

Raman study of the mechanisms of formation of water–monomethylhydrazine solid mixtures

J. C. Bureau, T. El Widadi, Z. Sassi and M. Diot

Laboratoire de Thermochimie Minérale, URA CNRS no. 116, Bât. 401, INSA de Lyon, 20 avenue Albert Einstein, F-69621 Villeurbanne Cedex (France)

M. T. Cohen-Adad and M. Ferriol

Laboratoire de Physico-Chimie Minérale II, URA CNRS no. 116, Université Claude Bernard Lyon I, 43 boulevard du 11 Novembre 1918, F-69622 Villeurbanne Cedex (France)

A. Laachach

ENIM, Rabat Agdal (Morocco)

Abstract

Water–monomethylhydrazine (MMH) mixtures have been investigated by means of Raman spectroscopy for the entire concentration range at room temperature and *vs.* temperature for some mixtures. The Raman spectra of the liquid mixtures have shown that several species coexist in solution. Spectroscopic features have been assigned to MMH dimers and MMH *n*-hydrates, confirming previous investigations performed in our laboratories using other techniques. It has been shown that solvation of MMH had a major influence on the C–N–N skeleton vibrations. For highly concentrated solutions in MMH, the presence of a high percentage of MMH dimers has been confirmed. A preliminary study of the effects of temperature on some water–MMH mixtures has shown that the skeleton frequencies are also perturbed by cooling.

1. Introduction

Water and monomethylhydrazine (MMH) mixtures have already been prepared and several of their physical and thermodynamical properties (phase equilibria, viscosity, density, molar volume etc.) have recently been investigated [1, 2]. In recent work [3] it was shown that several species (dimers, *n*-hydrates with *n* = 1 and 3) coexist in the liquid phase, which could lead to the formation of glasses or amorphous solids as the solutions are cooled down. In order to confirm the previous results and to study the formation of an expected organic glass, we have decided to undertake a systematic study of the whole concentration range by means of Raman spectroscopy, for the room temperature liquid solutions, before investigating the solid state.

2. Experiments

Throughout this paper, concentrations will be expressed in percentages by mole of MMH. MMH was both prepared and purified in our laboratory. In order

to control the accuracy of the mixture concentrations, MMH titrations were performed once the mixtures were prepared. It has been thus shown that the accuracy of our results was better than 5% (molar). The mixtures were placed in cells made of a Pyrex glass tube (internal diameter, 6 mm). The tubes were sealed on both sides, thus insulating the mixtures from any air damage. The cells were suitable to resist to the internal pressures induced by water expansion during solidification. The Raman spectra were recorded using a photon counter system mounted on a Coderg PH0 Raman laser spectrometer. The laser was a Spectraphysics 365–06 argon ion laser used with the green line (514.5 nm). Typical powers varied from 200 to 800 mW and were shown to have no influence on the cell temperature. The effects of polarization have not been studied. The Raman spectra were recorded immediately after preparing the mixtures, and the cells were sealed and kept in a dark place between experiments in order to limit the effects of the eventual decomposition of the mixtures themselves. No influence of time has been observed for periods up to 1 month. For the temperature effect studies, the cells were mounted in a cryostat enabling studies from 120 to 300 K.

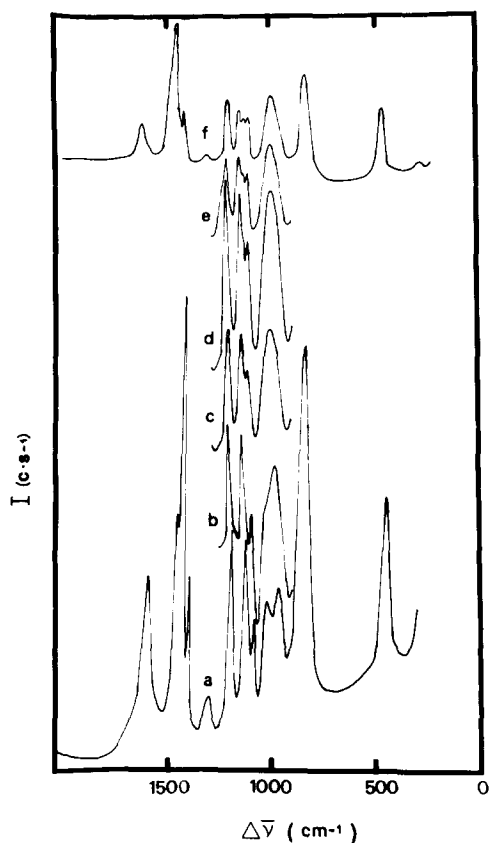


Fig. 1. Raman spectra of water-MMH mixtures in the liquid phase at room temperature *vs.* concentration (per cent by mole of MMH) (resolution, 4 cm^{-1}): spectrum a, 10%; spectrum b, 36%; spectrum c, 50%; spectrum d, 60%; spectrum e, 80%; spectrum f, pure MMH.

3. Results

Figure 1 shows typical Raman spectra of water-MMH mixtures in the liquid phase at room temperature. As shown in Fig. 1 the evolution of the spectral features depends on the concentration range. Within our experimental accuracy (about 4 cm^{-1}) it was observed that several frequencies varied *vs.* concentration, towards both lower and higher frequencies, but more generally towards lower frequencies, as the MMH concentration is increased. Some lines also exhibited a complex behaviour as both intensities and positions changed, and the concentration range can be roughly separated into two regions, either before or after 50%. The experimental frequencies are given in Table 1, and Fig. 2 gives a representation of the frequency *vs.* concentration behaviour.

The effects of temperature on water-MMH mixtures have been studied in the concentration range where the formation of a glass or an amorphous solid is expected [3]. The spectra have been recorded from ambient temperature to 150 K ($-123\text{ }^\circ\text{C}$). Figure 3 shows the

Raman spectra of a 36% water-MMH mixture *vs.* temperature. The same Raman lines as those involved with concentration effects reveal a constant modification as the temperature is lowered.

4. Discussion

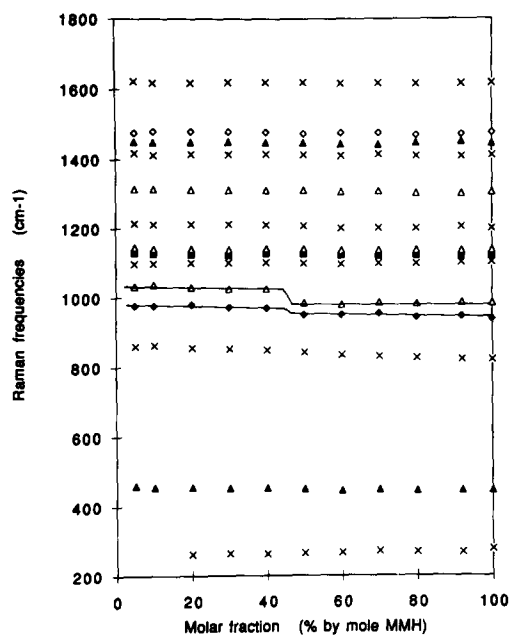
The behaviour of the Raman lines is typical of a system in which several chemical species coexist. With respect to the values of the frequency shifts ($\Delta\nu$ varying from 10 to 40 cm^{-1}) we can undoubtedly assume that no chemical reaction occurs. Nevertheless, the frequency shifts and intensity changes can be related to van der Waals' interactions, *i.e.* associations of molecules (n -mers or n -hydrates). In a first attempt, we have tried to assign the Raman lines using assignments given in previous papers [4–6]. Because of some inconsistencies in the assignments found in the literature, we have had to re-assign the major Raman frequencies in the light of our results. We have thus decided to undertake an assignment of the lines not only with the help of Raman spectra of hydrazine [7] and MMH, but also by analysing Raman spectra of symmetric dimethylhydrazine [4, 5, 8], methylamine [9] and dimethylamine [10]. The full development concerning our choices is described elsewhere and our assignments are given in Table 1.

Under such conditions, we can undoubtedly assign the frequencies strongly affected by concentration to the C–N–N skeleton motions. As the Raman lines we refer to are shifting in frequency, we shall refer to their values for pure MMH throughout this paper. As four lines are modified by concentration we assign the three lines at 445 cm^{-1} , 820 cm^{-1} and $937\text{--}983\text{ cm}^{-1}$ to respectively the bending, symmetric, and antisymmetric modes of the C–N–N skeleton. The fourth line at 1118 cm^{-1} is assigned to a combination mode involving a skeleton mode. Because of the superposition of the lines, it is difficult to assign that line precisely. Nevertheless, in the low concentration domain, where it will later be explained that few species are present in solution, we can tentatively assign this line to the $\nu_a + \nu_b$ combination. These assignments are confirmed by the shape of the four involved lines, as the line at 1118 cm^{-1} is just a broad shoulder instead of the three others which are narrow intense lines.

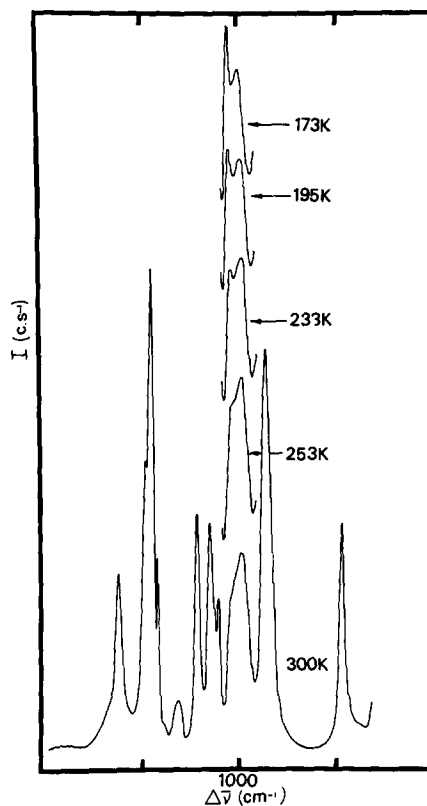
As the motions involved in the solvation are related to the skeleton, we have established a simple model of frequency calculation for these modes, assuming that solvation modifies the C–N–N angle ϕ . First of all, we have reduced the molecule to a three centre vibrator, *i.e.* we have made the assumption that, from the point of view of the C–N–N skeleton vibrations, the molecule could be represented by an $M_1\text{--}M_2\text{--}M_3$ system

Table 1. Raman frequencies of water–monomethylhydrazine mixtures in the liquid phase at room temperature *vs.* concentration

Raman frequencies (cm ⁻¹) for the following concentrations (% by mole of MMH)											Assignment
5	10	20	30	40	50	60	70	80	92	100	
		262	265	262	265	267	270	269	267		ν_a CH ₃ torsion δ
460	455	455	453	452	450	446	447	445	445	445	Skeleton bend
860	862	855	852	848	843	835	830	826	821	820	ν_b skeleton stretch + deformation mode
977	976	980	972	969	950	950	953	943	945	937	Skeleton stretch (in MMH <i>n</i> -hydrates)
1033	1037	1030	1025	1024	985	980	985	982	985	983	Skeleton stretch (in MMH dimers) + NH ₂ rocking
1098	1098	1100	1100	1100	1099	1096	1098	1098	1100	1102	NH bend
1130	1126	1124	1122	1126	1125	1121	1119	1121	1117	1118	$\nu_a + \nu_b$
1146	1141	1141	1138	1140	1140	1136	1136	1137	1135	1136	NH bend
1215	1211	1212	1211	1209	1207	1200	1200	1200	1203	1198	CH ₃ wagging
1315	1314	1312	1310	1309	1310	1305	1306	1301	1300	1303	NH ₂ wagging
1419	1412	1415	1414	1414	1413	1409	1414	1409	1407	1414	CH ₃ deformation
1451	1449	1450	1450	1447	1447	1443	1441	1447	1450	1444	CH ₃ deformation
1477	1480	1480	1478	1477	1473	1475	1475	1469	1470	1475	CH ₃ deformation
1624	1619	1619	1620	1620	1620	1616	1617	1616	1615	1617	NH ₂ scissors

Fig. 2. Variation in the Raman frequencies of water–MMH mixtures in the liquid phase at room temperature *vs.* concentration (per cent by mole of MMH).

($M_1 \equiv \text{CH}_3$; $M_2 \equiv \text{NH}$; $M_3 \equiv \text{NH}_2$). We have thus used a simple Wilson model [11, 12] to compute the variation in the C–N–N angle. The computations are described in detail elsewhere [13]. During the first step, we have computed the three force constants corresponding to the skeleton motions with the experimental frequencies corresponding to gaseous MMH and assuming that in the gas phase the C–N–N angle is close to 109.5°. Then, with the help of these force constant values, we

Fig. 3. Raman spectra of a water–MMH mixture (36% by mole of MMH) *vs.* temperature (resolution, 4 cm⁻¹).

have computed again the theoretical variations in the skeleton frequencies *vs.* the C–N–N angle. Figure 4 shows these variations. The poor accuracy for the frequency at about 445 cm⁻¹ can be explained by the fact that the matrices used in the computation were

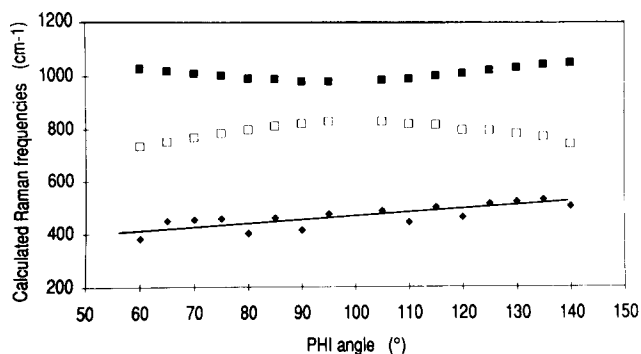


Fig. 4. Variations in the calculated skeleton vibrational frequencies ν (cm^{-1}) with the C–N–N angle ϕ (deg).

unconditioned, introducing a lack of precision in the computations. Nevertheless the behaviour of the lines at 445 and 937–983 cm^{-1} shows that the C–N–N angle is opened by solvation, which is not what would be expected from such systems. That means that, before solvation occurs, the MMH molecules are in a state which is more bent than that after solvation. In other words, before water addition, the MMH molecules are already submitted to interactions stronger than solvation, *i.e.* dimerization, because it is the only interaction that can be found in pure MMH, as the titrations have confirmed the good chemical quality of our products.

In order to check the validity of our assumptions, we have compared our results with those already obtained in our laboratories [3] which have shown that, for highly concentrated solutions in MMH, MMH dimers prevailed. As the MMH dimers are the major species in pure MMH, the MMH molecules are thus bent. Then, as water is added, dimers are gradually replaced by monohydrates. The water–MMH interactions being weaker than those between two MMH molecules, the opening of the C–N–N angle is observed. As the concentration in MMH is lowered, and while dimers vanish, MMH monohydrates are formed, followed by MMH trihydrates when the concentrations of MMH are less than 30% [3]. Of course, as we are concerned with the skeleton behaviour, we cannot differentiate the two hydrated species, the first molecule of water that fixes on MMH being the molecule that introduces the strongest interaction and the largest frequency shift on the skeleton vibrations. We have thus taken the two hydrate concentrations together and found the final assignment of the Raman lines, which can be summarized as follows.

(i) The lines which are strongly affected by solvation are related to the C–N–N skeleton vibrations. Three of them (445, 820 and 937–983 cm^{-1}) are related to the skeleton modes; a fourth line (at 1118 cm^{-1}) is a combination line.

(ii) The 937–983 cm^{-1} band is in fact a superposition of the antisymmetric mode for the dimers (at 937 cm^{-1}) and for the hydrates (at 983 cm^{-1}). Under such conditions, the 937 cm^{-1} line would totally vanish when the MMH concentration tends to zero, which is not observed experimentally, as a peak is still present for very low MMH concentrations at 935 cm^{-1} . This implies that a third line is superimposed on the skeleton vibration. This line is an NH_2 rocking mode, which is expected at that position and has already been assigned there by previous researchers [6].

(iii) No spectroscopic evidence can be found for the separation of the two hydrated species.

(iv) The behaviour of the line at 820 cm^{-1} is not well understood and our model cannot explain it: such a positive shift cannot be explained only in terms of the closing of the angle ϕ , and its continuous variation is not expected. Our model does not take into account the modifications that solvation could induce inside one or more of the three M_1 , M_2 , and M_3 groups. Another phenomenon could be responsible for this shift: the superposition of a deformation mode would forbid a precise positioning of the skeleton mode. We intend to refine our model, or better to use another model, to answer this question.

Concerning the temperature effects on water–MMH mixtures, the Raman spectra show that the natures of the species in solution are still involved in the explanation of the solution behaviour. Figure 4 shows that the major change in the spectrum is related to the 937–983 cm^{-1} band. With respect to what was found in room temperature spectra, the spectral features can be explained in terms of relative concentration changes between the MMH dimers and the hydrate species: the dimers increase in relative concentration and the relative amount of hydrates decreases. Even when the solid state is reached (173 K), for instance, the spectral features have not drastically changed, keeping the shape of what was observed in the liquid state. No lattice vibrations appeared, which would mean that the liquid state is kept in an amorphous or glassy state. Nevertheless, these are just preliminary observations and further experiments must be carried out to confirm the latter conclusions.

5. Conclusion

The Raman spectra of water–MMH mixtures have been investigated by means of Raman spectroscopy for the entire concentration range at room temperature. They have shown that several species coexist in solution. Spectroscopic features have been assigned to MMH dimers and MMH n -hydrates ($n = 1$ and 3), confirming previous investigations performed in our

laboratories using calorimetric techniques. It has been shown that solvation of MMH had a major influence on the C–N–N skeleton vibrations. For highly concentrated solutions in MMH, the presence of a strong percentage of MMH dimers has been confirmed. The separation of mono- and trihydrates has not been carried out, because of the identical spectroscopic behaviours of the two species in the 200–1600 cm⁻¹ range, and we intend to develop the study of the high frequency range. A preliminary study of the effects of temperature on some water–MMH mixtures has shown that the skeleton frequencies are also perturbed by cooling, increasing the relative proportion of MMH dimers with respect to the hydrated species.

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