7476 *J. Phys. Chem. A* **1997,** *101,* 7476−7485

Analysis of Stereodynamical Effects in Terms of Order Parameters and Steric Factors

Andreas Busalla* and Karl Blum

Institut für Theoretische Physik I, Universität Münster, Wilhelm-Klemm-Strasse 9, D-48149 Münster, Germany

Received: February 3, 1997; In Final Form: April 22, 1997[⊗]

General equations are derived for differential cross sections for collisions between anisotropic molecular ensembles and electrons or atoms. In the obtained expressions geometrical and dynamical factors are separated. The initial anisotropic axis distribution is characterized by "order parameters"; the information on the dynamics is contained in "steric factors". The results can be used to analyze experimental results and also as a basis for numerical calculations. Several examples are discussed in order to point out the geometrical importance of the relevant parameters for diatomic and polyatomic molecules. As an illustration, all relevant steric factors are numerically calculated for elastic collisions between electrons and anisotropic ensembles of CO molecules.

1. Introduction

The dependence of chemical reactivity on orientation and alignment of the reactants is a key issue in stereodynamics. Extensive investigations of steric effects have been performed. For a review of these developments, we refer to the articles by Bernstein et al.,[1] Simons,[2] Delgado-Barrio,[3] Loesch,[4] Parker and Bernstein,[5] and Stolte.[6] The treatment given in the present paper is also appropriate for molecule−surface scattering (see for example ref 7).

In the present paper we will develop and generalize the existing theories of stereodynamical effects. We will derive some basic formulas that will be useful for an exploitation of the spatial aspects of collisions with diatomic or polyatomic molecules. The prerequisite for measuring steric effects is the preparation of an anisotropic distribution of axes of the molecular target system prior to the reaction. Our first aim is therefore to characterize the anisotropy of the initial ensemble. We will discuss this in section 2 by developing the concept of "order parameter", introduced previously in other contexts (see for example the treatment by Michl and Thulstrup[8]). Some examples of experimental interest will be given in subsections 2.2 and 2.3 in order to clarify and visualize the geometrical importance of the order parameters.

Our main topic, the description of reactions between projectiles (electrons, atoms) and anisotropic molecular ensembles, will be developed in section 3. General equations will be described that relate the observable differential cross section to the order parameters and that will allow to identify the relevant "steric factors". These expressions generalize former results given in the literature (see e.g. ref 4 and references therein) and can be used for an analysis of experiments and as a basis for numerical calculations. The maximum information on the stereodynamical properties of the collision, which can be obtained under given experimental conditions, is contained in the full set of all independent steric factors.

A comparison of experimental and theoretical data for all relevant steric factors gives therefore the most detailed test of the theoretical model under the given experimental condition. The main experimental problem is therefore the measurement of all steric factors, and we briefly consider the "theory of measurement". By plotting experimental results, some immediate conclusions can be drawn on the directional properties of the collision, and we discuss this in section 4. In section 5 we will illustrate the theory with numerical results for elastic collisions between electrons and CO molecules. For a scattering energy of 10 eV all relevant steric factors are plotted as a function of the scattering angle, and their general behavior will be discussed. Finally, in section 6, we summarize our main results.

Throughout this paper the notation of Zare[17] will be used.

2. Order Parameter and Axis Distribution Functions

2.1. General Expressions. The description of orientational order plays an important role in the investigation of anisotropic systems. Its first objective consists of the identification of a set of parameters that characterize the sample of interest. Our first task is therefore to discuss a way to systematically introduce these parameters. Several formulations have been given in the literature (see e.g. ref 8 and references therein). Here we will apply and develop a description in terms of so-called "order parameters".[8,9]

Consider an ensemble of molecules with a nonuniform axis distribution. These can be molecules adsorbed at surfaces or in stretched polymers, or it may be the instantaneous axis distribution of an anisotropic ensemble of rotating molecules in the gas phase.

We introduce a right-handed coordinate system xyz which is defined by the process by which the anisotropic molecular system has been prepared ("director system"). If the distribution possesses a symmetry axis, this will be chosen as the z-axis. This might be the direction of an orientating static field, the electric field direction in laser pumping with linearly polarized light, or the molecular beam axis in supersonic expansion experiments.

We introduce a coordinate system $x'y'z'$ rigidly connected with the molecular framework. For diatomic molecules we will choose the internuclear axis as z'. For planar molecules the molecular plane will be taken as $y'z'$-plane. The orientation of the molecule with respect to the director system is specified by the three Euler angles $\alpha\beta\gamma$ (see Figure 1). Here, β is the angle between z and z'. α is the azimuth angle of z' in the director frame; that is, it defines a rotation around the sample z-axis. The third Euler angle γ specifies a rotation of the $x'y'$-plane around z'. For $\gamma = 0$ the x'-axis would lie in the zz'-plane.

The axis distribution of the molecular ensemble can be characterized in terms of the distribution function $W(\alpha\beta\gamma)$, defined in such a way that $W(\alpha\beta\gamma)\, d\alpha\, d\beta \sin\beta\, d\gamma$ is the probability of finding a molecule with $x'y'z'$-axes at a specific

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

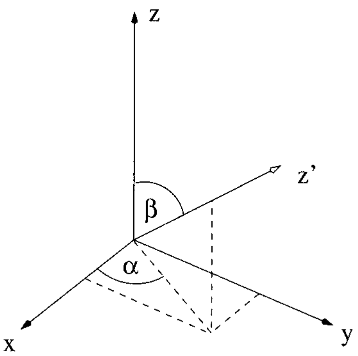

Figure 1. Relation between molecular system $x'y'z'$ and the director system xyz (only z' is shown).

orientation fixed by $\alpha\beta\gamma$. This function, as any other function of the Euler angles, can be expanded in terms of the rotation matrix elements $D^{(K)}_{Q'Q}(\alpha\beta\gamma)$:

$$W(\alpha\beta\gamma) = \sum_{KQQ'} \frac{2K+1}{8\pi^2} \langle D^{(K)}_{Q'Q}{}^*\rangle D^{(K)}_{Q'Q}(\alpha\beta\gamma) \tag{1}$$

We will use the convention of Zare,[17] that is,

$$D^{(K)}_{\mathbf{Q'Q}}(\alpha\beta\gamma) = \mathrm{e}^{-iQ'\alpha}\, d^{(K)}_{Q'Q}(\beta)\mathrm{e}^{-iQ\gamma} \tag{2}$$

We will normalize according to

$$\int_0^{2\pi}\mathrm{d}\alpha\int_0^{\pi}\mathrm{d}\beta\,\sin\beta\int_0^{2\pi}\mathrm{d}\gamma\; W(\alpha\beta\gamma) = 1 \tag{3}$$

The expansion coefficients $\langle D^{(K)}_{Q'Q}{}^*\rangle$ are defined by the relation

$$\langle D^{(K)}_{Q'Q}{}^*\rangle = \int_0^{2\pi}\mathrm{d}\alpha\int_0^{\pi}\mathrm{d}\beta\,\sin\beta\int_0^{2\pi}\mathrm{d}\gamma\; W(\alpha\beta\gamma)\, D^{(K)}_{Q'Q}{}^*(\alpha\beta\gamma) \tag{4}$$

where the star denotes the complex conjugate. Equation 4 is obtained by multiplying eq 1 with $D^{(K)}_{Q'Q}{}^*(\alpha\beta\gamma)$, integrating over all angles, and using the orthogonality of the D functions. The knowledge of the set of all relevant coefficients $\langle D^{(K)}_{Q'Q}{}^*\rangle$ completely specifies the distribution. The parameters $\langle D^{(K)}_{Q'Q}{}^*\rangle$ are usually called "*order parameters*".[8,9] For randomly oriented molecules $W(\alpha\beta\gamma)$ is constant, and all order parameters with $K \neq 0$ vanish.

In general, the sum over K is infinite. In several cases the sum is limited to a few terms. Excitation by light (from an initially isotropic ensemble) produces only order parameters with $K \leq 2$. For rotating molecules with sharp angular momentum J we have $K \leq 2J$.[9] In other cases it has been found that only the first few terms are of practical importance[6,10,11] (see also section 5).

For rotating molecules there is a close relationship between the axis distribution of an ensemble, described by order parameters, and its corresponding angular momentum distribution, described by state multipols $\langle T^{+}_{KQ}(J)\rangle$. The relevant relations for linear rotors, symmetric tops, and pendulum states can be found in the literature (e.g. ref 9) and will not be given here.

From the normalization condition (3) follows

$$\langle D^{(0)}_{00}{}^*\rangle = 1 \tag{5a}$$

From the definition (4) we obtain for example

$$\langle D^{(1)}_{00}{}^*\rangle = \langle\cos\beta\rangle \tag{5b}$$

which provides us with an average angle of orientation, and

$$\langle D^{(2)}_{00}{}^*\rangle = \langle {}^1/_2(3\cos^2\beta - 1)\rangle \tag{5c}$$

From the symmetry properties of the rotation matrices follows

(i) order parameters with $Q' = Q = 0$ are real (5d)

$$\text{(ii)}\quad \langle D^{(K)}_{Q'Q}{}^*\rangle = \langle D^{(K)}_{Q'Q}\rangle^* \tag{5e}$$

$$\text{(iii)}\quad \langle D^{(K)}_{Q'Q}{}^*\rangle = (-1)^{Q'-Q}\langle D^{(K)}_{-Q'-Q}\rangle \tag{5f}$$

where $\langle D^{(K)}_{Q'Q}\rangle$ is defined by eq 4 with $D^{(K)}_{Q'Q}$ substituted for $D^{(K)}_{Q'Q}{}^*$.

2.2. Conditions Following from the Symmetries of the Preparation Process. Equation 1 simplifies under certain conditions. We will consider here a few cases of practical interest. Assume that the anisotropic molecular ensemble has the following symmetry properties: (a) It is axially symmetric around z. (b) It is invariant under reflection in any plane through z (in particular in any zz'-plane). Both conditions are satisfied, for example, if an initially isotropic ensemble is aligned by pumping with linearly polarized laser light or by orienting the molecules with the help of an external electric field.[9]

Axial symmetry around z means that the probability $W(\alpha\beta\gamma)$ must be independent of α. From eqs 1 and 2 follows that this is only possible if all order parameters with $Q' \neq 0$ vanish. We obtain therefore for axially symmetric axis distributions

$$W(\beta\gamma) = \sum_{\mathrm{KQ}} \frac{2K+1}{4\pi} \langle D^{(K)}_{0Q}{}^*\rangle D^{(K)}_{0Q}(0\beta\gamma) \tag{6}$$

where an integration over α has been performed. Since the function $D^{(K)}_{0Q}(\alpha\beta\gamma)$ is independent of α, we have put $\alpha = 0$ in eq 6.

Let us now consider condition b. Since γ is the angle between the zz'-and $z'x'$-planes of a given molecule, it follows that γ is transformed into $(-\gamma)$ under a reflection in the zz'-plane. Invariance under this transformation requires

$$W(\alpha\beta\gamma) = W(\alpha\beta,-\gamma)$$

Substitution of this result into eq 4 and, using the symmetry properties of the rotation matrices, yields the condition

$$\langle D^{(K)}_{0Q}{}^*\rangle = \langle D^{(K)}_{0Q}\rangle \tag{7}$$

Hence, all nonvanishing order parameters are real.

A further conditions holds if the preparation process defines only an *axis*, but no *direction.* This is the case, for example, in excitation processes with linearly polarized light because of the rapid oscillation of its electric vector. Hence, the molecules are unable to distinguish head from tail, and we have the condition

$$W(\alpha\beta\gamma) = W(\alpha,\pi+\beta,\gamma) \tag{8}$$

Since

$$d^{(K)}_{0Q}(\beta) = (-1)^K d^{(K)}_{0Q}(\pi+\beta)$$

it follows that we shall only need to retain terms with K even in eq 6. In this case an equal number of molecules have z'-axis pointing in the $(+z)$ and $(-z)$ direction.

Of course, this result holds in any case if the molecules have themselves a nonpolar shape (e.g., homonuclear diatomics).

In general, we will call an axis distribution *oriented* if at least one order parameter with K odd is different from zero and *aligned* if only order parameter with K even contribute and simply *anisotropic* if at least one order parameter with $K \neq 0$ is nonvanishing.

2.3. Conditions Following from Internal Symmetries of the Molecular Shapes. Example. Internal symmetries of the molecules are in particular reflected by the γ-dependence of the distribution function. We give two examples in order to clarify further the geometrical importance of the order parameters.

(i) Diatomic Molecules. We choose the molecular axis $\vec{\mathbf{n}}$ as z'-axis. Because of the axial symmetry of the molecules around z', the x'- and y'-axis can be chosen arbitrarily, and the third Euler angle γ becomes superfluous. (Usually one sets $\gamma = 0$; that is, the molecular coordinate system is chosen in such a way that the x'-axis lies in the zz'-plane.) The molecular distribution must be independent of γ, and this requires that all order parameter with $Q \neq 0$ vanish (as follows by inspecting eqs 2 and 4). Equation 1 reduces to the expression

$$W(\alpha\beta) = \sum_{KQ'} \langle Y^{*}_{KQ'} \rangle Y_{KQ'}(\beta\alpha) \tag{9}$$

where we applied the relation $D^{(K)}_{Q'0}(\alpha\beta\gamma) = [4\pi/(2K + 1)]^{1/2}$ $Y^{*}_{KQ'}(\beta\alpha)$,the corresponding relation for the order parameters, and used that $W(\alpha\beta)$ is real. Furthermore, an integration over γ has been performed.

Assume now that the molecular axis distribution is axially symmetric with respect to the z-axis of the director system. In this case all order parameters with $Q' \neq 0$ vanish, and eq 9 reduces to an expression in terms of Legendre polynomials P_K(cos β)

$$W(\beta) = {}^1\!/_2 \sum_{K} (2K + 1) \langle P_K \rangle P_K(\cos\beta) \tag{10}$$

where we have integrated over α and where the relevant order parameters are defined by the relation

$$\langle P_K \rangle = \int_0^{\pi} \mathrm{d}\beta \, \sin\beta \, W(\beta) P_K(\cos\beta)$$

This case has often been discussed in the literature (see for example the reviews by Stolte,[6] Friedrich et al.,[10] Simons,[2] and Loesch[4]). The axis distribution is completely specified in terms of the set $\langle P_K \rangle$. The angle β specifies the directional vector correlation between the molecular axis and the "director" (z-axis).

(ii) Molecules with C_{2v} Symmetry. A rotation of the molecules around the C_2-axis (z') about an angle π leaves all observational properties invariant. Hence, we require

$$W(\alpha\beta\gamma) = W(\alpha\beta,\gamma+\pi)$$

Substitution of this condition into eq 4 and use of eq 2 yields the condition

$$\langle D^{(K)}_{Q'Q}{}^{*} \rangle = (-1)^{Q} \langle D^{(K)}_{Q'Q}{}^{*} \rangle \tag{11}$$

Only order parameters with Q even contribute.

A reflection in the molecular plane ($y'z'$-plane) transforms x' into $-x'$. Invariance under this condition yields

$$W(\alpha\beta\gamma) = W(\alpha\beta,\pi-\gamma) \tag{12}$$

Specializing to axially symmetric systems (eqs 6 and 10), we obtain that all order parameters with Q even are real.

Let us consider an explicit example: assume H_2O molecules have been aligned by pumping with linearly polarized laser light. In this case only parameters with $K = 0$ and $K = 2$ are nonvanishing (because of dipole selection rules). By using conditions 5f, 6, and 7 and the structural information contained in eqs 11 and 12, we obtain for the distribution function:

$$W(\beta\gamma) = \frac{1}{4\pi}\left[1 + 5\langle D^{(2)}_{00} \rangle \frac{1}{2}(3\cos^2\beta - 1) + 5\langle D^{(2)}_{02} \rangle 2\sqrt{\frac{3}{8}} \sin^2\beta \cos 2\gamma\right] \tag{13}$$

where we have inserted explicit expressions for D-functions. For diatomic molecules $\langle D^{(2)}_{02} \rangle$ would vanish, and the axis distribution would be completely determined by knowledge of the alignment parameter $\langle D^{(2)}_{00} \rangle$, given by eq 5c which measures the alignment of the molecular z'-axis with respect to z. For H_2O molecules we need an extra angle γ in defining the alignment of the $x'y'$-plane relative to the director system and an extra parameter

$$\langle D^{(2)}_{02} \rangle = (3/8)^{1/2} \langle \sin^2\beta \cos 2\gamma \rangle \tag{13a}$$

This parameter specifies the difference between the alignment of the x'- and y'-axis. If all molecules would be perfectly aligned with their z'-axis parallel to z, we have $\beta = 0$ and $\langle D^{(2)}_{00} \rangle = 1$, $\langle D^{(2)}_{02} \rangle = 0$. If the z'-axis of all molecules would be perpendicular to z, corresponding to $\beta = \pi/2$, we would have an alignment $\langle D^{(2)}_{00} \rangle = -{}^1\!/_2$. If in addition all x'-axes are perfectly aligned parallel to z ($\gamma = 0$), then $\langle D^{(2)}_{02} \rangle = (3/8)^{1/2}$. We would have $\langle D^{(2)}_{02} \rangle = -(3/8)^{1/2}$ if the y'-axes would all point in z-direction ($\gamma = \pi/2$).

At the first sight it might be surprising that the distribution function depends on the angle γ after excitation by linearly polarized light. We will discuss the physical reason for this in the Appendix.

3. Orientation/Alignment-Dependent Cross Sections

3.1. General Derivations. Steric Factors. In this section we will consider reactions between an ensemble of molecules and projectiles (atoms or electrons). We will derive some basic formulations useful for an exploitation of the spatial aspects of molecular processes, generalizing former attempts (see e.g. refs 12 and 13 and references therein). Assume that an anisotropic molecular ensemble has been prepared in the director system and that its axis distribution is given by eq 1. In order to have a definite situation in mind, we will consider freely rotating molecules in the gas phase with a nonuniform instantaneous axis distribution $W(\alpha\beta\gamma)$.

This ensemble reacts with a beam of projectiles. The reaction is most conveniently be described in a coordinate frame XYZ where the Z-axis is parallel to the initial relative wave vector $\vec{\mathbf{k}}_0$ and where the scattering plane ($\vec{\mathbf{k}}_0-\vec{\mathbf{k}}_1$-plane) is chosen as the XZ-plane where $\vec{\mathbf{k}}_1$ is the final relative wave vector (collision system). The relation between director and collision system is fixed by the three Euler angles $\epsilon\delta\chi$. Here, δ is the angle between z and Z, ϵ is the azimuth angle of z in the collision frame, and the third Euler angle χ refers to a rotation of the x-/y-axis around z. If the initial molecular ensemble is axially symmetric around z, then χ is superfluous and can always be put to zero, and the x-axis lies in the zZ-plane. This case is illustrated in Figure 2 where θ is the scattering angle. For example, if the molecular ensemble has been prepared by a static electric field $\vec{\mathbf{E}}||z$, then δ is the angle between $\vec{\mathbf{E}}$ and $\vec{\mathbf{k}}_0$. In

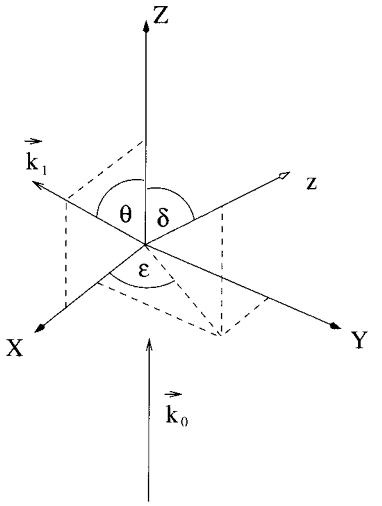

Figure 2. Scattering geometry. *XYZ* denotes the collision system. *Z* is parallel to $\vec{\mathbf{k}}_0$; the $\vec{\mathbf{k}}_0-\vec{\mathbf{k}}_1$ plane is the *XZ*-plane. θ is the scattering angle. δ and ϵ are polar and azimuth angle of the "director" (z), respectively, in the collision system.

supersonic expansions δ would be the angle between the molecular beam axis and $\vec{\mathbf{k}}_0$. The angle ϵ will allow to describe the *azimuthal steric effects*.[6]

Our basic approximation is that the collision time is much shorter than the average rotation time of the molecules. The "elementary" process is then a collision between a projectile and a molecule with a specified orientation of its axes $x'y'z'$. We will denote the differential cross section for the "elementary collision" by $\sigma(\theta,\alpha'\beta'\gamma')$, where $\alpha'\beta'\gamma'$ specify the orientation of $x'y'z'$ relative to the collision frame (see Figure 3). For inelastic collisions a sum over excited degenerate states is assumed to be included in $\sigma(\theta,\alpha'\beta'\gamma')$.

In our present case of interest the molecules are not sharply oriented but are distributed according to the prepared axis distribution (1). Thus, only the corresponding cross section $\sigma(\theta,\epsilon\delta\chi)$ can be measured. This observable is obtained by averaging $\sigma(\theta,\alpha'\beta'\gamma')$ over the given initial axis distribution.

$$\sigma(\theta,\epsilon\delta\chi) = \int_0^{2\pi}\mathrm{d}\alpha' \int_0^{\pi}\mathrm{d}\beta' \sin\beta' \int_0^{2\pi}\mathrm{d}\gamma'\, W(\alpha'\beta'\gamma')\, \sigma(\theta,\alpha'\beta'\gamma') \quad (14)$$

Here $W(\alpha'\beta'\gamma')$ is the distribution function of the initial molecules relative to the collision system. In order to separate geometrical and dynamical properties, we proceed as follows. Expanding the probability in terms of order parameters with respect to the *collision* system, we obtain similar to eq 1

$$W(\alpha'\beta'\gamma') = \sum_{kqq'} \frac{2k+1}{8\pi^2} \langle D^{(k)}_{q'q}{}^*\rangle D^{(k)}_{q'q}(\alpha'\beta'\gamma') \quad (15)$$

which gives

$$\sigma(\theta,\epsilon\delta\chi) = \sum_{kqq'} \frac{2k+1}{8\pi^2} \times \langle D^{(k)}_{q'q}{}^*\rangle \int_0^{2\pi}\mathrm{d}\alpha' \int_0^{\pi}\mathrm{d}\beta' \sin\beta' \int_0^{2\pi}\mathrm{d}\gamma'\, D^{(k)}_{q'q}(\alpha'\beta'\gamma') \times \sigma(\theta,\alpha'\beta'\gamma') \quad (16)$$

It is convenient to express the order parameters $\langle D^{(k)}_{q'q}{}^*\rangle$ in terms of the parameters $\langle D^{(K)}_{Q'Q}{}^*\rangle$ defined by eq 4 with respect to the *director* system since this will then easily allow to take the symmetries of the preparation process into account. The order parameters transform as irreducible tensors under rotation and have the simple transformation property

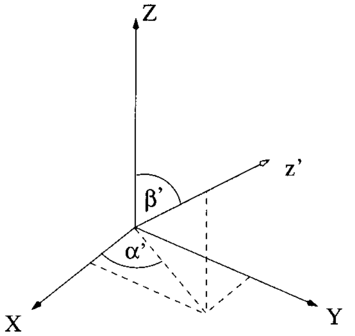

Figure 3. Relation between molecular system $x'y'z'$ and the collision system *XYZ* (only z' is shown).

$$\langle D^{(k)}_{q'q}{}^*\rangle = \delta_{kK}\delta_{qQ} \sum_{Q'} \langle D^{(K)}_{Q'Q}{}^*\rangle D^{(K)}_{q'Q'}{}^*(\epsilon\delta\chi) \quad (17)$$

which can be derived by using the corresponding transformation property of the rotation matrices[18]

$$D^{(k)}_{q'q}(\alpha'\beta'\gamma') = \delta_{kK}\delta_{qQ} \sum_{Q'} D^{(K)}_{q'Q'}(\epsilon\delta\chi)\, D^{(K)}_{Q'Q}(\alpha\beta\gamma)$$

Substitution of eq 17 into eq 16 yields finally

$$\sigma(\theta,\epsilon\delta\chi) = \sum_{Kq'QQ'} \frac{2K+1}{8\pi^2} \langle D^{(K)}_{Q'Q}{}^*\rangle D^{(K)}_{q'Q'}{}^*(\epsilon\delta\chi) \times \int_0^{2\pi}\mathrm{d}\alpha' \int_0^{\pi}\mathrm{d}\beta' \sin\beta' \int_0^{2\pi}\mathrm{d}\gamma'\, D^{(K)}_{q'Q}(\alpha'\beta'\gamma')\, \sigma(\theta,\alpha'\beta'\gamma') = \sum_{Kq'QQ'} \frac{2K+1}{8\pi^2} \langle D^{(K)}_{Q'Q}{}^*\rangle D^{(K)}_{q'Q'}{}^*(\epsilon\delta\chi)\, I^{(K)}_{q'Q}(\theta) \quad (18)$$

where the "steric factor" $I^{(K)}_{q'Q}(\theta)$ is defined by the integral. Equation 18 generalizes definitions given for diatomic molecules (see e.g. refs 12 and 13). The factors $I^{(K)}_{q'Q}(\theta)$ are responsible for the orientation alignment dependence of the cross sections and can in principle be determined experimentally (see for example the review by Loesch[4]).

For diatomic molecules we obtain from eq 18 by setting $Q = 0$:

$$\sigma(\theta,\epsilon\delta\chi) = \sum_{Kq'Q'} \langle Y^*_{KQ'}\rangle D^{(K)}_{q'Q'}(\epsilon\delta\chi)\, I_{Kq'}(\theta) \quad (19)$$

Here the steric factors $I_{\mathrm{Kq}'}(\theta)$ are defined by the relation

$$I^{(K)}_{q'0}(\theta) = 2\pi\left(\frac{4\pi}{2K+1}\right)^{1/2} I^*_{Kq'}(\theta) \quad (20)$$

with

$$I^*_{Kq'}(\theta) = \int_0^{2\pi}\mathrm{d}\alpha' \int_0^{\pi}\mathrm{d}\beta' \sin\beta'\, Y^*_{Kq'}(\beta'\alpha')\, \sigma(\theta,\alpha'\beta') \quad (21)$$

Finally, we list some symmetry properties of the steric factors. Generalizing the argumentation given in refs 9 and 13, we obtain equation

(i) the steric factors are real

$$I^{(K)}_{q'Q}(\theta) = I^{(K)}_{q'Q}{}^{*}(\theta) \tag{22a}$$

$$\text{(ii)}\quad I^{(K)}_{q'Q}(\theta) = (-1)^{Q-q'} I^{(K)}_{-q'-Q}(\theta) \tag{22b}$$

$$\text{(iii)}\quad I^{(K)}_{q'Q}(0) = I^{(K)}_{q'Q}(\pi) = 0 \qquad \text{for } q' \neq 0 \tag{22c}$$

3.2. Discussion and Examples. The advantage of eq 18 is that geometrical and dynamical factors are separated and can be determined independently of other. The initial axis distribution of the molecular target system is characterized by the order parameters $\langle D^{(K)}_{Q'Q}{}^{*}\rangle$ defined with respect to the director system, which allows to take easily the symmetry properties of the preparation process into account. The full information about the dynamics is contained in the steric factors which are most conveniently calculated in the collision frame. The elements $D^{(K)}_{q'Q'}(\epsilon\delta\chi)$ describe the geometry of the experiment, that is, the orientation of the director system relative to $\vec{\mathbf{k}}_0$ and $\vec{\mathbf{k}}_1$. δ is the angle between z and $\vec{\mathbf{k}}_0$ (Figure 2) and can be considered as an average angle of attack. ϵ is the angle between z and the XZ-plane (scattering plane). By varying ϵ, the azimuthal steric effects can be studied.[6]

The order parameters $\langle D^{(K)}_{Q'Q}{}^{*}\rangle$ in eq 18 can be expressed in terms of parameters that characterize the initial angular momentum distribution.[9] Inserting the relevant relations into eq 18, one obtains an expression that essentially describes the vector correlations between $\vec{\mathbf{k}}_0$, $\vec{\mathbf{k}}_1$, and the initial molecular angular momentum.

Let us specialize eq 18 to the case where the initial axis distribution is axially symmetric around z. From eq 6 we obtain by setting $Q' = 0$ in eq 18

$$\sigma(\theta,\epsilon\delta) = \sum_{Kq'Q} \frac{2K+1}{8\pi^2} \langle D^{(K)}_{0Q}{}^{*}\rangle D^{(K)}_{q'0}{}^{*}(\epsilon\delta 0)\, I^{(K)}_{q'Q}(\theta) \tag{23}$$

For diatomic molecules we obtain from eq 10 by setting $Q = 0$ in eq 23 and using eqs 20 and 22a

$$\sigma(\theta,\epsilon\delta) = \sum_{Kq'} \left(\frac{2K+1}{4\pi}\right)^{1/2} \langle P_K\rangle D^{(K)}_{q'0}{}^{*}(\epsilon\delta 0)\, I_{Kq'}(\theta) \tag{24}$$

The physical importance of the additional order parameters with $Q' \neq 0$, occurring in eq 23 has been discussed in section 2.3 (eq 13). It should be noted that "brute force" techniques are required in order to produce linear rotors in oriented states.[4,10]

Equations 18, 19, 23, and 24 show that the steric factors $I^{(K)}_{q'Q}(\theta)$ can in principle be determined experimentally by measuring $\sigma(\theta,\epsilon\delta\chi)$ for several angles δ and ϵ, if the order parameters are known. The main problem for theoreticians is to calculate the steric factors for reactions of interest as a function of energy and scattering angle. The numerical results will point out most favorable kinematical regions and will be helpful for experimentalists for planning measurements. A comparison between theoretical and experimental results for all relevant steric factors will provide a detailed test of the theory.

We will briefly consider an example assuming that only terms with $K = 0$ and $K = 2$ contribute to eq 24. Following Loesch and Stienkemeier[12] and making use of eq 22 we obtain

$$\sigma(\theta,\epsilon\delta) = \sigma_0(\theta) + (5/4\pi)^{1/2}\langle P_2\rangle[I_{20}(\theta)\, P_2(\cos\delta) + 2I_{21}(\theta)\, d^{(2)}_{10}(\delta)\cos\epsilon + 2I_{22}(\theta)\, d^{(2)}_{20}(\delta)\cos 2\epsilon] \tag{25}$$

$\sigma_0(\theta) = (1/4\pi)^{1/2} I_{00}(\theta)$ is the cross section for collisions with randomly oriented molecules. Equation 25 shows that under the assumed conditions three steric factors $I_{20}(\theta)$, $I_{21}(\theta)$, and $I_{22}(\theta)$ must be determined which requires three independent measurements. The dependence on the azimuth angle ϵ is particularly simple. A possible way of determining the steric factors would be to fix θ and δ and vary ϵ. Differential cross sections for electron collisions as a function of ϵ have been measured by Böwering et al.[14] (see also the review by Böwering[19]).

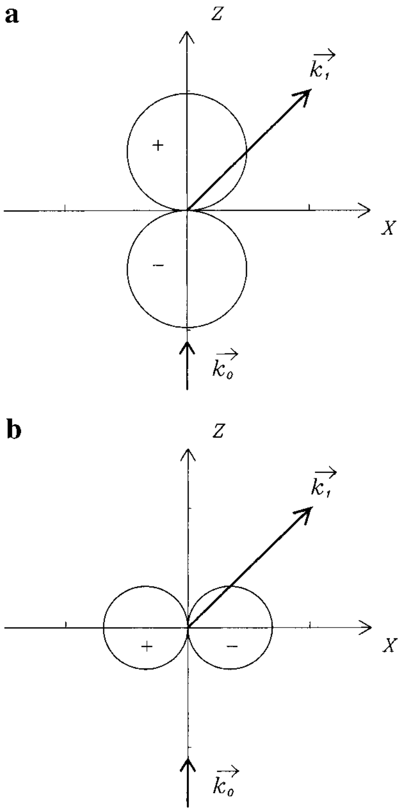

Figure 4. Polar plot of (a) $|Y_{10}(\beta'\alpha')|$ and (b) $|\mathrm{Re}(Y_{11}(\beta'\alpha'))|$ projected into the scattering plane.

It follows from eq 24 that for diatomic molecules a preparation of an initially *axially symmetric* ensemble is sufficient in order to determine all relevant steric factors. Equation 24 is therefore sufficient as a basis for a complete discussion.

The experimental situation is more complex for anisotropic ensembles of polyatomic molecules as follows by inspecting eq 23. Here, the steric factors depend on both, q' and Q. In order to see the consequences, consider for example molecules with C_{2v} symmetry. Assuming preparation by linearly polarised light only the order parameter $\langle D^{(2)}_{00}\rangle = \langle P_2\rangle$ and $\langle D^{(2)}_{02}\rangle = \langle D^{(2)}_{0-2}\rangle$ are nonvanishing as shown in section 2. Specialising eq 23 to this case, we obtain

$$\sigma(\theta,\epsilon\delta) = \sigma_0(\theta) + (5/8\pi^2)\sum_{q'} D^{(2)}_{q'0}{}^{*}(\epsilon\delta 0)[\langle P_2\rangle I^{(2)}_{q'0}(\theta) + \langle D^{(2)}_{02}\rangle(I^{(2)}_{q'2}(\theta) + I^{(2)}_{q'-2}(\theta))] \tag{26}$$

Equation 26 shows that by varying δ and ϵ only the brackets can be determined as a whole, but not the steric factors separately. In order to obtain more information, one has to prepare initial molecular samples without cylindrical symmetry.

4. Geometrical Interpretation of the Steric Factors

The initial molecular samples can be prepared experimentally in various ways. For example, preparation by linearly polarized light produces order parameters with $K = 0$ and $K = 2$ only. If molecules are oriented in external electric fields, also order parameters with K odd contribute. The steric factors, however, can be calculated independently of the experimental preparation process once and for all. In this section we will consider the geometrical importance of the steric factors for diatomic molecules. This discussion is closely related to former treatments in the literature (e.g., refs 4, 6, and 12), generalizes however certain aspects. In the following section we will illustrate our results with numerical data (Figures 6, 7).

Let us start with the factor

$$I_{10}(\theta) = \int_0^{2\pi} d\alpha' \int_0^{\pi} d\beta' \sin\beta' \, Y_{10}(\beta'\alpha')\, \sigma(\theta,\alpha'\beta')$$

$$= (3/4\pi)^{1/2} \int_0^{2\pi} d\alpha' \int_0^{\pi} d\beta' \sin\beta' \cos\beta' \, \sigma(\theta,\alpha'\beta') \quad (27)$$

The cross section $\sigma(\theta,\alpha'\beta')$ is weighted by the spherical harmonic $Y_{10}(\beta'\alpha')$ for any direction of β'. $Y_{10}(\beta'\alpha')$ is zero for $\beta' = \pi/2$ and maximal for axes parallel or antiparallel to $\vec{\mathbf{k}}_0$. It follows that molecules with axes perpendicular to $\vec{\mathbf{k}}_0$ do not contribute to $I_{10}(\theta)$ and that $I_{10}(\theta)$ picks out predominantly the contributions from axes directions parallel or antiparallel to $\vec{\mathbf{k}}_0$. Furthermore, $Y_{10}(\beta'\alpha')$ is positive for $0 \le \beta' \le \pi/2$ and negative for $\pi/2 \le \beta' \le \pi$. These properties are illustrated in Figure 4a, which shows the polar plot for $|Y_{10}(\beta'\alpha')|$ and where the sign of $Y_{10}(\beta'\alpha')$ is indicated by the ($\pm$) sign in the upper and lower lobe, respectively. Note that the factor $\sin\beta'$ in eq 27 is always positive in the integration region $0 \le \beta' \le \pi$.

Hence we can write

$$I_{10}(\theta) = \int_0^{\pi/2} d\beta' \sin\beta' \cos\beta' \, \sigma(\theta,\beta') - \int_{\pi/2}^{\pi} d\beta' \sin\beta' \, |\cos\beta'| \, \sigma(\theta,\beta') \quad (28)$$

where we have defined

$$\sigma(\theta,\beta') = (3/4\pi)^{1/2} \int_0^{2\pi} d\alpha' \, \sigma(\theta,\alpha'\beta')$$

Assume that $I_{10}(\theta)$ has been calculated or measured as a function of θ. Equation 28 allows then to draw some immediate conclusions from the results by inspecting the sign of the steric factors. If $I_{10}(\theta)$ is positive, then the first term in eq 28 is larger than the second one. This means that—on the average—$\sigma(\theta,\beta')$ is larger for molecular orientations within $0 \le \beta' < \pi/2$ (pointing in the upper lobe of Figure 4a) than for axes orientations within $\pi/2 < \beta' < \pi$ (pointing in the lower lobe of Figure 4a). The opposite result holds if $I_{10}(\theta)$ is negative. These results are clearly independent of the values of all other steric factors. It should be mentioned that this result for $I_{10}(\theta)$ allows no conclusion on the head/tail asymmetry of the full cross section. Several terms contribute to $\sigma(\theta)$ which may partly compensate each other. In order to obtain more detailed information, one has therefore to consider the steric factors individually.

Let us now consider $I_{11}(\theta)$, defined by

$$I_{11}(\theta) = \int_0^{2\pi} d\alpha' \int_0^{\pi} d\beta' \sin\beta' \, \mathrm{Re}(Y_{11}(\beta'\alpha'))\, \sigma(\theta,\alpha'\beta') \quad (29)$$

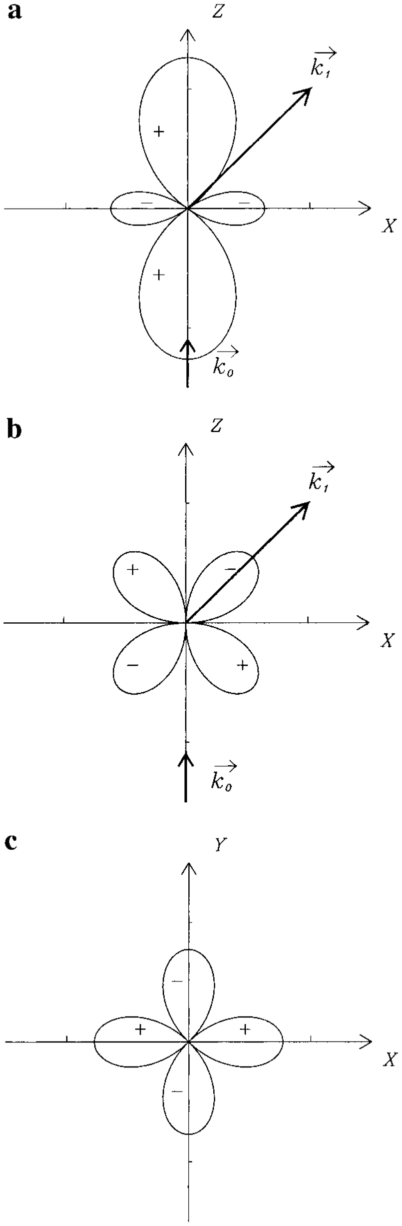

Figure 5. Polar plots of (a) $|\mathrm{Re}(Y_{20}(\beta'\alpha'))|$ and (b) $|\mathrm{Re}(Y_{21}(\beta'\alpha'))|$ projected into the scattering plane. Part c shows $|\mathrm{Re}(Y_{22}(\beta'\alpha'))|$ projected into the XY-plane of the collision system.

where the reality property (22b) of the steric factors has been taken into account. The polar plot of $|\mathrm{Re}(Y_{11}(\beta'\alpha'))|$, projected into the $\vec{\mathbf{k}}_0-\vec{\mathbf{k}}_1$ plane, is shown in Figure 4b, where the sign of $\mathrm{Re}(Y_{11}(\beta'\alpha'))$ is indicated by (+) and (−). The plot is axially symmetric around the X-axis. It follows that molecules oriented perpendicular to $\vec{\mathbf{k}}_0$ give the dominant contributions to $I_{11}(\theta)$ and that molecules oriented parallel or antiparallel to $\vec{\mathbf{k}}_0$ do not contribute at all. Furthermore, a positive sign of $I_{11}(\theta)$ indicates a preference for molecules with axes pointing in the left-hand lobe of Figure 4b, and vice versa if the sign of $I_{11}(\theta)$ is negative (in the sense explained above).

The three factors $I_{2q'}(\theta)$ can be discussed along similar lines. These factors are independent of the direction of the molecular axis and depend only on their alignment. The polar plots of $|\mathrm{Re}(Y_{2q'}(\beta'\alpha'))|$ correspond to the usual plots of d-orbitals, and their projection in the $\vec{\mathbf{k}}_0-\vec{\mathbf{k}}_1$ plane is given in Figure 5a,b. Figure 5c shows the projection of $|\mathrm{Re}(Y_{22}(\beta'\alpha'))|$ in the XY-plane. It is indicated in which parts of the lobes $\mathrm{Re}(Y_{2q'}(\beta'\alpha'))$ is positive or negative. From the sign of the corresponding steric factors one can read off which part of the lobes gives the dominant contributions (in the sense explained above for $I_{10}(\theta)$). In particular, $I_{22}(\theta)$ gives some information on the *azimuthal* steric effects. A similar analysis can be performed for the other steric factors.

In conclusion, an experimental determination of the steric factors give some immediate insight into the stereodynamical conditions of the reactions. A comparison between numerical and experimental data gives a very detailed test of how good the stereodynamics is described by the theory.

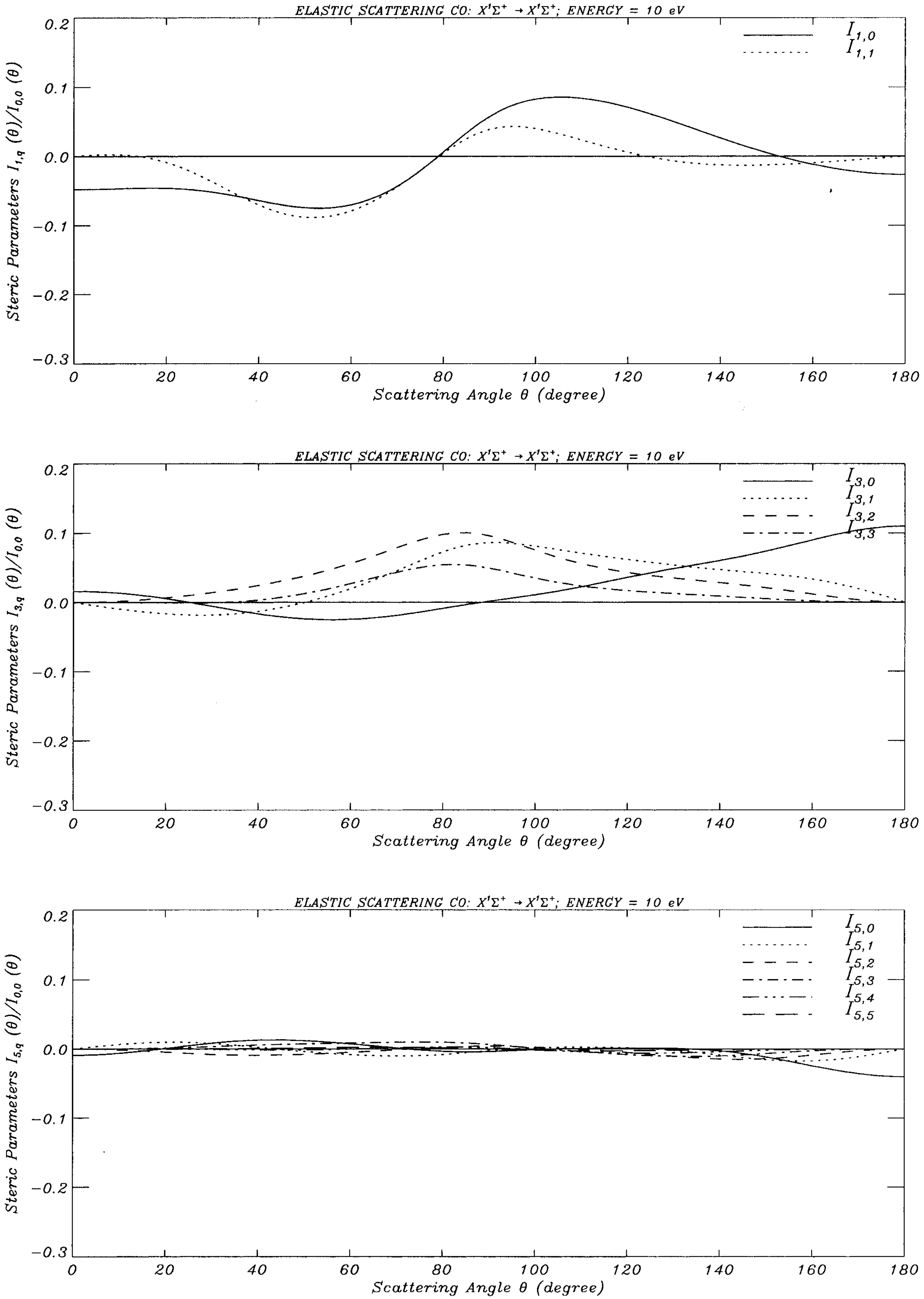

Figure 6. Numerical results for steric factors with *K* odd for elastic e$^-$−CO collisions.

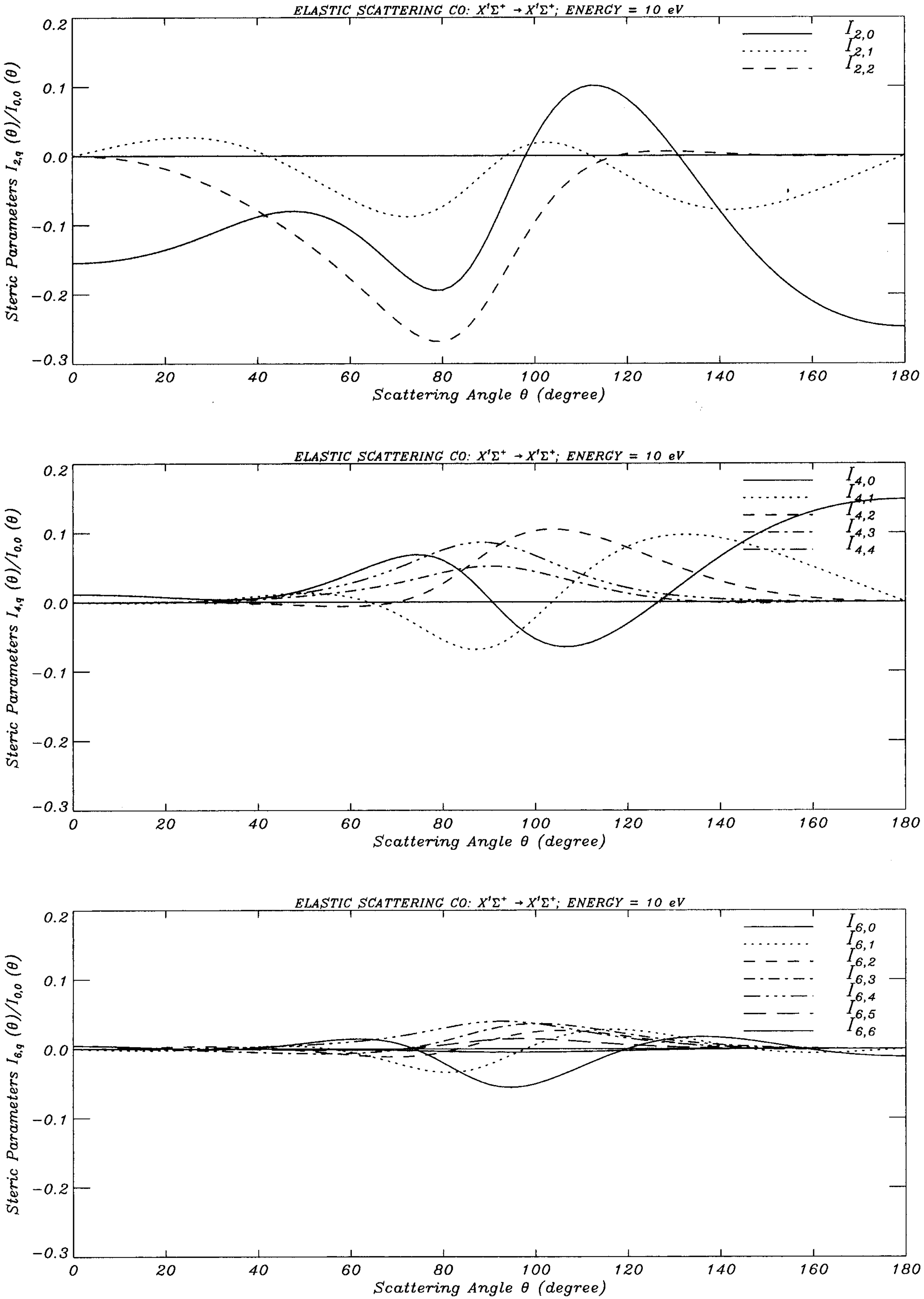

Figure 7. Numerical results for steric factors with *K* odd for elastic e$^-$−CO collisions.

5. Numerical Results for Elastic Collisions with CO Molecules

In order to illustrate the general results, presented in the preceding sections, we will give numerical results for the steric factors for elastic collisions between electrons and CO molecules in their vibrational and electronic ground state. Differential cross sections for elastic and inelastic $e^- - CO$ scattering for randomly oriented molecules have been obtained by Morgan and Tennyson[15] for collision energies below 12 eV, using **R**-matrix techniques. We refer to this paper for details of the basic numerical procedure.

Using the partial-wave **T**-matrix elements, obtained by Morgan and Tennyson, we calculated the steric factors up to $K = 6$ (see ref 16 for details). Results are shown in Figure 6 for steric factors with odd K and Figure 7 for even K. The corresponding factors $I_{Kq'}(\theta)$ with negative q' follow from eq 22b. In these calculation the direction of the molecular axis is from the C atom to the O atom.

The figures present the normalised steric factors $I_{Kq'}(\theta)/I_{00}(\theta)$ as a function of the scattering angle at a collision energy of $E = 10$ eV. Figure 6 shows the orientation effect upon the collision and Figure 7 the alignment effect. Magnitude and sign of the steric factors vary considerably with the scattering angle.

The results can be analyzed along the lines discussed in section 4. For example, $I_{20}(\theta)$ is mainly negative, indicating that contributions from molecules aligned mainly perpendicular to $\vec{\mathbf{k}}_0$ are larger than from molecules aligned in $\vec{\mathbf{k}}_0$ direction. From the negative sign of $I_{22}(\theta)$ one can deduce that an axis alignment perpendicular to the scattering plane is more favorable than an alignment in the plane.

An interesting result is that the steric factors vanish rapidly with increasing K. The factors with $K = 5$ and $K = 6$ are considerably smaller as the factors for $K \leq 4$. It can be expected that similar results hold for other reactions if the dependence of the cross sections $\sigma(\theta,\alpha'\beta'\gamma')$ on the direction of the molecular axes is not too strong. In addition, it has been shown for several cases that the order parameters become also small with increasing K,[10,11,14] so that the products $\langle P_K \rangle I_{Kq'}(\theta)$ decrease even more rapidly. Hence, it might be expected that one only need to retain the first few terms in eq 24 in many practical cases.

In concluding this section, we point out that no *general* conclusion can be drawn on the convergence of the expansions (18) and (19) (except for cases like excitation by polarized light where only terms up to $K = 2$ contribute). Our conclusions on the relative importance of the steric factors with different K are deduced from our numerical results. This situation may be different in other cases. However, one might expect that only few terms contribute to eqs 18 and 19 if the cross section depends only relative weakly on the axis orientation (if σ would be completely independent on the axis distributions only the term with $K = 0$ would be nonvanishing). Numerical calculations of the steric factors will therefore be very helpful as a guide to experimentalists.

6. Conclusions

By applying the concept of order parameters and by explicitly using their tensorial properties, we have derived general expressions for differential cross sections for collisions with anisotropic molecular ensembles. The derivations given here generalize previous formulations given in the literature.

Our main results are eqs 18 and 23 for polyatomic molecules and eq 24 for diatomics. In these expressions geometrical and dynamical factors are separated. The orientation and alignment of the initial target system are characterized by the order parameters. These parameters allow to take efficiently the symmetries of the preparation process into account and represent a systematic way of approaching the structural information contained in $W(\alpha\beta\gamma)$. The information on the directional properties of the collision is contained in the steric factors. The experimental geometry is explicitly described by the rotation matrix elements. These expressions might be useful for experimental and theoretical investigations of steric effects for elastic, inelastic, and reactive collisions. The theory of the measurement is briefly considered.

The main goal is the determination of the steric factors. A calculation of these parameters allows to point out favorable kinematical regions which will be useful for the planning of experiments. Measurements or calculation of the steric factors allow to draw some immediate conclusions on the stereodynamics of the collision as discussed in section 4 and illustrated in section 5. A comparison between theoretical and experimental data for all relevant steric factors would be the most detailed test of the theory under the given experimental conditions.

Appendix

In this appendix we will briefly consider the γ-dependence of the distribution function $W(\beta\gamma)$ after absorption of linearly polarized light. We will concentrate on molecules with C_{2v} symmetry, assuming that initially all molecules are in their electronic ground state (A_1). The relevant distribution function is given by eq 13.

The absorption probability of a transition is proportional to the square of the projection of the relevant electric dipole transition moment into the direction of the electric field vector of the light (z-axis), and this depends on the molecular orientation, that is, on β and γ. In order to obtain the formal relationship, one has to express the order parameters in terms of the components $M_{x'}$, $M_{y'}$, and $M_{z'}$ of the transition moments in the molecular frame and insert the results into eq 13. Here we will not give the derivations but only the final result (see for example ref 8, eq 4.71):

$$W(\beta\gamma) = A\{|M_{z'}|^2 \cos^2\beta + {}^1\!/_2[(|M_{x'}|^2 + |M_{y'}|^2) + (|M_{x'}|^2 - |M_{y'}|^2)\cos 2\gamma]\sin^2\beta\} \qquad \text{(A.1)}$$

where A is a constant. Let us consider an $A_1 \rightarrow B_1$ transition. Symmetry dictates that the transition moment is directed along the molecular x'-axis (which is perpendicular to the molecular plane). Only $M_{x'}$ is then different from zero and eq A.1 reduces to

$$W(\beta\gamma) = (A/2)|M_{x'}|^2 (1 + \cos 2\gamma)\sin^2\beta \qquad \text{(A.2)}$$

It follows that (for fixed $\beta \neq 0, \pi$) $W(\beta\gamma)$ is maximal for $\gamma = 0$ (x' lies within the zz'-plane) and zero for $\gamma = \pi/2$. In fact, in the latter case x' is perpendicular to the zz'-plane and therefore perpendicular to the electric field vector, and no absorption is possible. In other words, there is no excited molecule in a B_1 state with an orientation $\gamma = \pi/2$. The variation of $W(\beta\gamma)$ with the angle 2γ reflects the molecular symmetry.

For an $A_1 - A_1$ transition only $M_{z'}$ is nonvanishing, and only $M_{y'}$ contributes for an $A_1 - B_2$ transition. These cases can be discussed similarly. The β- and γ-dependence of the molecular distribution function is therefore a consequence of the relevant dipole selection rules, which in turn depend on the molecular symmetry.

References and Notes

(1) Bernstein, R. B.; Herschbach, D. R.; Levine, R. D. *J. Phys. Chem.* **1987**, *91*, 5366.

(2) Simons, J. P. *J. Phys. Chem.* **1987**, *91*, 5378.

(3) Delgado-Barrio, G. *Dynamical Processes in Molecular Physics*; IOP Publishing: Bristol, 1993.

(4) Loesch, H. J. *Annu. Rev. Phys. Chem.* **1996**, *46*, 255.

(5) Parker, D. H.; Bernstein, R. B. *Annu. Rev. Phys. Chem.* **1989**, *40*, 561.

(6) Stolte, S. *Ber. BunsenGes. Phys. Chem.* **1982**, *86*, 413.

(7) Geuzebroek, F. H.; Wiskerke, A. E.; Tenner, M. G.; Kleyn, A. W. *J. Phys. Chem.* **1991**, *95*, 8409.

(8) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarised Light*; VCH Publishers: New York, 1986.

(9) Blum, K. *Density Matrix Theory and Applications*, 2nd ed.; Plenum: New York, 1996.

(10) Friedrich, B.; Pullmann, D.; Herschbach, D. R. *J. Phys. Chem.* **1991**, *95*, 8118.

(11) Neitzke, H. P.; Terlutter, R. *J. Phys. B* **1992**, *25*, 1931.

(12) Loesch, H. J.; Stienkemeier, F. *J. Chem. Phys.* **1993**, *98*, 9570.

(13) Ostrawsky, C.; Blum, K.; Gillian, G. *J. Phys. B* **1995**, *28*, 2269.

(14) Böwering, N.; Volkmer, M.; Meier, Ch.; Lieschke, J.; Dreier, R. *J. Mol. Struct.* **1995**, *348*, 29.

(15) Morgan, L. A.; Tennyson, J. *J. Phys. B* **1993**, *26*, 2429.

(16) Busalla, A. *Diplomthesis*, University of Münster, 1997, unpublished.

(17) Zare, R. N. *Angular Momentum*; Wiley: New York, 1988.

(18) Edmonds, A. R. *Angular Momentum in Quantum Mechanics*; Princeton University Press: Princeton, NJ, 1957.

(19) Böwering, N. In *Selected Topics in Electron Physics*; Campbelly, D., Kleinpoppen, H., Eds.; Plenum Press: New York, 1996.