Spectroscopic Determination of the State-to-State Differential Cross Section by Velocity Selected Double Resonance

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We have measured the state-to-state differential scattering cross section (DCS) for a rotationally inelastic process using an entirely spectroscopic method. The system studied was $\mathrm{Li}_2(A^1\Sigma_u^+)$-Xe and the method utilizes two color sub-Doppler double resonance. Analysis of the shape of the double resonance line yields the final distribution of relative velocity vectors. This represents the first measurement of a state-to-state DCS using thermal cell spectroscopy. In addition we have determined, also for the first time, the dependence of the state-to-state DCS on initial relative velocity. Results are presented for the $\Delta j = 6$ rotationally inelastic process.

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Scattering cross sections differential in *angle* are generally measured by molecular beam methods. In molecular scattering, quantum state selection and detection are an essential prerequisite to meaningful analysis of the data and such enhancements add greatly to the cost and complexity of the experiment. An alternative approach is through Doppler-resolved double resonance spectroscopy [1,2] which may be performed in simple collision cells. Here we demonstrate that velocity selected double resonance (VSDR) may be used to give state-to-state cross sections for atom-molecule rotationally inelastic collisions that are differential in *angle* and relative velocity. These are the first purely spectroscopic measurements of such quantities for inelastic processes in molecules.

That information on angular distributions is contained in double resonance line shapes of atoms in thermal cells was first pointed out by Berman [3]. Gottscho *et al.* [4] extended this to rotationally inelastic collisions of molecules and determined energy averaged, most probable scattering angles for BaO colliding with argon. Of relevance are the experiments of Kinsey, Pritchard, and coworkers [5,6] who developed laser methods to determine velocity distributions, the velocity selection by Doppler shift method of Smith *et al.* [7,8], and most recently, a fully polarization-resolved, four-vector experiment by Collins, McCaffery, and Wynn [9]. Alternative treat-

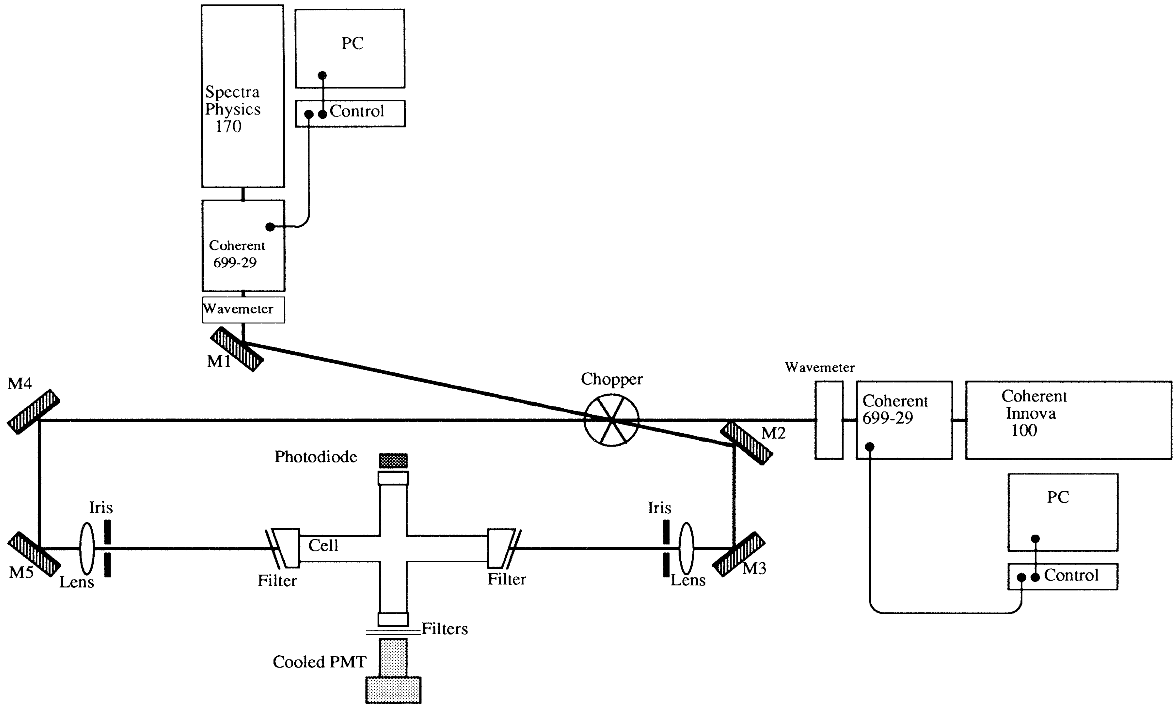

FIG. 1. Velocity selected double resonance experimental setup.

ments of optical-optical double resonance (OODR) line shapes [10,11] do not emphasize the extraction of the scattering angular variables but contribute valuable insights.

The method of sub-Doppler excitation results in a non-Maxwell-Boltzmann distribution of molecular speeds and a nonisotropic distribution of molecular vectors relative to the laser axis. Molecules excited at the line center will be moving in a plane perpendicular to the laser axis, with a Maxwell-Boltzmann speed distribution, whereas excitation at the far wings of the Doppler profile selects molecules moving at speeds approaching the upper bounds of the thermal distribution, with their velocity vectors aligned close to the laser axis. The routine described by Smith *et al.* [7] allows transformation from molecular to *relative* velocity distributions. This relative velocity selection method is most effective for light-molecule–heavy-atom systems.

We have studied inelastic collisions of Li_2 $(A^1\Sigma_u^+)$ molecules with Xe atoms from the $v = 16$, $j = 6$ level to $\Delta j = -2, -4, +2, +4, +6, +8, +10$. The experimental setup is shown in Fig. 1, and utilizes two narrow linewidth (~ 1 MHz) tunable dye lasers (Coherent model 699-29 Autoscan) to produce counterpropagating beams which become almost coaxial and interact with the lithium vapor contained inside a stainless steel sample vessel. The fluorescence produced is detected via a photomultiplier tube (EMI 9635QB) oriented at 90° to the two intersecting beams.

Two main methods are used to discriminate the desired two-photon process from unwanted signals. First, the lasers are intermodulated and the signal is amplified by a phase sensitive technique; second, extensive optical filtering (BG12+BG39+lens) is used prior to collection by the photomultiplier (PMT).

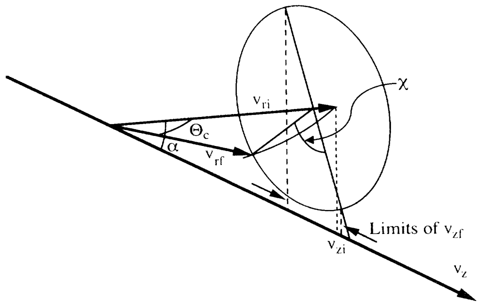

FIG. 2. Initial relative velocity vector is selected by pump laser detuning to be of length v_{ri} with angle α to the laser propagation (v_z) direction. After collision the velocity vector is scattered in-plane by Θ_c (the most probable scattering angle) and out-of-plane by angle χ. The final relative velocity vector v_{rf} forms a cone of vectors about v_{ri} the base of which (shown as a circle) is inclined to v_z. The range of projections of v_{rf} on the v_z axis gives the linewidth and the inclination of the circle determines the line shape.

The relationship between the scattering angle and the experimental line shapes is illustrated in Fig. 2.

The probability of selecting a relative velocity vector of magnitude v_r with angle α with respect to the laser axis, for a given selected molecular velocity component v_z, is [2,7]

$$P(\alpha, v_r|v_z) \propto v_r^2 \exp\left\{\frac{-v_r^2\sin^2\alpha}{2(s_a^2+s_m^2)} - \frac{(v_z - v_r\cos\alpha)^2}{2s_a^2}\right\}. \tag{1}$$

In (1), $s_x = (kT/w_x)^{1/2}$, where $x = m$ for molecule, $x = a$ for atom, and w is mass.

The change in the velocity component on collision is [2]

$$v_{zf} - v_z = u_{zf} - u_z = \frac{w_a}{w_a + w_m} v_{rf}\left[\cos\alpha\left(\cos\Theta_c - \frac{v_r}{v_{rf}}\right) - \sin\alpha\sin\Theta_c\cos\chi\right]. \tag{2}$$

$v_{rf} = (v_r^2 - 2\Delta E_r/\mu)^{1/2}$, where ΔE_r is the change in rotational energy and μ is the reduced mass for the collision.

Equation (2) relates the change in the velocity component with the angles Θ_c, the collision frame scattering angle, α, the angle between the initial velocity vector and the laser axis, χ, the out-of-plane scattering angle, and the molecular and atomic masses via the relationship of the vectors as illustrated in Fig. 2. The final velocity component distribution $P_{v_{zf}}(v_{zf}|v_z)$ is given by [2]

$$\begin{aligned} P_{v_{zf}}(v_{zf}|v_z) = \int_0^\infty \int_\infty^{-\infty} \int_0^\pi \int_0^\pi \int_0^{2\pi} & L\,(v_z'|v_z) P_{\Theta_c}(\Theta_c|v_r) P(v_r, \alpha|v_z') P_\chi(\chi) \\ & \times \delta\left[v_{zf} - v_z' - \frac{w_a}{w_a + w_m} v_{rf}\left[\cos\alpha\left(\cos\Theta_c - \frac{v_r}{v_{rf}}\right) - \sin\alpha\sin\Theta_c\cos\chi\right]\right. \\ & \times \sin\alpha\sin\Theta_c\, d\chi\, d\Theta_c\, d\alpha\, dv_z'\, dv_r, \end{aligned} \tag{3}$$

where $L(v_z'|v_z)$ is the Lorentzian distribution of selected velocity components.

Through Eq. (3) the shift and broadening of the velocity distribution as measured by the VSDR line shape may be related to the differential scattering cross section which is shown as the probability distribution $P_{\Theta_c}(\Theta_c|v_r)$.

TABLE I. $\Delta j = 6$: Parameters of the probability distribution $P(\Theta_c)$ (function given in text) obtained from line-shape fits.

Width, experimental linewidth (ms^{-1})	v_z Laser selected molecular velocity (ms^{-1})	V_{rp} Most probable relative velocity (ms^{-1})	Θ_{cp} Most probable scattering angle (°)	n
704±30	0±25	780	21±2	6
672±30	117±25	790±5	21±2	1
635±30	375±25	870±15	18±2	1
524±30	434±25	900±15	18±2	2
386±30	750±25	1110±20	12±2	1
350±30	914±25	1260±20	10±2	1
300±30	1125±25	1420±20	10±2	1
348±30	1320±25	1580±25	8±2	1

Table I presents the results of line-shape fitting using the analytical relation stated earlier [Eq. (3)]. In this example the probability function $P_{\Theta_c}(\Theta_c|v_r)$ was chosen for computational convenience; however, it provides a reasonable approximation to the primary feature of a differential scattering cross section (DCS) for a predominantly forward scattering system, and is discussed in greater detail in Ref. [2]. It takes the form

$$P_{\Theta_c}(\Theta_c|v_r) = \Theta_c \exp\{-n\Theta_c^2/2\Theta_{cp}^2\}.$$

The experimental line shapes exhibit two interesting trends. First, the double resonance linewidths reduce markedly as v_z increases; second, the linewidths increase dramatically with increasing Δj. In simple physical terms it can be seen from Fig. 2 that the linewidth is closely related to the projection of the scattering "circle" of the final velocity vectors on the v_z axis. Reduction in linewidth may come about through a reduction in α [known through Eq. (1)] or a reduction in Θ_c. The two general trends noted above in the data indicate that as v_z (and hence v_r) increases for a given Δj the most probable scattering angle becomes smaller, i.e., scattering is more forward peaked. It would be expected that as Δj increases (for a constant v_z) the scattering angle would increase.

Full analysis of the data is not yet complete but results for $\Delta j = 6$ illustrate the first of these trends. For low v_r, the scattering angle is highest since a substantial fraction of the momentum is required to open the channel. As the relative velocity increases this represents a diminishing fraction of the available kinetic energy and thus the scattering becomes more forward peaked. This trend is consistent with impulsive scattering off an elliptical hard wall potential [12,13].

There is little available data with which to compare our results since full state-to-state DCS measurements of rotationally inelastic transitions are rare. Comparison with data on Na_2–rare-gas collisions by Bergmann and co-workers [14] indicates that our DCS values peak at somewhat lower values than those shown in Ref. [14]. This is not surprising since the work cited on Na_2 was performed on the ground state of that molecule and our results are for the Li_2 $A^1\Sigma_u^+$ excited state. The intermolecular potential of this state of Li_2 with rare gases is known to be exceptionally anisotropic [15,16], which strongly aids rotational transfer.

In summary, therefore, we present for the first time a measurement of the state-to-state differential cross section using purely thermal cell spectroscopy. In addition, and also for the first time, the dependence of the state-to-state DCS on relative velocity has been measured. Results are presented as parameters of an assumed function for the DCS: the most probable scattering angle (Θ_{cp}) and width of the distribution (n). Values of Θ_{cp} and trends, as v_r is varied, are consistent with those expected for a rotationally inelastic process involving a strongly anisotropic intermolecular potential.

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