SIMPLE MODEL FOR Λ-DOUBLET PROPENSITIES IN BIMOLECULAR REACTIONS

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A simple geometric model is presented to account for Λ-doublet propensities in bimolecular reactions $A+BC \rightarrow AB+C$. It applies to reactions in which AB is formed in a Π state, and in which the unpaired molecular orbital responsible for Λ-doubling arises from breaking the B–C bond. The Λ-doublet population ratio $\Pi(A'):\Pi(A'')$ is predicted to be 2:1 provided that; (1) the motion of A in the transition state [ABC] determines the plane of rotation of AB; (2) the unpaired π orbital lying initially along the BC bond may be resolved into a projection onto the AB plane of rotation, which correlates with $\Pi(A')$, and a projection perpendicular to this plane, correlating with $\Pi(A'')$; (3) there is no preferred geometry for dissociation of [ABC]. The 2:1 Λ-doublet ratio is the "unconstrained dynamics prior" Λ-doublet distribution for such reactions.

1. Introduction

The electron configuration of a linear molecule in a Π state must be of the form π or π^3; in either case, there is an unpaired π orbital lying perpendicular to the internuclear axis. In the nonrotating linear molecule, the electronic angular momentum makes a projection on the internuclear axis of $\Lambda=1$, and the Π state is doubly degenerate due to the two possible directions of this projection [1,2]. If the molecule also rotates, interaction of the molecular rotational angular momentum with the electronic angular momentum splits this degeneracy, giving rise to two different energy levels, the Λ-doublet levels. In the limit of large molecular rotation, the unpaired π orbital acquires an additional symmetry with respect to reflection in the plane of rotation (see fig. 1). If this orbital is unchanged by reflection in the plane of rotation, the Π state Λ-doublet level is designated [3] as $\Pi(A')$; if it changes sign, it is called $\Pi(A'')$.

The $\Pi(A'):\Pi(A'')$ population ratio has a statistical prior of 1:1, based on the small size of the Λ-doublet splitting (typically less than 1 cm^{-1}) compared to thermal energies. However, numerous photodissociation and reactive scattering studies show that the Λ-doublet population ratio may deviate substantially from unity [3,4]. This is usually interpreted as resulting from some dynamical preference
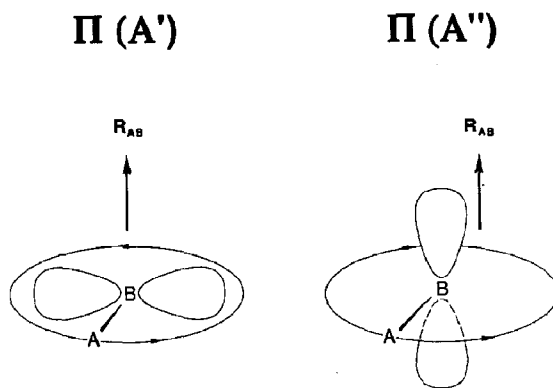

Fig. 1. The Λ-doublet components of a Π molecule in the high J limit.

for planar versus nonplanar breakup of the complex in photodissociation or reactive scattering. If a bond breaks to form an unpaired orbital on one of the resulting fragments, the lobes of this orbital are expected to point initially along the line of the broken bond. On the other hand, angular motion of the fragment in the complex during the bond breaking would lead to rotation of the fragment after the dissociation is completed. Thus, the orientation of the plane of rotation relative to the unpaired π orbital of the fragment gives information about the motion of A rel-

ative to the breaking bond during the dissociation.

Recently, several attempts have been made to describe theoretically the preference for population of different Λ-doublet levels (the Λ-doublet propensity) in specific systems. The methods used include both quasiclassical trajectory calculations [5] and quantum scattering calculations [6] on ab initio surfaces. In this Letter we present a simple geometrical model to describe the formation of the two Λ-doublet levels in the limit of large product rotation (high J limit) in a bimolecular reaction. We show that under a set of not too restrictive conditions the high J $\Pi(A'):\Pi(A'')$ population ratio is 2:1. This result can be used as a "reference state" which we call the "unconstrained dynamics prior". Deviations from the predicted ratio imply dynamical preferences in the reaction, e.g., restricted motion in the breakup of the collision complex. We compare the predictions of this model to the results of several experimental studies involving H-atom reactions.

2. Theory

Consider a bimolecular reaction that leads to the breakup of a triatomic [ABC] transition state to form products AB and C such that the diatomic product AB is formed in a Π state with the unpaired π orbital on AB arising from the breaking of the BC bond (later this triatomic case will be generalized). We describe the geometry of [ABC] as shown in fig. 2. The A atom is bonded to B at a distance r, and moves within the complex with instantaneous velocity vector v_A (which has components $v_\parallel$ and $v_\perp$, parallel and perpendicular to the AB bond axis). The AB bond and the velocity vector v_A determine the xy plane of the molecular coordinate system. The position of C is described by the angles θ and ϕ as shown.

The model we describe applies to any reaction that proceeds through such a transition state provided that the following three conditions are met:

(1) the plane of rotation of the AB product is determined by the motion (instantaneous velocity) of the A atom within the [ABC] transition state;

(2) the unpaired π orbital lying initially along the BC bond may be resolved into a projection onto the AB plane of rotation, which correlates with $\Pi(A')$, and a projection perpendicular to this plane, which
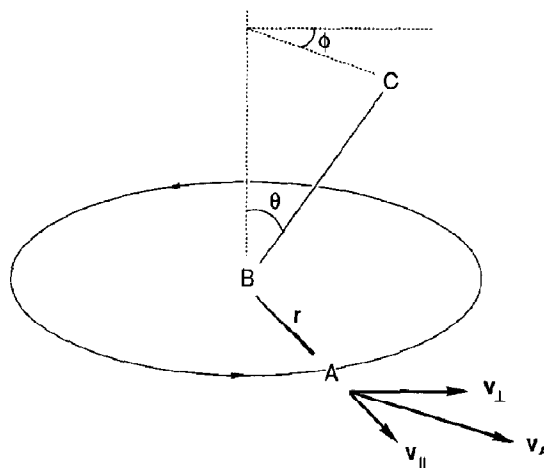

Fig. 2. The geometry of the [ABC] transition state. The instantaneous velocity vector of the A atom (v_A) and its components parallel and perpendicular to the AB bond axis ($v_\parallel$ and $v_\perp$) are shown. Atoms A and B are separated by distance r, and the plane of motion of A about B is indicated. The AB bond axis and v_A define the xy plane of the molecular coordinate system. C is oriented at angles θ and ϕ.

correlates with $\Pi(A'')$, as C separates from AB;

(3) there is no "preferred" orientation of C relative to AB for breakup of the transition state to occur, i.e. all angles θ and ϕ are equally likely in [ABC].

Condition (1) is important for our model, and can be brought about in a number of ways. For example, if the atom A is much lighter than the atom B ($m_A/m_B \ll 1$), then the force exerted on AB by the breaking BC bond is nearly on the center of mass of AB, and the resulting torque will be small. Thus the AB angular momentum will be determined primarily by the motion of A within the complex (specifically, by the component $v_\perp$ of v_A), and condition (1) will hold. Alternatively, if the A atom moves very rapidly within the complex (which is also facilitated if $m_A \ll m_B$), or if the forces exerted during the dissociation are weak, then the rotation of AB will also arise primarily from the motion of A. Because we are interested in the high J limit, we exclude the cases of small or zero $v_\perp$, as this would not lead to formation of AB with high J.

The breaking of the BC bond is taken to be as indicated in fig. 3. We describe in the following way the formation of the Λ-doublet levels in the high J limit. The unpaired π orbital on the AB molecule is
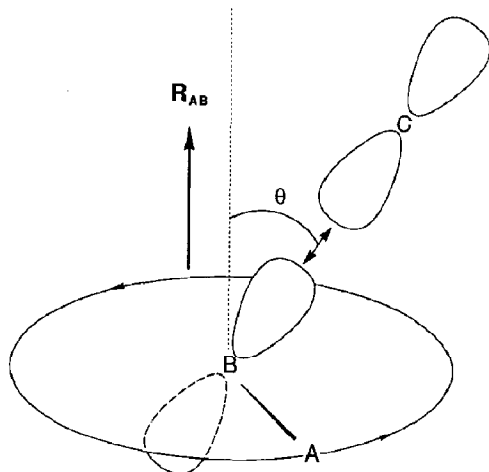
Fig. 3. Breakup of the [ABC] transition state. The axis of the broken BC bond (which is the axis of the unpaired π orbital on B) makes an angle θ with the AB fragment's nuclear rotational angular momentum vector, where θ is the angle of orientation of C with respect to the AB axis upon dissociation.

localized on the B atom and correlates asymptotically with the broken BC bond, making an angle θ with the AB rotational angular momentum vector $\mathbf{R}_{AB}$ as shown. This orbital orientation can be described as a linear combination of the limiting cases of the orbital oriented parallel or perpendicular to the plane or rotation of AB, i.e. of the two Λ-doublet levels. Thus, the wavefunction of the final state of the AB molecule will be a linear combination of the two Λ-doublet wavefunctions, as shown in fig. 4:

$$\Psi_{final} = a' [\Pi(A')] + a'' [\Pi(A'')], \qquad (1)$$

where the coefficients a' and a'' are the contribu-

tions from each Λ-doublet level to the final state. The contribution from the A' Λ-doublet level (π orbital parallel to the AB plane of rotation) will be just the projection of the axis of the π orbital onto the plane of rotation, i.e. $a' = \sin \theta$, whereas the contribution from the A'' Λ-doublet level (π orbital perpendicular to the AB plane of rotation) will be the projection of the π orbital onto an axis perpendicular to this plane (i.e. the axis of rotation), $a'' = \cos \theta$. Condition (2) implies that the projections a' and a'' remain unchanged throughout the dissociation.

In this discussion we have assumed that any projection of the forming unpaired π orbital (the breaking BC bond) onto the AB plane of rotation corresponds to a contribution from the A' Λ-doublet level. Initially, this projection may not be perpendicular to the AB axis. However, since the unpaired π orbital and the AB bond axis must be perpendicular in the final state of AB, we assume that the π orbital and the AB bond can reorient during the dissociation by the processes of rearrangement of the π orbital electron cloud and rotation of A about B (the latter facilitated by the rapid motion of A with respect to B and C). Any such reorientation would not affect the values of a' and a'': rotation of A about B does not change the position of the BC bond axis relative to the plane of rotation of AB, while condition (2) implies that rearrangement of the electron cloud would not mix A' and A'' states.

However, for some A+BC systems, such reorientation may not be possible for all [ABC] dissociation configurations. If reorientation is difficult or impossible for a given configuration, this can indicate that dissociation from that configuration is restricted or unallowed (in contradiction to condition (3)). Indeed, restriction of dissociation from cer-
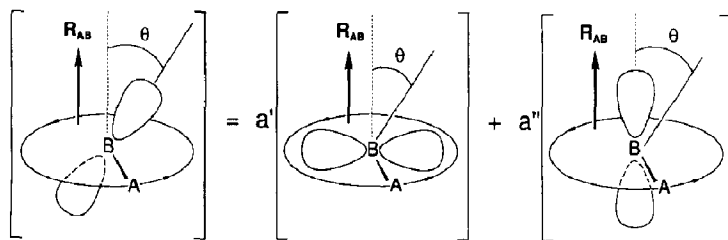

Fig. 4. Decomposition of the unpaired π orbital on AB into a linear combination of the wavefunctions of the two Λ-doublet levels.

tain transition state geometries leads to a predictably different result for the Λ-doublet ratio (see discussion in section 3).

Condition (3) dictates that there is no correlation between the position of C (or, equivalently, the motion of A) and the probability of dissociation. This case can be regarded as the "unbiased" case for breakup of the [ABC] transition state in the sense that the distribution of dissociation orientations will be random and unconstrained. Under these conditions, a simple heuristic argument correctly predicts the resulting Λ-doublet population ratio. Referring to fig. 2, we let the AB bond axis and the A atom velocity vector define the xy plane of the molecular coordinate system. As B and C separate, the unpaired π orbital on AB points along the BC axis (see fig. 3). The position of this orbital can be described as a linear combination of projections of its position vector on three mutually perpendicular axes in this system, two of which (x and y) lie in the plane of motion of A about B (which eventually becomes the plane of rotation of the AB fragment), and one of which (z) is perpendicular to this plane. Two of these three projections have the π orbital in the plane of rotation of AB, corresponding to the A' Λ-doublet level, while one projection has the orbital perpendicular to the AB plane of rotation, corresponding to the A" Λ-doublet level. Since the orientation of [ABC] upon dissociation is random (no preferred orientation), we would expect equal contributions from each of the three possible mutually perpendicular configurations when averaged over all possible [ABC] geometries. These considerations lead us to anticipate a Λ-doublet population ratio in the high J limit of

$$\Pi(A'):\Pi(A'')=2:1 . \tag{2}$$

The process of Λ-doublet formation is thus equivalent to randomly selecting in 3-D space a vector (the direction of the unpaired π orbital) and measuring its projection on a given plane (the AB plane of rotation). Because in 3-D there exist two degrees of freedom within a plane and one degree of freedom perpendicular to that plane, a randomly selected vector should, on average, have its projection in the plane and its projection perpendicular to the plane in the ratio 2:1. This result can also be obtained rigorously, as shown in the Appendix.

Our model thus predicts a Λ-doublet population

ratio of 2:1 in the high J limit for any reaction that satisfies the three conditions listed above. Note that this preference for the A' Λ-doublet level arises purely from geometrical considerations assuming a simple unconstrained model for the dynamics: no orientation preference in the breakup of [ABC]. In this model, the A' level is preferentially populated simply because, geometrically, more [ABC] dissociation trajectories have in-plane character than out-of-plane character (*not* because trajectories with in-plane character are preferred). Thus, the 2:1 Λ-doublet population ratio may be regarded as the prior Λ-doublet distribution for this type of bimolecular reaction. We call this Λ-doublet population propensity the *unconstrained dynamics prior*.

The key feature in this model is how the [ABC] transition state decomposes, not how it was formed. Thus, this model can be applied to either of the bimolecular reactions, $A+BC$ and $B+AC$, and it is valid both for direct reactions and for reactions that proceed via a long-lived complex. It can also describe unimolecular decompositions (e.g. photodissociation of the molecule ABC), provided that conditions (1)–(3) hold for the excited molecule. Further consideration shows that this model can be generalized to include cases where A and/or C consist of more than one atom provided that the three conditions listed above are satisfied.

3. Comparison to experiment

To test our model, we have collected in table 1 the observed OH (OD) Λ-doublet population ratios in the high J limit for reactions of the type $H(D) + OQ \rightarrow OH (OD) + Q$. We chose this class of reactions because the OH (OD) product is often formed with high rotational angular momentum, making classification into $\Pi(A')$ and $\Pi(A'')$ most meaningful [3]. Moreover, the lightness of the H (D) atom relative to the O atom, combined with its high velocity (especially for hot H or D atoms), lead us to expect that the motion of H (D) determines the plane of rotation of the OH (OD) product, as our model requires.

Table 1 shows that for many reactions, the observed $\Pi(A'):\Pi(A'')$ ratio is near or equal (within experimental error) to our predicted ratio of 2:1. Our

Table 1
Experimentally observed Λ-doublet population ratios in the high J limit for H-atom reactions

Reaction	Product probed	$\Pi(A')/\Pi(A'')$	Ref.
$H+O_2 \rightarrow O+OH$,	$OH(^2\Pi_{3/2}, v=0)$	2.06 ± 0.11	[7]
$E(H)=1.6$ eV	$OH(^2\Pi_{3/2}, v=1)$	1.93 ± 0.09	[7]
	$OH(^2\Pi_{1/2}, v=0)$	1.72 ± 0.15	[7]
	$OH(^2\Pi_{1/2}, v=1)$	1.84 ± 0.16	[7]
$H+O_2 \rightarrow O+OH$,	$OH(^2\Pi_{3/2}, v=0)$	2-3	[5]
$E(H)=1.0, 1.9,$			
$2.1, 2.3, 2.5$ eV			
$H+N_2O \rightarrow N_2+OH$	$OH(^2\Pi_{3/2,1/2}, v=0)$	1.8 ± 0.4	[8]
$E(H)=1.9$ eV			
$D+OCS \rightarrow OD+CS$,	$OD(^2\Pi_{3/2}, v=0)$	2.17 ± 0.22 [a]	[9]
$E(D)=2.5$ eV	$OD(^2\Pi_{1/2}, v=0)$	1.98 ± 0.19 [a]	[9]
$H+CO_2 \rightarrow OH+CO$,			
$E(H)=2.5$ eV	$OH(^2\Pi_{3/2,1/2}, v=0, 1)$	1.06 ± 0.21 [a]	[10]
$E(H)=1.86$ eV	$OH(^2\Pi_{3/2, 1/2}, v=0)$	0.98 ± 0.17	[11]
$H+NO_2 \rightarrow OH+NO$,	$OH(^2\Pi_{3/2,1/2}, v=0, 1)$	1.5 ± 0.2	[12]
$E(H)=$ thermal			
$H+ClO_2 \rightarrow OH+ClO$,	$OH(^2\Pi_{3/2,1,2}, v=0, 1)$	1.3 ± 0.3	[12]
$E(H)=$ thermal			

[a] Computed from the data given.

model offers a rationalization for these observations, including the results of our recent study [7] of the reaction $H+O_2 \rightarrow OH+O$. Indeed, this model correctly predicts the observed Λ-doublet propensity for all the hot H-atom reactions except one.

Deviations from our unconstrained dynamics prior do occur. For example, $H+CO_2 \rightarrow OH+CO$ has a Λ-doublet population ratio of about 1:1. One possible interpretation of this result is as follows. If [ABC] dissociates from a linear geometry, we expect the A' Λ-doublet to be formed exclusively, since in this case the BC bond lies in the plane of rotation of AB (see figs. 2 and 3). On the other hand, for dissociation from highly bent geometries where the ABC bond angle is nearly 90° and the motion of A is unconstrained, we expect equal contributions from A' and A''. Thus, the observed Λ-doublet population ratio for $H+CO_2$ may indicate a preference for decomposition of the [HOCO] transition state from a bent geometry that falls apart equally well for any motion of H.

In conclusion, we have developed a simple geometric model to predict Λ-doublet population ratios in bimolecular reactions forming products in Π elec-

tronic states. The model gives the ratio of 2:1 as the prior distribution for the $\Pi(A'):\Pi(A'')$ ratio in the high J limit, based on the fact that, in a random distribution of dissociation geometries, more configurations will lead to the A' Λ-doublet level than the A'' Λ-doublet level. Our model correctly predicts the experimental Λ-doublet distribution for a number of H-atom reactions. We can also interpret Λ-doublet distributions that differ from the unconstrained dynamics prior in terms of preferred or restricted dissociation geometries, so that, using this model, we can gain new insight into the dynamics of reactions of this type.

Acknowledgement

Appendix. Calculation of the $\Pi(A')/\Pi(A'')$ population ratio for unconstrained dynamics

Our model describes the probability to form either Λ-doublet level for a given [ABC] dissociation geometry. From eq. (1), this probability (denoted P' or P'', for the A' or A'' Λ-doublet level) is given by

$$P' = (a')^2 = \sin^2\theta, \quad P'' = (a'')^2 = \cos^2\theta . \quad (3)$$

To predict an experimental Λ-doublet distribution we must average this probability over all possible geometries (i.e. all r, θ and ϕ). This averaged probability, which we denote P_T, is given by

$$P_T = \frac{\int_r \int_\theta \int_\phi J(r, \theta, \phi)\, dr\, d\theta\, d\phi\, S(r, \theta, \phi)\, P(r, \theta, \phi)}{\int_r \int_\theta \int_\phi J(r, \theta, \phi)\, dr\, d\theta\, d\phi\, S(r, \theta, \phi)} , \quad (4)$$

where $J(r, \theta, \phi)$ is the Jacobian for this coordinate system (i.e. the "density" of geometries at a given r, θ, and ϕ); $S(r, \theta, \phi)$ is the probability for breakup of [ABC] at this r, θ, and ϕ; $P(r, \theta, \phi)$ is the probability to form the AB product in the given Λ-doublet level (P' or P'', as defined above); and the integral in the denominator is the normalizing constant.

For integration over θ and ϕ the Jacobian J is the familiar $\sin\theta$ weighting for integration over the surface of a sphere. We denote by $j(r)$ the r dependence of the Jacobian. The exact form $j(r)$ will be unimportant in our model, so we need not specify this function. Hence

$$J(r, \theta, \phi)\, dr\, d\theta\, d\phi = j(r)\sin\theta\, dr\, d\theta\, d\phi . \quad (5)$$

The function $S(r, \theta, \phi)$ represents the relative probability that [ABC] will dissociate with the geometry given by r, θ, and ϕ. Condition (3) states that S does not depend on θ or ϕ:

$$S(r, \theta, \phi) = \rho(r) . \quad (6)$$

Combining eqs. (3)–(6) to determine the probability to form AB in the A'' Λ-doublet level (P''_T), we find that

$$P''_T = \frac{\int_r \int_\theta \int_\phi j(r)\sin\theta\, dr\, d\theta\, d\phi\, \rho(r)\cos^2\theta}{\int_r \int_\theta \int_\phi j(r)\sin\theta\, dr\, d\theta\, d\phi\, \rho(r)}$$

$$= \frac{\int_{\theta=0}^{\pi}\sin\theta\cos^2\theta\, d\theta}{\int_{\theta=0}^{\pi}\sin\theta\, d\theta} = \frac{1}{3} . \quad (7)$$

This implies that

$$P'_T = 1 - P''_T = \tfrac{2}{3} \quad (8)$$

and it follows that

$$\Pi(A')/\Pi(A'') = P'_T/P''_T = 2 . \quad (9)$$

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