

## RAMAN SPECTROSCOPIC STUDIES OF NON-AQUEOUS SOLUTIONS

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**Abstract** - The techniques available for the application of Raman spectroscopy to the study of non-aqueous solutions are reviewed. Such techniques include operation at non-ambient temperature and pressure, and with corrosive liquids. The results from such studies are discussed under the headings: pure solvents and solvent mixtures; cation-solvent interactions; cation-ligand interactions; solvent-moderated ion-pair interactions.

### INTRODUCTION

The development of Raman spectroscopy for chemical purposes has a curious history. Shortly after its discovery this form of spectroscopy became the major source of information on the vibrational properties of molecules, and many important findings emerged - the identification of  $\text{Hg}_2^{2+}$  in aqueous solutions of mercury(I), and of  $\text{NO}_2^+$  as the active species in the sulphuric/nitric acid nitration mixture, to quote just two examples. Studies of infrared spectra were, until ca. 1945, mainly concerned with the overtone region (near infrared) in which glass is transparent, but these investigations were of necessity limited to those vibrations whose overtones are sufficiently intense for study. Then, with the introduction of the 'Infracord' machine, infrared spectroscopy became the most widely used vibrational technique in all fields except of aqueous solutions, where handling problems restrict the utility of infrared techniques. Much of the recent work on infrared spectra of non-aqueous solutions was reviewed at IV.ICNAS in Vienna by Popov (1).

The development of the laser has changed the situation once again. After a slow start, beginning in 1962, the main break-through came with the development in about 1970 of high-power, continuous sources, such as the  $\text{Ar}^+$  and  $\text{Kr}^+$  plasma which are eminently suitable for the excitation of Raman spectra. Thus the balance between the complementary techniques for i.r. and Raman spectroscopy has finally been attained with the development of simple, if rather expensive, Raman spectrophotometers.

However, the application of Raman spectroscopy to non-aqueous solutions has lagged behind other applications, except in the field of molten salts, which will not be discussed here. There is no obvious reason for this state of affairs. Our own interest dates from 1972 when I, with a background of co-ordination chemistry and J.B. Gill, with his background of thermodynamic studies of liquid ammonia solutions decided to join forces to investigate what was then almost virgin territory. The influence of our respective backgrounds will become plainly apparent when we discuss our results.

Raman spectroscopy is particularly well adapted for the study of solutions, since, as both incident and scattered radiation are usually in the visible region of the electromagnetic spectrum, any transparent material, including glass can serve as cell material. The cells do not need to be of high optical quality, and pyrex tube is in fact satisfactory for many purposes. For corrosive liquids, windows of corundum, cut with the optical axis perpendicular to the face to minimise window polarisation effects may be used (2). Indeed the whole cell may be made from this material, making the study of hydrogen fluoride solutions possible (3).

There is no difficulty in working at temperatures above ambient. The cell may be provided with a metal jacket through which flows liquid from a conven-

tional thermostat, or, for higher temperatures a simple wire-wound furnace may be used. Various designs may be used for sub-ambient temperatures (4). Our own design (5) emphasises the importance of the cryostat being top-loading and optically efficient, and has a single set of heated windows. If an evacuated jacket is used, as in the commercially available cryostats, a pair of windows will be required.

A typical instrumental set-up is shown in Fig.1. The laser beam enters the

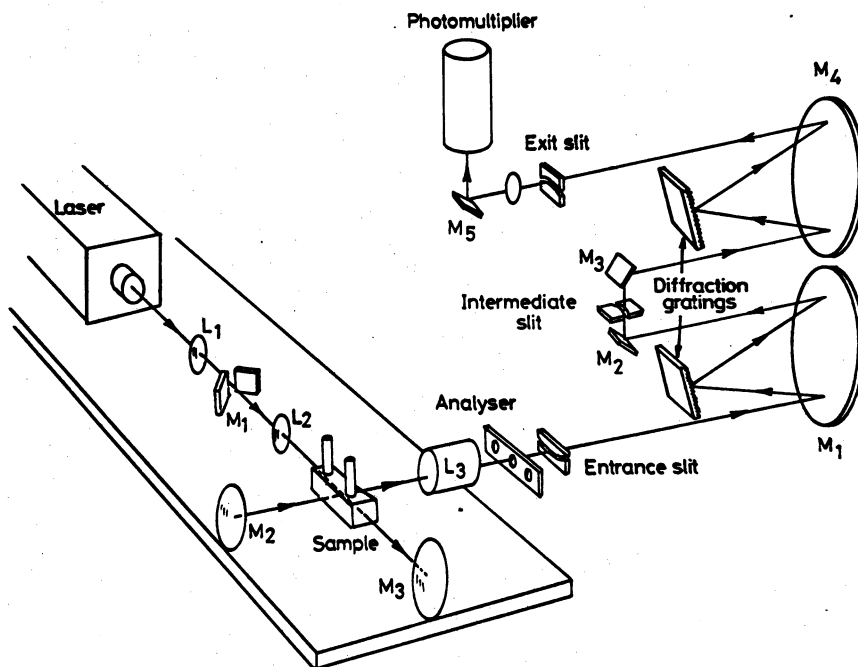


Fig.1 Schematic diagram of layout for laser-Raman spectroscopy using the Coderg spectrophotometer.

cell horizontally and the Raman radiation is collected in the same horizontal plane. The spectrometer must be of high quality, with at least two gratings to provide adequate discrimination against the Rayleigh scattered radiation. For solution work there is little need for a third monochromator, particularly if holographically ruled gratings are used. DC amplification of the photo-multiplier response is not inferior to photon counting, since solute spectra are usually not of low strength, but are measured against a fairly high solvent background. Instrumental operation presents no special problems.

There is some difficulty, however, in making quantitative measurements of Raman intensity, because of the single-beam nature of the experiment. Internal intensity standards are obviously possible, and scattering power may be corrected for the instrumental function and fourth-power-law variation, to give an "absolute" intensity (6). An external standard may be applied with a rotating cell technique (7).

The elimination of solvent spectra is also tricky, since a double-beam technique with variable solvent reference is not possible. One also meets the difficulty that the solvent's spectrum may not be invariant to changes of solute concentration. Thus, whether a rotating (8) or oscillating (9) arrangement is used for solvent spectrum subtraction, the process is never completely successful. The solvent spectrum, if assumed to be constant, may be subtracted digitally after suitable scaling. Another aspect of intensity measurement is the use of curve-resolution techniques, but a discussion of these is not appropriate here.

## RESULTS

In reviewing the results of Raman spectroscopic investigations one should always remember that Raman and infrared spectra are mutually complementary, and that other techniques such as n.m.r. and e.s.r. spectroscopy may be needed to resolve a problem fully. With those reservations we can consider the results under the headings: pure solvents and solvent mixtures; cation-solvent interactions; cation-ligand interactions; solvent-moderated ion-pair interactions. The examples chosen are but a representative selection of our recent results. A comprehensive review of Raman spectroscopic results for electrolyte solutions will appear shortly (10).

Pure solvents and solvent mixtures

The interest here centres on the intermolecular interactions and the state of solvent aggregation. A typical system studied is liquid hydrogen fluoride, Fig.2. From the spectra at a series of temperatures between  $-34$  and  $+49^{\circ}\text{C}$

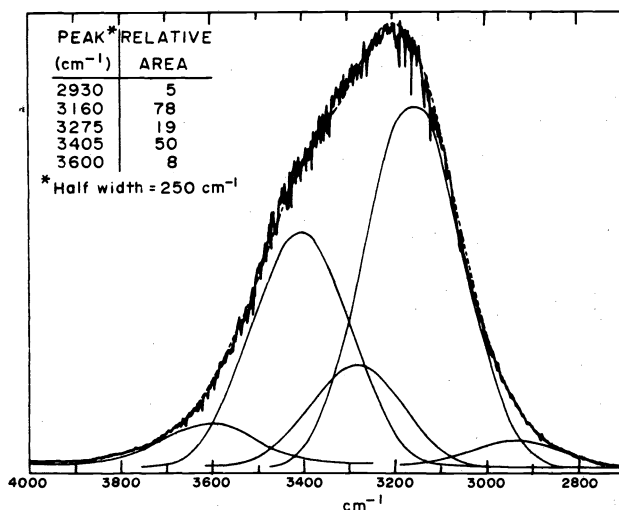


Fig.2 Resolved Raman spectrum of liquid HF at  $-34^{\circ}\text{C}$ . Reproduced, with permission, from ref.3.

and from previously reported vapour density data Sheft and Perkins concluded that no single oligomeric species was predominant (3). The situation regarding liquid ammonia is even more controversial. There is considerable evidence for some kind of molecular aggregation, but few reliable structural indications (10).

Cation-solvent interactions

Direct interaction of donor solvent molecules with acceptor cations should give rise to a well defined solvated cation complex. The totally symmetric stretching vibration of this complex will be Raman active, and its characteristics can be used to infer properties such as the coordination number of the cation. We have observed the appropriate band in liquid ammonia solutions of a wide variety of cations (11), and the results are shown in Fig. 3. The observations for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  have been confirmed by others (12), and values for  $\text{Ag}^+$  ( $260\text{ cm}^{-1}$ ) and  $\text{Pb}^{2+}$  ( $315\text{ cm}^{-1}$ ) are not shown. The conclusions are relatively straightforward. All the amines are octahedral except those of  $\text{Li}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^{2+}$ . Data, shown for comparison purposes, of the analogous aquo-complexes, suggest that coordination numbers in the two solvents are the same, with the probable exception of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$ . The latter is the most interesting, since it is clear that  $[\text{Ag}(\text{NH}_3)_2]^+$  is not present as it is in aqueous ammonia. The consequences of this are still being explored, but one system has already been examined in some detail, and this will be discussed next.

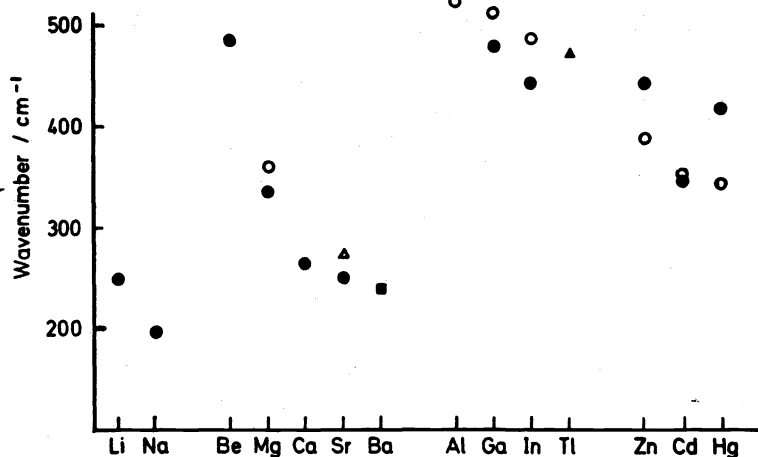


Fig.3 Raman-active M-NH<sub>3</sub> (●) and M-OH<sub>2</sub> (○) stretching vibration frequencies. Reproduced, with permission, from ref.11.

#### Cation-ligand interactions

It is well known that the complex  $[\text{Ag}(\text{CN})_2]^-$  is very stable in aqueous solution;  $\log \beta_2 > 20$ , and AgCN is insoluble. When  $\text{K}[\text{Ag}(\text{CN})_2]$  is dissolved in ammonia a redistribution occurs and "AgCN" and  $[\text{Ag}(\text{CN})_3]^{2-}$  species are formed (13). This is illustrated in Fig.4. The bands marked A belong to

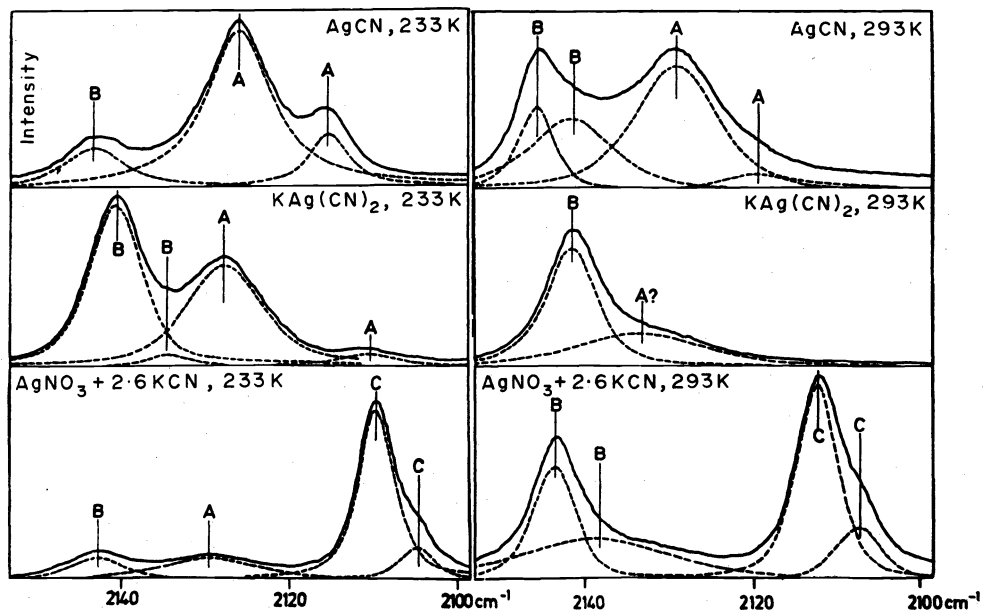


Fig.4 Raman spectra of cyano-silver complexes in liquid ammonia. Reproduced, with permission from ref.13.

a species of stoichiometry AgCN, B to  $[\text{Ag}(\text{CN})_2]^-$  and C to  $[\text{Ag}(\text{CN})_3]^{2-}$ . The stepwise equilibrium constants  $K_2$  and  $K_3$  are small and  $K_4$  is immeasurable.

Unfortunately we have no measure of  $K_1$  since we cannot observe free cyanide ions. However it is clear that the equilibria in ammonia and water are substantially different from each other.

Even more surprising is the fact that each cyano complex of silver(I) displays two prominent Raman bands. In the case of "AgCN" we have postulated that these originate from linkage isomerism involving the cyanide ion (13). If this interpretation is correct, it is the first time such isomerism has been observed and it is probable that anion solvation plays an important role in the process.

Other ligation studies mainly concern the nitrate ion, but these are intimately related to other forms of ion-pairing and will be passed over briefly (14). The main difference between aqueous and ammonia spectra is in the  $\nu_3$  region - the asymmetric N-O stretching vibration, where it seems that the solvent-nitrate interaction is weak, but not absent in ammonia.

#### Solvent-moderated ion pair interactions

We have studied in some detail ion-pairing in alkali metal salts of a wide variety of anions. We choose to illustrate the results mainly in terms of the cyanides. We obtain the first direct evidence (15) for the co-existence, in ammonia solution, of various types of ion-pair, though the assignments we make are rather speculative.

Some typical spectra are shown in Fig.5. The difference between NaCN and

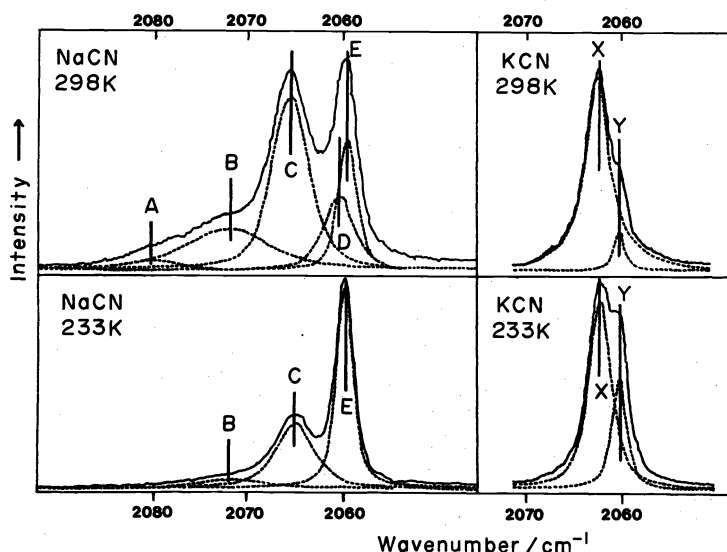


Fig.5 Raman spectra of liquid ammonia solutions of sodium and potassium cyanide. Reproduced, with permission from ref.15.

KCN is striking, and results from a weaker inter-ionic perturbation. We assign bands E and Y to the 'free' ion, and C and X to the solvent-shared ion pair, *i.e.* the pair formed from solvated cation in contact with the anion. Bands B and A probably represent contact ion-pairs, and D is problematical - there is some spectral and computational evidence for its presence, but it is insufficient for detailed characterisation.

The relative intensity of each component varies with varying concentration and temperature. A typical trend is shown in Fig.6. The concentration of 'free' ion decreases rather slowly, but the figure highlights a major problem. Results are needed at much lower concentration. This will be difficult to achieve using conventional Raman spectroscopy because of the increasing contribution from the solvent to the solute's spectrum. One possible way might be the use of Resonance Raman effect, in which enhanced intensity results when a molecule is irradiated at absorbent wavelengths. However, this will require the use of either coloured anions, or u.v. lasers (16).

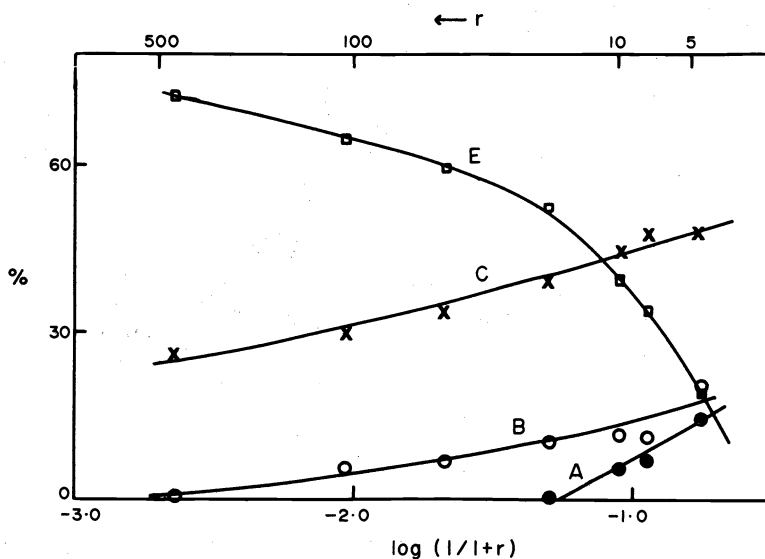


Fig.6 Variation with concentration of the relative intensities of Raman bands from sodium cyanide in liquid ammonia at 25°C. Reproduced, with permission from ref.15.

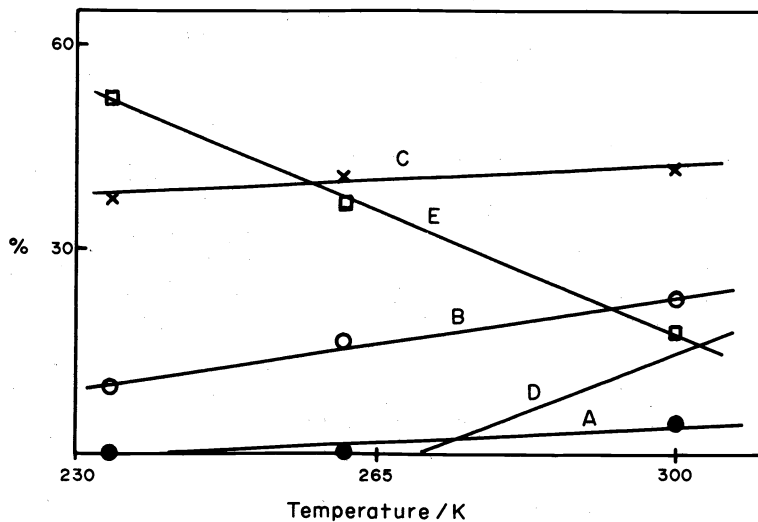


Fig.7 Variation with temperature of the relative intensities of Raman bands from sodium cyanide in liquid ammonia. Reproduced, with permission from ref.15.

Variation with temperature is shown in Fig.7 the proportion of 'free' ion rises as temperature falls. This is expected on the basis of dielectric constant considerations as  $\epsilon$  increases from 16 - 25 approximately.

To illustrate the variation with cation in more detail, we consider the thiocyanates in preference to cyanides; the trend is similar but the data are more extensive (17).

A typical spectrum is shown in Fig.8. The three bands appear in the Li, Na, K and Cs salt solutions, increasingly closer in frequency. Variation of the relative proportion of the 'free' ion with concentration is shown in Fig.9.

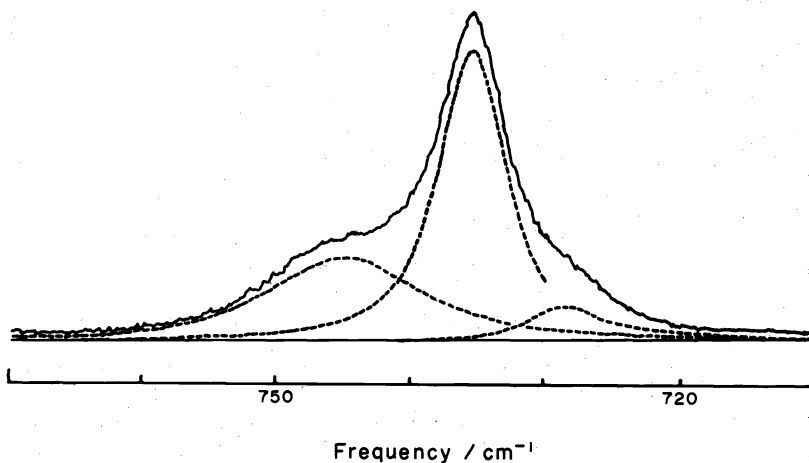


Fig.8 Raman spectrum of  $\text{NaNCS}:\text{NH}_3$  (1:20.8) mixture at  $25^\circ\text{C}$ .

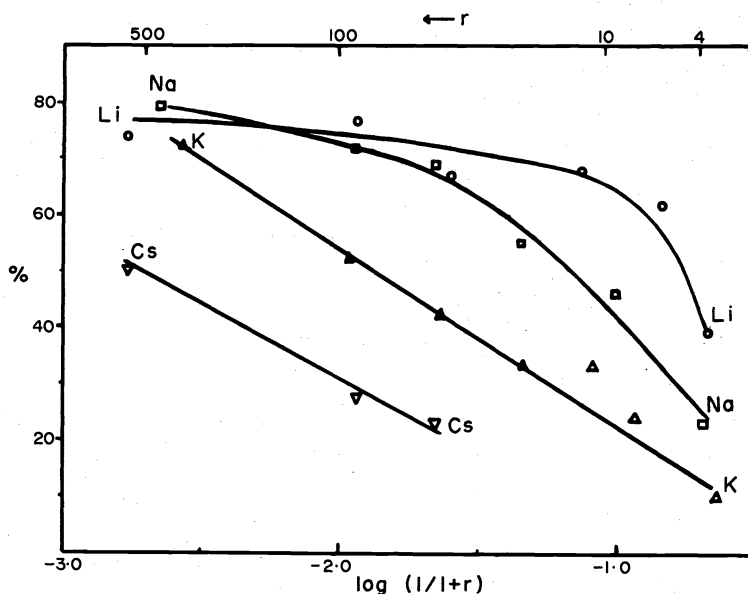


Fig.9 Variation with cation of relative proportion of 'free' thiocyanate ion in alkali metal salt solutions in liquid ammonia, as a function of concentration.

These trends are particularly difficult to interpret. At high concentrations the extent of ion-pairing, as judged by the proportion of 'free' ion present increases in the order  $\text{Li} < \text{Na} < \text{K} < \text{Cs}$ , but if one extrapolates to low concentration the order seems to be  $\text{K} < \text{Na} < \text{Li}$ . The latter is what one expects on the basis of size considerations, though the effective cationic charge is somewhat moderated by the polarisable ammonia ligands.

A possible explanation lies in the changing nature of the medium, from dilute solution to a quasi-lattice structure with locally ordered arrays of cations and anions. The factors determining the extent of ion-pairing are clearly quite different in the two limiting types of medium. If this is a medium effect, then Raman spectroscopy provides an excellent tool for its investigation.

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