CHAPTER III

MECHANICAL CHARACTERISTICS OF MECHANOLUMINESCENCE IN ORGANIC MOLECULAR CRYSTALS

3-1. INTRODUCTION

The outstanding parameter for describing the ML phenomenon and for its interpretation is the determination of the spectral distribution of the emitted light. Due to the low intensity and short duration of ML emission, initially it was not possible for a long time to obtain a plottable spectra. Recently the ML spectra were recorded accurately and were compared with other emission spectra of the respective substance, possibly with photoluminescence, electroluminescence, cathodoluminescence or gas discharge spectra. This allowed to draw important conclusions related to the excitation mechanism.

Another parameter is the duration of the light flashes. This quantity, however, cannot be considered as a constant and typical for a particular substance. It depends largely on the conditions of treatment. The classification of mechanoluminescent substances into A-types of short luminescence period \( \leq 10^{-4} \) sec and B-type of luminescence period greater than \( 10^{-4} \) sec proposed by Wolff et al (1955), therefore seems to be superficial.

Recently it has been realised that the ML is linked with other physical processes occurring in the crystal or on
its boundary surface. The ML research, therefore, is closely linked with the investigation of physical changes of the crystal in the course of its mechanical treatment. This includes primarily the following parameters: elastic and plastic deformations, fracture origin, production of potential difference, strain rate, conductivity, release of gases etc.

Despite of several works on ML, its mechanisms and mechanical characteristics are not satisfactorily understood to-date. Previous Studies were chiefly concerned with the identification of new mechanoluminescent substances (Imhof 1917, Levison 1904, Wolff et al 1952), the spectroscopy of ML (Hardy et al 1977, Nelson 1926, Wick 1937) and the relationships between ML and the physical properties of crystals (Sodomka 1974, Chudacek 1966, Meyer et al 1970, Albetta et al 1970). An essential step, in the understanding of ML, as in all luminescence research is the establishment of the signal to source correlation. As ML is produced during deformation of a crystal, a correlation between the ML intensity and the crystal deformation is expected. Todate neither the time dependence (kinetics) of ML nor the intensity dependence as a function of crystal deformation is satisfactorily understood. The present Chapter reports the mechanical characteristics of ML of crystals where the ML was excited impulsively by the impact of a moving piston on to the crystals. The crystals of p-anisidine,acenaphthene, N-acetylanthranilic acid, p-rhamnose, tartaric acid, and triglycine sulphate are
chosen for the present investigation. The ML spectra of p-anisidine, acenaphthene and N-acetylanthranilic acid are similar to their PL spectra, however, the ML spectra of β-rhamnose, tartaric acid and triglycine sulphate crystals are similar to the discharge spectra of surrounding gases.

3-2. EXPERIMENTAL

The crystals chosen for the present investigation were grown following the technique reported in Chapter II. The crystals were made to the required size by grinding and polishing. The size of the crystals used in the present investigation was 1.5x1.5x1.5 mm. The crystallographic axes along which the crystals were crushed are shown in Table 3-1.

The crystals were fractured by dropping a load of particular mass and shape from different heights and the ML intensities with different impact velocities were recorded using the experimental set up shown in Figure 3-1a. For the determination of the time dependence of ML, the crystal was placed on a transparent lucite plate inside a sample holder below the guiding cylinder. The luminescence was monitored from below the transparent plate by using an IP21 photomultiplier tube connected to systronics 515D oscilloscope having CRTP7 phosphorescent screen. In a dark room, a trace appeared on the oscilloscope screen, is visible
for more than a minute. The electrical connections of the photomultiplier tube is shown in Figure 3-1b. The response time in the microsecond range is necessary because we are interested in measuring the pulses due to ML emission which are of less than a millisecond duration. For this purpose, a resistance of 54.1 kΩ is connected between the anode and ground which decreases the response time of the photomultiplier-detector system. This arrangement makes the response time of our photomultiplier-detector system less than 5 μs. The response time of the photomultiplier can also be reduced by connecting condensers of appropriate values between the dynodes.

For eliminating the scattering of crystallite fragments, the crystal was covered with a thin aluminium foil and fixed with a adhesive tape. The aluminium foil was connected to one terminal of an 1.5 V battery which was connected to a resistance of 100 kΩ. The other end of resistance was connected to the metallic wire used for dropping the load through a frictionless pulley (Figure 3-1a). When the dropped load touched the aluminium foil on the crystal, a pulse appeared across the resistance of 100 kΩ. This pulse was used to trigger the oscilloscope. The ML intensity was monitored by the photomultiplier tube whose output was fed to one channel of the oscilloscope. For determining the rise and decay time of ML at different impact velocities, the trace on the oscilloscope screen was recorded.
The velocity of the load could be changed up to 400 cm/sec by changing the distance between the load to be dropped and the crystal on the lucite plate. For determining the effect of load on the ML intensity, the mass of the load to be dropped could also be changed. Since the pulley and guiding cylinder used were of negligible friction, the impact velocity $v_0$ was taken as $\sqrt{\frac{2gh}{2}}$, where $g$ is acceleration due to gravity and $h$ is the height through which the piston is dropped. Furthermore, this estimation does not make any difference because we are interested in making the relative measurements of ML.

The integrating sphere has been used by many workers for the accurate measurement of the efficiency of luminescence (Periasamy and Santhanam 1974, 1975, Zweig et al 1968, Bozman and Faulkner 1971). In all the works done on ML to date, the procedure similar to that described in the present investigation has been adopted. It has been found that when the crystals of small cross sectional area as compared to the light sensitive area of the photomultiplier tube is crushed close to the photomultiplier tube, the ML intensity measured will be proportional to the intensity of ML. Because of the limitations of our laboratory, we are not able to measure the ML intensity absolutely. However, we have normalized the ML intensity of all the crystals in terms of the ML intensity of sucrose crystals.
Fig. 3-1. (a) Schematic diagram of the experimental arrangement used for measuring the time dependance of ML in crystals (1-stand; 2-Pulley; 3-Metallic wire; 4-load; 5-Guiding cylinder; 6-Aluminium foil; 7-Crystal; 8-Transparent lucite plate; 9-Wooden block; 10-Photomultiplier tube; 11-Iron base mounted on a table, connecting wires)
Fig. 3-1. (b) Schematic diagram of the electrical circuit used for measuring the rise and decay times of ML.
For investigating the dependence of ML on the area of newly created surfaces of crystals, some simple experiments were conducted. For this experiment, the crystals were made to the required size by grinding and polishing or by cleaving. The size of the crystals used was 5x5x5 mm. However, the crystals used in cutting experiments were one mm thickness.

For the ML measurements, the crystal was fractured instantaneously by compressing it between the two jaws of a screw gauge. In an independent experiment, the crystals were cut instantaneously by a sharp blade. In this measurement, the total ML intensity was monitored by the technique described previously in Chapter II. In the cutting experiment, the area of newly created surfaces was calculated from the known dimension of the crystals. However, in the compressing experiment, the area of newly created surfaces $S$, is determined from the relation

$$S = 6 \left[ N_1 \left( \frac{M_1}{d} \right)^{2/3} + N_2 \left( \frac{M_2}{d} \right)^{2/3} + N_3 \left( \frac{M_3}{d} \right)^{2/3} + N_4 \left( \frac{M_4}{d} \right)^{2/3} \right] - S_o$$

where $d$ is density of the crystal and $S_o$ is surface area of the crystal before fracture. The crystallites formed after the fracture were divided into four groups. $M_1$, $M_2$, $M_3$ and $M_4$ denote the average mass of the crystallites of the first, second, third and fourth groups respectively. $N_1$, $N_2$, $N_3$ and $N_4$ denote the total number of crystallites of the first, second, third and fourth groups respectively. The newly created area due to the formation of some fine powders is neglected.
For each point, four crystals were studied. The error found in the measurement of ML intensity was ±6%.

3-3. RESULTS

Figure 3-2 shows the time dependence of the ML of p-anisidine crystals for different impact velocities. The ML appears after the impact of piston on to the crystal. At first, it increases with time, reaches its maximum intensity a few tenths of a millisecond after the impact, and then it decays. The peak in the ML versus time curve increases in intensity and shifts towards shorter time values with increasing impact velocities. There may be a small time lag between the impact of the piston on to the crystal and the appearance of ML, but we are not able to monitor it in the time scale used in the present investigation. The time dependence of other crystals like acenaphthene, N-acetylanthranilic acid, D-glucose, tartaric acid and triglycine sulphate is also similar to that of the p-anisidine crystals.

Figure 3-3 shows the plot of log I versus t, for rising and decaying portion of ML, at different impact velocities for p-anisidine crystals. It is seen that for rising portion of the ML, the plot of log I versus t is linear with a positive slope which suggests the relation.

\[ I = I_1 \exp (\lambda_1 t), \quad (3-2) \]

where \( I_1 \) and \( \lambda_1 \) are constants.
It is also seen from Figure 3-3 that for the decaying portion of ML with time, the plot of log I versus t is a straight line with a negative slope which supports the relation

\[ I = I_2 \exp (-\lambda_2 t) \]  

where \( I_2 \) and \( \lambda_2 \) are constant. The value of \( \lambda_1 \) and \( \lambda_2 \) increase with increasing values of the impact velocity of the piston. The physical meaning of the parameters \( I_1, I_2, \lambda_1 \) and \( \lambda_2 \) will be discussed in Chapter VI. The rise and decay portions of ML of other crystals also behave similar to that of p-anisidine crystals.

Figure 3-4 shows the dependence of peak intensity \( I_m \) of ML intensity versus time curve on the impact velocity \( V_o \). It is seen that for higher values of the impact velocity, the peak intensity \( I_m \) increases linearly with the impact velocity.

Figure 3-5 shows that the total intensity \( I_T \) of ML, defined as the area below the ML intensity versus time curve, initially increases with the impact velocity \( V_o \), and then it attains a saturated value for higher values of the impact velocity. Figure 3-6 shows that the plot of log \( I_T \) versus \( 1/V_o \) is a straight line with a negative slope which suggests the relation

\[ I_T = I_T^0 \exp (-\varphi_c / V_o), \]  

where \( I_T^0 \) and \( \varphi_c \) are constants. The physical significance of these constants will be discussed later in Chapter VI. The value of \( \varphi_c \) is different for different crystals and it is
Figure 3-7 shows the dependence of the time $t_m$ corresponding to peak in the ML intensity versus time curve on the impact velocity $V_0$, for p-anisidine and triglycine sulphate crystals. It is seen that $t_m$ decreases with increasing values of the impact velocity $V_0$. Figure 3-8 shows that for higher values of the impact velocity, the plot of $t_m$ versus $1/V_0$ is a straight line with positive slope.

The variation of total intensity $I_T$ of ML with the mass of the crystals for the impact velocity 313.2 cm/sec, is shown in Figure 3-9. Figure 3-10 shows the crystal mass dependence of the peak intensity $I_m$ of the ML versus time curve for a constant impact velocity of 313.2 cm/sec. It is found that after a minimum size of the crystals, the total ML intensity increases linearly with the volume or mass of the crystals, and the peak of the ML intensity versus time curve increases linearly with the area of cross-section of the crystals.

The dependence of total ML intensity of p-anisidine crystals on the impact velocity is shown in Figure 3-11 for different masses of the load dropped on the crystals. It is seen that for higher mass of the load, the total ML intensity attains a saturation value at lower values of the impact velocity as compared to that for lesser mass of the load.
The dependence of total ML intensity on the area of newly created surfaces of crystals is shown in Figure 3-12. It is seen that the total ML intensity is directly proportional to the area of newly created surfaces, although the ML efficiency is different for different crystals.

From the known ML intensity for a given mass of a crystal at an impact velocity 313.2 cm/sec, the relative integrated intensities per gm mole of the crystals were determined. No significant changes in ML activity were found with respect to the crushing direction of the crystals. For the determination of the approximate value of the PL efficiency, the PL is excited at 365 nm using the light coming from a 100 W mercury lamp placed at a fixed distance and the PL intensity was monitored and normalized accordingly.

It is to be noted that the absolute determination of PL efficiency needs the determination of absorption coefficient which is not done here. Table 3-1 shows that there is no systematic correlation between the ML and PL efficiencies of the crystals.

3-4. DISCUSSION

The ML excitation does not take place in the elastic and plastic regions of p-anisidine, acenaphthene, N-acetylanthranilic acid, \( \beta \)-rhamnose, tartaric acid and triglycine sulphate crystals. It appears only during the fracture of these crystals. The time duration of ML pulse due to the
motion of a single crack is in a microsecond range which is of the order of the time needed for a crack to move through the crystal. However, the time duration of a continuous ML pulse produced during the impact of a load on to the crystal is of the order of milliseconds and depends on the impact velocity. Thus the continuous ML signal produced during the impact should be the superposition of individual ML pulses produced during the motion of many cracks in the crystals. As such time dependence of ML produced during the impact of a load on to the crystal should be related to the number of mobile cracks produced in the crystals.

The linear correlation between the ML intensity and the area of newly created surfaces suggests that the atoms or molecules present on the newly created surfaces are subjected to strong deformation during the movement of cracks in the crystals. This finding may be of considerable importance in the further theoretical and experimental investigation of ML.

It has been found that the ML intensity is higher for values of the impact velocity. This fact indicates the creation of more surfaces at higher impact velocity. The increase in the ML intensity with the increasing size of the crystals may also be due to the creation of more surface area. The details of the ML excitation in the organic molecular crystals will be discussed in Chapter VI. The time dependence, impact velocity dependence and crystal size dependence of ML will also be discussed theoretically in Chapter VI.
Figure 3-2 shows the time dependence of ML intensity of p-Anisidine crystals for different impact velocities. Curves I, II, and III correspond to 313.2, 171.5, and 76.7 cm/sec, respectively.
Fig. 3-8.  The I versus \( t \) plot for \( \text{p-Anisidine} \) crystal.

(Curves I, II and III correspond to 313.2, 171.5 and 76.7 cm/sec respectively.)
Fig. 2. (a) Dependence of $I_m$ of photoluminescence crystals on the impact velocity.
Fig. 3-5. (a) Dependence of photoluminescent crystals on the impact velocity.
I - β - RHAMNOSE
II - TARTRIC ACID
III - TRIGLYCINE SULPHATE

IMPACT VELOCITY (cm/sec)

Fig. 5(c) Dependence of $I_x$ of non-stochiometric crystal on the impact velocity
Fig. 3-6. (Al)Plot of $I_p$ versus $1/V_0$ for the photoluminescent crystals.
Fig. 3-6. (b) Plot of \( \frac{1000}{V} \) versus \( \frac{1}{V_o} \) for the non-photoluminescent crystals.
Fig. 1-7. Dependence of $E_{10}$ on the impact velocity $V_o$.

I - O-anisidine
II - Triglycine sulphate

Impact Velocity (cm/sec)
$I_T (ARB. UNITS)$

1. $N$-ACETYLANTHRANILIC ACID
2. II - TARTARIC ACID
3. III - TRIGLYCINE SULPHATE
Fig. 1-12 Dependence of the total intensity of HL on the area of newly created surfaces.
<table>
<thead>
<tr>
<th>Crystals</th>
<th>P-Anisidine</th>
<th>Acenaphthene</th>
<th>N-Acetylanthranilic acid</th>
<th>f3-Rhamnose</th>
<th>Tartaric acid</th>
<th>Triglycine Sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML and PL efficiencies of the crystals</td>
<td></td>
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<td></td>
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<tr>
<td>Crystal Crushing Normalized system direction</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Activity (crystallo- with respect to graphic axis) to that of sucrose crystals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>0.43 ± 0.024</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>0.81 ± 0.053</td>
<td>0.31</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>0.52 ± 0.034</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>0.013 ± 0.006</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The table shows the normalized PL activity of various crystals with respect to that of acenaphthene crystals. It includes orthorhombic and monoclinic crystal systems.
Values of certain constants relate to the excitation of mechanoluminescence:

<table>
<thead>
<tr>
<th>Substance</th>
<th>V (cm/sec)</th>
<th>( \nu ) (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Anisidine</td>
<td>67.2</td>
<td>14.0</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>66.5</td>
<td>13.2</td>
</tr>
<tr>
<td>N-Acetylanilic acid</td>
<td>66.0</td>
<td>13.3</td>
</tr>
<tr>
<td>( \alpha )-Rhamnone</td>
<td>69.2</td>
<td>13.7</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>69.1</td>
<td>15.5</td>
</tr>
<tr>
<td>Triglycine sulphate</td>
<td>69.2</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Values of certain constants are related to the mechanical properties of crystals.

For calculation, when \( V = 313.2 \) cm/sec and \( V = 313.2 \) cm/sec, the crystal properties are:

\( \nu \approx 1.4 \times 10^{-2} \) cm/sec.
REFERENCES


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