

Interpolation model for molecular reorientation in gases and liquids

S K DEB and A K SOOD[†]

Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India

[†]Materials Science Laboratory, Indira Gandhi Centre for Atomic Research,
Kalpakkam 603 102, India

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Abstract. The interpolation model for molecular reorientation in gases and liquids has been extended to the case for symmetric top molecules. It has been compared with experimental correlation functions for linear as well as prolate and oblate symmetric top molecules. The agreement is excellent for systems where the intermolecular torque is small. With increasing torque, there is discrepancy at short times whereas at intermediate and long times the decay is described quite well. However for liquids at low temperatures, the description of molecular reorientation within the framework of this model is unsatisfactory.

Keywords. Molecular rotations; infrared line shapes; Raman line shapes; generalized extended diffusion models; interpolation model.

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1. Introduction

Reorientation dynamics of molecules in gases and liquids is being studied by a number of experimental techniques—the infrared and Raman spectroscopic techniques being the most widely used. The time-correlation function for molecular orientation vector as well as the angular velocity vector can be obtained from Fourier transform of vibration-rotation band profile in infrared and Raman spectra. The different experimental techniques and the different types of information obtained from these along with their advantages and disadvantages are reviewed in several articles (Gordon 1968; Steele 1976; Berne and Pecora 1976; McClung 1977; Vincent-Geisse 1980; Yarwood 1983 etc.). A complete understanding of the reorientation dynamics, however requires comparison of the experimental data with theoretical models. Of the several theoretical models for molecular reorientation in gases and liquids, the rotational diffusion model proposed by Debye (1928) has been the earliest and by far the simplest. This was subsequently generalized by Gordon (1966). Unlike Debye's model where the molecule reorients by infinitesimal angle, Gordon had introduced free rotation by finite angle between successive collisions. The Gordon's model, also known as the extended diffusion model (EDM) has two versions—the *M* and *J* diffusion models. The two models are indistinguishable at short times but the *J* diffusion model decays much faster than the *M* diffusion at long times. The EDM was extended to include molecules of different shapes and compared with various experimental data to obtain a clear understanding of the reorientation dynamics (McClung 1977). However, in spite of comparing a large number of experimental data, no broad consensus could be arrived