

Experimental angular correlation functions of molecules in liquids and crystals

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Experimental Angular Correlation Functions of Molecules in Liquids and Crystals

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Experimental Angular Correlation Functions of Molecules in Liquids and in Crystals

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Abstract. In this paper we describe the experimental investigation of molecular reorientation processes with the aid of angular correlation functions. After a brief summary of the theory the experimental limitations are outlined. Subsequently this method is applied to HCl and DCl dissolved in liquid tetrachlorides and to OD⁻-ions in alkali halides. Models for the short time behaviour of these dipoles are presented. The applicability of the angular correlation functions is extended to polyatomic molecules by group theoretical considerations. Experimental examples are presented.

Zusammenfassung. Die vorliegende Arbeit befasst sich mit der experimentellen Untersuchung von molekularen Reorientierungsprozessen mit Hilfe von zeitabhängigen Richtungskorrelationsfunktionen. Nach einer kurzen Zusammenfassung der Theorie werden die experimentellen Grenzen der Methode diskutiert. Als Anwendung werden die Systeme von HCl und DCl in flüssigen Tetrachloriden und von OD⁻-Ionen in Alkalihalogeniden untersucht. Das Kurzzeitverhalten dieser Dipole wird an Hand von Modellen gedeutet. Mit Hilfe gruppentheoretischer Methoden wird der Anwendungsbereich der Korrelationsfunktionen auf mehr als zwei-atomige Moleküle ausgedehnt und die Resultate an einigen experimentellen Beispielen erläutert.

1. Introduction

Since the days of P. Debye [1] considerable effort was taken to obtain information on the microscopic mechanism of reorientation of molecules in liquids and solids. Most of the work dealt with the measurement of spectroscopic line widths and relaxation times derived therefrom, yielding one single parameter to characterize the complicated processes [2]. Moreover, different spectroscopic techniques led to contradicting results.

Fortunately in recent years linear response theory [3, 4] provided the tool to interpret the line shapes of rotating molecules in terms of time-dependent correlation functions [5, 6]. These correlation functions are obtained as Fourier transforms of the corresponding line profiles. They give a detailed description of the average molecular motion over a restricted time range. In addition the introduction of correlation functions allows us to profit from the theory of stochastic processes [7, 8, 9, 10] and to test many of the deductions of the earlier theories on a more general basis.

The purpose of this study is to demonstrate the fruitfulness of the correlation function method as well as to discuss the inherent experimental limitations and difficulties. It is applied to the vibration-rotation spectra of diatomic and polyatomic molecules in liquids and diatomic impurities in alkali halides.

A number of excellent theoretical reviews exists on the subject [2, 4, 11-14]. The principal results necessary for the comprehension of the experimental work are summarized in Section 2. Section 3 is dedicated to the evaluation of correlation and