J-Selective Stark Orientation of Molecular Rotation in a Beam

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(Received 22 July 1992)

We propose a facile method to transform alignment of molecular rotation in a beam into transverse orientation with high efficiency via the second-order Stark effect in a homogeneous electric field $\mathcal{E}$. The calculated **J**-orientation magnitude for a specific rotational level J exhibits a regular structure of equidistant dispersion-form signals in $\mathcal{E}^2$ coordinates. Estimates performed for the NaK molecule show the possibility to produce rotational and isotopic selective **J** orientation for a fixed beam velocity **v**. The orientation appears in the direction perpendicular to the $(\mathbf{v},\mathcal{E})$ plane, and the optimal angle between **v** and $\mathcal{E}$ is 45°.

PACS numbers: 33.55.Be, 34.50.Lf

The interaction between molecules is known to be strongly dependent on their mutual orientation (steric effect). In order to perform direct experimental investigations of steric requirements in single-collision dynamics, beams of molecules are used with an anisotropic spatial distribution of molecular axes **R** and angular momenta **J** with respect to the reference axis **Z**. The distribution possesses *alignment* if it is unchanged upon reversing the direction of the **Z** axis and *orientation* if the distribution is changed. Both alignment and orientation of molecules in a beam can be produced using optical methods, such as optical pumping [1,2] and photodissociation [3] with polarized lasers (methods are summarized in [4,5]). Nevertheless, the laser-based methods are not always suitable owing to special requirements for the spectroscopic properties of the object, and therefore nonoptical methods are being developed extensively. A technique based on inhomogeneous-electric-field focusing via the first-order Stark effect [6–8] is applied to orient **R** in symmetric top molecules. The method is, however, not applicable to linear (including diatomic) molecules. The alignment of **J** in polar linear molecules can be achieved in some cases for low rotational states via the second-order Stark effect in an inhomogeneous field [9,10]. Very recently, the simple technique of orienting rotationally cooled polar molecules in a strong homogeneous external electric field of strength $\mathcal{E}$ was proposed by the research teams of Loesch [11] and Herschbach [5,12]. The method is based on the "brute force" influence on electric dipole moments μ when low rotational states are converted into pendular librators oscillating within a limited angle over the $\mathcal{E}$ direction, which is caused by hybridization of different J values. The method was applied to orient polar diatomic molecules such as ICl [13]. The molecules were cooled in a free jet expansion to low rotational energies $BJ(J+1)$ that are small with respect to $\mu\cdot\mathcal{E}$. This elegant technique is nevertheless restricted to small J values and cannot be considered as a method of orientation of molecular rotation because the latter is disturbed by the torque of an electric dipole in an external field, and the rotational spectrum undergoes a dramatic transformation into that reflecting pendular motion [14,15].

From another point of view, the same free jet expansion is known [5,16–18] as a facile method to produce a considerable degree of **J** alignment for diatomic molecules seeded in carrier gases. A substantial degree of alignment was found by Zare and co-workers [16] in a Na_2/Na supersonic beam, and later in some other mixtures [5,18], such as I_2 diluted in light gases H_2, He, etc. Anisotropic collisions in microscopic gas transport is a dominating process leading to preferential molecular rotation in a plane containing the beam axis **Z'**, Fig. 1. That means that **J** is aligned in a plane perpendicular to **Z'** and the spatial **J** distribution function $n(\theta')$ possesses axial symmetry about **Z'** having only even nonzero Legendre polynomial expansion coefficients a_K in

$$n(\theta')=n_0\sum_K a_K P_K(\cos\theta')\,. \tag{1}$$

In most cases, as considered herein, only a_0 and a_2 differ from zero ($a_0=1$ is supposed) and a_2 has a negative value up to about -0.5 [5,16].

As may be seen, there is a lack of simple nonoptical methods for facile *orientation* of molecular rotation of diatomic or linear molecules in a beam, leading to nonzero odd a_K values (only molecular-beam–surface collisions can be mentioned [19]). At the same time, owing to some specific manifestation in some elementary processes,

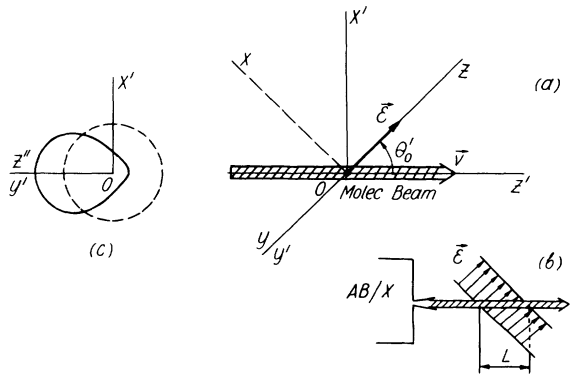

FIG. 1. Schematic of realization of alignment-orientation Stark conversion. (a) Choice of coordinate systems. (b) Possible realization scheme for AB molecules seeded in a free jet of X atoms. (c) Symbolic polar plot of **J** distribution.

it may be of importance [20] to increase the variety of possibilities to orient the angular momenta **J**. We are suggesting here a simple method of transition from alignment to orientation in a molecular beam. For this purpose one can use the effect of some external perturbation (external field, anisotropic collisions) capable of destroying the axial symmetry of the ensemble of particles. For some special cases such an effect has been known already for a long time [21,22]. As we are going to show here, the effect of a homogeneous electric field $\mathcal{E}$ on the beam of aligned polar linear molecules having velocity $\mathbf{v}\|\mathbf{Z}'$ [Fig. 1(a)] is able to produce significant J- and isotopic-selective alignment-orientation conversion.

Let the beam cross the field $\mathcal{E}$ region of length L [Fig. 1(b)], $\mathcal{E}$ forming an angle θ_0' with respect to **v** (it can be demonstrated that $\theta_0'=45°$ is an optimal value). Because of the quantum origin of the Stark effect the evolution of density matrix elements $f_{MM'}$ for the molecules in a beam must be considered. Choosing the quantization axis $\mathbf{Z}\|\mathcal{E}$, Fig. 1(a), and neglecting relaxation processes in a beam, we get

$$f_{MM'}={}^0f_{MM'}e^{-i\omega_{MM'}L/v},\quad \omega_{MM'}=(E_M-E_{M'})/\hbar\ , \tag{2}$$

where ${}^0f_{MM'}, f_{MM'}$ are density matrix elements before and after crossing the field $\mathcal{E}$ region, and $E_M, E_{M'}$ are the energies of the M, M' magnetic sublevels. In order to connect ${}^0f_{MM'}$ with the classical alignment parameter a_2 as defined in the $X'Y'Z'$ coordinate system [Fig. 1(a)], we will use the approach developed in Ref. [23]. For this purpose the angular momentum distribution $n(\theta',\varphi')$, which in general depends on both spherical angles θ' and φ', must be expanded over spherical functions Y_{KQ} [4,24],

$$n(\theta',\varphi')=n_0(4\pi)^{-1/2}\sum_{KQ}(2K+1)^{1/2}{}'\rho_Q^K(-1)^Q \times Y_{KQ}(\theta',\varphi')\ . \tag{3}$$

Using Eqs. (1) and (3) we can connect a_K with the *classical polarization moments* ${}'\rho_Q^K$, getting ${}'\rho_0^0=a_0=1$ and ${}'\rho_0^2=a_2/5$, supposing hereafter $a_K=0$ for $K>2$. Then, using the Wigner D matrix [25], we transform ${}'\rho_0^K$ into polarization moments $\rho_Q^K={}'\rho_0^K D_{0Q}^{(K)}(0,\theta_0',0)$ in the XYZ coordinate system with $\mathbf{Z}\|\mathcal{E}$, thus obtaining nonzero transverse alignment ρ_Q^2 values with $Q=\pm1,\pm2$. Further, we are using the fact [23] that in the $J\gg1$ limit the classical polarization moments ρ_Q^K equal their quantum analog ${}^0f_Q^K$ defined as expansion coefficients of density matrix ${}^0f_{MM'}$ over irreducible tensor operators,

$${}^0f_{MM'}=\sum_{KQ}(2K+1)(2J+1)^{-1}(-1)^Q{}^0f_Q^K C_{JMKQ}^{JM'}\ , \tag{4}$$

where $C_{aa\,b\beta}^{c\gamma}$ are Clebsch-Gordan coefficients. That means that, as a result of transformation $a_2\rightarrow{}'\rho_0^2\rightarrow\rho_Q^2\rightarrow{}^0f_Q^2\rightarrow{}^0f_{MM'}$, we get ${}^0f_{MM'}$ and place them into (2). As may be seen from the reverse of Eq. (4), in the XYZ coordinate system

$$f_Q^K=\sum_{MM'}C_{JMKQ}^{JM'}f_{MM'}=\sum_M C_{JMKQ}^{JM+Q}{}^0f_{M\,M+Q}e^{-i\omega_{M\,M+Q}L/v}\ , \tag{5}$$

and if M sublevels are split in the field $\mathcal{E}$ nonequidistantly, ${}^0f_{MM}$, ${}^0f_{M\,M+1}$, and ${}^0f_{M-1\,M+1}$ produce not only transverse alignment f_Q^2, but also *transverse orientation* f_Q^1, components. This orientation appears in the direction perpendicular to the $(\mathbf{v},\mathcal{E})$ plane, or along the **Y** axis [cf. Fig. 1(a)], thus breaking axial symmetry of the **J** distribution over the beam axis $\mathbf{Z}'\|\mathbf{v}$ as is schematically shown in Fig. 1(c). Note that because the field $\mathcal{E}$ is not acting on ${}^0f_{MM}$, f_0^2 remains unchanged and the appearance of longitudinal orientation f_0^1 along the beam axis is excluded.

In order to calculate what fraction of alignment a_2 is transformed into transverse orientation, we must use a coordinate system with the $\mathbf{Z}''$ axis parallel to the direction of orientation created, namely, $\mathbf{Z}''\|\mathbf{Y}$, Fig. 1(a). In such a system the transverse orientation components $\rho_{\pm1}^1$ (the classical analog of $f_{\pm1}^1$) are transformed into one "longitudinal" component ${}'\rho_0^1$. This allows one to come back to a corresponding Legendre polynomial coefficient ${}'a_1=3{}'\rho_0^1=3\sqrt{2}\,\mathrm{Im}\rho_1^1$. In order to obtain ρ_1^1 the form of the Stark effect must be specified. We will use the Stark energy expression for a rigid-rotor-type diatomic (or linear) molecule, neglecting hyperfine interaction, in the form [26,27]

$$E_M=\frac{\mu^2\mathcal{E}^2}{hB}\left[\frac{J(J+1)-3M^2}{2J(J+1)(2J-1)(2J+3)}\right], \tag{6}$$

B being the rotational constant. This leads to an expression for ${}'a_1$ of the form

$${}'a_1=A\sum_{l=0}^{J-1}(2l+1)(J+l+1)(J-l)\sin[(2l+1)\varphi]\ , \tag{7}$$

where A is a normalizing factor, and φ is equal to

$$\varphi=\frac{3\pi}{J(J+1)(2J-1)(2J+3)}\frac{\mu^2\mathcal{E}^2}{h^2B}\frac{L}{v}\ . \tag{8}$$

Calculation allows us to determine the efficiency factor for alignment-orientation conversion: $\kappa={}'a_1/a_2$; cf. Figs. 2, 3, and 5. As may be seen from Fig. 2, in $\varphi\sim\mathcal{E}^2$ coor-

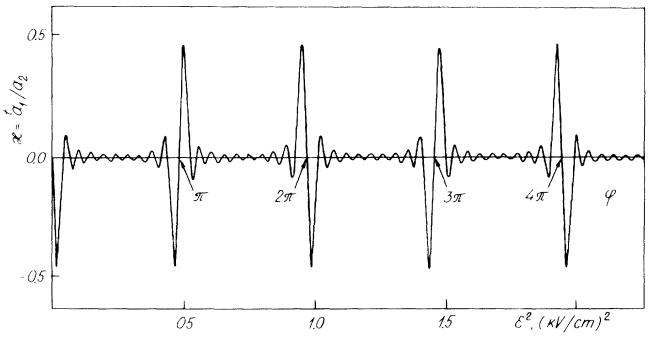

FIG. 2. SOG structure for conversion efficiency ${}'a_1/a_2=\kappa(\varphi)$. $\mathcal{E}^2$ values correspond to an example of NaK molecule with $J=10$.

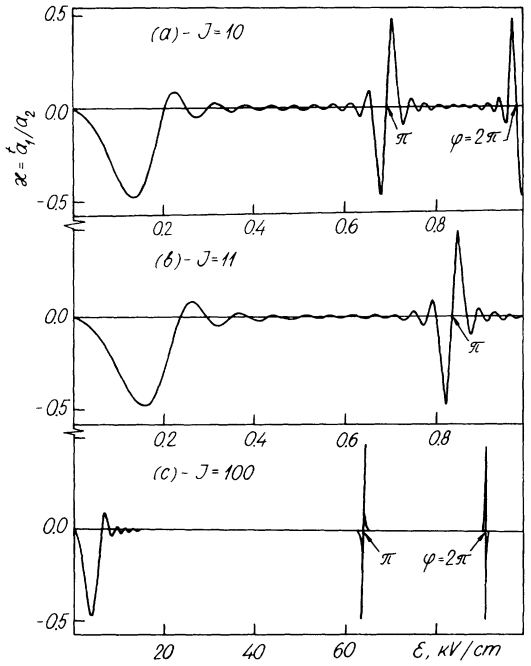

FIG. 3. Alignment-orientation conversion parameter κ dependence on electric field strength $\mathcal{E}$ as calculated for a $^{23}Na^{39}K$ ($X^1\Sigma$) molecule. (a) $J=10$. (b) $J=11$. (c) $J=100$.

dinates, orientation appears in the form of some regular structure. Such a "Stark orientation grill" (SOG) exhibits equidistantly spaced alternating dispersion-form "principal" orientation signals centered at positions $\varphi=n\pi$, $n=1,2,\ldots$, corresponding to field strength $\mathcal{E}_n^2$ values,

$$\mathcal{E}_n^2=\frac{nh^2BvJ(J+1)(2J-1)(2J+3)}{3L\mu^2}. \tag{9}$$

Between the centers of adjacent principal signals secondary maxima of a similar form can be distinguished. As J increases from 10 to 100 (Fig. 3), the principal $\kappa(\varphi)$ signals become relatively sharper (cf. Fig. 4), and secondary peaks, while increasing in number, become negligible in their effect. Such behavior of appearing orientation reminds one of a diffraction-grating-signal characteristic pattern for the $\kappa(\varphi)$ dependence; however, being linear with respect to $\sin[(2l+1)\varphi]$, cf. Eq. (7) (not squared, like in the case of a diffraction grating), this leads to dispersion-form signals. The amplitude values of $|\kappa(\varphi)|$ are sufficiently large, being equal to ≈ 0.468 for $J\geq 5$.

Let us examine as a concrete example, a polar NaK molecule, for which noticeable alignment in a supersonic beam can be expected, similar to the case of Na_2/Na [16,17]. A mixed halogen diatomic molecule, such as IBr, could also be considered as a convenient object [5,28]. Values of $\mathcal{E}^2$ and $\mathcal{E}$ for NaK in its electronic ground $X^1\Sigma$ state obtained from Eqs. (7)–(9), assuming [29] $\mu=2.667$ D, $B=0.0905$ cm^{-1}, $L=5$ cm, and $v=10^5$ cm s^{-1}, are given in Figs. 2 and 3 for $J=10$, 11, and 100. Values of the field strength $\mathcal{E}_1$ for $n=1$ corresponding to the location of the zero point for the first principal signal (taking place for $\varphi=\pi$) are given in Fig. 4. The signal width $\Delta\mathcal{E}_1$, defined as the distance between positions of maximum and minimum orientation values for the first principal signal, is also shown in Fig. 4. As may be seen, the relative signal width $\Delta\mathcal{E}_1/\mathcal{E}_1$ diminishes with the growth of J. It is interesting that the $\mathcal{E}_1$ difference for different J allows, in principle, for production of orientation only for a selected J level; cf. Figs. 3(a) and 3(b) for $J=10$ and 11. Moreover, selectivity of the SOG structure may allow one to resolve (orient separately) different isotope molecules. Figure 5 gives an example allowing one to compare orientation signals for $^{23}Na^{39}K$ and $^{23}Na^{41}K$. The values of $B=0.0886$ cm^{-1} and $v=9.8425\times10^4$ cm s^{-1} were taken for the $^{23}Na^{41}K$ molecule, assuming that changes in the numerical value of B are caused by changes in the moments of inertia of the molecule [27] and changes in v are caused by changes

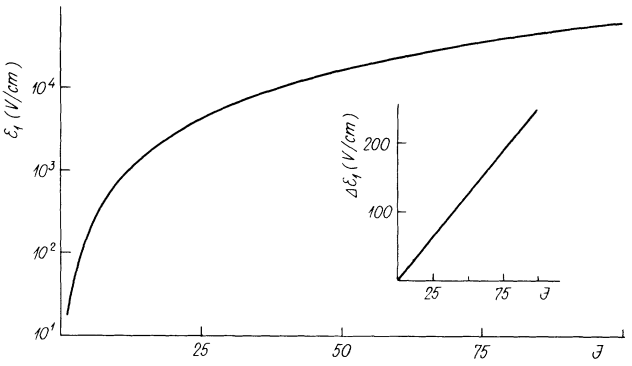

FIG. 4. Calculated J dependence of first-order ($\varphi=\pi$) signal position $\mathcal{E}_1$ and signal width $\Delta\mathcal{E}_1$.

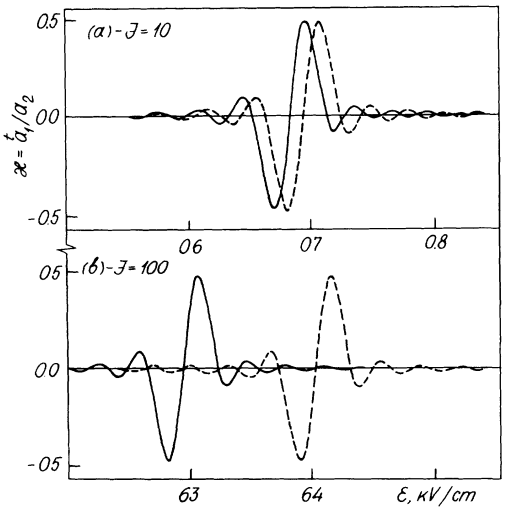

FIG. 5. First-order ($\varphi=\pi$) orientation maxima calculations for $^{23}Na^{41}K$ isotopic molecule. (a) For $J=10$. (b) For $J=100$. Dashed curves reproduce signals for $^{23}Na^{39}K$.

in molecular mass. The isotopic shift is in principle resolvable, even for $J=10$ [cf. Fig. 5(a)], growing dramatically for $J=100$ [Fig. 5(b)]. Of course, the expected resolution takes place for a monoenergetic beam of molecules with fixed v value. From another point, however, for a given J value beam molecules with definite v can be oriented selectively. For a beam with a given, say, Maxwellian v distribution it may turn out to be more convenient to use the zero-order ($\varphi=0$) SOG signal, namely, the first minimum in Fig. 3, despite the loss in J selectivity. In fact, it requires considerably smaller electric field values of only about 135 V/cm for $J=10$; even a field strength of 4 kV/cm needed for $J=100$ does not seem too excessive. It must be emphasized that here we need much smaller electric field values than in the "brute force" method [11–15] and higher J values can be oriented. In contrast to the brute force method, the rotational movement remains undisturbed here because of the small value of $\mu\mathcal{E}_1/B$, being about 0.34 for $J=10$ and 31.7 for $J=100$, which leads to $\mu\mathcal{E}_1/BJ(J+1)<4\times10^{-3}$.

The simplest and most straightforward method of registering the produced orientation is to detect changes in the degree of laser-induced-fluorescence circularity excited from the oriented state level. In order to extract alignment and orientation parameters, the approach developed by Zare and co-workers [30] can be used. It is not excluded that the registration procedure could be more effective using modulation of the electric field amplitude $\mathcal{E}_1\pm\Delta\mathcal{E}_1/2$ with phase-sensitive detection.

Though the discussed picture may be somewhat idealized by choosing favorable conditions, it seems that the simplicity of the experimental realization, combined with the J selectivity of the SOG structure of conversion from alignment to transverse orientation of molecular rotation in a beam, allows one to perform different variants of this method, only partly touched upon in the present paper.

Support from the Latvian Science Council (Grant No. 90.467) is gratefully acknowledged.

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