

- (1978).
6. P. B. Visscher, *Phys. Rev.* **B13**, 3272 (1976).
 7. G. C. Hartmann and J. Noolandi, *J. Chem. Phys.* **66**, 3498 (1977).
 8. D. Y. Kim, S. Shin, and K. J. Shin, *Bull. Kor. Chem. Soc.* **7**, 271 (1986).
 9. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
 10. F. C. Collins and G. E. Kimball, *J. Colloid Sci.* **4**, 425 (1949).
 11. G. D. Smith, *Numerical Solution of Partial Differential Equations: Finite Difference Methods* (Oxford Univ. Press, London, 1978).

Energy Transfer Between Diatomic Molecules

Yoo Hang Kim*

Department of Chemistry, Inha University, Incheon 160

Hyung Kyu Shin

Department of Chemistry, University of Nevada, Reno, Nevada 89557, U.S.A. Received November 13, 1986

The effects of initial vibrational energy on VV energy transfer in the collinear collision of two diatomic molecules, either homonuclear or heteronuclear, has been studied over a range of collision energies in classical mechanics. When initial vibrational energy is very large, only a small fraction of vibrational energy in the excited molecule is transferred to the colliding partner. In this case, the VV step is found to be strongly coupled with VT during the collision. At low collision energies, energy transfer in the homonuclear case of $O_2 + O_2$ with small initial vibrational energy is found to be very inefficient. In the heteronuclear case of $CH + HC$ with the initial energy equivalent to one vibrational quantum, VV energy exchange is found to be very efficient at such energies. Between 0.3 and 0.5 eV, nearly all of vibrational energy of the excited molecule with one to about three vibrational quanta in $CH + HC$ is efficiently transferred to the colliding partner through pure VV process in a sequence of down steps during the collision. The occurrence of multiple impacts during the collision of two heteronuclear molecules and the collisional bond dissociation of homonuclear molecules are also discussed.

Introduction

Both approximate and exact calculations of collisional energy transfer in classical mechanics have been made in large numbers over the last two decades and the results are well documented in a number of standard references¹⁻¹³. Most of such calculations are based on the collision of two harmonic oscillators with no initial vibrational energy. Carrying out exact calculations numerically for anharmonic oscillators is no more difficult than that of the harmonic case, and in such more realistic calculations the binding potential of the oscillators is usually assumed by the Morse function^{1,14}.

Relatively little has been done, however, in the way of classical calculations involving anharmonic oscillators with initial vibrational energy. In such a case there is an important feature of vibration-to-vibration (VV) energy transfer, and information on the efficiency of VV energy exchange and the extent of VV contribution to overall energy transfer processes are valuable in studying, among others, chemical reaction dynamics and the performance of chemical lasers^{11,12,15,16}. Of particular interest in such studies is energy transfer to or from excited molecules with regard to the influence of initial vibrational excitation on the accumulation of internal energy and subsequent bond dissociation. The classical equations of motion for systems of this type can be solved numerically with a digital computer. Typical calculations describe the time evolution of dynamical variables such as trajectory and internal coordinates. Energy transfer between vibrational motions

or between translational and vibrational motions can be extracted from these calculations. The present work is concerned with such calculations carried out in order to study vibrational energy exchange between two Morse oscillators interacting collinearly—one with initial vibrational energy and the other with no energy. The specific systems considered are the collisions of $O_2 + O_2$ and $CH + HC$ representing homonuclear and heteronuclear molecules, respectively, in the collision energy range of 0–2 eV. Particular emphasis will be given to the effects of varying initial vibrational energy in $CH + HC$.

In the $CH + HC$ collision system, two light hydrogen atoms are located between two heavy carbon atoms. When a collision occurs the two hydrogen atoms oscillate back and forth, thus causing multiple impacts and making the collision dynamics very interesting. This system also closely resembles the interaction of the hydrocarbon chain and mimics the quenching of the vibrationally excited molecules by hydrocarbons.

Collision Model

In the collision, one of the molecules (say molecule 1) with initial vibrational energy $E_{v,1}$ collides with molecule 2, which has no initial vibrational energy. The binding potential of each molecule is assumed by the Morse function

$$V_{u,i}(y_i) = D_{e,i} (e^{-b_i y_i} - 1)^2; \quad i = 1 \text{ or } 2, \quad (1)$$

where D_e is the well depth of the Morse potential and b is an

intramolecular potential constant related to other constants as $b = (M/2D_3)^{1/2}\omega$, M and ω being the reduced mass and the angular frequency of the oscillator; y_i is the vibrational coordinate measuring the displacement of the i th oscillator bond from its equilibrium value d_i . Throughout this paper, subscripts 1 and 2 represent molecules 1 and 2, respectively. The potential energy between two collinearly interacting molecules is assumed to be determined by an exponentially repulsive energy acting between the inside atoms $O\cdots O$ in $O_2\cdots O_2$ or $H\cdots H$ in $CH\cdots HC$ in analogy to previous calculations on vibrational energy transfer^{14,17,18}

$$V_1(x, y_1, y_2) = Ae^{-z/a} = Ae^{-x/a} e^{-\gamma_1(d_1+y_1)/a} e^{-\gamma_2(d_2+y_2)/a} \quad (2)$$

$$= A' e^{-x/a} e^{-\gamma_1 y_1/a} e^{-\gamma_2 y_2/a},$$

where the inside atom-atom distance z is $x - \gamma_1(d_1+y_1) - \gamma_2(d_2+y_2)$, $A' = Ae^{\gamma_1 d_1/a + \gamma_2 d_2/a}$, and x is the distance between the centers of mass of the colliding molecules. Here, $\gamma_1 = \gamma_2 = m_O/(m_O + m_O) = 1/2$ in $O_2(E_{v,1}) + O_2$ or $\gamma_1 = \gamma_2 = m_C/(m_H + m_C) = 0.922$ in $CH(E_{v,1}) + HC$.

Energy Transfer Expressions

The time evolution of vibrational energy in molecule 2 with no initial vibrational energy can be written as¹⁴

$$\Delta E_2(t) = D_{e,2} [e^{-b_2 y_2(t)} - 1]^2 + \frac{1}{2} M_2 \dot{y}_2^2(t), \quad (3)$$

where the dot means the derivative with respect to time. Here $y_2(t)$ and $\dot{y}_2(t)$ are solutions of the equations of motion

$$\mu \ddot{x} = -\frac{\partial V}{\partial x}, \quad M_i \ddot{y}_i = -\frac{\partial V}{\partial y_i}; \quad i = 1 \text{ or } 2, \quad (4, 5)$$

where $V = V_{M,1}(y_1) + V_{M,2}(y_2) + V(x, y_1, y_2)$, μ is the reduced mass of the collision system, and the relation $A' = E$, the initial collision energy, is introduced to set the energy scale.

The solutions of the equations of motion can be obtained by numerically integrating the following six first order differential equations derivable from Eqs. (4) and (5) and the potential expression,

$$\frac{dx}{dt} = \dot{x}$$

$$\frac{d\dot{x}}{dt} = \frac{A'}{\mu a} e^{-x/a} e^{-\gamma_1 y_1/a} e^{-\gamma_2 y_2/a}$$

$$\frac{dy_i}{dt} = \dot{y}_i; \quad i = 1 \text{ or } 2 \quad (6a) - (6f)$$

$$\frac{d\dot{y}_i}{dt} = \frac{2D_{e,i} b_i}{M_i} (e^{-b_i y_i} - 1) e^{-b_i y_i}$$

$$- \frac{A' \gamma_i}{M_i a} e^{-x/a} e^{-\gamma_1 y_1/a} e^{-\gamma_2 y_2/a}; \quad i = 1 \text{ or } 2$$

with the equation of motion of molecule 1 in the initial region ($t \rightarrow -\infty$)

$$y_1 = -\frac{1}{ab_1} \ln(1 - \alpha) + \frac{1}{ab_1} \ln[1 + \alpha^{1/2} \sin(\Omega t + \delta)] \quad (7a)$$

$$\dot{y}_1 = \frac{\alpha^{1/2} \Omega}{\sigma ab_1} [\cos(\Omega t + \delta) / \{1 + \alpha^{1/2} \sin(\Omega t + \delta)\}] \quad (7b)$$

where

$$\alpha = \frac{E_{v,1}}{D_{e,1}}, \quad \sigma = \frac{1}{a} (E/\mu)^{1/2}$$

and $\Omega = b_1 [2(D_{e,1} - E_{v,1})/M_1]^{1/2}$.

We shall represent the vibrational energy of molecule 1 by $E_{v,1}(t)$. Then the energy gained (or lost) by the molecule due to the collision at t is $E_{v,1}(t) - E_{v,1}(-\infty)$, where $E_{v,1}(-\infty) \equiv E_{v,1}$. As the collision starts, the vibrational energy either decreases from $E_{v,1}$ if the energy transfer is VV and/or $V \rightarrow T$ or increases from $E_{v,1}$ if it is $T \rightarrow V$. However, it is convenient to consider $E_{v,1}(t)$ instead of the difference $E_{v,1}(t) - E_{v,1}$ and treat it as a measure of the time evolution of the vibrational energy of molecule 1

$$\Delta E_1(t) = E_{v,1}(t) = D_{e,1} [e^{-b_1 y_1(t)} - 1]^2 + \frac{1}{2} M_1 \dot{y}_1^2(t), \quad (8)$$

where $y_1(t)$ and $\dot{y}_1(t)$ are solutions of the equations of motion for the initial values $y_1(-\infty)$ and $\dot{y}_1(-\infty)$ obtained from $E_{v,1} = D_{e,1} [e^{-b_1 y_1(-\infty)} - 1]^2 + \frac{1}{2} M_1 \dot{y}_1^2(-\infty)$, the equation which is valid as $t \rightarrow -\infty$, where the interaction potential is zero. Note that for molecule 2, $y_2(-\infty)$ and $\dot{y}_2(-\infty) = 0$. When $t = -\infty$, $\Delta E_1(-\infty) = E_{v,1}$, the initial vibrational energy of molecule 1. The values of $y_1(-\infty)$ and $\dot{y}_1(-\infty)$ depend on the initial phase δ of the molecule, so does the time evolution of vibrational energies given by Eqs. (3) and (8); i.e., $\Delta E_i(t, \delta)$. When the limiting values of $y_i(t)$ and $\dot{y}_i(t)$ are used in these equations, we then find $\Delta E_i(+\infty, \delta)$. Thus, for a given phase, the vibrational energy of molecule 1 starts out with $E_{v,1}$ and varies as the collision progresses according to Eq. (8), then finally settling to a constant value $\Delta E_1(+\infty, \delta)$ as the collision completes. On the other hand, the vibrational energy of molecule 2 starts out with zero and the finally reaches $\Delta E_2(+\infty, \delta)$. For a given collision energy, therefore, amounts of energy transfer at different phases (i.e., different trajectories) will have to be averaged over $\delta = 0$ to 2π to obtain the energy transfer $\Delta E_i(+\infty) = (2\pi)^{-1} \int_0^{2\pi} \Delta E_i(+\infty, \delta) d\delta$, which we shall express as ΔE_i for simplicity throughout the following section. Similarly, the phase-dependent quantity $\Delta E_i(t, \delta)$, which determines the vibrational energy of the i th molecule during the collision, will be simply expressed as $\Delta E_i(t)$.

The equations of motion will be integrated numerically starting with a large value of x and the specified values of $y_i(-\infty)$ and $\dot{y}_i(-\infty)$. We then follow the collision system through the interaction region and determine $y_i(t)$ and $\dot{y}_i(t)$ out to large separation. Phase effects can be particularly important at higher collision energies, so many trajectories will have to be selected to obtain reliable results. The values of phase-averaged energy transfer ΔE_i presented below are believed to be accurate to about 10-20%. A sufficient condition for the phase step $\Delta\delta$ to give this degree of accuracy is about 0.5° for $CH(0.95D_e) + HC$ in the collision energy range considered; i.e., about 720 points were required before the phase averaged ΔE_i converged. For $O_2(h\nu) + O_2$, about 360 points were required. For molecule 2, no such many trajectory sampling is necessary since the molecule has no initial vibrational energy. The time-integration limits are typically from $t = -10^{-12}$ to $+10^{-12}$ s. The integration time step Δt used in the calculation is related to the reduced energy $\epsilon = E/h\nu$ and the number of

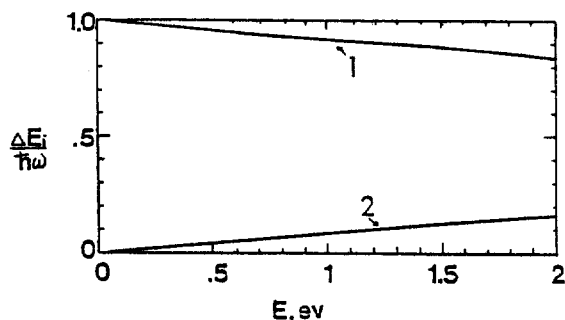


Figure 1. Dependence of vibrational energy transfer $\Delta E_i/\hbar\omega$ on the collision energy E in $O_2(\hbar\omega) + O_2$. Throughout the figures, 1 and 2 stand for, respectively, molecules 1 and 2.

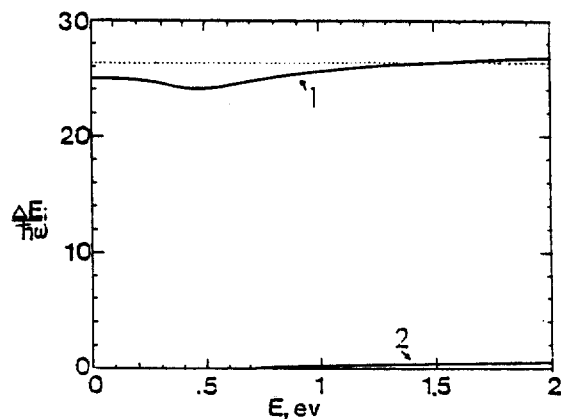


Figure 2. Dependence of vibrational energy transfer $\Delta E_i/\hbar\omega$ on the collision energy E in $O_2(0.95D_e) + O_2$. Dotted line indicates $D_e/\hbar\omega$.

steps n by $\Delta t = 2.9 \times 10^{-12}/n\epsilon^{1/2}$ s in $O_2(E_{v,1}) + O_2$ and by $\Delta t = 1.4 \times 10^{-12}/n\epsilon^{1/2}$ s in $CH(E_{v,1}) + HC$. The Number of steps will be adjusted so as to maintain Δt within the range of 1/30–1/50 of the vibrational period. In the calculation, we use $D_e = D_e^\circ + \frac{1}{2}\hbar\omega$ with $D_e^\circ(O_2) = 5.08$ eV and $D_e^\circ(CH) = 3.47$ eV from standard tables¹⁹ along with $\alpha = 0.2 \text{ \AA}^{-1}$.

Results and Discussion

A. $O_2 + O_2$

Figure 1 shows the effects of varying the initial collision energy of two oxygen molecules on $\Delta E_i/\hbar\omega$, where molecule 1 has initial energy equivalent to one vibrational quantum $\hbar\omega$; i.e., $O_2(\hbar\omega) + O_2$. (One quantum of O_2 is equivalent to $0.038D_e$). The energy transfer $\Delta E_i/\hbar\omega$ rises from zero nearly linearly as E increases reaching 0.16 at $E = 2$ eV, while $\Delta E_i/\hbar\omega$ decreases from the initial value of one to 0.84 at $E = 2$ eV as the result of VV exchange. In the collision energy range considered, the extent of VV exchange gradually increases as E increases, but only a small fraction of vibrational energy is transferred from $O_2(\hbar\omega)$ to O_2 by collision. Note that the sum of $\Delta E_i/\hbar\omega$ is very close to one indicating that the contribution of $T \rightarrow V$ or $V \rightarrow T$ mode in both molecules is not important.

When molecule 1 is highly excited, only a small fraction of vibrational energy is transferred to molecule 2. In fact, as shown in Fig. 2, when molecule 1 has initial vibrational energy $0.95D_e$, which is equivalent to $25.1\hbar\omega$, the fraction of the vibrational energy of molecule 1 transferred to molecule 2 through VV is much less than that in the previous case, where molecule

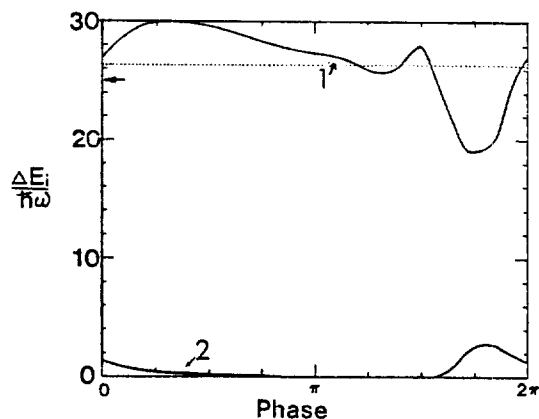


Figure 3. Phase dependence of vibrational energy transfer in $O_2(0.95D_e) + O_2$ at $E = 2$ eV. The arrow on the ordinate locates $E_{v,1} = 25.1\hbar\omega = 0.95D_e$. Dotted line indicates $D_e/\hbar\omega$.

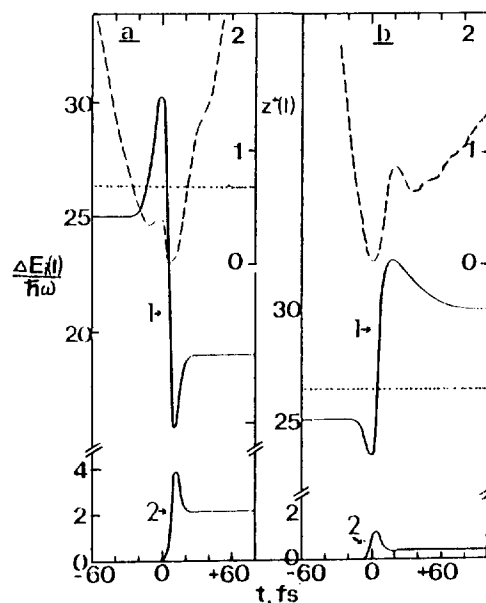


Figure 4. Time evolution of vibrational energy $\Delta E_i(t)/\hbar\omega$ in $O_2-(0.95D_e) + O_2$ at (a) $\delta = 310^\circ$ and (b) $\delta = 50^\circ$; $E = 2$ eV. Also shown is $z^*(t)$ in $\text{\AA}$. Solid curves: $\Delta E_i(t)/\hbar\omega$; dashed curves: $z^*(t)$. Dotted line indicates $D_e/\hbar\omega$.

1 initially has only $0.038D_e$, or $\hbar\omega$, although *absolute magnitude* of the energy gained by molecule 2 is larger. For example, at $E = 1, 1.5$, and 2 eV, the amounts of vibrational energy transferred to molecule 2 are 0.32, 1.6, and 2.0% of the initial vibrational energy of molecule 1, respectively, in $O_2(0.95D_e) + O_2$. The corresponding values in $O_2(\hbar\omega) + O_2$ are as large as 8.1, 12, and 16%. When $E < 1$ eV, the amount of energy transferred to molecule 2 is very slight. In the figure we find that after a decrease from 25.1 near $E = 0.5$ eV, molecule 1 actually gains energy from translational motion. Above $E = 0.8$ eV, $\Delta E_i/\hbar\omega$ is greater than 25.1 and near $E = 2$ eV, the vibrational energy of molecule 1 becomes greater than the dissociation energy, so the molecule will dissociate. Thus, we see that in the E range considered, molecule 2 gains only a very small fraction of vibrational energy in the highly excited molecules.

It is interesting to study the effects of the phase relationships of molecule 1 to energy transfer. In Figure 3 we show the phase dependence in $O_2(0.95D_e) + O_2$ at $E = 2$ eV. Molecule 1 can gain a substantial amount of energy from translation

between $\delta=0$ and $3\pi/2$, while not much activities are going on in molecule 2. In this phase range, ΔE_1 is greater than the dissociation energy. Only between $3\pi/2$ and 2π , the vibrational energy of molecule 1 remains below the dissociation limit and there is a substantial VV exchange. For the representative phase of each of these two regions, we plot the time evolution of vibrational energy, $\Delta E_i(t)/\hbar\omega$, at $E=2$ ev in Figure 4. For $\delta=310^\circ$ of the latter region, $\Delta E_1(t)/\hbar\omega$ rises to a maximum value of 30.4 and then rapidly decreases to 15.8 as the collision progresses. The initial increase of about $5\hbar\omega$ in $\Delta E_1(t)/\hbar\omega$ is due to the $T \rightarrow V$ step and the decrease, which involves an enormous amount of energy, is the result of both $V \rightarrow T$ and VV. As t continues to increase, $\Delta E_1(t)/\hbar\omega$ increases to its limiting value $\Delta E_1/\hbar\omega = 19.0$. All these energy transfer steps take place on a subpicosecond time scale during the collision. The peak of $\Delta E_1(t)/\hbar\omega$ rises above the dissociation limit, but the energy stays in molecule 1 for a time shorter than the vibrational period, so the molecule will not dissociate. Note that the collision begins near $t = -30$ fs and is essentially over at $+30$ fs. Also plotted in the figure is $z^*(t) = x(t) - y_1[y_1(t) - y_1(-\infty)] - y_2[y_2(t) - y_2(-\infty)]$, which is a measure of the inner O...O distance. The appearance of two minima in this plot indicates that the inner O atoms suffer two impacts during the collision. Figure 4a shows that as $\Delta E_1(t)/\hbar\omega$ decreases from the maximum to the minimum between $t=0$ and $+10$ fs, $\Delta E_2(t)/\hbar\omega$ rises to a maximum through VV exchange and then levels off to the limiting value $\Delta E_2/\hbar\omega$ for $t > +30$ fs. So the build-up of vibrational energy in molecule 2 does not start until molecule 1 gains a large amount of energy from translational motion. As shown in the figure, there is no activity in molecule 2 between $t = -30$ fs and zero, where $\Delta E_1(t)/\hbar\omega$ rapidly increases due to the first impact. The magnitude of energy transferred to molecule 2 is substantial, but it is only a small fraction of the initial vibrational energy of molecule 1. We now consider the case $\delta = 50^\circ$. Unlike the previous phase case, $\Delta E_1(t)/\hbar\omega$ now decreases to a minimum value as the collision begins and then sharply increases due to the $T \rightarrow V$ step; see Figure 4b. During the initial decrease of $\Delta E_1(t)/\hbar\omega$, molecule 2 quickly adjusts its motion to receive vibrational energy through VV exchange but the extent of the initial decrease is not large, so the energy transferred to molecule 2 is relatively small. The vibrational energy of molecule 1 exceeds D_e , when the molecule gains a large amount of energy ($\cong 9\hbar\omega$) from translation. And in this case, the energy resides in the molecule long enough to cause dissociation. Thus, the dissociation is characterized by an initial decrease followed by a sharp increase of $\Delta E_1(t)/\hbar\omega$ finally producing a small amount of energy transfer to molecule 2. The calculation shows that as the colliding molecules approach each other the bond of molecule 1 is stretched in the dissociative case, whereas it is compressed in the nondissociative case. We see in Figure 4b that $z^*(t)$ increases less sharply than the previous case because $y_1(t)$ also increases as the fragments of molecule 1 fly apart. As seen in Figure 3, ΔE_1 is greater than D_e over a wide range of phase. Hence, trajectories leading to dissociation is far more numerous than nondissociative ones considered in Figure 4a. In both dissociative and nondissociative cases, translational motion is heavily involved in producing $T \rightarrow V$ and $V \rightarrow T$ steps during the collision, thus competing with the VV step. Although it is not shown, we find similar variations of $\Delta E_i(t)/\hbar\omega$ with t in $O_2(\hbar\omega) + O_2$ with a significant VT contribution. In the latter case, however, $\Delta E_1(t)/\hbar\omega$ never ex-

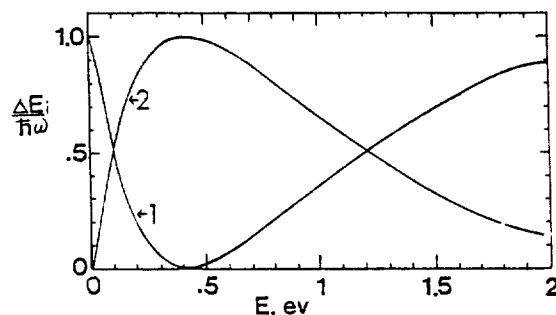


Figure 5. Dependence of vibrational energy transfer $\Delta E_i/\hbar\omega$ on the collision energy E in $CH(\hbar\omega) + HC$.

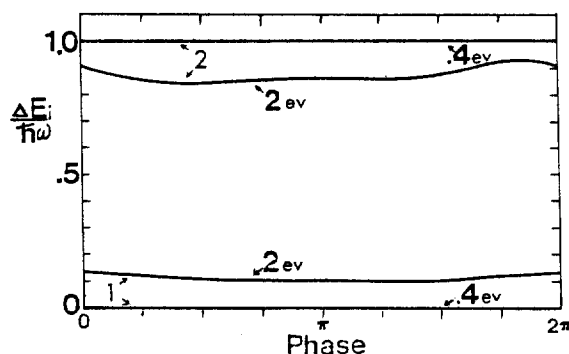


Figure 6. Phase dependence of vibrational energy transfer in $CH(\hbar\omega) + HC$ at $E=0.4$ and 2 ev.

ceeds the dissociation limit, and furthermore, $z^*(t)$ always takes only one sharp minimum (i.e., a one-impact collision).

We remark in passing that when a random distribution of the initial phases of molecule 1 is assumed, the probability of collisional dissociation can then be determined as the fraction of phases leading to $\Delta E_1 \geq D_e$; i.e., $P_d = \frac{1}{2\pi} \sum_i \delta_i(\Delta E_1 \geq D_e)$. From Figure 3, we thus find $P_d = 0.686$ for $O_2 - (0.95D_e) + O_2$ at $E=2$ ev.

B. $CH + HC$

In Figure 5, we show the energy dependence of $\Delta E_i/\hbar\omega$ for $CH(\hbar\omega) + HC$, where $\hbar\omega = 0.097D_e$. The variations of energy transfer with E are entirely different from those of the previous cases of $O_2 + O_2$. The curves are symmetrical to each other and it is evident that an efficient VV exchange is taking place. The variation of the curves suggests a characteristic oscillation of vibrational energy between the molecules giving rise to pronounced resonances. The sum of $\Delta E_i/\hbar\omega$ is essentially unity, clearly indicating the occurrence of a pure VV step with no conversion of internal energy to translational motion. As shown in the figure, the energy exchange is quite appreciable even when E is as low as 0.05 ev. As E increases to 0.1 , 0.3 , and 0.5 ev, the vibrational energy gained by molecule 2 increases to 0.501 , 0.961 , and $0.984\hbar\omega$, respectively. At $E=2$ ev, about 12% of the vibrational energy of molecule 1 is transferred to molecule 2 when the collision is over. Near $E=0.4$ ev, $\Delta E_2/\hbar\omega = 1$, thus indicating the complete VV exchange—exact resonance. Therefore, a study of the time evolution of vibrational energy near $E=0.4$ ev would be of interest in analyzing the dynamics of exact-resonance collisions; this we present in the following.

The phase dependence of $\Delta E_i/\hbar\omega$ for $CH(\hbar\omega) + HC$ at

$E = 0.4$ eV is very weak. The values of $\Delta E_i/\hbar\omega$ vary very slowly between 4.65×10^{-4} and 4.69×10^{-4} in the entire range of $\delta = 0$ to 2π , while $\Delta E_2/\hbar\omega$ remains at 0.9995: see Figure 6. In the figure, we also plot the $E = 2$ eV case for comparison. We now choose $\delta = \pi$ and calculate the time evolution $\Delta E_i(t)/\hbar\omega$ at $E = 0.4$ eV. In Fig. 7 we first consider the time variation of $z^*(t)$, which is a measure of the H...H distance. In the CH...HC configuration, the C atoms "squeeze" the H atoms into close proximity of each other. The light H atoms then encounter each other in this close-in collision many times (a multiple-impact collision^{5,14}) and at each impact they are compressed toward their respective C atoms, thus producing the strong perturbing force on the vibrational motions. Initially, molecule 1 has vibrational energy equivalent to $\hbar\omega$, whereas molecule 2 is vibrationally "frozen", and the oscillatory variation of $z^*(t)$ seen in the figure at large negative t is due to the vibration of molecule 1. After the collision the molecules recede from each other and $z^*(t)$ again undergoes the same variation because molecule 2 now has vibrational energy $\hbar\omega$ while molecule 1 settles down to rest. This situation is clearly seen from the time evolution of $y_i(t)$ also plotted in the figure. Molecule 1 undergoes free Morse oscillation at large negative t , but its amplitude starts to decrease near $t = -20$ fs, at which $y_2(t)$ begins to take a noticeable value. The displacement $y_2(t)$ grows, while $y_1(t)$ tends to diminish as t increases. After $t = +30$ fs, $y_1(t)$ vanishes but $y_2(t)$ takes full Morse oscillation with a period of about 11 fs, as is for molecule 1 at large negative t .

As shown in Fig. 7, noticeable changes in $\Delta E_i(t)/\hbar\omega$ start near $t = -35$ fs, and then $\Delta E_1(t)/\hbar\omega$ reaches its limiting value $\Delta E_1/\hbar\omega$ near $t = +30$ fs, whereas $\Delta E_2(t)/\hbar\omega$ reaches its limiting value at $t = +40$ fs, so the duration of collision for the VV exchange can be estimated as about 75 fs. During this time

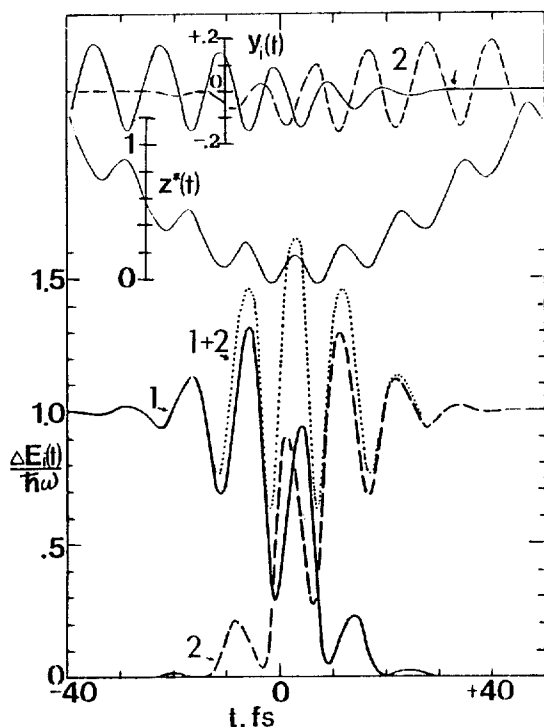


Figure 7. Time evolution of vibrational energy $\Delta E_i(t)/\hbar\omega$ in CH($\hbar\omega$) + HC at $\delta = \pi$; $E = 0.4$ eV. Also shown are $z^*(t)$ and $y_i(t)$ in Å. "1+2" represents the sum of $\Delta E_i/\hbar\omega$.

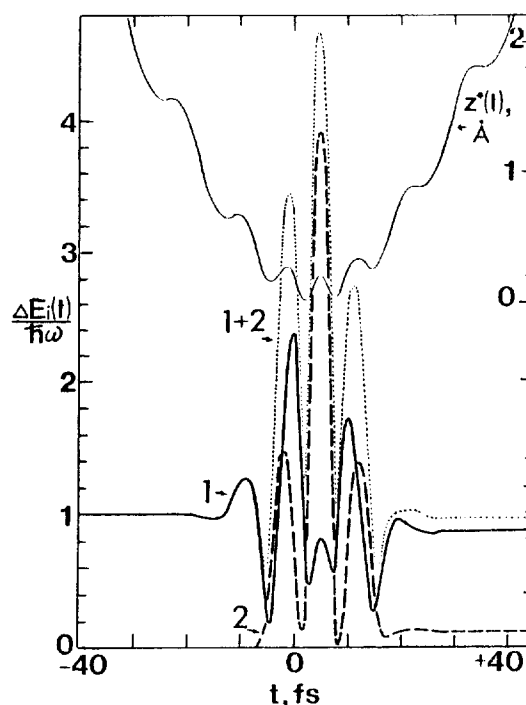


Figure 8. Time evolution of vibrational energy $\Delta E_i(t)/\hbar\omega$ in CH($\hbar\omega$) + HC at $\delta = \pi$; $E = 2$ eV. Also shown is $z^*(t)$ in Å.

period, the perturbation causes part of energy to flow back and forth many times between the molecules with a characteristic frequency of about 11 fs, finally settling to the limiting values of $\Delta E_1/\hbar\omega = 4.67 \times 10^{-4}$ and $\Delta E_2/\hbar\omega = 0.9995$. Unlike the homonuclear case $O_2 + O_2$, molecule 1 loses (or molecule 2 gains) energy in a sequence of many down (or up) steps. As seen in Figure 7, molecule 1 starts out with $E_{v,1} = \hbar\omega$ and takes a sequence of translation-assisted energy transfer steps losing 0.020, 0.056, 0.25, 0.40, 0.045, 0.045, and 0.020 $\hbar\omega$, finally reaching $4.67 \times 10^{-4} \hbar\omega$. Since the amount of energy associated with the first and last steps is negligible, this collision can therefore be treated as essentially a five-step process. The duration of each step is ≈ 11 fs, which is very close to the vibrational period.

The phase dependence of $\Delta E_i/\hbar\omega$ at $E = 2$ eV is somewhat significant; see Figure 6. The time evolution of vibrational energy for $\delta = \pi$ for this case is shown in Figure 8. From the $z^*(t)-t$ plot also shown in the figure, we notice that the H atoms approach close proximity of each other six times in the collision range of $t = -20$ to $+30$ fs. Of particular interest in the study of collisions involving heteronuclear molecules is the question of impact multiplicity¹⁴. At low collision energies a general calculation of the multiplicity of impacts is extremely difficult, depending on the law of force of each oscillator as well as its phase at the beginning of the collision. From the number of minima of the $z^*(t)-t$ plot and from comparing each minimum with the variation of $\Delta E_i(t)/\hbar\omega$, we may conclude that there are six impacts between the H atoms producing multiple energy transfer steps during the collision. The general feature of the $\Delta E_i(t)/\hbar\omega-t$ plots is similar to that for the $E = 0.4$ eV case, but we now find that the sum of $\Delta E_i(t)/\hbar\omega$ can become much greater than one. The maximum peak leads to the sum 4.7 compared to 1.6 for the lower energy case. Thus, the VV step is strongly coupled with VT during the collision. This

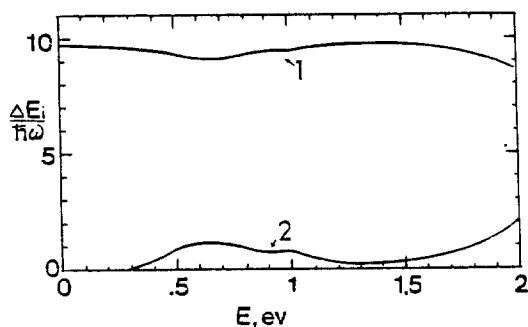


Figure 9. Dependence of vibrational energy transfer $\Delta E_i/\hbar\omega$ on the collision energy E in $\text{CH}(0.95D_e) + \text{HC}$.

coupling leads to a small extent of VV exchange when the collision completes. As in the $E=0.4$ eV case, molecule 1 starts out with $\hbar\omega$ and takes a sequence of energy transfer steps. Because of the strong VV-VT coupling, however, the sequence now involves both energy-gaining and energy-losing steps.

When molecule 1 in $\text{CH} + \text{HC}$ is initially highly excited with vibrational energy equivalent to $0.95D_e$ (i.e., $9.76\hbar\omega$), the E -dependence of $\Delta E_i/\hbar\omega$ is somewhat irregular as shown in Figure 9, and unlike $\text{CH}(\hbar\omega) + \text{HC}$, the clear case of complete VV exchange is no longer seen. In this collision it is difficult to remove a large fraction of energy from $\text{CH}(0.95D_e)$ by either VV or VT step especially at lower collision energies. But absolute energy transfer from the excited CH to the collision partner is quite significant at $E=2$ eV, see Figure 9. As shown in the figure, the fraction of the vibrational energy of molecule 1 transferred to molecule 2 is small and the energy transfer contains a significant VT contribution. For example, at $E=0.4$ eV, $\Delta E_1/\hbar\omega=9.55$ and $\Delta E_2/\hbar\omega=0.40$. Since $E_{v,1}=9.76\hbar\omega$ in $\text{CH}(0.95D_e) + \text{HC}$, molecule 2 gains $0.21\hbar\omega$ of its energy from molecule 1 and the remaining $0.19\hbar\omega$ from translational motion. Note that in $\text{CH}(\hbar\omega) + \text{HC}$ at $E=0.4$ eV, there is nearly complete VV exchange. Except at $E=2$ eV, the fraction of vibrational energy transferred to molecule 2 in this collision is much smaller than that in $\text{CH}(\hbar\omega) + \text{HC}$. For example, at $E=1$ and 1.5 eV, the extents of VV exchange are about 8 and 2%, respectively, but those in $\text{CH}(\hbar\omega) + \text{HC}$ are as large as 64 and 68%. At lower energies, the difference in percentages becomes even greater. It should be important to note that in the E range considered, $\Delta E_i/\hbar\omega$ never exceeds the dissociation limit.

We now analyze the time evolution of vibration energy in $\text{CH}(0.95D_e) + \text{HC}$. To do this we first consider phase effects at $E=2$ eV in Figure 10. Both curves exhibit a highly structured dependence on phase and are nearly symmetrical to each other, thus indicating the occurrence of some VV exchange. The exchange process takes place over the entire phase range.

Although it is significant between $\delta=0$ and $\frac{1}{4}\pi$, VV exchange is not very efficient in the remaining range. We choose one phase from each of these two ranges and analyze the time evolution $\Delta E_i(t)/\hbar\omega$ in Figure 11. For $\delta=20^\circ$, VV exchange is quite efficient and the gross behavior of the time evolution is similar to that of $\text{CH}(\hbar\omega) + \text{HC}$ at $E=0.4$ eV shown in Figure 7. Molecule 1 starts out with $9.76\hbar\omega$ and then takes five energy transfer steps to reach $\Delta E_1=1.48\hbar\omega$. Here, the molecule gains energy at the last step, but the amount of energy gained is negligible. However, at $\delta = \frac{1}{2}\pi$, as shown

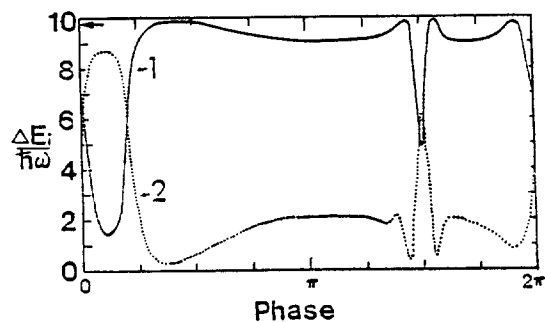


Figure 10. Phase dependence of vibrational energy transfer in $\text{CH}(0.95D_e)$ at $E=2$ eV. The arrow on the ordinate locates $E_{v,1}=9.76\hbar\omega=0.95D_e$.

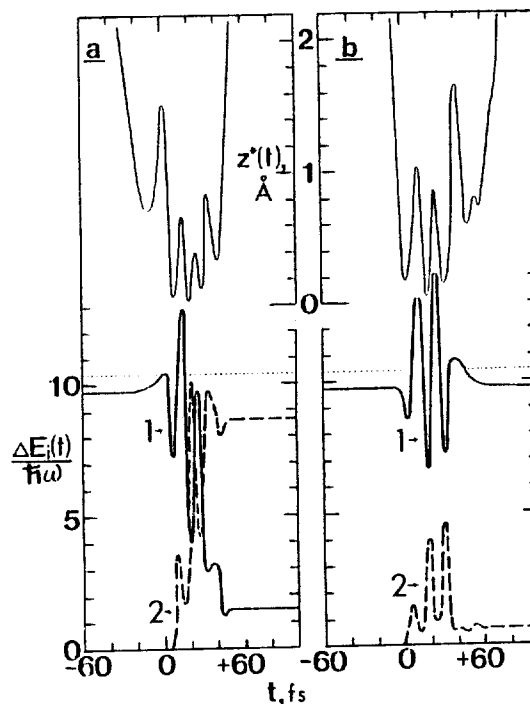


Figure 11. Time evolution of vibrational energy $\Delta E_i(t)/\hbar\omega$ in $\text{CH}(0.95D_e) + \text{HC}$ at (a) $\delta=20^\circ$ and (b) $\delta=90^\circ$; $E=2$ eV. Also shown is $z^*(t)$ in Å. Dotted line indicates $D_e/\hbar\omega$.

in Figure 11b, VV exchange is not efficient. Since there are far more trajectories which belong to the latter class than the former, the phase-averaged energy transfer $\Delta E_2/\hbar\omega$ is only 2.10; see Figure 9. Molecule 1 takes four energy transfer steps, two energy-losing and two energy-gaining, each of which containing a large contribution of translational motion. The dynamical aspect of these steps is particularly interesting. Molecule 1 starts out with $E_{v,1}=9.76\hbar\omega$, and its energy begins to decrease toward $8.53\hbar\omega$ as the colliding molecules approach each other to suffer their first impact. At this step, molecule 1 thus transfers $1.23\hbar\omega$ to molecule 2. When they start to recede upon the impact, molecule 1 gains a large amount of translational energy. The energy $\Delta E_1(t)$ is now as large as $13.2\hbar\omega$, which is far above D_e . Note that this large amount of energy stays in molecule 1 for ≈ 9 fs, which is shorter than the vibrational period, so the molecule will not dissociate. This highly excited molecule then stretches its bond violently causing the H atom to suffer another impact with the other H. At

this instant, $\Delta E_1(t)$ drops to $6.69\hbar\omega$; the lost energy is taken up by molecule 2 through VV and translational motion through $V \rightarrow T$. Immediately after the second impact, molecule 1 becomes again strongly compressed and reaches $\Delta E_1(t) = 14.1\hbar\omega$ thus gaining energy as large as $7.41\hbar\omega$. This time the energy stays in molecule 1 for only ≈ 7 fs. Part of this energy is from molecule 2, whose energy now decreases from 3.97 to $0.905\hbar\omega$, and the rest from translation. Then, the molecules repeat the expansion-compression process to suffer the third impact. As molecule 1 stretches out its bond to suffer the impact, $\Delta E_1(t)$ decreases from 14.1 to $7.23\hbar\omega$, while $\Delta E_2(t)$ increases from 0.905 to $4.57\hbar\omega$. As the hydrogen atom of molecule 1 moves away from the impact region (i.e., the bond is compressed), $\Delta E_1(t)$ increases from 7.23 to $10.8\hbar\omega$, whereas $\Delta E_2(t)$ decreases from 4.57 to $0.576\hbar\omega$. Note that as $\Delta E_1(t)$ approaches $10.8\hbar\omega$, there is a large increase in the $H \cdots H$ separation. Now the H atoms approach for the final impact at which $\Delta E_1(t)$ decreases to $9.80\hbar\omega$. In this case the H atoms undergo a soft impact at an $H \cdots H$ distance much larger than the previous impacts. After this impact, the molecules move out of the interaction region, so the atoms can no longer suffer further impact. The last minimum of the $z^*(t)$ - t plot appears to indicate a superposition of two impacts. Since it appears at a large $z^*(t)$, the vibrational energy of molecule 1 evolves with time as if the last encounter consists of only one impact. On the other hand, the $\Delta E_2(t)/\hbar\omega$ curve does show some residual variation at this encounter, but it deviates only slightly from the limiting value $\Delta E_2/\hbar\omega = 6.27$. We therefore find that molecule 1 transfers its energy through a sequence of four steps, each with -1.23 , -1.84 , $+0.54$, and $+2.57\hbar\omega$, respectively, where a negative (positive) sign stands for energy-losing (energy-gaining). These numbers indicate that there is essentially no net energy transfer in molecule 1. The sequence takes place over a time range of about 70 fs.

Thus, at low collision energies (< 2 ev), the fraction of vibrational energy in the excited molecule transferred to molecule 2 in $CH(E_{v,1}) + HC$ is very large when $E_{v,1} = \hbar\omega$, but it becomes small when $E_{v,1}$ is as large as $0.95D_e$. Furthermore, the energy transfer takes place through a stepwise process. Note that strong-collision models in unimolecular reaction theories assume transfer of a large fraction of vibrational energy from the excited molecule in a single-step process²⁰. To analyze the dependence of VV exchange on initial excitation in an orderly manner we now calculate the fractional energy transfer $\Delta E_i/E_{v,i}$ for $E_{v,i}/D_e = 0.1 - 0.95$ at $E = 0.1, 0.2, \dots, 0.5$ ev; the results are shown in Figure 12. The phase dependence of energy transfer at these energies is very weak and we take the $\delta = \pi$ case in the calculation. When $E_{v,i}/D_e$ is small, there is pure VV exchange. For example, when $E_{v,i}/D_e = 0.1$, nearly all of the initial vibrational energy of molecule 1 is transferred to molecule 2 at $E = 0.3 - 0.5$ ev, but at 0.1 ev the exchange is only about 50%. Since $\hbar\omega$ is about one-tenth of D_e , we find in Figure 12 that CH with initial vibrational energy up to about three quanta can efficiently undergo VV exchange with the collision partner which has no initial energy at $E \approx 0.4$ ev. As $E_{v,i}$ increases, the exchange process rapidly becomes very inefficient. Near $E_{v,i}/D_e = 0.7$, no VV exchange takes place; furthermore, the sum of $\Delta E_i/E_{v,i}$ is one indicating that VT transfer is also absent. When the collision energy is 0.1 ev, there is essentially no VV exchange for $E_{v,i} > 0.3D_e$. It is interesting to note that when $E_{v,i} \approx 0.90D_e$, the VV step appears

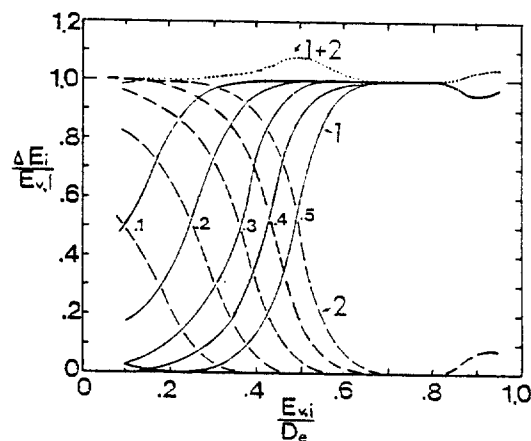


Figure 12. Dependence of vibrational energy transfer on the initial vibrational energy of molecule 1. The fractional energy transfer $\Delta E_i/E_{v,i}$ is plotted against $E_{v,i}/D_e$ for $CH(E_{v,1}) + HC$ at $E = 0.1 - 0.5$ ev. The curves between $E_{v,1}/D_e = 0.8$ and 0.95 are for $E = 0.5$ ev. The sum $(1+2)$ of $\Delta E_i/E_{v,i}$ is also for $E = 0.5$ ev (see text).

again, but the extent of VV exchange is not significant. Between $E_{v,i}/D_e = 0.8$ and 0.95 , the curves of $\Delta E_i/E_{v,i}$ for $E = 0.1 - 0.4$ ev lie above that for 0.5 ev, and the curves of $\Delta E_2/E_{v,1}$ lie below that for 0.5 ev. For clarity, we therefore show only the curves of $\Delta E_i/E_{v,i}$ for the $E = 0.5$ ev case in Figure 12.

The determination of the types of energy transfer processes (VV, $V \rightarrow T$, $T \rightarrow V$, etc.) and the extent of each process is a difficult task in both experimental and theoretical studies of molecular energy transfer¹⁵. However, such information can be readily extracted from the present calculations; the results are listed in Table 1. As shown in Figure 12, the vibrational energy of molecule 1 in $CH(E_{v,1}) + HC$ falls far below $E_{v,1}$ at small $E_{v,1}/D_e$ values as a result of Vv energy transfer to molecule 2. On the other hand, molecule 2 can gain not only vibrational energy from molecule 1 but also translational energy. For example, when $E_{v,1}/D_e = 0.5$ at $E = 0.4$ ev, molecule 2 gains $0.842\hbar\omega$ (i.e., $\Delta E_2/E_{v,1} = 0.164$) with 74% of it through VV and 26% through $T \rightarrow V$. In the table we list the fractional contributions of VV and $T \rightarrow V$ in molecule 2. When there is energy transfer to molecule 2, the $T \rightarrow V$ contribution, in general, increases with increasing $E_{v,1}$. At $E = 0.1 - 0.5$ ev, the removal of vibrational energy from $CH(E_{v,1})$ with $E_{v,1}$ up to about $0.3D_e$ (i.e., $\approx 3\hbar\omega$) by HC involves pure VV step, but when $E_{v,1}$ is larger, the energy gained by molecule 2 contains a substantial $T \rightarrow V$ contribution. In the collisions with $E_{v,1}$ greater than $0.5D_e$, however, the energy gained by molecule 2 is only a small fraction of $E_{v,1}$.

We finally note that although calculations are not performed in this work, the collisional characteristics of $HC + CH$ are expected to be similar to those of $O_2 + O_2$, a homonuclear case, and the magnitude of its energy transfer would be far less than that of $CH + HC$ ²¹. We further expect the efficiency of VV exchange in the collinear collision of $CH + CH$ to be an intermediate between those of $CH + HC$ and $HC + CH$.

Concluding Comments

We may make the following concluding comments on the collinear model in which vibrational energy could be transfer-

Table 1. Dependence of the Fractional Contribution of VV and T→V Processes to the Vibrational Energy $E_{v,1}$ at $E=0.1-0.5$ ev.

	$E_{v,1}/D_e$	0.10	0.20 ^a	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95
$E=0.1$ ev	$\Delta E_2/E_{v,1}$	0.494	0.212	0.331(1) ^b	0.287(2)	0.142(3)	0.235(5)	0.663(4)	0.262(1)	0.434(3)	0.887(3)
	VV(%)	98	92	78	76	c	c	c	93	c	c
	T→V(%)	2	8	22	24	c	c	c	7	c	c
0.2 ev	$\Delta E_2/E_{v,1}$	0.820	0.665	0.324	0.574(1)	0.622(2)	0.320(3)	0.983(3)	0.186(1)	0.163(1)	0.113(2)
	VV(%)	99	97	88	80	63	c	c	91	73	c
	T→V	1	3	12	20	37	c	c	9	27	c
0.3 ev	$\Delta E_2/E_{v,1}$	0.973	0.888	0.721	0.289	0.419(1)	0.352(2)	0.219(2)	0.466(2)	0.575(1)	0.102(1)
	VV(%)	100	99	95	83	70	48	c	c	68	71
	T→V(%)	0	1	5	17	30	52	c	c	32	29
0.4 ev	$\Delta E_2/E_{v,1}$	1.00	0.979	0.906	0.681	0.164	0.190(1)	0.606(2)	0.175(3)	0.869(1)	0.405(1)
	VV(%)	100	100	98	92	74	60	c	c	68	59
	T→V(%)	0	0	2	8	26	40	c	c	32	41
0.5 ev	$\Delta E_2/E_{v,1}$	0.983	1.00	0.978	0.882	0.483	0.651(1)	0.202(2)	0.573(2)	0.792(1)	0.919(1)
	VV(%)	100	100	100	97	82	68	c	c	65	58
	T→V(%)	0	0	0	3	18	32	c	c	35	42

^a Each column reads as, for example, when the collision energy E is 0.1 ev and the initial vibrational energy of molecule 1, $E_{v,1}$, is $0.20D_e$, the energy gained by molecule 2 is $0.212E_{v,1}$, of which 92% comes from molecule 1(VV) and 8% from translational motion (T→V). ^b Parentheses include negative powers of ten; e.g., $0.331(1)=0.331 \times 10^{-1}$. ^c Percent contribution is not listed because the fraction of energy transfer to molecule 2 is negligible.

red from one of the colliding molecules to the other in the collision energy range 0–2 ev.

(1) It is difficult to remove a large fraction of vibrational energy in the highly excited molecule by the collision partner with no vibrational energy. This is especially so in the collisions involving homonuclear molecules (i.e., O_2+O_2). The reason for this is that the VV step competes with VT, which plays an important role in transferring energy into or from the vibrational motions during the collision. Thus, when the collision is over, only a small fraction of the initial vibrational energy is transferred. This statement applies to both homonuclear and heteronuclear cases, although the fraction of energy transfer is larger in the latter case.

(2) In a heteronuclear case of CH+HC, the removal of vibrational energy in the excited molecule having energy up to about three vibrational quanta through VV is very efficient. In the collision energy range of 0.3–0.5 ev, there is total transfer of vibrational energy between the colliding molecules through a sequence of energy-losing steps in molecule 1 and energy-gaining steps in molecule 2. For the case with a highly excited molecule, the sequence involves both energy-losing and energy-gaining steps. In the collision of two homonuclear molecules, which does not involve a stepwise process, transfer of energy from the excited molecule is highly inefficient, but becomes less so as the collision energy increases. In general, VV exchange in the collision of two heteronuclear molecules with the lighter atoms inside is more efficient than that between homonuclear molecules because of repeated impacts between the atoms producing a sequence of energy transfer steps during the collision.

(3) A highly excited O_2 in the homonuclear case can

dissociate by gaining additional energy from translational motion in the energy range considered, but in CH+HC the vibrational energy of such an excited molecule always remains below the dissociation limit when the collision completes.

Acknowledgement. The authors gratefully acknowledge the financial support from the Ministry of Education.

References

1. R. J. Harter, E. B. Alterman, and D. J. Wilson, *J. Chem. Phys.* **40**, 2137 (1964).
2. J. D. Kelley and M. Wolfsberg, *J. Chem. Phys.* **44**, 324 (1966).
3. B. Stevens, *Collisional Activation in Gases* (Pergamon Press, London, 1967).
4. G. M. Burnett and A. M. North, editors, *Transfer and Storage of Energy by Molecules*, Vol. 2, *Vibrational Energy* (Wiley-Interscience, New York, 1969).
5. D. Secrest, *J. Chem. Phys.* **51**, 421 (1969).
6. D. Rapp, *Quantum Mechanics* (Holt, Rinehart, and Winston, New York, 1971), Chapter 24.
7. E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Oxford Univ. Press, London, 1974).
8. W. R. Gentry and C. F. Giese, *J. Chem. Phys.* **63**, 3144 (1975).
9. H. K. Shin in *Dynamics of Molecular Collisions*, Part A, edited by W. H. Miller (Plenum, New York, 1976), pp. 131–210.
10. W. R. Gentry in *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979), pp. 391–425.
11. J. T. Yardley, *Introduction to Molecular Energy Transfer*

- (Academic Press, New York, 1980).
12. I. W. M. Smith (ed.), *Physical Chemistry of Fast Reactions*, Vol. 2, *Reaction Dynamics* (Plenum, New York, 1980).
 13. R. T. Skodje, W. R. Gentry, and C. F. Giese, *Chem. Phys.* **74**, 347 (1983).
 14. T. Ree and H. K. Shin, *J. Chem. Phys.* **84**, 5545 (1986).
 15. S. R. Leone, *J. Phys. Chem. Ref. Data*, **11**, 953 (1982).
 16. R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques* (Oxford Univ. Press, London, 1982), Chapter 7.
 17. B. Gazdy and D. A. Micha, *J. Chem. Phys.* **82**, 4926 (1985).
 18. M. Page, E. S. Oran, J. P. Boris, D. Miller, R. E. Wyatt, H. Rabitz, and B. A. Waite, *J. Chem. Phys.* **83**, 5635 (1985).
 19. G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, Princeton, NJ, 1950), Table 39.
 20. M. Quack and J. Troe in *Gas Kinetics and Energy Transfer*, Vol. 2, (Chemical Society, London, 1977), pp. 177-201.
 21. H. K. Shin, *J. Chem. Phys.* **49**, 3964 (1968).

Syntheses of Alternating Head-to-Head Vinyl Copolymers and Vinyl Terpolymers via Ring-Opening Mechanism. Ring-Opening Polymerization of Substituted-3,4-dihydro-2H-pyrans

Ju-Yeon Lee

Department of Chemistry, Inje College, Aebang-Dong, Kimhae 600-60

Iwhan Cho

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131

Received December 16, 1986

2-Ethoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran (**1_a**), 2-n-butoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran (**1_b**), 2-isobutoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran (**1_c**), and 2-ethoxy-6-methoxy-3-methyl-5-cyano-3,4-dihydro-2H-pyran (**1_d**) were prepared by (4 + 2) cycloaddition reaction of methyl α -cyanoacrylate with the corresponding alkyl vinyl ethers. Compounds **1_{a-d}** were ring-open polymerized by cationic catalyst to obtain alternating head-to-head (H-H) copolymers. For comparison, head-to-tail (H-T) copolymer **3**, was also prepared by free radical copolymerization of the corresponding monomers. The H-H copolymer exhibited minor differences in its ¹H NMR and IR spectra, but in the ¹³C NMR spectra significant differences were observed between the H-H and H-T copolymers. Glass transition temperature (*T_g*) of H-H copolymer was higher than that of the H-T copolymer, but thermal decomposition temperature of the H-H copolymer was lower than that of the H-T copolymer. Compounds **1_a**, **1_b**, and **1_c** copolymerized well with styrene by cationic catalyst, but compound **1_d** failed to copolymerize with styrene. All of the H-H and H-T copolymers were soluble in common solvents and the inherent viscosities were in the range 0.2-0.4 dl/g.

Introduction

Vinyl polymers of head-to-head (H-H) structure are expected to show different properties from those of conventional head-to-tail (H-T) polymers, and extensive interest has been focused on the synthesis and characterization of H-H polymers. So far, various H-H polymers have been prepared and their properties were found to differ significantly from those of H-T polymers¹⁻⁸. The synthetic schemes hitherto applied to prepare H-H polymers have been by the reactions on polymers such as the radical 1,4-polymerization of 2,3-diphenylbutadiene, followed by selective hydrogenation to H-H polystyrene². However, it is often difficult to get clean and complete reactions in these synthetic methods.

We have reported a new synthetic route to H-H alternating copolymers by cationic ring-opening polymerization of substituted-3,4-dihydro-2H-pyrans⁹⁻¹³. These substituted pyrans were prepared by (4 + 2) cycloaddition reaction of cyanoacrylate or vinyl ketones with alkyl vinyl ethers, and have various cation-stabilizing groups at proper positions of the pyran ring.

This work is now extended to the construction of H-H copolymers of another pair of vinyl monomers. The present report describes the syntheses and ring-opening polymerization of 2,3,5,6-tetrasubstituted-3,4-dihydro-2H-pyrans. Properties of the resulting H-H copolymers were compared with those of the corresponding H-T copolymers which were prepared by free radical copolymerization of the corresponding monomers.

Results and Discussion

Compounds **1_{a-d}** were prepared according to a procedure similar to that reported earlier^{12,14} from methyl α -cyanoacrylate and the corresponding alkyl vinyl ethers (Scheme 1). In dilute benzene solution, substituted 3,4-dihydro-2H-pyrans were obtained in high yield at room temperature and only a trace amount of poly(methyl α -cyanoacrylate) was formed. The chemical structures of the substituted pyrans were identified by ¹H NMR (Figure 1 and Figure 2) and IR spectra. Spectral data indicated that **1_d** was a mixture of the *cis*- and