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Publisher: Taylor & Francis

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## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

### Laser - Induced Luminescence in Trans- (CH)<sub>x</sub>

K. Iwahana<sup>a</sup>, P. Knoll<sup>a</sup> & H. Kuzmany<sup>a</sup>

<sup>a</sup> Inst. f. Festkörperphysik der Univ. Wien and Ludwig Boltzmann-Inst. f. Festkörperphysik, A-1090, Vienna, Austria

Version of record first published: 17 Oct 2011.

To cite this article: K. Iwahana, P. Knoll & H. Kuzmany (1985): Laser - Induced Luminescence in Trans- (CH)<sub>x</sub>, Molecular Crystals and Liquid Crystals, 117:1, 255-258

To link to this article: <http://dx.doi.org/10.1080/00268948508074633>

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## LASER - INDUCED LUMINESCENCE IN TRANS - (CH)<sub>x</sub>

K. IWAHANA, P. KNOLL, H. KUZMANY

Inst. f. Festkörperphysik der Univ. Wien and Ludwig Boltzmann-  
Inst. f. Festkörperphysik, A-1090 Vienna/ Austria

**Abstract** Irradiating trans-(CH)<sub>x</sub> with laser light in the visible range can give a strong enhancement of background in Raman spectra. We distinguish between two cases: (1) Irradiating with laser powers less than 100 mW; in this case pure polyacetylene is very insensitive to irradiation. Exposing trans-(CH)<sub>x</sub> to air, the oxygen which is reversibly incorporated into the material makes the polymere very sensitive to irradiation. This results in the appearance of a broad unstructured luminescence during irradiation at room temperature. (2) Irradiating with more than 100 mW: In pure trans-polyacetylene this yields a very strong, structured luminescence showing an unusual behaviour with some characteristics of hot luminescence.

## INTRODUCTION

Investigating artificially introduced defects on trans polyacetylene we found that irradiation with light does not strongly influence the prominent Raman peaks but causes a significant enhancement of background.<sup>1</sup> A more detailed investigation showed that oxygen plays an important role during irradiation.<sup>2</sup>

In this contribution we give a study on the influence of several parameters as e.g. laser power, temperature, oxygen concentration etc. on the luminescence behaviour in order to get a better understanding of defects in polyacetylene.

The observation of luminescence in Raman spectra of pristine trans (CH)<sub>x</sub> has been reported recently from other laboratories as well.<sup>3,4</sup> However, we feel that in all cases the sample quality and sample handling plays a dominant role.

## IRRADIATION WITH 457,9 nm AND 100 mW

Irradiating a standard quality sample at room temperature with a line focussed laser yields a characteristic luminescence as shown

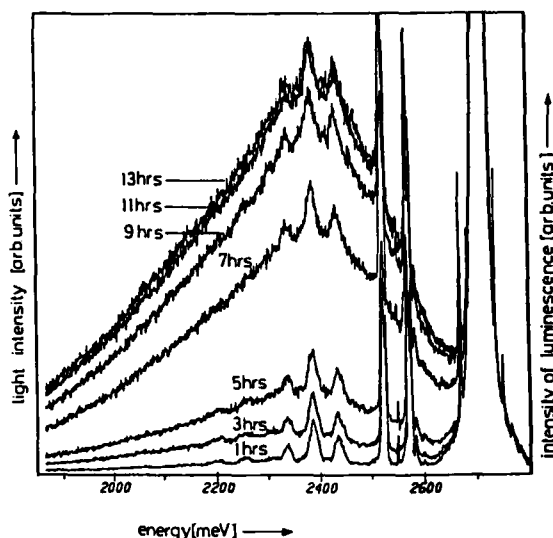


FIGURE 1 Luminescence of trans (CH) as a function of laser irradiation at room temperature.

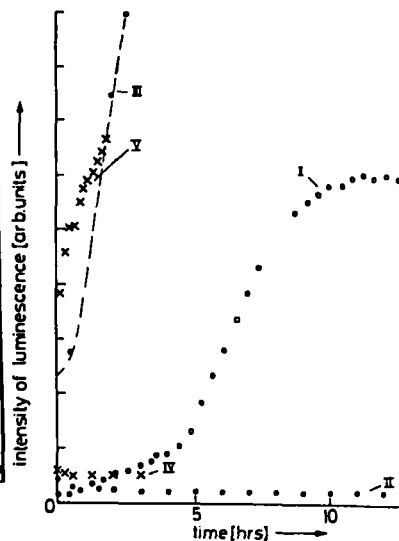


FIGURE 2 Influence of parameters like Temperature (I,II) oxidation (III), pumping (IV) and doping (V) on the luminescence.

in Fig.1.

Depending on irradiation time a broad luminescence around 2.4 eV appears in addition to the well known Raman lines. Except for these lines and their overtones no significant structure of this luminescence was observed. The response of the luminescence on the laser irradiation was found to depend critically on several parameters like irradiation temperature, exposure to air, doping etc. The influence of these parameters is shown in Fig.2. Curve I shows the behaviour of the peak intensity of the luminescence of Fig.1. After a characteristic incubation time the luminescence rises rapidly up to a saturation value after 10 hours irradiation. At low temperatures (curve II) no laser induced luminescence was observed whereas irradiation at room temperature during exposure to air yields a very strong enhancement of the luminescence (curve III). Repeating the same experiment with a sample exposed to air for fourteen days but subsequently very carefully pumped at around  $10^{-2}$  mbar over several days gives no increase in Raman background (curve IV). This experimental result suggests that oxygen which is reversibly incorporated into the material is responsible for the observed laser induced luminescence. Since on the other hand oxygen acts as a dopant for the polymer it is

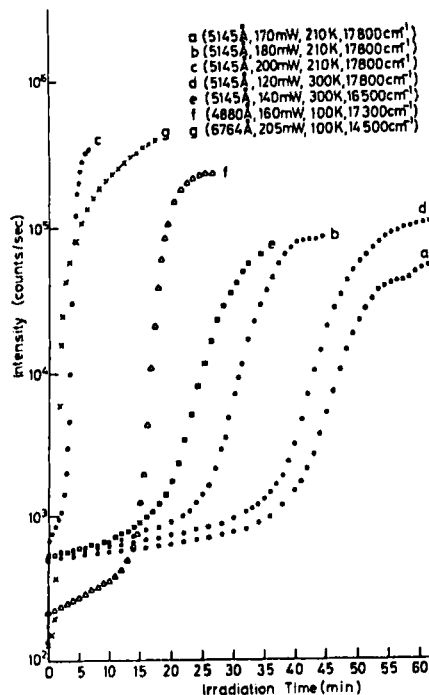


FIGURE 3 Peak intensity of luminescence of trans-(CH)<sub>x</sub> after irradiation with high laser power.

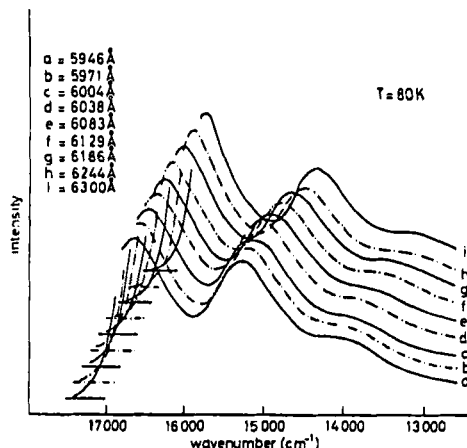


FIGURE 4 Luminescence of irradiated trans-(CH)<sub>x</sub> for various exciting laser lines.

suggested that the luminescence is due to the oxidized state of the chain. In order to check this suggestion irradiation of an electrochemically ClO<sub>4</sub><sup>-</sup> doped trans-(CH)<sub>x</sub> was performed. A similar strong enhancement of the background as for the sample exposed to air was observed which supports the idea that this luminescence is rather related to the oxidized chain than to the dopant molecule.

#### IRRADIATION WITH INTENSE LASER LIGHT

Increasing the laser power to more than 100 mW the behaviour of the background becomes more dramatic. Even without oxidation we

obtained a strong luminescence after a quite short irradiation time as shown in Fig.3. Although the curves of Fig.3 are very similar to curve III of Fig.2 the resulting luminescence is different. As Fig.4 shows a strong, broad and well structured luminescence is observed. This structure is particularly well pronounced at temperatures below 100 K. Like a first order Raman line the peaks shift with the exciting laser frequency. A more detailed description of this behaviour is given in Ref.5.

#### DISCUSSION

A general property of the luminescence described above is the characteristic behaviour with irradiation time (Fig.2 and 3). Assuming a simple model where the generation rate of luminescence centers depends on concentration of unconverted material and laser power gives an exponential increase in intensity  $I = A \cdot (1 - \exp(-k \cdot t))$ . This explains the increasing and saturating part of the luminescence. Within this very simple model the incubation time may be explained by assuming a second mechanism which causes decrease of luminescence centers. This gives an additional decreasing term  $I = B \cdot \exp(-l \cdot t)$ . An initial decrease in background luminescence is indeed observed in curve II of Fig.2, for example. Thus, if the parameters  $k$  and  $l$  have a proper temperature dependence this model can give a similar behaviour as observed. However, we cannot give a quantitative explanation for this phenomenon at present.

Acknowledgement This work was supported by the "Stiftung Volkswagenwerk".

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