Reaction Dynamics
Recent Advances

Edited By
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"One amusing characteristic of
Chemists is their tendency to
talk as if they can really 'see'
atoms and molecules as clearly
as objects in the everyday world."

—I.W.M. Smith
Nature, 343, 691 (1990)

Preface

The award of the Nobel Prize in chemistry for the year 1986 to Professors D.R. Herschbach, Y.T. Lee and J.C. Polanyi could be considered an indication of the field of molecular reaction dynamics coming of age. That does not mean to say that there have not been much development after 1986. On the contrary, the activity has fluorished much more intensely. Much more refined state-to-state information has become available on the most fundamental $H + H_2$ reaction; "dynamical stereochemistry" has gotten into the parlance of the dynamicists; the shift from scalar to vector observables is noticeable; photodissociation has gotten beyond the state-to-state level; gas-surface scattering has benefitted from the developments in molecular beam and laser techniques; and more recently, the femtosecond transition state spectroscopy is being used to probe the transition state and "to observe molecular vibration and rotation". Fully converged three dimensional quantum mechanical calculations using accurate ab initio potential-energy surfaces have definitely become "practicable" if one has access to Cray or any of its cousins. Classical trajectories are being computed merrily for anything ranging from $H + H_2$ collisions to protein dynamics. It has been shown that chaos is not all that chaotic, that it has far reaching implications to intra- as well as inter-molecular processes and that some of it might be "observed". Present day detailed dynamical studies are not confined to gas phase only. Some of the barrierless isomerization reactions have become amenable to time-resolved laser spectroscopy. Theory has kept pace with experiments.

To review all the developments in the field of molecular reaction dynamics would be an undertaking we could not venture into. Instead we have highlighted some of them which fall right in our alley.

I am grateful to all the contributors for their valuable contributions and co-operation. But for the referees who took the time out to critically examine the earlier versions of the manuscripts, this volume would not be in its present form. I am grateful to all of them. It is a pleasure to place on record the fact that this volume emerged as a consequence of the two Winter Schools on Molecular Reaction Dynamics organized at IIT Kanpur and to acknowledge the continued support from the Department of Science and Technology, New Delhi. Finally, we thank Mr. N.K. Mehra of Narosa Publishing House for encouraging us into this exercise, gently reminding us of the deadlines and finally bringing the volume in the form seen by the readers.

<div align="right">N. Sathyamurthy</div>

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Contents

1. Molecular Beams and Clusters

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Abstract

Precise knowledge of intermolecular potential, which is at the heart of understanding macroscopic properties of matter, is most directly probed through measurements of scattering cross sections. High resolution differential elastic cross section data along with bulk properties can determine inert gas potentials to within 1% precision. Comparable precision in atom-diatom potential is achievable through high resolution differential cross section measurement and accurate evaluation of quenching of the diffraction structure. Rotationally inelastic differential cross section measurements provide direct information on potential anisotropy.

Supersonic expansion of pure and mixed gases lead to formation of pure and mixed clusters of various composition and sizes. Identification and characterization of clusters which provide linkage between gaseous phase and solid phase, is achieved through mass spectrometry, laser spectroscopic techniques, scattering measurements and a combination of all of them.

1. INTRODUCTION

Thermal energy atomic and molecular beam techniques are playing a very important role in the investigation of physical and chemical properties of matter. First important application of the atomic beam technique was the famous Stern-Gerlach experiment where atoms of silver were separated in an inhomogenous magnetic field depending on their spin state. Subsequently atomic beams found wide application in magnetic resonance studies [1]. Chemical application of molecular beams in a sustained manner has come into existence from sixties onwards. It is now a major and sensitive tool for probing intermolecular forces, energy transfer dynamics, biomolecular reaction dynamics, ultrasensitive spectroscopy and molecular structure, surface structure and surface reactions, catalysis, intramolecular processes, photodissociation dynamics, microelectronics and many other aspects of immense interest in chemistry and chemical physics. Precise knowledge of intermolecular forces is at the heart of understanding macroscopic properties of matter. Traditional sources of information on intermolecular forces are the bulk properties like virial coefficients, transport properties of dilute gases etc. which provide information on the "averaged"

potential. In contrast, scattering of two atoms or molecules provides a direct method for determination of interaction potentials between colliding partners. Several reviews [2–8] in this field bring out the developments in the field over the initial fifteen years or so. Theoretical developments in many of these aspects have kept pace with the experimental progress.

An important spin-off of molecular beam research is the development of supersonic jets and supersonic beams. In view of their special characteristics, they could foster the generation of van der Waals clusters, metal and semiconductor clusters of various sizes and compositions. The study of such clusters is of prime importance because they serve as a definitive approach to the study, at a molecular level, of what is frequently referred to as the aggregated or "fifth state" of matter [2] having properties between gaseous and solid (or liquid) state. It is one of the challenging problems in chemical physics to elucidate factors which influence the variation in electronic and thermochemical properties, spectroscopic features, reactivity and other properties of matter during its course of change from gaseous to condensed phase.

In view of limitation of space and time, we will presently restrict ourselves to the discussion of only certain aspects of molecular beam chemistry. Our present discussion will concern with the latest developments in molecular beam elastic and inelastic scattering studies for precise determination of intermolecular potentials and the study of van der Waals clusters.

2. MOLECULAR BEAM SCATTERING AND INTERMOLECULAR FORCES

2.1 Elastic Scattering
Body of literature on intermolecular forces is presently far too large. Existing reviews and books [8–17] cover different facets of this complex subject. The reviews by Buck and Pauly are in particular useful for knowing about the quality and quantity of information on intermolecular forces contained in scattering data of different types (diffraction, rainbow etc.) and also about methods of extracting such information the best way. For inert gases such two body potentials are known very accurately (~ 1%) from use of multiproperty analysis [20, 21]. Further, all the rare gas systems [17] have the same reduced functional form (within ~ 1%) of the potential. A decisive contribution to the present knowledge of van der Waals interaction comes from atomic and molecular beam measurements of scattering cross sections [8, 17–19]. A direct inversion procedure, which leads from scattering results to intermolecular potential energy curves, has been attempted only in a few particularly favourable cases [21], where isotropic atom-atom interactions are involved and high resolution conditions in angle and energy are obtained in the experiments. However, if for a given system in addition to scattering results other properties sensitive to the potential, e.g. spectroscopic and thermophysical data are available, a combined analysis of all these data can extend the range of validity of the potential energy function and improve its reliability [11, 22–23].

In general, two kinds of scattering measurements are made—differential and

integral cross sections. The former (DCS) for two colliding atoms provides detailed information on the interaction potential of van der Waals systems. The rainbow scattering angle provides probably the most direct and unique measure of the potential well depth ε, while the diffraction oscillations give a direct measure of the diameter σ of the repulsive wall (and thus the location of the potential minimum r_m). Typically, rainbow oscillations are easily observable for heavy systems and diffraction oscillations for light ones. The observation of both types of oscillations in the thermal energy range for rare gas-rare gas systems has so far presented a challenge to the experimentalists because of resolution problems. While most of the rare gas potentials are known within 1% of the true potentials in the attractive and low repulsive regions, there are still discrepancies concerning some unlike rare gas pairs e.g. Ne-heavier rare gas systems.

For atom-diatom scattering non-spherical part of the potential can significantly alter the observed cross sections e.g. quenching of total DCS and the glory amplitudes in integral cross sections. However, an approach similar to that used for rare gases can be extended to atom-diatom systems. The precise measurement of total DCS and accurate evaluation of quenching of diffraction structure within the framework of infinite order sudden (IOS) approximation, coupled to absolute integral cross sections and second virial coefficients also lead for systems like He interacting with N_2, O_2 and NO [24], Ar interacting with N_2 and O_2 [25] and NO scattered by Ar and Kr [26] to rather precise determination of potential energy surfaces (PES). In particular the absolute position of the repulsive wall of the spherical potential has been determined with a precision of about 1% and well depth to within 5% uncertainties, comparable to those achieved for the corresponding He-Ar system [20]. Further, rotational anisotropy has been found to agree with the results obtained from rotationally inelastic DCS data [27]. However, while for spherical systems the determination of the potential can be very accurate and conclusive [28, 29], for non-spherical systems its validity remains confined within the limits of the approximate schemes of analysis employed, since it is still impracticable to perform exact quantum calculations for potential fitting purposes [24].

2.1.1 Experimental technique

The study of differential cross section involves measurement of the spatial distribution of the particles around the scattering centre while in integral cross section study one measures the attenuation of the incident beam by the scattering medium (e.g. a scattering chamber or a second molecular beam). Further, it is often necessary to characterize the pre-collision and post-collision state of the interacting atomic or molecular species either by use of mechanical devices, electric and magnetic fields or lasers. In modern molecular beam scattering machines one almost invariably uses supersonic beam sources for reasons of better beam intensity and better beam quality.

In order to perform crossed molecular beam scattering experiments we have to look for beam detectors sensitive to flux $< 10^9$ molecules/s. Properties of a number of currently used detectors are listed in Table 1. Ions are easily detected

with multipliers where they trigger secondary electron generation. Most of the neutral particle detection techniques, therefore, depend on their conversion to ions. With the availability of intense and tunable laser sources, two-photon ionization [30] and resonance enhanced multiphoton ionization [31] methods are also used. Both methods can be made state and species selective and two photon ionization efficiency of 20% is very promising.

Table 1.   Properties of molecular beam detectors

Detector	Detected molecules	Detection efficiencies (cts./molecule)	Detector length	Response time
Open secondary electron multipliers	Ions, metastables	≤ 1	1 mm	ns
Surface ionization	Alkali halides and alkali metals	< 0.1–1	1 mm	μs to ms
Electron bombardment ionization	All	$\sim 10^{-4}$	1 cm	μs
Laser induced fluorescence	Na_2, LiH, NO etc.	0.02	1 cm to 1 μm	ns[b]
Bolometer and tunable ir laser	HF, CO, NH_3 etc.	10^{5a}	—	s[b]
cw two photon and pulsed multiphoton ionization	Na_2, K_2, large organic molecules	0.2 (TPI) 10^{-4} (MPI)	—	ns[b]

[a]Noise equivalent estimated for 2 s averaging time and 0.2 eV/molecule.
[b]Species and state selective.

Typical experimental systems for differential and integral cross section studies are shown in Figs.1 and 2. The necessary corrections required to take into account non-ideal experimental conditions are discussed in the literature. The geometric arrangement used in recent precision measurement of DCS by the Italian group [24] has the following characteristics: the collision volume is always contained in the detector viewing angle, which for a point collision zone is 0.5°, narrow divergence in angle (0.4 to 1.8°) and velocity spread (FWHM 3.5 to 20%) of the colliding beams.

2.1.2 Rare gas data
Rare gases offer the simplest systems for precise determination of interaction potential. Only when the two body potential is known precisely at all internuclear distances can serious work on problems of three body forces in dense phases can be initiated. Study of elastic scattering in inert gas systems has come a long way since the early sixties. The quality of DCS data available then and now are shown in Figs. 3 to 5. It is apparent from Fig. 5 that the high degree of instrumental sophistication allows us to resolve experimentally the fine features of the quantum scattering theory and thus derive the intimate details of the potential energy curves.
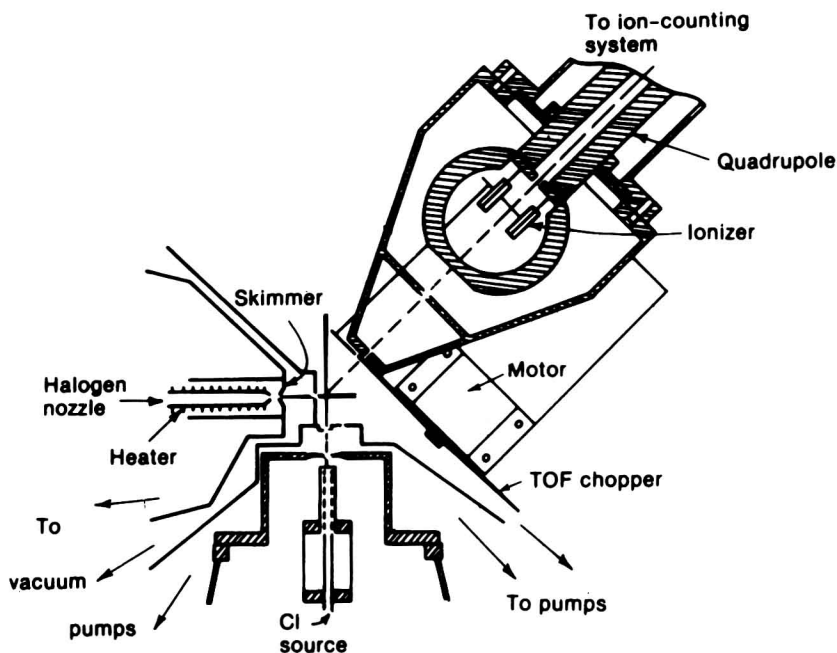
Fig. 1. Schematic diagram of crossed molecular beam apparatus showing arrangement for differential pumping for detector and source chambers and beam geometry (from J.J. Valentini et al, J. Chem. Phys. **67**, 4866, (1977)).
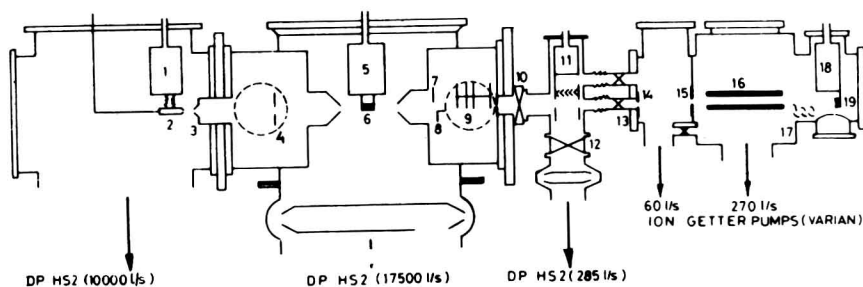

Fig. 2. Schematic diagram of apparatus used to measure integral cross section using crossed molecular beams : 1. liquid N_2 cold trap, 2. nozzle, 3. skimmer, 4. collimator, 5. liquid He/H_2 cryostat, 6. multichannel source for secondary beam, 7. shutter, 8. chopper, 9. velocity selector, 10. butterfly valve, 11. liquid N_2 cold trap, 12. VAT valve, 13. straight through valve, 14 and 15. collimators, 16. quadrupole mass filter with electron impact ion source, 17. multiplier (off axis), 18. liquid He cryostat and 19. beam trap (apparatus used in Goettingen).

For low B $(B = 2\mu\varepsilon r_m^2/\hbar^2 < 300)$ values no pronounced rainbow structure is expected. As B increases in going from He_2 to Xe_2 angular spacing and amplitude of identical particle oscillations progressively decrease and finally disappear due to finite apparatus resolution but rainbow structures do survive. In recent experiments with crossed molecular beams very high resolution elastic DCS
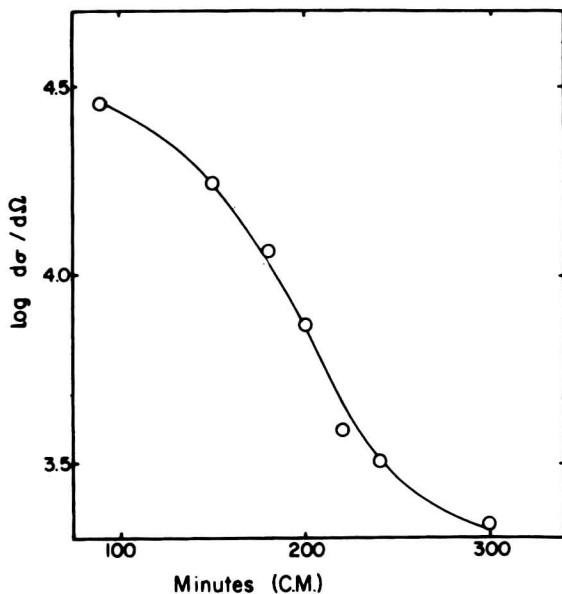
Fig. 3. Low resolution differential cross section for Ar on Ar [10].

data have been obtained [28] at thermal energies for Ne-He, Ne-Ar, Ne-Kr and Ne-Xe scattering in which diffraction quantum oscillations were superimposed on the main rainbow structure. In Fig. 6 we report the three best available potentials for Ne-Xe together with energies obtained by Maitland and Wakeham [33] from direct inversion of transport properties. As can be seen the differences in the potentials are very small (a few percent). Nevertheless, these DCS data are able to discriminate between them. None of the available potentials provides a good fit to the experimental data (see Fig. 5). The NLB (Ng, Lee and Barker) potential [34] gives the diffraction oscillations which are increasingly shifted towards too large angles with increasing scattering angle with respect to experimental data. This is because the low repulsive wall is too inward (r_m = 3.745 Å) located on the distance scale. The CPV (Candori, Pirani and Vecchiocattivi) potential [22] gives diffraction oscillations almost perfectly in phase having the correct r_m (r_m = 3.90 Å), but the location of the rainbow and general slope of the cross section curve is not in agreement with the experiment, because of too shallow a well (ε = 6.05 meV) and of incorrect slope of the outer potential wall in the region of the inflection point, just the domain of rainbow scattering. The prediction of the A (Aziz) potential having the correct r_m (r_m = 3.872 Å) follows rather closely in phase and period the experimental data. However, it does not predict the general fall off of the rainbow as well, indicating that the shape of the outer wall and/or the well depth is not correctly accounted for. The inverted energies of Maitland and Wakeham [33] give a σ value of 3.502 ± 0.009 Å which is slightly out of bounds of the direct determination (σ = 3.47 ± 0.02 Å) of the Perugia group. Clearly, presently available DCS data permit sophisticated refinement of
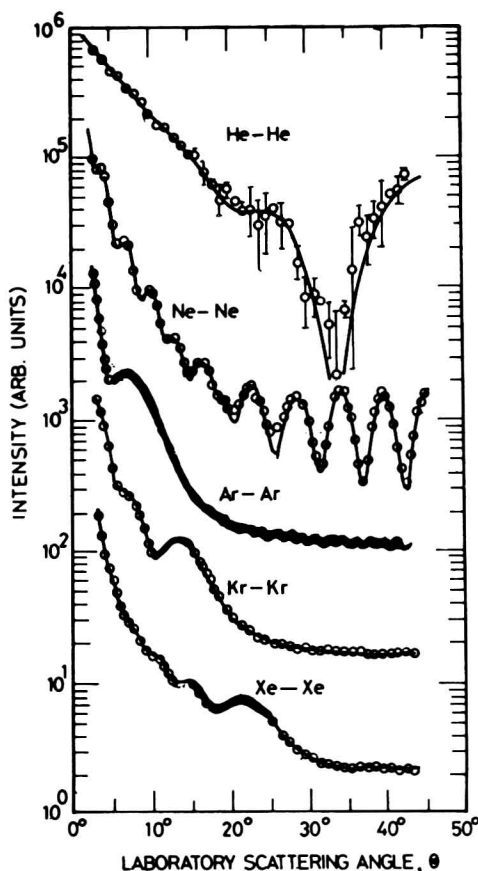
Fig. 4. High resolution differential cross section of like inert gas partners(after Y.T. Lee).

the unlike inert gas pair potential by simultaneously analysing them with other properties.

2.1.3 Atom-diatom systems

It is possible to extend to some simple atom-diatom systems the same approach used for the rare gas systems. Precise measurements of total DCS and accurate evaluation of the quenching of the diffraction structure within the framework of infinite order sudden (IOS) approximation, coupled to total integral cross sections, second virial coefficients and semiempirical long range coefficients, also lead for systems like He and other rare gases interacting with N_2, O_2 and NO to rather precise determination of some aspects of the PES. In particular, the absolute position of the repulsive wall of the spherical potential has been determined with a precision of 1% and the well depth of about 5%. These uncertainties are comparable to those achieved for He-Ar isotropic system.

As seen from Figs. 7 and 8, a pronounced quenching of the diffraction structure occurs in He-O_2, He-N_2 and He-NO cases with respect to corresponding isotropic
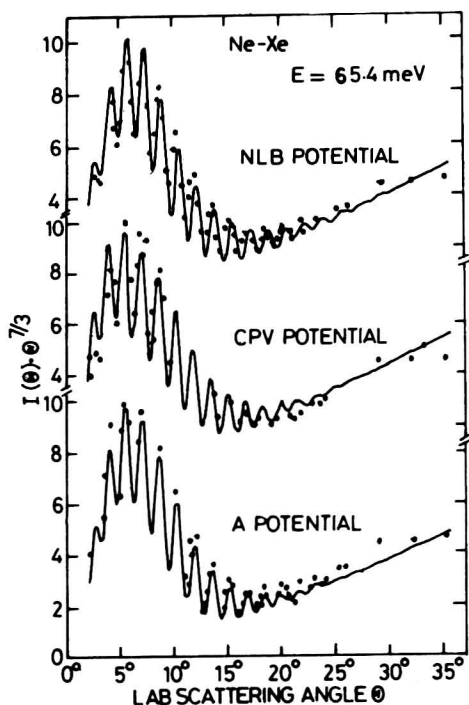
Fig. 5. Very high resolution elastic differential cross section data multiplied by $\theta^{7/3}$ for Ne-Xe system compared with predictions from different interatomic potentials. Upper curve: potential of Ng et al [34], middle curve: potential of Candori et al [22], lower curve: potential of Aziz [20].
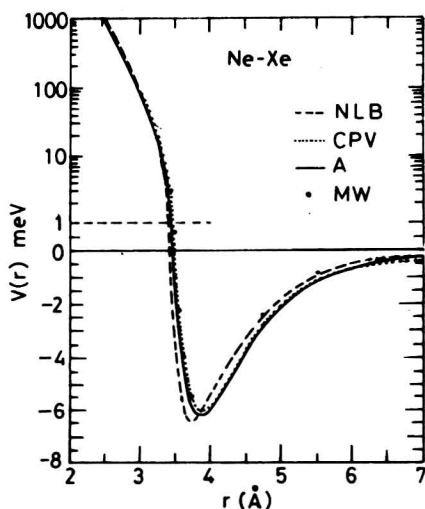

Fig. 6. Various interatomic potentials for Ne-Xe system as quoted in Fig. 5. Dots represent energy values obtained by Maitland and Wakeham [33].