

Optical preparation of oriented and aligned reagents

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Expressions used for describing the optical preparation of oriented and aligned reagents are derived. For a parallel transition, the probability of orienting and aligning a symmetric top by excitation with circularly polarized radiation is given. [S1050-2947(97)03812-2]

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The individual encounters between reagents and the separation of products from the transition state for a reaction are intrinsically anisotropic because of the chemical shapes of reagents. In most cases, geometric constraints on chemical reactivity are inferred from indirect evidence. For example, in the calculation of bimolecular rate constants from the kinetic theory of gases, a steric factor is introduced, based on the idea that some collisions are more effective than others in promoting a reaction [1]. The value of the steric factor is adjusted to bring experiment in accord with the hard-sphere collision model. More sophisticated theories of reaction rate constants also confront the question of what role reagent approach geometry plays, but this is usually hidden in the assumed structure of the transition state. Clearly, a need exists for experiments that observe directly the effect of the chemical shapes of reagents on the reaction.

It was realized in the early days of molecular-beam experiments that state-selective collision experiments would significantly deepen our understanding of collision dynamics. Attempts have been made to select atomic m levels or aligned rotational levels of molecules using inhomogeneous fields [2–5]. This technique has been applied with great success to the salt molecules, such as TIF [6], CsF [7], and LiF [8], to polar symmetric top molecules, such as CH₃I [9] and CF₃I [10], to paramagnetic molecules, such as NO [11], and using molecular-beam magnetic resonance techniques to H₂ [12]. For other systems, orientation is much less convenient. Moreover, even in the best circumstances, external field orientation often leads to a poor degree of spatial control whose exact characterization often presents difficulties. On the other hand, a limitation of this technique is the restriction to small (j, m) quantum numbers, at least for experiments aiming at high state selectivity. Recently, optical techniques have been used extensively to align the reagent rotation [13–20]. Specifically, for a symmetric top molecule, when the optical pumping process is not so strong, the angular probability of aligning the rotation level (J, K) by excitation with linearly polarized light is given by [14]

$$P_{JK}(\theta) = \frac{1}{4\pi} [I + A_0(J, K)P_2(\cos\theta)], \quad (1)$$

where θ is the angle between the molecular axis and the electric vector of the polarized radiation and $P_2(\cos\theta)$ is the second-order Legendre polynomial. $A_0(J, K)$ is the alignment parameter, which ranges from +2 for $P_{JK}(\theta) \propto \cos^2\theta$

to -1 for $P_{JK}(\theta) \propto \sin^2\theta$. However, as Green and Zare pointed out [15], when a molecule was photodissociated by circularly polarized light, the fragments would be oriented. Similarly, the target molecules may be oriented by absorption of circularly polarized light. In this paper, an explicit expression for the absorption of circularly polarized light by a symmetric top to produce oriented and aligned excited targets is given.

The wave function of a symmetric top is described by the total angular momentum J , its projection K on the top axis (also called the figure axis), and its projection M on the space-fixed axis of quantization, i.e., by $|JKM\rangle$. It has the explicit form

$$|JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D_{KM}^J(\phi, \theta, \chi), \quad (2)$$

where D_{KM}^J is a rotation matrix and ϕ, θ, χ are the three Euler angles relating the body-fixed to space-fixed frames. Therefore, when the top is in the state $|JKM\rangle$, the probability $P_{JKM}(\phi, \theta, \chi)$ of finding the top axis pointing into the solid angle element $d\Omega = d\phi \sin\theta d\theta d\chi$ is given by

$$P_{JKM}(\theta)d\Omega = |D_{KM}^J(\phi, \theta, \chi)|^2 d\phi \sin\theta d\theta d\chi, \quad (3)$$

which is seen to be independent of the angles ϕ and χ . Once again this satisfies the normalization

$$\int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\chi \langle JKM|JKM\rangle = 1. \quad (4)$$

The selection rules for infrared (or microwave) dipole transitions between nondegenerate vibrational levels of a symmetric top for a parallel band are $\Delta J = 0, \pm 1$ and $\Delta K = 0$ if $K \neq 0$, and $\Delta J = \pm 1$ and $\Delta K = 0$ if $K = 0$, since the change in the dipole moment (as well as the permanent dipole moment) is along the direction of the top axis [21]. Then the probability amplitude of finding the symmetric top in the state $|JKM\rangle$ following the dipole absorption of left- or right-circularly polarized light ($j_{\text{ph}} = 1, m_{\text{ph}} = 1$ or -1) is proportional to the product of the Wigner coefficients $\langle J''M'', 11|JM\rangle \langle J''K'', 10|JK\rangle$ or $\langle J''M'', 1-1|JM\rangle \langle J''K'', 10|JK\rangle$, where $|J''K''M''\rangle$ is the initial state of the symmetric top. Here only left-circularly polarized light is treated. Thus the angular distribution of top axes is given by

$$P_{JK}(\theta) = \sum_{M''} \langle J''M'', 11 | JM \rangle^2 \times \langle J''K'', 10 | JK \rangle^2 |D_{KM}^J(\phi, \theta, \chi)|^2, \quad (5)$$

where a sum is performed over the initial M'' states, which are assumed to have a random distribution. The problem is to evaluate the sum

$$S(J, K) = \sum_{M''} \langle J''M'', 11 | JM \rangle^2 |D_{KM}^J|^2. \quad (6)$$

This is readily accomplished using a form of the inverse Clebsch-Gordan series [22]

$$\langle j_1 m_1, j_2 m_2 | j_3 m_3 \rangle D_{k_3 m_3}^{j_3} = \sum \langle j_1 k_1, j_2 k_3 - k_1 | j_3 k_3 \rangle D_{k_1 m_1}^{j_1} \times D_{k_3 - k_1 m_2}^{j_2}. \quad (7)$$

With the identification

$$\begin{aligned} j_1 &= J'', & m_1 &= M'', & k_1 &= K'', \\ j_2 &= 1, & m_2 &= 1, & k_2 &= K - K'', \\ j_3 &= J, & m_3 &= M, & k_3 &= K, \end{aligned}$$

Eq. (6) becomes

$$\langle J''M'', 11 | JM \rangle D_{KM}^J = \sum_{K''} \langle J''K'', 1K - K'' | JK \rangle \times D_{K''M''}^{J''} D_{K-K'', 1}^1. \quad (8)$$

Squaring both sides of Eq. (8) and summing over M'' yields

$$\begin{aligned} & \sum_{M''} \langle J''M'', 11 | JM \rangle^2 |D_{KM}^J|^2 \\ &= \sum_{M''} \left[\sum_{K''} \langle J''K'', 1K - K'' | JK \rangle D_{K''M''}^{J''} D_{K-K'', 1}^1 \right]^* \\ & \times \left[\sum_{K'} \langle J''K', 1K - K' | JK \rangle D_{K''M''}^{J''} D_{K-K', 1}^1 \right]. \quad (9) \end{aligned}$$

The left-hand side of Eq. (9) is recognized as $S(J'', K'')$, the sum to be evaluated, by unity of the rotation matrices

$$\sum_{M''} D_{K-K'', M''}^{J''} * D_{K-K', M''}^{J''} = \delta_{K''K'}, \quad (10)$$

and the right-hand side of Eq. (9) simplifies to

$$S(J'', K'') = \sum_{K''} \langle J''K'', 1K - K'' | JK \rangle^2 |D_{K-K'', 1}^1|^2, \quad (11)$$

where the sum over K'' is from $K - 1$ to $K + 1$. Thus Eq. (11) has the explicit value

$$S(J'', K'') = \langle J''K - 1, 11 | JK \rangle^2 |D_{11}^1|^2 + \langle J''K, 10 | JK \rangle^2 |D_{01}^1|^2$$

$$+ \langle J''K + 1, 1 - 1 | JK \rangle^2 |D_{-11}^1|^2. \quad (12)$$

Clearly, Eq. (5) is evaluated explicitly as

$$\begin{aligned} P_{JK}(\theta) &= \langle J''K'', 11 | JK'' + 1 \rangle^2 |D_{11}^1(\phi, \theta, \chi)|^2 \\ &+ \langle J''K'', 10 | JK'' \rangle^2 |D_{01}^1(\phi, \theta, \chi)|^2 \\ &+ \langle J''K'', 1 - 1 | JK'' - 1 \rangle^2 |D_{-11}^1(\phi, \theta, \chi)|^2. \quad (13) \end{aligned}$$

Using explicit expressions for the Wigner coefficients and the identities

$$|D_{11}^1(\phi, \theta, \chi)|^2 = \frac{1}{4}(1 + 2 \cos \theta + \cos^2 \theta), \quad (14)$$

$$|D_{01}^1(\phi, \theta, \chi)|^2 = \frac{1}{2} \sin^2 \theta, \quad (15)$$

$$|D_{-11}^1(\phi, \theta, \chi)|^2 = \frac{1}{4}(1 - 2 \cos \theta + \cos^2 \theta), \quad (16)$$

$P_{JK}(\theta)$ can be recast in the familiar form

$$P_{JK}(\theta) = \frac{1}{4\pi} [1 + O_0(J, K)P_1(\cos \theta) + A_0(J, K)P_2(\cos \theta)], \quad (17)$$

where

$$P_1(\cos \theta) = \cos \theta \quad (18)$$

and

$$P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2 \quad (19)$$

are the first- and the second-order Legendre polynomial, respectively. $O_0(J, K)$ is defined as an orientation parameter.

For a P branch transition in which $J = J'' - 1$,

$$O_0(J'', K'') = \frac{3K''}{2(J'' + 1)}, \quad (20)$$

$$A_0(J'', K'') = \frac{3K''^2 - J''^2 - J''}{2(2J'' + 3)(J'' + 1)}; \quad (21)$$

for a Q branch transition in which $J'' = J$,

$$O_0(J'', K'') = -\frac{3K''}{2J''(J'' + 1)}, \quad (22)$$

$$A_0(J'', K'') = \frac{J''^2 + J'' - 3K''^2}{2J''(J'' + 1)}; \quad (23)$$

and for an R branch transition in which $J'' = J + 1$,

$$O_0(J'', K'') = -\frac{3K''}{2J''}, \quad (24)$$

$$A_0(J'', K'') = \frac{3K''^2 - J''^2 - J''}{2J''(2J'' - 1)}. \quad (25)$$

Equation (17) reduces to Eq. (1), i.e., only the alignment of reagents is prepared by absorption of circularly polarized radiation, when $K''=0$. Equations (20) and (22) as well as Eq. (24) hold only for $K'' \neq 0$; moreover, it shows, particularly when $K'' = \sqrt{J''(J''+1)}/3$, that pumping of the reagents can produce a high degree of orientation, but totally without alignment. This is similar to orienting reagents by external electric and magnetic fields.

The above results are satisfied only for absorption of left-circularly polarized light. For right-circularly polarized, $O_0(J'', K'')^{\text{right}} = -O_0(J'', K'')^{\text{left}}$ and $A_0(J'', K'')^{\text{right}} = A_0(J'', K'')^{\text{left}}$. In addition, it is an easy matter to derive the corresponding expressions for a perpendicular band in which the changing dipole moment is perpendicular to the top axis. This treatment has demonstrated that absorption of circularly polarized light may be used to prepare reagents with known orientation and alignment whose degree of orientation can often be chosen to be high. It has been assumed that the optical pumping process is not so strong that the equal population distribution of magnetic sublevels is disturbed.

Traditionally, the oriented reagents were prepared by using a hexapole-rod arrangement with alternating positive and negative charges on the rods to generate an inhomogeneous electric field. Within the hexapole electric field, molecules in a state $|JKM\rangle$ that exhibit a first-order Stark effect experience a radial force, which, to first order, is given by [25]

$$\Gamma_{JK} = \frac{6\mu V_0}{r_0^3} \frac{KM}{J(J+1)} r, \quad (26)$$

where μ is the molecular electric dipole moment, r_0 is the radial distance from the hexapole axis to the electrode rods, r is the radial distance from a molecule to the axis, V_0 is the applied voltage on the hexapole rods, and M is the projection J in the electric field direction. Assuming that θ is the angle between the molecular axis and the electric field direction, we can rewrite Eq. (26) according to Ref. [22]

$$\Gamma_{JK}(\theta) = O(J, K) P_1(\cos\theta), \quad (27)$$

where

$$O(J, K) = \frac{6\mu V_0}{r_0^3} r \frac{K}{J+1}. \quad (28)$$

Clearly, the (J'', K'') dependence of $O_0(J'', K'')$ in Eq. (17) is the same as that of $O(J, K)$ in Eq. (27). For the optical method, the molecules of the single rotational state may be oriented. Molecules in states with the same value of the ratio $KM/J(J+1)$ for the hexapole focusing technique, however, will be focused on the same point, with the position of that point depending on factors such as the molecular-beam velocity and the electric-field strength. This leads to the molecules at the different rotational levels all being ori-

ented. Moreover, unlike circularly polarized light, particularly a laser, the hexapole focusing technique is much less convenient to operate and to control and is restricted to molecules with small- J levels that exhibit a first-order Stark effect and to molecular-beam experiments. The orientation of molecules that have a permanent electric-dipole moment but no component of angular momentum along their molecular axis is possible using homogeneous electric fields via the second-order Stark effect but, as Brooks pointed out [4], the field strengths required to achieve significant orientation of thermal molecules would be extremely high.

Since Zare [14] gave formulas for the alignment prepared by a one-photon absorption for diatomic molecules and for symmetric tops, a number of workers applied this technique and related optical excitation methods to prepare aligned samples, including Collins *et al.* [26], who studied the inelastic scattering of electronically excited $\text{Li}_2(A)$ molecules from xenon, Zacharias and co-workers [27,28], who investigated inelastic scattering of C_2H_2 prepared by stimulated Raman pumping (SRP), and Sitz and Farrow [29], who used SRP to prepare aligned samples of N_2 and probed the decay of the alignment by multiphoton ionization. The primary work in the field of reaction dynamics using laser-aligned reagents has come from Zare and co-workers [30–32] and Loesch and co-workers [33–36]. More recently, Zhang *et al.* [16] reported an experimental study of photodissociation of aligned HF molecules prepared by linearly polarized IR radiation. Moreover, a consequence of the excitation with linearly polarized is that the excited molecules are prepared in the upper state with their angular-momentum vectors and internuclear axes aligned (as opposed to oriented), so that collisions can be studied in which side-on and end-on geometries are distinguished, but the ‘‘heads-vs-tails’’ collisions possible for oriented molecules cannot be distinguished. Obviously, oriented and aligned molecules prepared by the absorption of circularly polarized light will be useful for studying collision processes and chemical reaction dynamics.

The methods mentioned above can only be suitable for optical orientation and alignment in weak laser fields. However, it should be pointed out that target molecular systems may be oriented or aligned by strong optical pumping [23,24,37–39]. For example, the alignment and orientation of polar and nonpolar molecules can be prepared by either the laser-induced ac Stark effect [37] or the dynamic Stark effect [38]. Moreover, alignment and orientation of target molecule can also be achieved by stimulated Raman scattering [39]. In those cases, the effect on alignment and orientation of target molecules occurs in the same way for all m sublevels. In strong and very strong laser fields, the distributions of the m sublevels will not be uniform and thus explicit formulas about angular distributions of molecular axes is difficult to derive.

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