3.1. INTRODUCTION

In this chapter we aim to provide a general indication of the present situation in the correlation of the frequencies and intensities of absorption bands with substituent effects. We have made no attempt to include all the extant references to this subject. Since 1947 many authors have compared spectral parameters with sigma values; however many of the series of compounds used were extremely limited in substituent type and many of the experimental procedures employed gave only approximate results, or are ill-defined. We have therefore usually omitted reference to such work. Further, in order to limit the length of this chapter we have not often discussed, or in many cases specifically mentioned, work published before 1960. Two books by C. N. R. Rao provide reasonable coverage of references to infrared\(^1\) and ultraviolet spectroscopy\(^2\) until 1960, and other summaries and reviews appeared in the 1950s and early 1960s covering correlations of features of infrared\(^3\)\textsuperscript{-10} and
ultraviolet\textsuperscript{11} spectra with substituent effects. More recent reviews\textsuperscript{12-15} of Linear Free Energy Relationships make little or no mention of correlation with quantities derived from optical spectroscopy. Thus, in his recent book, Wells\textsuperscript{12} makes only passing mention of the subject and, in fact, suggests that as far as the ultraviolet region is concerned 'no real success has been obtained in attempts to correlate this type of spectroscopic data'. This, we believe, may give the erroneous impression that little progress has been made or can be made in this field. Equally, a recent review by Shorter\textsuperscript{15} devotes little space to correlations of infrared spectral results with sigma values and gives only one example for ultraviolet spectra.

A recent book on infrared group-frequencies by Bellamy,\textsuperscript{16} a book\textsuperscript{17} on the infrared spectra of benzene and its derivatives, and a review on infrared intensities by Wexler\textsuperscript{18} are valuable sources of primary references but are not complete. The other limitation on the approach we have adopted is to avoid widening the scope of this chapter to such an extent as to make it a mere list of references. Thus we make no reference, or only passing reference, to solvent or steric effects on absorption bands. This means that we have, where possible, given preference to data for non-interacting solvents, and have avoided series such as ortho-substituted benzenes. Since the field is not well understood at present, we have also given preference to results for simple substituents rather than those where d-orbital and mass effects might be involved.

We treat infrared results first and have subdivided the discussion into a consideration of (a) frequency, (b) intensity measurements. The limited number of references to Raman spectroscopy are included in the latter. Ultraviolet results are then considered under analogous headings. Finally we have attempted to indicate where we think progress might be made in the next few years.

3.2. THE INFRARED REGION: GENERAL CONSIDERATIONS

Since the general introduction of double-beam automatic-recording infrared spectrometers in 1947, many workers have considered the effect of structure on characteristic group vibrations. We give first a brief description of the relevant theory. A more detailed account can be found in several excellent monographs and reviews (see, for example, references 19–22).

The frequency at which an infrared absorption occurs is determined by the elasticity of the bond concerned. Thus the absorption corresponding to a C\texthyphen\equiv\textdegree C triple bond stretching vibration absorbing a quantum of energy occurs at a higher frequency than that for a C\equiv C double bond, which in turn occurs at a higher frequency than that for a C\textendash C single bond. Certain requirements must be met before we can expect a particular absorption to be closely related to the electrical effects of changing substituents in the molecule. First, we must make measurements under the same conditions of phase or solvent, and must avoid specific solvent\textendash solute interactions such as hydrogen-bonding. The measurements should therefore preferably be made on compounds in the gas phase, but solutions in an inert solvent represent a more