Atom-Molecule Scattering: Classical Simplicity beneath Quantum Complexity

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Analysis of scattering angle (θ_p) versus velocity for $(A)^1\Sigma_u^+ Li_2$-Xe inelastic collisions reveals the process in classical rather than quantal terms. The parallel component of velocity is scattered unchanged and the perpendicular component is converted into molecular rotation. For each Δj channel, the only perpendicular component is $v_{\rm th}$, the channel-opening velocity. Hence direction of the incident velocity *and* scattering angle are determined by a vector relationship with $v_{\rm th}$ and $v_r^i \cos\theta_p$ the perpendicular and parallel components of v_r^i, respectively. The results suggest classical relations underly the complexities of quantal scattering with momentum disposal the guide to outcome. [S0031-9007(96)00477-2]

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Theories of collision-induced state change in diatomic molecules have reached a degree of maturity such that they are regarded as a reliable guide to actual events. Despite this, quantum scattering theory in its rigorous or approximate forms is characterized by a *lack* of transparency regarding the underlying physics of the process. As a result, few simple rules of thumb are available to explain even the most common experimental observables. It may be significant that the development of theory has taken place in the absence of extensive experimental data of quality sufficient to provide a critical test of the basic concepts. This is a reflection of the difficulty (and expense) of collision dynamics experiments that have the highest degree of resolution.

The state-to-state differential scattering cross section (DCS) is the experimental quantity expected to provide the most stringent test of theory; it represents the *least* averaged of the measurements experimentalists strive to make. Practical difficulties have severely limited the number of systems studied but two main categories of collision system may be distinguished. The first of these includes H_2 and its isotopomers with the lighter rare gases. Here rotational levels are well spaced and a transition represent a sizable fraction of the collision energy. The DCS for these systems show diffraction oscillations as the dominant feature [1,2]. The second category includes heavier molecules where RT is a small fraction of the collision energy. Oscillatory structures are much less prominent, the DCS exhibiting smooth rotational rainbow features as exemplified by Na_2–rare gas collisions [3,4].

More recently we have demonstrated an entirely spectroscopic approach to this problem which holds promise that the determination of the state-to-state DCS and its velocity dependence might become relatively routine [5]. The method has given very precise rotationally resolved DCS for the collision system $(A)^1\Sigma_u^+ Li_2$-Xe for a wide range of initial velocities [6]. This collision pair would fall into the second of the two categories described above.

In this Letter we analyze data from that experiment and find that *vector* relationships govern the outcome of scattering events in a previously unsuspected fashion. The most probable scattering angle (θ_p) for a quantum-state resolved collision-induced inelastic transition appears to be determined only by the initial relative velocity (v_r^i) and the channel opening, or threshold velocity $v_{\rm th}$. Plots presented below indicate that the scattered relative velocity (v_r^f) is that component of v_r^i *parallel* to the surface of the repulsive intermolecular potential. The perpendicular component is consumed by the process of rotational transfer (RT).

That velocity, quantum state, and scattering angle-resolved molecular collision dynamics experiments should be capable of analysis in simple classical terms might at first sight appear a disappointing outcome. In fact this is far from the case; indeed we believe that very significant insights into collision-induced processes are contained in the experimental discovery reported here. The results suggest that underlying the oscillatory fine structure that characterizes quantum scattering there may be a coarser graining rooted in the classical mechanics of the collision. In a search for "rules of thumb" to aid our understanding of collision dynamics, simple classical models in which *vector* properties dominate may provide valuable new insights. Our analysis of the scattering data is of this nature and when taken in conjunction with the angular momentum (AM) theory of RT [7] we show that a complete picture of the collisional process emerges.

The data for this analysis were obtained using experimental methods outlined in Ref. [6]. The state-to-state DCS is extracted from spectral line shapes in a velocity selected double resonance experiment. Initial velocity selection is by pump laser detuning within the Doppler profile. This creates a known distribution of molecular velocities in the $(A)^1\Sigma_u^+$ state of Li_2 and standard transformations give relative velocity distributions when a collision partner is introduced. The reorientation, and change in length, of the relative velocity vector after collision is measured from the line-shape change using a narrow line probe laser. Results on the system $(A)^1\Sigma_u Li_2$ colliding

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with Xe are differential both in angle and relative velocity (v_r^i) and have full quantum state resolution [6].

Tables in [6] list the most probable scattering (rainbow) angle for a number of different v_r^i values for rotationally inelastic collision-induced transitions with $\Delta j = -4$ to $+10$. Relative velocities in this experiment were quite sharply defined because of the favorable molecule-atom mass ratio and varied over the range 800–2500 ms^{-1}. Two main trends in the data have already been remarked upon [6]. First the rainbow angle was found to increase with Δj for a fixed value of v_r^i and, second, θ_p decreases as v_r^i increases for each Δj transition. Neither of these observations is surprising.

However, a most unexpected result is obtained when the vector relationships in each scattering event are analyzed in detail. The data reveal surprising constraints that govern the outcome which become apparent on plotting *excess* velocity against the parallel component of initial relative velocity $v_\parallel^i$ using experimental values of v_r^i, Δj, and θ_p. The excess velocity v_{ex} is the velocity acting in the direction of v_r^i after the channel-opening velocity v_{th} has been subtracted. Thus $v_{\mathrm{ex}} = v_r - v_{\mathrm{th}} \sin\theta_p$.

These quantities are plotted in Fig. 1 for the data sets $\Delta j = -4, 2, 4, 6, 8$, and 10 using a range of v_r^i for each and θ_p values obtained by the full line-shape fitting method [6]. (Note that in calculating $v_\parallel^i$ we have assumed that only the parallel component is scattered. Justification for this is given below.) A straight line plot is obtained with slope close to 45°, i.e., the numerical values of v_{ex} and $v_r^i \cos\theta_p$ are closely similar.

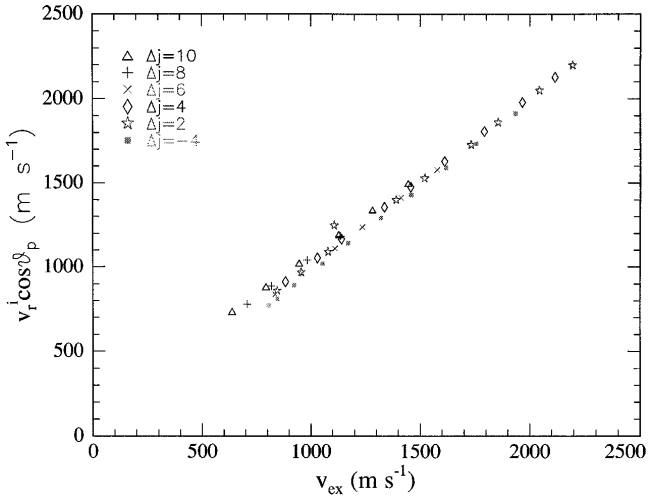

FIG. 1. Plot of excess velocity (defined as $v_r^i - v_{\mathrm{th}} \sin\theta_p$) versus $v_r^i \cos\theta_p$ (the parallel component of v_r^i if the scattered relative velocity is also parallel to the surface). The slope is 45° when plotted on identical scales. Data are for $\Delta j = -4, 2, 4, 6, 8$, and 10. Relative velocities for each Δj range from 860 to 2140 ms^{-1}.

The significance of this is readily seen in Fig. 2, a hard ellipse (HE) view of rotationally inelastic scattering [8]. Figure 2 depicts the special case in which the scattered velocity v_r^f is parallel to the ellipse surface. Only for this case is there a relationship between the scattering angle θ_p and angles subtended by the *incoming* velocity vector. Thus, the linear relationship involving incoming velocity and outgoing angle over a range of velocities, scattering angles, and Δj values displayed in Fig. 1 indicates that there is *no perpendicular component in the scattered velocity.* Furthermore, the 1:1 relationship between v_{ex} and $v_r^i \cos\theta_p$ tells us that the only perpendicular component of the *initial* velocity is v_{th}, the threshold velocity for that Δj channel. This observation is of considerable stereodynamical significance as we discuss further below.

Data from the Li_2-Xe experiment [6] indicate that the principal features of the scattering process are best understood in terms of the fate of excess linear momentum. This discovery has important implications in the context of the recently introduced angular momentum model [7] which is based on the postulate that RT is controlled by the conversion of linear momentum of relative motion to rotational angular momentum at the repulsive wall of the intermolecular potential. The probability density of this process may readily be calculated [7] from the (generally known) distribution function for v_r and an empirical probability density for the effective impact parameter b_n. This latter function has been shown to be an average of radial and angular repulsive anisotropy [9].

The underlying physics of RT becomes transparent in this model with the main features: exponential-like decay of rates, strong propensity to conserve m_j, having clear physical origins. The model allows the prediction of RT rates using readily available data, namely, the diatomic bond length, atomic masses, and velocity distribution [10]. We have also shown that it may form the basis of a straightforward inversion routine yielding contours of the repulsive potential from experimental data [11].

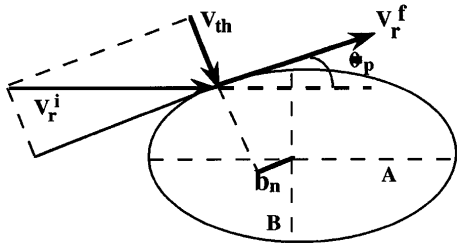

FIG. 2. Vector relationship between v_r^i, the threshold velocity v_{th}, and the most probable scattering angle θ_p that the analysis of the text implies. This relationship is found for each value of v_r^i, Δj, and θ_p reported in [6]. Note that this implies that the direction of the incident trajectory and most probable scattering angle are determined by the values of v_r^i and v_{th} and that it is the disposal of the parallel and perpendicular components of the incident relative momentum which determines the overall outcome.

In generating AM from the linear momentum of relative motion, the threshold velocity for each channel plays a key role in a process linear in v_r. When taken together with the scattering data, this suggests that in collision-induced RT our "unit of currency" might usefully be taken to be *linear momentum* and its (partial) conversion into AM regarded as the prime driving force for the process. This contrasts the approach in which kinetic energy is our basic unit and its conversion to potential energy is the focus of RT calculations. A major advantage of a momentum-based interpretation is that instead of complexity and lack of insight the process becomes physically transparent and conceptually simple. Its use as the basis of an inversion routine is an added bonus [11].

In the momentum "currency" the principal features of rotationally inelastic scattering may be summarized as follows. That portion of the incident relative momentum needed to open the Δj channel is converted to AM via the relation $\Delta j = \mu v_{\mathrm{rel}} b_n$. Probabilities for state-to-state RT follow on expressing this equation as a joint probability of the random variables that comprise it [7,9,10]. The excess momentum is the parallel component and this is scattered unchanged. The most probable scattering angle appears to be determined by simple vector relationships that follow from knowledge of the magnitude of v_r^i and of the perpendicular component, namely, v_{th}.

We note that, of course, the relationships deduced here between incident and scattered relative velocities and the scattering angles themselves are the *most probable* values of what generally are reasonably narrow distributions. As rotational inelasticity increases, the spread of scattering angle increases. The experimental study [6] reported data only from relatively low angle scattering processes, the maximum for $\Delta j = 10$ being 30°. It is possible that deviations from the simple picture presented here will be observed for processes characterized by much larger scattering angles.

In conclusion, we have found that in the system studied a remarkably simple vector relationship governs the most probable scattering angle. For a given Δj value, the trajectory of v_r^i is such that the total velocity component perpendicular to the potential wall is sufficient just to open that channel. This threshold momentum is converted into rotational angular momentum. The excess momentum is parallel to the potential wall and is scattered unchanged. Thus simple vector relations determine the stereodynamics of the collision and the scattering angle, both of which may be predicted once initial velocity is known and Δj specified. These observations are quite surprising since state-to-state DCS and their velocity dependence are expected to be very sensitive to the intermolecular potential and to provide a test of the validity of scattering theory methods.

This work has shown that the main features of RT and inelastic scattering are most simply understood in terms of the fate of the incident linear momentum. Physical insight, rules of thumb, and genuine predictive power follow. Here, experimental data reveal that *vector* relations govern the RT and scattering processes and that the threshold momentum plays a key role. This appears to raise fundamental questions as to the nature of the controlling processes in collision events and we hope to explore this further in the context of other collision-induced processes.

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