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Shape of Molecular Infrared Absorption and Raman Scattering Lines as Probe of Hindered Molecular Motion and Site Symmetry in Crystals

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Abstract

New symmetrized angular auto-correlation functions (ACFs) are applied to the theoretical description of the line-shape of internal modes in the polarized light scattering and infrared absorption spectra of molecular crystals. The model of hindered molecular motion (HMM) used to simulate the ACFs involves a molecular rearrangement by means of random angular jumps of an intramolecular vector between its hindered states in different potential wells whereas the probability density of the vector orientation is continuously distributed over the angles. The hindered states are classified according to the irreducible representations of a point symmetry group of the molecule motion. The ACFs of first and second ranks, which are important in molecular spectroscopy, are presented in an explicit form as a function of the crystal orientation in an axial laboratory coordinate frame. They depend on both the motion and site symmetry of the molecule through the correlation times and dynamic weights of the hindered states, respectively. The quantitative data important for practical applications are tabulated. The surface-plot graphs drawn for the initial amplitude of the ACFs show how an ACF anisotropy varies on changing the dynamic weights. The polycrystalline ACFs are in an agreement with the ACFs corresponding to rotation diffusion models. Therefore, the present theory of HMM can be considered as a general one and can be used in a description of the line extension caused by HMM in condensed matter. Some well known experiments on infrared, Raman and Rayleigh spectroscopy in molecular monocrystals and liquids show the reliability of the theory. © 1998 John Wiley & Sons, Ltd.