Part I

Studies on Elastic Scattering Processes in Molecular Collisions
Chapter I: Introduction
With the rapid advances during the last decade in the experimental techniques, molecular beam scattering study has become one of the potentially best sources of information on intermolecular forces. This is particularly so as the more conventional methods like the transport and equilibrium properties of gases are not likely to yield more detailed informations than which have already been obtained from them during the last three decades. This is mainly due to the fact that the bulk properties as studied are the averages over the velocity distribution so that it is not possible to derive precise informations from them.

The study on the elastic scattering processes in molecular collisions can yield informations on the spherical part of the interaction. In principle, informations on the non-spherical interactions can be derived from the inelastic collisions. However, due to the experimental difficulties no sufficiently extensive and reliable inelastic scattering data have till now been produced which may be used for this purpose.

The rigorous quantum treatments of the elastic scattering process have till now been confined to the lighter systems. For the heavier systems, quantum calculations become very laborious and generally classical or semi-classical treatment is used. Some of the features of the scattering process cannot however be explained by using classical method for which semi-classical treatment is necessary.
One method for the determination of the intermolecular potential from the scattering cross section data is to assume a particular form for the potential with several adjustable parameters which are to be determined from the experimental data. This method has the basic limitation of assuming a functional form for the potential which naturally introduces constraints. The other method which is known as 'inversion' is the direct determination of the potential from the experimental data. At present considerable efforts are being made to develop this method. Exact solutions of the inversion problem exist essentially for the two cases for which either the phase shifts for a fixed angular momentum are known for all energies or the phase shifts are known for all the angular momenta at a fixed energy. Even these requirements on the initial information do not result in any solution which is unique and always valid. In the first case, all the eigen values of negative energy for the corresponding angular momentum must be considered. In the second case, only certain classes of potentials can be inverted in a unique manner. Generally these methods cannot be applied due to some practical limitations and several indirect methods have been proposed by some workers. Since certain features of the elastic scattering process such as rainbow structure, glory undulations etc. are strongly influenced by the interaction over certain ranges of the interparticle separation, it is possible to build up by parts an overall picture of the potential for a given system.
Due to the difficulties in computations and lack of sufficiently accurate and extensive data the inversion method has till now been applied successfully only in few cases. Under the circumstances at present both the methods of the determination of intermolecular forces from scattering data are being used. In this thesis, we have dealt with two interesting aspects of this problem.

Till recently most of the methods for inversion have been for the differential scattering cross section data using classical mechanics. The differential scattering cross sections are comparatively difficult to measure accurately and only recently such accurate data are being produced. The total scattering cross section which can be measured more easily has not been used for the inversion. Miller\textsuperscript{11} has suggested a semi-classical inversion method for the determination of the intermolecular potential from the energy dependence of the total cross-section in the region where the eikonal approximation is valid and the potential is monotonic. That is, this method is likely to yield informations on the repulsive part of the interaction potential. This part of the potential cannot be determined satisfactorily from the transport properties data as such high temperatures are difficult to attain in the laboratory. At present accurate total cross section data are available in the thermal energy range and it is likely that such data in the high energy range will be available in the near future\textsuperscript{12}. It is therefore essential to examine the
feasibility of this method for inversion from total cross section data. With this end in view in Chapter IV (Sec. 1) of this thesis we have applied to He-He system Miller's method for inversion and some interesting conclusions have been drawn.

The study of the rainbow scattering phenomenon is one of the most sensitive methods for obtaining information about intermolecular forces\textsuperscript{3,5}. Experiments performed earlier\textsuperscript{12,14} yielded only a few rainbow maxima and minima. With the improvement of experimental techniques, recently, several systems have been studied\textsuperscript{15,16} which have revealed a large number of maxima and minima in the rainbow structure. Such types of studies are expected to increase in the near future. For ready interpretation of the experimental data, it is necessary to have the positions of maxima and minima for different commonly used forms of intermolecular potential models. Till recently only the positions of first three maxima and minima were available in the tabular form mainly for the Lennard-Jones type potentials\textsuperscript{14,9}. Berry\textsuperscript{17} has suggested a method based on the uniform approximation which holds good at all angles near and at a distance from the rainbow angle. With the availability of this uniform approximation which has rendered computations much simpler, positions of large number of maxima and minima have been calculated in Chapter IV (Sec. II) of this thesis for the Lennard-Jones (12:6) and Kihara core potential at different energies and quantum parameters. The results have been utilized to obtain the force parameters for some systems for which a large number of well resolved rainbow peaks are available.