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Single-Parameter Quantification of the Sensitivity of a Molecular Collision to Molecular Polarization[†]

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This article introduces the concept of intrinsic entropy, S, of a molecular collision. Defined in rigorously quantum mechanical terms as the von Neumann entropy of the intrinsic density matrices of reagents and products, the intrinsic entropy is a dimensionless number in the $0 \leq S \leq 1$ range. Its limits are associated with situations where the collision cross section is due to a single combination of reagent and product polarizations ($S = 0$) or where there is absolutely no selectivity with respect to the molecular polarizations ($S = 1$). The usefulness of the intrinsic entropy as a quantifier of the sensitivity of a molecular collision to molecular polarizations is demonstrated with examples for the benchmark $H + D_2$ reaction.

1. Introduction

Molecular collisions pervade virtually all of chemistry. This makes them a primary target for the sort of investigations whose ultimate goals are deep and thorough understanding and characterization of the fundamental processes underpinning chemical phenomena. A preferred modus operandi of these investigations is to consider isolated (gas-phase) collisions between atoms and small molecules, which are the most amenable to detailed and accurate experimental or theoretical studies. Particular attention is paid to intra- and intermolecular interactions, represented by the potential energy surface(s) that influence the motion of nuclei, and to the unfolding of that motion (the collision dynamics) as the collision partners approach, interact, and recoil.[1]

The properties that quantify the collision dynamics can be divided in two broad classes: scalar and vector.[1,2] Scalar properties are those that do not depend on spatial directions; prime examples are the integral cross section (roughly speaking, the collision probability regarded as a function of the collision energy and the atomic and molecular states) and the product state distribution. Vector properties do depend on spatial directions; prime examples are the differential cross section (DCS, roughly speaking, the collision probability regarded as a function also of the scattering angle, which is the angle between the relative velocities of reagents and products) and the various polarization-dependent (or tensor) cross sections. These are cross sections that, on top of the parameters listed above, also depend on the multipolar (or tensorial) components of the atomic and molecular polarizations (spatial distributions of angular momenta and internuclear axes).[3,4]

Since vector properties provide additional, more detailed information about the collision dynamics, their importance has long been recognized.[5,6] Furthermore, since the theoretical but especially the experimental techniques for their study have steadily progressed, the interest in and activity around vector properties have steadily increased.[7] A problem that remains, however, is that stereodynamics studies (that is, studies of vector properties of molecular collisions) can, and almost invariably do, involve a vast amount of data. One pressing question, for experimentalists and theoreticians alike, is the following: *where is the interesting information?* At heart, this is a question about the sensitivity of the collision stereodynamics to its parameters (collision energy, initial state, final state, scattering angle). What one wants to know is whether there are particular regions of the parameter space where the parameter values are highly correlated, or where the reaction properties are strongly dependent on the parameter values.

In this article we introduce a concept that should prove useful in addressing this question. For reasons to be made clear later, we call it the *intrinsic collision entropy*. For a given combination of parameters other than the molecular (reagent and product) polarizations, the intrinsic collision entropy (S) is a dimensionless number that can be defined so as to lie in the $0 \leq S \leq 1$ range, with the lower and upper limits having well-defined meanings. If $S = 0$, the collision cross section is entirely due to a single combination of reagent and product polarizations. If $S = 1$, all reagent and product polarizations that can contribute to the collision cross section do so equally — that is, there is absolutely no selectivity with respect to the molecular polarizations. We should also mention that the intrinsic entropy is fully defined within the framework of quantum mechanics and that its calculation does not require any approximation.

Although the intrinsic entropy may prove to be important on its own, the point we want to make in this article is that this quantity allows one to completely bypass the explicit consideration of molecular polarizations in the analysis of the sensitivity of a collision to stereodynamical parameters. Furthermore, the intrinsic entropy precisely and unambiguously *quantifies* the sensitivity of the collision to molecular polarizations. A question such as "how sensitive is this collision to molecular polarization?" can be answered not only with qualitative terms such as "very" or "not so much", but also with a number whose value must lie between zero and one.

The remainder of the article is organized as follows. Section 2 is devoted to the theory; it starts with brief reviews of two concepts that are essential for the definition of the intrinsic collision entropy (intrinsic collision properties[11,12] and canonical

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collision mechanisms[12]) before turning to the definition of the intrinsic entropy itself. Section 3 presents numerical examples, all of which refer to $H + D_2 \rightarrow HD + D$, the simplest and best characterized of all reactive molecular collisions.[13] Section 4 closes the paper with a summary of its main points and an outlook.

2. Theory

2.1. Intrinsic Collision Properties. We have discussed the need for distinguishing the intrinsic, extrinsic, and observable properties of molecular collisions in past publications;[11,12] what follows is but a short review.

The *intrinsic properties* of a collision are those that describe the collision process itself rather than a particular experimental realization of it. For example, a collision may have the following intrinsic property: its cross section is maximum when the reagents approach each other with a particular mutual orientation. This particular collision geometry is characteristic of the collision and completely independent of experimental observations; in fact, it is even independent of whether an experimental technique that can make the reagents approach each other and collide in the specified way actually exists. In metaphorical terms, one could say that intrinsic properties are associated with what the collision “wants” rather than with what the collision “gets”.

In contrast, the *extrinsic properties* of a collision describe a particular experimental setup rather than characteristics of the collision process itself. For example, let us imagine an experiment in which the reagents are prepared so as to approach each other with a particular mutual orientation. This particular collision geometry is characteristic of the experiment and independent of the collision dynamics. It is therefore an extrinsic property. In metaphorical terms, one could say that extrinsic properties are associated with what the collision “gets” rather than with what the collision “wants”.

The *measurable properties* of a collision result from the interplay between intrinsic and extrinsic properties; in the metaphorical terms used above, from the balance between what the collision “wants” and what it “gets.” For example, the value of the collision cross section measured in the experiment described in the previous paragraph would depend on how the reagents were prepared (that is, on the extrinsic properties of the collision) but also on the extent to which the collision dynamics favors or disfavors the experimentally selected collision geometry (this is an intrinsic property of the collision).

When a theoretician performs a quantum scattering calculation, the main output of the calculation is the scattering matrix. The elements of this matrix are probability amplitudes for the transitions between all the possible initial (reagent) and final (product) states. As the scattering matrix elements are independent of any experimental consideration, they are fully intrinsic quantities. As a consequence, every collision property that depends on no dynamical parameter other than the scattering matrix elements is also an intrinsic property. As we will see below, this is indeed the case for the intrinsic collision entropy.

When a theoretician performs a wavepacket calculation, he or she must decide on the form of the initial wavepacket. As this theoretician-made decision is independent of the collision dynamics, the form of the initial wavepacket is an extrinsic property of the collision. The observed wavepacket evolution results from a combination of extrinsic and intrinsic factors (respectively, initial wavepacket form and collision dynamics). Note, however, that one can use wavepacket calculations to obtain values of scattering matrix elements.[14] This shows that although the values of intrinsic properties cannot be directly observed, they can be inferred from the values of observed and extrinsic properties. In principle, this should also be the case in experimental studies. In practice, however, it would be difficult because of the large amount of experimental information required.

Let us consider a mathematical example. We assume that a quantum scattering calculation has been performed for a reactive collision, $A + BC \rightarrow AB + C$. This resulted in a set of scattering matrices whose elements, $S^{JE}_{\mathbf{p}_n\mathbf{r}_m}$, are labeled by the total angular momentum quantum number (J), by the total energy (E), and by two collective indices. The $\mathbf{r}_m$ collective index singles out one of the states of the reagent basis set used in the calculation, $\{|\mathbf{r}_m\rangle, m = 1, 2, ...\}$. Similarly, $\mathbf{p}_n$ singles out one of the states of the product basis set used in the calculation, $\{|\mathbf{p}_n\rangle, n = 1, 2, ...\}$.

Let us now consider two collision experiments, a and b, in which two different reagent states are used:

$$|\Psi_a\rangle = \frac{|\mathbf{r}_1\rangle - |\mathbf{r}_2\rangle}{\sqrt{2}} \tag{1a}$$

$$|\Psi_b\rangle = \frac{|\mathbf{r}_1\rangle + |\mathbf{r}_2\rangle}{\sqrt{2}} \tag{1b}$$

We assume that the $|\mathbf{r}_1\rangle$ and $|\mathbf{r}_2\rangle$ basis states are degenerate, which implies that the $|\Psi_a\rangle$ and $|\Psi_b\rangle$ states are time-independent.

If summed over product states, the integral cross sections of the two experiments are respectively given by

$$\sigma_a(E) = N\sum_{nJ}(2J + 1)\frac{\left|S^{JE}_{\mathbf{p}_n\mathbf{r}_1} - S^{JE}_{\mathbf{p}_n\mathbf{r}_2}\right|^2}{2} \tag{2a}$$

$$\sigma_b(E) = N\sum_{nJ}(2J + 1)\frac{\left|S^{JE}_{\mathbf{p}_n\mathbf{r}_1} + S^{JE}_{\mathbf{p}_n\mathbf{r}_2}\right|^2}{2} \tag{2b}$$

where N is a flux factor. Note the following:

- The scattering matrix elements depend on the reaction under study, but not in any way on the “experimental” reagent states, $|\Psi_a\rangle$ and $|\Psi_b\rangle$. The values of the scattering matrix elements are intrinsic to the reaction.
- The “experimental” reagent states are chosen arbitrarily and do not depend on the quantum scattering results. In particular, they need not coincide with any of the reagent basis states used in the scattering calculation. The “experimental” reagent states are extrinsic to the reaction.
- The integral cross section is a measurable property whose value depends on the (intrinsic) scattering matrix elements and also on the (extrinsic) reagent states.

2.2. Canonical Collision Mechanisms. In general, molecular collisions involve an incoherent superposition of a number of separate coherent processes.[15] For this reason, one must in general describe the initial (reagent) and final (product) states using density matrices rather than wave functions.[16] If $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ are, respectively, the density matrices of reagents and products, they are related by[17]

$$\boldsymbol{\rho}' = \mathbf{f}\boldsymbol{\rho}\mathbf{f}^{\dagger} \qquad (3)$$

$$\boldsymbol{\rho} = \mathbf{f}^{\dagger}\boldsymbol{\rho}'\mathbf{f} \qquad (4)$$

where **f** is the scattering amplitude matrix.

If the reagents are unpolarized, their state is an equally weighed incoherent superposition of the states in the angular momentum-space reagent state basis set,

$$\{|b_i\rangle\}, \quad i = 1, 2, ..., n \qquad (5)$$

One has

$$\boldsymbol{\rho} = \frac{1}{n}\mathbf{I}_n \qquad (6)$$

where $\mathbf{I}_n$ is the $n \times n$ identity matrix. This result is actually independent of the basis set chosen to describe the reagents and implies

$$\boldsymbol{\rho}' = \frac{1}{n}\mathbf{f}\mathbf{f}^{\dagger} \qquad (7)$$

In general, the density matrix of eq 7 is not diagonal. The reason is that the pure product polarization states formed in the collisions involving each of the pure reagent states (the $|b_i\rangle$ states) need not coincide with the states in the angular momentum-space product state basis set,

$$\{|b'_i\rangle\}, \quad i = 1, 2, ..., n' \qquad (8)$$

However, once the $\boldsymbol{\rho}'$ matrix has been obtained as indicated above, one can easily diagonalize the matrix and thus determine the product states that make $\boldsymbol{\rho}'$ diagonal. Note the following:

- Diagonalization of $\boldsymbol{\rho}'$ is equivalent to its decomposition into pure-state density matrices,

  $$\boldsymbol{\rho}' = \sum_{i=1}^{n'} w_i \boldsymbol{\rho}'^{(\mathrm{pure})}_i \qquad (9)$$

  where the pure-state density matrices are those corresponding to the eigenvectors of $\boldsymbol{\rho}'$ and the w_i (the statistical weights of the pure states[16]) are the eigenvalues of $\boldsymbol{\rho}'$.
- As every pure product state associated with a nonzero eigenvalue must be in a one-to-one relation to a pure reagent state,[12] determination of the pure product states implies determination of the corresponding pure reagent states associated to them:

  $$\boldsymbol{\rho}^{(\mathrm{pure})}_i = \mathbf{f}^{\dagger}\boldsymbol{\rho}'^{(\mathrm{pure})}_i\mathbf{f} \qquad (10)$$

- Had we started this derivation using unpolarized products and eq 4 rather than unpolarized reagents and eq 3, we would have obtained the same results, except for an exchange of the symbols referring to reagents or products.

This implies that through diagonalization of either

$$\mathbf{R} = \mathbf{f}^{\dagger}\mathbf{f} \qquad (11)$$

or

$$\mathbf{P} = \mathbf{f}\mathbf{f}^{\dagger} \qquad (12)$$

(note that the two matrices have the same norm, Tr(**R**) = Tr(**P**), whatever the representation used for reagent and product states) one can (i) determine all the pure states of reagents and products that are involved in the collision, (ii) put the pure reagent and pure product states in one-to-one correspondence, and (iii) determine the statistical weight of each pure collision process in the overall collision.

Let us now introduce some terminology. Since **R** and **P** are, respectively, density matrices of reagents and products, and since they are entirely determined by the scattering amplitude matrix (an intrinsic quantity whose determination involves no dynamical parameter other than the scattering matrix[17]), we shall refer to **R** and **P** as the *intrinsic density matrices* of reagents and products. Since we have a criterion (a "canon", diagonalization of **R** and **P**) to determine the pure asymptotic states, we shall refer to them as the *canonical states* of the reagents and products of the collision. Since each canonical reagent state is pure and in one-to-one correspondence with an (also pure) product canonical state, the two are related by a pure transformation—a fully coherent collision mechanism. We shall refer to each of these as a *canonical collision mechanism.*

The statistical weight of each canonical mechanism, that is, its contribution to the overall collision, is given by the corresponding eigenvalue (it must be the same regardless of whether the matrix that is initially diagonalized is **R** or **P**, see ref 12). As each of these eigenvalues is a DCS,[12] we shall refer to each of them as a *canonical differential cross section* (for short, canonical DCS). Note that, because the "conventional" DCS (the observable property resulting from collision of unpolarized reagents) is defined as the average rather than the sum of the DCSs associated with the various reagent substates, the relation between the conventional and canonical DCSs reads

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\omega} = \frac{1}{n}\sum_{i=1}^{n}\frac{\mathrm{d}\sigma^{(\mathrm{can})}_i}{\mathrm{d}\omega} \qquad (13)$$

where $\mathrm{d}\sigma/\mathrm{d}\omega$ is the conventional DCS and the $\mathrm{d}\sigma^{(\mathrm{can})}_i/\mathrm{d}\omega$ are the canonical DCSs.[12]

We should emphasize that what is unique about the canonical mechanisms is not the decomposition of the DCS. If the superscript referring to canonical mechanisms is discarded, eq 13 holds for every complete set of pure reagent states. This is because, whatever the complete set of pure reagent states, it is always true[16] that

$$\sum_{i=1}^{n}\boldsymbol{\rho}^{(\mathrm{pure})}_i = \mathbf{I}_n \qquad (14)$$

the $\rho^{(\mathrm{pure})}_i$ pure-state density matrices need not be those defined by eq 10. Instead, what is unique to the canonical decomposition of the dynamics of a reaction is the complete separation of the pure, independent processes that underlie it. This would not be the case if the analysis was done, say, in terms of the rotational substates of reagents and products. The initial and final states

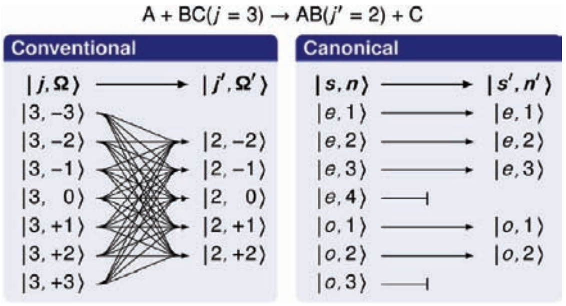

Figure 1. Two representations of the scattering amplitude of the A + BC($j = 3$) → AB($j' = 2$) + C reaction; atoms A and C carry no angular momentum, and the vibrational quantum numbers of the BC and AB molecules are fixed. The arrows represent nonzero scattering amplitudes. (Left) A conventional representation in terms of the helicity substates of reagents and products (j and Ω are, respectively, angular momentum and helicity quantum numbers; unprimed symbols refer to the BC reagent, primed symbols to the AB product). Note that every reagent state can be transformed into every product state; the asymptotic states are all entangled. (Right) In the canonical representation,[12] the reagent and product states are labeled by symmetry, s (must be even, e, or odd, o), and by decreasing order of the corresponding canonical DCS, n [the DCS is the squared modulus of the scattering amplitude; one has DCS(e_1) ≥ DCS(e_2) ≥ DCS(e_3) ≥ DCS(e_4), and similarly for the reactions involving odd-symmetry canonical states]. Note that the canonical representation allows for direct identification of asymptotic states that do not participate in the dynamics (in this example, reagent states |e,4⟩ and |o,3⟩ do not react), and also that each reagent state that does react can only be transformed into one product state; the asymptotic states are all disentangled.

would be then entangled and not in one-to-one correspondence (see Figure 1).

2.3. Intrinsic Collision Entropy. In classical probability theory a state is a distribution of probabilities over the possible outcomes of a measurement. If we represent it by

$$\mathbf{P} = \begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_n \end{pmatrix} \tag{15}$$

where the p_i are the probabilities of observing the various outcomes (they must satisfy $p_i \geq 0$ and $\Sigma_i p_i = 1$), then the Shannon entropy,[18]

$$S(\mathbf{P}) = -k \sum_{i=1}^{n} p_i \ln p_i \tag{16}$$

where k is a positive number, is only one of many possible mathematical definitions of entropy,[19] but arguably the most telling of them all.[20] Its quantum counterpart is the von Neumann entropy,[21]

$$S(\boldsymbol{\rho}) = -k\mathrm{Tr}(\boldsymbol{\rho} \ln \boldsymbol{\rho}) = -k \sum_{i=1}^{n} w_i \ln w_i \tag{17}$$

where $\boldsymbol{\rho}$ is an $n \times n$ density matrix satisfying $\mathrm{Tr}(\boldsymbol{\rho}) = 1$ and the w_i are its eigenvalues [as density matrices are positive semidefinite, it is always true that $w_i \geq 0$; note also that the eigenvalues of $\boldsymbol{\rho}$ are the statistical weights of the pure states that are mixed in it and satisfy $\Sigma_i w_i = \mathrm{Tr}(\boldsymbol{\rho})$]. The von Neumann entropy is the Shannon entropy of the spectrum of $\boldsymbol{\rho}$ and varies from zero for pure states to $k \ln n$ for $\boldsymbol{\rho} = \mathbf{I}_n/n$, the maximally mixed state.[20]

Like the Shannon entropy, the von Neumann entropy is a functional of a state (in quantum mechanics, a state is a density matrix), possesses a number of useful mathematical properties,[22] and can be singled out from several possible definitions of entropy by natural requirements. In the case of the von Neumann entropy, an important "natural requirement" is that it be the smallest entropy among all of those that could be defined as the Shannon entropy of the probability distribution for the eigenvalues of some observable.[20]

Now let us recall some of the quantities involved in the determination of the canonical mechanisms of a collision. We had two intrinsic density matrices, **R** and **P**, whose nonzero eigenvalues coincide.[23] These eigenvalues—the canonical DCSs—give the probabilities (strictly speaking, differential cross sections) that each canonical mechanism will contribute to the overall collision. Therefore, we can use the canonical DCSs to define the intrinsic von Neumann entropy of a molecular collision; we shall refer to it as the *intrinsic entropy* of the collision.

The only, and very slight, complication is the following: as defined in eqs 11 and 12, **R** and **P** do not have unit trace; their eigenvalues, the canonical DCSs, do not add to 1. To deal with this all one needs to do is renormalize the intrinsic density matrices so as to have $\mathrm{Tr}(\mathbf{R}) = \mathrm{Tr}(\mathbf{P}) = 1$. We can then define the intrinsic entropy as

$$S = -k \sum_{i=1}^{N_{\mathrm{can}}} w_i \ln w_i \tag{18a}$$

$$k = (\ln N_{\mathrm{can}})^{-1} \tag{18b}$$

$$w_i = \frac{1}{s} \frac{\mathrm{d}\sigma_i^{(\mathrm{can})}}{\mathrm{d}\omega} \tag{18c}$$

$$s = \sum_{i=1}^{N_{\mathrm{can}}} \frac{\mathrm{d}\sigma_i^{(\mathrm{can})}}{\mathrm{d}\omega} \tag{18d}$$

where N_{can} is the number of canonical collision mechanisms and the choice of k value, eq 18b, was made so that we have 1 as the maximum S value (normalization ensures that the minimum value is $S = 0$). Note also that eq 18b, together with the normalization of the intrinsic density matrices to unit trace, implies that the entropy as defined here is as a dimensionless quantity.

Like the other properties associated with canonical collision mechanisms, the intrinsic entropy is an intrinsic property of the collision. It gives us direct information about the dynamical transformation—in this case, about the extent to which the collision favors or disfavors particular canonical mechanisms, particular pairs of canonical reagent and product states, and particular pairs of correlated reagent and product polarizations. Note also that the intrinsic entropy is entirely defined by the eigenvalues of the intrinsic density matrices, **R** and **P**. Explicit consideration of the canonical reagent and product states (the eigenvectors of **R** and **P**, respectively) is not required.

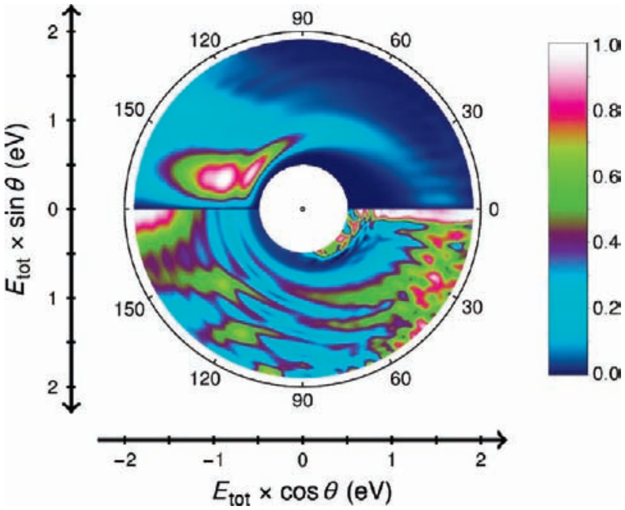

Figure 2. Cylindrical−coordinate plots of the differential cross section (top half) and intrinsic entropy (bottom half) of the $H + D_2(v = 0, j = 1) \rightarrow HD(v' = 0, j' = 1) + D$ reaction as a function of total energy (radius) and scattering angle (cylindrical angle). The DCS was multiplied by the volume element, sin θ. The color indicates the value of each quantity as a fraction of its maximum value over all energies and scattering angles (the numerical value of the maximum is unspecified for the DCS, and $S = 1$ for the intrinsic entropy).

3. Example: The $H + D_2$ Reaction

We have written that use of the intrinsic entropy allows one (i) to bypass the explicit consideration of molecular polarizations in the analysis of the sensitivity of a collision to stereodynamical parameters and (ii) to quantify that sensitivity. We shall now provide illustration of those points, taking as our example the

$$H + D_2(v,j) \rightarrow HD(v',j') + D \tag{19}$$

isotopic variant of the hydrogen-exchange reaction (v and j are vibrational and rotational angular momentum quantum numbers, respectively). As "the simplest of chemical reactions", the H_3 system has long been regarded as a very important benchmark in studies of reaction dynamics, and in particular as the first choice for tests of new approaches to the problem. This has led to a large number of accurate experimental and theoretical results, to a thorough description of many aspects of its dynamics[13] and in particular to recent interesting insights into the collision mechanisms.[24−28] Its stereodynamics is less well characterized.[11]

The results we present below have used as input the scattering matrices obtained in previously reported time-independent quantum scattering calculations run on the BKMP2 potential energy surface.[29,30] We ask our readers to consult the original papers if they are interested in details of the scattering calculations or potential energy surface.

Let us now turn to the examples. Figure 2 shows data for the reaction of eq 19 when $v = v' = 0$ and $j = j' = 1$. The figure is as follows:

- The data plotted are the DCS (in arbitrary units, so that it can be considered as the sum or as the average of the canonical DCSs) and the intrinsic entropy as functions of the total energy and the scattering angle (respectively, E_{tot} and θ).
- The plot uses cylindrical coordinates.
- The radius is the total energy. Its maximum value is 1.9 eV. The outermost, black circle appears at $E_{tot} = 2$ eV.
- The cylindrical angle is θ. Its value ranges from 0 to 180°. The directions associated with particular θ values are identified by the tics on the outermost, black circle.
- In the top half of the plot, z is the DCS multiplied by the volume element, sin θ.
- In the bottom half of the plot, z is the intrinsic entropy, S.
- The color indicates the value of each quantity as a fraction of its maximum value. In the top half, the maximum is the largest value of DCS × sin θ over all energies and scattering angles. In the bottom half, the maximum value is always $S = 1$.

One sees, for instance, that the DCS (top half of the plot) is relatively large in the $135° < \theta < 180°$, $0.5 \text{ eV} < E_{tot} < 1.5$ eV region; note that the figure only provides relative DCS magnitudes—the actual DCS values are not specified. One also sees that in the $\theta \approx 0$, $E_{tot} \approx 0.75$ eV region the intrinsic entropy (bottom half of the plot) quickly changes from its minimum ($S = 0$) to its maximum ($S = 1$) value; note that here the figure does provide the absolute S value (its maximum is always $S = 1$). Let us now raise some questions that can be answered by inspection of Figure 2 and others similar to it.

Where Is the Reaction Most Sensitive to Molecular Polarization? The answer is, where $S \rightarrow 0$. Inspection of Figure 2 reveals that this happens in three qualitatively distinct cases.

The first case appears near or below the total energy threshold ($E_{tot} \lesssim 0.65$ eV). This observation is not difficult to rationalize. Near the threshold, tunneling is important. As the tunneling probability quickly decays with barrier height and width, and both of them depend on the approach and recoil geometries, the reaction probability is highly sensitive to molecular polarization. Alas, the DCS in this region is small.

The second case appears when the total energy is large and the scattering angle is in the $\theta \approx 60−150°$ interval. In this region the intrinsic entropy has several local minima, but they appear where the DCS is negligibly small.

The third case is the most interesting. In a narrow total energy interval centered at $E_{tot} \approx 0.85$ eV, the intrinsic entropy approaches $S = 0$ throughout the $\theta \approx 120−180°$ region. In this region the DCS is large. In fact, the two most prominent maxima of the DCS lie close to each other and are separated precisely by the low-entropy region we have identified (see Figure 3 for a more detailed view). As there is no obvious reason why this should happen, this region would be a good target for the investigation of molecular polarization effects.

Where Is the Reaction Least Sensitive to Molecular Polarization? The answer is, where $S \rightarrow 1$. Inspection of Figure 2 reveals that this happens in the forward scattering, $\theta \approx 0$ region. Because of the multiplication of the DCS by sin θ, Figure 2 does not allow for visualization of the DCS in this region. We note, however, that what happens there is well-known:[13] the DCS features very fast oscillations that are due to interference effects. The information we get from Figure 2 is that the interference effects involve all of the canonical states.

In General, How Sensitive to Molecular Polarization Is the Reaction? Inspection of Figure 2 reveals that in the regions where the reaction probability is large the value of the intrinsic entropy is $S \approx 0.1−0.5$. These values seem surprisingly low (and, therefore, the stereodynamical selectivity seems surprisingly high) for a reaction that no chemist would normally think of as susceptible to pronounced steric effects. In fact, the explanation is simple. Because we are considering a $j = j' = 1$ case, we have only three reagent polarization states (three "p orbitals"), only three product polarization states (three "p orbitals" again), and only three canonical collision mechanisms.

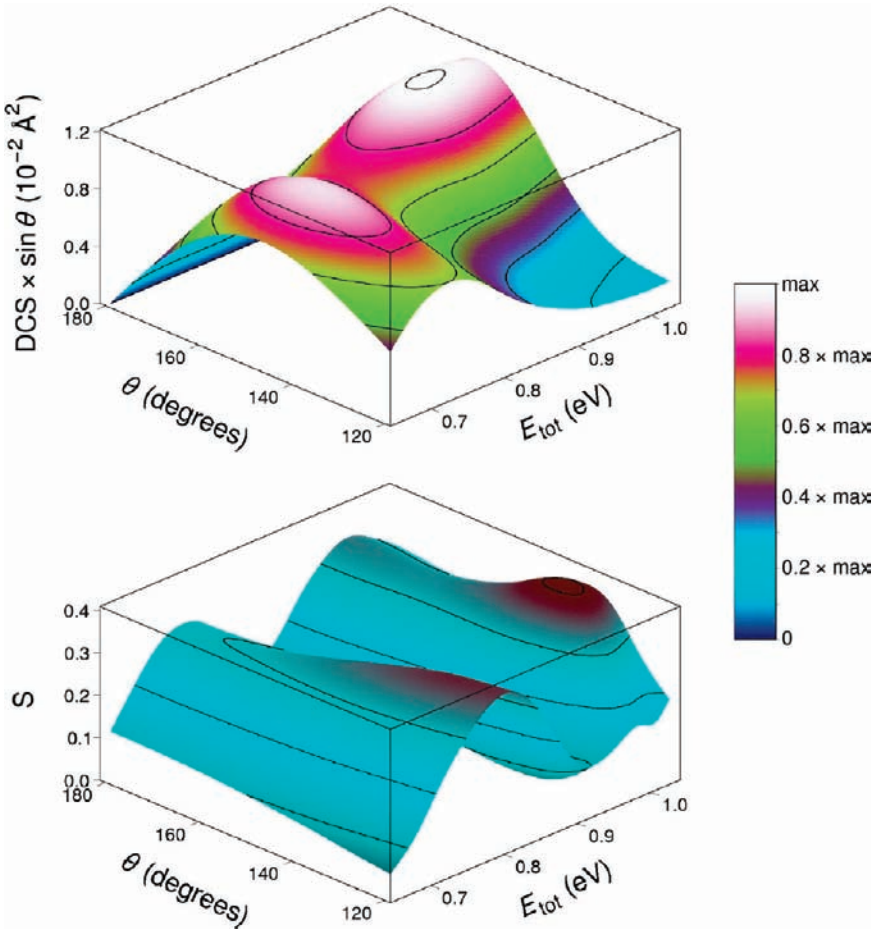

Figure 3. A different view of the DCS (top) and intrinsic entropy (bottom) of Figure 2 in the $E_{tot} = 0.65-1.05$ eV, $\theta = 120-180°$ region. The two close-lying DCS × sin θ maxima are separated by a region where the intrinsic entropy is very low. Colors as in Figure 2.

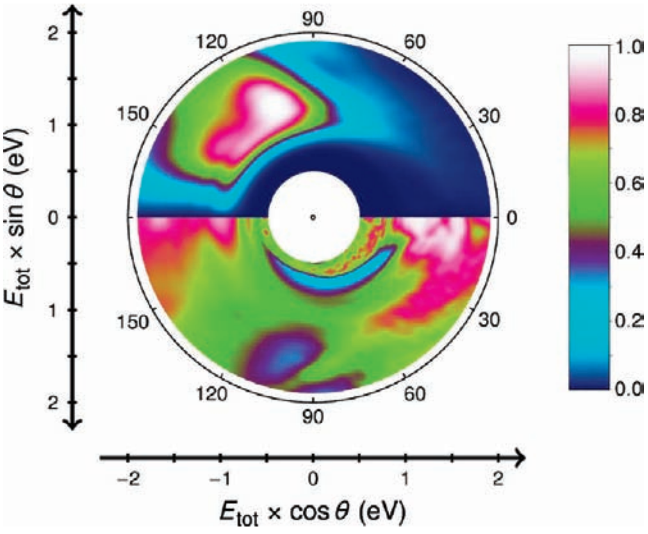

Figure 4. As Figure 2, but for the H + $D_2(v = 0, j = 5) \rightarrow$ HD$(v' = 0, j' = 5)$ + D reaction.

Each of the canonical mechanisms involves states that in a sense are very different from the others. This large difference between the canonical states, and the small number of them, explain the low intrinsic entropy, which is not so surprising after all. If the reaction involved a larger number of canonical mechanisms, the typical entropy should be higher. And this is indeed the case, as one can see by inspecting Figure 4. The plots there are as in Figure 2, but the initial and final angular momentum quantum numbers were changed to $j = j' = 5$. In this case there are 11 reagent polarization states, 11 product polarization states, and therefore 11 canonical mechanisms. As expected, the intrinsic entropy is invariably larger than in the $j = j' = 1$ case. One finds that $S > 0.5$ wherever the DCS is not negligible.

How Does the Sensitivity to Molecular Polarization Change with Reagent and Product States? We have seen that if the number of canonical mechanisms increases, the sensitivity to molecular polarizations decreases. But what if the number of canonical mechanisms stays constant while reagent and/or product quantum numbers change?

Figure 5 presents two examples involving change of rotational quantum number. The situation is as in Figure 2 (where we had $v = v' = 0$ and $j = j' = 1$), except that either the reagent or else the product rotational quantum number (not both) has been increased to 5. In the $j = 1, j' = 5$ case there are eight product states that are not formed, whereas in the $j = 5, j' = 1$ case there are eight reagent polarization states that do not react. In either case we have three canonical mechanisms, three reagent states that do react, and three product states that are actually formed.

Comparison of the top panel of Figure 5 to Figure 2 shows that when only the product rotational quantum number is changed, the intrinsic entropy values associated with relatively large DCSs do not change appreciably; one finds $S \approx 0.2-0.5$. On the other hand, comparison of the bottom panel of Figure 5 to Figure 2 shows that when the reagent rotational quantum number is the one that increases, the intrinsic entropy increase is significant; where the DCS is large, we now find $S \approx 0.6-0.9$. If we assume that other aspects of

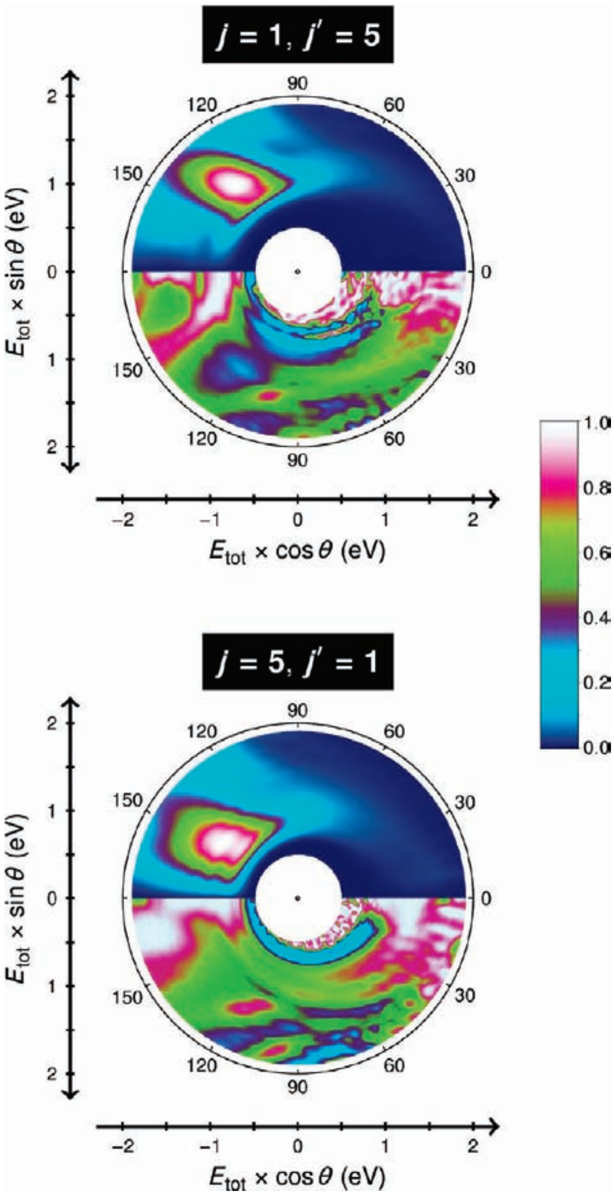

Figure 5. As Figure 2, but for the H + $D_2(v = 0, j) \rightarrow HD(v' = 0, j')$ + D reaction with $j = 1$ and $j' = 5$ (top panel) or $j = 5$ and $j' = 1$ (bottom panel).

the dynamics are less important, the indication is that the reaction we are considering is more sensitive to HD than to D_2 polarization [note that although we are assuming D_2 to be a reagent and HD a product, the results we are presenting in this section also apply to the reverse reaction, D + $HD(v', j') \rightarrow D_2(v, j)$ + H].

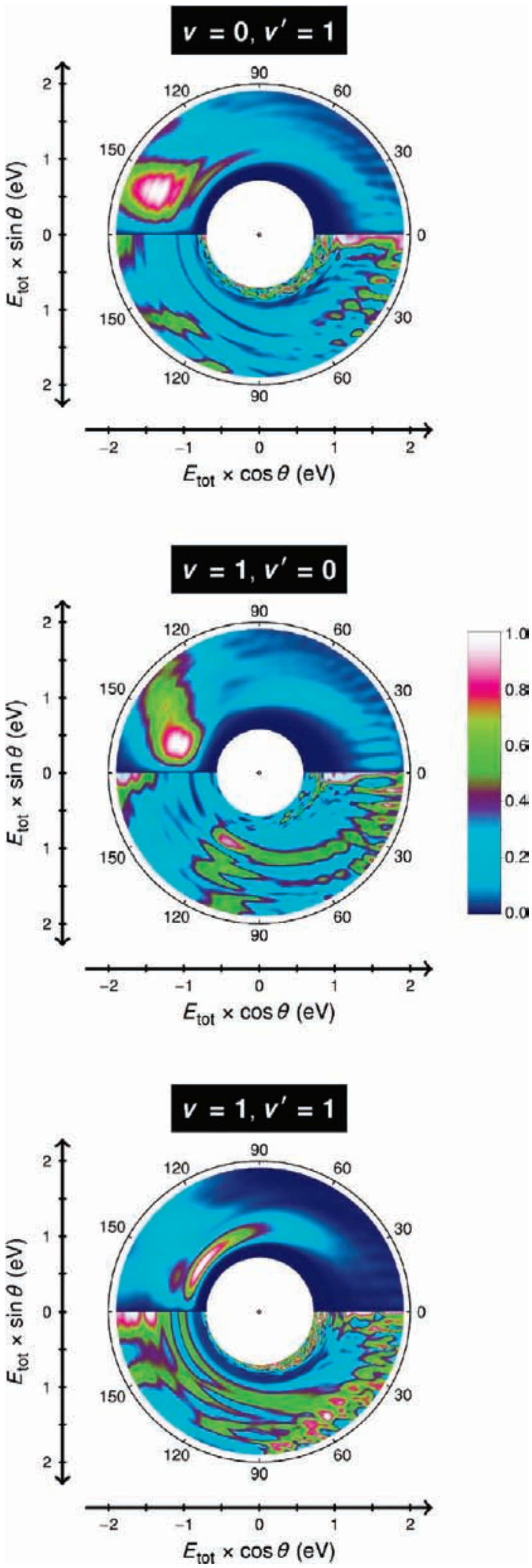

Figure 6. As Figure 2, but for the H + $D_2(v, j = 1) \rightarrow HD(v', j' = 1)$ + D reaction with $v = 0$ and $v' = 1$ (top panel), $v = 1$ and $v' = 0$ (middle panel) or $v = v' = 1$ (bottom panel).

As our last example, let us consider changes of vibrational quantum number. Figure 6 presents cases that again are similar to that of Figure 2 (where we had $v = v' = 0$ and $j = j' = 1$), except that we have added one quantum of vibration to the product diatomic (top panel of Figure 6), to the reagent diatomic (middle panel), or to both (bottom panel). Note that in all these cases the number of canonical mechanisms is $2j + 1 = 2j' + 1 = 3$. The $v \neq v'$ cases (top and middle panels of Figure 6) are the most striking. Where the DCS is large the intrinsic entropy is very low; the typical values are in the $S \approx 0-0.3$ interval. Furthermore, they share a feature that is quite distinct from what we have discussed so far. At $E_{tot} \approx 1-1.6$ eV, the DCS has a moderate-intensity tail that spreads all the way from the backward ($\theta > 90°$) to the forward ($\theta < 90°$) hemisphere. This tail is associated with high intrinsic entropy, $S \approx 0.6-0.9$ in the $v = 1$, $v' = 0$ case. Although this sort of DCS tail has attracted considerable attention in the past,[13,31] it is something of a surprise to find it associated with a pronounced loss of selectivity with respect to molecular polarizations.

4. Summary and Outlook

The intrinsic entropy, S, of a molecular collision is the von Neumann entropy of the intrinsic density matrices of reagents and products. Because it quantifies the distribution of the collision probability over the independent, canonical mechanisms of the collision (each of them associated with a correlated pair of pure reagent and product polarization states), it is a quantitative indicator of the sensitivity of the collision to the reagent and product polarizations. When the intrinsic entropy reaches its lower or upper limit, $S = 0$ or $S = 1$, that sensitivity is, respectively, maximum or nonexistent.

The intrinsic entropy is an interesting sensitivity quantifier not only because it is a single, dimensionless number lying in a well-defined range, but also because its evaluation does not require explicit consideration of molecular polarizations. As demonstrated through exam of examples concerning state-to-state $H + D_2$ reactions, this makes the intrinsic entropy useful also as a simple "filter" of the large amount of data one normally is confronted with in stereodynamical studies.

Through cursory inspection of a few plots in which we contrasted the differential cross section of a state-to-state $H + D_2$ reaction to its intrinsic entropy, we could easily locate regions of the parameter space (more specifically, total energy and scattering angle values) where pronounced polarization effects take place, regions where such effects are of little relevance, and trends associated with change of the asymptotic vibrational and angular momentum quantum numbers. Had we tried to do that through explicit consideration of molecular polarizations, the task would have been challenging.

Consider, for example, the simplest of our examples: those involving reagents and products with a single quantum of rotational excitation (that is, $j = j' = 1$). In these cases, the polarizations of reagents and products are each determined by four polarization moments (one component of the rank-1 polarization tensor, three components of the rank-2 polarization tensor[32]), all of them having values dependent on the choice of reference frames. Let us assume that under a particular combination of energy and scattering angle there is maximum selectivity with regard to molecular polarizations: there is a single reagent (product) state that reacts (is formed), and reagent (product) states with polarizations orthogonal to that do not react (are not formed) at all. In terms of the intrinsic entropy, this is an $S = 0$ situation. In terms of polarization moments, the situation is not immediately obvious: some polarization moments may have large magnitude, other may be small or even zero.[33] It is not necessarily the case that at least one of the polarization moments must reach one of the extremes of its range of allowed values, and if one or more of the polarization moments do reach an extreme value, that does not necessarily imply that the reaction proceeds through a single pair of reagent and product polarization states. Even by simultaneously considering eight polarization moments, without further analysis one cannot conclude that this is a case of maximum sensitivity to molecular polarization. And this is a simple case: if the angular momentum quantum numbers were $j = j' = 5$, one might have to consider as many as sixty polarization moments for reagents and sixty more for products. The bottom line is this: a set of polarization moments is a set of numbers that collectively provide direct quantification of molecular polarization, but not direct quantification of the sensitivity of a collision to molecular polarization. This is done by the intrinsic collision entropy.

Studies of collision stereodynamics have long proved fertile ground for the development of innovative theoretical approaches. Past examples include the concept of the chemical shape of colliding molecules,[6] the stereodirected representation of the scattering,[34] the decomposition of the scattering amplitude into near-side and far-side components,[35] and others.[5,9,36,37] Like all of those, the theory of canonical collision mechanisms (and the intrinsic entropy concept as part of it) has its advantages and disadvantages.

There are two main advantages. First, the theory of canonical collision mechanisms is formulated in rigorously quantum mechanical terms; it requires no approximation, classical, semiclassical, or otherwise. Second, it is entirely developed in terms of intrinsic collision properties; for this reason, it provides direct insight into the transformation that is effected by the collision. The second advantage, however, can be seen as a disadvantage: the predictions of the theory are not directly observable. Intrinsic properties cannot be directly measured. Instead, they must be inferred from the correlation between extrinsic and observable collision properties. Albeit not impossible, in general the task is experimentally difficult. We note, however, that the canonical mechanisms theory does lead to explicit predictions about possible and not-too-difficult experimental observations (indeed, we have seen a few in this article).

We conclude with a brief consideration of possible extensions of our approach. For good reasons, information theory uses a plethora of entropy definitions.[38] Some of these may be very helpful in further characterizing the relations between the asymptotic states of a collision system. Relative entropies, in particular, have caught our attention; that happened because of their usefulness in characterizing the geometry of the space of states, and in particular because relative entropies are related to the metric of this space.[20] Consider, for instance, the observation we made in section 3 regarding the "large differences" among the asymptotic canonical states when we only had three canonical mechanisms. Those "differences" are not related to the overlap between canonical states (canonical state are always orthogonal[12]), but rather to some sort of geometric distance. Characterization of the geometry of the space of states associated with a collision is a project of interest to us, and we expect to report on it in the future.

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