A mathematical model of localized molecular-ion, and molecular-exciton states in a dielectric medium is described. This model is shown to provide a quantitative description of the lineshapes and temperature dependence of photoemission and UV absorption from molecular glasses and pendant-group polymers. Its extension to describe electron transfer in these systems is indicated. Attention is focused on polystyrene, poly(2-vinyl pyridine), and molecular glasses of 2-ethyl benzene, isopropylbenzene and 2-ethyl pyridine as model systems. Application of the model to describe contact charge exchange in copolymers of polystyrene, poly(methyl methacrylate) and poly(2-vinyl pyridine) correctly predicts the steady-state charge exchange among these materials.
INTRODUCTION

The nature of the electronic states associated with injected charges and optical excitations in polymeric and molecular solids has been a subject of renewed interest in recent years both because of the increasing use of such materials in electronic devices and because a question has arisen concerning the appropriateness of traditional one-electron energy band theory for the description of these states.\textsuperscript{1-3} In particular, it has been suggested that under many circumstances charges injected into polymeric and molecular materials are more analogous to localized molecular ions in solution than to the extended "Bloch" states which are thought to be associated with electronic motion in metals and common covalent semiconductors.\textsuperscript{1,2} Consequently, a suspicion has been growing that semiconducting organic solids should not be regarded as "organic semiconductors" in the traditional sense, in spite of an extensive early literature in which energy-band models were applied to interpret measurements of their optical and transport properties.\textsuperscript{4}

This paper is devoted to the presentation of a recently-developed "relaxation-localization" model of localized molecular-ion and exciton states in polymers and molecular glasses. This model was proposed initially to interpret photo-emission measurements from two pendant-group polymers: polystyrene and poly(2-vinyl pyridine).\textsuperscript{2,5} It next was utilized in the prediction and subsequent observation\textsuperscript{6} of surface states of molecular solids as well as of the temperature dependence of photoemission and UV absorption linewidths of molecular films.\textsuperscript{2,3,7} Having proven successful in describing the spectroscopic properties of typical pendant-group polymers and molecular glasses, the model most recently has been extended to provide a description of electron-transfer processes in both these materials and molecularly-doped polymers.\textsuperscript{8} Therefore it affords a unified and experimentally-verified microscopic description of electron ionization, excitation and transfer processes in a variety of molecular and polymeric materials.

The basic concepts on which the relaxation-localization model is based are simple.\textsuperscript{3,9} The molecular character of the solid state leads to weak interactions between the molecular entities and hence to a high degree of disorder. Contributions to the disorder are both static (e.g., local variations in composition and/or structure) and dynamic (e.g., thermally induced vibrations) in nature. The static disorder localizes both injected charges as molecular ions and injected excitations as molecular excitons. Once localized, these entities interact strongly with the (dynamic) charges which they induce in the surrounding dielectric medium. The induced charges in turn can be described