Single Collision Studies of Vibrational Energy Transfer Mechanisms

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Chemists have appreciated that the rates of collisional production and deexcitation of highly energized molecules can have profound effects on the overall kinetics of chemical reactions since at least as early as Lindemann's hypothesis.[1] Expressed in current terms, the Lindemann mechanism for a unimolecular reaction is[2]

$$A + M \xrightarrow{k_1} A^* + M \quad (1)$$

$$A^* + M \xrightarrow{k_2} A + M \quad (2)$$

$$A^* \xrightarrow{k_3} B \quad (3)$$

where A is the reactant species, B represents the products, and M is any species present in the system. A* is a reactant molecule with sufficiently high internal energy, predominantly vibrational, to undergo transformation 3, and k_3 is the decomposition rate constant for the energized reactant. Steps 1 and 2 represent the collisional production and deexcitation of A*. In steady state, the overall rate of reaction is

$$k_3[A^*] = \frac{k_1 k_3 [A][M]}{k_2 [M] + k_3} \quad (4)$$

and is clearly sensitive to k_1 and k_2 as well as to k_3. For low-pressure gas-phase reactions ($k_2[M] \ll k_3$) the overall reaction rate is completely determined by the intermolecular energization rate. Although we shall not present other examples in detail, it should be clear that collisional energy transfer plays an important role in any thermal reaction having an energy barrier which can be overcome by internal excitation.

Experimental and theoretical investigations of collisional energy transfer processes have a long history.[3-5]

In the past decade the development of infrared gas lasers has led to rapid growth in studies of energy transfer in small molecules.[6] This has happened in part because lasers offer great flexibility and specificity in producing and monitoring excited-state populations and in part because intermolecular energy transfer plays an important role in the operation of gas lasers.[7,8] Recently laser excitation of molecular vibrations has been used to enhance chemical reaction rates,[9] and isotopically selective rate enhancement is under active consideration as a practical technique for isotope separation.[10] A crucial limitation to the efficiency of most laser excitation rate enhancement schemes is the collisional transfer of energy out of the initially excited molecule.[11]

Despite the importance of intermolecular energy transfer in a great variety of chemical situations and the attention which the subject has consequently received, a good understanding of the detailed mechanisms involved in collisional shuttling of energy from one molecule or degree of freedom to another is lacking

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in most instances. The reason for this is that most experimental studies of collisional energy transfer have been performed under bulk conditions. Their results are averages of the outcomes of individual collisions over an ensemble of colliding molecules. The information obtained is very useful for determining the rate constants governing energy-transfer processes of interest. However, detailed information about the results of single collisions is necessary for the development of a complete understanding of intermolecular energy transfer.

In the development of chemistry it has often been the case that valuable general insight has been obtained through the detailed investigation of a few prototypical systems. The study of vibrational energy transfer for single collisions in simple systems having a variety of interaction mechanisms can yield general insights into the dynamics of inelastic collisions. A type of experiment yielding detailed information about intermolecular interactions involves forming a beam of molecules or ions, directing the beam into a target of molecules which act as collision partners, and measuring the resulting scattered intensity as a function of scattering angle and final speed. (In the following, we shall conform to the common usage of the terms speed and velocity as equivalent.) This kind of experiment has recently been performed in several laboratories,[12-17] and much valuable insight into the dynamics of vibrational excitation and deexcitation has been obtained for a variety of systems. In the following discussion we shall focus on a series of experiments[18-20] aimed at obtaining a detailed understanding of the mechanisms responsible for the deactivation of a highly vibrationally excited polar diatomic molecule. We shall indicate how pertinent molecular beam experiments are performed, how their results can be interpreted to obtain an understanding of collision dynamics, and how the mechanism of vibrational energy transfer changes as the nature of the interaction between the diatomic molecule and its collision partner varies.

Experimental Approach

In order to study vibrational deactivation processes, one needs a source of vibrationally excited molecules. A chemical technique is useful for producing a molecular beam in which essentially all of the molecules are highly vibrationally excited. We make use of the
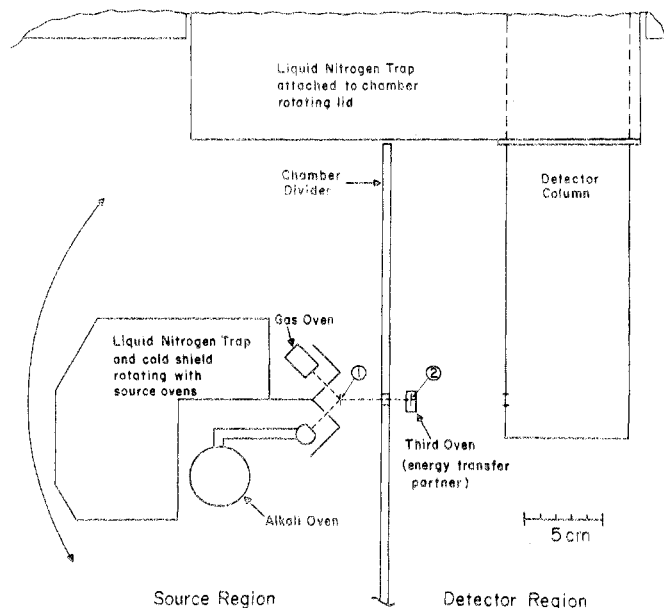
Figure 1. Simplified schematic of the apparatus used for energy-transfer studies. Both source ovens and associated cold trapping rotate in the plane of the paper about interaction zone 1 as a center. The detector column rotates with the vacuum chamber lid in a plane perpendicular to the paper with interaction zone 2 as a center. The third oven is actually above the plane of the paper.

extremely exothermic reaction between potassium and bromine (eq 5, where the dagger indicates vibrational

$$K + Br_2 \rightarrow KBr^\dagger + Br \qquad (5)$$

excitation). The energetics of (5) have been carefully studied in a series of molecular beam experiments.[21-24] The average vibrational excitation of $KBr^\dagger$ is about 41 kcal/mol, and the vibrational energy distribution has a full width at half intensity of about 10 kcal/mol; the rotational and translational energy distributions are roughly characterized by temperatures of 1500 and 750 K, respectively. Consequently, vibrational energy exceeds both the distribution width and the energy in other product degrees of freedom. Thus (5) is potentially a means of preparing molecules for investigating energy transfer in collisions of highly vibrationally excited molecules at relatively low translational and rotational energies. These are processes of importance in the course of highly endothermic reactions in thermal systems.[25]

Figure 1 illustrates schematically how we use (5) in what might be called a tandem molecular beam technique to obtain data on vibrational deactivation. Only the heart of the apparatus is illustrated; practically important but conceptually peripheral items such as vacuum pumps and chamber walls are not shown. The source region contains two ovens from which a beam of Br_2 and one of K emanate. These two beams intersect in interaction zone 1 to produce $KBr^\dagger$. A portion of this $KBr^\dagger$ passes through a slit in the chamber divider

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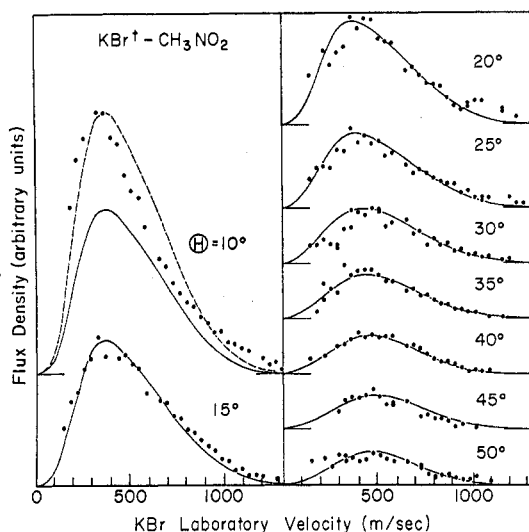(20) F. F. Crim, H. B. Bente, and G. A. Fisk, *J. Phys. Chem.*, 78, 2438 (1974).

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Figure 2. Typical laboratory data. Scattered flux density of potassium bromide as a function of KBr laboratory velocity at various laboratory angles Θ. Flux density is the signal intensity per unit angle normalized through division by the total scattered KBr intensity. The points are experimental measurements, and the solid curves are the results of model calculations. No adjustments of the relative intensities for the solid curves are made; the broken curve is scaled to match the measurements at Θ = 10°. The KBr† beam is at Θ = 0°, and the CH_3NO_2 beam is at Θ = 90°.

into the detector region. As indicated in Figure 1, both source ovens and their associated cold trapping rotate about interaction zone 1. For an angle of 60° between the initial K direction and the normal to the chamber divider, we find that the KBr† "beam" entering the detector region is virtually uncontaminated by K.

After passing into the detector region, KBr† enters interaction zone 2 where it intersects a beam of energy-transfer partners emanating from the third oven. The processes occurring in zone 2 are the ones of interest. The detector column rotates about interaction zone 2 as a center. Its motion occurs in a plane including the KBr† and energy-transfer partner beams. The detector consists of a slotted disc velocity analyzer behind which a surface ionization filament is mounted. This filament converts incoming alkali halide species to ions which are collected on a metal plate. The resulting current is measured with an electrometer, and its magnitude is displayed on a strip chart recorder.

Our data are measurements of the intensity of scattered potassium bromide as a function of its laboratory scattering angle Θ and of its final laboratory velocity. Figure 2 displays the data for the scattering of KBr† by CH_3NO_2. The initial direction of the KBr† beam is Θ = 0° and that of the CH_3NO_2 beam is Θ = 90°. The solid dots are laboratory data, and the solid curves are the predictions of a model discussed below. These data are typical of those collected for the various systems we shall discuss and represent a wealth of information concerning vibrational energy transfer mechanisms. Although the data are obtained in a laboratory fixed-coordinate system, they are by far more easily interpreted when expressed in a coordinate system moving with the center of mass, cm, of the colliding pair of molecules. One can often obtain a qualitative feeling for the kinds of interactions responsible for a given cm scattering intensity distribution from simple visual inspection. It is often possible to

obtain a good representation of the cm intensity distribution from the observed laboratory distribution by using computer-based transformation routines. We have found such routines very helpful[18-20] and shall concentrate in the following on interpretation of data transformed to the cm system.

Polar Scattering Partners

As a first illustration of the use of scattering results to draw inferences about the dynamics of energy-transfer processes, we discuss the scattering of KBr† by a series of polar molecules: CH_3OH,[18] H_2O,[18] NH_3,[18] and CH_3NO_2.[20] A common physical aspect of these four scattering systems suggests that they might yield readily interpretable scattering intensities. All the polar partners considered have appreciable dipole moments, varying from 1.5 D for NH_3 to 3.5 D for CH_3NO_2.[26] Ground vibrational state KBr has a substantial dipole moment, ~11 D, and KBr† has an even larger one, ~17 D.[27] As a result of the large dipole moments associated with all the molecules under consideration, strong attractive forces exist between KBr† and any of the polar partners. For instance, on the basis of electrostatic interactions and hard core repulsions, ignoring any possible chemical effects, KBr† is bound to CH_3OH by over 20 kcal/mol. Given the expected binding energies, a simple Rice–Ramaberger–Kassel (RRK) statistical treatment[2] predicts that KBr† should form a short-lived collision aggregate, or complex, with any of the polar partners. The average lifetime of the complex before decomposition into the original molecules occurs should be several vibrational periods, perhaps the order of one rotational period. Statistical theories propose that during this lifetime energy initially present as vibrational excitation of KBr† becomes randomly distributed among available degrees of freedom of the complex, resulting in efficient vibrational deactivation of KBr†.

If an energy-randomizing collision complex is involved in the KBr†–polar molecule collision systems, the cm scattering distribution should show several characteristic features. First, there should be no correlation between the angular and speed distributions resulting from the decay of a randomized complex. That is, the overall intensity distribution is factorable into terms depending on cm scattering angle, θ, and final cm velocity, u (eq 6). Second, the velocity distribution $U(u)$

$$I(\theta,u) = T(\theta)U(u) \tag{6}$$

should have a single broad peak and be roughly, though not precisely, thermal in shape. Finally, the angular distribution $T(\theta)$ for a complex having a lifetime long compared to its rotational period should be symmetric about θ = 90°. For lifetimes comparable to or shorter than a rotational period, this symmetry is distorted because of the large probability that the complex will break up before completing a rotation.

Figure 3 presents the cm scattering intensity distribution for the KBr†–CH_3OH system in the form of a contour map. The origin of the map is at the tip of the vector labeled V_{cm}, and the most probable velocities in the two initial beams are displayed to give an idea of the relation between the laboratory and cm coor-

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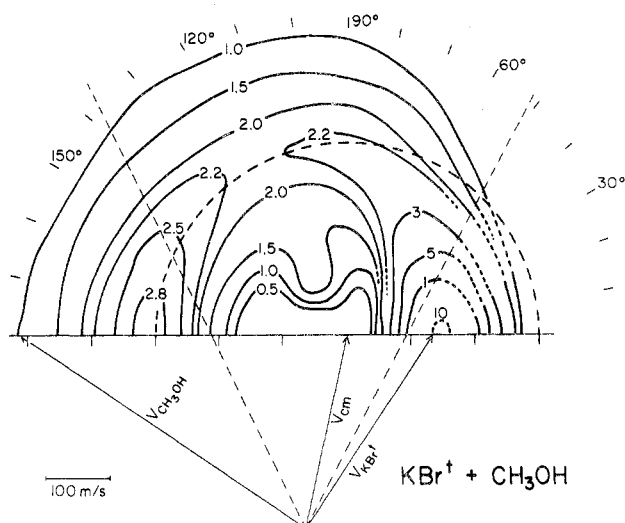
Figure 3. Center of mass contour map of intensities in the $KBr^\dagger$-CH_3OH system. Origin of the center of mass coordinate system is at tip of V_{cm}. The lower half of map is omitted because it is merely the reflection of the upper half.

dinate systems. Laboratory data collected between angles indicated by the two dashed lines were used in the analysis. The dashed regions of the contours fall within the laboratory direction of the $KBr^\dagger$ beam where data cannot be obtained. For $\theta \leq 80°$, elastic scattering, resulting from collisions in which the partners do not approach closely enough to form a complex, contributes importantly to the overall intensity, and the factoring predicted by (6) is not possible. For larger angles, however, all the features associated with a short-lived complex are evident. The velocity distribution can be obtained by reading intensities along any ray from the origin; it is sensibly independent of angle and has the expected single maximum and roughly thermal shape. The intensity distribution is approximately symmetric about $\theta \approx 110°$, indicating that a complex with lifetime comparable to a rotational period is responsible for the observed distribution.

The qualitative understanding of scattering in the $KBr^\dagger$-CH_3OH system obtained through inspection of Figure 3 generalizes to the other polar partners studied and can be quantified easily. Decay energetics and angular distributions arising from energy randomizing complexes have been discussed elsewhere,[18,28-30] and only a few central points are summarized here. The probability of a final relative translational energy E_T is

$$P(E_T) = A(E_T)N^+(E - E_T) \tag{7}$$

where E is the total energy of the system and $N^+(E - E_T)$ is the energy level density of the active vibrations and rotations, excepting the decay coordinate, at the critical configuration for complex decay. In the analysis discussed here, E is taken to be the average total energy of the system. That this is a reasonable approximation

follows from the earlier remarks concerning $KBr^\dagger$ energetics. A more elaborate treatment, in which the detailed distribution of E is considered, would not significantly change the results reported. In the limit of high total energy and low-frequency vibrations, the classical approximation (8) is valid. $A(E_T)$ is determined by

$$N^+(E - E_T) \sim (E - E_T)^n \tag{8}$$

mined by the interaction force constants in the entrance and exit channels and by the initial relative translational energy. The appropriate force constants are calculated using the Keesom–Linder[31] approximation for the interaction of two rotating dipoles. The exponent n in (8) is given by (9), where s is the number

$$n = s + (r/2) - 2 \tag{9}$$

of active vibrations in the complex, including the separation coordinate, and r is the number of active rotations. Angular distributions for decay products of long-lived complexes are determined by angular momentum considerations.[29] For short complex lifetimes, these distributions are modified using a factor[30] determined by the ratio of the mean complex lifetime to the rotational period, τ/τ_R. The model discussed here has only two adjustable parameters, n and τ/τ_R; it adequately reproduces both the shape and relative intensities of the measured laboratory distributions (Figure 2).

Lin and Rabinovitch[32] have called the temporary low-frequency modes of a complex, which correlate with rotations and translations of the separated partners, transitional modes and have discussed intermolecular energy transfer in terms of these modes. The analysis described above[18] is consistent with the idea that only the transitional modes and the $KBr^\dagger$ vibration participate in energy randomization in complexes formed between $KBr^\dagger$ and CH_3OH, H_2O, or NH_3. All of these complexes are characterized by $\tau/\tau_R \approx 0.3$, or a lifetime of about 10^{-12} s, and by n ranging from 3.5 to 4. Complex formation and energy randomization followed by eventual decay of the complex very efficiently deactivate $KBr^\dagger$. According to this model, an average of 80% (34 kcal/mol) of the initial $KBr^\dagger$ vibrational excitation is converted to rotational and translational energies of the separating collision partners. CH_3NO_2 has a larger dipole moment than do the other polar partners and possesses three low-frequency skeletal vibrations involving atoms in the vicinity of the dipole.[20] Analysis of $KBr^\dagger$-CH_3NO_2 scattering distributions[20] indicates that the complex lifetime is about 5×10^{-12} s and that three CH_3NO_2 internal vibrations participate in energy randomization. Although the criteria for participation of a skeletal vibration in energy redistribution are not well established, low frequency and good coupling to the initial $KBr^\dagger$ vibration seem necessary.

Nonpolar Scattering Partners

The systems discussed thus far represent a fairly general limiting kind of collision dynamics. Strong attractions hold the two interacting molecules together long enough for the energy-transfer process to be essentially statistical. Repulsive forces are doubtless

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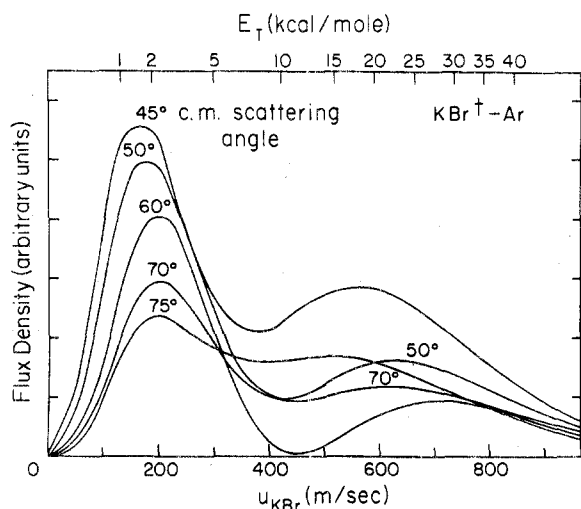
Figure 4. Center of mass flux densities as functions of final KBr cm velocity at several cm scattering angles for the KBr†–Ar system. The final relative translational energy of the collision pair is shown on the upper axis.

involved in the detailed dynamics of the energy-transfer processes, but in the statistical limit it is neither necessary nor possible to investigate their effects directly. In this sense, these systems exhibit attraction-dominated dynamics. We shall now discuss the results of scattering experiments performed in systems for which attractions are minimized and repulsive forces dominate the energy-transfer process. The nonpolar scattering partners investigated are Ne, Ar, N_2, CO, and CO_2.[19] The KBr†–nonpolar partner attractions are about an order of magnitude smaller[19,33] than those in the KBr†–polar partner systems, and no complex formation is expected.

Figure 4 displays cm intensity distributions in the KBr†–Ar system in the form of intensity vs. velocity plots at several scattering angles. It is clear that the velocity distribution is not independent of scattering angle and that its form is not that associated with the collision complex mechanism. For all angles there is a peak at low velocity representing nearly elastic scattering and another at higher velocity arising from interactions which very efficiently convert vibrational to translational energy. Such interactions are typically associated with strongly repulsive impacts between two particles, and simple model calculations[19,34] based on a hard-sphere collision between Ar and the vibrating KBr† molecule yield energy transfers in rough agreement with those observed. We therefore infer that repulsive forces dominate in generating the distributions displayed in Figure 4. Scattering distributions in the other KBr†–nonpolar partner systems are qualitatively similar to those presented in Figure 4. Analysis of the distributions[19,35] indicates that for the molecular partners vibration–vibration energy transfer competes effectively with vibration–translation conversion.

In order to quantify the inference drawn from Figure 4 that repulsive forces dominate interactions between KBr† and nonpolar partners, a full treatment of the collision dynamics must be performed. A statistical
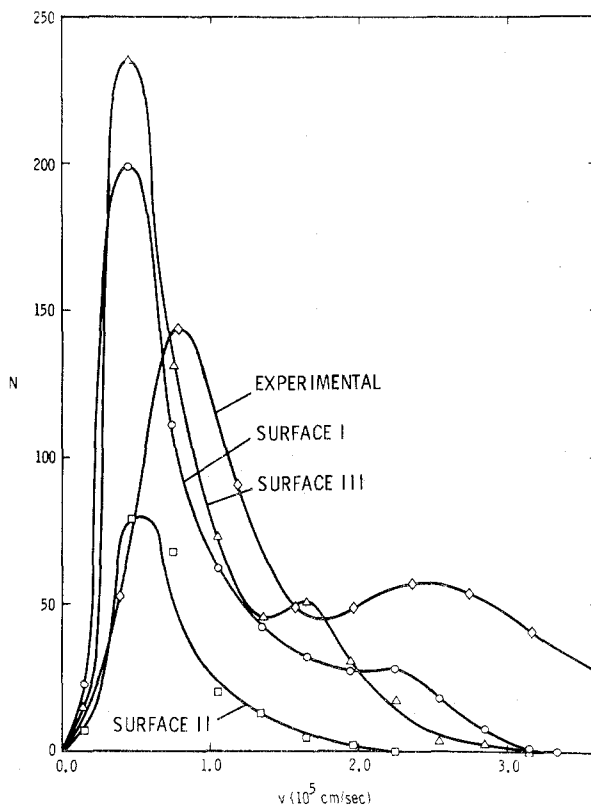
Figure 5. Center of mass scattering intensity as a function of final overall relative velocity, v, at cm scattering angle $\theta = 70°$ as inferred from experiment (◊). Number of trajectories in the range $60° < \theta < 80°$ as calculated for surface I (O), surface II (□), and surface III (△), grouped into successive intervals of width 3×10^4 cm/s. The area under experimental curve is matched to that under curve for surface I.

treatment is not appropriate; thus the interactions between vibrational, rotational, and translation motions in three dimensional collisions must be considered explicitly. An analytic treatment is not possible, but a three-dimensional classical trajectory study of the KBr†–Ar system has recently been completed.[33] Figure 5 presents the calculated velocity distributions for scattering to cm angles between 60 and 80° and compares them to the $\theta = 70°$ experimental curve (Figure 4). As has previously been discussed,[36] the computer-based transformation routines used to generate cm intensities from laboratory data determine the locations of maxima much more reliably than they determine relative magnitude. More weight should therefore be placed on existence and location of high-velocity peaks than on their intensities relative to those of the low-velocity peaks when comparing trajectory calculations with a cm curve inferred from experiment. Three different potential-energy surfaces were treated in the trajectory study, and on all three the interactions leading to the conversion of large amounts of vibrational energy to translation were strongly repulsive. Attractions did play a role in the overall dynamics, however, as can be seen by comparing the three surfaces and the results calculated using them.[33] Surface I was constructed from a simple, experimentally referenced, model of the interactions present in the KBr†–Ar system. Surface II is a purely repulsive one obtained from surface I by deleting all attractions. Surface III

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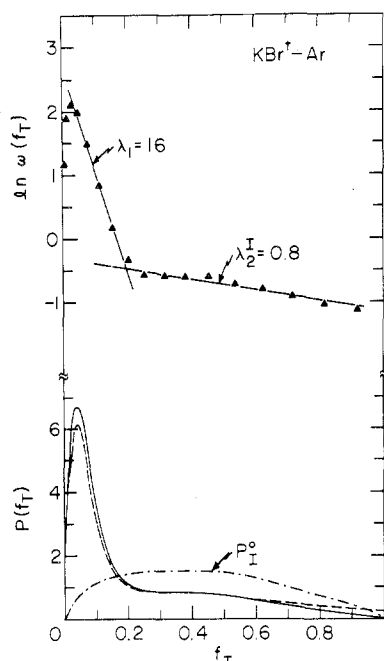
Figure 6. Surprisal analysis for KBr†–Ar. The broken curve is the final translational energy distribution of KBr averaged over the cm angular range 50° to 80°, and the solid curve is the same distribution adjusted to pass through zero at $f_T = 1$. The atom–diatom equilibrium distribution, $P°_I$, is shown as a dot-dashed curve. All distributions are normalized to unit area. Solid symbols are values of ln $\omega(f_T)$ and exhibit two linear regions as indicated.

was obtained by adding a spherically symmetric attractive part, having the same well depth as the attractive part of surface I, to surface II. Surfaces I and III thus differ in the shapes of their attractive wells; surface I channels incoming Ar preferentially to the K end of KBr and surface III does not. Reference to Figure 5 indicates that only the distribution calculated for surface I has a high-velocity peak in essentially the same location as that observed experimentally. The gathering and channeling effects of the attractive part of the potential are important, although they are not responsible for the actual transfer of large amounts of energy.

Even though detailed distributions such as those presented in Figure 4 are not amenable to simple statistical treatments, there is a sense in which the KBr†–nonpolar partner systems behave nearly randomly. Figure 6 presents an information theoretic treatment[35] of the data obtained from Figure 4 after averaging the velocity distributions over all experimentally accessible cm scattering angles. The lower portion of the figure displays the experimental and microcanonical equilibrium probabilities that a given fraction, f_T, of the total system energy will appear as translation. The natural logarithm of the ratio ω of these two probabilities is a measure of the deviation of the observed distribution from that associated with microcanonical equilibrium and is displayed in the upper portion of the figure. The interpretation of such plots has been discussed in detail recently.[37] The values of λ are the negatives of the slopes of the linear regions and can be related to effective temperatures.[37] The larger value of λ associated with small f_T corre-

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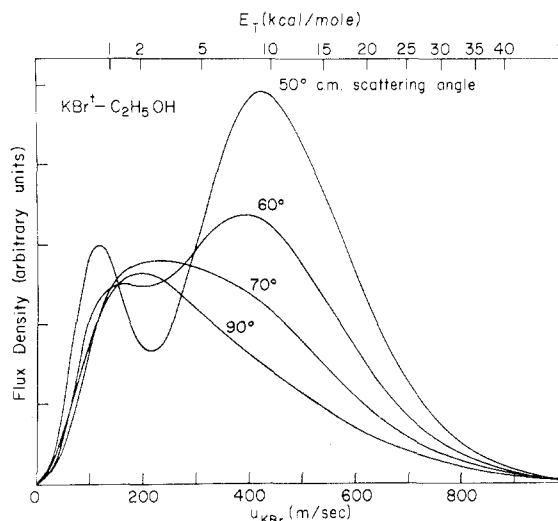
Figure 7. Center of mass intensities for the KBr†–C$_2$H$_5$OH system presented with the same conventions used for Figure 4.

sponds to nearly elastic scattering and large deviations from microcanonical equilibrium. The smaller value of λ is associated with large energy transfer and a nearly random final state distribution. For all $f_T \geq 0.2$ the value $\lambda = 0.8$ adequately represents the observed distribution, and most of the rest of the distribution is well represented by $\lambda = 16$. All other nonpolar partners yield surprisal plots which are well characterized by two straight line segments over almost the entire f_T range.[35,36] This introduces the possibility that a modified statistical model might be adequate for describing final energy distributions (but *not* angularly resolved energy distributions) in these systems if a general scheme for predicting λ's could be found.

Other Polyatomic Partners

In the previous sections we have discussed systems in which either attractive or repulsive forces are of predominant importance in energy-transfer processes. Here we briefly discuss results obtained in systems exhibiting the importance of both kinds of forces. Data were collected[20] for the scattering of KBr† by C$_3$H$_8$, (CH$_3$)$_2$O, and C$_2$H$_5$OH, molecules having dipole moments of 0, 1.3,[26] and 1.7 D,[26] respectively. These data, in combination with those for the nonpolar partners Ar and CO$_2$, describe a series of partners having different structures and long-range interactions with KBr† but similar masses.

Figure 7 presents center of mass results for the KBr†–C$_2$H$_5$OH system; results for the other systems were very similar. The curve for 50° shows a low- and a high-velocity peak as did the distributions for the nonpolar systems. At larger angles the high-velocity peak diminishes in intensity, and at 90° a single smooth peak is observed. Although the shape of the curve at 90° strongly suggests that attractive forces are important, it cannot be fit quantitatively using the collision complex model. There is more intensity at high velocity for the experimental 90° curve than is predicted by the complex model,[20] and therefore we cannot assume that a simple transition between repulsion-dominated and attraction-dominated interactions takes place as the scattering angle increases from 60 to 90°. At fixed θ, a simple measure of the extent of vibration–translation energy transfer is the difference be-

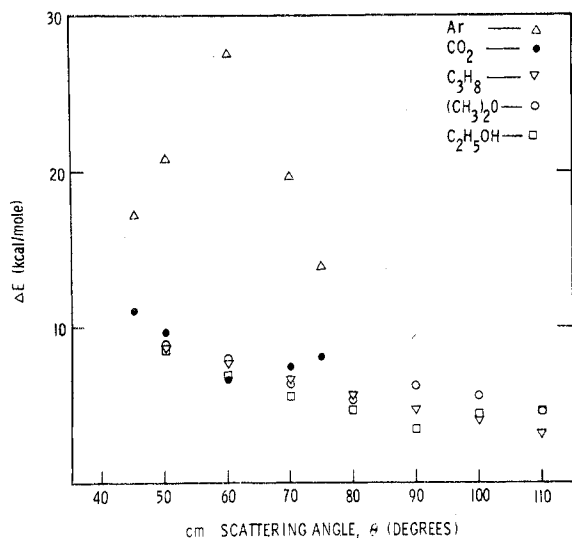**Figure 8.** Characteristic energy transfer, ΔE, as a function of cm scattering angle for the scattering of $KBr^\dagger$ by Ar, CO_2, C_3H_8, $(CH_3)_2O$, and C_2H_5OH.

tween the relative translational energy corresponding to the maximum intensity in the high-velocity region and the initial relative translational energy. This quantity is designated ΔE and is plotted as a function of θ in Figure 8 for all the partners having molecular weights between 40 and 46. Within the experimental uncertainty, the ΔE's for all the molecular partners are the same at a given cm scattering angle. This observation coupled with the remarks at the end of the preceding section suggests that it may well be possible to find a fairly general quasi-statistical theory which will treat collision dynamics in systems not involving atomic collision partners or complex formation.

In this Account we have tried to indicate why energy transfer warrants thorough investigation. We have illustrated one set of techniques appropriate for studying vibrational energy transfer at the single collision level and have showed how scattering distributions in prototype systems can be interpreted qualitatively. A discussion of the quantitative interpretation of data in simple systems dominated by either attractive or repulsive forces was given and the features present in more complicated systems were discussed briefly. We have tried to show how molecular beam studies can yield a worthwhile reward in terms of an improved understanding of the mechanisms responsible for vibrational energy transfer.

An Atom Dipole Interaction Model for Molecular Optical Properties

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A simple way to understand the origin of various optical effects in many substances is based on an atom dipole interaction model. The atoms in a molecule are regarded as isotropic particles which interact by way of the dipole moments induced in them by an external field. Since the dipole fields are anisotropic, the molecule as a whole becomes anisotropic. This model was first proposed by Gray[1] in 1916 to account for optical rotation and by Silberstein[2] in 1917 to account for molecular anisotropies exhibited by the depolarization of scattered light and by the electrooptical Kerr effect. The qualitative predictions of Silberstein's theory provided an important insight during the early part of this century, and served as a basis for correlating anisotropy data with molecular structure in the work of Cabannes,[3] Stuart,[4] and others. Before the advent of electronic computers, however, it was difficult to treat the model quantitatively for polyatomic molecules. Consequently, the model has until recently played little role in the quantitative theory of molecular properties, and little was known about its quantitative validity.

From the early studies it could be expected that the model would provide some information on molecular optical properties outside of absorption bands. It might, therefore, be a useful alternative to quantum mechanical dispersion theory in such cases, since the latter requires a detailed knowledge of many electronic transitions in order to make calculations analogous to those which can be performed with relatively little empirical information for the atom dipole interaction model. In recent years we have found that the model is approximately valid for many polyatomic molecules. Thus it is possible to predict signs and approximate magnitudes of properties (e.g., optical rotations and

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