Angular Scattering Distribution By Doppler Spectroscopy: $Na(3P_{1/2})+Ar \rightarrow Na(3P_{3/2})+Ar$

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We have developed a new method for determining state-resolved differential cross sections in inelastic collisions. A single-frequency laser provides level-specific detection of scattered atoms, while the Doppler shift of the same laser provides a completely nonmechanical angular selectivity in the detection. We have used this technique to make the first measurement of an alkali fine-structure transfer cross section in which both the scattering angle and final state are determined.

In this Letter, we describe a new technique for inelastic differential cross section measurements which uses a laser to detect both the energy level and angular distribution of scattered atoms. Since the laser detection of the scattered atoms can be accomplished on a time scale of nanoseconds, the method is suitable for the study of scattering into short-lived states. We have applied this method to the measurement of the differential cross section for $Na(3P_{1/2}) + Ar \rightarrow Na(3P_{3/2}) + Ar$. Because of the short lifetime of the Na $3P$ levels and the small energy defect (17 cm^{-1}) of the process, this measurement has been impossible to make by any previous technique.

In our method, a laser is used to excite fluorescence from only those atoms which have been scattered into a specific level. The Doppler shift, which causes the laser frequency seen by any scattered atom to depend on the projection of its velocity along the laser beam, provides additional selectivity for the scattering angle as well as the level.

The relationship between the Doppler shift of the analysis laser and the scattering angle in the center-of-mass (COM) system can be made quite simple. Figure 1 shows a velocity vector diagram for a Na-Ar collision. The velocity vectors for Na atoms scattered by an angle θ in the COM system form a cone centered on the axis of relative velocity between the Na and Ar. Since each of these vectors has the same velocity component along the relative velocity axis, a laser beam directed along this axis will be resonant at the same frequency for all atoms scattered by θ.

With the laser so directed, and tuned to a given frequency, the number of atoms excited by the laser is proportional to the number of atoms scattered by angle θ into the desired state. If we take the laser offset frequency $\Delta\nu = 0$ to correspond to the frequency needed to excite forward-scattered ($\theta = 0$) atoms of the correct level, for the laser directed in the same direction as the initial Na velocity in the COM system (copropagating), we have

$$\Delta\nu = (\cos\theta - 1)\frac{v_{\rm rel}}{\lambda}\frac{M_{\rm Ar}}{M_{\rm Ar} + M_{\rm Na}}, \qquad (1)$$

where $v_{\rm rel}$ is the relative velocity, M is the atomic mass, and λ is the laser wavelength. For counter propagation of the analysis laser the sign of $\Delta\nu$ is reversed. Note that θ is the COM scattering angle and that no transformation between COM and laboratory coordinates is necessary. By observing the fluorescent intensity excited by the laser as a function of $\Delta\nu$, one obtains a direct measure of the relative differential cross section $d\sigma(\theta)/d\Omega$:

$$I(\Delta\nu) = K d\sigma(\theta)/d\Omega, \qquad (2)$$

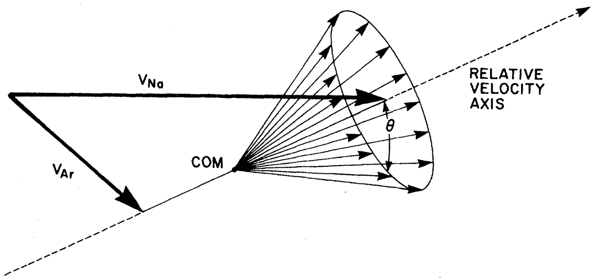

FIG. 1. Velocity vector diagram. Bold vectors are initial laboratory velocities, light vectors are scattered Na velocities in the COM system for scattering through angle θ at different φ.

where $\Delta\nu$ and θ are related as in Eq. (1) and K is a proportionality constant. Some of the particular advantages of this technique compared with conventional methods with mechanical selection of the scattering angle of detected atoms are as follows: (1) It provides level specificity; (2) detection takes place in a time comparable to the radiative lifetime after the scattering; (3) all atoms scattered by θ in the COM system are available for detection, rather than only a subset scattered by a particular azimuthal angle. This results in a substantial increase in sensitivity.[1]

We have applied this new technique to the measurement of fine-structure-transfer (FST) collisions in Na-Ar, using it to make the first measurement of the differential cross section for this process. This is an appealing application because alkali-rare-gas excited-state collision processes have been actively studied both experimentally and theoretically and have emerged as a major testing ground for theories and experiments of excited-state atomic interactions. For Na-Ar there exist both crossed-beams[2] and cell measurements[3] of the velocity dependence of the FST total cross section. Both pseudopotential[4] and *ab initio*[5] calculations of the relevant $A\Pi$ and $B\Sigma$ excited-state potential curves have been made, and the *ab initio* results show good agreement with the Rydberg-Klein-Rees (RKR) curve determined for the $A\Pi$ state from molecular spectroscopy.[6] Close-coupling calculations of the differential cross section for the process studied have been made using the *ab initio* potentials.[5] These predict large oscillations, at wide angles, in the level-resolved differential cross section, but not in the sum of inelastic and elastic cross sections. Hence, it is not possible to observe these oscillations in "conventional" excited-state differential scattering studies in which the Na is detected after it has decayed.[7,8] Our measurements, because of their combined level and angular sensitivity, are the first to show these oscillations. Consequently, the theory can now be subjected to entirely new tests.

Our experimental arrangement is as follows: An atomic beam of Na is excited by a single-frequency dye laser operating on the $3S_{1/2}(F=2) \rightarrow 3P_{1/2}(F=1, 2)$ transition (see Fig. 2). Because of the Doppler shift, the excited atoms are in two narrow velocity groups corresponding to the two $3P_{1/2}$ hyperfine levels. This velocity-selected beam of excited atoms collides with an atomic beam of Ar from a supersonic nozzle having a velocity full width of less than 10% and an angular FWHM (full width at half-maximum) of about 0.1 radian. The analysis laser, a Coherent 599 laser operated at 5683 Å using Rhodamine 110, is directed along the relative velocity axis and tuned to the $3P_{3/2} \rightarrow 4D_{5/2}$ transition, exciting Na atoms which have undergone the $3P_{1/2} \rightarrow 3P_{3/2}$ FST process. The population of the $4D$ states is monitored by observing the cascade $4P \rightarrow 4S$ radiation at 3302 Å. The differential cross section is determined by measuring the number of photons at 3302 Å as a function of the analysis-laser frequency. The angular resolution in the measured differential cross section near 90° (COM) is limited to ~5° FWHM by the velocity spread of the atomic beams. Spectroscopic width and structure, and power broadening of the $3P_{3/2}$ state also degrade the resolution somewhat. The resolution is worse near 0° and 180°.

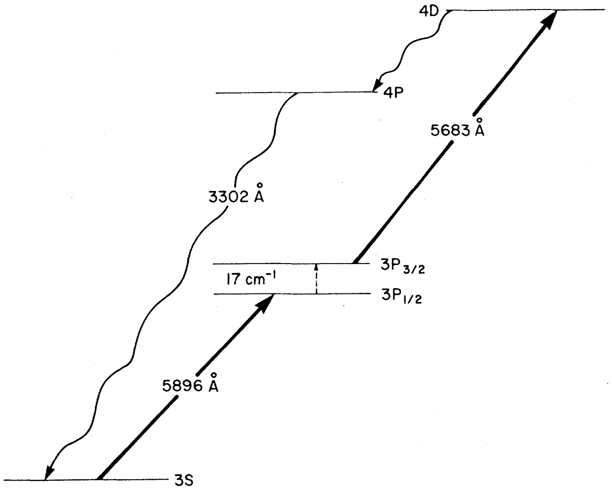

FIG. 2. Na energy levels with excitation (straight) and decay (wavy) transitions shown. The FST collision is shown dashed.

Figure 3(a) shows such an experimentally determined differential cross section for mean collision energies of 0.121 and 0.143 eV, for the two $3P_{1/2}$ hyperfine states excited. The analysis laser was directed along the COM Na velocity. In the same figure, the data are compared with normalized predictions of the theory of Saxon, Olson, and Liu[5] for these energies suitably averaged over the velocity and angular widths of the atomic beams, the widths of the transitions involved, the $3P$ hyperfine structure, and the $4D$ fine structure. Figure 3(b) shows the same cross section for the opposite direction of propagation of the analysis laser. The large feature at ~1 GHz on the frequency scale is due to forward-scattered

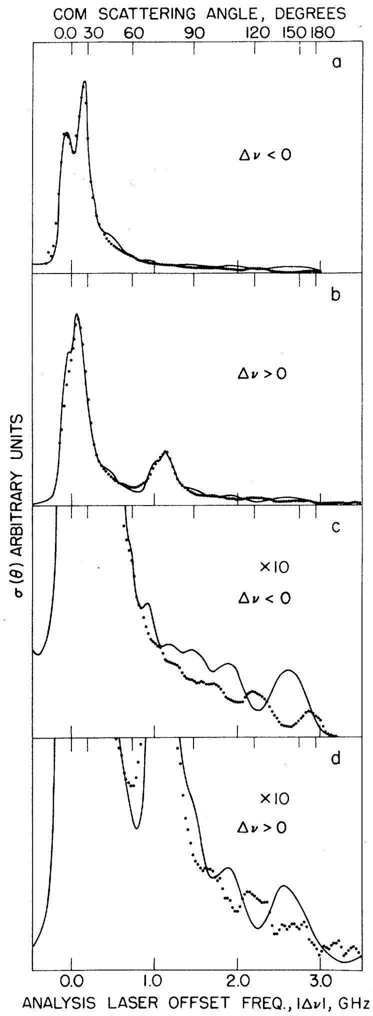

FIG. 3. Experimental (points) and theoretical Na-Ar FST cross sections: (a) copropagating analysis laser; (b) counter-propagating analysis laser; (c) magnified view of (a); (d) magnified view of (b).

Na atoms excited to the $4D_{3/2}$ states, which are separated from the $4D_{5/2}$ by 1028 MHz. This feature is off scale to the left in Fig. 3(a). The structure in the forward-scattered peaks in Figs. 3(a) and 3(b) is caused by the two velocity groups of $3P_{1/2}$ atoms. The difference in appearance of this structure in the two figures can be understood by considering the distribution of scattered atoms among the $3P_{3/2}$ hyperfine levels. We have been able quantitatively to account for this difference in the theoretical curves by using the relative $\sigma(j,m_j \rightarrow j',m_j')$ given by the calculations of Elbel,[9] assuming that the nuclear spin orientation is unaffected by the collision.

Figures 3(c) and 3(d) show a magnified view of Figs. 3(a) and 3(b). The oscillations at large angles, which are due to interference between paths involving the Σ and Π potential curves of the molecule NaAr, are clearly seen in the experimental and theoretical cross sections. These oscillations cannot be seen in experiments which fail to distinguish elastic and inelastic processes, since they are out of phase for the two processes and cancel in the sum.[5]

The general features of the experimental and theoretical cross sections are in fair agreement. The relative magnitudes of forward and large-angle scattering correspond fairly well and the spacing and depth of the oscillations are similar. It is clear, however, that the phase of the oscillations is not well reproduced by the theory. Since no systematic errors big enough to account for this difference can be found, we attribute it to inaccuraacies in the potentials used for the scattering calculation. We feel that the $A\Pi$ potential determined from spectroscopic data by the RKR technique (extended, if necessary, to larger and smaller internuclear separation in accord with *ab initio* calculations) would not introduce significant uncertainty into calculations of the differential cross sections measured here. Therefore adjustment of the $B\Sigma$ state to give cross sections in accord with our measurements would provide definitive new information about this potential.

In summary, we have demonstrated a new method for measuring differential inelastic cross sections of individual final levels. In contrast to techniques using movable particle detectors,[7,8] our method offers improved sensitivity at some sacrifice in angular resolution, and measures the desired level-specific differential cross section rather than a sum of several such cross sections. The angular resolution of the present experiment could easily be improved by using sources with less velocity spread and by reducing the laser power to eliminate power broadening. The use of Fourier-transform Doppler spectroscopy[1] would result in a further improvement in angular resolution and could also provide speed resolution. There are many collision processes in which the advantages of the method presented here are well matched to the scientific problem. For example, the recently reported study by Bergmann *et al.*[10] of inelastic collisions of Na_2, where mechanical selection of the scattering angle and laser selection of the final level was used, is an excellent candidate for our method.

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[1] J. L. Kinsey, J. Chem. Phys. 66, 2560 (1977).

[2] W. D. Phillips, C. L. Glaser, and D. Kleppner, Phys. Rev. Lett. 38, 1018 (1977).

[3] J. Apt and D. E. Pritchard, Phys. Rev. Lett. 37, 91 (1976).

[4] J. Pascale and J. Van de Planque, J. Chem. Phys. 60, 2278 (1974).

[5] R. P. Saxon, R. E. Olson, and B. Liu, J. Chem. Phys. 67, 2692 (1977).

[6] R. E. Smalley, D. A. Auerbach, P. S. H. Fitch, D. H. Levy, and L. Wharton, J. Chem. Phys. 66, 3778 (1977).

[7] G. M. Carter, D. E. Pritchard, M. Kaplan, and T. W. Ducas, Phys. Rev. Lett. 35, 1144 (1975).

[8] R. Düren, H. O. Hoppe, and H. Pauly, Phys. Rev. Lett. 37, 743 (1976).

[9] M. Elbel, Z. Phys. 248, 375 (1971); see also J. C. Gay and W. B. Schneider, Z. Phys. A278, 211 (1976).

[10] K. Bergmann, R. Engelhardt, U. Hefter, P. Hering, and J. Witt, Phys. Rev. Lett. 40, 1446 (1978).

Double-Quantum Saturation Spectroscopy in Hydrogen: Measurement of the $3P_{3/2}$-$3D_{3/2}$ Lamb Shift

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Very narrow saturated double-quantum transitions (2^2S-$3^2S, 3^2D$) have been observed for atomic H in a He-H_2 dc discharge using rf and a cw dye laser. The H $3P_{3/2}$-$3D_{3/2}$ Lamb shift has been measured directly by comparing single- and double-quantum saturation signals to be $-5.5(0.9)$ MHz, confirming that $3D_{3/2}$ lies lower than the $3P_{3/2}$ state. Further applications of the method are discussed.

Saturation spectroscopy[1,2] in hydrogen using single-photon transitions is limited in resolution by the natural lifetime of the broad resonant P levels. Double-quantum transitions between the longer-lived ^2S or ^2D levels, however, will in principle be narrower by more than one order of magnitude, e.g., by a factor of 30 for 2^2S-3^2S compared to the intermediate 2^2S-3^2P transitions, as has been pointed out several years ago.[3] More general theoretical analyses of saturated double-quantum transitions using lasers had been worked out even earlier.[4]

We have demonstrated the feasibility of Doppler-free double-quantum saturation spectroscopy (DQS) of atomic hydrogen using saturated, polarized absorption[2] for the optical transitions 2^2S-n^2P, $n \geq 3$, and a simultaneous rf or microwave transition $[n^2P$-n^2S $(-n^2D)]$. This method is a practicable alternative to the not yet accomplished possibility of infrared two-photon spectroscopy of excited ^2S (^2D) hydrogenic states. It has the advantage that very low laser intensities (e.g., <20 mW/cm^2 for H_α D_1, $2S_{1/2}$-$3P_{1/2}$) are sufficient to saturate the optical transition. With the high absorption attainable in the He-H_2 dc discharge, the double-quantum transitions can readily be observed with the convenient detection method of saturation or polarization spectroscopy, i.e., as a change in the transmitted laser-probe-beam intensity or polarization. Narrow transitions have also been observed in hydrogen with a purely radio-frequency double-quantum method resulting in a precise determination of the $3S_{1/2}$-$3D_{5/2}$ separation.[5]

The experimental setup is shown in Fig. 1. A single-mode cw dye laser (Coherent Inc. Model 599, Rhodamine 101 dye) pumped by the 568.2-nm line of a Kr^+ laser (Spectra-Physics Model 171) provides 50 mW at H_α, $\lambda = 656.3$ nm, with a bandwidth of about 1 MHz. A wide discharge tube (5.5 cm i.d.) without wall coating filled with a He-H_2 (1 to 15%) mixture is used to generate the metastable $H^*(2s)$ atoms. It has several advantages compared to a conventional narrow (1-cm-diam) Wood's discharge tube with pure H_2 and a wall coating of P_2O_5 and H_2O. The H_α polarization signals are of similar strength for discharge current densities lower by more than a factor of 3. With currents of 50 to 500 mA provided by a hot cathode, $H^*(2s)$ densities of $10^9/$