

Probing the Intermolecular Potential: Spectroscopy or Molecular Beam Scattering?

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1 Introduction

Many of the most significant developments in chemistry this century have relied heavily on the contributions spectroscopy has made to the subject. Often this has been in the form of molecular identification or of structure determination. On the other hand, at a more fundamental level, spectroscopy has provided most of the remarkably precise detail that we possess on individual molecules and which underpins our understanding of macroscopic chemical behaviour. Still to be revealed is the nature of the dynamical forces that give rise to chemical or physical change, the motivation for the work described in this review.

The origin of this all-pervading influence of spectroscopy is the unique capability of light to act as a *quantum state* probe, a characteristic that results from the very specific properties carried by the photon. As a result, the interaction of light with atoms and molecules is reasonably predictable from rigorous or approximate selection rules. Using spectroscopic methods we are now in a position to investigate, say, the forces within molecules, the dynamics of deactivation of excited species and many other *intramolecular* processes that are of chemical significance.

When we come to enquire about the forces *between* molecules, in the past spectroscopy has been less evident and the main techniques of investigation have been (atomic and) molecular beam scattering. This is partly a consequence of the transitory nature of the interaction between species in the gas phase which makes the design of an appropriate spectroscopic probe more difficult. However, the success of early atomic beam scattering experiments in unravelling details of the interatomic potential appears also to have been influential in the design of probes of the *intermolecular* interaction.

A significant new factor that enters in experiments involving *molecules* is that the kinetic energy of collision may be converted into internal (or potential) energy of the molecule and thus not be observable as recoil velocity and deflection angle of the colliding species. The need for detailed knowledge of the complete (kinetic and potential) energy balance before a picture

of the intermolecular potential could emerge has led to a re-evaluation of the scattering method for interactions involving molecules.

A complete picture of energy disposal in collisional (reactive or non-reactive) events requires knowledge of internal energies of colliding species and their velocities before an interaction and the new values after. One component of this complex requirement may be simplified since it is the *relative* velocity before and after the collision that is significant. The need to know internal molecular energies however means that the distribution of population over molecular rotational, vibrational and electronic states must be determined, before and after collision.

This latter requirement is so plainly suited to spectroscopic methods that the interfacing of lasers to molecular beam scattering experiments was a natural development. At this point it is worth noting that internal state selection prior to interaction may be achieved with some degree of effectiveness using a supersonic jet expansion and thus the problem often reduces to quantum state *detection*. However, despite this, the full determination of the energy budget in collisional interactions of molecular species remains dauntingly complex and few experimentalists have achieved this level of specification.

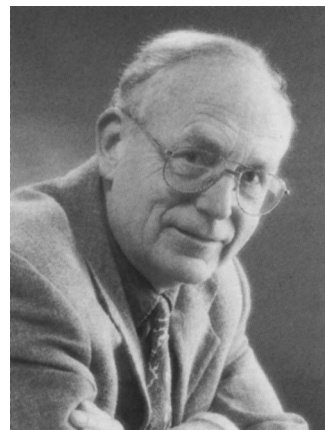
1.1 Spectroscopic Approaches

Parallel to the development of molecular beam methods for studying intermolecular interactions has been one which focused on quantum state changes within the interacting species, with no attempt to define precisely the kinetic energy component of the energy balance equation. This arose in part from technological developments in the form of lasers capable of transferring substantial numbers of molecules into a single molecular quantum state. Transfer out of this to some other quantum state by an intermolecular interaction may then be monitored in one of a variety of ways to give state-to-state transition rates or cross-sections. A motivation of this was the search for selection (or propensity) rules analogous to those found in spectroscopy which would give insights into the nature of the process.^{2,3} Figure 1 illustrates the complexity of the collisional problem by comparison to that involving the photon-molecule interaction.

One of the advantages of spectroscopic experiments is the relative ease with which they may be performed. For example, much useful work has been done in simple glass or metal collision cells. In addition, the ease with which samples may be changed and experiments performed had led to a sizeable database of rates and cross-sections in which many molecules and collision partners have been investigated. This contrasts molecular beam scattering studies which require a longer term commitment to a particular system and consequently the database is smaller.

The combination of spectroscopy and molecular beam scattering raises the possibility that all components of the energy equation may be determined; kinetic energies from scattering and potential energy from internal state distributions determined by spectroscopy. The second major development in reaction and collision dynamics experiments involved the interfacing of lasers to the molecular beam apparatus to facilitate state-to-state measurements. Much important new data has emerged from these demanding experiments. However, each increase in sophistication represents a quantum leap in the cost of an experiment since two-laser molecular beam experiments are now commonplace and those involving

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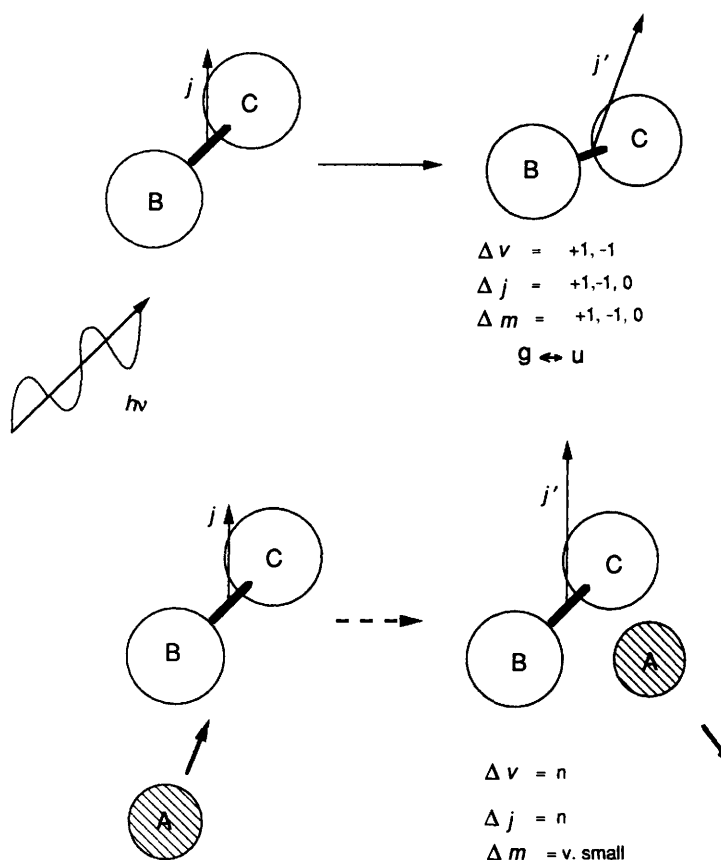


Figure 1 This figure schematically contrasts the photon-molecule interaction, for which there are known rules of engagement, with that for the atom-molecule encounter where few rules appear to control the outcome. The curious restriction on m that is frequently found in atom-diatom elastic and inelastic collisions is the subject of detailed discussion in ref. 1.

three or four lasers are not unknown. Despite such ingenious experiments, true insight into the controlling forces in the most fundamental of chemical processes still remains elusive.

In this review, the focus is on experiments that to an extent represent a de-sophistication of the way in which intermolecular interactions are studied. Thus spectroscopy, with its inbuilt capability to determine potential energy disposal becomes the starting point and to this is added, also spectroscopically, the facility to select and determine the relative kinetic energy of the interacting species. The result is an all spectroscopic method of obtaining the state-to-state differential scattering cross-section for non-reactive or reactive collisions. Although the methods described will generally require two lasers, the experiments are simple collision cell spectroscopic ones with the many advantages such an approach brings.

It will be apparent from the preceding paragraph that the very active field of van der Waals spectroscopy in which the long-range intermolecular forces are observed directly through bound-state spectroscopic methods on species at ultra-low temperatures will not be part of this review. This spectroscopic method continues to be very powerful in the experimental determination of intermolecular forces.⁴

Here we address the question of how velocity determination may be added to the inherent quantum state selectivity of radiation, how selectively may it be employed and how diagnostic of changes in relative velocity such a method might be. The mechanism through which velocity selection and detection is achieved is the Doppler effect, a phenomenon that has long frustrated the search by spectroscopists for higher and higher resolution in atomic and molecular spectroscopy. Sub-Doppler laser spectroscopy, under the right conditions, can specify or determine the complete energy budget of a molecule, kinetic and potential. In addition, the presence of a unique axis, the light propagation direction, to which all measurements are referenced, allows velocity magnitudes and directions to be ascertained.

1.2 Molecular Velocities; Directions, Magnitudes and Distributions

Scattering experiments are fundamentally about changes in velocity; more precisely they are about changes in velocity distributions. It may at first sight seem paradoxical that in order to investigate the potential energy surface, experiments that focus on accurate kinetic energy determination are devised. It will be apparent from the foregoing discussion that changes in kinetic energy are a reflection of processes on the potential energy surface and that in molecules, kinetic-potential energy interconversion is a major complicating factor.

In order to know what has happened to the initial relative kinetic energy of the reactants it is essential to map the destinations of products. Initial and final kinetic energies are in the form of relative velocity distributions. The angular distribution of product relative velocities, from a known reactant distribution, is the quantity known as the differential scattering cross section (DCS). Clearly the DCS is all-important in any attempt to balance the kinetic energy budget.

Discussions of velocity distributions in any context tend rapidly to become very mathematical since the distribution functions of unselected and selected velocities are quite complex. As a result it is easy to lose sight of the physical processes involved. This next section will attempt to illustrate velocity distributions in a pictorial fashion in order to develop a physical picture of the scattering process and the distributions of velocities that result from using molecular beam or laser methods.

The distribution of molecular velocities in a gas cell depends, as is well known, on the temperature of the cell and the masses of the individual molecules. It is important to distinguish distributions of molecular velocities from those of molecular speeds. The Maxwell-Boltzmann distribution of velocities is given by the expression $f(v_x) = (m/2\pi kT)^{1/2} \exp(-mv_x^2/2kT)$ for the x component. Probability distributions of molecular velocities peak at zero

velocity. The distribution function of molecular speeds has the more familiar form, that of the Maxwellian distribution:

$$f(v) = 4\pi(m/2\pi kT)^{3/2}v^2 \exp(-mv^2/2kT) \quad (1)$$

It is the presence of the term v^2 weighting the probability distribution that gives the speed distribution function its characteristic shape, the peak of which shifts with temperature and with mass.

In processes that are initiated by collisions it is the *relative* speed distribution that is most relevant. The motion of two independent particles may be decomposed into that of the relative motion and the motion of the centre-of-mass. Only the former can induce a collision. The relative speed in effect is a velocity since in each individual collision event, the direction is specified as that between the colliding centres. Like molecular speeds, these directions are randomly oriented in space. The distribution of relative velocities has the form of a speed distribution. This particular point is rarely emphasised in textbooks and is often the source of confusion. A useful way of visualising this is to consider an extreme example such as that of collisions between a gas and a stationary partner, a solid surface for example.

The distribution of relative velocities in a gas has Maxwellian form with the collision system reduced mass substituted for molecular mass. The mean relative velocity is given by $8kT/\pi\mu^{1/2}$ where μ is the reduced mass of the colliding pair. We can see that the mean velocity will be high when one of the colliding partners is a light atom or molecule and that the mean velocity will be low when both species are heavy. This represents the ‘natural’ distribution of velocities that the molecular dynamics experimenter must manipulate in order to achieve a distribution of known directions and magnitudes in the experimental frame. Although this is not a central part of this review, a brief discussion of molecular beams experiments is given here in order that the Doppler selection technique may be set in context.

In molecular beam scattering experiments, the colliding species enter the scattering chamber initially through a small hole in the sample-containing section of the apparatus. Two main regimes exist, the first when the hole is small compared to the mean free path of the colliding species and the second when the hole is large compared to the mean free path. The former condition causes the sample species to effuse into the chamber with a velocity distribution very similar to that inside the container. The latter condition, particularly when combined with high pressure conditions in the sample container, gives rise to the supersonic expansion. In this, internal motions of the molecules undergoing expansion are converted into highly directional flow as a result of large numbers of collisions, generally with a carrier gas such as He or Ar which form part of the expansion.

Figures 2(a) and 2(b) show the velocity distributions that characterise the effusive and the supersonic nozzle. In many respects, the supersonic nozzle produces an ideal velocity distribution for molecular dynamics experiments since the distribution of velocities may be very narrow and the molecules have generally been cooled to their lowest quantum states. However, the effusive expansion does give the experimenter the opportunity to vary both selected velocity and initial quantum state by means of additional selective devices. This is less straightforward in the case of the supersonic expansion, although the mean velocity may be changed by changing the mass of the species undergoing expansion.

Velocity selection of reactants beginning with distributions as described above has been a central theme in molecular beam studies. Detection of reaction product velocity distributions generally utilises angularly variable, time-of-flight detectors. These methods give product velocity distributions in the coordinate frame defined by the experiment. Transforming these distributions to give the equivalent function in the collision frame is less straightforward and laboratory frame-to-collision frame transformations often cause loss of specificity of the detail of an experiment.

Mechanical methods of velocity selection do not represent the sole techniques available. In principle, any physical phenomenon that is affected by molecular velocities represents potentially a method of velocity selection. The Doppler effect is one such and, as

is well known, the absorption frequency apparently exhibited by an atom or molecule is a function of the speed of that molecule in the direction of the light beam. To the spectroscopist the Doppler effect represents an unwelcome intrusion into the serious business of greater and greater spectral resolution since the distribution of molecular velocities causes line-broadening. True to the principle that each problem constitutes an opportunity in disguise, a growing number of researchers have utilised the Doppler effect either to select or to detect molecular velocities in molecular dynamics experiments.

1.3 Molecular Velocity Selection via the Doppler Shift

Spectral lines are not infinitely narrow in the gas phase and among the many broadening mechanisms are the lifetime of the excited species, with consequent uncertainty in the absorption frequency, and that due to random motion of the species. Transition frequencies of moving molecules are shifted from the unperturbed resonance frequency by an amount proportional to the speed of the molecule *relative to that of the probing light beam*. For light species at room temperature and for heavier molecules at elevated temperatures, molecular speeds of several thousand metres per second are not uncommon, leading to linewidths broadened to several GHz. The basic relation between observed absorption frequency ω_a , unperturbed resonant frequency ω_0 and molecular velocity along the laser propagation direction v_z is:

$$\omega_a = \omega_0(1 + v_z/c) \quad (2)$$

In equation 2 c is the speed of light.

The Doppler shift is a form of *inhomogeneous* line broadening, in contrast to that due to the uncertainty in lifetime, and excitation into a specific region of the line profile will result in the selection of only a sub-set of the molecules that undergo the transition. In certain circumstances therefore a narrow line laser may be used to select a sub-group of molecules of definable velocity by tuning the laser into a specific region of the Doppler profile (this process is frequently referred to as *detuning* since perfect *tuning*, *i.e.* line centre, excites only $v_z = 0$ components). Using commercially available cw dye lasers, this selection process may be very precise indeed in the selection of v_z . Conversely, the shift of resonant absorption from line centre may be used to determine the distribution of molecular

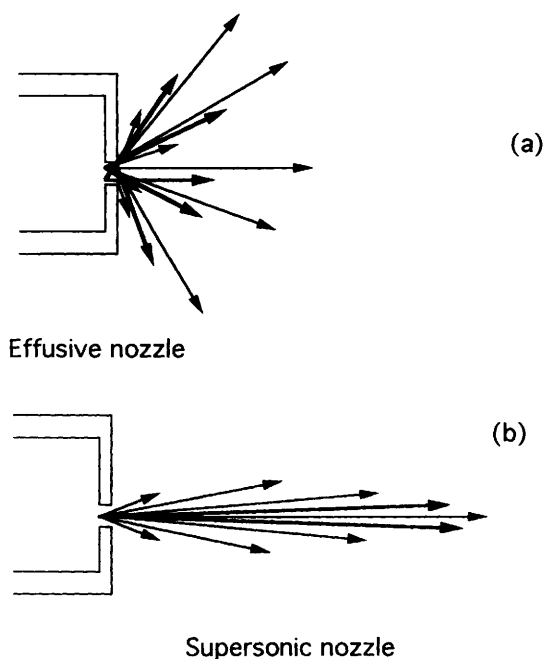


Figure 2 Pictorial view of the velocity distributions from: (a) an effusive source and (b) a supersonic nozzle. Arrow length is a representation of speed, and thickness a measure of probability.

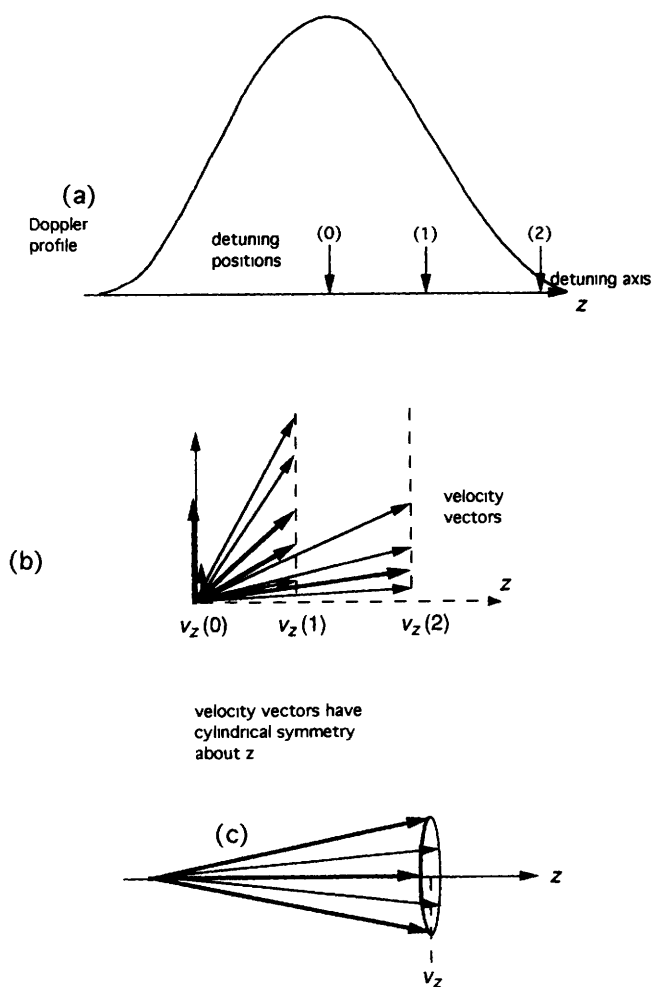


Figure 3 (a) A typical gas phase rovibronic Doppler profile with three detuning positions highlighted (b) The range of molecular velocities accessed by each of these laser-selected wavelengths. It is apparent that large detunings select velocity distributions similar in form to those of the supersonic nozzle (c) Each detuning wavelength selects z components of velocity and hence there is cylindrical symmetry about the z axis

v_z values. Figure 3 illustrates the process of molecular velocity selection by wavelength selection in different regions of the Doppler profile.

The suggestion that Doppler shift measurements could be used to define or to determine velocity distributions of molecules in scattering experiments was first made by Kinsey.⁵ He demonstrated that the velocity distribution of products from a scattering experiment could be determined from Doppler scan lineshape measurements made as a function of the direction of the incident light. The Fourier transform of the Doppler profile obtained with incident light along θ , ϕ , say, is the same as the three-dimensional Fourier transform of the full velocity distribution evaluated on a line in Fourier space parallel to the θ , ϕ direction. By scanning at a number of angles it is possible to reconstruct the entire Fourier map which may then be inverted to the velocity distribution.

In addition to providing a new method for tackling the complex problem of simultaneous quantum state and velocity distributions of products, there are additional advantages inherent in the method. Kinsey drew attention to a signal-to-noise gain, equivalent to the Fellgett advantage, that make Fourier transform methods the most favoured for IR and NMR instrumentation. He calculated⁵ a gain of up to 10^4 for Fourier transform Doppler methods over conventional techniques. A further advantage is the simplicity of transformation from laboratory to collision frame coordinates, discussed in more detail below.

The Doppler shift method was demonstrated experimentally by Phillips, Serrin, Ely, Pritchard, Way and Kinsey⁶ who determined the

differential cross-section (DCS) for the fine structure transition in excited sodium in collisions with Ar. Further experimental developments led to determination of velocity distribution of products in rotationally inelastic scattering for Na_2 -rare gas collisions.⁷

1.4 Relative Velocity Determination Using Spectroscopy

A particularly significant development in the context of this review was by Smith, Scott and Pritchard⁸ who demonstrated that the Doppler selection method could be used to specify relative velocities using a straightforward transformation of laser frequency within the Doppler profile (the laser detuning). This, it should be emphasised, is not a special spectroscopic trick but consists mainly in appropriate choice of molecule for excitation and collision partner. An example illustrates this. If our target molecule, whose velocity has been selected by a Doppler shift technique, collides with an infinitely massive partner (a surface, say), the relative velocity is then very well defined since it is identical with the molecular velocity. As the collision partner becomes less massive, the precision of the transformation from molecular to relative velocity is reduced owing to target motion. Smith *et al.*⁸ used sub-Doppler selection of relative velocity to obtain, for the first time, the dependence of state-to-state rotational transfer cross-section on initial relative velocity.

The key equation in this selectivity was derived by Smith *et al.* which relates laser detuning via the z -component of selected molecular velocity to the distribution function of relative velocities. This is written in equation 3 in the form of a probability distribution (or density) which gives the probability of finding a relative velocity of magnitude v , whose angle of inclination to the z -axis (the direction of propagation of the light beam) is α , once the z -component of molecular velocity v_{mz} has been specified. This equation is

$$P(v, \alpha | v_{mz}) \propto v^2 \exp\left(\frac{-v^2 \sin^2 \alpha}{2(s_a^2 + s_m^2)} - \frac{(v_z - v_r \cos \alpha)^2}{2s_a^2}\right) \quad (3)$$

In equation 3, $s = m_m/m_a$. Distributions of the form given in equation 3 are best illustrated pictorially. Figure 4 presents the distributions of relative velocity as a function of laser detuning for the collision pair Li_2 -Xe. It can be seen that for frequencies close to the centre of the Doppler profile, values of α range widely about the perpendicular. Selectivity in magnitude from line centre excitation also lacks high precision.

Excitation in the wing of the Doppler profile leads to greatest selectivity of both angle and magnitude. In the extreme wing, relative velocities become closely locked to the laboratory axis with the high value of molecular velocity translated directly into relative motion. It is of course one of the ironies of experimental work that this ideal distribution should be that which is least accessible in practice, in this case because signal strength is much reduced.

With the relationship of equation 3 we have the basis of a new use for spectroscopy, namely as an alternative to the molecular beam apparatus. It should also be borne in mind that any method based on high resolution spectroscopy has quantum state selectivity naturally built in. This in principle may be very specific indeed. A feature to note is that equation 3 relates relative velocity vectors to the laboratory frame directly. This contrasts the situation in a crossed molecular beam experiment in which the collision-laboratory frame transformation may be a difficult and error-prone process.

There is an additional advantage that follows from tying the velocity vector to the laser propagation direction which stems from the fact that internal molecular vectors may also be aligned in the excitation process either parallel or perpendicular to this same axis. These might, for example, be the transition dipole moment or the rotational angular momentum vector. The ability to specify the directions of these vectors relative to one another before a collision and to determine them after is of great significance for the field of collision and reaction dynamics as we discuss later in this review.

2 Effect of Collisions

If we can go from laser detuning via the molecular velocity distributions to those of relative velocity, then clearly we can reverse this process to obtain relative velocity distributions from spectroscopic

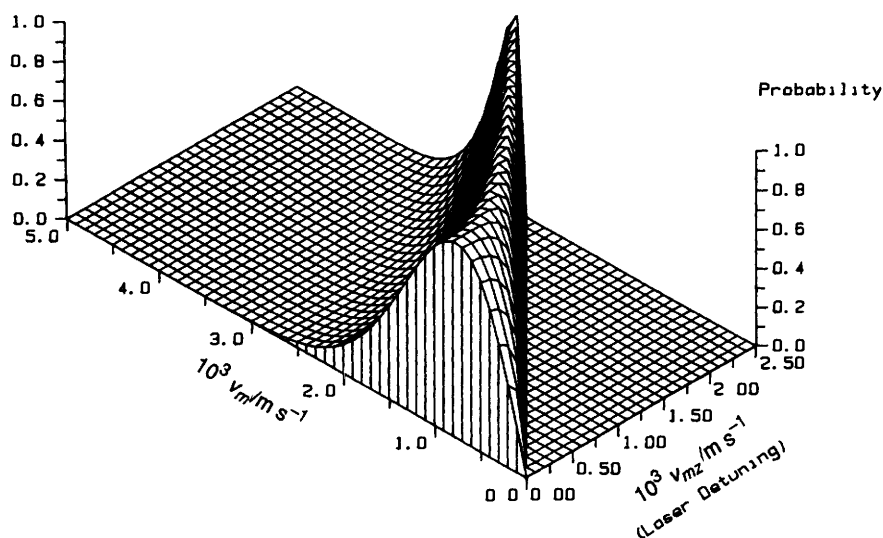


Figure 4 Three-dimensional plot of probability of selecting molecular velocity v_m as a function of laser detuning, $i.e.$ of increasing v . The example shown is for L_{12} -Xe at 1000 K in a thermal cell

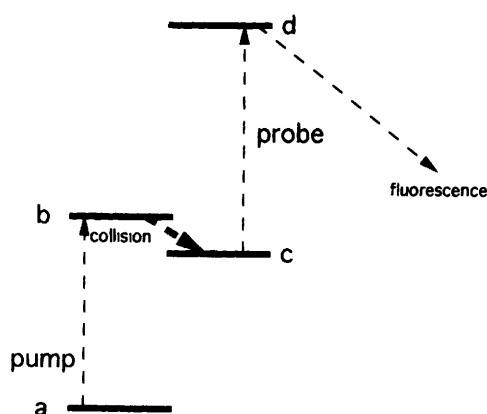


Figure 5 Two-laser double resonance configuration for probing the result of a collision taking molecules from state (b) to state (c)

lineshapes. This might be done as part of the analysis of a traditional molecular beam experiment in the mode of Kinsey or alternatively following a velocity selection process (see below) in which translationally hot atoms produced by photolysis have kinetic energies sufficiently large that they dominate the relative velocity equation. However, were this to follow the kind of velocity determination by Doppler selection described above then we would have a wholly spectroscopic technique for determining state-to-state differential scattering cross-sections. A double resonance spectroscopic configuration would be needed for this process, of the kind illustrated in Figure 5, but two-laser experiments are now relatively common and relatively cheap compared to the most sophisticated of molecular beam methods.

This then is the basis of the method described in this review. We have from the earlier section a relation between laser wavelength and relative velocity magnitude and direction. We now need to consider the effect of collisions on velocity distributions and on the experimental observable, the double resonance lineshape. This is discussed below, again using a mix of pictorial representation and of mathematical description. We begin with a qualitative consideration of the velocity changes induced by a non-reactive collision and their effect on the lineshape.

To simplify this discussion we assume that the initial distribution of relative velocities may be replaced by a single vector v_i representing the most probable value selected by the laser. From earlier discussions on velocity selection it will be apparent that detuning the laser into the wings of the Doppler profile increasingly narrows

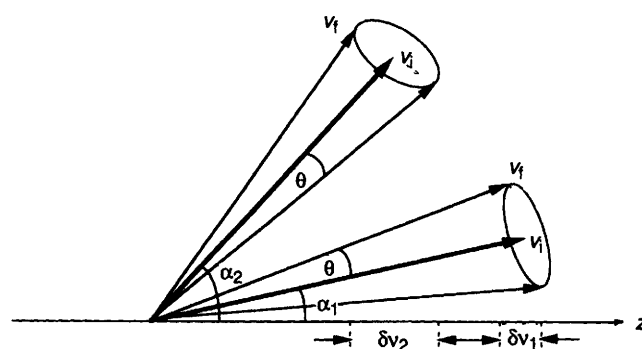


Figure 6 An illustration of the effect of angle α (that between z axis and velocity direction) on the velocity selected double resonance (VSDR) linewidth. Initial v_i is the same in each case as is the scattering angle θ . The double resonance linewidth is given by the projection of the base of the scattering cone on the frequency axis. As α increases, for a given scattering angle, so does the projection on the z axis.

the distribution towards this ideal representation. First we assume the system undergoes an *elastic* collision, *i.e.* no change in internal quantum state of the molecule and hence no change in relative velocity (though of course, atom and molecule velocities may change individually). Some interaction takes place and this is reflected in a change in direction of v_i , or *scattering* through the scattering angle θ . This can be shown diagrammatically as in Figure 6. Note that the length of v_i is unchanged and that scattering through angle θ may take place over a range of angles (χ) to the initial plane.

The effect of this on an experimental double resonance lineshape is shown qualitatively in Figure 6. Clearly for a given elastic (or inelastic) process, the more closely parallel the initial vector is to the z -axis, the narrower will be the final lineshape, given by the projection of the base of the scattering cone on the z -axis. This is shown in Figure 6.

When the process is *inelastic*, changes in internal energy are at the expense of magnitude of relative velocity. Thus for the case, say, of rotational excitation, v_i would be *shortened* and deflected through angles θ, χ as shown in Figure 7. Two instances are shown in this figure. Initial v_i is kept constant in each case but two different values of scattering angle θ are shown together with a qualitative representation of the expected lineshapes. Again the lineshape is a function of the size of the scattering cone base and its angle of inclination to the z -axis. The experiment therefore reveals the origins of collision broadening in gas phase spectroscopy and fur-

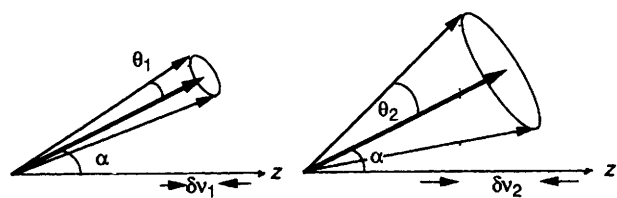


Figure 7 This shows the effect of different scattering angles (θ) on the VSDR linewidth. In the two cases shown, initial relative velocity is identical but different scattering angles produce cones of different base diameter and hence different linewidth.

therefore it is apparent that the width of the double resonance line contains valuable information on the distribution of the final v_r vectors which may be related to the scattering angle.

From this simple pictorial example it is apparent that the kind of information normally associated with molecular beam experiments, *i.e.* the angular distribution of the relative velocity vectors, may be obtained from a purely spectroscopic method. The two examples given above are useful in that they form the basis of a simple test of the experiment and its ability to measure velocity magnitudes and angular distributions. Thus we anticipate that for a given selected initial v_r , the double resonance linewidth should increase markedly with rotational inelasticity (*i.e.* as θ increases) and furthermore we would expect that for a given inelasticity (*i.e.* fixed θ) the linewidth should vary predictably with laser detuning. Thus lines should be narrow when v_r^i is selected in the Doppler wing and broad when tuned close to line centre.

The foregoing discussion took place in terms of an idealised distribution of relative velocity vectors whereas in fact it is the molecular velocity distribution that gives us optical access to velocity selection through the Doppler effect. This is treated fully in the theory but can be represented pictorially using Newton diagrams to represent molecular, atomic and relative velocities in a molecular dynamics experiment. Figure 8 shows such a diagram with initial and final velocity combinations representing an idealised scattering experiment in which initial atom and molecular velocities and directions are known. The outcome is a scattering event of the kind described in detail above but now we show explicitly the fate of the atomic velocity vector. In each case the relative velocity is shown as the resultant of the atomic and molecular velocities.

These may also be displayed on the same diagram as mass-weighted relative motions of atom and molecule in the centre-of-mass (c.o.m.) frame with the motion of c.o.m. shown separately. The broken line in Figure 8 represents this c.o.m. motion (which has no influence on the dynamics). Atomic, molecular and relative

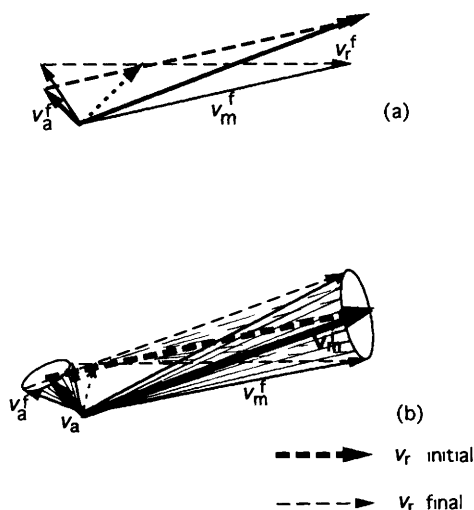


Figure 8 Representation of the velocities of atom (v_a), molecule (v_m) and relative motion (v_r) before (heavy arrows) and after (light arrows) a collision. (b) The cone of final atomic, molecular and relative vectors resulting from scattering.

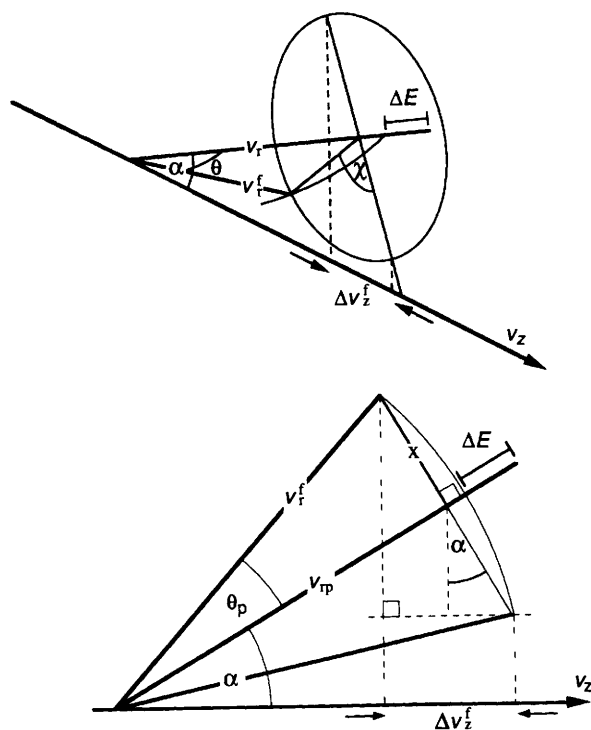


Figure 9 Illustration of a simple geometric relationship between linewidth and most probable scattering angle for the ideal case of a single vector.

velocity scattering cones are shown together with the projection of molecular and relative velocities on the quantisation axis. Although this is a more complex picture than those used above to describe the principle of the double resonance method, it illustrates all atomic and molecular motions and shows that the detection of the spread of molecular velocities via the double resonance lineshape is also a measure of the spread of the final relative velocity vector.

In this section qualitative arguments have been presented and used to describe how relative velocity magnitudes and angles may be determined spectroscopically. A simple relationship exists between the scattering angle and double resonance linewidth. This is illustrated in Figure 9 which shows a planar cut through the scattering cone to include v_r^i and the z -detuning axis. The geometric relationships are evident from the figure as is the direct relationship between scattering angle (θ) and linewidth (Δv_z^f) of the spectroscopic signal.⁹

To derive an expression we begin with the relations, $\sin \theta = x/v_r^f$, $\sin \alpha = \Delta v_z^f/2x$, $\cos \alpha = v_m^f/v_r^f$. From these it is straightforward to obtain equation 4.

$$\sin \theta = \frac{\Delta v_z^f}{2 \left(v_r^i^2 - \frac{2\Delta E}{\mu} \right)^{1/2} \left[1 - \left(\frac{v_m^i}{v_r^i} \right)^2 \right]^{1/2}} \quad (4)$$

This qualitative view of velocity selection and of the scattering process is valuable in visualising the experiment and in making a rapid analysis of the double resonance data. A full treatment of this lineshape is more complex and has been addressed by more than one author. One approach has been in the context of velocity changing collisions (VCC) and dephasing collisions in Na(²P)–rare gas atom interactions.¹⁰ These elastic interactions cause subtle changes to the lineshape in a double resonance experiment as Gallagher and colleagues have demonstrated¹¹ and contribute to the lineshape of the ‘parent’ transition. Inelastic processes cause a more substantial redistribution of the initial velocity vectors and these authors have studied fine-structure changing collisions using the velocity selected double resonance (VSDR) method.¹¹ To analyse data they utilised a theoretical treatment which expresses scattering amplitudes in terms of the kernels and frequencies of the collision integrals through a series of velocity averaging steps.

A density matrix formalism was employed by Liu and Dickinson¹² in a more general treatment that includes both atomic

and molecular systems. The density matrix permits m -degeneracy to be included *via* its irreducible components and these authors have chosen to express the two-step double resonance lineshape in terms of the collision integral. This may then be related to the generalised cross-section. Liu and Dickinson give full expressions for the atomic and the molecular inelastic transition cases.

There is a pragmatic approach to the analysis of double resonance lineshapes.^{13,14} It is the DCS that we wish to extract from experiment, which measures the redistribution of velocity vectors causing the lineshape to broaden on collision. A simple approach would be to assume some functional (parameterised) form for the DCS and to vary the parameters until the *shape* of the double resonance line can be duplicated. This is the basis of the method we have used and is described in more detail below. For a full description of the process however it is necessary to give the theoretically derived expression for the double resonance lineshape. This can be found in recent publications¹³ and was derived using probability density expressions for the variables that are involved in the selection, the collision and the detection processes.

The linewidth expression is given as a probability density of the final velocity component distribution $P(v_{mz}|v_m)$

$$P(v_{mz}|v_m) = \iiint P(v_m|v) P(\theta|v_r) \times P(v_r|\alpha|v_m) P(\chi) \sin\alpha \sin\theta_i d\alpha d\theta dv_r \quad (5)$$

There are kinematic constraints on this equation, represented by δ functions in the full expression.¹³ These are not given here and the reader is referred to the above mentioned publications for complete expressions. The quantities on the right of equation 5 represent the following probabilities: the distribution of z -axis velocity projections given a specified laser detuning (v_z), the distribution of in-plane scattering angles, $i.e.$ the DCS (note this is velocity dependent), the distribution of relative velocity magnitudes and their angle of inclination to the z -axis for a specified z -component of initial relative velocity, and finally the distribution of out-of-plane scattering χ . Note that this is generally assumed to be isotropic.

Thus in equation 5, the DCS is the only unknown function and by using an assumed form for this on a trial and error basis, a best fit to the lineshape may be used to refine the parameters of the DCS function. This is usually done with a series of nested integrations until reproduction of the experimental lineshape is satisfactory.¹⁴ Note that the linewidth in the *absence* of collisions will be determined by a number of factors. The natural lifetimes of all states involved, *i.e.* levels a, b, c and d of Figure 5, will determine the unperturbed double resonance linewidths and additional broadening factors such as power broadening *etc.* must be eliminated. In this we assume such effects to be small compared to inelastic collision velocity redistribution effects.

3 Experimental Realisation

In science it is rare for a field of research to have no prehistory and VSDR is not thus marked. Some twenty years ago, Berman¹⁵ outlined the theoretical basis of the measurement of the DCS in atom-atom collisions using double resonance methods of the kind discussed here. He also pointed out some of the advantages of spectroscopy over scattering methods, in particular the direct linking of laboratory and collision frames referred to earlier. The theoretical development by Berman was somewhat different from that outlined above. Berman derived expressions that relate line broadening to the collision kernels, quantities utilised for many years in theories of line broadening and representing the probability of a (state-to-state) collision induced velocity change. Generally this velocity is that of the probed species.

In this review we have focused on the reorientation of the relative velocity vector as a result of the collisions with explicit expressions given for the angular distribution. This leads to a ready visualisation of the result of a collisional interaction although the net result is the same as the theoretical treatment first outlined by Berman. The first systematic measurements of molecular lineshapes following collision-induced state change in a sub-Doppler double resonance

experiment were by Gottscho, Field, Bacis and Silvers.¹⁶ BaO was the molecule chosen and this represented the first wholly spectroscopic state-to-state velocity selection and detection experiment. Elastic and rotationally inelastic processes were studied with some variation of initially selected velocity. The unfavourable mass ratio in the systems studied (BaO-Ar, CO₂) prevented these authors from making the molecule-relative velocity transformation that is the feature of the treatment described in this review.

By assuming negligible velocity change consequent on small Δv changes, Gottscho *et al.* were able to obtain scattering angle data. The most striking feature of their results was the dramatic line narrowing that occurred on changing collision partner from Ar to CO₂. This was explained by the authors in terms of the long-range forces that are anticipated to be important in the case of BaO-CO₂ collisions.

The development outlined in this review describes a process by which the relative velocity of the collision is selected prior to collision and then detected after the interaction. The first experimental lineshapes in a VSDR experiment were reported by Reid, McCaffery and Whitaker,¹⁷ in which the physical basis of the experiment was described. Further refinement of the experiment was necessary before fully reliable lineshapes and DCS functions were obtained and a description of experiment and results are given in recent publications.^{14,18}

Figure 10 shows the experimental arrangement used by Collins *et al.*¹⁴ Two single frequency cw dye lasers form the principal optical elements but this level of sophistication is not essential. The requirement is that the laser linewidth be narrow compared to the Doppler width of the probe species and for very light molecules numerous laser systems fulfil this criterion. One laser (the *pump* laser) excites a narrow velocity distribution of molecules to a specific electronic, vibrational and rotational (E, v, J) state. This creates a population 'spike' in a specific level of the upper state as shown diagrammatically in Figure 11. The narrowness of the spike reflects the velocity selection process as discussed in detail above. It is also affected by collisional interactions, some of which are energetic enough to change the quantum state of the molecule and others which are less violent. In this second category are elastic collisions

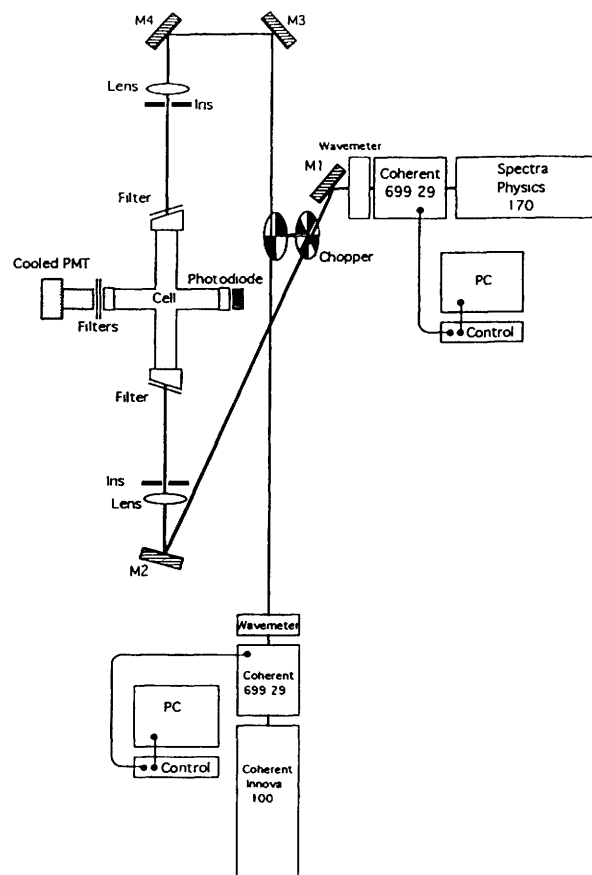


Figure 10 Experimental set up for the VSDR experiment

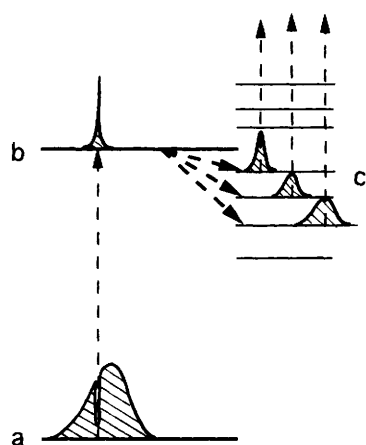


Figure 11 Schematic diagram to illustrate the production of velocity-selected excited states from the Doppler profile and the broadening that would occur as a result of quantum state change in the excited state.

which cause velocity redistribution, and hence line broadening, and phase-changing collisions that interrupt the wavetrain of the radiating molecule also broadening the observed linewidth.

The last two categories of collision are found experimentally to have only a very small effect compared to those which cause a quantum state change. This is shown schematically in Figure 11. The major line broadening effects are the result of the inelastic collision causing the quantum state change and may be analysed in terms of the theory discussed above.

Double resonance experiments are capable of giving spurious results and it is important to use experimental methods that discriminate against unwanted signals and also to know well the spectroscopy of the system under investigation. Two-photon processes with pump and with probe lasers must be eliminated, for example, and checks made for (linear) dependence of signal on both lasers. In the experimental set up in the author's laboratory,¹⁴ pump and probe lasers are modulated at different frequencies and signal detected at the *sum*. This intermodulation method eliminates many spurious signals. Sharp cut-off filters eliminate spontaneous emission from the first excited state and background from the heated cell.

The experimental method may be varied quite widely according to the demands of the investigation and equipment availability. For example the pump laser might be an IR source and ground state processes investigated. The method would then have similarities to a technique used in photofragmentation experiments, known as overtone mediated photodissociation.¹⁹ This would eliminate problems arising from spontaneous emission from the initial level. For enhanced sensitivity, the probe laser(s) might be chosen to excite, directly or indirectly, the ionisation continuum. Again, this would help overcome some difficulties described above which occur with optical detection of two signals from lasers of similar frequency. Pulsed or cw lasers may be used in principle.

This is probably a good point at which to emphasise the advantage of optical methods of velocity selection and detection, some of which were described by Berman¹⁵ many years ago and are briefly referred to above. Most obvious is the high degree of quantum state selectivity that results from using narrow line lasers. Individual electronic, vibrational and rotational states may be accessed relatively easily and a process investigated systematically as a function of each of these. The selection and detection process may be of fine structure (spin-orbit) and hyperfine (nuclear spin) states. Detuning of the laser from line centre gives molecular velocities directly and these may be transformed into relative velocities with the laser propagation direction as the axis of quantisation. It is this last fact that gives the technique particular strength since the transformation from laboratory to collision frame coordinates is a source of considerable uncertainty in molecular beam experiments.

In addition to these features the use of polarised light in selection and detection adds a major new dimension which results from the directionality of the electric vector of the radiation field. The nature

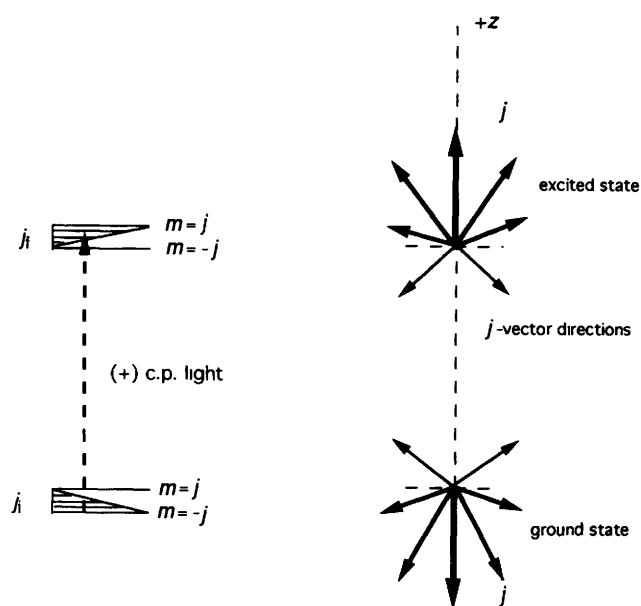


Figure 12 Effect of circularly polarised excitation on ground and excited state m -populations. The resulting distribution of j -vectors for each state is shown on the right.

and directional properties in the molecular frame of particular transitions are well known from spectroscopy. For instance, electronic transition moments in diatomic molecules may be polarised along or perpendicular to the bond and it is straightforward to determine which is the case for a particular transition. Optical excitation in an isotropic medium is a process of *photoselection* and only those molecules whose transition moments have projection along the direction of the electric vector of the light beam will be excited. Again, this is with reference to the direction defined by the laser beam.

More precise identification of molecular direction comes from the use of linearly or circularly polarised light when rotational resolution is achieved. These two forms of polarisation achieve molecular directionality through the different distributions of magnetic sub-states that they excite.²⁰ Here the m states represent projections of the rotational angular momentum vector on the propagation direction. For a given value of j the rotational angular momentum, $(2j + 1)$, m states are possible ranging from j to $-j$. Excitation using circularly polarised light generally biases the m state distribution towards j or $-j$ in a dipolar array of populations whilst use of linearly polarised light gives a quadrupolar distribution that peaks either around $m = 0$ or simultaneously at j and $-j$. This is shown pictorially in Figure 12, which also displays how knowledge of m state distribution gives molecular directionality.

Much of this is well known and has been widely used in molecular dynamics experiments for a number of years. What is novel in the application described here lies in the fact that the radiation used for state selection and molecular directionality *via*, say, the m dependence is that used also for *relative velocity* selection. Thus the possibility exists of building in directly a correlation between the vectors representing the relative velocity direction and those describing the molecule's orientation, with both being referenced to the propagation direction of the lasers. Some years ago, Herschbach and coworkers²¹ realised the importance of detailed, correlated knowledge of directionality of velocity, angular momentum and transition moment vectors in collisional processes. They introduced the term *vector correlation* to molecular dynamics together with an extensive theoretical formalism, much of which has its origin in nuclear physics.

It will be evident from the foregoing that as more vectors are correlated in an experiment, the fewer are the averaging assumptions that must be made leading to greater detail in the interpretation of results. A typical two-vector correlation experiment is an older-style molecular beam measurement with well defined initial relative

velocity before collision and distribution of velocities detected after. When laser detection of product angular momentum direction is added, a three-vector correlation may be obtained. Most informative is the four-vector correlation experiment and the VSDR experiment described here, when used with full polarisation of light in both selection and detection is the basis of such an experiment. This was first demonstrated by Collins *et al.*²² who described the first four-vector correlation molecular dynamics experiment.

3.1 Some Results

The VSDR method of obtaining the DCS is very new and only one molecule atom collision system has been investigated using this technique to date. However, it is worth emphasising that the measurement of the state-to-state DCS is sufficiently difficult that these quantities have been evaluated (by combined laser and molecular beam methods) on very few occasions indeed. A full description of the results obtained in this work is given in the original publications but here a brief summary is given to demonstrate that the theory outlined in earlier sections does indeed appear to work and to give results that do reliably represent the state-to-state DCS and its velocity dependence.

Figure 13 shows some of the VSDR lineshapes obtained in the experiment of Collins *et al.*¹⁴ displayed in a way that shows the dependence upon ΔJ (upper plots) and on selected velocity (lower plots). Note that these are normalised. The signal intensity drops considerably as the pump laser begins to probe the outer regions of the Doppler profile and as inelasticity increases. The variation of VSDR linewidth as ΔJ increases is particularly marked. Initial rela-

tive velocity is approximately constant for each experiment and the linewidth can be seen to increase from around 50 m s^{-1} to close to ten times this value for $\Delta J = 10$ (Table 1). The signal-to-noise ratio deteriorates somewhat as inelasticity increases, nevertheless the trend is apparent and rotational inelasticities of up to 20 angular momentum units in Li_2 were observed.

The examples shown are for ΔJ increasing. Similar, though significantly not identical, results are found for ΔJ decreasing. It is worth reflecting again on the process involved that yields these lineshapes. Note that initially a narrow distribution of velocities is selected and is maintained through *elastic* collisions. This is apparent from the $\Delta J = 0$ lineshape. As collisions occur, the experiment monitors in turn those in which relative velocity has been converted into rotational angular momentum. The velocity vectors will shorten therefore and be distributed about the most probable scattering angle in a manner that reflects the shape of the intermolecular potential and the distribution of available velocities. The projection of this distribution of final velocities on the z -axis (the wavelength axis) is what is measured in the experiment and displayed in Figure 13. In this context therefore, the steady increase of linewidth with inelasticity is what would be expected on simple physical grounds. A pictorial representation of this process is given in Figure 7.

A second significant trend can be seen in the lineshapes displayed in Figure 13 which plots VSDR shapes for the $\Delta J = 4$ process as the relative velocity of collision increases. A marked narrowing of the lineshape is seen as the pump laser moves into the wings of the Doppler profile to select higher-velocity encounters. A simple physical explanation of this process is illustrated in Figure 6. As the selected velocities become more parallel to the

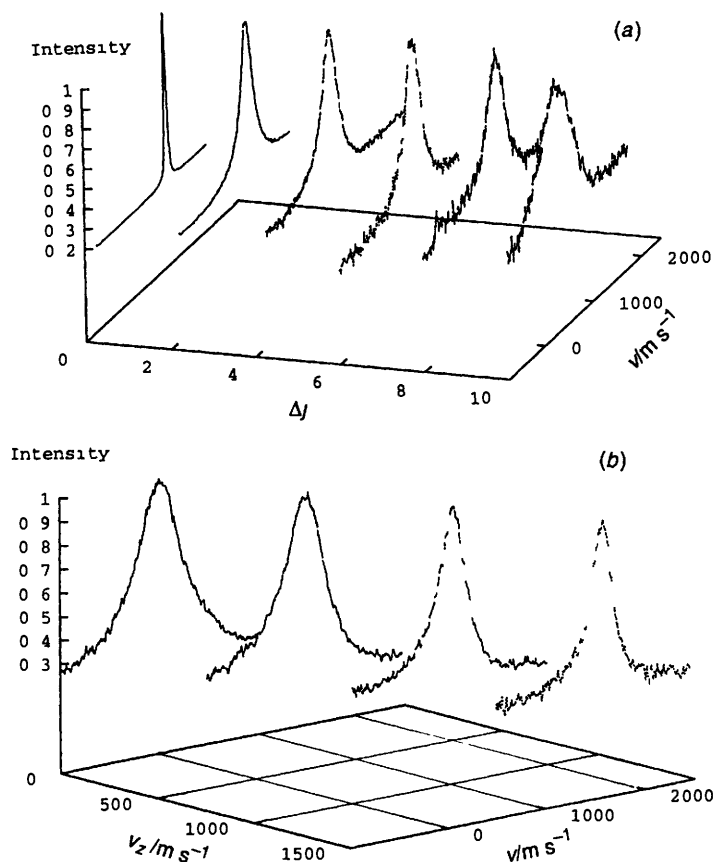


Figure 13 Some VSDR lineshapes for the case of $\text{Li}_2(\text{A}^1\Sigma_u)-\text{Xe}$. (a) The dependence of lineshape on rotational inelasticity for the same detuning. The steadily increasing linewidth is a manifestation of increasing scattering angle, shown schematically in Figure 7. (b) The effect of velocity selection on a given inelastic process. The linewidths narrow appreciably as detuning increases owing to the change in the projection of the scattering cone base on the frequency axis, as indicated in Figure 6.

Table 1 Most probable scattering angles for the $\Delta j = 10$ transition calculated from full fitting analysis (l.a) and the single vector model (s.v.). The double resonance linewidth is taken as the fwhm value.

ν_z m s ⁻¹	⁷⁷ Li ₂ -Xe		$\Delta j = 10$	
	Linewidth m s ⁻¹	Linewidth m s ⁻¹	ν_{rp} m s ⁻¹	θ_{cp}° ($\pm 1^\circ$)
	$\Delta j = 10$	$\Delta j = 0$		s.v. l.a.
0	756	67	780	32
-184	732	66	800	30
-331	726	65	850	28 30
-534	676	63	960	25 26
-699	645	61	1070	25 17
-902	581	57	1230	20 14
-1067	506	54	1370	16 12
-1251	449	53	1520	14 10
-1399	455	52	1650	14
-1601	398	50	1840	11

laser axis they project a narrower distribution on that axis. For the same inelasticity and hence the same cone of scattering, the z-axis projection will be smaller and the VSDR linewidth narrower. The observed linewidth trend follows this intuitive argument in respect of its main features and this provides useful evidence that the experiment is indeed sensitive to the quantities that it purports to measure. There is more detail to be extracted from these lineshapes concerning change in collision trajectories as velocity increases which not relevant to this survey but is discussed in the original paper.

An analysis of the data shown in Figure 13 and of other results is given by Collins *et al.*¹⁴ in terms of an impulsive collision at the hard wall of the intermolecular potential with torque generated through the anisotropic component of the repulsive potential. A hard ellipse provides a useful basic model for this and the trends described in the previous paragraphs are well accounted for using these simple concepts.

3.2 Further Developments

The determination of scattering quantities, particularly the state-to-state DCS, is very new and the full range of contexts in which it may be adopted is as yet unexplored. Alternatives to the method described above do exist, which will be described briefly and consist mainly of variations on the double resonance theme. The VSDR experiment is basically a four-level double resonance, three of which are coupled by radiation and the fourth by collision. Several configurations are possible, two of which are shown in Figure 13. The first of these will be recognisable as the basis of the VSDR experiment described above. It highlights a potential disadvantage of the method in that the probe laser explores the second (or higher) electronic excited state of the system. The experimenter may have to identify and characterise this higher lying level since knowledge of the high-lying regions of many molecules is often sparse. The main problems would emerge as the results of line-broadening perturbations: predissociation for example, though it should be emphasised that knowledge of the *identity* of the final state is not essential.

A more useful configuration may turn out to be that of Figure 14(b) or (c). In these only the first excited electronic state is involved and molecular constants and occurrence of perturbations are more often known for this level. Special experimental techniques are needed for these experiments since of course, level 3 [and level 2 in case (c)] will generally be populated in Boltzmann fashion and it is the population due exclusively to collisional transfer from level 1 that we wish to identify. One advantage of the VSDR configuration (a) is that population of level 3 (under single collision conditions) may only be *via* level 2. The use of a high power, modulated IR pump laser would provide the basis of a

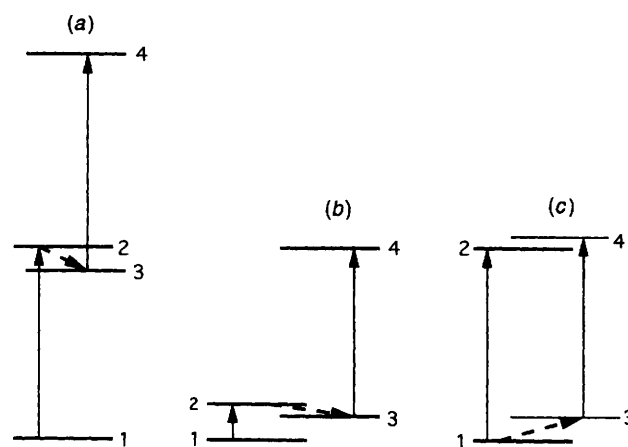


Figure 14 Double resonance configurations suitable for VSDR.

configuration (c) experiment. A sensitive method based on configuration (b) is one in which the level 1 molecules are labelled using polarised light and the probe searches for this polarisation label in the molecules of level 3.

This particular experiment, known as laser polarisation spectroscopy (LPS) is well known as the basis of a highly selective spectroscopic technique.²³ Its physical basis is as follows. The pump laser polarises a specific rotational level of the molecule by excitation with circularly polarised light. This selectively depletes *m*-states of the lower level by transferring them to the excited state.²⁰ The probe laser is linearly polarised using the first of two polarising prisms, crossed with the first, is placed *after* the sample but before the detector. For most wavelengths therefore no light passes to the detector since the polarisers are crossed. If the probe laser comes into coincidence with a transition that originates on the pumped ground state however this situation changes. Transitions sharing a common ground state with the pumped level appear to be optically active and such transitions become circularly dichroic and birefringent. Under the right experimental circumstance, the former of these dominates and a Lorentzian double resonance lineshape results. A detailed description of LPS may be found in the comprehensive text on laser spectroscopy by Demtröder.²⁴

The major use of the LPS method has been a means of simplifying complex molecular spectra for the purpose of identification since only transitions originating on the pumped level are seen strongly. However, as noted in the original work by Schawlow, and known from specific studies of *m*-transfer rates,²⁵ the polarisation label survives elastic and inelastic collisions and thus LPS is potentially a method *via* which *collisional* population may be detected. Apart from the instances cited below, the method has not been used to study collisions systematically. This is surprising since the technique is potentially very sensitive by virtue of the null background away from resonance. Furthermore, the existence of a collisional LPS signal contains important dynamical information. It tells us that some fraction of the original *m*-state distribution must have been retained. In fact the original Schawlow study demonstrated that the polarisation label is preserved through both vibrationally and rotationally inelastic collisions under conditions representing many collisional interactions.

A great advantage of the LPS method is the ability to study *ground* states of molecules. In this way it should be possible to compare the double resonance method with more conventional molecular beam techniques. Only two studies so far have been made. Note that in order to utilise the methods described above it is essential to excite with narrow line laser radiation, preferably to utilise a heavy collider in order to determine *relative* velocities and, most important of all, to resolve pure dichroism signals (Lorentzian lineshapes) in order to identify the broadening arising from velocity changes. The study of collisional LPS lineshapes in NaK-K collisions by Kasahara *et al.*²⁶ represents a very significant development since they demonstrated that high quality lineshapes could be

obtained for highly inelastic processes. They also showed that collisions energetic enough completely to randomise velocity distributions still were accompanied by a high degree of polarisation. More recently, Wilson and McCaffery²⁷ have obtained velocity-selected polarisation double-resonance (VSPDR) lineshapes for Li_2 and Na_2 in collision with Xe from which most probable scattering angles may be extracted. Li_2 proved to be unusual in that the smallest inelasticity was accompanied by a very wide velocity distribution, quite unlike the behaviour of this molecule in the excited state. A possible explanation for this behaviour is the presence of reactive atom-molecule collisions.

Technological advances can be expected to play a role in the development of spectroscopic methods of determining velocity distributions. Lasers with wide tuning range based on parametric amplification in solids will play a significant role in investigating molecules that cannot be accessed using cw tunable devices based on organic dye solutions. High power pulsed lasers bring new problems to a spectroscopic investigation e.g. low duty cycle, nonlinear effects and others. However they offer great advantages in terms of wavelength range and, of course, the possibility of time resolution. This latter property would be valuable in extending the LPS technique. Using cw lasers, the effective sampling time is that which the molecule spends in the probing beam.

3.3 Other Spectroscopic Strategies

A very significant development in recent years has been the use of lineshape analysis to probe the products of photodissociation experiments using polarised laser-induced fluorescence (LIF). Dixon²⁸ has shown that careful lineshape analysis of individual rotational transitions allows the experimenter to correlate product state velocities and rotational angular momentum and to link these to laboratory coordinates *via* the transition dipole moment. This has now become an essential component of modern fragmentation experiments and yields insights into the mode through which dissociation occurs.

A recent and novel development utilises 'hot' atoms produced with very high velocities by photodissociation. Such suprathermal atoms are in effect velocity polarised and in subsequent bimolecular reactions²⁹ can have sharply defined *relative* velocities. Knowledge of the photodissociation asymmetry (β parameter)²⁸ allows us to link the distribution of initial relative velocities to the laboratory frame and Doppler-resolved polarised LIF investigation of the products of the reaction yields data on translational and rotational anisotropies relative to the laboratory axis. In the best of circumstances therefore it is possible to correlate initial and final relative velocities and product rotational alignment with both initial and final relative velocities.

There are strong similarities here to the VSDR experiment and hence sub-Doppler probing of the products would be expected to yield the DCS as well as other vector correlations. Recently this has been achieved and reactive scattering experiments have been carried out in thermal cells using spectroscopic methods and have yielded data of quality normally associated with the best of molecular beam experiments. An impressive range of systems has already been investigated using these basic principles, emphasising perhaps one of the advantages of spectroscopic methods cited earlier in this review, namely the ease of switching the molecular species involved in the study.

Wolfrum³⁰ reported rotational alignment of OH produced by the reaction of velocity polarised H atoms with O_2 and Bersohn and coworkers³¹ utilised suprathermal H atoms in collision with polyatomic deuterides followed by Doppler analysis of displaced D atoms to investigate the mechanism of substitution in tetrahedral analogues of methane. Hancock and coworkers³² measured vector correlations in product species CO following the reaction of photolytically produced $\text{O}(^3P)$ with CS. Simons and coworkers²⁹ have studied the reaction of hot $\text{O}(^1D)$ atoms with N_2O to produce NO, interpreting the results as evidence of direct stripping dynamics and collinear collision geometry. The method clearly has considerable potential in a diverse range of systems as Zare and colleagues

demonstrate,³³ in the measurement of state-to-state DCS for the reaction $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{H}$ using photolytically produced hot H atoms as the reaction initiator.

4 Summary

The use of purely spectroscopic methods in the study of collision-induced change has taken a major step forward very recently. Of particular significance is the selection and/or detection of molecular and relative velocities by constructive use of the Doppler effect. In this way all components of the energy exchange, kinetic and potential, may be determined experimentally. In this review, methods by which this may be accomplished are described and some results of recent experiments shown. Some of the advantages of a purely spectroscopic approach are discussed and contrasted with the molecular beam approach. New and very detailed information on collisions and reactions could result from a more accessible technique and it is conceivable that widespread use of spectroscopic methods will reveal the underlying principles governing the basic processes of chemistry.

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