

## V-RT TRANSFER: A STUDY OF TWO OPPOSING DYNAMIC CONSTRAINTS\*

Avia KAFRI and Ronnie KOSLOFF

*Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel*

Received 20 December 1976

A procedure for the estimation of the relative rates of energy transfer among the vibrotational states of a diatomic molecule in a nonreactive collision is presented. It is found that these rates are dominated by two opposing dynamical constraints: 1. Inertia of the linear momentum of the relative motion. 2. The tendency to conserve the molecular angular momentum. The detailed product distributions are constructed by a procedure which maximizes the entropy of the density matrix subject to the dynamical constraints. The results are compared to experimental measurements and quantum mechanical calculations.

### 1. Introduction

When a molecule collides with an atom, a rearrangement of its energy may occur. How this energy is partitioned among the vibration, rotation and translation is the subject of this investigation. The results presented in this paper, suggest that the internal energy partitioning is governed mainly by two opposing dynamical constraints:

- (a) The tendency to conserve the linear momentum of relative motion.
- (b) The inertia of the angular momentum of the colliding molecule.

Processes of energy transfer are of practical importance in fields such as chemical reaction kinetics [1], gas dynamics [2,3], upper atmosphere phenomena [4], and even astrophysics [5,6]. Moreover, energy transfer collisions form an important class of elementary molecular processes, and as such are of great theoretical interest.

For some systems, energy disposal has become available through experiment [7-11] and through calculations, either by classical trajectory studies [12], or quantum mechanical approximations [13,14]. Nonetheless, there is a need for a simple theory by means of which detailed cross sections can be predicted and classified, and which preserves the physical picture of the molecular encounter. This was the ori-

gin of mechanical models such as the well known Landau-Teller model for V-T transfer [15] or its elaboration to include V-R-T transition by Moore [16].

In this paper we want to present a procedure based on the information theoretic approach, which takes into consideration dynamical characteristics of the molecular encounter. The procedure is based on a maximum entropy of a generalized density matrix. We make use of the correlation between reactants and products as constraints defining the joint distribution. As a direct consequence of the formalism the microscopic reversibility is built in.

In the analysis of vibrotational (V-RT) detailed cross sections we notice a few significant features. The dominant fact is the shift of the most probable rotational number with the variation of  $\Delta v$  (the change in the vibrational number). This is common for both reactive [17] and nonreactive collisions [7].

More detailed examination of the shift reveals the following facts:

- (a) The shift increases with the initial rotation.
- (b) The shift is proportional to the reduced mass of the colliding partner, and inversely proportional to the molecular reduced mass.
- (c) The shift is invariant to small changes in the initial translational energy.

Another interesting feature is the increase of the rotational distribution width with  $|\Delta v|$ .

The outcome of our procedure is consistent with these observations. The resulting rotational and trans-

\* Work supported by the Stiftung Volkswagenwerk.

lational joint distribution of the products in nonreactive molecular collisions is of the form:

$$P(j', E_T' | j, E_T; E) = P^0(j', E_T' | j, E_T; E) \exp(-\lambda \Gamma^2 - \alpha \Delta j^2), \quad (1)$$

when  $\Gamma$  is the linear momentum transfer and  $\Delta j$  is the angular momentum transfer.  $\lambda$  and  $\alpha$  are coupling parameters between the reactants and products.

The method we have employed is discussed in section 2. A detailed exposition of the maximum entropy procedure in the density matrix formalism can be found in appendix A.

Section 3 describes the product rotation and translation distributions, subject to dynamical constraints. Section 4 gives a summary of approximate analytic expressions of vibration rotation distributions for thermal reactants. (In appendix B we present the detailed derivation of these formulas.) The connection to the exponential gap law is also demonstrated in section 4. Section 5 compares and applies the results of the investigation to experimental and computational results.

## 2. General framework

In molecular collisions there exist two limits of behavior. A statistical limit which can be defined by a lack of correlation between reactants and products. All the final states are equally probable irrespective of the initial conditions, subject to conservation laws [18–21] (such as energy and angular momentum conservation). The other extreme is a narrow delta function distribution. The actual case is somewhere in between these extremes.

Our procedure improves the results of the statistical theory by including dynamic correlations between the reactants and products. The method we use to include these correlations is to translate them to constraints on a generalized density matrix. Because of the symmetry of the constraints, microscopic reversibility becomes automatically built-in. In appendix A we give the detailed discussion of the formalism and the results applicable to V-RT energy transfer.

We have limited our discussion to atom-molecule collisions, although an extension of the theory to molecule-molecule collisions is possible.

In seeking variables to describe the collision, we look for the variables which are conserved when no interaction takes place. Vectors are preferable to scalars (like the internal energy) since they carry more information.

Our first choice of variable is the relative momentum transfer

$$t = p' - p \quad (2)$$

$p$  and  $p'$  are the initial and final momentum of the relative motion.

In elastic scattering all physical behavior can be described by this variable, because as a vector quantity, it describes the angular distribution.

The qualitative success of the Born approximation [22] to describe inelastic scattering leads us to the conclusion that the momentum transfer variable is a good choice. The Born approximation is a method to describe the molecular encounter by defining the probability amplitude of the momentum transfer.

Our next choice of variable is the angular momentum transfer:

$$\Delta j = j' - j, \quad (3)$$

$j$  and  $j'$  are the initial and final molecular angular momentum. This is a natural choice because it is immediately connected to the conservation of the total angular momentum.

## 3. Translational and rotational distributions, subject to dynamical constraints

### 3.1. The momentum transfer distribution

The simplest assumption that can be made on the momentum transfer is that there is no preference to any angle in space because of symmetry considerations. (This assumption is similar to the random walk assumption.) Therefore, the first moment of the momentum transfer vanishes.

We maximize the entropy of the density matrix subject to the constraint of a known second moment of  $t$ ,  $\langle t^2 \rangle = \gamma^{-1}$ .

In the classical limit we obtain:

$$P(t) dt = \exp(-\gamma t^2) t^2 dt d\Omega. \quad (4)$$

To obtain the distribution of the recoil energy con-

ditioned on the initial translation we first integrate over the spatial angles  $\Omega$ . We get to the scalar measure of the momentum transfer:

$$\Gamma^2 = [(E'_T)^{1/2} - (E_T)^{1/2}]^2 \quad (5)$$

(cf. appendix A).

To a good approximation the conditional translational distribution is:

$$P(E'_T | E_T; E) = P^0(E'_T | E_T; E) \exp \{-\lambda [(E'_T)^{1/2} - (E_T)^{1/2}]^2\}, \quad (6)$$

where  $\lambda = 2\mu\gamma$ .  $P^0(E'_T | E_T; E)$  is simply the prior distribution function (see appendix A). (The parameter  $\lambda$  can be estimated from the potential surface [23].)

We dispense with further discussion of the problem of the momentum transfer distribution since it can be found elsewhere [24–26].

### 3.2. The rotation angular momentum distribution

To obtain the rotation angular momentum distribution we used the same procedure as for obtaining the density matrix of the linear momentum. Again, we adopted the unbiased assumption that all directions in space of  $\Delta j$  transitions are equally probable, so that the first moment of  $\Delta j$  vanishes

$$\langle \Delta j \rangle = 0, \quad \langle \Delta j^2 \rangle = \alpha^{-1}. \quad (7)$$

Subject to these moments, we obtain the conditional distribution (up to a normalization factor):

$$P(j' | j, E'_T, E_T, E) = \sum_{k=|j-j'|}^{j+j'} (2k+1) \exp[-\alpha k(k+1)]. \quad (8)$$

Both the linear momentum transfer and the angular momentum transfer distributions depend on a temperature-like parameters  $\lambda^{-1}$  and  $\alpha^{-1}$ . When  $\lambda$  and  $\alpha$  tend to zero, the distributions become statistical.

### 3.3. Joint distributions of the products

#### 3.3.1. The joint distribution translation rotation

The rotation and translation are dependent variables, therefore the joint distribution is constructed from a marginal translational distribution and a conditioned rotation.

In a single collision we have the vector equation of the total angular momentum conservation:

$$J = l + j = l' + j'. \quad (9)$$

Consequently,  $\Delta l = -\Delta j$ . Likewise, any probability moment of eq. (9) must hold

$$\langle \Delta l^n \rangle = \langle (-\Delta j)^n \rangle. \quad (10)$$

From symmetry consideration  $\langle \Delta j \rangle$  vanishes, and the second moment equation gives us the desired correlation between translation and rotation:

$$\langle \Delta l^2 \rangle = \langle (\mathbf{b} \times \mathbf{p} - \mathbf{b}' \times \mathbf{p}')^2 \rangle \quad (11)$$

( $\mathbf{b}$  and  $\mathbf{b}'$  are the initial and final impact parameters).

If the correlation between  $\mathbf{b}$  and  $\mathbf{p}$  is neglected and we assume that  $\langle \mathbf{b}^2 \rangle$  is proportional to the total cross section, using microscopic reversibility of the detailed cross sections:

$$\langle \mathbf{b}^2 \rangle \mathbf{p}^2 = \langle \mathbf{b}'^2 \rangle \mathbf{p}'^2, \quad \text{define } b_{av}^2 = (\langle \mathbf{b}^2 \rangle \langle \mathbf{b}'^2 \rangle)^{1/2}, \quad (12)$$

we get

$$\langle \Delta l^2 \rangle = \langle (\mathbf{b} - \mathbf{b}')^2 \rangle \mathbf{p} \mathbf{p}' + b_{av}^2 \mathbf{p}^2. \quad (13)$$

Hence the  $\Delta j$  correlation parameter is given by

$$\alpha^{-1} = a (E'_T E_T)^{1/2} + c \Gamma^2,$$

$$a = 2\mu \langle \Delta \mathbf{b}^2 \rangle, \quad c = 2\mu b_{av}^2. \quad (14)$$

We can identify the two sources of orbital angular momentum transfer, the first being a change in impact parameter, namely a measure of the unisotropy of the potential surface, and the second caused by linear momentum change.

To obtain the joint distribution translation and rotation we multiply eq. (6) with eq. (8). Treating  $j$  in the classical limit, we obtain:

$$P(j', E'_T | j, E_T; E) = P^0(j', E'_T | j, E_T; E) \exp(-\lambda \Gamma^2 - \alpha \Delta j^2), \quad (1)$$

and  $P^0(j', E'_T | j, E_T; E)$  can be approximated by the usual prior:  $N(2j'+1)(E'_T)^{1/2}$ . It should be emphasized that the exponent in eq. (1) obeys microscopic reversibility.

Treating the angular momentum transition as a vector quantity we have to take into consideration certain restrictions on orientation. A list of orientational correlations has been collected by Case and Hershbach [27]. In the absence of relevance our formal way of attacking the problem ensures the existence of all the

geometrical correlations. However, it is a different case when there are new orientational correlations between reactants and products. An example is helicity conservation on which there is a large amount of theoretical and computational material, proving that in many cases, the product helicity has a strong correlation to the initial one [28,29]. In appendix A we give an example of a distribution derived under the assumption of helicity conservation.

### 3.4. Rigid rotor rotation distributions

When a rigid rotor collides with an atom, the two terms in eq. (1) operate in essentially the same direction. This is easily seen by noting that  $t$  and  $\Delta j$  are approximately the same variables since

$$E'_T + E'_R = E_T + E_R, \quad |t| = (2\mu)^{1/2} |(E'_T)^{1/2} - (E_T)^{1/2}| \\ \approx (2\mu)^{1/2} |(E'_R)^{1/2} - (E_R)^{1/2}| \approx (2\mu B_e)^{1/2} |j' - j|. \quad (15)$$

This is the situation at low energies and small momentum changes so that a single term in the exponent of (1) suffices. This term can also be approximated by the equation:

$$P(E'_R | E_R; E) \quad (16)$$

$$= P^0(E'_R | E_R; E) \exp\{[\lambda + (2E_R B_e c)^{-1}] |\Delta E_R|\},$$

which is the exponential gap law well documented for R-T energy transfer [30,31]. At high collision energies, approximations (15) and (16) deteriorate and both terms in (1) need to be explicitly present, where  $E'_T = E_T + E_R - E'_R$ .

### 3.5. The joint distribution rotation vibration

We get this distribution by a change of variable. In the rigid rotor approximation:

$$E'_T = E_T + \Delta v + \Delta R, \quad (17)$$

where  $\Delta v = E_v - E'_v$  and  $\Delta R = E_R - E'_R$ .

Examining eq. (1) we find that the first term  $\lambda \Gamma^2$  prefers transitions in which the internal energy is conserved ( $\Delta v + \Delta R = 0$ ). On the other hand, the term  $\alpha \Delta j^2$  prefers angular momentum conserving transitions. This competition between the two dynamical constraints is the origin of the shift of the most prob-

able rotation with the change in the vibrational energy. To demonstrate this phenomenon explicitly, we have expanded the exponent to the second order in  $\Delta v$  and  $\Delta R$  around the global maximum (the elastic transition). The result is

$$P(\Delta v, \Delta R | E_v, E_T; E) = P^0(E'_v, E'_R; E) \quad (18) \\ \times \exp\{-(\lambda/4E_T)[(\Delta R + \psi \Delta v)^2/\psi + (1-\psi)\Delta v^2]\},$$

where

$$\psi = \lambda a B_e E_R / (1 + \lambda a B_e E_R), \quad (19)$$

$B_e$  is the molecular rotational constant,  $a$  is defined by eq. (14).

In the classical limit (for high values of  $jj'$ ) we can neglect the contribution of  $P^0$ . Therefore, the most probable rotation is obtained when:

$$\Delta R = -\psi \Delta v.$$

Because  $0 \leq \psi \leq 1$ , this equation describes the two limits of the competition between the minimum momentum transfer when  $\psi = 1$  and the minimum  $j$  transfer when  $\psi = 0$ .

## 4. The rotation vibration distribution for thermal reactants

We first consider thermal reactants of which the initial translation is coupled to a heat bath (when  $\beta = 1/kT$ ). In principle, the constants  $\lambda$ ,  $a$  and  $c$  in eqs. (1) and (14) are energy dependent. If the variation of parameters is moderate, or we know the energy dependence of the constraints, we can integrate numerically eq. (1). However, simple analytic expressions are more convenient. This can be achieved by finding an analytic approximation for the temperature averaging integrals which is possible for a few limiting cases (for details see appendix B).

### 4.1. R-T transition

In this case:

$$P(\Delta R | E_R; \beta) = P^0(\Delta R | E_R; \beta) \exp(-\beta \theta_R |\Delta R|), \quad (20)$$

where

$$\theta_R = [(1 + \lambda a B_e E_R) / \beta a B_e E_R]^{1/2},$$

in cases where the expansion of eq. (18) is valid. If the momentum transfer term dominates then:

$$\theta_R = \frac{1}{2} [-1 + (1 + 4\lambda/\beta)^{1/2} \{1 + [\beta E_R B_c (a\lambda/\beta + c)]^{-1}\}],$$

when  $\lambda/\beta \rightarrow \infty$  the two  $\theta_R$  coincide.

#### 4.2. V-T transition

In this case we have a double integration on  $E'_R$  and  $E_T$  and we obtain:

$$P(\Delta v|E_R; \beta) = P^0(\Delta v|E_R \beta) \exp(-\beta \Lambda |\Delta v|), \quad (21)$$

when  $\Lambda = [(1 - \psi)\lambda]^{1/2}/\beta$ .

Reviewing the set of formulae for the rotational and vibrational distributions for thermal reactants we observe that they are the exponential gap law as discussed by Procaccia and Levine [31,32]. Both parameters  $\theta_R$  and  $\Lambda$  can be obtained by the synthesis method of Procaccia and Levine [31,32]. The temperature dependence of  $\Lambda$  and  $\theta_R$  predicted in eqs. (20) and (21) is qualitatively the same.

### 5. Application to experimental and computational results

As was seen in the above paragraph, our functional form resembles the exponential gap law closely. We therefore did not see a need to repeat results which have been confirmed by numerous cases [31,32]. We, however, have considered only the cases where the exponential gap law is not adequate.

#### 5.1. Fixed energy calculations

A vast number of quantum mechanical calculations has been recently worked out for molecular hydrogen relaxation processes [13,14]. In this paper we have considered the coupled state calculations of Alexander and McGuire on the He+H<sub>2</sub> and He+D<sub>2</sub> reactions [14]. We focus our attention on the vibration rotation relaxation cross sections of the  $v=1, j=0$  state to the  $v'=0, j'$  states.

As was previously noticed qualitatively [7,14,16] and as presented in section 3 there is a competition between the minimum  $j$  transfer and the minimum momentum transfer. This result we have confirmed quantitatively in what follows.

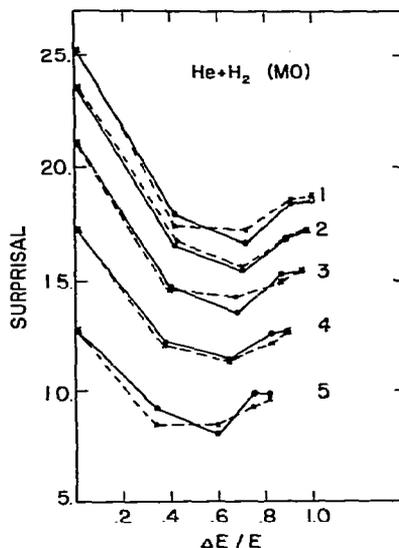


Fig. 1. Surprisal plots of the detailed yield function  $y = (E_T)^{1/2} \alpha$  ( $v=1, j=0 \rightarrow v=0, j'$ ) for the system  $\text{He} + \text{H}_2$ , for five different initial energies. The  $(\cdot)$  refers to the calculation of Alexander and McGuire [13] for the MO potential. The X's are reproduced through eq. (22) where the fitted parameters are summarized in table 1 and are the same for all energies. The surprisal is  $I = \log y/y^0$  where  $y^0 = c(E_T E'_T)^{1/2}$ . The initial translational energies are: (1)  $4.99 \times 10^{-3}$  eV; (2)  $1.098 \times 10^{-2}$  eV; (3)  $2.398 \times 10^{-2}$  eV; (4)  $5.398 \times 10^{-2}$  eV; (5)  $1.140 \times 10^{-1}$  eV.  $E$  is the total energy above the ground state. The difference between this surprisal and that of Alexander [33] is in the  $(2j'+1)$  term which we omitted from our pre-exponent  $P^0$  (see text).

In the coupled states calculation [14] only helicity conserving states are gathered into the  $S$  matrix. For  $j=0$  only  $m'=0$  exists. In eq. (8) only one term is left over and we obtained for the surprisal:

$$I = \lambda \Gamma^2 + \alpha j'(j'+1) + \lambda_0. \quad (22)$$

Figs. 1–4 present the surprisal plots for the cross sections for different initial energy for different potential and collision partners. The graphs compare the computed results from ref. [14] to those computed by the use of eq. (22).

In order to determine the coupling parameters we separate the different contributions to the surprisal. When we examine the energy level scheme we find that the  $v=1, j=0$  state is almost resonant to the  $v=0, j=8$  state. Effectively the momentum transfer term

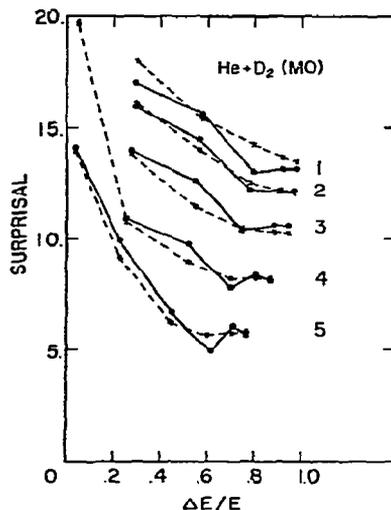


Fig. 2. Surprisal plots of the detailed yield function for the system  $\text{He} + \text{D}_2$  in the MO potential. All conditions are the same as for fig. 1.

$\lambda \Gamma^2$  vanishes and we are left with only the  $j$  transfer term. Conversely, in the  $\nu=1, j=0 \rightarrow \nu=0, j=0$  transition only the momentum transfer exists.

Fig. 5 demonstrates the linear dependence of the  $\nu=1, j=0 \rightarrow \nu=0, j=0$  surprisal on the squared momen-

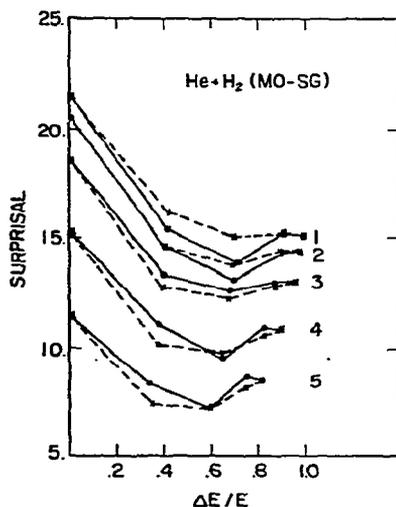


Fig. 3. The same as fig. 1 for the HO potential.

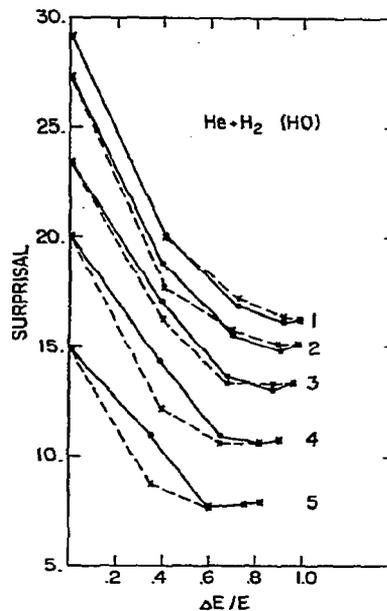


Fig. 4. The same as fig. 1 for the MO-SG potential.

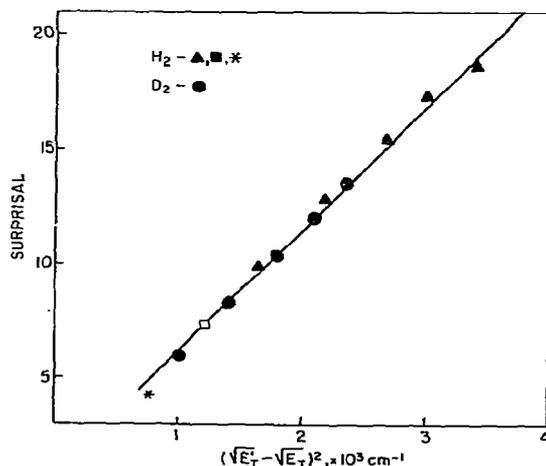


Fig. 5. Surprisal plot of the detailed yield function  $y(\nu=1, j=0 \rightarrow \nu=0, j=0)$  versus the momentum transfer (for the MO potential). The absence of the rotational transfer term enables us to determine the dependence of the surprisal on the momentum transfer. One straight line is sufficient both for the  $\text{D}_2$  points as well as the  $\text{H}_2$  points. This suggests that  $\lambda$  is mass invariant. The points denoted by  $\square, \star$  correspond to  $E_T = 0.214$  and  $0.414$  eV, respectively.

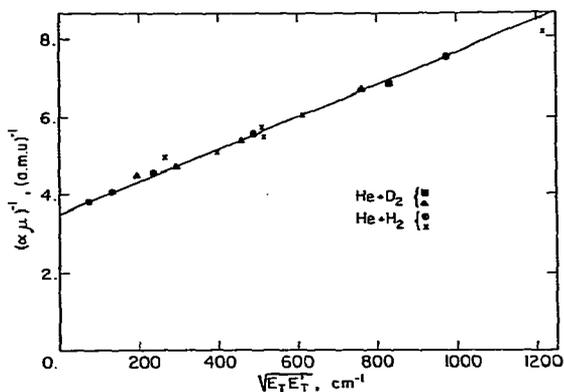


Fig. 6. A plot of the mass invariant angular momentum coupling constant  $(\alpha\mu)^{-1}$  versus  $(E_T E_T')^{1/2}$  for the system He+H<sub>2</sub> (D<sub>2</sub>). In the transition  $\nu=1, j=0 \rightarrow \nu=0, j=8$  for H<sub>2</sub>, the momentum transfer is negligible hence  $\alpha = (I - \lambda_0)/\Delta j(\Delta j + 1)$  ( $I$  is the surprisal,  $\lambda$  is a normalization constant). For the system He+D<sub>2</sub> and the transitions  $\nu=1, j=0 \rightarrow \nu=0, j=6$  for H<sub>2</sub>, the momentum transfer term  $\lambda\Gamma^2$  is subtracted. The slope is  $\langle \Delta b^2 \rangle = (0.26 r_0)^2 = 0.04 \text{ \AA}^2$ .

tum transfer. Note that  $\lambda$  is isotopic invariant and energy independent at least for cases where  $E_T \leq 0.2 \text{ eV}$ .

The next step is the determination of  $\alpha$ . The transitions with negligible momentum transfer contribution are to be considered first. A linear dependence of  $\alpha^{-1}$  on the product of the initial and final momentum  $p p'$  is found. For mixed transitions the momentum transfer term  $\lambda\Gamma^2$  is subtracted from the surprisal. The points on the plot which belong to states of which  $\Gamma^2 \neq 0$  suggest that  $b_{uv}^2$  [eq. (12)] is small, suggesting that efficient vibration transitions occur only for close to collinear configurations. This is consistent with the small total  $V-V$  relaxation cross section. Fig. 6 demonstrates the functional dependence of  $\alpha^{-1}$  on  $(E_T E_T')^{1/2}$ . Eq. (14) predicts that  $(\alpha\mu)^{-1}$  is mass invariant. This prediction is confirmed by fig. 6 since the points of He+D<sub>2</sub> system fit to the same line of He+H<sub>2</sub>. The interesting feature is the finite intercept, suggesting that  $j$  transfer term is finite when  $E_T = 0$ . The dependence of  $\alpha^{-1}$  on  $(E_T E_T')^{1/2}$  suggested by fig. 6 is:  $(\alpha\mu)^{-1} = \alpha_0/\mu + \langle \Delta b^2 \rangle (E_T E_T')^{1/2}$ . This function was checked also for higher  $E_T$  up to 0.414 eV. The fitted  $\alpha$  from the results of ref. [14] for  $E_T = 0.414 \text{ eV}$  deviates from the extrapolated line of fig. 6 by 8%.

Figs. 1 and 2 demonstrate the fit of eq. (22) to the

Table 1

A summary of the parameters used for the fit of the surprisals given by eq. (22)

System	Potential	$hc\lambda$ (10 <sup>3</sup> cm)	$\alpha^0/\mu$ (amu <sup>-1</sup> )	$(\langle \Delta b^2 \rangle)^{1/2}/r_0$ <sup>a)</sup>
He+H <sub>2</sub>	MO	5.7	3.5	0.26
He+D <sub>2</sub>	MO	5.7	3.5	0.26
He+H <sub>2</sub>	HO	4.9	3.1	0.24
He+H <sub>2</sub>	MO-SG	4.8	2.8	0.28

a)  $r_0$  is the equilibrium diatomic separation.

surprisal plots of the inelastic cross sections of He+H<sub>2</sub> and He+D<sub>2</sub>. The fitted parameters are summarized in table 1. The same parameters were sufficient for all the initial energies. Figs. 3 and 4 demonstrate the same functional fit for the molecular potentials HO and MO-SG. (We kept the original notation of ref. [14] for the various potential surfaces.)  $\lambda$  is a measure of the stiffness of the potential. The larger  $\lambda$  value for the HO surface is consistent with the fact that the harmonic oscillator is more rigid than the Morse oscillator.

The success of the functional fit of eq. (22) to the quantitative as well as qualitative features of VR-T relaxation and its parametrization to a few energy independent constants, gives us the benefit of a simple extrapolation. The fitted parameters present a way to classify the potential surfaces to  $j$  transfer and momentum transfer. The mass invariance of the parameters suggests that the constants are only potential-dependent [23].

In a recent paper, Alexander [33] concluded that the nonlinearity of the surprisal is caused by the nonclassical behaviour of the system. In our opinion the oscillation around the predicted line may be a quantum effect. However, the main feature is a consequence of the two conflicting dynamical constraints.

## 5.2. Thermal translation experiments

An exposition of the phenomena significant in V-RT transitions was presented by the high resolution experiment of Enen and Ottinger [7]. The experimental system was composed of Li<sub>2</sub> <sup>1</sup>B<sub>u</sub> (in a specific  $\nu, j$  state) colliding with an inert gas maintained at a constant temperature. The results of the vibrotational distributions (for the two initial  $\nu, j$  states) is reproduced in figs. 7 and 8. The shift of the most probable rota-

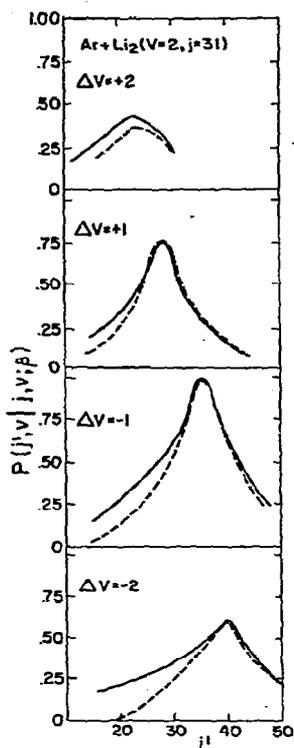


Fig. 7. Detailed normalized rate constants for the collision  $A_T + L_{i2}$  ( $v=2, j=31$ ). The solid line was reproduced from the measurements of Enen and Ottinger [7]. The dashed line displays the fitted distribution based on eq. (1) when the initial translation was averaged numerically on a Boltzmann ensemble. The fitted parameters are summarized in table 3.

tion for each vibrational change is noticed clearly. As a representative case we display a quantitative fit of the vibrotational distribution derived by a numerical integration of the initial translation in eq. (1) (averaged over a Boltzmann distribution). The same parameters were used for the two initial  $v, j$  states (table 2 summarizes the fitted parameters). The small differences between the fit and the experimental data is within the experimental error set by the authors, (20% for V-V transitions.) Partly it may be caused by secondary relaxation processes [7]. In what follows we focus our attention on the major features of the distributions.

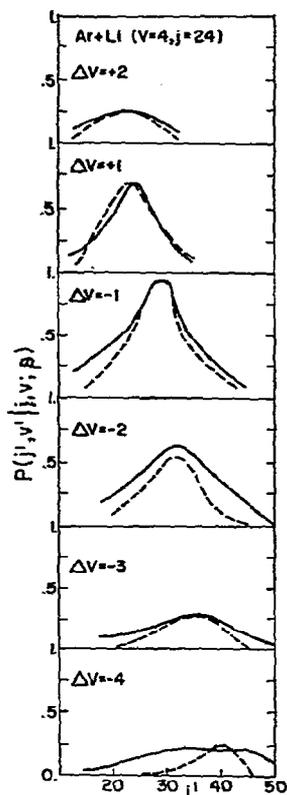


Fig. 8. The same as fig. 7, for the initial conditions  $A_T + L_{i2}$  ( $v=4, j=24$ ) we used the same fitted parameters for both initial conditions.

### 5.2.1. The shift

As can be seen in figs. 7 and 8 the two initial  $j$  states reproduce different shifts of the maximum rota-

Table 2

A summary of the parameters used for the fit of the vibrational distribution function for the system  $L_{i2} + A_T$

$hc\lambda$ (cm)	$\lambda\omega_e$ <sup>a)</sup>	$\langle b^2 \rangle / r_0^2$	$\langle b^2 \rangle$ ( $\text{Å}^2$ )	$\langle (\Delta b^2) \rangle^{1/2} / r_0$ <sup>b)</sup>	$\langle (\Delta b^2) \rangle^{1/2}$ ( $\text{Å}$ )
$1.1 \times 10^{-3}$	3	29	80	0.16	0.45

a)  $\omega_e$  is the harmonic vibrational energy separation.

b)  $r_0$  is the equilibrium diatomic distance.

Table 3

A comparison between the predicted and measured shift for different colliding partners and initial conditions [based on eq. (19)]

System	State	$\psi$ measured <sup>a)</sup>	$\psi$ predicted
Li <sub>2</sub> + Ar	$j = 31 \nu = 2$	0.55	0.47
Li <sub>2</sub> + Ar <sup>b)</sup>	$j = 24 \nu = 4$	0.34	0.34
Li <sub>2</sub> + Xe	$j = 31 \nu = 2$	0.51	0.51
Li <sub>2</sub> + Xe	$j = 24 \nu = 4$	0.35	0.38
Li <sub>2</sub> + He	$j = 31 \nu = 2$	0.34	0.23
Li <sub>2</sub> + He	$j = 24 \nu = 4$	0.20	0.15

a) The measured values are from ref. [7]. b) Reference.

tional states within the vibrational manifold. In our fit we have used the same potential parameters to describe the two distributions. This brings us to the conclusion that the difference in the shift is a consequence of the change in the initial rotational state, in accordance with eq. [19]. The larger shift for higher initial  $j$  simply reflects the increase of rotational energy spacing.

Eq. (19) can give an approximation of the dependence of the shift on the molecular parameters. If we assume that the potential surface is similar for different colliding partners, we can use eq. (19) to calculate the change in the shift due to the mass effect. If  $\lambda$  is mass invariant, the mass dependence is the ratio of the relative motion reduced mass to the molecular reduced mass. Table 3 presents the use of eq. (19) to predict the shift for different colliding partners and different initial rotation.

The reason that the translation does not appear in eq. (19) is that it plays two opposite roles which cancel each other out. First, it increases the orbital angular momentum and hence the  $j$  changes, but it also makes a momentum change easier because  $\Gamma$  is a decreasing function of the initial translational energy.

Another interesting feature is the increase of the width of the vibrotational distributions when departing from the resonant  $\nu$  state. Examining eq. (13) we identify this phenomena to be a consequence of the increase of the angular momentum transfer  $\alpha^{-1} = \langle \Delta l^2 \rangle$  with the increase in the momentum transfer  $\epsilon$ .

The large  $b_{av}^2 \approx 80 \text{ \AA}^2$  found in our fit (the estimate of the total cross section) is consistent with the measured large inelastic cross section of  $\approx 60 \text{ \AA}^2$ .

## 6. Concluding remarks

The competition between the propensity to conserve the angular momentum and the tendency to conserve linear momentum, has been found to play a major role in the determination of the vibrotational distribution. We have presented a consistent procedure based on the maximum entropy of a generalized density matrix, the outcome of which has a simple functional form. The parameters  $\lambda$ ,  $a$ ,  $c$  have a physical significance. Therefore, they can be estimated from general features of the molecular interaction. This enables us to predict detailed product state distributions. On the other hand, our procedure provides an opportunity to estimate and to classify the dynamical features of the molecular interaction such as the stiffness of intramolecular potential, the directionality of the potential surface and especially the total cross section out of raw data.

## Acknowledgement

We wish to thank Professor R.D. Levine and Dr. A. Ben-Shaul for constructive suggestions and discussions.

## Appendix A

### A.1. Procedure for obtaining detailed cross sections in the density matrix scheme

A scattering event is defined by a set of dynamical variables which commute with the asymptotic hamiltonian of the entrance and exit channels. The interaction potential generates correlations among variables of the different channels. Therefore it is convenient to describe the scattering event in the tensor product of the asymptotic variables [36]. In any experiment the dynamical variables are to some extent random. Moreover, the interaction may be unknown or random.

The density matrix of von Neuman [34,35] is tailored to deal with a random state vector. In order to deal with the random nature of the molecular encounter we introduce a generalized density matrix defined on the tensor product space. In this space the probability distribution of a dynamical variable  $a$  is:

$P(a) = \text{Tr}(a \cdot \rho) / \text{Tr}(\rho)$ , where  $a$  is the projection operator of the variable  $a$  in the tensor product space,  $\rho$  is the density matrix,  $\text{Tr}$  denotes the trace operation.

Lacking any prior information on the interaction we obtain the familiar statistical theory [27,18,19] by using the procedure of von Neuman of equating the diagonal elements to one and zero otherwise. This ensures that the statistical density matrix is invariant under the transformations of the base set. The choice of boundary conditions will make a selection of the statistical theory. (For example, a time box or a space box.) The statistical theory plays the role of degeneracy in the statistical mechanics of stationary states. (An excellent discussion of the problem can be found elsewhere [20,21].)

Dealing with the density matrix one can define a normalized submatrix in which part of the indices are fixed. Evaluating the trace of this submatrix, we obtain the conditional distribution, subject to the selection of these variables.

Our next step is to include all available information in the construction of the density matrix. We follow the well known procedure of Jaynes [37] of obtaining the canonical distributions, which was first introduced into the molecular dynamic domain by Ben-Shaul, Levine and Bernstein [38-40]. We maximize the entropy of the density matrix  $\text{Tr}(\rho \ln \rho)$  subject to certain constraints which we have on the collision. The dynamical constraints imposed by the interaction do not commute with the asymptotic observables. Namely, a correlation exists between the magnitude and phases of the variables of the different channels. The  $P$  matrix (the squares of the elements of the  $S$  matrix) lost information on relative phases. Therefore the derivation of the probability distribution through maximizing the entropy of the  $P$  matrix is not adequate.

The generalized density matrix is equivalent to the  $S$  matrix, since the information of the relative phases exists in nondiagonal elements of the density matrix. A convenient way of solving the maximum entropy procedure is to describe information as probability moments of the physical variables that take place in the chemical encounter.

The analytic behaviour of the  $S$  matrix ensures the convergence of the procedure to the exact solution, if we have enough moments. This procedure enables us to use general features of the interactions to construct the probability distributions. On the other hand, meas-

ured distributions can be used to gain knowledge on the interaction potential. To minimize the computational effort we sought the moments that converge the density matrix as fast as possible. The preferred variables are those which define a correlation between the entrance and exit channels. When these correlations are turned off, our procedure reduces to the prior yield function [20,41].

For convenience we summarize the main results of the Jaynes procedure for the density matrix [42,43]. Define  $\langle a_n \rangle = \text{Tr}(a_n \cdot \rho)$  the density matrix which leads to maximal entropy is given by  $\rho = \exp(\sum \lambda_n a_n)$ . In the representation where  $a_n$  is diagonal the Lagrange multiplier  $\lambda_n$  is given by  $\lambda_n = -(\langle a_n \rangle)^{-1}$  in the classical limit.

### A.2. The final translational distribution conditioned on the given initial variables

As we noticed in section 2 we chose the momentum transfer  $t = p' - p$  to define the correlation between the initial and final translation.

If we have no information on the detailed dynamics, we necessarily have the symmetry that will cancel out the first moment of  $t$

$$\langle t \rangle = 0. \quad (\text{A.1})$$

Assuming a known second moment of  $t$ :

$$\langle t^2 \rangle = \gamma^{-1}. \quad (\text{A.2})$$

We then construct the momentum transfer submatrix, subject to the above constraints:

$$\rho_{t\bar{t}} = N \delta(t - \bar{t}) \exp(-\gamma t^2), \quad (\text{A.3})$$

where  $N$  is the normalization factor,  $N^{-1} = \text{Tr}(\rho_{t\bar{t}})$  which can be evaluated analytically [26] and is dependent on  $p$ ,  $E$  through the limits of the integration.

When we have information on angular correlations (for example a high polarizing potential) we construct simultaneously the joint angular and translational distribution. This construction is complicated because not all of the variables commute. A solution of the maximum entropy density matrix procedure under such conditions can be found elsewhere [42]. Obviously, in the classical limit this problem does not exist.

In order to obtain the translational distribution, we change variables to  $p$ ,  $p'$  and  $\Omega$ ,  $\Omega$  is the scattering angle. We average over  $\Omega$  for each specified  $p$  and  $p'$ .

(This is equivalent to the trace operator over the subspace of the spatial angle  $\Omega$ .)

$$\begin{aligned} \rho_{pp'}^{\bar{p}\bar{p}'} &= Np^2 \int e^{-\gamma^2} \frac{\partial(t\Omega')}{\partial(p'\Omega)} d\Omega \delta(p-\bar{p}) \delta(p'-\bar{p}') \quad (\text{A.4}) \\ &= 2\pi N p^2 p'^2 e^{-\gamma(p^2+p'^2)} \int_{-1}^1 e^{-\gamma p p' x} dx \\ &\times \delta(p-\bar{p}) \delta(p'-\bar{p}') \\ &= 2\pi N p^2 p'^2 e^{-\gamma(p-p')^2} [(1-e^{-4\gamma p p'})/2\gamma p p'] \\ &\times \delta(p-\bar{p}) \delta(p'-\bar{p}'). \end{aligned}$$

To obtain the probability distribution of  $E'_T$  conditioned on a given value of  $E_T$  we sum over the internal variables  $j, m, j', m'$  and get:

$$P(E'_T|E_T; E) = P^0(E'_T|E_T) \exp\{-\lambda[(E_T)^{1/2} - (E'_T)^{1/2}]^2\} Z, \quad (\text{A.5})$$

where  $\lambda = 2\mu\gamma$ ,  $\mu$  is the reduced mass of the relative motion and

$$Z = \{1 - \exp[-\lambda(E_T E'_T)^{1/2}]/2\lambda(E_T E'_T)^{1/2}\}.$$

In the limit when  $E_T$  or  $E'_T$  or  $\lambda$  tend to zero,  $Z$  tends to  $\frac{1}{2}$ . In cases of statistical rotations we obtain for the classical limit

$$P^0(E'_T|E_T; E) = 4\pi\mu^{3/2} N (E'_T)^{1/2} (E - E'_T).$$

### A.3. The conditional distribution $P(j'|E'_T, E_T, j; E)$

In this section we evaluate the rotational distribution in cases where a correlation between the internal angular momentum in the reactants and products channel exists. In addition, we define helicity to be the component of the total angular momentum  $J$  along the relative distance  $R$  in the atom-diatomic molecule:

$$h = J \cdot R / |R| = j \cdot R / |R|, \quad h' = j' \cdot R' / |R'|. \quad (\text{A.6})$$

The change of the helicity during the collision is given by  $\Delta h = h - h'$ . We present the correlation between the molecular angular momentum in the entrance and exit channels by the two constraints:

$$\langle \Delta j \rangle = 0, \quad \langle \Delta j^2 \rangle = \alpha^{-1} \neq 0, \quad (\text{A.7, A.8})$$

where  $\Delta j = j' - j$ .

The averaging process in (A.7) and (A.8) is carried over all  $J$  values.

Since  $\Delta h$  and  $\Delta j$  do not commute, we prefer to deal with the distribution of  $j'$  conditioned on a given

$\Delta h$ , in order to avoid laborious algebra [42]. As an example we shall deal with the case of a sharp helicity conservation, namely:

$$P(h, h') = \delta_{hh'}. \quad (\text{A.9})$$

This is the case of coupled states approximation [14]. We start from the statistical assumption, namely where the dynamical constraints (A.7), (A.8) and (A.9) are turned off. The submatrix under consideration is obtained by the von Neuman procedure, namely

$$\rho_{jmj'm'}^{\bar{j}\bar{j}'\bar{m}\bar{m}'} = \delta_{\bar{j}\bar{j}'} \delta_{\bar{j}'\bar{j}'} \delta_{\bar{m}\bar{m}'} \delta_{\bar{m}'\bar{m}'}. \quad (\text{A.10})$$

Now we turn on the helicity dynamical constraint (A.9). We define a coordinate system where the  $z$  axis is parallel to the initial linear momentum. The density matrix at a given initial and final translational energy and at a scattering angle  $\Omega$  is given by:

$$\begin{aligned} \rho_{jmj'm'}^{\bar{j}\bar{j}'\bar{m}\bar{m}'} &= \delta_{\bar{j}\bar{j}'} \delta_{\bar{j}'\bar{j}'} \delta_{\bar{m}\bar{m}'} \\ &\times \sum_{h'h'} D_{m'h'}^{\bar{j}}(-\Omega) D_{\bar{m}'\bar{m}}^{\bar{j}'}(-\Omega) \delta_{h'h'} \delta_{m'h'}. \quad (\text{A.11}) \end{aligned}$$

where  $D_{m'h'}^{\bar{j}}(\Omega)$  are the Wigner matrices [43] and  $m$  is the initial helicity.

In cases where there is a lack of correlation the density matrix is reduced to the unity matrix. If we turn off the constraint of the helicity conservation, then by using the orthogonality relation of the Wigner matrices [43]

$$\begin{aligned} &\int D_{m_1 m_2}^{j_1 j_2}(\Omega) D_{m_1' m_2'}^{j_1' j_2'}(\Omega) d\Omega \\ &= \delta_{j_1 j_2} \delta_{m_1 m_1'} \delta_{m_2 m_2'} (2j_1 + 1)^{-1} \quad (\text{A.12}) \end{aligned}$$

integrating over the scattering angles and carrying the summation over  $h', \bar{h}'$  will bring us back to the statistical  $\rho$ , namely (A.10).

In order to carry out the maximum of entropy procedure consistent with the dynamical constraints (A.7) and (A.8) we change the representation from  $jmj'm'$  set into  $jj'\Delta jM$  set ( $M$  is the  $z$  component of  $\Delta j$ ). The transformation is carried out by the use of Clebsch-Gordan coefficients [43]

$$|jmj'm'\rangle = \sum_M \langle jmj'm' | jj'\Delta jM \rangle |jj'\Delta jM\rangle. \quad (\text{A.13})$$

In this representation the density matrix consistent with (A.9) and at a given scattering angle  $\Omega$  is given by:

$$\rho_{jj'\Delta jM} = \delta_{\bar{j}\bar{j}} \delta_{j'\bar{j}'} \sum_{m\bar{m}} \sum_{m'\bar{m}'} \delta_{m\bar{m}} \delta_{h'\bar{h}'} \delta_{mh'} D_{m'h'}^{j'}(-\Omega)^* \times D_{m'\bar{h}'}^{\bar{j}'}(-\Omega) \langle jmj'm' | jj'\Delta jM \rangle \langle \bar{j}\bar{j}'\bar{\Delta}\bar{j}\bar{M} | \bar{j}\bar{m}\bar{j}'\bar{m}' \rangle. \quad (\text{A.14})$$

The distribution function of  $\Delta j$  consistent with (A.7) and (A.8) which leads to maximal entropy is given up to a normalization factor by:

$$P(\Delta j) = \exp(-\alpha \Delta j^2). \quad (\text{A.15})$$

Therefore the desired density matrix consistent with the constraints (A.7), (A.8) and (A.9) is derived by multiplication of the right-hand-side of (A.14) with (A.15), since (A.14) is diagonal in  $\Delta j$  and  $\Omega$ . The density matrix defined above is functionally dependent on the scattering angle through the Wigner matrices and  $\alpha$ . In cases where  $\alpha$  is a slow varying function of  $\Omega$  as compared to  $D_{m_1 m_2}^j(\Omega)$  use can be made of the orthogonality relation (A.11).

In such a case we have:

$$\rho_{jj'\Delta jM} = \delta_{\bar{j}\bar{j}} \delta_{j'\bar{j}'} \sum_{m\bar{m}} \langle jmj'm' | jj'\Delta jM \rangle \langle \bar{j}\bar{j}'\bar{\Delta}\bar{j}\bar{M} | \bar{j}\bar{m}\bar{j}'\bar{m}' \rangle \times \exp\{-\alpha \Delta j(\Delta j+1)\} (2j'+1)^{-1}. \quad (\text{A.16})$$

By the use of the orthogonality of the Clebsch-Gordan coefficient we finally get:

$$\rho_{jj'\Delta jM} = \delta_{\bar{j}\bar{j}} \delta_{j'\bar{j}'} \delta_{\Delta j \bar{\Delta} j} \delta_{M \bar{M}} \exp[-\alpha \Delta j(\Delta j+1)] (2j'+1)^{-1}. \quad (\text{A.17})$$

To compute the probability distribution of  $j'$  conditional on  $j$  we take the trace of the density matrix, i.e. sum over  $m\bar{m}$  and  $\Delta j, \bar{\Delta} j$ . For an initially unpolarized beam, we have

$$P(j' | j, E_T'; E_T; E) = \sum_{k=|j-j'|}^{i+j'} (2k+1) \exp[-\alpha k(k+1)] (2j'+1)^{-1}. \quad (\text{A.18})$$

The origin of the factor  $(2j+1)^{-1}$  is the strict constraint of the helicity conservation. If we turn off constraints (A.7) and (A.8) the trace is equal to  $2j+1$  states for each  $j$  and  $j'$  pair. On the other hand, if there is no restriction on the final helicity imposed by

the reactants channel, the factor  $(2j'+1)^{-1}$  is cancelled out as can be seen from (A.10).

In cases where the correlation between the helicity of the reactants and products is not as strict as up to a  $\delta$  function, the construction of the distribution function is analogous. The main modification needed is the substitution of (A.9) by the relevant joint distribution  $P(h'h')$ . This will affect the stage of summation over the values of the initial and final helicities. Another complication can arise if  $\alpha$  is not a slow varying function of  $\Omega$ . Therefore one cannot use the orthogonality of the Wigner matrices. However these problems can be overcome by numerical integration and summation.

In cases where the distributions of the helicity change  $\Delta h$  and the change in the molecular angular momentum  $\Delta j$  are broad enough, we can use the classical approximations [26] and need not care about the commutation relations of  $\Delta h$  and  $\Delta j$ .

## Appendix B

### B.1. Temperature averaging integrals

The purpose of appendix B is to obtain simple analytic expressions for detailed rate constants or cross sections of which part or all of the initial degrees of freedom are coupled to a heat bath. We also want to display the limits of applicability of our results.

The procedure employed is the steepest descent method. We follow the discussion of Morse and Feshbach [44] but modify it slightly to be applicable to our purpose.

The general form of the integral we want to approximate is

$$I = \int_{x_0}^{\infty} f(x) \exp[J(x)] dx, \quad (\text{B.1})$$

when  $f(x)$  and  $J(x)$  are analytic functions of  $x$  and  $J(x)$  has only one maximum  $\bar{x}$  in the region  $x_0 \leq \bar{x} < \infty$ .

The method of approximation is based on expanding the integrand around the principle value  $\bar{x}$ .

We define  $\bar{x}$  as the solution of

$$J'(\bar{x}) = 0. \quad (\text{B.2})$$

We then define:

$$\omega^2 = J''(\bar{x}) - J(x). \quad (\text{B.3})$$

Substituting (B.3) and (B.2) into (B.1), we get:

$$I = \exp[J(\bar{x})] \int_{\omega_0}^{\infty} f[x(\omega)] \exp(-\omega^2) (dx/d\omega) d\omega, \quad (\text{B.4})$$

when

$$\omega_0 = [J(\bar{x}) - J(x_0)]^{1/2}.$$

Our next step is to expand  $f[x(\omega)] (dx/d\omega)$  in a MacLorren series in  $\omega$  and we integrate each term separately.

Our approximation consists of the first term:

$$I \approx \exp[J(\bar{x})] f(\bar{x}) [2\pi/J''(\bar{x})]^{1/2} [1 + \text{erf} f(\omega_0)]/2, \quad (\text{B.5})$$

where  $\text{erf} f(x)$  is the standard error function [43].

### B.2. Criteria for a good approximation

In order to eliminate all odd terms in the expansion  $\omega_0$  has to be large:

$$J(\bar{x}) - J(x_0) \gg 1. \quad (\text{B.6})$$

We estimate the remaining terms of the expansion by the  $\omega^2$  term. For (B.5) to be a good approximation, we want this term to be small:

$$\frac{5 f'(\bar{x}) J'''(\bar{x})}{2 f(\bar{x}) [J''(\bar{x})]^2} + \frac{f''(\bar{x})}{f(\bar{x}) J''(\bar{x})} + \frac{5 [J'''(\bar{x})]^2}{2 [J''(\bar{x})]^3} - \frac{1}{4} \frac{J''''(\bar{x})}{[J''(\bar{x})]^2} \ll 1. \quad (\text{B.7})$$

If (B.6) and (B.7) are satisfied, we obtain for our approximation:

$$I = \exp[J(\bar{x})] f(\bar{x}) [2\pi/J''(\bar{x})]^{1/2}. \quad (\text{B.8})$$

### B.3. Translation dominant vibration rotation distributions

In this section we average the initial translation in eq. (1) over a Boltzmann distribution. We define

$$\Delta = E_v + E_R - E'_v - E'_R, \quad (\text{B.9})$$

and the detailed rate constant:

$$P(E'_v, E'_R | E_v, E_R; \beta) = Q^{-1} \int_{x_0}^{\infty} [x(x+\Delta)]^{1/2} (2j'+1) (2j'+1) \times \exp(-\beta x + \lambda \Gamma^2 - \alpha \Delta j^2) dx, \quad (\text{B.10})$$

where

$$x_0 = \max\{-\Delta, 0\}, \quad \Gamma^2 = [(x+\Delta)^{1/2} - (x)^{1/2}]^2, \quad \alpha^{-1} = a [x(x+\Delta)]^{1/2} + c \Gamma^2, \quad (\text{B.11})$$

and  $Q$  is the translation partition function. In what follows, we assume that the momentum transfer distribution dominates. Therefore we identify:

$$J(x) = -(\beta x + \lambda \Gamma^2), \quad (\text{B.12})$$

$$f_1(x) = [x(x+\Delta)]^{1/2}, \quad f_2(x) = \exp(-\alpha \Delta j^2).$$

Employing equation (B.8) we obtain our approximation for (B.10)

$$P(E'_v, E'_R | E_v, E_R; \beta) = \bar{P}(E'_v, E'_R | E_v, E_R; \beta) \times \exp[-\beta(\Lambda|\Delta| - \tilde{\alpha} \Delta j^2)], \quad (\text{B.13})$$

where

$$\Lambda = \frac{1}{2} (1+4\lambda/\beta)^{1/2}, \quad \tilde{\alpha} = \frac{(1+4\lambda/\beta)^{1/2}}{\beta|\Delta|(a\lambda/\beta+c)}.$$

and

$$\bar{P}(E'_v, E'_R | E_v, E_R; \beta) = [2(\pi)^{1/2}/Q] \beta^{-1/2} \Delta^{3/2} (\lambda/\beta)^2 \times (1+4\lambda/\beta)^{-5/4} (2j'+1) (2j'+1) \exp A, \quad (\text{B.14})$$

where  $A = \min\{\beta\Delta, 0\}$ . (Note: Since we average the yield function, our integral obeys microscopic reversibility, except for the Boltzmann factor  $e^{(-\beta E^T)}$ . Therefore, the only difference between the endothermic regions is the multiplication by  $\exp(\beta\Delta)$  for the endothermic transition.)

The criterion (B.6) becomes

$$|\Delta| \beta [(1+2\lambda/\beta - (1+4\lambda/\beta)^{1/2})] \gg 1, \quad (\text{B.15})$$

which means that  $\Delta$  has to be large in units of  $\beta$  and  $\lambda$  has to be far from the statistical limit compared to  $\beta$ .

Criterion (B.7) leads only to one new conclusion — that both  $a$  and  $c$  cannot be too small in units of  $\lambda\Delta j^2$ . When there is no change in vibration we can use the approximation that

$$(\Delta j)^2 \approx \Delta R^2/2E_R B_e \quad (\text{B.16})$$

and we obtain for the rigid rotor transition:

$$P(E'_R|E_R; \beta) = \tilde{P}(E'_R|E_R; \beta) \exp(-\beta\theta_R|\Delta|), \quad (\text{B.17})$$

where

$$\theta_R = \frac{1}{2} [-1 + (1 + 4\lambda/\beta)^{1/2} \{1 + [\beta E_R B_e (\alpha\lambda/\beta + c)]^{-1}\}]. \quad (\text{B.18})$$

#### B.4. Vibration rotation distributions – general case

Another alternative of obtaining a simple approximation is to integrate eq. (18) using the method presented in section A of this appendix. We obtain

$$P(E'_v, E'_R|E_v, E_R; \beta) \approx \tilde{P}(E'_v, E'_R|E_v, E_R; \beta) \quad (\text{B.19})$$

$$\times \exp\{-\beta\Lambda[(\Delta R + \psi\Delta V^2)/\psi + (1-\psi)\Delta V^2]^{1/2}\},$$

where  $\Lambda = (\lambda/\beta)^{1/2}$  and

$$\tilde{P}(E'_v, E'_R|E_v, E_R; \beta) = (2)^{1/2} \pi/Q [\bar{x}(\bar{x} + \Delta)]^{1/2}$$

$$\times (\beta^{-1/2} \bar{x}) (2j+1) (2j'+1) \exp A, \quad (\text{B.20})$$

where  $A = \min\{\beta\Delta, 0\}$ ,

$$\bar{x} = \frac{1}{2} (\lambda/\beta)^{1/2} [(\Delta R + \psi\Delta v)^2/\psi + (1-\psi)\Delta v^2].$$

Condition (B.6) for this approximation is always satisfied. Condition (B.7) leads to the following inequality:

$$\frac{3}{8} \{[(\Delta R + \psi\Delta v)^2/\psi + (1-\psi)\Delta v^2] \lambda\beta\}^{-1/2} \ll 1, \quad (\text{B.21})$$

which is similar to (B.15) but is also good in the statistical limit when  $\lambda \rightarrow 0$ .

For  $\Delta v = 0$  we get the rigid rotor distribution:

$$P(E'_R|E_R; \beta) = \tilde{P}(E'_R|E_R; \beta) \exp(-\beta\theta_R|\Delta R|),$$

$$\theta_R = [(1 + \lambda\alpha B_e E_R)/\beta\alpha B_e E_R]^{1/2}, \quad (\text{B.22})$$

which is the same as (B.18) for  $\lambda/\beta \rightarrow \infty$ .

#### B.5. V-T transitions

We integrate with the same method (B.19) over  $\Delta R$  and obtain

$$P(E'_v|E_v, E_R; \beta) = \tilde{P}(E'_v|E_v, E_R; \beta) \exp(-\beta\Lambda\Delta v), \quad (\text{B.23})$$

where  $\Lambda = [(1-\psi)\lambda/\beta]^{1/2}$ ,

and

$$\tilde{P}(E'_v|E_v, E_R; \beta) = (2^{3/2} \pi^{1/2} / \beta^{1/2} Q B_e) \exp(A)$$

$$\times [E_R(E_R - \psi\Delta v)]^{1/2} \bar{x} [\bar{x} + (1-\psi)\Delta v]^{1/2}, \quad (\text{B.24})$$

where

$$\bar{x} = \frac{1}{2} |\Delta v| [\lambda/\beta(1-\psi)]^{1/2}.$$

#### References

- [1] R.D. Levine and R.B. Bernstein, *Molecular reaction dynamics* (Clarendon Press, Oxford, 1974).
- [2] R.D. Levine and J. Jortner, *Molecular energy transfer* (Wiley, New York, 1976).
- [3] S. Ormond, *Rev. Mod. Phys.* 47 (1975) 193.
- [4] J.W. McGowan, R.H. Kummeler and F.R. Gilmore, *Advan. Chem. Phys.* 28 (1975) 379.
- [5] S.I. Chu, *Astrophys. J.* 206 (1976) 640.
- [6] R. Kosloff, A. Kafri and R.D. Levine, *Astrophys. J.*, to be published.
- [7] G. Ennen and Ch. Ottinger, *Chem. Phys.* 3 (1974) 404.
- [8] R.B. Kuzel, J.I. Steinfeld, D.A. Hetzenbuhler and G.E. Leroy, *J. Chem. Phys.* 55 (1971) 4822, and references therein.
- [9] K. Bergman and W. Demtröder, *J. Chem. Phys.* 38 (1965) 136.
- [10] P. Villarego, *J. Chem. Phys.* 49 (1968) 2523.
- [11] E.H. Fink, D.L. Akins and C.B. Moore, *J. Chem. Phys.* 56 (1972) 900.
- [12] M.D. Pattengill, *Chem. Phys. Letters* 36 (1975) 25.
- [13] H. Rabitz and H. Zarur, *J. Chem. Phys.* 61 (1974) 5076.
- [14] M.H. Alexander, *Chem. Phys. Letters* 38 (1976) 417; 40 (1976) 101; M.H. Alexander and P. McGuire, *J. Chem. Phys.* 64 (1976) 452.
- [15] L.D. Landau and E. Teller, *Phys. Z. Sowjetunion* 10 (1936) 34.
- [16] C.B. Moore, *J. Chem. Phys.* 45 (1965) 2979.
- [17] R.D. Levine, R.B. Johnson and R.B. Bernstein, *Chem. Phys. Letters* 19 (1975) 1.
- [18] J.C. Light, *J. Chem. Phys.* 40 (1964) 3221; R.A. White and J.C. Light, *J. Chem. Phys.* 55 (1971) 379.
- [19] W.H. Miller, S.A. Safron and D.R. Herschbach, *Faraday Discussions Chem. Soc.* 44 (1967) 108; *J. Chem. Phys.* 56 (1972) 3581; W.H. Miller, *J. Chem. Phys.* 52 (1970) 543.
- [20] A. Ben Shaul, *Chem. Phys.* 18 (1977) 13.
- [21] A. Ben Shaul, R.D. Levine and R.B. Bernstein, *J. Chem. Phys.* 61 (1974) 4937.
- [22] A. Kafri, Y. Shimon, R.D. Levine and S. Alexander, *Chem. Phys.* 13 (1976) 323.
- [23] R. Kosloff, A. Kafri and R.D. Levine, to be published.
- [24] A. Kafri, E. Pollak, R. Kosloff and R.D. Levine, *Chem. Phys. Letters* 33 (1975) 201.

- [25] E. Pollak, Ph.D. Thesis, Hebrew University, Jerusalem (1976).
- [26] A. Kafri, Ph.D. Thesis, Hebrew University, Jerusalem (1976).
- [27] D.A. Case and D.A. Herschbach, *J. Chem. Phys.* 64 (1976) 4212.
- [28] M. Tamir and M. Shapiro, *Chem. Phys. Letters* 31 (1975) 166.
- [29] P. McGuire and D. Kouri, *J. Chem. Phys.* (1974) 2488.
- [30] J.C. Polanyi and K.W. Woodall, *J. Chem. Phys.* 56 (1972) 1363.
- [31] R.D. Levine, R.B. Bernstein, P. Kahana, I. Procaccia and E.T. Upchurch, *J. Chem. Phys.* 64 (1976) 796; and I. Procaccia and R.D. Levine, *Physica* 82A (1976) 623.
- [32] I. Procaccia and R.D. Levine, *J. Chem. Phys.* 64 (1975) 808; 63 (1975) 4261, and references therein.
- [33] M. Alexander, *Chem. Phys. Letters* 40 (1976) 267.
- [34] J. von Neuman, *Mathematical foundation of quantum mechanics* (Princeton Univ. Press, USA, Princeton, 1965).
- [35] L.D. Landau and E.M. Lifshitz, *Quantum mechanics*, 2nd Ed. (Pergaman Press, London, 1965).
- [36] R.E. Turner and R.F. Snieder, *Can. J. Phys.* 54 (1976) 1313.
- [37] E.T. Jaynes, *Phys. Rev.* 108 (1957) 171.
- [38] A. Ben Shaul, R.D. Levine and R.B. Bernstein, *J. Chem. Phys.* 57 (1972) 5427.
- [39] R.B. Bernstein and R.D. Levine, *Advan. Atom. Mol. Phys.* 11 (1975) 215.
- [40] G.L. Hofacker and R.D. Levine, *Chem. Phys. Letters* 15 (1972) 165 and R.D. Levine and R.B. Bernstein, *Accounts Chem. Res.* 7 (1974) 393.
- [41] R.D. Levine and R.D. Bernstein, in: *Dynamics of molecular collisions*, ed. W.H. Miller (Plenum, New York, 1975).
- [42] D.J. Scalapino, Ph.D. Thesis, Stanford University, Palo Alto, Cal., USA (1961).
- [43] A.R. Edmonds, *Angular momentum in quantum mechanics* (Princeton Univ. Press, Princeton, 1960).
- [44] P.H. Morse and H. Feshbach, *Methods of theoretical physics*, part I (McGraw-Hill, New York, 1953) pp. 434-443.
- [45] M. Abramowitz and I.A. Stegun, eds. *Handbook of mathematical functions* (Dover, New York, 1964).