1. Introduction

The previous chapters have been primarily concerned with the theoretical description of electron–molecule scattering processes and with the appropriate comparisons between theory and experiment. The emphasis has tended to be on reaction mechanisms, rather than on the spectroscopy of the molecular states involved in the reactions. In the present chapter we take a different and complementary approach, and deal mainly with the use of electron–molecule collisions as a spectroscopic tool for investigating the electronic structure of simple molecules. We shall see that there is considerable information to be gained from electron scattering spectroscopy which is not available from optical experiments.

In Section 2 we consider the spectroscopy of negative-ion resonances. These resonances appear as sharp changes in electron–molecule scattering cross sections at low incident electron energies (typically 1–10 eV). An example is shown in Fig. 1, taken from the work of Sanche and Schulz.\(^1\) This spectrum shows the yield of electrons that pass through a sample of NO gas without being elastically or inelastically scattered. As the incident electron energy is varied the yield of transmitted electrons fluctuates rapidly. This yield is differentiated before being displayed in the spectrum, to make the fluctuations more visible. The analysis of this spectrum will be discussed in Section 2.1.

The structures which appear in electron scattering spectra such as that shown in the figure are caused by the formation of molecular negative ions \(M^-\) which quickly decay (with a lifetime typically in the range \(10^{-15}\) to \(10^{-12}\) s) by any of the routes that are energetically accessible. This can be illustrated by writing

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where $M^{*-}$ is the temporary negative ion and $n, v,$ and $J$ represent the set of electronic, vibrational, and rotational quantum numbers of the molecule. When inelastic scattering occurs at least one of the quantum numbers $n_f, v_f,$ and $J_f$ is different from the initial set $n_i, v_i,$ and $J_i$. Resonances may appear in any of the accessible decay routes. The incident electron energy at which a resonance occurs is given by the difference between the energy of the initial state of the target molecule and that of the negative ion. The observed energy width of a resonance depends on the natural decay width of the negative ion and the width introduced by the finite resolution of the electron energy analyzers. Therefore the energies, and sometimes also the widths, of the negative-ion states come directly from the experimental measurements. Other spectroscopic properties of interest are the symmetries and potential energy functions of these short-lived molecules. The experimental energy resolution and theoretical interpretation have now reached the stage at which most or all of these properties can be deduced for resonant states of several simple molecules.

In Section 3 we consider the use of the electron energy-loss technique to