RAMAN SPECTROSCOPY OF SIMPLE ORGANIC LIQUIDS IN AN EXTERNAL ELECTRIC DC FIELD

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ABSTRACT

Simple liquids have been investigated on the influence of electric fields on Raman scattering. Changes in intensities and depolarization ratios are found.

1.INTRODUCTION

Pre-breakdown conditions in liquids under electric stress have rarely been investigated by spectroscopic means up to now. Modern laser techniques have recently opened this field, however, to the experimentator.

2.EXPERIMENTAL

In our experiments /1/ we have performed measurements of Raman scattering in simple liquids under the influence of high quasi-static electric fields. The field-strengths applied have been in the range from 10^5 up to 1.2×10^6 V/cm. The highest field-strengths exceed the static breakdown strengths of the liquids by more than a factor of 2. Breakdown was avoided by applying the fields only for 50 - 500 ns. Raman spectroscopy was performed by use of a Q-switched, frequency-doubled Nd^+-YAG-laser with puls durations of 30 ns, peak-powers of 40 kW, and a wavelength of 530 nm.

3.RESULTS

In most of our measurements we found that electric fields change both the intensity as well as the depolarization ratio of various Raman bands, while no marked influence on the wave-number was observed. In general the following trend was found: For moderate fields ($\lesssim$ 500 kV/cm) both Raman intensities and depolarization ratios increased with field-strength. In the most favourable cases intensity enhancements of 6 and depolarization ratios of 0.75 could be observed. With even higher field-strengths both values were found to decrease gradually and had nearly reached the initial level when breakdown occurred finally. Lower levels than the initial one were never to be observed. Furthermore the increase was dependent on duration of the field pulses. Larger durations yielded smaller increase. The results for various liquids are summed up in Tab. 1. This behaviour, which was qualitatively the same in all liquids investigated, was complicated by a number of facts. So a severe influence of contamination was found in some cases. In Nitrobenzene, Acetonitrile, Benzene, and Methanol addition of small amounts of water caused vanishing of the enhancements observed previously. It was observed that the influence of contamination was the same, at least qualitatively, for various Raman bands in the same liquid. On the other hand, pure cyclohexane showed no field-induced enhancement. After 1:1 mixing with benzene even the bands of cyclohexane were found to be enhanced by the field.

Raman measurements performed after switching off the field showed the enhancement to decay with a remarkably long time-constant. In CS_2 the enhancement relaxed exponentially with a life-time of about 400 μs. In pure C_6H_6 a life-time of about 100 ns was found, while after mixing 10 % C_6H_6 and 90 % CCl_4, the life-time of Raman enhancement was extended to about 500 ns.

4. DISCUSSION

The severe influence of contaminations and the long life-times in our opinion give reason to believe a complex intermolecular mechanism to be responsible for the observed intensity enhancement. So an interpretation of our observation by simple physical models concerning the properties of the single molecule seems not to be possible. In addition all nonlinear molecular parameters known up to now which would explane a field dependence of Raman intensity by singel molecules would yield much smaller effects. Therefore we assume some early stage of chemical interaction induced by the field to be responsible for the enhancement in Raman intensities and depolarization ratios.

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Compound	wave number cm^{-1}	field strength kV/cm	pulse duration ns	intensity enhancement
nitrobenzene	3081	650	100	3
acetonitrile	2253			3
	2943	650	100	3
methanol	2835			2
	2944	500	100	2
benzene	3048/61	650	80	2.5
	992	650	80	1.8
cyclohexane	2852	500	100	1
	2924			1
cyclohexane (+benzene 1:1)	2852	500	100	2
	2924			2

Tab. 1: Maximum intensity enhancement

REFERENCES

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