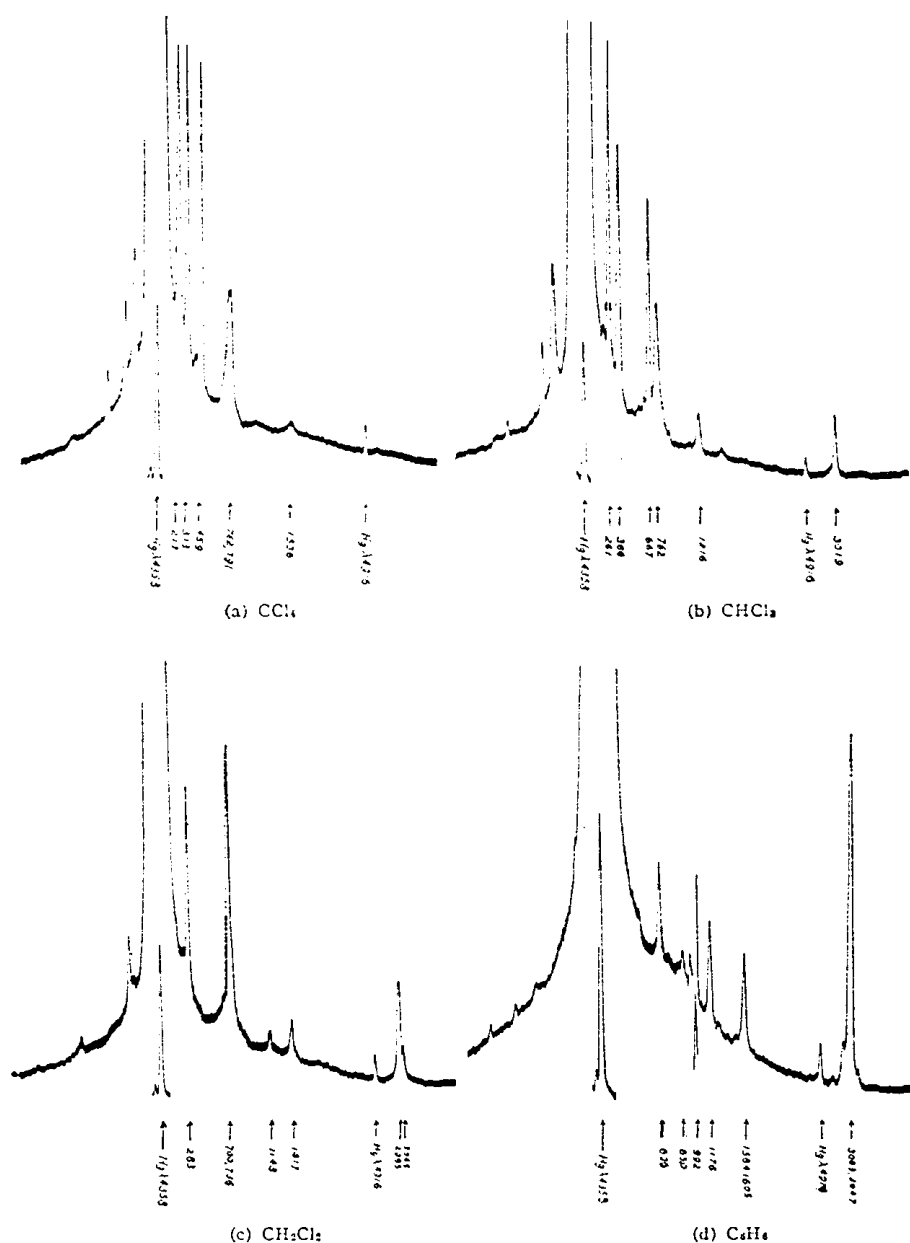


FIG. 4. Recorded Raman spectrograms of CCl_4 , CHCl_3 , CH_2Cl_2 , and C_6H_6 .