Collisionally Induced Vibrational Energy Transfer

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Note

I wrote this paper in my 2nd year of grad school. It was not intended for publication but to help give me a better grasp of what was happening in the system I was studying (NO2). AS I was working on my thesis it became clear to me that vibrational energy transfer was a key ingredient of what I was observing in my experimentation. Also, it helped give me a basis to discuss vibrational energy transfer in the short course on Chemical Lasers and Kinetics that I taught in my 3rd year.

Introduction

Consider a system consisting of an oscillator AB and a collision partner C. The oscillator may in general be diatomic or polyatomic, and the collision partner may be monatomic, diatomic, or polyatomic. At infinite separation between AB and C the interparticle forces are assumed to go to zero, and the Hamiltonian for the system can be expressed as

$$H^0 = T_{AB} + T_C + V_{AB}^{\text{int}} + V_C^{\text{int}}$$

where

- $T_{AB} = -\frac{\hbar^2}{2\mu_{AB}}\nabla_{AB}^2$ is the kinetic energy operator for AB,
- $T_C = -\frac{\hbar^2}{2\mu_C}\nabla_C^2$ is the kinetic energy operator for C,
- V_{AB}^{int} is the internal potential energy operator for AB, and
- V_C^{int} is the internal potential energy operator for C.

Suppose that we allow AB and C to approach each other to a point where the intermolecular forces are no longer negligible. We represent this interaction energy operator by H', which must be included in the Hamiltonian. The collision occurs, and as the particles recede $H' \to 0$, leaving us with the pre-collision form of the Hamiltonian. This problem is ideally suited to treatment by time-dependent perturbation methods, which we now develop.

Time-Dependent Equations

The time dependence of the Schrödinger equation is expressed by

$$i\hbar\,\dot{\Psi} = H\Psi$$

where Ψ is the total, time-dependent wave function and H is the total, time-dependent Hamiltonian. We can write H as the sum of a time-independent and a time-dependent term,

$$H = H^0 + H'$$

where H' will be called the time-dependent perturbation. The Schrödinger equation can now be written as

$$i\hbar\,\dot{\Psi} = (H^0 + H')\Psi.$$

We expand the wave function Ψ in the time-independent wave functions ϕ_n, which are solutions of $H^0\phi_n = E_n\phi_n$:

$$\Psi = \sum_n C_n\,(t)\,\phi_n\,e^{-iE_nt/\hbar}$$

so that the time dependence is carried in the expansion coefficients $C_n(t)$. Furthermore,

$$\dot{\Psi} = -\frac{i}{\hbar}\sum_n C_n\,(t)\,E_n\,\phi_n\,e^{-iE_nt/\hbar} + \sum_n \dot{C}_n\,(t)\,\phi_n\,e^{-iE_nt/\hbar}.$$

Substituting into the time-dependent Schrödinger equation gives

$$\sum_n C_n\,(t)E_n\phi_n e^{-iE_nt/\hbar} + i\hbar\sum_n \dot{C}_n\,(t)\phi_n e^{-iE_nt/\hbar} = \sum_n C_n\,(t)E_n\phi_n e^{-iE_nt/\hbar} + \sum_n C_n\,(t)H'\phi_n e^{-iE_nt/\hbar}$$

or

$$i\hbar\sum_n \dot{C}_n\,(t)\,\phi_n\,e^{-iE_nt/\hbar} = \sum_n C_n\,(t)\,H'\phi_n\,e^{-iE_nt/\hbar}.$$

Define the angular frequency ω_{kn} as

$$\omega_{kn} = \frac{E_k - E_n}{\hbar}.$$

The complete set of ϕ_n is orthonormal, so multiplying both sides of the equation by ϕ_k^* and integrating gives

$$i\hbar\,\dot{C}_k(t)\,e^{-iE_kt/\hbar} = \sum_n C_n\,(t)\big(\int \phi_k^* H'\phi_n\,d\tau\big)e^{-iE_nt/\hbar}$$

$$\dot{C}_k(t) = \frac{1}{i\hbar}\sum_n \big[C_n(t)\big(\int \phi_k^* H'\phi_n\,d\tau\big)e^{i\omega_{kn}t}\big].$$

Note that the expansion is over a complete set of eigenfunctions: where they are discrete they are summed, and where they are continuous they must be integrated. Integration over any continuum eigenfunctions needed to ensure completeness of the set has been implicitly assumed above.

Returning to the problem, replace the perturbation H' by $\lambda H'$ and express the coefficients as a power series in λ:

$$C_n(t) = \sum_{j=0}^{\infty} C_n^{(j)}\,(t)\,\lambda^j.$$

This series is assumed to be a continuous and analytic function of λ for $\lambda \in (0,1)$. Substituting this expression, equating like powers of λ, and then setting $\lambda = 1$ gives

$$\dot{C}_k^{(0)}(t) = 0$$

$$\dot{C}_k^{(j+1)}(t) = (i\hbar)^{-1} \sum_n \left[\left(\int \phi_k^* H' \phi_n \, d\tau \right) C_n^{(j)}(t) \, e^{i\omega_{kn} t} \right].$$

In principle, then, successive integrations give approximate solutions to any desired order in the perturbation. By not carrying this out indefinitely we introduce the first approximation of the treatment.

That $\dot{C}_k^{(0)}$ is zero implies that the $C_k^{(0)}$ are constant in time. We assume the system to be in a precisely defined state initially, so that all $C_k^{(0)}$ are zero except the one describing that state. Integrating the first-order equation then gives

$$C_k^{(1)}(t) = (i\hbar)^{-1} \int_{-\infty}^{t} \left(\int \phi_k^* H'(t') \, \phi_m \, d\tau \right) e^{i\omega_{km} t'} \, dt'$$

where the wave function ϕ_m describes the initial state and ϕ_k the final one. The constant of integration and the limits have been chosen so that

$$C_k^{(1)}(-\infty) = 0.$$

The probability of the system being in state m is $|C_m^* C_m|$, which is initially equal to 1. The probability of the system being in state k after a time t under the influence of the perturbation H' is

$$|C_k^*(t) \, C_k(t)|.$$

Since the colliding particle starts at $t = -\infty$ and we follow it to $t = +\infty$, the probability of going from an initial state i to a final state f is

$$p_{i,f} = \left| C_f(\infty) \right|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} \left[\int \phi_f^* H' \phi_i \, d\tau \right] e^{i\omega_{fi} t'} \, dt' \right|^2.$$

This is the first-order perturbation result, provided we can find an expression for H' as a function of time.

Semi-Classical Approach

We set up the model as follows:

1. AB is the oscillator and has its center of mass at a fixed position.
2. C approaches AB along the vibration coordinate with a relative kinetic energy of approach (at infinite separation)

$$\varepsilon_k = \frac{\mu v_0^2}{2}.$$

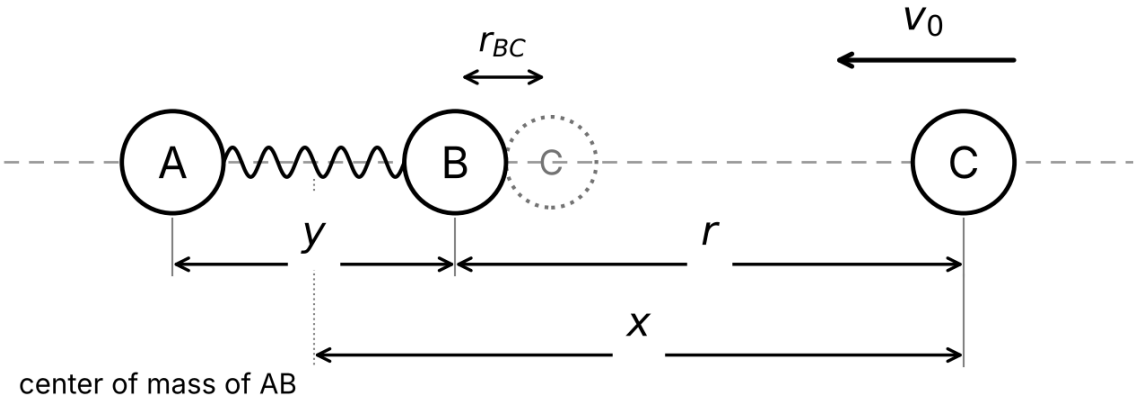


Figure 1. Collinear collision geometry. C approaches the oscillator AB with velocity v_0; y is the A–B separation, r the B–C separation, x the distance from the center of mass of AB to C, and r_{BC} the distance of closest approach.

The potential energy of the system is assumed to have the form $V = V_0 e^{-\alpha r}$, where α is a range parameter and r is the distance between AB and C. This distance is

$$r = x - \left(\frac{M_A}{M_A + M_B}\right) y$$

for C colliding with B, and

$$r = x - \left(\frac{M_B}{M_A + M_B}\right) y$$

for C colliding with A. Letting $V_0 = 1$, we can write

$$V(x, y) = \exp\left\{-\alpha\left[x - \left(\frac{M_A}{M_A + M_B}\right) y\right]\right\}.$$

At the distance of closest approach (r_{BC}) we therefore have

$$V(x_0, y_0) = \varepsilon_k = \exp\{-\alpha r_{BC}\}$$

$$r_{BC} \simeq x_0 - \left(\frac{M_A}{M_A + M_B}\right) y_0$$

where y_0 is the equilibrium value of the harmonic oscillator coordinate y.

The potential energy can be rewritten as

$$\begin{aligned} V(x, y) &= \varepsilon_k \exp\left\{-\alpha\left[x - \left(\frac{M_A}{M_A + M_B}\right) y - r_{BC}\right]\right\} \\ &= \varepsilon_k \exp\left\{-\alpha\left[(x - x_0) - (y - y_0)\left(\frac{M_A}{M_A + M_B}\right)\right]\right\} \end{aligned}$$

or

$$V(X, Y) = \varepsilon_k \, e^{-\alpha X} \, e^{\alpha Y M_A/(M_A + M_B)}$$

where $X = x - x_0$ and $Y = y - y_0$. Therefore

$$V(X,Y) = V(X)\,V(Y).$$

To assign a collision trajectory, suppose that $V(Y) \simeq 1$:

$$V(X,Y) \simeq V(X) = \varepsilon_k\, e^{-\alpha X}.$$

The total energy of the system (discounting internal energy) is

$$\varepsilon_k = V(X) + \frac{\mu\, v(X)^2}{2}$$

where $v(X) = dX/dt$. Rearranging gives [Note 1]

$$\int_{X_0}^{X_t} \left[\frac{2\varepsilon_k}{\mu}(1 - e^{-\alpha X})\right]^{-1/2} dX = \int_0^t d\,t.$$

The solution for position as a function of time is implicit in the relation

$$e^{-\alpha X} = \operatorname{sech}^2\left(\frac{\alpha v_0 t}{2}\right)$$

which results from integrating the equation above. Since the potential does not depend strongly on Y (that is, $\alpha Y \ll 1$), we can write

$$V(Y) = e^{\alpha Y M_A/(M_A+M_B)} \simeq \left\{1 + \left(\frac{M_A}{M_A + M_B}\right)\alpha Y\right\}.$$

The potential $V(X,Y)$ can now be written in the form $V(Y,t)$:

$$V(Y,t) = \varepsilon_k \left\{1 + \alpha Y \left(\frac{M_A}{M_A + M_B}\right)\right\} \operatorname{sech}^2\left(\frac{\alpha v_0 t}{2}\right).$$

This expression gives the perturbation energy as a function of time t and of the displacement Y from the oscillator's equilibrium position. If the total wave function is separable into a product of electronic, vibrational, rotational, and translational wave functions,

$$\Psi = \phi_{\text{elect}}\,\phi_{\text{vib}}\,\phi_{\text{rot}}\,\phi_{\text{trans}}$$

then (assuming they are properly normalized) all of them factor out and integrate to unity except the vibrational wave function, which can be expressed as a function of Y. The matrix element factors into a time-dependent and a time-independent part [Note 2]:

$$H'_{if}(t) = F(t) \int_{-\infty}^{\infty} \phi_f\,(Y)\,Y\,\phi_i(Y)\,dY$$

where

$$F(t) = \frac{\partial}{\partial Y}\{V(Y,t)\} = \alpha\,\varepsilon_k \left(\frac{M_A}{M_A + M_B}\right) \operatorname{sech}^2\left(\frac{\alpha v_0 t}{2}\right).$$

From the perturbation theory result, the transition probability is

$$p_{i,f} = \frac{\alpha^2 \varepsilon_k^2}{\hbar^2}\left(\frac{M_A}{M_A + M_B}\right)^2 \left|\int_{-\infty}^{\infty} \phi_f^*\; Y\,\phi_i\,dY\right|^2 \left|\int_{-\infty}^{+\infty} \operatorname{sech}^2\left(\frac{\alpha v_0 t}{2}\right) e^{i\omega_{fi} t}\,dt\right|^2.$$

The squared time integral has the value [Note 3]

$$\frac{16\pi^2\omega_{fi}^2}{\alpha^4 v_0^4}\operatorname{cosech}^2\left(\frac{\pi\omega_{fi}}{\alpha v_0}\right)$$

so that

$$p_{i,f} = \frac{4\pi^2\omega_{fi}^2\mu^2}{\alpha^2\hbar^2}\left(\frac{M_A}{M_A+M_B}\right)^2 \operatorname{cosech}^2\left(\frac{\pi\omega_{fi}}{\alpha v_0}\right)\left|Y_{if}\right|^2$$

where $\left|Y_{if}\right|^2$ is the square of the matrix element inducing the harmonic oscillator transitions. These are well known and have the following properties [Note 4]:

$$\left|Y_{n,n+1}\right|^2 = \frac{n+1}{2\beta}, \qquad \left|Y_{n,n-1}\right|^2 = \frac{n}{2\beta}, \qquad \beta = \frac{m\,\omega}{\hbar}$$

$$\left|Y_{if}\right|^2 = 0 \quad \text{if } \Delta n \neq \pm 1.$$

These equations define the transition probability per collision for a given $\varepsilon_k = 1/2\,\mu v_0^2$.

Here $\mu = M_C(M_A+M_B)/(M_A+M_B+M_C)$ is the reduced mass of the AB–C collision pair, which appears in ε_k and in the thermal average below, and $m = M_A M_B/(M_A+M_B)$ is the reduced mass of the oscillator, which appears in β [Note 8].

Thermal Averaging

The observed probability is the one integrated over a Maxwell–Boltzmann distribution of energies. Since the mechanics were solved in one dimension, the one-dimensional distribution should be used for consistency:

$$dn = n\left(\frac{\mu}{2\pi kT}\right)^{1/2} e^{-\mu v_0^2/2kT}\,dv_0.$$

In the transition probability we used v_0, but this should properly be v_a, the velocity corresponding to the average of the kinetic energies of approach and recession. This introduces into the trajectory calculation the collisional symmetrization that was previously ignored. The velocities v_0 and v_a are related by

$$\mu v_0^2 = \mu v_a^2 - \hbar\omega \quad \text{for deactivation}$$

$$\mu v_0^2 = \mu v_a^2 + \hbar\omega \quad \text{for activation.}$$

We make the further simplification that, since $\pi\omega \gg \alpha v_a$ for an adiabatic collision,

$$\operatorname{cosech}(x) \simeq 2\exp(-x).$$

The velocity distribution is integrated from 0 to ∞, since we are interested only in velocities directed toward the target. If we define

$$A = \frac{16\pi^2\omega^2\mu^2}{\alpha^2\hbar^2}\left(\frac{M_A}{M_A+M_B}\right)^2\left|Y_{if}\right|^2\left(\frac{\mu}{2\pi kT}\right)^{1/2}$$

then the averaged transition probability is

$$\bar{p}_{if} = A \int_0^\infty e^{-2\pi\omega/\alpha v_a}\; e^{-\mu v_0^2/2kT}\, dv_0.$$

Using the relations between v_a and v_0 this becomes

$$\bar{p}_{if} = A\, e^{\pm\hbar\omega/2kT} \int_0^\infty \exp\left[-\frac{2\pi\omega}{\alpha v_a} - \frac{\mu v_a^2}{2kT}\right] dv_a$$

where the + sign refers to deactivation and the − sign to activation. The integrand is a sharply peaked function of v_a and contributes significantly to the transition probability only near a critical velocity v_a^*, found by setting the derivative of the exponent to zero:

$$v_a^* = \left(\frac{2\pi\omega kT}{\alpha\mu}\right)^{1/3}.$$

Expanding the exponent about v_a^* gives the approximation [Note 5]

$$-\frac{2\pi\omega}{\alpha v_a} - \frac{\mu v_a^2}{2kT} \simeq -3\left(\frac{\pi^2\omega^2\mu}{2\alpha^2 kT}\right)^{1/3} - \frac{3}{2}\frac{\mu}{kT}(v_a - v_a^*)^2.$$

With the definition

$$B = A\, e^{\pm\hbar\omega/2kT} \exp\left[-3\left(\frac{\pi^2\omega^2\mu}{2\alpha^2 kT}\right)^{1/3}\right]$$

we can write

$$\bar{p}_{if} = B \int_0^\infty \exp\left\{-\frac{3}{2}\frac{\mu}{kT}(v_a - v_a^*)^2\right\} dv_a$$

which is readily evaluated to give [Note 6]

$$\bar{p}_{if} \simeq B\left(\frac{2\pi kT}{3\mu}\right)^{1/2}.$$

If we label the initial and final states by the vibrational quantum number n and restrict ourselves to transitions with $\Delta n = \pm 1$, it follows immediately that

$$\bar{p}_{n,n-1} = \bar{p}_{n-1,n}\, e^{\hbar\omega/kT}$$

and that

$$\bar{p}_{n,n-1} = n\,\bar{p}_{1,0}.$$

Modifications to the Treatment

Several modifications can be made to this treatment that give some interesting results.

Multiquantum transitions can be treated readily by keeping higher-order terms in the expansion

$$e^{CY} = 1 + CY + \frac{(CY)^2}{2!} + \cdots$$

For the first term the matrix element vanishes by orthogonality of the vibrational wave functions. The second term gives a non-vanishing matrix element for states whose vibrational quantum numbers differ by 1, the third term for those with $\Delta n = \pm 2$, and so on. As expected, the probabilities fall off rapidly with increasing Δn. Alternatively, one can use anharmonic wave functions and compute the matrix element of the Y term; this gives non-vanishing probabilities for $\Delta n = \pm 2$ and higher, depending on how far the anharmonicity is carried.

For complex vibrational energy transfer such as

$$AB(v_1 = n,\ v_2 = k) + C \rightarrow AB(v_1 = n - 1,\ v_2 = k + 1) + C$$

the process can be regarded as a simultaneous deactivation of mode 1 and activation of mode 2. Since the probability of two events occurring simultaneously may be approximated by the product of the individual probabilities,

$$\bar{p}_{n,n-1}^{\,k,k+1} = \bar{p}_{n,n-1} \cdot \bar{p}_{k,k+1}$$

which will be proportional to [Note 9]

$$e^{\hbar(\omega_1 - \omega_2)/2kT}.$$

An identical result is obtained for V → V transfer, as in

$$AB(v_1 = n) + CD(v_2 = k) \rightarrow AB(v_1 = n - 1) + CD(v_2 = k + 1).$$

Complex V → T transfer, as well as V → V transfer, can thus be expressed in terms of the probabilities of individual simple V → T transfers.

If there is an attractive force with a potential well of depth ε_a, a factor $e^{\varepsilon_a/kT}$ is added to the velocity distribution function. This is a constant and integrates out; it merely multiplies the probability given earlier.

To take collisional symmetry into account (C colliding with A as well as with B, whereas the trajectory calculation assumed collision with B only), note that for a collision at the A end the coupling factor $M_A/(M_A + M_B)$ becomes $M_B/(M_A + M_B)$. The transition probability depends on the square of this factor, so averaging over the two ends of the molecule replaces $\left(M_A/(M_A + M_B)\right)^2$ wherever it appears (in $p_{i,f}$, A and B) by [Note 7]

$$S_{AB} = \frac{1}{2}\left[\left(\frac{M_A}{M_A + M_B}\right)^2 + \left(\frac{M_B}{M_A + M_B}\right)^2\right] = \frac{M_A^2 + M_B^2}{2(M_A + M_B)^2}.$$

For a homonuclear oscillator $S_{AB} = 1/4$, the same as the unsymmetrized value. For a light–heavy molecule such as HCl, $S_{AB} \approx 0.47$, compared with 7.7×10^{-4} for collisions at the Cl end alone: collisions at the light end dominate the energy transfer.

Collecting the results, the symmetrized, thermally averaged probability of deactivating the first vibrational level is

$$\bar{p}_{1,0} = \frac{8\pi^2 \omega \mu^2 S_{AB}}{\sqrt{3}\,\alpha^2 \hbar\, m} \exp\left[-3\left(\frac{\pi^2 \omega^2 \mu}{2\alpha^2 kT}\right)^{1/3} + \frac{\hbar\omega}{2kT}\right]$$

with $\bar{p}_{n,n-1} = n\,\bar{p}_{1,0}$ and $\bar{p}_{n-1,n} = \bar{p}_{n,n-1}\, e^{-\hbar\omega/kT}$, multiplied by $e^{\varepsilon_a/kT}$ if there is an attractive well.