VIBRATIONAL-ROTATIONAL EXCITATION AND DEACTIVATION OF CH_4 - TYPE TETRAHEDRAL MOLECULES

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ABSTRACT

The classical trajectory calculations had been carried out to study energy transfer in methane - argon collisions. The average energy transfer is calculated for the temperature and molecule internal energy wide range.

To calculate the nonequilibrium unimolecular reaction rate constant at the low pressure limit it is necessary to determine the average energy transferred by a collision between translational and inner degrees of freedom. The average energy transferred determines the probabilities of transition between energy levels and thus the molecules energy distribution.

This work was undertaken to calculate using the classical trajectory method the average energy $\langle \Delta E \rangle$ trasferred per collision between methane and argon. The classical trajectory calculations had been carried out earlier to study energy transfer in atom - triatom collisions (He, Ar - O_3, H_2O) [1].

The potential surface of the methane molecule is presented by expression

$$U = \sum_{i=1}^{4} D_i \left[\exp(-\beta_i \Delta R_i) - 1\right]^2 + \frac{1}{2} \sum_{i>j} k_{ij} \Delta \varphi_{ij}$$

where D_i are the dissociation energies, β_i are Morse coefficients, ΔR_i are lengthenings for i-bonds, k_{ij} are hardness coefficients, $\Delta \varphi_{ij}$ are the valent angles changes.

The interaction between the molecule and the heat-bath gas atom is described with the Lennard-Jones (6 - 12) potential.

For the atom - molecule trajectory there are a number of variables that have to be defined at the start of each trajectory. We assume that at the start of each trajectory the molecule passes through its equilibrium configuration, the initial direction and values of the atoms' momenta being randomizated but normalized to give a definite internal energy of the system. For the majority of calculations the vibrational and rotational energies of the molecule were set at their classical equipartition corresponding to the temperature under consideration. Hence each rotational degree of freedom was given an initial energy 1/2 kT. The impact parameter and the vibration phase were given by the standart calculation methods [2]. The average energy transferred per collision is the result of statistical averaging of number of trajectories.

The average vibrational energy transferred per collision

$< E_V >$ is most important to be known for the rate constant calculations. Therefore in our calculations the internal energy of the molecule was divided into the vibrational and the rotational components. The CH_4 molecule rotational energy was calculated from the inertia momenta at a given time. The vibrational energy E_V was calculated from the difference of the molecule total internal and the rotational energy.

In the Fig.1 the rotational energy E_R of CH_4 is presented vs. time at the internal energy of the molecule corresponding to the temperature of 2000 K. Oscillations of E_R are of the same order of magnitude of kT and are determined with the molecule inertia momenta varying during the molecule vibrations. Therefore at the calculations of the average transferred energy smoothed rotational (and vibrational) energies were used.

In the Fig.2 histogramm is shown which characterizes the distribution of E_V value determined from the trajectory calculations at 500 K and internal energy of CH_4 4.5 eV for Ar as the heat-bath gas. The exponential model is seen to be a good approximation to the V - T transition probabilities.

In the table average energies transferred per collision between CH_4 and Ar are given. E_V is seen to increase with both translational temperature and molecule internal energy.

REFERENCES

(1) A.J. Stace and J.N.Murrell, J.Chem.Phys., 68, 3028 (1978).

(2) D.L. Bunker,"Atomic and Molecular Scattering" in "Methods in Computational Physics"(Academic Press, New York and London, 1971).

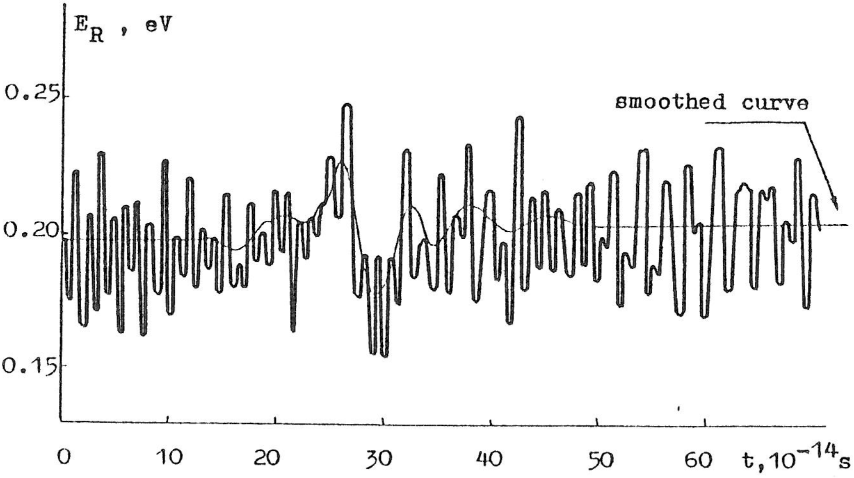

Fig.1. Methane molecule rotational energy E_R vs. time

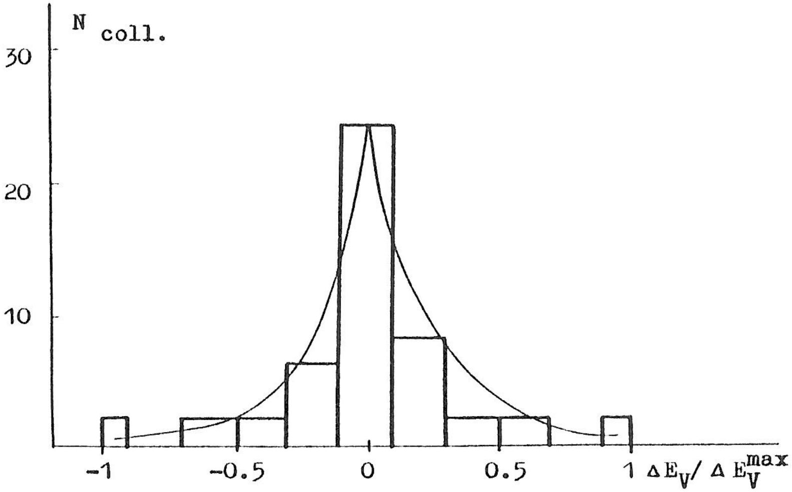

Fig.2. Histogramm of the transition probability function determined from the classical trajectory calculations. The curves are the transition probability function calculated using exponential model

Table. Average vibrational energies transferred per collision between CH_4 and Ar (eV)

T , K E_{int}, eV	500	2000	5000
0.45	$4.72 \cdot 10^{-4}$	$5.50 \cdot 10^{-3}$	-
1.806	$6.40 \cdot 10^{-3}$	$3.32 \cdot 10^{-3}$	$2.95 \cdot 10^{-2}$
4.5	$1.62 \cdot 10^{-2}$	$2.73 \cdot 10^{-2}$	$4.13 \cdot 10^{-2}$