Erc.Üni.Fen.Bil.Derg., 5, 1-2 (1989), 762-769

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

Fahrettin GÖĞTAŞ and Nuri KOLSUZ
Department of Physics, Fırat University, 23119 Elazığ, TURKEY

ABSTRACT

The quantum-mechanically calculation of the vibrational energy transfer in the nonreactive -collinear-inelastic collisions of fouratom-fouratom which has the form of $X_2Y_2+X_2Z_2$ is presented. The method has been applied to the $C_2H_2+C_2H_2$, $C_2H_2+C_2D_2$, and $C_2D_2+C_2D_2$ collision systems.

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

ÖZET

$X_2Y_2+X_2Z_2$ formundaki dört atom-dört atom nonreaktif-kolineer-inelastik çarpışmasında titreşim enerji transferinin kuantum mekaniksel hesabı gösterilmiş. Metod $C_2H_2+C_2H_2$, $C_2H_2+C_2D_2$ ve $C_2D_2+C_2D_2$ 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 fouraotom-fouratom-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;

$$X_2Y_2(n_1,n_2,n_3)+X_2Z_2(n_4,n_5,n_6) \quad X_2Y_2(n_1',n_2',n_3')+X_2Z_2(n_4',n_5',n_6') \tag{1}$$

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 intermoleculer 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 comparision 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

$$H_T = T(x)+H_{ABCD}(Q_1,Q_2,Q_3)+H_{EFGH}(Q_4,Q_5,Q_6)+V(x,Q_1,Q_2,Q_3,Q_4,Q_5,Q_6) \tag{2}$$

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 follow:

$$H_{ABCD} = -\frac{n^2}{2}\sum_{i=1}^{3}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\prod_{i=1}^{3}\lambda^2_i Q_i^2 \qquad (3)$$

$$H_{EFGH} = -\frac{n^2}{2}\sum_{j=4}^{6}\frac{\partial^2}{\partial Q_j^2} + \frac{1}{2}\prod_{j=4}^{6}\lambda^2_j Q_j^2 \qquad (4)$$

$$T(x) = -\frac{h^2}{2\mu}\frac{\partial^2}{\partial x^2} \qquad (5)$$

and

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

In the Eqs. 4 and 5, λ_i($\lambda_i=4\pi^2\nu_i^2$) are energy parameters, μ is the reduced mass of the whole system, and V_o and α are parameters which characterize the interaction potential. The parameter V_o doesn't effect 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 $a_1=(1/2m_A)^{1/2}$, $a_3=(m_B/m_Am_1)^{1/2}$, $a_4=(1/2m_E)^{1/2}$, and $a_6=(m_F/m_Em_2)^{1/2}$ where m_1 and m_2 are mass of the ABCD and EFGH molecules, respectively. σ 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 funcitons. We can easily construct the close-coupling system of equations for the collision system.

$$-\frac{d^2}{dx^2}\Psi_n(X) - k_n^2\Psi_n(X) + \sum_{n'}V_{nn'}(X)\Psi n'(X) = 0 \qquad (7)$$

where

$$k_n^2 = (2\mu/n^2)[E - \epsilon_n] \qquad (8)$$

E is the total collison energy, ϵ_n is the molecular harmonic value for the state $n(n=n_1,n_2,n_3,\ldots n_6)$ of four atom-four atom collision system, and

$$V_{nn'}(x) = (2\mu/h^2)\, V_o e^{-\alpha(x-\sigma)} \prod_k < n|e^{a_k\Omega_k}|n' > \qquad (9)$$

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

$$[-\frac{d^2}{dx^2}\,\underline{I} + \underline{V}(x)]\;\underline{\Psi}(x) = \underline{k}^2\;\underline{\Psi}(x) \qquad (10)$$

where $\underline{I}$ is the unit matrix, $\underline{k}^2$ is the wave number element of the scattered wave which is given by Eq.8 and $\underline{V}(x)$ 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 probabilites, namely

$$P_{ijklmn\;\;i'j'k'l'm'n'} = |S_{ijklmn\;\;i'j'k'l'm'n'}|^2 \qquad (11)$$

Hence, the energy transfered from the ijklmn state to the all excited states can be calculated by equation

$$\Delta E_{ijklmn} = \sum_{i'j'k'l'm'n'} P_{ijklmn\;\;i'j'k'l'm'n'} |E_{i'j'k'l'm'n'} - E_{ijklmn}| \qquad (12)$$

We have applied this method to the system of C_2H_2+C_2H_2, C_2H_2+C_2D_2, and C_2D_2+C_2D_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 C_2H_2+C_2H_2, C_2H_2+C_2D_2, and C_2D_2+C_2D_2 systems, respectivelly, 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. Th variations of the transfered energy according relative collisic energy are ploted 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. $P(T\text{-}V)_A > P(T\text{-}V)_S$, and the transition probabilities between two symmetric modes are larger than those for two antisymmetric modes. That is, $P(V\text{-}V)_{S\rightarrow S} > P(V\text{-}V)_{A\rightarrow A}$.

There are many degenerate states for C_2H_2+C_2H_2, and C_2D_2+C_2D_2 collision systems because incoming molecule is the same as the target molecule.But there is not any degenerate state for C_2H_2+C_2D_2, collision system in the energy range studied.

Transition probabilities to doubly degenarate 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 0.60×10^{-3}. The total transfered energy increases with increasing mass of the incoming molecule as expected.

REFERENCES

[1] D.Rapp, and T. kassal, Chem. Phys., 69, 61(1969).

[2] D.Secrest and B.R.Johnson, J.Chem. Phys., 45, 407(1971).

[3] H.K.Shin, in Dynamics of Molecular Collisions, Ed.by.W.H.Miller (plenum Press, New York, 1976), Part A, p.131.

[4] Ş. Erkoç, J.N. Murrel and D.C. Clary, Chem. Phys. Letters, 79, 264(1980).

[5] D.C. Clary, Molec. Phys., 39, 1295(1980).

[6] B.R. Johnson, J.Chem. Phys., 84, 176(1986).

[7] A.Berki and Ş. Erkoç, Chem.Phys., Letters, 79, 261(1981).

[8] Ş.Erkoç and N. Kolsuz, Chem.Phys. Letters, 109, 56(1984).

[9] C.H. Becker, J.Chem.Phys., 76, 5928(1982).

[10] M.H. Alexander, J.of Chem.Phys., 59, 6254(1973).

[11] S.C. Choen and M.H. Alexander, J.Chem.Phys., 61, 3967(1974).

[12] D.C. Clary, Molec. Phys., 42, 1121(1981).

[13] E. İltan, Ş.Erkoç and S. Özder, DOĞA, TUJ, Phys. and Astrophys, 11, 65(1971).

[14] R.G. GORDON, Meth.Comput. Phys., 10, 81(1971).

[15] R.G. GORDON, J.Chem.Phys., 51, 14(1969).

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

	C_2H_2	C_2D_2
1. Frequences (cm^{-1})		
	ν_1 : 3374	2700
	ν_2 : 1974	1762
	ν_3 : 3287	2427
2. Bond distances (A°)		
	X_{10} : 1.06	1.06
	X_{20} : 1.20	1.20
	X_{30} : 1.06	1.06
3. The potential Parameters		
	α (a_o^{-1}) : 2.10	2.10
	V_o(eV) : 900	900

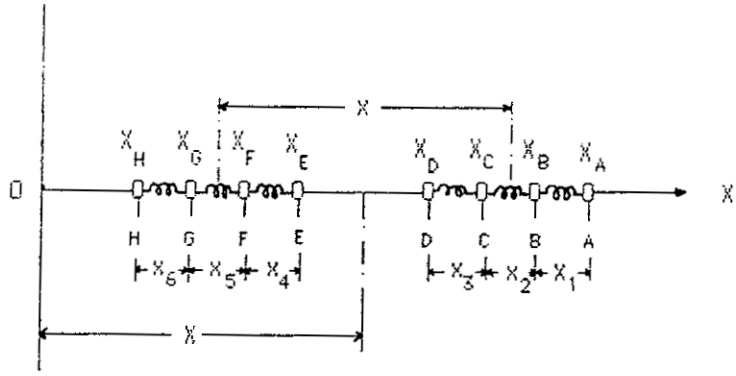

Figure - 1 : Schematic representation of the $X_2Y_2+X_2Z_2$ collinear collision system.

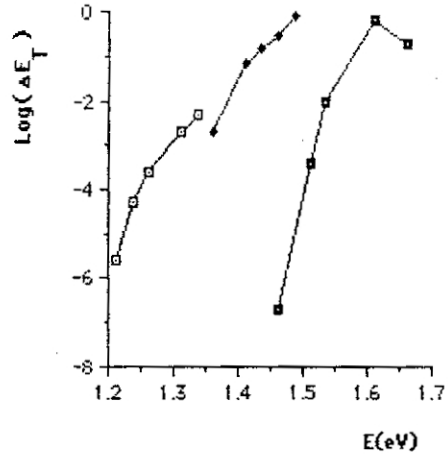

Figure - 2 : The variation of the transfered energy versus relative collision energy for (⊡) C_2D_2+C_2D_2, (◆) C_2H_2+C_2D_2 and (■) C_2H_2+C_2H_2, collision systems, respectively.