

Determination of population, alignment, and orientation using laser induced fluorescence with unresolved emission. II

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When an anisotropic ensemble of isolated atoms or molecules absorbs radiation from a polarized laser beam and the resulting fluorescence is collected independent of wavelength (1 + 1 unresolved LIF) with optional polarization analysis, the moments of the spatial distribution of the angular momentum J of the initial state in the ensemble may be determined. Previously, work by A. C. Kummel, G. O. Sitz, and R. N. Zare [J. Chem. Phys. **88**, 7357 (1988)] correctly derived what possible moments can be found when cylindrical symmetry is present. This work shows that several additional alignment moments, not mentioned in KSZ, can be found in ensembles having noncylindrical symmetry.

Previous work by Kummel, Sitz, and Zare (KSZ)¹ considered the problem of determining the orientation and alignment of the angular momentum of a sample of molecules using laser induced fluorescence (LIF) detection. In this method the sample absorbs polarized radiation in a one-photon process and the resulting one-photon fluorescence is collected with no wavelength resolution (1 + 1 unresolved LIF) and optional polarization analysis. In general, the spatial distribution of a particular state J of the molecules can be expressed in an expansion of real spherical harmonics,² and the expansion coefficients, $A_{q\pm}^{(k)}$, are called the real moments of the angular momentum distribution. For 1 + 1 LIF, there are, in general, 25 such moments with the index k ranging from 0 to 4, and the index $q\pm$ ranging from $-k$ to $+k$. The $k = 0$ moment, $A_{0+}^{(0)}$, carries information about the relative population of the state J of the ensemble while the $k \neq 0$ moments carry information about the angular momentum polarization of the ensemble. The 24 $k \neq 0$ moments are conveniently subdivided into 10 moments with k odd ($k = 1, 3$) which describe the orientation, and 14 moments with k even ($k = 2, 4$) which describe the alignment. Often symmetry conditions, such as the presence of cylindrical symmetry, greatly reduce the number of moments present in the system.

Previous studies done by Case, McClelland, and Herschbach³ required the use of several geometries to determine all the moments. In contrast, KSZ considered various excitation-detection geometries in which the excitation direction and the detection direction are fixed throughout an experiment. This choice was purposeful because in most experiments it is difficult to alter the excitation-detection geometry. In particular, KSZ examined three right-angle excitation-detection geometries, called Case I, Case II, and Case III. In Case I, the probe laser propagates along the laboratory z axis and the fluorescence is detected along the laboratory y axis; for Case II the probe laser propagates along the x axis and the fluorescence is detected along the z axis; for Case III the probe laser propagates along the y axis and the fluorescence is detected along the z axis. In each of these cases (as

well as for any fixed excitation-detection geometry), KSZ noted that the measured moments are actually apparent moments, i.e., represent simple sums of the real moments of the molecular ensemble.

To extract the real moments from the apparent moments, KSZ outlined a procedure to determine the alignment moments, called a double delta scan, and a procedure to determine the orientation moments, called a double beta scan. These experiments involve two angles. Δ_a is defined as the angle between the polarization vector of the probe laser beam (adsorbed photon) and a convenient axis of the lab frame (the x axis for Case I and the z axis for Cases II and III). Δ_d is the angle between the major axis of the detector polarizer, and an appropriate axis of the lab frame (the z axis for Case I, the x axis for Case II, and the z axis for Case III). These angles are determined by the linear polarizer placed between the probe laser and the sample for Δ_a and between the sample and the detector for Δ_d . For a double delta scan, one of the angles, Δ_a , is varied for several values of Δ_d , or vice versa. The resulting data then can be fit in a least-squares manner to determine the real alignment moments [see Eq. (15a) of KSZ].

To determine the orientation moments a separate experiment, a double beta scan, was suggested by KSZ. This experiment involves two elliptical polarizations. β_a is the angle between the major axis (\hat{B}) of a linear polarizer (the x_a axis for Case I and the z_a axis for Cases II and III) in front of the probe beam and the major axis of a quarter-wave plate subsequently used to create the ellipticity. The value of β_a establishes the degree of ellipticity of the incident radiation. β_d is a function of the angle between the major axis direction of the detector quarter-wave plate (z_d axis for Case I, the x_d axis for Case II, and the z_d axis for Case III) and the major axis of the linear polarizer in front of the detector (\hat{B}). For a double beta scan, β_a is varied for several values of β_d or vice versa, while Δ_a and Δ_d are held fixed. The resulting data then can be fit in a least-squares manner to determine the real orientation moments [see Eq. (16a) of KSZ].

The double delta and double beta scan methods are quite convenient to use from the viewpoint of an experimentalist and provide much more precise information on the angular momentum polarization than experiments with unpolarized detection. When cylindrical symmetry is present,

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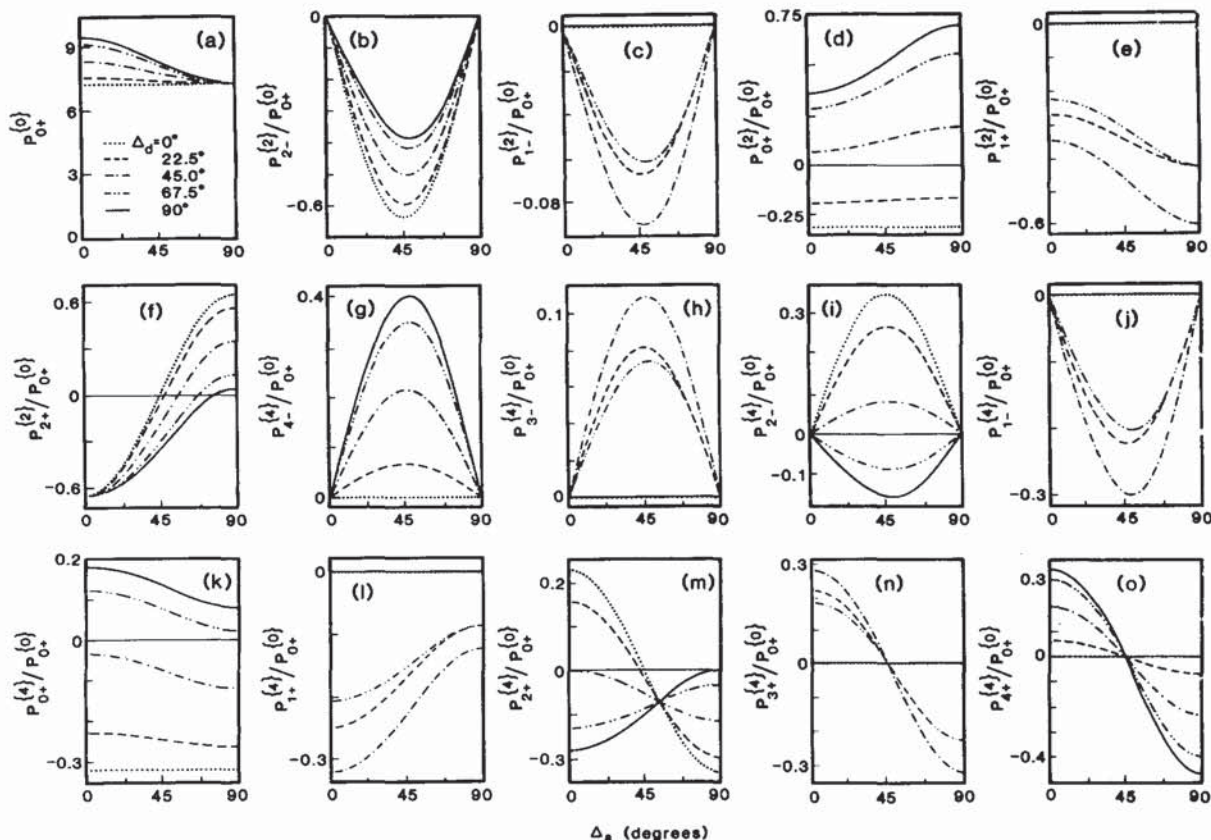


FIG. 1. A "double delta scan": The moments of the line strength factors $P_{q\pm}^{(k)}$ for Case I geometry vs the angles of linear polarization of the probe light Δ_a and the emitted light Δ_d for the P branch of $J = 20$ at $\beta_a = 0^\circ$ and $\beta_d = 0^\circ$ in the LIF of $\text{CN}(^2\Sigma^-2\Sigma^-2\Sigma^-)$.

the results of KSZ are correct, but when noncylindrically symmetric moments exist in the molecular ensemble, detailed examination of KSZ shows that they failed to state that the double delta scan can yield information on several additional moments which cannot be determined for unpolarized detection. These moments escaped notice by KSZ because they vanish for certain common angles between the analyzing polarizer and the lab frame. For example, when Δ_d is 0° or 90° , the line strengths $P_{1-}^{(2)}, P_{1+}^{(2)}, P_{3-}^{(4)}, P_{3+}^{(4)}, P_{1-}^{(4)}, P_{1+}^{(4)}, P_{3-}^{(2)}$ in Case I, and $P_{2-}^{(2)}, P_{1+}^{(2)}, P_{2-}^{(4)}, P_{1+}^{(4)}$ in Case II all equal zero.⁴ This paper clarifies this problem and extends the analysis presented by KSZ.

We find that when using linearly polarized detection, we are sensitive in general to $k = 0, 2, 4$ and all q . Figure 1 of this paper is an extension of Fig. 6 in KSZ. It depicts the line strengths for a "double delta scan," $P_{q\pm}^{(k)}$, vs Δ_a and Δ_d at $\beta_a = 0^\circ$ and $\beta_d = 0^\circ$. Once again, this is calculated for the LIF of the $B^2\Sigma^+ - X^2\Sigma^+$ states of CN for Case I geometry. As is evident from Fig. 1, we need only to vary Δ_d between 0° and 90° in order to span the space. We can directly use a linear least-squares fit to the following equation [modified from Eq. (15a)–(15d) in KSZ] to determine the real moments:

$$I(\Delta_n, J_i, J_e) = \mathbf{P}_{q\pm}^{(k)}(\Delta_n, J_i, J_e) a_{q\pm}^{(k)}(J_i), \quad (1a)$$

TABLE I. The apparent moments for a "double delta scan" as a function of the reduced moments of the ground state distribution for $J = 20$ for a heteronuclear diatomic molecule (CN) with case (b) coupling and $I = 1$ undergoing $^2\Sigma^-2\Sigma^-2\Sigma^-$ LIF with unresolved emission.

Case I geometry		
$A_{1-}^{(2)}$ (app)	$= A_{1-}^{(2)} + 3.245A_{3-}^{(4)} - 1.227A_{1-}^{(4)}$	(P branch)
$A_{1-}^{(2)}$ (app)	$= A_{1-}^{(2)} + 2.715A_{3-}^{(4)} - 1.026A_{1-}^{(4)}$	(Q branch)
$A_{1-}^{(2)}$ (app)	$= A_{1-}^{(2)} + 2.319A_{3-}^{(4)} - 0.876A_{1-}^{(4)}$	(R branch)
$A_{1+}^{(2)}$ (app)	$= A_{1+}^{(2)} + 0.490A_{3+}^{(4)}$	(P branch)
$A_{1+}^{(2)}$ (app)	$= A_{1+}^{(2)} - 1.039A_{3+}^{(4)}$	(Q branch)
$A_{1+}^{(2)}$ (app)	$= A_{1+}^{(2)} + 0.350A_{3+}^{(4)}$	(R branch)
$A_{3+}^{(4)}$ (app)	$= A_{3+}^{(4)} - 0.529A_{1+}^{(4)}$	(P branch)
$A_{3+}^{(4)}$ (app)	$= A_{3+}^{(4)} + 0.005A_{1+}^{(4)}$	(Q branch)
$A_{3+}^{(4)}$ (app)	$= A_{3+}^{(4)} - 0.529A_{1+}^{(4)}$	(R branch)
Case II geometry ⁴		
$A_{2-}^{(2)}$ (app)	$= A_{2-}^{(2)} + 3.470A_{2-}^{(4)}$	(P branch)
$A_{2-}^{(2)}$ (app)	$= A_{2-}^{(2)} + 2.903A_{2-}^{(4)}$	(Q branch)
$A_{2-}^{(2)}$ (app)	$= A_{2-}^{(2)} + 2.479A_{2-}^{(4)}$	(R branch)
$A_{1+}^{(2)}$ (app)	$= A_{1+}^{(2)} + 0.464A_{3+}^{(4)}$	(P branch)
$A_{1+}^{(2)}$ (app)	$= A_{1+}^{(2)} - 1.580A_{3+}^{(4)}$	(Q branch)
$A_{1+}^{(2)}$ (app)	$= A_{1+}^{(2)} + 0.331A_{3+}^{(4)}$	(R branch)
$A_{1+}^{(4)}$ (app)	$= A_{1+}^{(4)} + 0.378A_{3+}^{(4)}$	(P branch)
$A_{1+}^{(4)}$ (app)	$= A_{1+}^{(4)} + 1.145A_{3+}^{(4)}$	(Q branch)
$A_{1+}^{(4)}$ (app)	$= A_{1+}^{(4)} + 0.378A_{3+}^{(4)}$	(R branch)

where

$$\begin{aligned}
 n &= 0 \rightarrow n_{\max}, \\
 (k, q) &= (0, 0 +), (2, 2 -), (2, 1 -), (2, 0 +), (2, 1 +), \\
 &\quad (2, 2 +), (4, 4 -), (4, 3 -), (4, 2 -), (4, 1 -), \\
 &\quad (4, 0 +), (4, 1 +), (4, 2 +), (4, 3 +), (4, 4 +).
 \end{aligned} \tag{1b}$$

The matrix notation used above is identical to that used in KSZ: a vector is indicated by boldface, and the rectangular array is denoted by a boldface symbol with a tilde. The subscript on Δ_n denotes the measurement number, with n_{\max} being equal to the number of polarization angles employed. Three of the additional moments reported here are linearly independent, $(k, q) = (2, 1 -), (2, 1 +), (4, 3 +)$ for Case I and $(k, q) = (2, 2 -), (2, 1 +), (4, 1 +)$ for Case II, while the remainder are dependent $(k, q) = (4, 3 -), (4, 1 -), (4, 1 +)$ for Case I and $(k, q) = (4, 2 -), (4, 3 +)$ for Case II. Table I lists the apparent moments as a linear combination of the reduced moments of the ground state distribution for a diatomic molecule (CN) undergoing $^2\Sigma^- \rightarrow ^2\Sigma^- \rightarrow ^2\Sigma^-$ LIF with unresolved emission. The coefficients were derived numerically by using a linear least-squares fit to Eq. (12a) of KSZ:

$$\begin{aligned}
 P_{q\pm}^{(k)}(J_i, J_e, J_f; \Omega) (\text{dep}) \\
 = \sum_{k'q'} c(k, q, k', q', J_i, J_e, J_f) P_{q'\pm}^{(k')}(J_i, J_e, J_f; \Omega) (\text{ind}). \tag{2}
 \end{aligned}$$

Regarding a double beta scan experiment, we note that Eqs. (16a)–(16c) of KSZ are correct provided that Δ_a and Δ_d are fixed at 0° or 90° relative to the appropriate lab axes as described in the original paper. If Δ_a or Δ_d are varied from these settings, then the experiment becomes sensitive to $k = 0-4$ and all q , and Eqs. (16a)–(16c) would need to be modified appropriately. However, such an experiment would generally be unnecessary and complicated.

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⁴The results for Case III are obtained from Case II as explained in KSZ. $P_{4-}^{(4)} = 0$ for all three branches for Case II geometry.