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# Raman Study of Glassy Aqueous Solutions of Magnesium Salts: $MgCl_2$ , $Mg(NO_3)_2$ , $MgSO_4$ and $Mg(ClO_4)_2$

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**Raman spectra were obtained for aqueous solutions of  $MgCl_2$ ,  $Mg(NO_3)_2$ ,  $MgSO_4$  and  $Mg(ClO_4)_2$  in both liquid and glassy states. Spectral changes associated with the transition from the liquid to the glassy state were studied for the Raman OH stretching spectra, and the restricted translational Raman bands of the low-frequency Raman spectra of the glassy solutions were characterized. It is shown that the spectral features and peak frequencies are greatly dependent on the chemical natures of the anions.**

## INTRODUCTION

We have shown previously<sup>1,2</sup> that Raman spectra for glassy aqueous solutions can provide useful information on the structural characteristics of both the solvent and the solute in the solutions, unobtainable from those for the solutions at ordinary temperatures. Numerous Raman studies<sup>3-5</sup> have been reported for aqueous electrolyte solutions at ordinary temperatures. In these studies, it was often noted that the anion is a dominant factor in determining the Raman spectral features of water in an aqueous electrolyte solution. In fact, the Raman OH bands are little affected when the cations are changed from lithium to caesium ions in aqueous alkali metal halide solutions at room temperature.<sup>6</sup>

The main advantage of the Raman spectroscopy of glassy aqueous solutions is the feasibility of obtaining a clear low-frequency Raman spectrum ( $<400\text{ cm}^{-1}$ ) without a significant Rayleigh scattering wing.<sup>1,2</sup> Thus, as an extension of a previous study on aqueous  $LiX$  and  $CaX_2$  ( $X = Cl$ , Br and I),<sup>7</sup> it is of interest to see what spectral features are observed in the low-frequency Raman spectra of glassy aqueous solutions of inorganic electrolytes other than metal halides.

In this study, we chose aqueous solutions of magnesium salts [ $MgCl_2$ ,  $Mg(NO_3)_2$ ,  $Mg(ClO_4)_2$  and  $MgSO_4$ ] because they have glass-forming composition regions,<sup>8</sup> and because these four are common inorganic anions. Our main objective was to examine the effects of anions on the Raman bands of water in both the OH stretching and the low-frequency ( $10-400\text{ cm}^{-1}$ ) regions.

## EXPERIMENTAL

All aqueous magnesium salt solutions were prepared by dissolving the crystalline magnesium salts by weight in

distilled water. The concentration of all the solutions were set to  $R = 16$  ( $R = \text{moles of water}/\text{moles of salt}$ ). We chose this concentration because all the solutions are glass-forming at  $R = 16$ , so that comparison of the spectra can be made at the same concentration of magnesium ions.

Details of the Raman measurements were essentially the same as previously reported.<sup>1,7</sup>

As a glass is in a non-equilibrium quenched state, the observed Raman spectrum was expected to be dependent on the cooling rate from the liquid to the glassy state and the thermal history of the glass. However, we found that changes in the cooling rate ( $300-600\text{ K min}^{-1}$ ) gave rise to only small Raman spectral changes in these magnesium salt solutions.

## RESULTS AND DISCUSSION

### OH stretching Raman spectra

The OH stretching Raman spectra for both the liquid state at room temperature and the glassy state at liquid nitrogen temperature are shown in Figs 1-4.

In these concentrated solutions, water molecules surrounding the cations and anions play an important role in determining the spectral features. As each magnesium ion strongly binds six water molecules and the anions are also hydrated, although barely enough to complete their inner hydration spheres, it is considered that most water molecules are strongly polarized in a field between cations and anions. Hence there should be little intrinsic water-like structure in these solutions, at least at room temperature, as inferred from an x-ray diffraction study<sup>9</sup> of concentrated aqueous  $LiCl$  solutions and from a Raman study<sup>10</sup> of hydrated  $Mg(NO_3)_2$  melts. Narten *et al.*<sup>9</sup> showed in an x-ray diffraction study that the basic water structure diminishes with increasing  $LiCl$  concentration and disappears at  $R = 10$  or less.

A common feature observed in these Raman spectra is that the low-frequency region ( $3100-3300\text{ cm}^{-1}$ )

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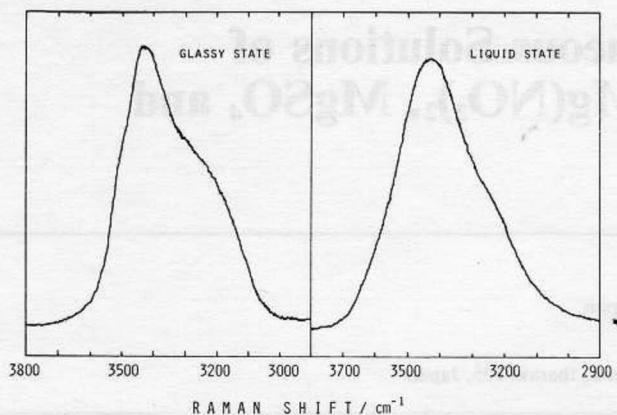


Figure 1. Raman spectra of aqueous  $MgCl_2$  solution ( $R=16$ ) in both liquid and glassy states.

increases in intensity on going from the liquid to the glassy state. We consider that this is a reflection of the partial recovery, on vitrification, of the basic water-like structure, which was disrupted by dissolved ions at room temperature. This increasing intensity trend in the lower frequency region with decreasing temperature is in agreement with observations on amorphous ice<sup>11</sup> and the temperature dependence of the OH stretching contours of water in the temperature range 4–90 °C.<sup>12</sup> Amorphous solid water and polycrystalline ice, where all the water molecules are strongly coupled with hydrogen bonds, have a very sharp peak at *ca* 3100  $cm^{-1}$ .<sup>11</sup>

Another common feature is that the OH stretching spectrum shifts as a whole to lower frequency by about 50  $cm^{-1}$  when the aqueous solution is vitrified. It is well established<sup>13</sup> that the decrease in the OH stretching frequency is a manifestation of an increase in hydrogen bond strength.

Comparison of the spectra for the liquid and glassy states shows clearly that the characteristics of the spectral features pertinent to each anion are more enhanced in a Raman spectrum for a glassy solution. As the concentration of magnesium ions in these solutions is the same, we can regard the differences in the spectral features as anionic effects.

Among these four anions, perchlorate is the most powerful structure breaker. In fact, the peak frequency of the OH stretching Raman spectrum is the highest (3545  $cm^{-1}$  at room temperature).

There has been some controversy about the nature of the high-frequency region of the Raman OH stretching

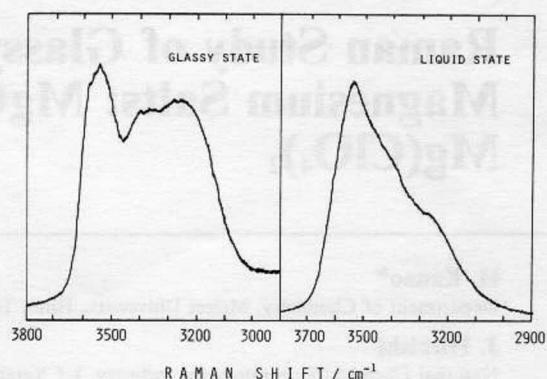


Figure 3. Raman spectra of aqueous  $Mg(ClO_4)_2$  solution ( $R=16$ ) in both liquid and glassy states.

spectrum for aqueous perchlorate solutions: Walrafen<sup>14</sup> argued that 'free' OH groups in a perchlorate solution are the cause of the high-frequency Raman peak, whereas others<sup>15,16</sup> maintain that the peak is due to the vibrations of the OH groups weakly hydrogen bonded to perchlorate ions. The latter view is now more strongly supported and accepted.<sup>15–17</sup>

An interesting aspect of the perchlorate solution is that the significant amounts of 'nearly free' hydrogen bonds produced by perchlorate ions in the solution are preserved even in the glassy state.<sup>17</sup> Together with the data for aqueous calcium perchlorate solutions,<sup>17</sup> we know that the contour apparently envelops two distributions: a higher one at *ca* 3585  $cm^{-1}$  and the other at *ca* 3545  $cm^{-1}$ . As the salt concentration increases, the lower frequency component becomes more intense than the higher frequency component. In the interpretation of the similar trapezoidal bands in the Raman spectrum of 2.0 M  $Na[PF_6]$  solution, Scherer<sup>16</sup> ascribed the lower frequency component to the  $\nu_1$  mode of the  $H_2O$  molecules having two weakly hydrogen-bonded OHs and the higher-frequency component to the  $\nu_1$  mode of the  $H_2O$  molecules with one weakly hydrogen-bonded OH. In the OH stretching vibrational region there is an approximately linear relationship between the OH stretching frequency and the hydrogen bond strength<sup>13</sup> and a lowering of the OH stretching frequency by *ca* 60  $cm^{-1}$  corresponds to 1 kcal mol<sup>-1</sup>.<sup>13</sup> Accepting this relationship, and knowing that the  $\nu_1$  band of water in the gas phase is 3657  $cm^{-1}$ , we estimate the strength of hydrogen bonding between a water molecule and a

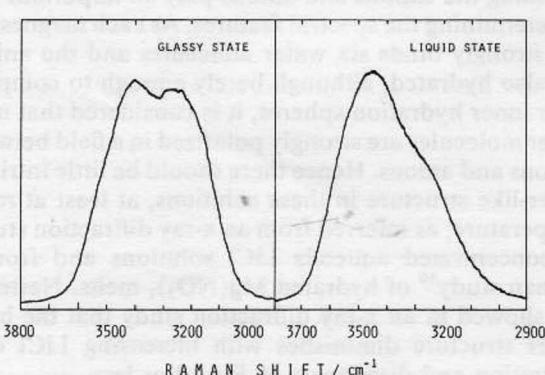


Figure 2. Raman spectra of aqueous  $Mg(NO_3)_2$  solution ( $R=16$ ) in both liquid and glassy states.

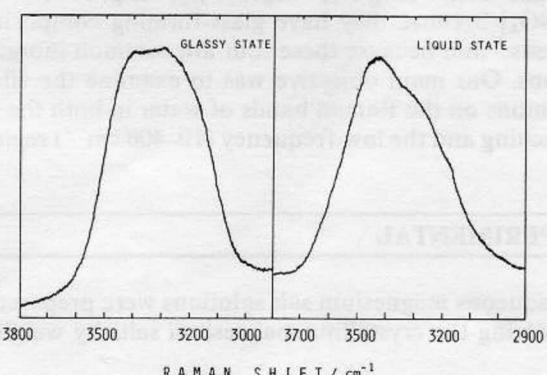


Figure 4. Raman spectra of aqueous  $MgSO_4$  solution ( $R=16$ ) in both liquid and glassy states.

**Table 1.** Frequencies of the Raman peaks (in  $\text{cm}^{-1}$ ) in the glassy Mg salt solutions

Solute	$\nu_{\text{OH}}$ band <sup>a</sup>	$\delta_{\text{OH}}$ band <sup>b</sup>	$\nu_{\text{OH}-\text{X(O)}}$ peak <sup>c</sup>	$\delta_{\text{OH}-\text{X(O)}}$ peak <sup>d</sup>
$\text{MgCl}_2$	$3430 \pm 5$ ( $3435 \pm 5$ ) <sup>e</sup>	$1660 \pm 3$ ( $1654 \pm 3$ ) <sup>e</sup>	$190 \pm 3$	$55 \pm 3$
$\text{Mg(NO}_3)_2$	$3400 \pm 5$ ( $3450 \pm 5$ ) <sup>e</sup>	$1658 \pm 3$ ( $1660 \pm 3$ ) <sup>e</sup>	— <sup>f</sup>	— <sup>f</sup>
	3350 ± 5			
$\text{MgSO}_4$	$3400 \pm 5$ ( $3425 \pm 5$ ) <sup>e</sup>	$1670 \pm 3$ ( $1645 \pm 3$ ) <sup>e</sup>	$210 \pm 3$	$65 \pm 3$
	3290 ± 5			
$\text{Mg(ClO}_4)_2$	$3545 \pm 5$ ( $3545 \pm 5$ ) <sup>e</sup>	$1625 \pm 3$ ( $1632 \pm 3$ ) <sup>e</sup>	$200 \pm 5$	$50 \pm 3$
	3250 ± 5			

<sup>a</sup>The peak frequencies for the OH stretching Raman spectrum.  
<sup>b</sup>The H-O-H bending Raman band.  
<sup>c</sup>The higher peak for the restricted translational lattice-like vibrations ranging from ca 10 to ca 300  $\text{cm}^{-1}$ .  
<sup>d</sup>The lowest frequency peak for the restricted translational lattice-like vibrations.  
<sup>e</sup>Values in parentheses are for the liquid state at room temperature.  
<sup>f</sup>The restricted rotational Raman bands of nitrate ions overlap with the restricted translational water Raman bands so that frequency assignments of the latter bands are impossible.

perchlorate ion to be *ca* 1 kcal mol<sup>-1</sup>, much weaker than the strength of strong hydrogen bonds in pure water, which is calculated to be *ca* 7 kcal mol<sup>-1</sup> (the  $\nu_1$  band of strongly hydrogen bonded water molecules in pure water is at 3225  $\text{cm}^{-1}$ ).<sup>12</sup>

The significant increase in intensity of the low-frequency region in the Raman spectrum for the glassy perchlorate solution indicates that water molecules not existing in the vicinity of perchlorate ion(s) tend to restore strong hydrogen bonds at low temperatures. The weakness of hydrogen bonds between perchlorate ions and their coordinated water molecules may be a cause of the re-formation of strong hydrogen bonds among water molecules at low temperatures.

With the chloride solution, the peak frequency at 3435  $\text{cm}^{-1}$  remains virtually unchanged from the liquid to the glassy state. The peak is mainly due to the OH stretching vibrations of water molecules coordinated to chloride ions. It is now well known that, owing to the pre-resonance Raman effect, the intensity of a Raman spectrum for an aqueous metal halide solution increases with increase in halide (except F<sup>-</sup>) concentration.<sup>7,17</sup> The charge-transfer states of hydrogen bonds between halide ions and their coordinated water molecules are the cause of the pre-resonance Raman effect.<sup>18</sup> It was found long ago that the intensities of Raman bands for aqueous halide solutions increase significantly with increase in halide concentration.<sup>19</sup> However, the importance of pre-resonance Raman effects on these intensity changes has not been appreciated until recently.<sup>7,18</sup>

The spectral shape of the OH stretching vibrations does not change much, compared with that for the perchlorate solution, from the liquid to the glassy state. There are two important factors for characterizing spectral changes in the halide solutions although they are intimately associated and are simply inseparable: the first is the change of the charge-transfer states of the hydrogen bonds between halide ions and their coordinated water molecules, which give rise to the pre-resonance Raman effect, and the second is the structural changes associated with temperature change. The apparently small spectral changes in the chloride solution from the liquid to the glassy state may be due to the cancellation of the two factors.

The OH stretching spectral contours for the sulphate and nitrate solutions are similar in the liquid state at

room temperature. However, the Raman spectra for the glassy solutions show more distinct features, although some similarities still remain. Both spectra have two maxima: the higher frequency maximum is mainly ascribed to the stretching vibrations of water molecules coordinated to anions and the lower frequency maximum to the stretching vibrations of water molecules having a more intrinsic water-like structure in the glassy state. The frequency of the lower frequency maximum for the glassy nitrate solution is *ca* 3250  $\text{cm}^{-1}$  and that for the sulphate solution is *ca* 3290  $\text{cm}^{-1}$ .

Strauss and Symons<sup>20</sup> carried out infrared and Raman studies of the solvation of ions in water and methanol at low temperatures. According to their results, the band maxima for the OH stretching mode of HOD molecules hydrogen-bonded to anions are as follows: Cl<sup>-</sup> 3370, NO<sub>3</sub><sup>-</sup> 3410, SO<sub>4</sub><sup>2-</sup> 3465 and ClO<sub>4</sub><sup>-</sup> 3530  $\text{cm}^{-1}$  at 170 K. Our results (Table 1) show a similar trend.

From the Raman spectrum for the glassy sulphate solution, it is difficult to deduce the peak frequency for the OH stretching mode of the water molecules hydrated to sulphate ions because of the broadness of the band top (3250–3400  $\text{cm}^{-1}$ ). However, from the observations that the peak frequencies of other three solutions change little from the liquid to the glassy state, it is expected that the peak frequency should shift little for the MgSO<sub>4</sub> solution on vitrification. In fact, there is a small hump at *ca* 3400  $\text{cm}^{-1}$  in the Raman spectrum top. An important result obtained from the constancy of the peak frequencies in these four solutions on vitrification is that the local water structures around anions remain virtually unchanged from the liquid state at room temperature to the glassy state at liquid nitrogen temperature.

Chang and Irish<sup>10</sup> carried out some Raman studies of aqueous Mg(NO<sub>3</sub>)<sub>2</sub> solutions including hydrated melts of Mg(NO<sub>3</sub>)<sub>2</sub>. As expected, there are significant similarities between the spectra of crystals of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and its saturated solution.<sup>10</sup> Our spectrum for the Mg(NO<sub>3</sub>)<sub>2</sub> solution (*R* = 16) at room temperature is similar to that of the saturated solution, suggesting that the basic water structures in the vicinity of cations and anions are increasingly similar to those of hydrated melts as the salt concentration increases.

The Fermi resonance also affects the Raman OH stretching spectrum. The importance of the Fermi resonance has often been noted<sup>12,21-23</sup> and detailed analyses

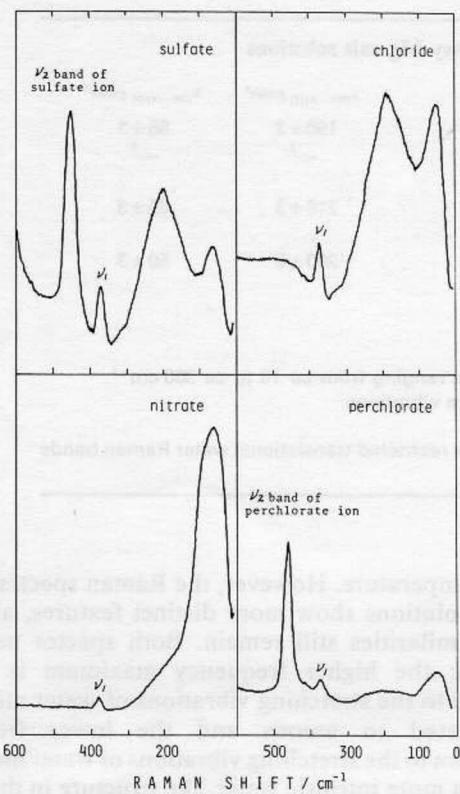


Figure 5. Raman spectra in the restricted translational vibration region ( $<400\text{ cm}^{-1}$ ) for the  $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{MgSO}_4$  solutions in the glassy state.

$\nu_1$ : Raman  $\nu_1$  band for  $[\text{Mg}(\text{OH}_2)_6]^{2+}$  ions.

for pure water and amorphous ice were made by Scherer<sup>16</sup> and Sceats *et al.*<sup>22</sup> A weak dip at  $3300\text{--}3350\text{ cm}^{-1}$  for every Raman spectrum for the glassy solution is a clear indication that the Fermi resonance is more important at low temperatures.

Before going on to a discussion of the restricted translational Raman bands, it should be mentioned that the  $\delta_{\text{OH}}$  band, apparently appearing as a single envelope, reflects the average solution structure. Interestingly, the peak frequencies vary in the order of the strength of the hydrogen bonds between water molecules and anions:  $\delta_{\text{OH}}(\text{SO}_4^{2-}) > \delta_{\text{OH}}(\text{Cl}^-) > \delta_{\text{OH}}(\text{NO}_3^-) > \delta_{\text{OH}}(\text{ClO}_4^-)$ . The same trend was observed by Ritzhaupt and Devlin<sup>24</sup> in an infrared study.

### Restricted translational Raman spectra

Raman spectra for the restricted translational vibrations in the glassy solutions are shown in Fig. 5. We can see the  $\nu_1$  (totally symmetric vibration) band of  $[\text{Mg}(\text{OH}_2)_6]^{2+}$  ions at  $370\text{ cm}^{-1}$  in all Raman spectra. As the inner-sphere coordination around an  $\text{Mg}^{2+}$  ion consists exclusively of water molecules, the Raman band at  $ca\ 370\text{ cm}^{-1}$  can be used as an internal intensity standard for comparison of the intensities of low-frequency Raman bands for these magnesium salt solutions.

Among the four spectra, the spectral features for the nitrate solution are completely different from the others

because the intense restricted rotational Raman bands of nitrate ions overlap the restricted translational Raman bands of water molecules in the solution. Therefore, it is almost impossible to obtain the genuine spectral features of the restricted translational water Raman spectrum for the nitrate solution.

The strength of the restricted translational Raman bands for the glassy  $\text{MgCl}_2$  solution is mainly due to the pre-resonance Raman effect arising from the charge-transfer states of the hydrogen bonds between chloride ions and water molecules. As has been noted briefly in the discussion of the OH stretching spectra for the chloride solution, the intensity of the Raman spectrum increases with increase in halide concentration. In this connection, it should be pointed out that the  $\delta_{\text{OH}\cdots\text{X}(\text{O})}$  band shows a larger enhancement than the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  band with increase in halide concentration.<sup>7</sup> In the glassy  $\text{CaCl}_2$  solution ( $R = 16$ ), the  $\delta_{\text{OH}\cdots\text{X}(\text{O})}$  band is higher than the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  band.

The restricted translational Raman bands for the glassy perchlorate solution are very weak. We consider that the weakness of the bands is mainly due to the weak hydrogen bonds between perchlorate ions and water molecules and to the disruption of strong hydrogen bonds among water molecules arising from the largeness of perchlorate ions. We have already observed that the weaker the hydrogen bonds become, the weaker becomes the band at  $ca\ 200\text{ cm}^{-1}$  compared with the band at  $ca\ 50\text{ cm}^{-1}$ . The higher frequency peak at  $ca\ 200\text{ cm}^{-1}$  is usually ascribed to the hydrogen bond stretching vibration [ $\nu_{\text{OH}\cdots\text{X}(\text{O})}$ ] and the lower frequency one at  $ca\ 50\text{ cm}^{-1}$  to the hydrogen bond bending vibration [ $\delta_{\text{OH}\cdots\text{X}(\text{O})}$ ].<sup>25</sup>

The broadness of the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  band for the perchlorate solution shows that there is a wide energy distribution of hydrogen bonds in the solution. This is consistent with the observation that the Raman OH stretching spectrum has a wide spectrum, as seen in Fig. 3.

With the glassy sulphate solution, the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  band intensity at  $ca\ 210\text{ cm}^{-1}$  is much higher than the  $\delta_{\text{OH}\cdots\text{X}(\text{O})}$  band at  $65\text{ cm}^{-1}$ . The frequency of the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  peak is nearly the same as that of amorphous ice ( $ca\ 217\text{ cm}^{-1}$ ).<sup>26</sup> In this respect, we can say that sulphate ion is the weakest structure breaker of the three ions (perchlorate, chloride and sulphate).

There is a strong correlation between the frequencies of the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  and  $\delta_{\text{OH}\cdots\text{X}(\text{O})}$  bands and the average strength of the hydrogen bonds. Both the  $\nu_{\text{OH}\cdots\text{X}(\text{O})}$  and  $\delta_{\text{OH}\cdots\text{X}(\text{O})}$  bands have higher frequencies as the average strength of hydrogen bonds increases.<sup>7</sup> Thus, together with the previous results for glassy  $\text{LiX}$  and  $\text{CaX}_2$  solutions ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ),<sup>7</sup> it is evident that restricted translational Raman bands, although obscured in a Raman spectrum for the liquid state at room temperature, can provide valuable information about solution structures.

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