THE HARMONIC ENERGY TRANSFER IN THE FOUR ATOM-FOUR ATOM NONREACTIVE-COLLINEAR-INELASTIC COLLISIONS

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ABSTRACT

The quantum-mechanically calculation of the vibrational energy transfer in the nonreactive -collinear-inelastic collisions of fouratom-fouratom which has the form of X₂Y₂+X₂Z₂ is presented. The method has been applied to the C₂H₂+C₂H₂, C₂H₂+C₂D₂, and C₂D₂+C₂D₂ collision systems.

DÖRT ATOM-DÖRT ATOM NONREAKTİF-KOLİNEER-INELASTİK ÇARPIŞMALARINDA HARMONİK ENERJİ TRANSFERİ

ÖZET

X₂Y₂+X₂Z₂ formundaki dört atom-dört atom nonreaktifi-kolineer-inelastik çarpışmasında titreşim enerji transferinin kuantum mekaniksel hesabu gösterilmiştir. Metod C₂H₂+C₂H₂, C₂H₂+C₂D₂ ve C₂D₂+C₂D₂ çarpışma sistemlerine uygulanmıştır.

The theory of the energy in molecular collisions has great importance for the understanding of most physical problems in chemical reactions and in most gas laser systems. For that reason, there has been much work done in recent years on this subject.

So for, atom-diatom [1-3], atom-triatom [4-6], atom-fouratom [7], atom-fouratom and diatom-fouratom [8], diatom-diatom [9-11], diatom-triatom [12], and finally triatom-triatom [13] nonreactive collisions have been carried out.
In this work, we have investigated the energy transfer in four-atom-four-atom-nonreactive-collinear-inelastic collision systems for the first time. The collision system may be expressed in the terms of vibrational quantum numbers as the following:

\[ X_2Y_2(n_1,n_2,n_3)+X_2Z_2(n_4,n_5,n_6) \rightarrow X_2Y_2(n'_1,n'_2,n'_3)+X_2Z_2(n'_4,n'_5,n'_6) \]  

(1)

Where \( n_i \) and \( n'_i \) are vibrational quantum numbers before and after collisions of the incoming and target molecules, respectively.

The general solution of the problem is very difficult and various approximations are introduced. First of all, the problem is restricted to the collinear collision model. Second, the vibrations of both molecules are assumed to be of the harmonic oscillator type. Finally, we are assumed a repulsive exponential potential function to represent the intermolecular interaction which only consisted of the interaction between two nearest atoms of the collision system.

Our objective in studying the collinear four atom-four atom collision is not primarily to allow a direct comparison between theory and experiment but to establish bench marks by which can be extended to three dimensional collisions.

The Hamiltonian in mass-weighted normal coordinates for four atom-four atom collision system (see fig.1) is

\[ H_T = T(x) + \tilde{H}_{HCD}(Q_1 Q_2 Q_3) + \tilde{H}_{EPH}(Q_4 Q_5 Q_6) + V(x, Q_1 Q_2 Q_3 Q_4 Q_5 Q_6) \]  

(2)

Where \( Q_1 \) and \( Q_3 \) represent the symmetric and antisymmetric stretching modes of the X-Y bonds, respectively, and \( Q_2 \) represents the stretching mode of the X-X bond for the \( X_2Y_2 \) molecule. \( Q_4 \), and \( Q_6 \) represent the symmetric and antisymmetric stretching modes of the X-Z bonds, respectively, and \( Q_5 \) represents the stretching mode of the X-X bond.
for $X_2Z_2$ molecule. $H_{ABCD}$ and $H_{EFGH}$ represent the internal Hamiltonian of the $ABCD$ and $EFGH$ molecules, respectively. $V$ is the interaction potential between two nearest atoms of molecules.

The terms in the total Hamiltonian may be expressed in terms of normal coordinates as follows:

$$H_{ABCD} = -\frac{n^2}{2} \sum_{i=1}^{2} \frac{\delta^2}{\delta Q_i^2} + \frac{1}{2} \sum_{i=1}^{5} \lambda_i Q_i^2$$

$$H_{EFGH} = -\frac{n^2}{2} \sum_{j=4}^{7} \frac{\delta^2}{\delta Q_j^2} + \frac{1}{2} \sum_{j=4}^{10} \lambda_j Q_j^2$$

$$T(x) = -\frac{\hbar^2}{2\mu} \frac{\delta^2}{\delta x^2}$$

and

$$V(x,Q_1,Q_2,Q_3,Q_4,Q_5,Q_6) = V_o \exp[-\alpha (x-a_1Q_1-a_2Q_2-a_3Q_3-a_4Q_4-a_5Q_5-a_6Q_6 - d)$$

In the Eqs. 4 and 5, $\lambda_i (i=1,2,3,4,5)$ are energy parameters, $\mu$ is the reduced mass of the whole system, and $V_o$ and $\alpha$ are parameters which characterize the interaction potential. The parameter $V_o$ doesn't affect the transition probabilities [1]. The coefficients $a_2$ and $a_5$ in the interaction potential are zero, so that, one can expect that the transition probabilities to these modes will be very small. Other coefficients are given as $a_1=(1/2m_1)^{1/2}$, $a_3=(m_2/m_1)^{1/2}$, $a_4=(1/2m_2)^{1/2}$, and $a_6=(m_5/m_6)^{1/2}$ where $m_1$ and $m_2$ are mass of the $ABCD$ and $EFGH$ molecules, respectively. $\sigma$ is the sum of the distances, at equilibrium, between the center of masses of the molecules and their end atoms. Using the total Hamiltonian expression in the Schrödinger equation and harmonic basis functions. We can easily construct the close-coupling system of equations for the collision system.

$$-\frac{d^2}{dx^2} \psi_n(x) - k_n^2 \psi_n(x) + \sum_{n'} V_{nn'}(x) \psi_{n'}(x) = 0$$

(7)
where
\[ k_n^2 = (2 \mu / n^2) [E - \epsilon_n] \quad (8) \]

\( E \) is the total collision energy, \( \epsilon_n \) is the molecular harmonic value for the state \( n(n=n_1, n_2, n_3, \ldots n_5) \) of \( \text{four atom-four atom collision system} \), and

\[ V_{nm'}(x) = (2\mu / h^2) V_0 e^{-\alpha (x-\sigma)} \langle n | e^{\beta kx} | n' \rangle \quad (9) \]

Equation 7 can be represented in matrix form as follow [8]

\[ \frac{d^2}{dx^2} \left[ \mathbf{I} + V(x) \right] \psi(x) = k^2 \psi(x) \quad (10) \]

where \( \mathbf{I} \) is the unit matrix, \( k^2 \) is the wave number element of the scattered wave which is given by Eq.8 and \( V(x) \) is the interaction matrix. The elements of interaction matrix (or coupling matrix) are given by Eq.9.

We have used Gordon's method [14,15] to calculate the scattering matrix, which gives the transition probabilities, namely

\[ P_{ijklmn} i'j'k'1'm'n' = |S_{ijklmn} i'j'k'1'm'n'|^2 \quad (11) \]

Hence, the energy transferred from the \( ijklnm \) state to the all excited states can be calculated by equation

\[ \Delta E_{ijklmn} = \sum_{i'j'k'l'1'm'n'} |P_{ijklmn} i'j'k'1'm'n' E_{ijklmn} - E_{ijklmn}| \quad (12) \]

We have applied this method to the system of \( \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_2 + \text{C}_2\text{D}_2 \), and \( \text{C}_2\text{D}_2 + \text{C}_2\text{D}_2 \) and we have calculated the transition probabilities and the energy transfer according to the relative collision energy for these systems.
The numbers of open channels of three collision systems considered in this work are different for a given collision energy; for instance, at 1.450 eV, there are 3, 9, and 19 open channels for \( \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_2 + \text{C}_2\text{D}_2 \), and \( \text{C}_2\text{D}_2 + \text{C}_2\text{D}_2 \) systems, respectively, and at 1.500 eV there are 11, 17, and 25 open channels for those collision systems, respectively. So that the range of collision energy for these three systems are different for low lying transitions. For this reason, different collision energy ranges for each collision system are considered in the calculations.

The parameters used in the calculations are given in Table 1. The variations of the transferred energy according relative collision energy are plotted in the Figure 2.

The results show that the T-V transitions (Figure 2) to antisymmetric modes are larger than those to the symmetric modes, i.e. \( \Pr(T-V)_A > \Pr(T-V)_S \), and the transition probabilities between two symmetric modes are larger than those for two antisymmetric modes. That is, \( \Pr(V-V)_S \rightarrow S > \Pr(V-V)_A \rightarrow A \).

There are many degenerate states for \( \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \), and \( \text{C}_2\text{D}_2 + \text{C}_2\text{D}_2 \) collision systems because incoming molecule is the same as the target molecule. But there is not any degenerate state for \( \text{C}_2\text{H}_2 + \text{C}_2\text{D}_2 \), collision system in the energy range studied.

Transition probabilities to doubly degenerate states are equal. For example, the harmonic energies for both \( n=4(001000) \) and \( n=5(000001) \) states are equal, so that this state is doubly degenerate, and the transition probability to both \( n=4 \) and \( n=5 \) state has the same value of \( 0.60 \times 10^{-3} \). The total transferred energy increases with increasing mass of the incoming molecule as expected.
REFERENCES


Table 1. The parameters used in the calculation [8].

<table>
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<tr>
<th></th>
<th>$C_2H_2$</th>
<th>$C_2D_2$</th>
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<td>3. The potential Parameters</td>
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<td>$V_0 (eV)$</td>
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Figure 1: Schematic representation of the $X_2Y_2+X_2Z_2$ collinear collision system.
Figure - 2: The variation of the transferred energy versus relative collision energy for (■) C₂D₂+C₂D₂, (♦) C₂H₂+C₂D₂ and (▲) C₂H₂+C₂H₂, collision systems, respectively.