Two-Color Sub-Doppler Circular Dichroism: A Four-Vector Correlation Molecular-Dynamics Experiment

T. L. D. Collins, A. J. McCaffery, and M. J. Wynn
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, United Kingdom

(Received 4 September 1990)

In molecular collision and reaction dynamics the precision of data obtainable from an experiment is determined by the extent the vectors of linear and angular momentum are specified. The highest degree of specification comes from four-vector correlation, two before and two after the collision. Here we introduce the new technique of two-color sub-Doppler circular dichroism and demonstrate the first four-vector correlation molecular-dynamics experiment. Results are given for elastic and inelastic collisional processes between Li_2 and the rare gases Ar and Xe.

PACS numbers: 34.50.−s, 34.40.+n

In molecular collision and reaction dynamics, the hierarchy of vector correlations has proved to be a valuable classification technique.[1] This approach emphasizes the importance of directional observables and has led, aided by experimental advances, to the emergence of the new field of dynamical stereochemistry.[2]

Traditional methods of achieving correlation of momentum (or velocity) vectors have generally relied on molecular-beam experiments.[3] However, it is known that sub-Doppler spectroscopic techniques provide a valuable additional device through which both magnitude and direction of atomic and molecular velocities may be assigned.[4-9] When such sub-Doppler methods are allied to high-precision polarization excitation and detection the possibility exists for high-order vector correlation experiments.

We have recently demonstrated[10] and analyzed[11] atom-diatom collision dynamical data from a three-vector correlation experiment that yielded direct information on stereochemical dynamics. In that work, Doppler velocity selection was allied to high-precision polarization techniques in the entrance and exit channels to specify initial relative momentum v_i together with the magnitude and dominant multipole distribution of the rotational angular momentum vector j_i. Following inelastic collisions the state multipoles of the final j_f distribution were determined as a function of laser detuning. This $(v_i j_i j_f)$ correlation was observed for rotationally inelastic collisions between Li_2 $(A\,{}^1\Sigma_u^+)$ and Xe.

In this Letter we report the extension of this technique to give the first four-vector correlation experiment. This method allies polarization methods of high precision and sensitivity with sub-Doppler pump and probe which provide velocity and angle discrimination in input and output channels. The pump laser is circularly polarized and thus a Lorentzian velocity distribution of oriented molecules is excited, leaving a similarly oriented hole in the ground-state velocity distribution. The probe laser measures the shift and broadening of this distribution in either labeled state, as a circular dichroism (CD) following collision. It thus becomes a four-vector correlation experiment in which $(v_i v_f j_i j_f)$ are correlated.

Here we describe the results of such a study of elastic and inelastic collisions in Li_2-Xe and -Ar but emphasize that the technique is of wide applicability since reactive and nonreactive collisions may be studied using this or closely related methods. Its strength is that laboratory-frame observations of gas-phase collisional processes may be interpreted in the molecule or the collision frame with all relative directional processes specified in that frame. To obtain data of this dynamical specificity from simple-collision-cell experiments suggests that a wide range of processes will soon be studied and a real possibility exists that intermolecular potentials will be obtained from such experimental data.[12]

Experimental description.—The determination of initial and final relative momentum- (velocity-) vector magnitudes and directions by Doppler shift has been described by us recently.[5,13] Figure 1 illustrates the general principle. In brief, the relation between laser detuning v_L and molecular velocity magnitude and direction is given by[5]

$$P(v_L,v_r,\alpha)=v_r^2\exp\left[\frac{-v_r^2\sin^2\alpha}{2(s_a^2+s_m^2)}\right]\times\exp\left[-\frac{(v_L-v_r\cos\alpha)^2}{2s_a^2}\right],$$

where $s_x=(m_x/kT)^{1/2}$.

The pump laser selects this distribution from the Doppler profile and the probe laser examines the shift and width of the distribution following collision. It has been shown that the shift may be related to the scattering angle through the following relation:[13,14]

$$\Delta v_{mz}=\left[\frac{m_a}{m_a+m_m}\right]v_r\cos\alpha(\cos\theta_c-1)\,.$$

Use of a light molecule with heavy collider atom allows molecular velocity and relative velocity to be interrelated with some precision. This line-shift method thus permits the vv correlation to be obtained, yielding the

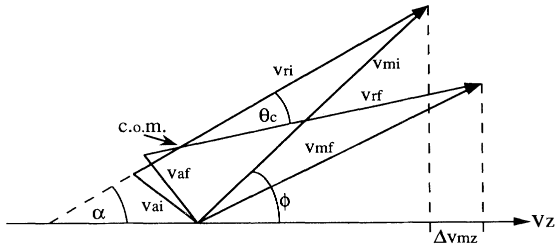

FIG. 1. A Newton diagram showing the relationship between the relative velocity vectors and the molecular velocity vectors, before and after collision. The angle θ_c is the center-of-mass scattering angle.

most probable scattering angle.

Correlation to the angular momentum vector is achieved using circularly polarized pump and probe. Excitation in this fashion produces excited molecules having a dipolar distribution of j vectors relative to the propagation direction and thus j and v are parallel in the wings but perpendicular at line center.

The probe laser measures the sub-Doppler circular dichroism (SDCD), i.e., the difference in absorption coefficient for left and right circularly polarized light of the pumped distribution following collision. This is measured in two separate ways: first, as a probe of the near Lorentzian spike of population excited by the pump into the Li_2 A state, or alternatively, as a probe of the hole left behind in the ground state. Thus we are able to study separately Li_2 rare-gas collisions for ground- and first-excited-state Li_2 molecules.

The SDCD signal is in one sense a measure of the double-resonance line shape but in addition it yields the loss of correlation of final with initial j-vector directions. Its shift and shape give the vv correlation information, i.e., the differential scattering cross section, while the shape and magnitude of the CD signal relative to the quantity $\sigma^+ + \sigma^-$, which is measured simultaneously, yields the jj and the jv correlation.

A single-frequency tunable ring dye laser (pump) is circularly polarized using a Fresnel rhomb and is directed into a heated cell containing lithium metal and buffer gas where it overlaps the probe laser. The second laser is also a single-frequency tunable source and is passed through a second Fresnel rhomb and then a photoelastic modulator just prior to entering the cell. The CD is detected from the difference in fluorescence intensities for left and right circularly polarized probe light. This yields a direct measure of the $K=1$ state multipole (orientation) of the j distribution while the sum of these is proportional to the $K=0$ or population moment. The former signal comes from a lock-in detector while the latter is obtained using a dc amplifier.

The pump laser excites a narrow, but variable, distribution of velocity vectors from the Doppler profile of a $(v'',j'')=(1,14)$ level of $X\,^1\Sigma_g^+$ Li_2 to (15,15) of $A\,^1\Sigma_u^+$. This spike in the A state possesses well defined velocity and angle relative to the laser propagation axis and a well characterized distribution of j-vector directions referenced to the same axis. The hole remaining in the X-state distribution is similarly well defined. The probe laser measures the CD of this spike or of the hole by exciting to (v,j) levels of the $G\,^1\Pi_g$ state in the former case, or from (v'',j'') levels of X state in the latter. In this way collisions of ground-state or of excited-state Li_2 with the collision partner could be studied. Experiments were performed for $\Delta j=0$ and $\Delta j=2$ processes by careful choice of probe laser frequency. Signals for the inelastic process could not be obtained on studying the hole in the X-state profile. In experiments on the A-state spike, a very wide range of initial velocities (out to $\sim 4800\ \mathrm{ms}^{-1}$) could be studied by tuning the pump laser because of the excellent signal-to-noise ratio.

A phenomenological expression for the Doppler-free laser-induced CD may be obtained from derivations of line profiles in polarization spectroscopy. We may write[15]

$$I^+ - I^- = \tfrac{1}{2} IL\Delta\alpha ,$$

where I is the probe beam intensity, L is the path length of the pumped region, and $\Delta\alpha = \alpha^+ - \alpha^-$ is the difference in absorption coefficient for left and right circularly polarized light. This expression assumes $\Delta\alpha L \ll 1$. $\Delta\alpha$ is related to the pump intensity and absorption cross section through known expressions given full identification of initial and final states. The CD detection method relies on the retention of some memory of initial orientation through elastic and inelastic collisions. There is experimental[16,17] and theoretical[11,18] evidence of strong m conservation under these collisional circumstances both for excited and for ground molecular states. We have recently reviewed this topic[11] and from this discussion it will be apparent that we may use elastic circular polarization ratios to calibrate inelastic values and thus evaluate the jj correlation from the SDCD magnitude.

Results.—The main purpose of this Letter is to demonstrate the first realization of the four-vector correlation experiment in molecular collision dynamics. This is illustrated in a study of elastic and inelastic collisions between Li_2 molecules and argon or xenon atoms. Some sub-Doppler double-resonance CD line shapes are shown in Figs. 2 and 3. Figure 2 displays two CD signals, one with pump laser tuned to line center and the other well into the wing at a relative velocity of $\simeq 1800\ \mathrm{m\,s}^{-1}$. These both represent an X-A, A-G double resonance and thus collisions of the excited A state with xenon atoms are probed. In this figure the upper line shape represents the circular dichroism in the form $\sigma^+ - \sigma^-$ while the lower curve in each case is the "unpolarized" intensity measured as $\sigma^+ + \sigma^-$. The former signal in density-matrix terms represents the $K=1$ or orientation multipole while the latter is a close approximation to the $K=0$ or population multipole. Their ratio yields the jj

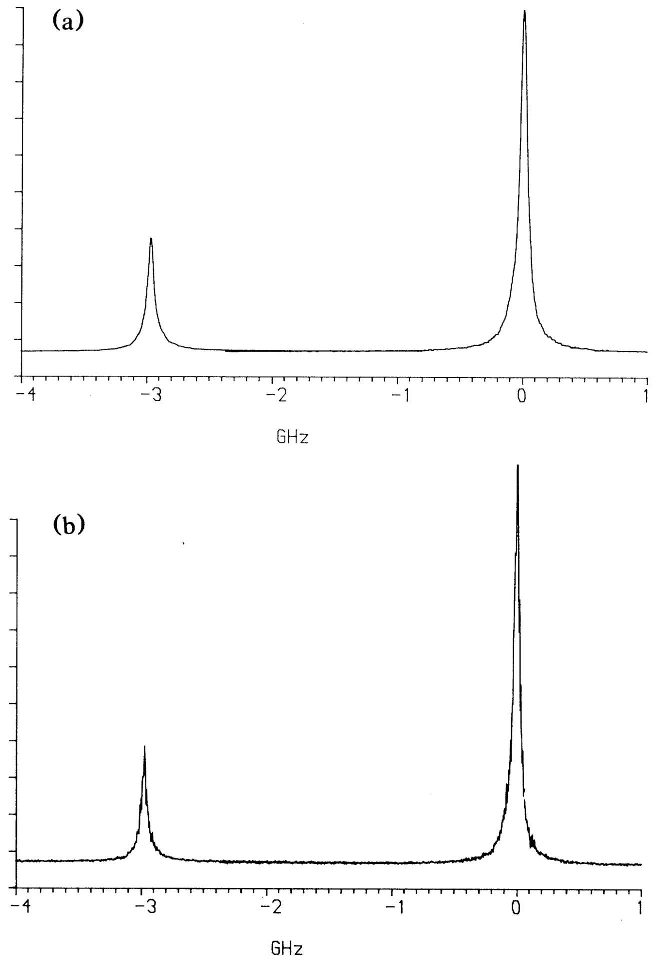

FIG. 2. Sub-Doppler line shapes showing the ac (upper) and dc components of the signal, at line center ($v_L \simeq 0$), and at $v_L \simeq 1800\ \mathrm{m\,s^{-1}}$.

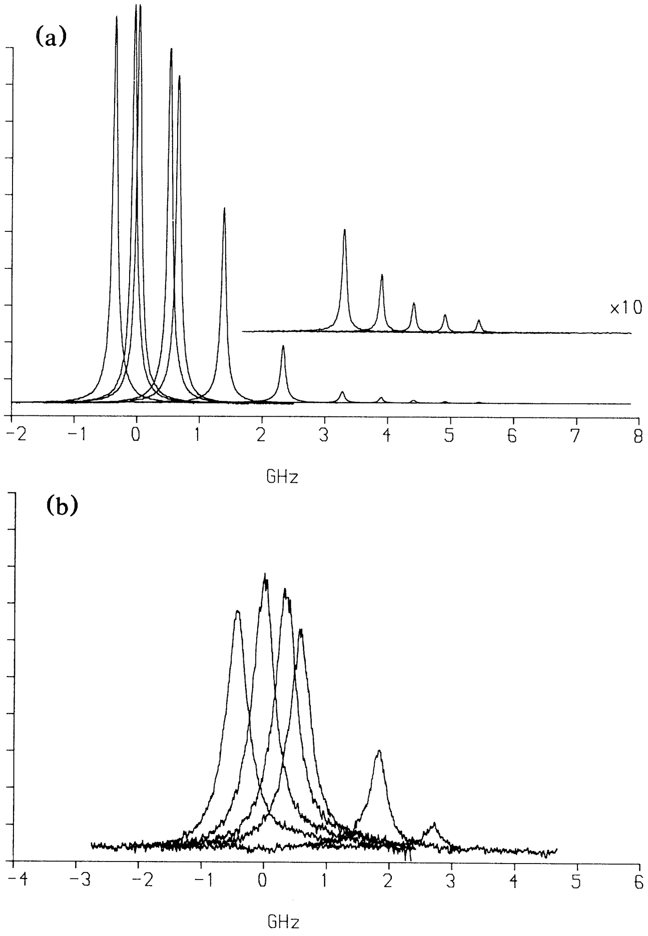

FIG. 3. Two Doppler scans are shown for the Li_2-Ar system. In both scans the pump excites in the *X-A* transition manifold, while the probe excites the *A-G*. The top scan is for $\Delta J = 0$, and the bottom for $\Delta J = +2$.

correlation. Further, we may infer the moments of the projection of *j* on the final relative velocity axis.

Information on the differential scattering cross section comes from the shift and broadening of the line shape. Figure 3 illustrates two sets of data, where the pump laser has been successively stepped across the Doppler profile. The upper scan illustrates the $\Delta J = 0$, elastic process, while the lower scan shows the $\Delta J = +2$, inelastic process in the Li_2-Ar system. In these examples only the CD signal is shown. Figure 4 illustrates a range of SDCD line shapes for the alternative experiment *X-A*, *X-A* where now collisions of the rare gas with ground-state lithium molecules are probed. This signal is considerably more noisy since now there are numerous competing processes which will attempt to repopulate the pumped hole from surrounding quantum states. However, this is an experimental configuration of considerable potential since it may be adapted to the study of reactive collisions. Further developments of this double-resonance technique in which pump and probe originate on the ground potential-energy surface may be anticipated.

In conclusion, we have presented, for the first time, data from a four-vector correlation molecular-dynamics experiment. The method is a two-color sub-Doppler optical-optical double resonance in which diatomic molecules are selected in relative velocity and *j*-vector orientation (as well as in quantum state) prior to collision by a narrow line circularly polarized pump laser. The shift, broadening, and magnitude of the probe circular dichroism signal may be analyzed to give the scattering angle and the *j*-vector reorientation for preselected relative velocities.

This represents the highest level of vector correlation in structureless-atom–Σ-state-diatomic scattering and is therefore of considerable significance as a molecular-dynamics experiment. Our data are preliminary and are for rotationally elastic and inelastic collisions but the

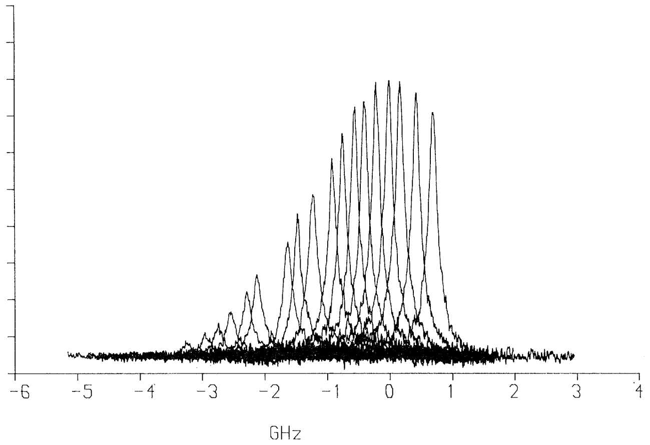

FIG. 4. A Doppler scan for the alternative experiment where pump and probe beams excite in the X-A band. The system used is Li_2-Ar, and $\Delta J = 0$.

technique has wider capabilities. It is not limited to optical frequencies, and pump or probe lasers might just as easily be infrared and ultraviolet sources. Extension of the method to study reactive collisions is readily envisaged.

We thank the Science and Engineering Research Council for financial support and for a studentship to T.L.D.C.

[1] D. A. Case and D. R. Hershbach, Mol. Phys. **30**, 1537 (1975).

[2] See J. Phys. Chem. **91**, 5365–5515 (1987).

[3] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford Univ. Press, New York, 1987).

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

[5] K. L. Reid, A. J. McCaffery, and B. J. Whitaker, Phys. Rev. Lett. **61**, 2085 (1988).

[6] J. A. Serri, J. L. Kinsey, and D. E. Pritchard, J. Chem. Phys. **75**, 633 (1981).

[7] N. Smith, T. P. Scott, and D. E. Pritchard, J. Chem. Phys. **81**, 1229 (1984).

[8] P. Houston, J. Chem. Phys. **91**, 5338 (1987).

[9] C. P. Fell, A. J. McCaffery, K. L. Reid, A. Ticktin, and B. J. Whitaker, Laser Chem. **9**, 219 (1988).

[10] K. L. Reid, A. J. McCaffery, C. P. Fell, and A. Ticktin (to be published).

[11] K. L. Reid and A. J. McCaffery (to be published).

[12] A. J. McCaffery and Z. T. Alwahabi, Phys. Rev. A (to be published).

[13] K. L. Reid and A. J. McCaffery (to be published).

[14] R. A. Gottscho, R. W. Field, R. Bacis, and S. J. Silvers, J. Chem. Phys. **73**, 599 (1980).

[15] W. Demtröder, *Laser Spectroscopy* (Springer-Verlag, Berlin, 1982).

[16] M. D. Rowe and A. J. McCaffery, Chem. Phys. **43**, 35 (1979).

[17] A. Mattheus, A. Fischer, G. Ziegler, E. Gottwald, and K. Bergmann, Phys. Rev. Lett. **56**, 712 (1986).

[18] V. Khare, D. J. Kouri, and D. K. Hoffman, J. Chem. Phys. **76**, 4493 (1982).