

CHAPTER-VIII

Infrared and Raman Spectra of Solutions of Some Alkali and Alkaline Earth Metal Perchlorates in Propylene Carbonate

Investigations on Raman and infrared spectra in aqueous and non-aqueous solutions have been extensively used to explore the types of interactions arising in electrolyte systems¹⁻⁶. The present chapter reports the results of infrared and Raman spectral investigations of $\text{Ba}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2$, LiClO_4 and NaClO_4 in propylene carbonate (PC). The perchlorate salts have been chosen because of the small charge densities of perchlorate anions and their relatively weak tendency to form complex ions, particularly with cations of the alkali and alkaline earth metals. PC has generated much interest as a solvent medium for electrochemical studies⁷ relating to high energy batteries^{8,9} and free radical species¹⁰. Hence, it is of much interest to study the behaviour of electrolytes in such a solvent medium. The present chapter is believed to shed new light on the nature of intermolecular and interionic interactions in PC.

Experimental

Propylene carbonate (E. Merck, Germany; > 99% pure) was purified as described in Chapter - II.

Calcium (II) perchlorate and Strontium (II) perchlorate were prepared by neutralising the corresponding carbonates with perchloric acid. Anhydrous barium (II) perchlorate and magnesium (II) perchlorate were commercially available (Fluka). All these perchlorate salts were purified by at least triple recrystallisation from distilled water and dried at 373 K in vacuum over silica gel for few days¹¹.

Lithium perchlorate (Fluka, >99% pure) and sodium perchlorate (AR, E. Merck, Germany) were purified according to the procedure given in Chapter - II.

All solutions were prepared at 25°C and the perchlorate concentrations were determined with an Orion ion-selective electrode meter (model EA 920) after standardisation with known solution of the perchlorate electrode system.

Laser Raman spectroscopic measurements were made at 25°C with a DILOR Z24 RAMAN spectrometer using 4880 Å^o excitation. The spectral slit width was kept at $\sim 4 \text{ cm}^{-1}$. The laser power used was 300 mW. The spectra were recorded by the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras.

The infrared spectral measurements were made at 25°C on a Perkin-Elmer 983 spectrophotometer. Polythene windows were used for all measurements.

All spectra were scanned at least twice to ensure repeatability.

Results

Infrared spectra of pure propylene carbonate and of $\text{Ca}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, $\text{Ba}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$ in PC at 298K are shown in Figs. 1-5. The principal bands observed for the pure solvent (PC) and its solutions have been listed in Tables 1 and 2 respectively.

Partial band assignments have been made for the infrared spectrum of PC (Table 1). The carbonyl stretching band appears at 1790 cm^{-1} . Four bands are observed in the C-O stretching region at 1182, 1118, 1050 and 1076 cm^{-1} . The 1468 cm^{-1} line has been assigned to the CH_3 deformation mode and CH_3 symmetric stretching frequency appears at 2985 and 2915 cm^{-1} . The IR spectrum of pure PC agreed well with those found in the literature^{2,12,13}.

We found that the spectra of calcium, strontium, barium and magnesium salt solutions showed several changes from that of pure PC. The 1790 cm^{-1} C = O stretching line of pure PC is used as the reference for intensity changes.

In all the salt solutions, a slight downward shift of the 1790 cm^{-1} and 1182 cm^{-1} bands was noticed. The intensities of the

peaks corresponding to the 1790 cm^{-1} and 1182 cm^{-1} bands of pure PC are found to be in the order:



In the infrared spectra of all the salt solutions, two new bands appear at $\sim 940\text{ cm}^{-1}$ and $\sim 624\text{ cm}^{-1}$, the later of which arises due to the triply degenerate bending vibration of perchlorate ion. The origin of the band at 940 cm^{-1} is not properly understood since the totally symmetric vibration of perchlorate ion is infrared inactive (it appears in the Raman spectrum).

The Raman spectra of pure PC and of LiClO_4 , NaClO_4 , $\text{Ba}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$ in PC at 298K are shown in Figs. 6-10. Some important bands observed for PC are recorded in Table 1. The Raman frequencies observed are given in Table 3. Comparison of the Raman bands of pure PC with literature values was not possible, because this solvent was not studied by Raman spectral techniques so far. The lines at 3001 and 2769 cm^{-1} have been assigned to the components of a Fermi resonance doublet arising out of the interaction between the symmetric CH_3 stretching mode (2892 cm^{-1}) and the first overtone of the CH_3 deformation mode (2949 cm^{-1}), the fundamental of which is found at 1473 cm^{-1} in pure PC.

Like the infrared spectrum of pure PC, the carbonyl stretching in the Raman spectrum occurs at 1799 cm^{-1} . But only two bands

are observed in the C-O region namely at 1188 and 1138 cm^{-1} ; the other two bands observed in the infrared spectrum of PC remain absent from the Raman spectrum because of the fact that they might be only infrared active. Both 1799 cm^{-1} and 1188 cm^{-1} bands of pure PC exhibited similar changes in frequency and intensity in the salt solutions as that of the infrared spectra.

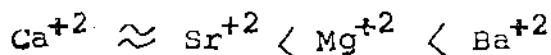
A new band appears at $\sim 940 \text{ cm}^{-1}$ in the solution spectra. This band is attributed¹⁴ to the infrared forbidden totally symmetric vibration of perchlorate ion.

Discussion

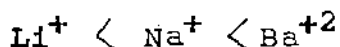
Because of the large dipole moment (4.94 D)¹⁵ propylene carbonate molecules should orient themselves with the negative poles in the direction of the cations and the positive poles in the direction of the anions. Thus it would seem that cations should disturb primarily the C = O band and only indirectly affect the C-O band. The disturbances caused by the cations will tend to weaken the C = O band because of the decrease in the electron density in this bond, in part, as a result of the flow of part of the s electrons in the direction of the free electron pairs of the oxygen atom of the C = O group. As a result of the induction effect the electron density in the C-O bonds within the ring should also decrease but the extent of weakening of the bond will be less than in the case of the C = O bond. It would seem that this type of change should lead to a

considerable decrease in the 1790 cm^{-1} band frequency and a smaller decrease in the 1182 cm^{-1} band frequency. In the present study, the intensities of both 1790 and 1182 cm^{-1} bands were found to decrease for all the salt solutions compared to the solvent spectrum; the extent of decrease in intensity was greater in the case of 1790 cm^{-1} band than in the case of 1182 cm^{-1} bands in all cases. This obviously indicates that the linkages of the metal ions with the PC molecule are actually taking place through the $\text{>C}=\text{O}$ group. But the frequencies corresponding to CH_2 stretching and CH_2 deformation modes of pure PC are not affected to a considerable extent in presence of these salts. This observation is in excellent agreement with the electron density distribution of the propylene carbonate molecule. The semi empirical molecular orbital calculation² shows a considerable electron density on the ring oxygen as well as on the carbonyl oxygen (Fig. 1 of Chapter 1). It is reasonable to assume that the interaction of cations with PC is not restricted to the carbonyl oxygen atom and may also involve extensive ring interactions. The positive centres, on the other hand, are much less accessible to anions. This agrees with observations that PC is a poor anion solvator². Exactly the same conclusion has been derived from the conductometric and viscometric investigations of alkali metal salts in this medium^{16,17}.

From the trends in the frequencies of the bands corresponding to 1790 and 1182 cm^{-1} bands in pure PC, it appears that the interactions of the cations with carbonyl oxygen increase in the order:



On the basis of the frequency shifts of the C = O band for the investigated perchlorates, the strength of the disturbance for the cation would seem to follow the order:



This indicates that the greatest changes occur in the propylene carbonate for $\text{Ba}(\text{ClO}_4)_2$ system, though Li^{+} ion has the maximum charge density amongst the three ions compared (Na^{+} and Ba^{+2} ions have almost the same charge density). On the basis of the charge density, Li^{+} ion should interact most strongly with the C = O group of propylene carbonate molecules. But the reverse is observed in the present investigation. This obviously, is an indication of the fact that the extent of the changes of the Raman spectral parameters is dependent not only on the charge density of the disturbing ions but also on their surface area. This is particularly important in the comparison of the action of cations belonging to different groups of the periodic system of elements. Thus, in the present study, the maximum interaction of Ba^{+2} with propylene carbonate molecules can be ascribed to the maximum surface area of the Ba^{+2} ion (as a matter of fact Ba^{+2} ion has about five times the surface of Li^{+} ion and twice that of Na^{+} ion). The observed differences in the change of frequency can not be explained on the basis of the fact that there are two perchlorate ions for every barium cation, since in accordance with the assumptions made, the anions should

lead to an increase in the frequency of the 1799 cm^{-1} band and a decrease in the frequency of the 1188 cm^{-1} band.

However, the observed differences in the behaviour of the cations may not depend only on such quantities as charge density or surface area of ions. Other factors leading to specific interactions may also play a role here, such as acceptor hybridisation of ions etc. The model given here, however, needs theoretical support and some calculations will be attempted in future in this direction.

Table 1. Infrared and Raman Spectra of liquid PC (cm^{-1})

Infrared	Raman	Assignment
2985 (s)	3001 (s)	CH_3 antisym. str.
2915 (s)	2949 (vs)	CH_3 sym. str.
1790 (vs)	1799 (s)	$\text{>C} = \text{O}$ str.
1468 (m)	1473 (m)	CH_3 def.
1182 (s)	1188 (s)	O-C-O skeletal str.
918 (w)	931 (w)	C-O-C sym. mode

vs = very strong; s = strong; m = medium; w = weak

Table 2. Infrared Spectra of PC and various Salt Solutions (cm^{-1})

PC	$\text{Ca}(\text{ClO}_4)_2$	$\text{Sr}(\text{ClO}_4)_2$	$\text{Ba}(\text{ClO}_4)_2$	$\text{Mg}(\text{ClO}_4)_2$
2985 (m)	2982 (m)	2980 (m)	2980 (m)	2980 (m)
2915 (s)	2915 (s)	2915 (s)	2920 (s)	2915 (s)
2345 (w)	2345 (w)	2340 (w)	2340 (w)	2345 (w)
1790 (vs)	1778 (vs)	1780 (vs)	1784 (vs)	1790 (vs)
-----	1620 (s)	1620 (s)	1610 (s)	1618 (s)
1548 (m)	1550 (m)	1546 (s)	1548 (s)	1548 (m)
1468 (m)	1470 (s)	1474 (s)	1474 (s)	1470 (m)
1445 (m)	1443 (m)	1443 (s)	1444 (s)	1444 (s)
1383 (s)	1383 (s)	1380 (s)	1382 (s)	1382 (s)
1344 (s)	1344 (s)	1345 (s)	1344 (s)	1344 (s)
1182 (s)	1177 (sh)	1177 (sh)	1180 (m)	1176 (m)
1118 (s)	1140 (sh)	1143 (sh)	1144 (w) 1115 (w)	1135 (sh) 1112 (w)
1050 (m)	-	1054 (sh)	1050 (w)	1054 (w)
1076 (sh)	1085 (s)	1080 (s, broad)	1080 (w)	1079 (vw)
959 (w)	956 (w)	960 (w)	955 (w)	956 (w)
-	940 (w)	940 (w)	944 (sh)	940 (w)
918 (w)	920 (w)	920 (w)	917 (w)	920 (w)
846 (m)	844 (m)	850 (m)	846 (s)	846 (m)
772 (s)	775 (s)	775 (vs)	774 (vs)	776 (vs)
708 (s)	708 (s)	708 (s)	708 (s)	708 (s)
626 (w)	624 (vs)	625 (vs)	624 (vs)	622 (vs)
532 (w)	536 (w)	533 (m)	536 (m)	532 (vw)
440 (vw)	448 (vw)	444 (vw)	440 (m)	448 (m)

vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

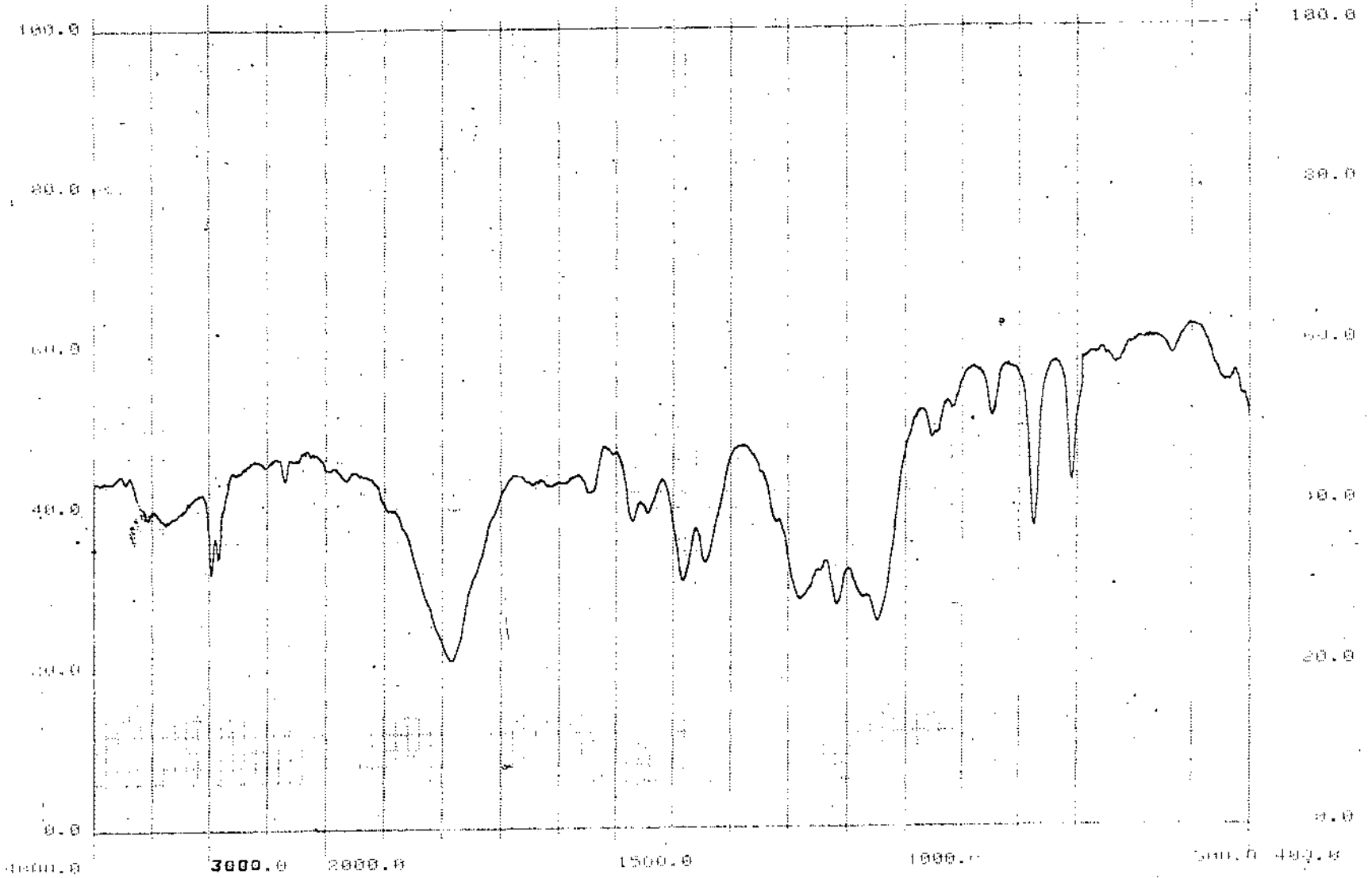
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Table 3. Laser Raman Spectra of PC and various Salt Solutions(cm^{-1})

PC	LiClO_4	NaClO_4	$\text{Ba}(\text{ClO}_4)_2$	$\text{Mg}(\text{ClO}_4)_2$
3001 (s)	2986 (s)	2984 (s)	2974 (s)	
2949 (vs)	2944 (vs)	2927 (vs)	2919 (vs)	
2892 (s)	2877 (s)	2870 (s)	2857 (s)	
2769 (m)	2756 (m)	2745 (m)	2740 (m)	
1799 (s)	1790 (vs)	1767 (m)	1758 (m)	1784 (m)
1508 (m)	1489 (s)	1465 (m)	1453 (m)	1486 (m)
1473 (m)	1460 (m)	1437 (m)	1424 (m)	1460 (m)
1245 (m)	1228 (s)	1209 (m)	1201 (m)	1227 (m)
1188 (m)	1158 (m)	1131 (m)	1127 (m)	1151 (m)
1138 (m)	1122 (m)	1108 (m)	1101 (m)	1124 (m)
-	1068 (m)	1041 (m)	1038 (m)	1058 (m)
974 (s)	960 (s)	-	-	959 (s)
-	935 (s)	941 (s)	937 (s)	934 (s)
931 (m)	913 (s)	920 (s) 899 (sh)	913 (s) 900 (sh)	
861 (s)	853 (vs)	836 (vs)	838 (s)	851 (s)
728 (s)	716 (s)	702 (s)	705 (s)	716 (s)
653 (m)	658 (m)	625 (m)	626 (m)	631 (m)
-	546 (s)	537 (s)	-	541 (s)
464 (m)	457 (s)	451 (s)	449 (m)	455 (m)
326 (w)	315 (w)	320 (w)	-	317 (w)

vs = very strong, s = strong, m = medium, w = weak, vw = very weak;

sh =

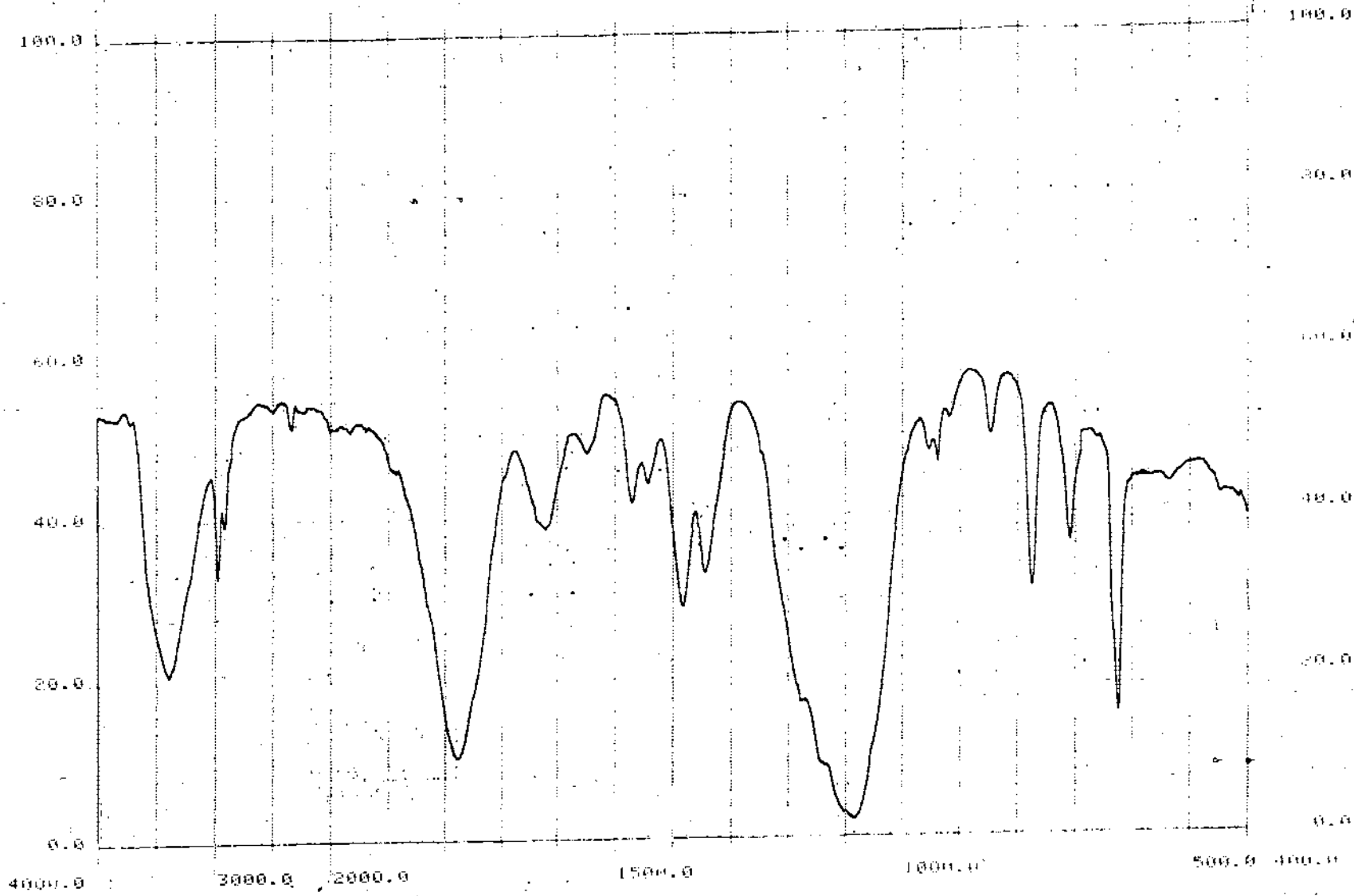


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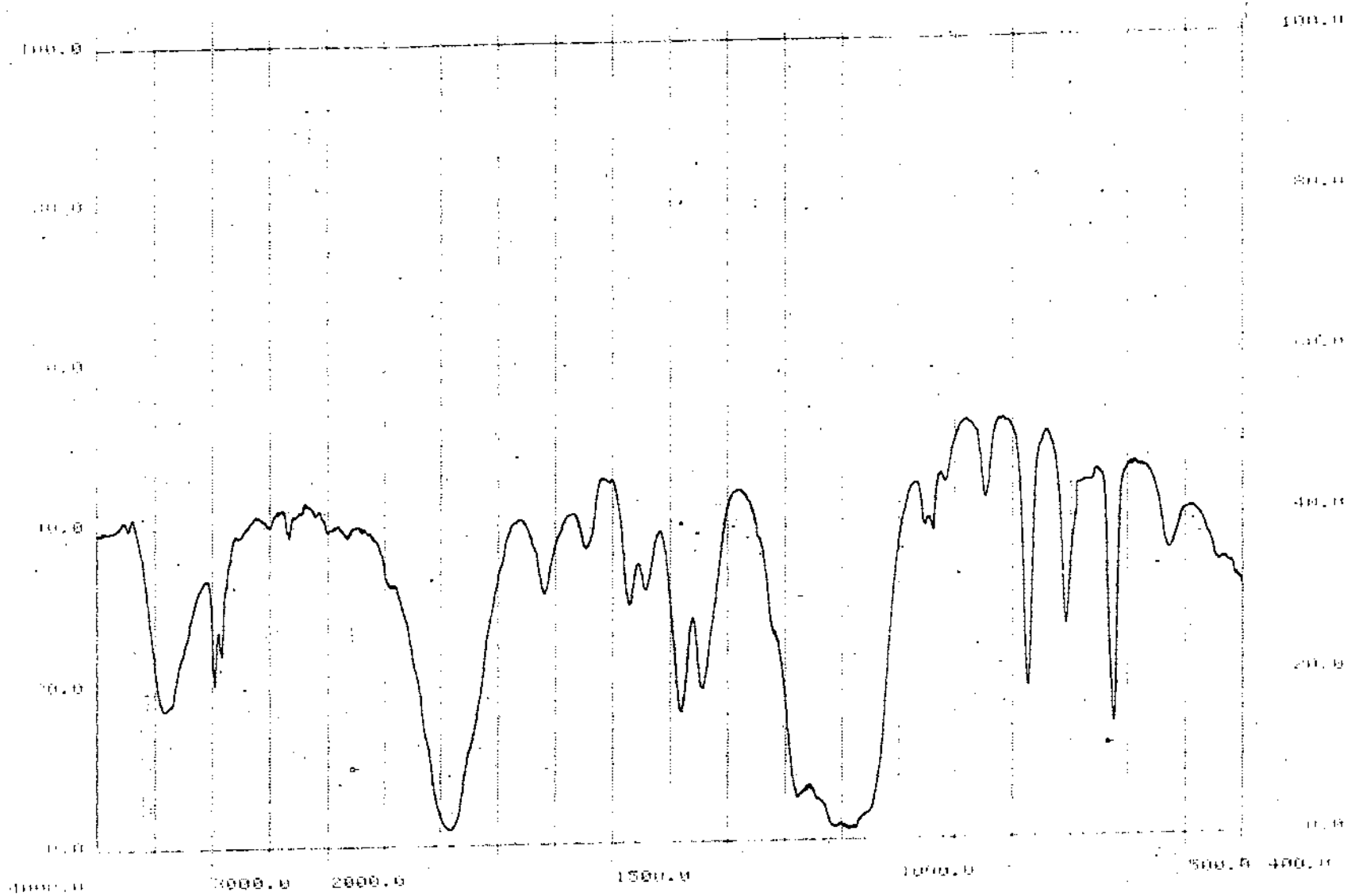
Fig.1 I.R. spectrum of propylene carbonate (PC)



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Fig.2 I.R. spectrum of $\text{Ca}(\text{ClO}_4)_2$ in Propylene Carbonate



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Fig. 3 I.R. spectrum of $\text{Sr}(\text{ClO}_4)_2$ in Propylene Carbonate

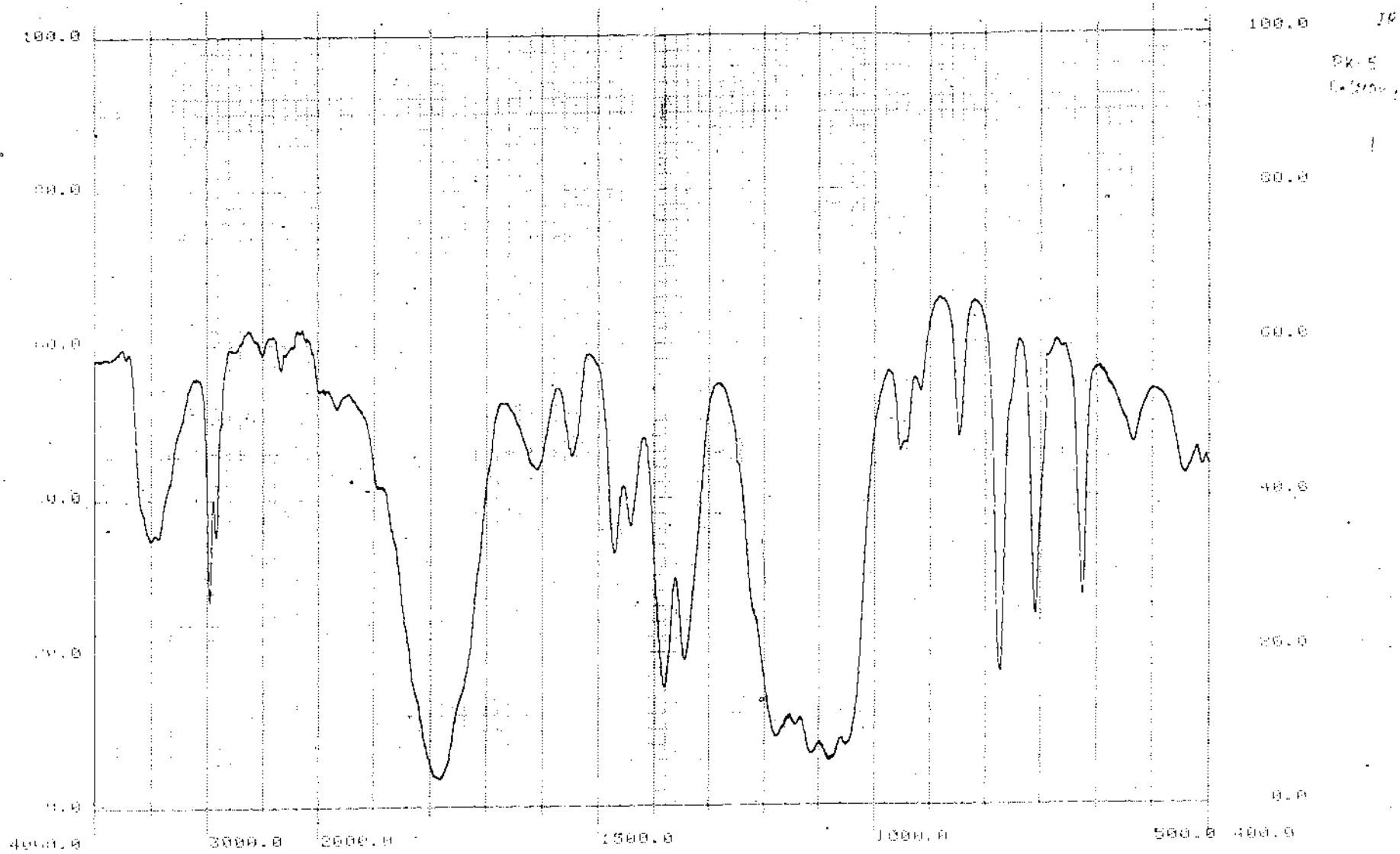
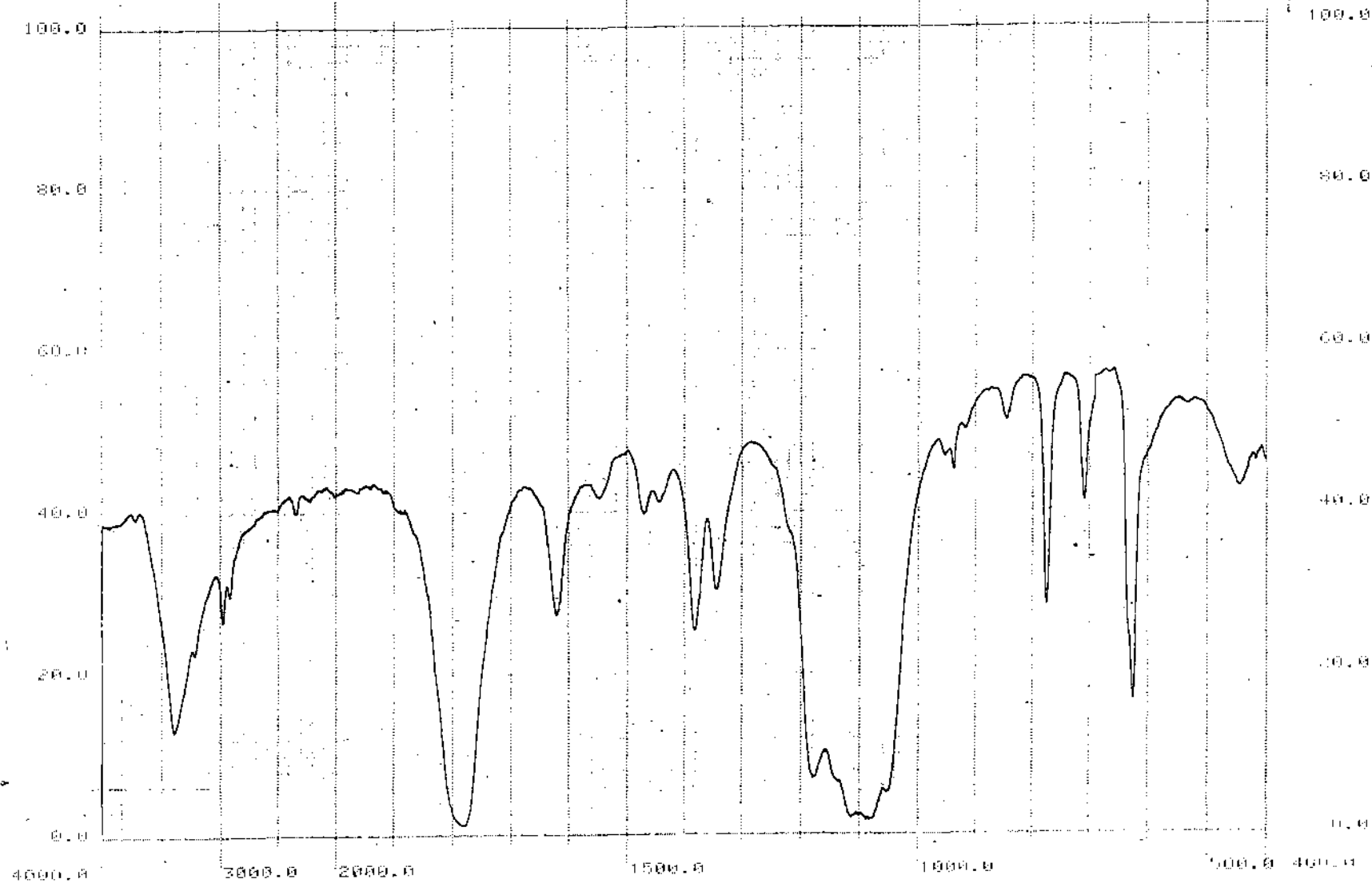


Fig.4 I.R. spectrum of $Ba(ClO_4)_2$ in Propylene Carbonate



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Fig.5 I.R. spectrum of $Mg(ClO_4)_2$ in Propylene Carbonate

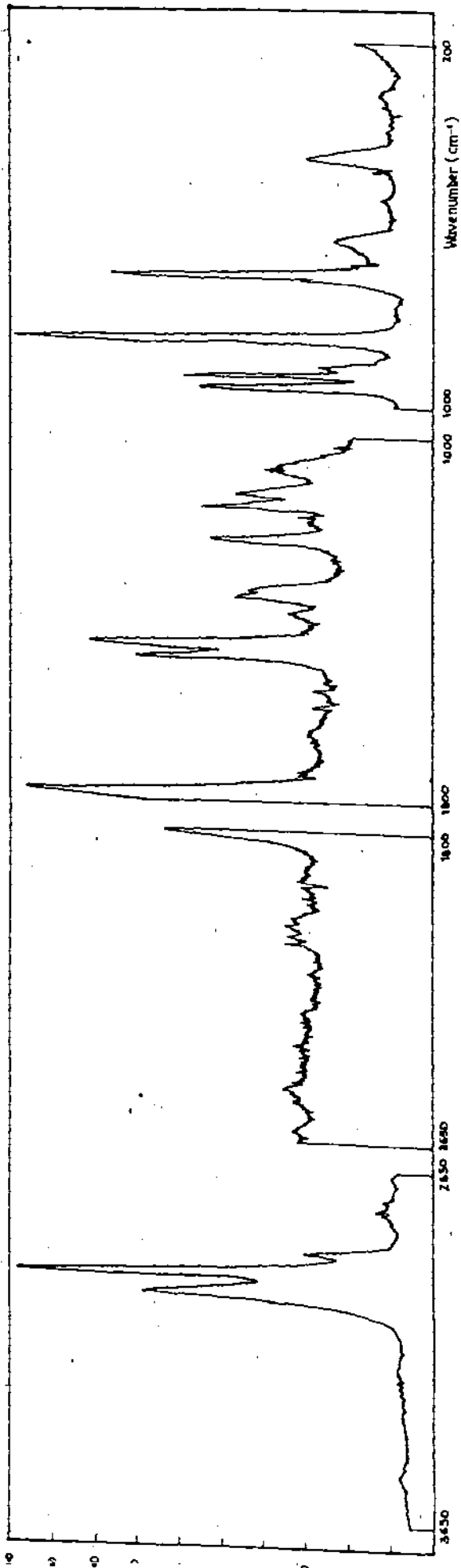


Fig-7 Raman Spectrum of LiClO_4 in PC

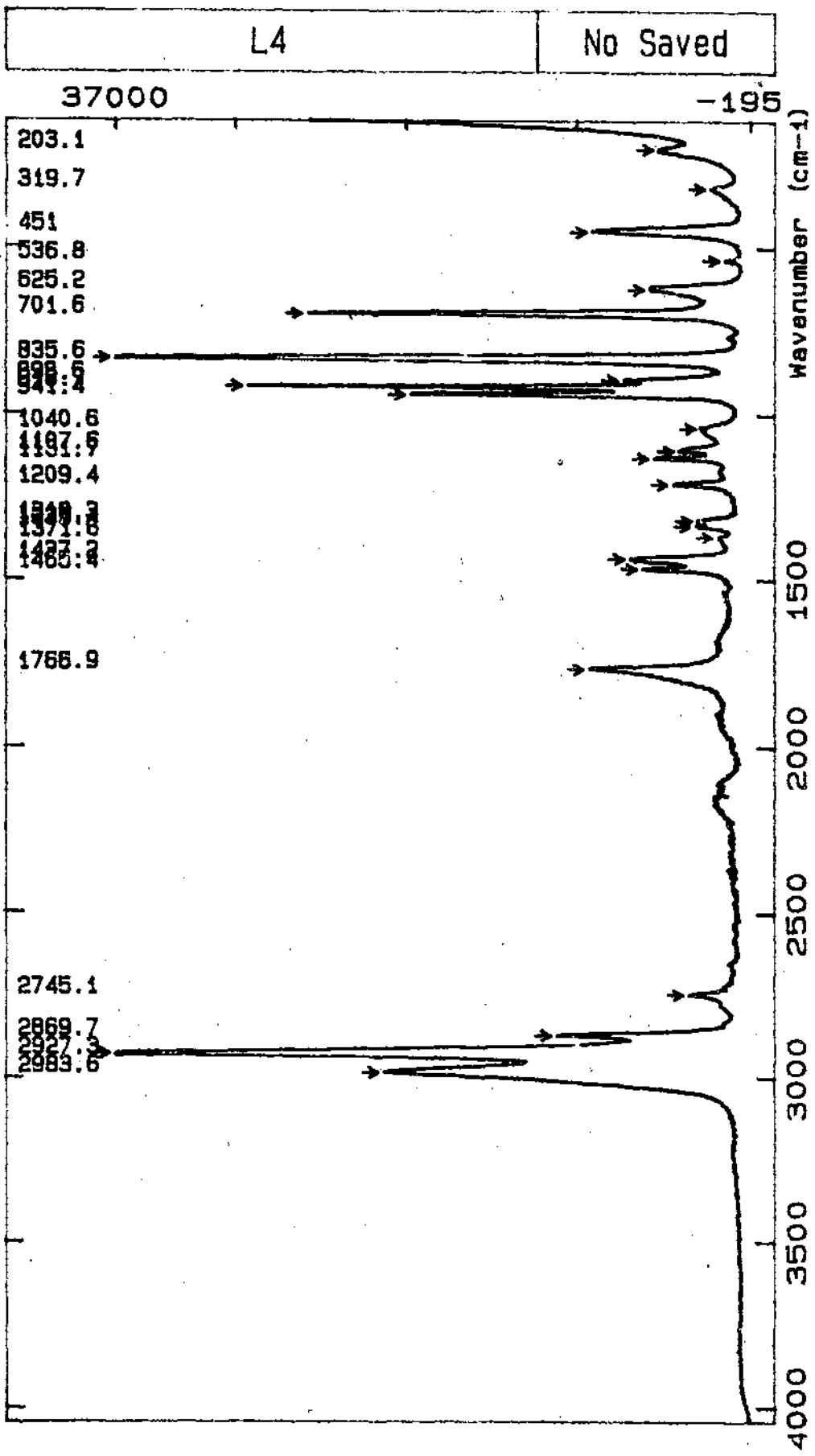


Fig. 8 Raman spectrum of NaClO₄ in propylene carbonate

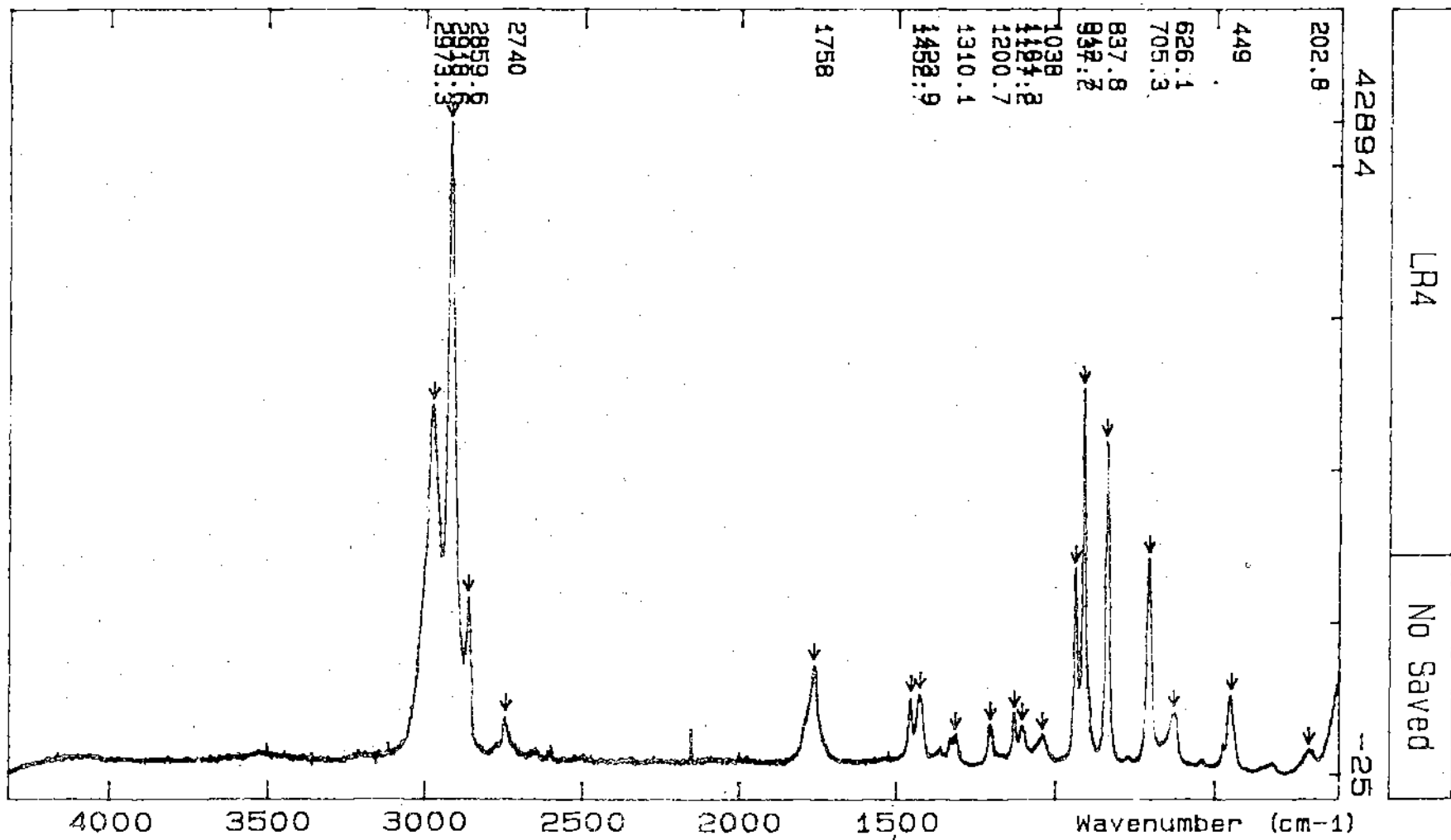


Fig.9 Raman spectrum of $Ba(ClO_4)_2$ in propylene carbonate

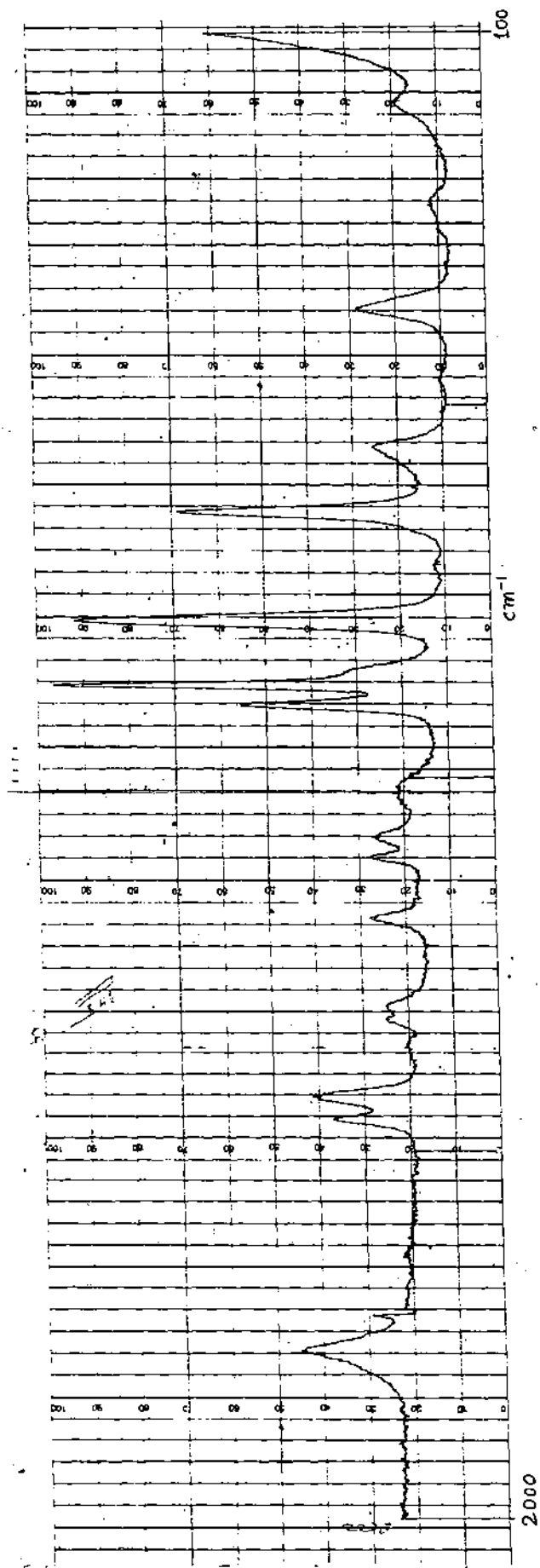


Fig. 10 Raman spectrum of $\text{Mg}(\text{ClO}_4)_2$ in propylene carbonate

R E F E R E N C E S

1. E.G. Höhn, J.A. Olander and M.C. Day, *J. Phys. Chem.*, 73, 3880, 1969.
2. H.L. Yeager, J.D. Fedyk and R.J. Parker, *J. Phys. Chem.*, 77, 2407, 1973.
3. R.E. Hester and R.A. Plane, *Spectrochim. Acta*, 23A, 2289, 1967.
4. K. Balasubrahmanyam and G.J. Janz, *J. Am. Chem. Soc.*, 92, 4189, 1970.
5. S.A. Al-Baldaui, M.H. Brooker, T.E. Gough and D.E. Irish, *Can. J. Chem.*, 48, 1202, 1970.
6. C.C. Addison, D.W. Amos and D. Sutton, *J. Chem. Soc (A)*, 2285, 1968.
7. W.H. Lee, in *Chemistry of Non-aqueous Solvents*, ed. J.T. Lagoski, Academic Press, New York, 1976, Vol. 4, Ch. 6.
8. R.J. Jasinski, *High Energy Batteries*, Plenum Press, New York, 1967.
9. R.J. Jasinski, *J. Electroanal. Chem.*, 15, 89, 1967.
10. R.F. Nelson and R.N. Adams, *J. Electroanal. Chem.*, 13, 184, 1967.
11. H. Doe, K. Wakamiya and T. Kitagawa, *Bull. Chem. Soc. Jpn.*, 60, 2231, 1987.
12. N.B. Colthup, L.H. Daly and S.E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, N.Y., 1964, p. 379.
13. J.L. Hales, J.I. Jones and W. Kynaston, *J. Chem. Soc. (A)*, 618, 1957.
14. A.D.F. Pullin and J.M. Pollock, *Trans. Faraday Soc.*, 54, 11, 1958.

15. R.F. Kempa and W.H. Lee, *J. Chem. Soc.*, 1936, 1958.
16. P.K. Muhuri and D.K. Hazra, *J. Chem. Soc., Faraday Trans.*, 87, 3511, 1991.
17. L.M. Mukherjee, D.P. Boden and R. Lindauer, *J. Phys. Chem.*, 74, 1942, 1970.