Dynamical angular momentum models for rotational transfer in polyatomic molecules

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We propose a model for collision-induced rotational transfer (RT) in polyatomic molecules based on the *angular momentum (AM) sphere*, a classical representation of the dynamical motion of the rotational AM vector in the molecular frame. The model develops further that proposed by us [AlWahabi *et al.*, J. Chem. Soc., Faraday Trans. **85**, 1003 (1989)] in which RT probabilities are related to the AM *gap* linking initial and final $N_{k_a k_c}$ states. The AM sphere representation embodies the full internal motion of the molecule via its effect on the inertial axes and the trajectory of the individual rotational state vectors. In this representation there is no unique AM gap for a particular transition between states of nominally well-defined $N_{k_a k_c}$ and here we propose and test several models for obtaining the distance in AM space between initial and final trajectories. Models are evaluated from their ability to fit data on NH_2–H collisions. We find that even the simplest approximations, such as shortest distance in AM space, give good fits to data sets but the best fits are obtained when both AM trajectory *and* molecular geometry are averaged over. © *1995 American Institute of Physics.*

I. INTRODUCTION

The problems involved in rationalizing collision-induced rotational transfer (RT) in polyatomic molecules are formidable. There is little guidance on what are the underlying principles that control the process, e.g., early studies that appeared to demonstrate that long-range forces were dominant seem less relevant in light of more recent experiments. Furthermore, the complex dependence of eigenstate energies on the internal quantum numbers indicates that simple energy gap relationships are unlikely to be helpful. Of particular relevance here is the angular momentum (AM) model proposed recently by us which shows promise in providing new insight into the physical basis of RT. This was first formulated as an AM *gap* relation using data in atom–triatomic molecule collisions[1] and later developed as an alternative theoretical approach to diatomic RT.[2] Most recently this AM theory, in which the probability of linear to angular momentum transfer is calculated explicitly, has been used as the basis of a fitting law[3] with some indications of predictive power.

In this contribution we consider in more detail the application of the AM model to RT in polyatomic molecules. We begin by pointing out that despite the success of the original AM gap model for the case of atom–triatom collisions,[1] there is a flaw in the physical assumptions upon which it is based, amplified further in Sec. II but briefly is this. The model assumes that rotational AM in a polyatomic may be represented by vectors that are *fixed* in the molecule frame and correspond to specific values of total AM and its projection on inertial *a* and *c* axes. It is well-known that k_a and k_c cannot simultaneously be good quantum numbers in an asymmetric rotor, the classical origin of this being the precessional motion which the AM vectors undergo in the molecule frame. This motion is slow compared, say, to the time taken for a collision but an experiment will sample all regions of the AM vector's trajectory. The dynamical motion of the AM vector is central to the proper description of AM change since, in effect, a collision causes the AM vector to hop from its initial trajectory to some other. The details of initial and final AM vector precessional motion will be important, therefore, in determining the probability of AM change.

The experimental determination of state-to-state RT rates in polyatomics can often pose severe problems arising from the presence of more than one inertial axis of rotation. This, together with vibrational modes which may couple strongly with rotations, give rise to complex energy level patterns. For these and other reasons, few rotationally resolved studies of collisional state change have appeared in the literature. Interpretation of collision experiments in polyatomic molecules was strongly influenced by the work of Oka[4] whose double resonance experiments indicated a dominant role for long-range forces. Selection and propensity rules were developed for collision-induced transitions. For interactions between polar species, these gave a satisfactory description of the observed transition probabilities. More recently it has become apparent that long-range interactions alone may be insufficient to describe collisional RT in polyatomics.[5,6] Collisions of polar molecules with atoms or small molecules often yields data that is not readily explained by a simple multipolar expansion[7] and it is clear that further state resolved experiments on polyatomic molecules are needed.

RT in polyatomic molecules has particular relevance to the development of our physical picture of collisional quantum state change. These mostly have come from studies on diatomics. Particularly important however is the change in relationship between energy and angular momentum on going to polyatomics arising from the fact that the energy of a state is determined by the magnitude and *direction* in the molecular frame, of the rotational angular momentum vector.
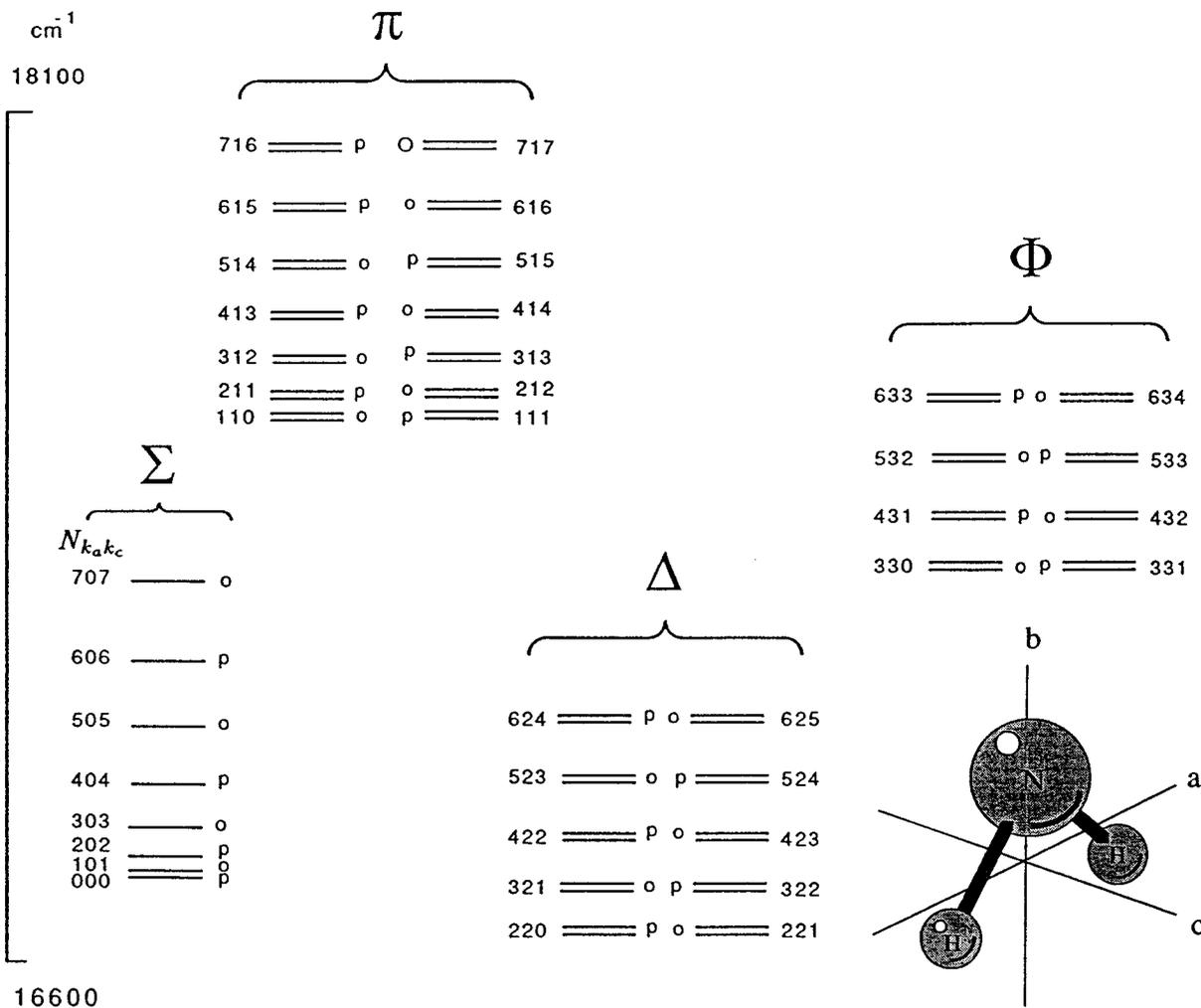
FIG. 1. Energy level diagram for the (0,9,0) vibrational manifold of the $A\ ^2A_1$ electronic state of NH_2. The energy levels are indexed by $N_{k_a k_c}$.

As a result it becomes possible to distinguish an angular momentum based dependency in RT from one based on energy change. A recent example of this is the work of Kroes and Rettschnick[8] who demonstrated that H_2–glyoxal rotationally inelastic scattering is dominated by AM transfer rather than energy transfer and there is evidence that energy gap relations are inadequate for describing RT in polyatomic molecules.[9]

We have reported results from an extensive study of state-to-state RT in the asymmetric rotor NH_2.[1] The motivation for this work was to address the questions raised in the preceding paragraph but also the intention was to add to the sparse data base of available fully state resolved RT rates in symmetric and asymmetric rotors. Approximately 100 state-to-state rates were measured[10,11] with full resolution of initial and final $N_{k_a k_c}$ states, of spin branching and polarization. Note that in asymmetric rotors with electron spin, N is the total rotational angular momentum and k_a, k_c are the projections of N on the inertial a and c axes. Spectroscopic states are indexed in these quantum numbers though only N and *one* of the projections are simultaneously good quantum numbers as noted above. Collision-induced transfer was measured both within and across the k_a stacks within a single

vibrational level and also between vibrational levels. This data set, together with the pioneering contribution to RT in triatomic radicals by Dixon and Field,[12] represents one of the most extensive currently available on a polyatomic molecule.

The experimental data revealed new insights into the nature of RT.[1] No correlation could be established between data sets on the basis of magnitude of energy change except in the trivial sense that transfer *within* k_a stacks follow energy gap laws. However, this is not diagnostic of mechanism since the energy levels within stacks are related to N in the same way as are those of a diatomic molecule to rotor AM. It is the transitions *across* the k_a stacks that are expected to distinguish between energy- and angular momentum-based models. For interstack transitions it is possible in some cases that an increase in magnitude of rotational angular momentum can result in a decrease in rotational energy due to the strong dependency of the energy on the direction of the AM vector in the molecule frame. This is evident from the set of energy levels for the (0,9,0) vibrational manifold of the $A\ ^2A_1$ electronic state of NH_2 shown in Fig. 1. The inability of energy gap models to fit this data is spectacular in some data sets[10,11] where an inverse dependency on energy gap may be detected. When RT rates are plotted against the angular mo-
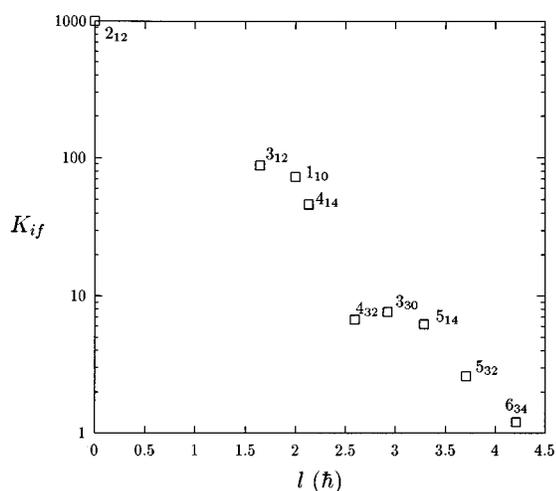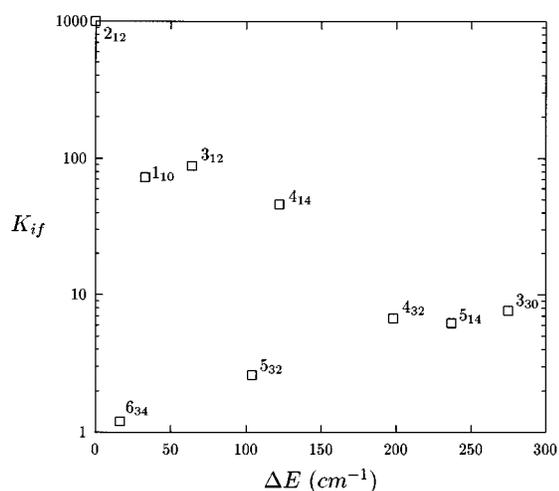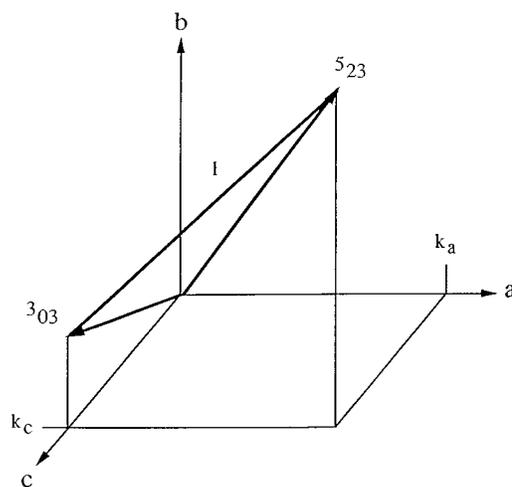
FIG. 3. Fixed vector model of the rotational angular momentum of an asymmetric rotor showing the molecule-fixed projections of the 3_{03} and 5_{23} states. The vector **l** represents the transferred AM.

FIG. 2. Semilog plots of RT rates in NH_2–H collisions vs energy gap ΔE and vs angular momentum gap **l**. The initially populated state is 2_{12}.

ment (AM) gap however, an excellent correlation is obtained.[1] This is shown for one data set (that from the 2_{12} state induced by collisions with H atoms) in Fig. 2.

The nature of the plot of rates vs transferred AM is of interest. The rates fall exponentially with the amount of transferred AM. This latter quantity was defined as the length of the vector that couples initial $N_{k_a k_c}$ to final $N_{k_a k_c}$ in the molecular frame. Here we extend and develop the simple AM model proposed in Ref. 1. Explicit recognition is made of the dynamical nature of the rotational AM vectors in the molecule frame and we show that a classical representation of rotational AM leads to a three-dimensional picture which can form the basis of a more physically reasonable model of AM changes in RT. We refer to this model as the angular momentum sphere representation to distinguish it from the fixed vector model first proposed in Ref. 1.

II. FIXED VECTOR (FV) MODEL

We first briefly outline the FV model as proposed in Ref. 1. The rotational states of an asymmetric top molecule may be labeled by the three quantum numbers N, k_a, and k_c. As

mentioned above, N is the rotational AM and k_a, k_c are projections of N on the molecular a and c axes in the respective oblate and prolate symmetric top limits. A rotational state may be represented in this model by a vector of length $\sqrt{N(N+1)}$ with components k_a and k_c. Two states of well defined $N_{k_a k_c}$ are shown in Fig. 3 together with the vector **l** joining them. In this model, **l** represents the AM transferred by collision in the transition from an initial state, $N_{k_a k_c}$, to a final state $N'_{k'_a k'_c}$. The magnitude of **l** may be calculated from geometric considerations to be[1]

$$l^2 = -2(N^2 + N - k_a^2 - k_c^2)^{1/2}(N'^2 + N' - k_a'^2 - k_c'^2)^{1/2}$$
$$+ N^2 + N - 2k_a k_a' - 2k_c k_c' + N'^2 + N'. \qquad (1)$$

Rates of collisional transfer in the $^2A_1$ state of NH_2 were found to scale exponentially with the magnitude of the vector **l** in a simple relationship of the form

$$k_{N_{k_a k_c} \to N_{k_a k_c}} = a \, \exp(-b|l|) \,. \qquad (2)$$

Despite the success of the FV model in fitting the rates of collision-induced RT in $^2A_1$ NH_2–H collisions the model cannot be regarded as a satisfactory representation of the process. A more physically reasonable representation would take into account the dynamical motion of the AM vector in the molecule frame. This precession is the classical origin of our inability to simultaneously quantify k_a and k_c. The motion is slow on the time scale of a collision but will be averaged over during an experiment and therefore the interaction will explore all regions of the trajectory of the AM vector. This extension of the FV angular momentum model to allow for dynamical motion of the rotational AM vector in the molecule frame is now described.

III. THE AM SPHERE

The vector model may be extended to include the dynamical motion of the rotational AM vector J. Note that in this work we use the more general notation J for the rota-
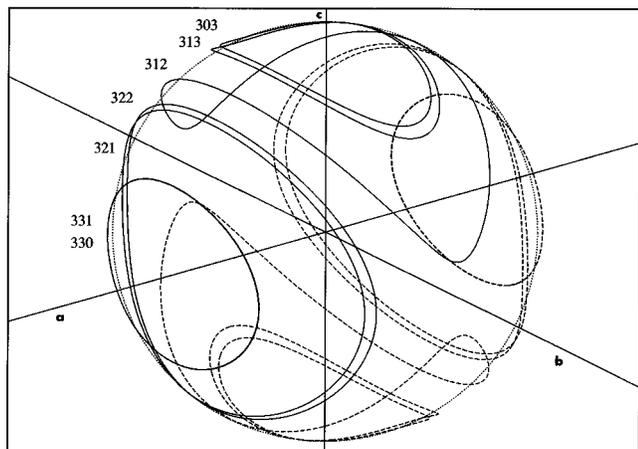
FIG. 4. The AM sphere for the $J=3$ rotational levels of NH_2 showing the classical trajectories of the individual $N_{k_a k_c}$ state vectors in the molecule frame. Note that for this representation, NH_2 is in its ground state equilibrium configuration since this separates individual trajectories more clearly than do the excited state geometries.

FIG. 5. Angular momentum (half) spheres for the $J=1$, 3, and 5 rotational levels of NH_2.

tional AM vector where for the case of NH_2, $J = \sqrt{N(N+1)}$. In the rigid symmetric rotor, rotational AM trajectories display uniform motion in the molecule-fixed frame which become nonuniform in the case of the asymmetric rotor. In both cases J follows a fixed periodic trajectory determined by the classical mechanics of the rotating system.[13,14] For example, in the case of NH_2 the motion of each $N_{k_a k_c}$ state within a J level is derived from the rotational Hamiltonian

$$H = AJ_a^2 + BJ_b^2 + CJ_c^2. \tag{3}$$

Diagonalization of the corresponding matrix provides the eigenvalues $E(N_{k_a k_c})$.

On expressing the Hamiltonian in terms of the spherical polar coordinates $J, \theta,$ and ϕ the classical trajectory of the $N_{k_a k_c}$ state vector is obtained from those values of θ, ϕ which fulfill the condition

$$E(\theta, \phi) = E(N_{k_a k_c}). \tag{4}$$

The set of trajectories of a single J level form an *angular momentum sphere* of radius $\sqrt{N(N+1)}$. These are closely related to the rotational energy trajectories described by Harter and Patterson.[15] A description of the classical motion of rigid rotors has been given by Zare.[16]

An example of the trajectories that comprise the $J=3$ level of NH_2 is shown in Fig. 4. The trajectories are sensitive to bond angle and rotational constants of the triatomic and, as we discuss in greater detail below, change dramatically as these change. The example shown in Fig. 4 is for the $^2B_1$ ground state of NH_2 which is more bent than the excited state and consequently the component trajectories of $J=3$ are well separated. As Fig. 3 shows, the trajectories of individual $N_{k_a k_c}$ state vectors vary considerably, exhibiting uniform motion around the a axis in the 3_{30} but becoming markedly nonuniform as the c-axis component increases in say the 3_{03}. Motions around each inertial axis are separated by the *separatrix* which is shown in the figure. Trajectories close to the
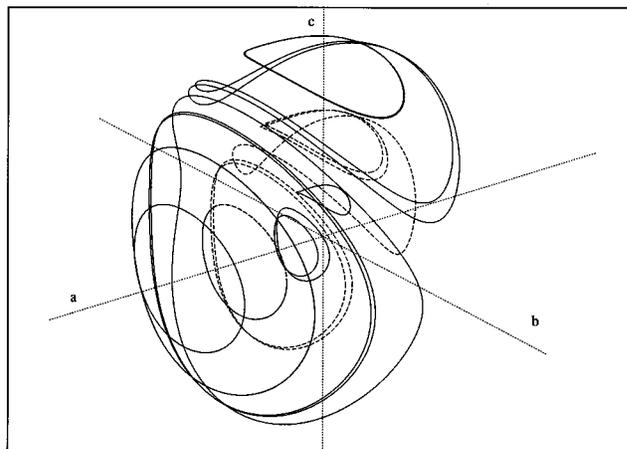
separatrix are less stable than those that remain close to an axis.[15,16]

When a series of J levels is considered, a set of concentric AM spheres is formed as shown in Fig. 5 which illustrates the trajectories for the levels of $J=1$, 3, and 5. There are several aspects of the AM sphere to be considered in relation to rotational transfer which in this model consists of a collision-induced hop from one trajectory to another, with the appropriate change in length and direction of J caused by the collision. This change may take place within a J sphere and thus represent a jump between the trajectories of Fig. 5 or may involve transitions between spheres. What is apparent from the topography of the J sphere is that unlike the FV model, there is no unique value of $\mathbf{l}$ for a given $N_{k_a k_c} \rightarrow N'_{k'_a k'_c}$. The length of the vector $\mathbf{l}$ coupling two trajectories will depend on the initial and final positions on the trajectory that are coupled. Note that of course the *energy* change in such a transition will be independent of start and end positions on the AM trajectories.

There are some other noteworthy points regarding the AM spheres and transitions between state vector trajectories. *Intra*stack transfer in which only one component changes (e.g, $\Delta k_a = 0, \Delta k_c \neq 0$) will have a direct relationship with energy change while *inter*stack transitions in which both components change will have a dependency on θ, ϕ values of initial and final J. The *minimum* value of $\mathbf{l}$ between any two states will lie in the a,c plane. This can clearly be seen in Fig. 3 for transitions within one J state but also applies between J levels. It is important to note that the precessional angular velocity of the J vectors is generally not uniform and has a marked θ, ϕ dependence for certain trajectories, those directed along the c axis for example. This may be important in collisional transfer out of a specified level since the turning points of the trajectory may have a dominant influence in RT processes.

IV. CALCULATIONS BASED ON THE AM SPHERES

The use of the AM sphere in interpreting collision experiments is new and clearly there will be no universally agreed method of use. As we have seen from the preceding section and as is apparent from the figures, there is no unique

value of **l**, the length in angular momentum space between initial and final precessing *J* vectors. We have therefore investigated a number of approaches based on simple physical principles in order to determine the ways in which to best use the AM sphere representation. The criterion used is best fit of experimental RT rates to magnitude of transferred AM (**l**) calculated by making certain assumptions regarding the dominant processes in the collision-induced transfer. Plots are on a semilogarithmic scale consistent with the notion of an inverse exponential dependence on magnitude of transferred AM. It is impossible in this process to escape making a comparison with the quality of fit yielded by the FV model for which correlation coefficients are generally excellent. However, we should not rule out the possibility that the excellence of fit to the FV model in this instance is misleading and perhaps due to factors arising from the highly excited bend vibration. We are seeking a model with general applicability but have relatively little in the way of data sets for rigorous testing.

A. Minimum transfer (MT) model

Our first attempt to use the AM sphere to predict RT rates was based on observation that RT scales exponentially with the inverse of the *magnitude* of AM transferred. It could therefore be argued that the *minimum* AM path should be that most favored for RT. As described above, this would lead to **l** vectors that lie in the *ac* plane of Figs. 4 and 5 since the minimum distance in AM space between trajectories lies in this plane. This is the basis for the first calculation. RT rates for a number of data sets were plotted in semilog form against transferred AM **l** calculated with the "minimum distance" model. In this calculation the geometry of NH_2 was taken to be that of the $^2A_1$ excited state in its equilibrium configuration in which the bond angle is 144°.[12]

One such plot is shown in Fig. 6(a) using data from the $N_{k_a k_c}$ level 2_{12}. Note that all data referred to in this work (and most of that in Ref. 1) was taken on NH_2 in its $(\nu_1, \nu_2, \nu_3) = (0,9,0)$ level. We discuss the significance of this high degree of bend vibrational excitation below. Figure 6(a) is interesting in that the basic exponential dependence on transferred AM is reproduced but the fit to data points is not as good as the FV model. The correlation coefficient for this same data set using the FV model is 0.990 while that for the AM sphere with shortest distance in AM space is 0.95. Thus although the physical picture is improved by allowing for *J*-vector precession in the molecular frame, the fit to data using the MT approximation is worsened compared to the FV model.

B. Turning point (TP) model

The MT model used above might be considered physically unreasonable since the point in the AM trajectory at which the jump takes place in this picture will be that at which the *J* vector is moving most rapidly. The precessing vector moves most *slowly* at the turning points of the trajectory. These generally will not lie in the *ac* plane. A more realistic model therefore would give greater weight to the slower regions on the trajectory. Our next simple model was
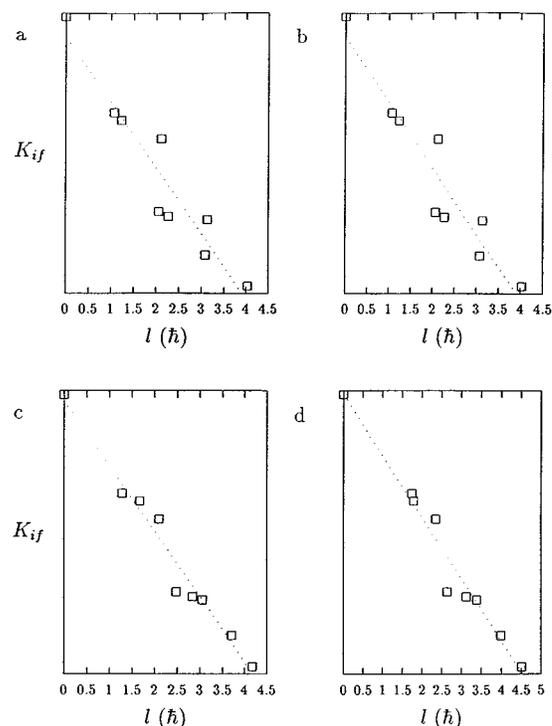

FIG. 6. The semilog plots shown here represent fits to data from the 2_{12} level of NH_2 using the different approximations described in detail in the text. In each case data (squares) are plotted against calculated values of transferred AM **l**. The dotted line is a best fit assuming an inverse exponential dependence on the length of **l**. (a) Calculations assume equilibrium geometry for NH_2 (bond angle 144°), AM jumps represent the shortest distance between the two chosen trajectories. (b) Calculations assume equilibrium geometry but AM jumps take place from the point on the initial trajectory that the vector spends the longest time. (c) Calculations assume the precessing vector is averaged around the positive quarter of its trajectory to give an (averaged) equivalent *static vector* which has been time-weighted. The calculations are based on the AM sphere for the NH_2 bond angle of 95°. (d) Calculations assume an average **l** by taking each point on the (positive quarter of) the initial trajectory and calculating the distance to all points on the final vector. The results are then averaged to give the average **l** value. The calculations are based on the AM sphere for the NH_2 bond angle of 95°.

one in which the point of minimum precessional velocity on the initial trajectory was identified and the minimum distance in AM space to the final trajectory from this point was calculated. The speed of the precessional motion is readily calculated since the program that reproduces the trajectories calculates position for fixed angular intervals which enables angular velocity ω to be obtained from the rate of change of *J* with respect to θ and ϕ.

The result of calculations from the AM sphere based on this turning point approximation are shown in Fig. 6(b). This is also the equilibrium configuration with data from the 2_{12} level. As in the case of the shortest distance model, the basic form is reproduced with reasonable fit to data, though not as good as the FV result. The correlation coefficient is again 0.95. Thus again an improved physical basis to the AM dependency has led to a slightly poorer fit to data.

C. Average vs equilibrium geometry

At this point it is useful to consider in more detail the shape of the NH_2 molecule with which the collision partner
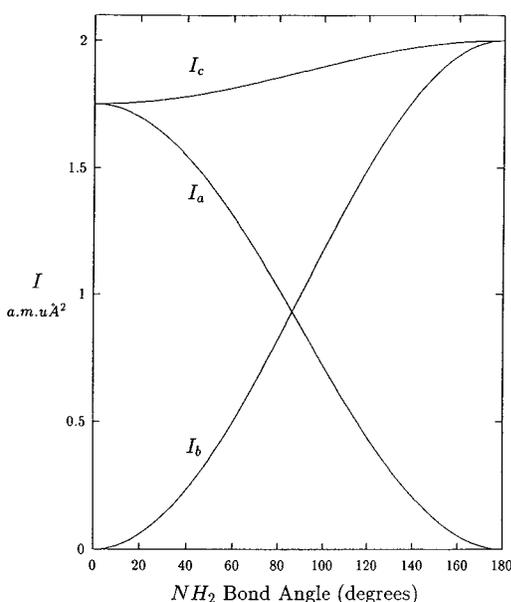
FIG. 7. Plot of inertial constants of NH_2 vs bond angle.

TABLE I. Correlation coefficients from least squares fit of the inverse exponential AM transfer law to RT data from the 2_{12} rotational level of $NH_2(A\ ^2A_1)$. The AM transfer l is calculated on the AM sphere from the various models discussed in the text.

NH_2 ($A\ ^2A_1$) bond angle	MT	TP	J_{av}	l_{av}
144°	0.950	0.950	0.959	0.937
107°	0.979	0.982	0.972	0.966
97°			0.983	0.982
95°			0.986	0.984
90°			0.980	0.984
75°			0.969	0.938

will on average interact. This is significant since the precise AM trajectories and hence the substructure of an AM sphere for a particular J value is very sensitive to the details of the molecular shape. That this will be so can be seen from the plot (Fig. 7) of moment of inertia (I_a, I_b, and I_c) as a function of bond angle. The experimental data which we are fitting was carried out on NH_2 having nine quanta of the bend vibration and the collisional RT experiment will sample the molecule in a wide range of geometries. This may affect the results in a manner that is not compensated for in the simple AM sphere calculations described above.

The first two sets of calculations were performed on the "equilibrium" AM sphere, i.e., assuming that the geometry of the molecule is that of the equilibrium configuration with bond angle 144°. This represents the minimum point on the potential surface of the $^2A_1$ excited state.[12] A more appropriate geometry might be an average of the motion of the molecule in its (0,9,0) vibrational level in this state. Our next refinement of the AM sphere calculation computes this average geometry and then calculates l values for this average AM sphere. The average geometry was calculated from the potential[12] by first fitting the dependence on bend angle (θ) to a simple polynomial function. This was used to compute the rate of change of potential with bend angle θ from which the average value of θ could be obtained:

$$\langle\theta\rangle = \Sigma\ \theta|dV(\theta)/d(\theta)|/\Sigma|dV(\theta)/d(\theta)|. \quad (5)$$

Using this expression and the published $^2A_1$ potential the value $\langle\theta\rangle = 106.7°$ was obtained. This bond angle generates new rotational constants and a different AM sphere to that of the equilibrium geometry. New values of **l** were calculated for this AM sphere using the two approaches described above, i.e., (i) minimum distance in AM space (the MT model) and (ii) turning point models. Results using this AM sphere are encouraging since they show improved correlation with the RT data. The results of calculations for the 2_{12} level,

summarized in Table I, show an improvement in the correlation coefficient to 0.979 in the case of the MT model and 0.9872 for the TP case.

Summarizing these first approaches to the use of the AM sphere we note that both equilibrium and average geometries give good fits to data but those obtained with the average bond angle of 106.7° were noticeably better. Use of the TP approximation generally produces better fits than the MT approach. Correlation coefficients are consistently better with the former approach for both geometries. This is encouraging since better fits appear to follow as the physical model of the interaction is improved. The average geometry is more appropriate for NH_2 (0,9,0) data and the assumption that the turning points of the AM trajectories have a dominant influence is also a reasonable one. We next discuss how these simple models may be improved.

D. Average vector (J_{av}) and average l (l_{av}) models

The success of the average geometry TP model has indicated that improvements can come from improving the physical representation for the calculation. These in effect consist of attempts to average over the complete trajectory in order to compute a true value of **l** in addition to finding the most appropriate NH_2 configuration for the calculation. The two **l** averaging approximations consist either in summing over (a portion of) the J trajectory to give an average vector (J_{av} approximation) or of averaging the computed AM space jump to give an average **l** value (l_{av} model).

In the J_{av} approximation, the path of the precessing vector around the positive quarter of its trajectory was averaged to give an equivalent static vector. This was done incorporating a time weighting obtained, as before, through knowledge of the angular velocity ω. This average static vector was then used in the calculation of l in a manner related to that described under the FV model. However, in this instance the magnitude of l is a function of projections on all three inertial axes. The l_{av} approach is somewhat different. Here the average transferred AM is found by taking each point on the initial trajectory and calculating l to all points on the final trajectory (again within the positive quarter of the J motion). All points on the initial trajectory are summed and the results averaged. Time weighting of the kind described above was also used.

These two models were used on RT data using a number of different molecular geometries. These included both the

equilibrium, bond angle 144°, the average (106.7°), and a number of bent configurations to probe the effect of geometry change on the fits. Rotational constants were recalculated for each new configuration and the bond angles 97°, 95°, 90°, and 75° were used since these are close to the turning point in the (0,9,0) level of $^2A_1$. Results of the calculations for the J_{av} and l_{av} models for the initial level 2_{12} using the turning point geometry of NH_2 with a bond angle of 95° are shown in Figs. 4 and 5. The results of this calculation are summarized in Table I for the data set originating from the 2_{12} level. As seen from the table, there is an improvement in quality of fit using both J_{av} and l_{av} models. These are best at the angle corresponding to the turning point of the potential surface representing the bend coordinate (approx. 95°) and suggest that the interaction is dominated by this configuration of the NH_2 molecule. Physically this is not unreasonable in view of the length of time spent at the turning points relative to other positions.

V. DISCUSSION AND CONCLUSIONS

The AM gap law[1] originally proposed for RT in polyatomics represented a new approach to RT in molecules featuring an (inverse) exponential dependence on transferred AM instead of the more usual transferred energy. There is increasing evidence of the unsuitability of energy gap relations in the RT of polyatomic molecules[9] and the data we reported on NH_2–H collisions[1] strongly indicates that the energy gap has little influence. Notwithstanding these comments it will be evident that RT *within k* stacks, which comprises much of the state-to-state RT data that is available on polyatomics, may be fit with energy *or* AM gap laws. As discussed earlier such processes, which are akin to RT in diatomics, are not diagnostic of mechanism. The exponential AM dependence noted first in Ref. 1 has been developed into a simple but powerful new theory of RT in diatomic molecules.[2,3] There is also evidence of the inadequacy of the long-range interactions alone to account for all observations of RT in polyatomic molecules.

It is important to recognize the dynamical nature of the AM vector in the molecule frame in the case of nonlinear molecules. Here this dynamical motion is explicitly included in the consideration of collision-induced transitions for the first time. This motion is completely described in the framework of the AM sphere representation that we present in this work and use as the basis for interpreting collisional processes in molecules. The AM sphere representation of classical motion of the AM vector is shown to be a very useful means of visualizing RT. Since it constitutes a plot of trajectories in angular momentum space defined by the individual molecule and its characteristic inertial moments, the AM sphere provides a basis for calculating the length of the AM vector that causes a transition from one trajectory to another.

The AM sphere may be adapted to include the additional complication of angular momenta arising from molecular vibrations, electronic orbital, or spin angular momenta as has been demonstrated in the case of the closely related rotational energy surfaces by Harter and co-workers[15] in an extensive series of applications. It is readily seen from the AM trajectories displayed in Figs. 4 and 5 that there is no unique

value of AM change when the orbital angular momentum of a collision transforms one trajectory to another. In this work we propose a number of simple models for calculating the magnitude of $\mathbf{l}$, the transferred AM. Note that *all* of these gives a very good account of the data we use as our test of model quality and therefore are all a very substantial improvement on a law based on the energy gap. Furthermore, all will give an excellent fit to the intra-*k* stack data that comprises much of the available data on RT in polyatomics.

Several approaches to calculation of the AM gap in the AM sphere representation are proposed and tested. Each has a firm basis in the physics of the interaction between an atom and a molecule undergoing vibrational and rotational motion. These are not necessarily exhaustive and other methods of using the AM sphere representation may exist. A major hinderance is the paucity of data with which to compare predictions. Here we test the models by their ability to fit sets of data obtained on NH_2–H collisions, an extensive set in which wide changes of N, k_a, and k_c have been detected. However, despite the quality and quantity of these RT rate constants this data is not ideal as an unambiguous test of the models we propose here since RT is of molecules excited with nine quanta of the bend vibration. This is sufficient to change the molecular geometry from a prolate symmetric top at the center of the oscillatory motion to an oblate top at the extremes of the bend.

This motion in the bend coordinate may be the origin of the excellent fits obtained using the FV model and suggests that this simple model may be inappropriate for molecules initially in low vibrational states. Despite the success of this model in fitting NH_2–H data the lack of account of the dynamical motion of the AM vector in the molecule frame is a serious flaw and the AM sphere model proposed here rectifies this. It may be that for highly vibrationally excited species the FV model may represent a useful approximation. However, we feel that one or another of the AM sphere-based techniques for estimating $\mathbf{l}$, the transferred AM will prove more satisfactory. We have found that the best fit to data using the AM sphere is obtained when the AM vector trajectory is averaged over via the J_{av} or the l_{av} approximations. It is clear that the method is sensitive to the effective geometry that the collision partner experiences, i.e., an *average* configuration rather than the equilibrium. The NH_2 data appears to be dominated by the turning point geometry in the bend vibration.

As more extensive data sets of RT in polyatomic molecules become available the usefulness of the models proposed here based on the AM sphere representation may be tested. Light triatomics will be particularly useful since their spectral features are often well separated and well characterized. The series of measurements by Steinfeld and colleagues[17] on spherical and symmetric top hydrides using infrared double resonance techniques have demonstrated the high selectivity of RT in such molecules. The AM sphere, which embodies the molecular symmetry and the disposition of the inertial axes in an angular momentum representation, may provide the key to the understanding of these and other collision-induced processes where simple energy gap relations have proved to be inadequate.

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