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# The calculation of TV, VT, VV, VV' – rate coefficients for the collisions of the main atmospheric components

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**Abstract.** The first-order perturbation approximation is applied to calculate the rate coefficients of vibrational energy transfer in collisions involving vibrationally excited molecules in the absence of non-adiabatic transitions. The factors of molecular attraction, oscillator frequency change, anharmonicity, 3-dimensionality and quasiclassical motion have been taken into account in the approximation. The analytical expressions presented have been normalized on experimental data of VT-relaxation times in N<sub>2</sub> and O<sub>2</sub> to obtain the steric factors and the extent of repulsive exchange potentials in collisions N<sub>2</sub>-N<sub>2</sub> and O<sub>2</sub>-O<sub>2</sub>. The approach was applied to calculate the rate coefficients of vibrational-vibrational energy transfer in the collisions N<sub>2</sub>-N<sub>2</sub>, O<sub>2</sub>-O<sub>2</sub> and N<sub>2</sub>-O<sub>2</sub>. It is shown that there is good agreement between our calculations and experimental data for all cases of energy transfer considered.

**Key words.** Ionosphere (Auroral ionosphere; ion chemistry and composition). Atmospheric composition and structure (Aciglow and aurora).

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## Introduction

Vibrational excitation of atmospheric molecules is important for the thermal structure of the atmosphere and may significantly change the chemical structure through modification of the normal reaction rates. Whereas the rotational and translational modes of the molecules with short relaxation times may be equilibrated during atmospheric disturbances (auroral precipitation, artificial heating etc.), the vibrational degrees of freedom will

definitely not be equilibrated, thus enhancing the chemical activity of atmospheric components.

The reactions involving vibrationally excited molecules are believed to be faster than the corresponding ground level reactions, because they occur on potential energy surfaces which have little or no activation barriers and are highly exothermic (Rusanov and Fridman, 1984). When the vibrational temperature of the molecular atmospheric components is sufficiently enhanced, the rates of reactions



may be greatly increased causing effective NO production in thin layers during auroral beam-plasma instabilities (Mishin *et al.*, 1989; Aladjev and Kirillov, 1995, 1997). The effect of selective reactant excitation on the rates of chemical reactions has been shown by Eyring *et al.* (1980), and Smith (1980). With an activation barrier displaced into the “exit valley” of the potential, vibrational energy was again found to promote reaction much more effectively than relative translational energy.

Also vibrationally excited molecules play a significant role in the ionic chemistry and thermal balance of the upper atmosphere. For example, the chemistry of ion O<sup>+</sup> in F-region of the ionosphere is very dependent on the vibrational temperature of ionospheric components. Nonlinear theory of the production of main ionospheric maximum was developed by Richards and Torr (1986), and Vlasov and Izakova (1989). It was found that enhanced vibrational excitation of atmospheric components results in the increase of O<sup>+</sup> losses and the decrease of electron concentration. The collisions of excited N<sub>2</sub> with thermal ionospheric electrons promote the heating of the electron gas and, under conditions of enhanced F region electron densities, N<sub>2</sub> may act as a small net source of electron thermal energy (Richards *et al.*, 1986).

An understanding of rates of different plasma-chemical processes involving excited molecules helps to

explain the role of vibrationally excited particles in the balances of ionospheric plasma because the ionospheric components can be excited to high vibrational levels during natural and artificial atmospheric disturbances. The classical, semiclassical, quasiclassical and exact quantum mechanical models developed to calculate the energy transfer in nonreactive vibrational-translational and vibrational-vibrational molecular collisions have been reviewed in Rapp and Kassal (1969), Nikitin (1974a, b), Nikitin and Osipov (1977) and Billing (1986). The purpose of this study is to show that the first-order perturbation approximation (FOPA) of the calculation of energy transfer between molecules in the absence of non-adiabatic transitions gives the TV, VT, VV and VV'-coefficients corresponding to the experimental data if the factors of molecular anharmonicity, frequency shift, attraction etc. are included. The present method is applicable to transitions involving the exchange of one or more quanta. Application is made to the N<sub>2</sub>-N<sub>2</sub>, O<sub>2</sub>-O<sub>2</sub>, N<sub>2</sub>-O<sub>2</sub> molecular collisions.

### Vibrational-translational energy transfer (TV and VT-process)

The basic model for the investigation of vibrational-translational energy transfer is the collinear collision between a oscillator and an incident particle interacting through a repulsive exponential potential. Let us consider the collinear collision of harmonic oscillator AB and a structureless particle C, shown in Fig. 1. The harmonic oscillator AB has the classical oscillator frequency  $\omega$ , and the repulsive interaction potential between the atom C and the nearest atom of the harmonic oscillator, B, is assumed to be exponential. The Hamiltonian of the interaction is equal to:

$$H = \frac{P_R^2}{2\mu} + \frac{p_r^2}{2M} + \frac{M\omega^2(r - r_e)^2}{2} + A_0 \exp[-\alpha(R + \lambda r)] , \quad (3)$$

in which  $R$  is the distance between C and the AB centre of mass,  $r$ , the oscillator coordinate, is the separation of A and B,  $r_e$  is the equilibrium value of  $r$ ,  $P_R$  and  $p_r$  are the conjugate impulses,  $M$  is the oscillator reduced mass  $m_A m_B / (m_A + m_B)$ ,  $\mu$  is the reduced mass of C on AB, or  $(m_A + m_B)m_C / (m_A + m_B + m_C)$ ,  $m_A, m_B, m_C$  are the masses, respectively, of atoms A, B, C,  $A_0$  and  $\alpha$  are constants determining the amplitude and the range of intermolec-

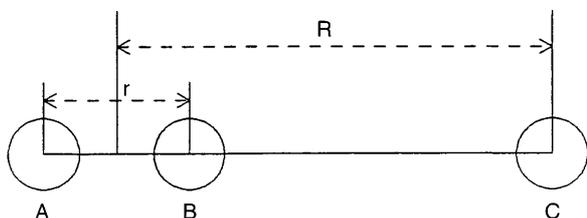


Fig. 1. The collinear collision of the molecule AB and a particle C

ular forces,  $\lambda = m_A / (m_A + m_B)$ . We suggest that the relative velocity of AB and C at  $t = -\infty$  has the value  $v$ .

For calculational purposes, it is convenient to define the dimensionless quantities  $z = \alpha R + z_0$ ,  $x = \alpha(r - r_e)(M/\mu)^{1/2}$ ,  $\tau = \omega t$  (Nikitin, 1974b). Then the Hamiltonian Equation (3) becomes in the classical case

$$H^{CL} = E_0 \left[ \frac{\dot{z}^2}{2} + \frac{\dot{x}^2}{2} + \frac{x^2}{2} + \exp(-z + \sqrt{m}x) \right] , \quad (4)$$

where

$E_0 = \mu\omega^2/\alpha^2$ ,  $\exp(z_0 + \alpha\lambda r_e) = E_0/A_0$ ,  $m = \lambda^2\mu/M$ . The equations of translational and vibrational motions for the system can be shown to be:

$$\ddot{z} = \exp(-z + \sqrt{m}x) \quad (5)$$

$$\ddot{x} + x + \sqrt{m} \exp(-z + \sqrt{m}x) = 0 . \quad (6)$$

Since  $x \ll 1$ , one can perform an approximate integration of Eq. (5) and (6) neglecting  $x$  in the exponential term. The result of the integration is

$$\exp(-z) = E_z \operatorname{sech}^2 \left( \sqrt{\frac{E_z}{2}} \tau \right) \quad (7)$$

$$\begin{aligned} \frac{\Delta E_{TV}^{CL}}{E_0} &= \lim_{\tau \rightarrow \infty} \frac{m}{2} \left\{ \left| \int_{-\infty}^{\tau} \exp[-z(s)] \sin(\tau - s) ds \right|^2 \right. \\ &\quad \left. + \left| \int_{-\infty}^{\tau} \exp[-z(x)] \cos(\tau - s) ds \right|^2 \right\} \\ &= 4mE_z [\pi\xi \cdot \operatorname{csch}(\pi\xi)]^2 . \end{aligned} \quad (8)$$

Here it is suggested that the oscillator was not excited originally,  $E_z = \alpha^2 v^2 / 2\omega^2$  is the energy of relative motion on infinite distance at  $\tau = -\infty$  for unity reduced mass of AB and C,  $\xi = \omega/\alpha v = (2E_z)^{-1/2} \gg 1$  is the Massey factor.

The expression (8) is identical with the energy amount which can be obtained from an approximate semiclassical calculation (Rapp and Kassal, 1969). In the semiclassical calculation, the molecule AB is treated as a quantum mechanical system with discrete vibrational levels. The relative translational motion of the molecule and the particle C is treated classically, see Eq. (7).

The possibility of vibrational-translational energy transfer (TV or VT-process from vibrational level  $n$  to  $m$ ) calculated according to the semiclassical FOPA is equal to

$$P_{nm}^{SC} = |r_{nm}|^2 \left| \frac{1}{\hbar} \int F(t) \exp(i\omega_{nm}t) dt \right|^2 , \quad (9)$$

where  $\hbar$  is Planck constant,  $\hbar\omega_{nm} = |E_n - E_m|$ ,  $E_n$  and  $E_m$  are the energies of vibrational levels  $n$  and  $m$ ,  $F(t)$  is the power acting on the oscillator,

$$r_{nm} = \int \Psi_n(r - r_e) \Psi_m dr , \quad (10)$$

where  $\Psi_n, \Psi_m$  are the wave function of levels  $n$  and  $m$ . For the harmonic oscillator

$$|r_{n,n+1}|^2 = (n+1)|r_{01}|^2 = (n+1) \frac{\hbar}{2M\omega_{01}}$$

and the possibility of  $n \leftrightarrow n+1$  energy transfer is proportional to that of  $0 \leftrightarrow 1$ :

$$P_{n,n+1}^{SC} = (n+1)P_{01}^{SC} . \quad (11)$$

It can be shown that the energy calculated according to Eq. (8) is related to the semiclassical possibility:

$$\Delta E_{TV}^{CL} = P_{01}^{SC} \hbar\omega_{01} .$$

Kelley and Wolfsberg (1966) have calculated the classical energy transfer to the oscillator by two methods. The approximate procedure neglected the effect of the oscillator motion on the external collisional motion in coordinate  $R$ . The exact procedure has taken into account the influence of the oscillator motion on the external collisional motion. It was found that the ratio of approximate and exact energy transfers is not equal to unity and depends only on  $m$ :

$$\mathfrak{R} = \exp(1.685m) . \quad (12)$$

Secrest and Johnson (1966) presented an exact quantum-mechanical solution for vibrational-translational transition probabilities in the collinear collision of a particle with a harmonic oscillator. They have found that their results did not reduce to the first-order distorted-wave approximation (FODWA) and the probabilities of Secrest and Johnson (1966) appear to be proportional (but not equal) to the probabilities of FODWA.

Rapp and Kassal (1969) believed that the reason for the failure of the FODWA is intimately related to the failure of the approximate classical calculations of Kelley and Wolfsberg (1966). This is the quantum-mechanical analogy of the classical approximate procedure, because the wave function in coordinate  $r$  is totally independent of coordinate  $R$ . Therefore, the FODWA must fail to agree with the exact quantum-mechanical calculations to the same extent that the approximate classical calculations fail to agree with the exact classical calculations.

The factor (12) may be regarded as a correction factor for the usual FODWA transition probabilities and approximate classical calculations. It is also interesting to note that the revised FODWA given by Mies (1964) leads to a correction factor expressible as  $(1 - m + \dots)$ .

As was pointed out in Nikitin (1974a, b), Nikitin and Osipov (1977) and Nikitin *et al.* (1989), the disagreement of the approximate calculation of energy transfer with the exact one is reduced in the classical case if the frequency shift factor is taken into account. Let us consider the approximate equation of oscillator motion with the frequency shift (obtained from the Hamiltonian Equation (4)):

$$\ddot{x} + (1 - \sqrt{m}x_0)x = (1 - \sqrt{m}x_0)x_0 , \quad (13)$$

in which the place of potential energy minimum  $x_0$  is determined by the expression

$$x_0 + \sqrt{m} \exp(-z + \sqrt{m}x_0) = 0 . \quad (14)$$

The comparison of TV-energy transfer for the case of oscillator frequency change with the expression (8) (Nikitin 1974a, b; Nikitin and Osipov, 1977; Nikitin *et al.*, 1989) gives the factor

$$f_{sh} = \frac{J_1^2(2\sqrt{m})}{m} . \quad (15)$$

Here  $J_1$  is the Bessel function. When the mass factor  $m$  is less than about 1/2, the approximate formula

$$f_{sh} \approx \left(1 - \frac{m}{2}\right)^2 \quad (16)$$

may be used.

The formula (16) can be obtained if Green's method is applied to calculate the net amount of vibrational energy transferred to the oscillator (Kirillov, 1997). Green's function of the Eq. (13) is equal to Baz *et al.* (1971):

$$G(\tau, s) = [\zeta(\tau)\zeta^*(s) - \zeta^*(\tau)\zeta(s)]/W(\zeta, \zeta^*) , \quad (17)$$

where the solution of homogeneous Eq. (12) is

$$\zeta(\tau) \approx e^{i\tau} \left[ 1 + im\sqrt{\frac{E_z}{2}} \tanh\left(\sqrt{\frac{E_z}{2}}\tau\right) \right] \quad (18)$$

and

$$W(\zeta, \zeta^*) = \dot{\zeta}\zeta^* - \dot{\zeta}^*\zeta . \quad (19)$$

The integration of the product of the function on the right side of (13) and Green's function (17) leads to the factor (16) (Kirillov, 1997).

To obtain the averaged possibility of vibrational-translational energy transfer  $v = 0 \leftrightarrow v = 1$ , the expression (8) must be integrated over a normalized Maxwell distribution of relative collision velocities along the line of centres. The resulting averaged transition probability is

$$\langle P_{01}^{SC} \rangle = Z_v Z_{tr} ,$$

where the vibrational and translational factors  $Z_v$  and  $Z_{tr}$  are as follows:

$$Z_v = \lambda^2 \frac{\mu}{M} \frac{2\pi^2\Theta}{\Theta'} , \quad (20a)$$

$$Z_{tr} = \sqrt{\frac{2\pi}{3}} \left(\frac{\Theta'}{\pi\Theta}\right)^2 \left(\frac{\Theta'}{T}\right)^{1/6} \exp\left[-\frac{3}{2}\left(\frac{\Theta'}{T}\right)^{1/3}\right] , \quad (20b)$$

$$\Theta' = \frac{4\pi^2\omega_{01}^2\mu}{\alpha^2 k} , \quad \Theta = \frac{\hbar\omega_{01}}{k} .$$

Here  $k$  and  $T$  are the Boltzmann constant and the translational temperature.

The calculation of vibrational-translational energy transfer could be easily extended to the case of an anharmonic oscillator by replacing the harmonic AB wave functions by anharmonic wave functions where the frequency for the transfer  $n \leftrightarrow n+1$  is equal to

$$\omega_{n,n+1} = \omega_{01}(1 - 2x_e n) , \quad (21)$$

where  $x_e$  is the anharmonic constant. Taking into account the frequency reduction in (21) and the dependence of translational and vibrational factors  $Z_{tr}$  and  $Z_v$  on the frequency of the transfer (20a, b), one can obtain the correction factor in the  $n \leftrightarrow n+1$  energy transfer for the anharmonic oscillator:

$$f_{an} = \exp \left[ 2x_e n \left( \frac{\Theta'}{T} \right)^{1/3} \right] \left( 1 - \frac{8}{3} x_e n \right) . \quad (22)$$

The expression (20b) was obtained for the repulsive exponential potential. In fact, there is an effect of a long-range attractive potential on the energy transfer. A procedure for the determination of the effect of attraction was suggested in Nikitin (1974a). To obtain the factor of this attraction we have used the relation between interaction times  $\tau''$ ,  $\tau'$  with and without the attraction, respectively, following Nikitin (1974a):

$$\tau'' = \tau' \left[ 1 - \frac{2}{\pi} \sqrt{\frac{\varepsilon}{E}} \right] , \quad (23)$$

where  $E$  is the relative energy of the molecule and the particle at infinite separation before collision and  $\varepsilon$  is the depth of the potential well. Place the Eq. (23) into the expression for a probability of oscillator excitation, (proportional to  $\exp(-2\pi\xi)$  in adiabatic collisions according to Eq. (8)), and average over the Maxwell distribution. The integrated function in this case is Nikitin (1974a):

$$f(y) \sim \exp \left[ -y - \left( \frac{2\gamma}{\sqrt{y}} \right) \left( 1 - \frac{C}{\sqrt{y}} \right) \right] , \quad (24)$$

where

$$C = \frac{2}{\pi} \sqrt{\frac{\varepsilon}{kT}} , \quad y = \frac{E}{kT} , \quad \gamma = \pi\xi .$$

The function (24) has its maximum near the exponential extremum and the integration over the Maxwell distribution yields the factor  $\exp(-3\gamma_0^{2/3} + 2C\gamma_0^{1/3})$ , where  $\gamma_0 = y_0^{3/2}$  (Kirillov, 1997). So the factor of the attraction is equal to:

$$f_{at} = \exp \left[ \frac{2}{\pi} \sqrt{\frac{2\varepsilon}{kT}} \left( \frac{\Theta'}{T} \right)^{1/6} \left( 1 - \frac{2x_e n}{3} \right) \right] . \quad (25)$$

The exponential power in Eq. (25) is  $\sqrt{2}$  greater than the one obtained in Nikitin (1974a).

Although the one-dimensional collision study leads to a functional form of the transition probabilities, it is necessary to estimate the possibility of vibrational-translational energy transfer for 3-dimensional case, as made by Schwartz and Herzfeld (1954), Calvert and Amme (1966), and Hansen and Pearson (1970). The three-dimensional model is needed to fit both the slope and the absolute magnitude of the experimental relaxation rates to our theoretical estimations. In this study the treatment of 1-dimensional calculation is extended to a collision in three dimensions by introducing the steric factor  $P_{st}$ .

The first effect of the 3-dimensionality results from the necessity of taking into account the contributions of non-collinear collisions. Since the collision of the molecule AB with the particle C may not be linear, a consideration of the effect becomes necessary. The second important effect accounted for by the factor  $P_{st}$  is caused by the non-zero-impact parameter collisions. It is obvious that an accurate prediction of the value of the steric factor  $P_{st}$  is practically impossible.

If the vibration is treated as if it is a breathing vibration in a nearly spherical molecule, one may expect for the diatomic molecule, that the value  $P_{st}$  for vibrational-translational transition probability is equal to  $\langle \cos^2(\theta) \rangle = 1/3$  where  $\theta$  is the angle between molecular axis and  $R$  (Schwartz and Herzfeld, 1954; Billing, 1986). The conclusion is based on the suggestion of very weak interaction at angles  $\theta \sim \pi/2$ . Quantum-mechanical calculations of the real potential surfaces show stronger angular interaction at  $\theta \sim \pi/2$  than in the case of the pairwise potential (Nikitin *et al.*, 1989). So, in fact, one may expect greater magnitudes of  $P_{st}$ .

Thus, the transition probability for the binary collision in which target molecule AB undergoes a VT or TV-transition  $n \leftrightarrow n+1$  upon the impact of an incident particle C is as follow:

$$\langle P_{n,n+1} \rangle = (n+1) P_{st} f_{an} f_{at} f_{sh} Z_v Z_{tr} f_{qu} , \quad (26)$$

where all factors (11), (15), (20a), (20b), (22), (25) have been taken into account and the value of quasiclassical factor

$$f_{qu} = \exp \left( \pm \frac{\hbar\omega_{n,n+1}}{2kT} \right) \quad (27)$$

can be obtained in the case of quasiclassical consideration (Landau and Lifshitz, 1965; Nikitin, 1974a). Signs + and - are to be used for VT and TV-processes, respectively. The rate coefficient of vibrational-translational energy transfer  $n \leftrightarrow n+1$  can be described by the equation:

$$k_{n,n+1} = \langle P_{n,n+1} \rangle \sqrt{\frac{8kT}{\pi\mu}} \pi R_0^2 , \quad (28)$$

where  $R_0$  is the gas-kinetic radius of the collision.

### Vibrational-vibrational energy transfer (VV and VV'-process)

The simple FOPA calculation can be extended to the case of vibrational-vibrational energy transfer between molecules. Let us consider two diatomic molecules AB and CD colliding head-on (Fig. 2). As in a previous section, the intermolecular potential is assumed to be purely repulsive between B and C, in analogy to previous calculation of vibrational-translational energy exchange. The Hamiltonian of the interaction is equal to

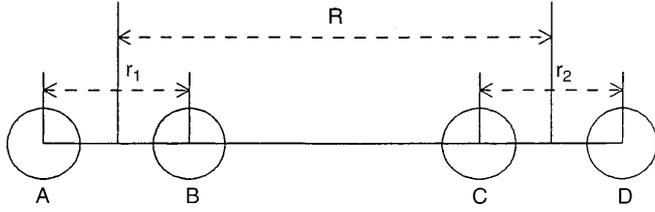


Fig. 2. The collinear collision of the molecules AB and CD

$$H = \frac{P_R^2}{2\mu} + \frac{P_{r_1}^2}{2M_1} + \frac{M_1\omega_1^2(r_1 - r_{1e})^2}{2} + \frac{P_{r_2}^2}{2M_2} + \frac{M_2\omega_2^2(r_2 - r_{2e})^2}{2} + A_0 \exp[-\alpha(R + \lambda_1 r_1 + \lambda_2 r_2)] , \quad (29)$$

in which the distance between centres of mass of AB and CD is  $R$ , the respective oscillator coordinates in AB and CD are  $r_1$  and  $r_2$ ,  $r_{1e}$  and  $r_{2e}$  are the equilibrium separations in AB and CD,  $P_R, p_{r_1}, p_{r_2}$  are the conjugate impulses,

$$M_1 = m_A m_B / (m_A + m_B), M_2 = m_C m_D / (m_C + m_D),$$

$\mu$  is the reduced mass of CD on AB, or  $(m_A + m_B)(m_C + m_D) / (m_A + m_B + m_C + m_D)$ ,  $m_A, m_B, m_C, m_D$  are the masses, respectively, of atoms A, B, C, D,  $\lambda_1 = m_A / (m_A + m_B)$ ,  $\lambda_2 = m_D / (m_C + m_D)$ . As in the case of vibrational-translational calculation we suggest that the relative velocity of AB and CD at  $t = -\infty$  has the value  $v$ , but the oscillator CD is initially vibrationally excited and the energy of the vibration is

$$E_{vib2} = \frac{M_2\omega_2^2(r_{2\max} - r_e)^2}{2} = \hbar\omega_2 .$$

Using the dimensionless quantities  $z = \alpha R + z_0, x_1 = \alpha(r - r_{1e})(M_1/\mu)^{1/2}, \tau = \omega_1 t$ , we obtain the following approximate expression for the Hamiltonian (29) in the classical case:

$$H^{CL} \approx E_0 \left[ \frac{z^2}{2} + \frac{\dot{x}_1^2}{2} + \frac{x_1^2}{2} + \frac{\hbar\omega_2}{E_0} + \exp(-z + \sqrt{m}x_1) \left\{ 1 + B \cos\left(\frac{\omega_2}{\omega_1}\tau + \delta\right) \right\} \right] , \quad (30)$$

where we neglect the energy loss of the CD oscillator and use for the amplitude of the CD vibration  $\lambda_2\alpha(2\hbar/M_2\omega_2)^{1/2} = B \ll 1$ , and we have  $E_0 = \mu\omega_1^2/\alpha^2$ ,  $\exp[z_0 + \alpha(\lambda_1 r_{1e} + \lambda_2 r_{2e})] = E_0/A_0, m = \lambda_1^2\mu/M, \delta$  is the phase of CD oscillation at  $t = 0$ .

The equation of vibrational motion of the AB molecule is

$$\ddot{x}_1 + x_1 + \sqrt{m} \exp(-z + \sqrt{m}x_1) \left\{ 1 + B \cos\left(\frac{\omega_2}{\omega_1}\tau + \delta\right) \right\} = 0 \quad (31)$$

and taking into account the expression for translational motion (7) the vibrational-vibrational energy transfer can be obtained as

$$\frac{\Delta E_{VV}^{CL}}{E_0} = \lim_{\tau \rightarrow \infty} \frac{mB^2}{2 \cdot 4} \left\{ \left| \int_{-\infty}^{\tau} \exp[-z(s)] \sin(\tau - s) \cos\left(\frac{\omega_2}{\omega_1}s + \delta\right) ds \right|^2 + \left| \int_{-\infty}^{\tau} \exp[-z(s)] \cos(\tau - s) \cos\left(\frac{\omega_2}{\omega_1}s + \delta\right) ds \right|^2 \right\} \approx mB^2 E_z [\pi\xi \cdot \operatorname{csch}(\pi\xi)]^2 , \quad (32)$$

where  $E_z = \alpha^2 v^2 / 2\omega_1^2$  and  $\xi = (\omega_2 - \omega_1) / \alpha v$ .

The energy amount in Eq. (32) can be calculated according to semiclassical FOPA. The approximation gives the following expression for VV and VV' energy transfer:

$$Q_{nn'}^{mm'SC} = |r_{nm'}|^2 |r_{mm'}|^2 \left| \frac{1}{\hbar} \int F(t) \exp(i\omega_{nn'}^{mm'} t) dt \right|^2 , \quad (33)$$

$$\hbar\omega_{nn'}^{mm'} = |E_n + E_m - E_{n'} - E_{m'}| ,$$

where  $E_n, E_m$  are the vibrational energies of AB and CD before the collision and  $E_{n'}, E_{m'}$  are the ones after the collision. The calculation of the integral in Eq. (33) leads to the expression

$$Q_{nn'}^{mm'SC} = Z_{nn'}^{AB} Z_{mm'}^{CD} \frac{8\mu}{\hbar^2 \alpha^2} \frac{\mu v^2}{2} [\pi\xi \cdot \operatorname{csch}(\pi\xi)]^2 . \quad (34)$$

Here the vibrational factors are

$$Z_{nn'}^{AB} = \alpha^2 \lambda_1^2 |r_{nn'}^{AB}|^2 , Z_{mm'}^{CD} = \alpha^2 \lambda_2^2 |r_{mm'}^{CD}|^2 . \quad (35)$$

As in the case of VT-energy transfer there is the relation of classical and semiclassical calculations

$$Q_{01}^{10SC} \hbar\omega_{01}^{AB} = mB^2 E_z [\pi\xi \cdot \operatorname{csch}(\pi\xi)]^2 E_0 \approx \Delta E_{VV}^{CL} .$$

To obtain the factor of frequency shift for VV and VV'-energy transfer one has to consider Eq. (13) but here the minimum of potential surface is determined from the equation

$$x_0 + \sqrt{m} \exp(-z + \sqrt{m}x_0) \left[ 1 + B \cos\left(\frac{\omega_2}{\omega_1}\tau + \delta\right) \right] = 0 .$$

Green's function of Eq. (13) is similar the one calculated according to Eqs. (19–21), since the amplitude of CD oscillations in small  $B \ll 1$ . The integration of Eq. (13) for vibrational-vibrational energy transfer leads to the factor (16).

The integration of Eq. (34) over the Maxwell distribution gives the expression

$$\langle Q_{nn'}^{mm'SC} \rangle = Z_{nn'}^{AB} Z_{mm'}^{CD} \frac{8\mu kT}{\hbar^2 \alpha^2} F(\gamma) , \quad (36a)$$

$$F(\gamma) = \int_0^\infty \gamma^2 \operatorname{csc} h^2 \left( \frac{\gamma}{\sqrt{y}} \right) \exp(-y) dy , \quad (36b)$$

$$\gamma = \frac{\pi |E_n + E_m - E_{n'} - E_{m'}|}{\hbar\alpha} \sqrt{\frac{\mu}{kT}} .$$

The function  $F(\gamma)$  is expressed as (Keck and Carrier, 1965):

$$F(\gamma) \approx \frac{1}{2} \left[ 3 - \exp\left(-\frac{2\gamma}{3}\right) \right] \exp\left(-\frac{2\gamma}{3}\right) \quad (37a)$$

for the quasisonant transfer ( $\gamma \approx 1$ ) and

$$F(\gamma) \approx 8 \sqrt{\frac{\pi}{3}} \gamma^{7/3} \exp(-3\gamma^{2/3}) \quad (37b)$$

for a very large resonance defect ( $\gamma \gg 1$ ).

The factor of the attraction of the molecules can be obtained as in the case of VT-calculation. The interaction time according to Eq. (23) has to be inserted in the integral (36b). For a very large resonance defect  $\gamma \gg 1$  the factor is

$$f_{at} = \exp(2C\gamma^{1/3}), \quad (38a)$$

and for a small resonance defect  $\gamma \approx 0$  the factor is

$$f_{at} = 1 + \sqrt{\pi}C + C^2. \quad (38b)$$

Thus, the FOPA transition probability for the binary collision in which target molecule AB undergoes a VV or VV'-transition  $n \rightarrow n'$  upon the impact of an vibrationally excited molecule CD is as follows:

$$\langle Q_{nn'}^{mm'} \rangle = P_{st}^{AB} P_{st}^{CD} f_{at} f_{sh} Z_{nn'}^{AB} Z_{mm'}^{CD} \frac{8\mu kT}{\hbar^2 \alpha^2} F(\gamma) f_{qu}, \quad (39)$$

where all factors (16), (36a), (36b), (37a), (37b), (38a), (38b) have been taken into account. The value of the quasiclassical factor is equal to

$$f_{qu} = \exp\left(\pm \frac{\hbar \omega_{nn'}^{mm'}}{2kT}\right), \quad (40)$$

where signs + and – are to be used for excess and defect energy VV or VV'-processes, respectively. It is suggested that the contribution of the different orientations of the AB and CD molecules has been included in the multiplying of steric factors in Eq. (39). For the case of a breathing vibration in a nearly spherical molecule, the averaged value of the multiplying for the vibrational-vibrational transition probability is equal to  $\langle \cos^2(\theta_1) \rangle \langle \cos^2(\theta_2) \rangle = 1/9$ , where  $\theta_1$  and  $\theta_2$  are the angles between molecular axes and  $R$  (Billing, 1986). The influence of the anharmonicity will be taken into account in the calculations of the factors  $f_{sh}$ ,  $f_{qu}$ ,  $F(\gamma)$  and vibrational factors (35), which depend on the frequencies of the vibrations.

The rate coefficient of vibrational-vibrational energy transfer can be obtained as in the case of TV, VT-transfer (28), i.e., by multiplying the probability (39) by the averaged thermal velocity and gas-kinetic cross section.

### Results of the calculation and the comparison with experimental data

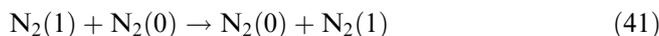
The expression (28) has been normalized on the experimental data of VT-relaxation time in  $N_2$  and  $O_2$  from (Millikan and White, 1963; Zabelinskii *et al.*, 1985) to obtain the magnitudes of steric factors and the extent of

repulsive exchange potentials. The magnitudes of  $\varepsilon$  are taken from Radzig and Smirnov (1980) and the gaskinetic radii of  $N_2$  and  $O_2$  molecules from Polak *et al.* (1973) and Camac (1961). We use the relation of VT-relaxation time with the rate coefficient according to Nikitin (1974a).

The fitted magnitudes of the steric factors are 0.73 for  $N_2$ - $N_2$  collisions and 0.44 for  $O_2$ - $O_2$  collisions. The fitted magnitudes of  $\Theta'_{N_2-N_2} = 8.44 \cdot 10^6$  and  $\Theta'_{O_2-O_2} = 3.16 \cdot 10^6 K$  correspond to  $\alpha_{N_2-N_2} = 39 nm^{-1}$  and  $\alpha_{O_2-O_2} = 45 nm^{-1}$ . The values are in good agreement with recent quantum-mechanical calculations 36 and 42  $nm^{-1}$ , respectively (van der Avoird *et al.*, 1986, Wormer and van der Avoird, 1984).

The interest in the study of relaxation processes in gases has resulted in the accumulation of a large body of experimental data concerning the rate constants of vibrational energy transfer in molecular collisions. In particular this concerns the rate coefficients of VV and VV'-processes in the collisions of the main atmospheric components  $N_2$  and  $O_2$ . In accordance with the formula (39) we have calculated the rate coefficients of VV and VV'-energy transfers for the collisions  $N_2$ - $N_2$ ,  $O_2$ - $O_2$ ,  $N_2$ - $O_2$ . The factor of attraction has been taken into account according to Eq. (38a) for  $\gamma > (\pi/4)^{3/2}$  and Eq. (38b) for  $\gamma < (\pi/4)^{3/2}$ .

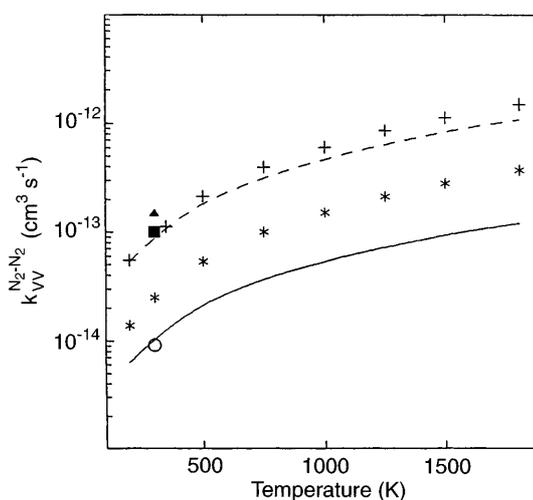
In the calculation of the rate coefficient for the resonant process



we have used  $\alpha_{N_2-N_2} = 39 nm^{-1}$ . The formula obtained for the process (41) is the following:

$$k_{VV}^{N_2-N_2} = 0.91 \cdot 10^{-13} \left(\frac{T}{300}\right)^{3/2} cm^3 s^{-1}. \quad (42)$$

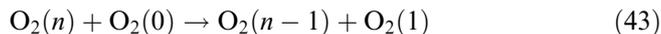
The temperature dependence of Eq. (42) is shown in Fig. 3. Here the experimental estimations of Suchkov



**Fig. 3.** The temperature dependence of the rate coefficient for the process  $N_2(1) + N_2(0) \rightarrow N_2(1) + N_2(0)$ : dashed line; our calculation; solid line; semiclassical trajectory calculation of Billing and Fisher (1979), Billing (1986), experimental data of Suchkov and Shebeko (1981): crosses; Akishev *et al.* (1982): stars; Valyanskii *et al.* (1984a): triangle; Valyanskii *et al.* (1984b): square; Gordeev and Shahatov (1995): circle

and Shebeko (1981), Akishev *et al.* (1982), Valyanskii *et al.* (1984a, b), and Gordeev and Shahatov (1995) for the rate coefficient are presented. There is good agreement of the formula with experimental data of Suchkov and Shebeko (1981), and Valyanskii *et al.* (1984a, b) and some excess over the estimations of Akishev *et al.* (1982) and Gordeev and Shahatov (1995). Also the semiclassical trajectory calculation of Billing and Fisher (1979) and Billing (1986) is presented in Fig. 3 showing good agreement with two smaller experimental estimations.

In the calculation of the rate coefficient for the process

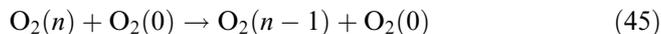


we have used  $\alpha_{\text{O}_2-\text{O}_2} = 45 \text{ nm}^{-1}$ . The formula obtained for the process (43) is the following:

$$k_{VV}^{\text{O}_2-\text{O}_2} = \frac{n}{1 - \frac{n-1}{66}} P_{st}^{\text{O}_2} P_{st}^{\text{O}_2} f_{at} f_{sh} 8.4 \cdot 10^{-17} T^{3/2} \frac{1}{2} \left[ 3 - \exp\left(-\frac{2\gamma}{3}\right) \right] \exp\left(-\frac{2\gamma}{3} - \frac{17.3(n-1)}{T}\right),$$

$$\gamma = \frac{9.76(n-1)}{\sqrt{T}}. \quad (44)$$

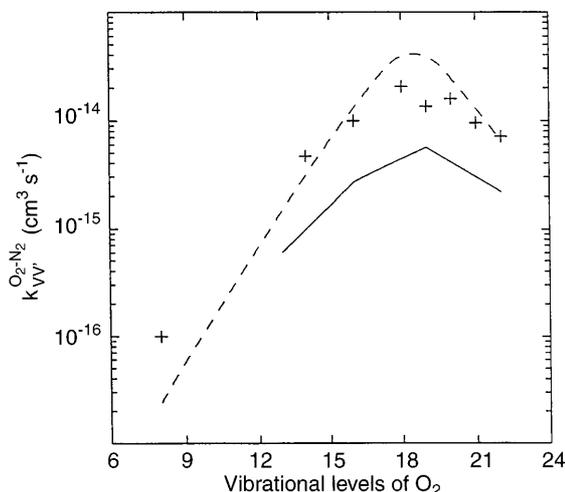
The dependence of the sum of rate coefficients of VV-processes (43) and VT-processes



on vibrational levels  $n$  at temperature 300 K is compared with experimental data of Park and Slanger (1994) in Fig. 4. Also the semiclassical trajectory calculations of Billing and Kolesnick (1992) are presented here.

To calculate the rate coefficients for  $\text{N}_2\text{-O}_2$  collisions we suppose from Billing (1994)

$$\alpha_{\text{N}_2-\text{O}_2} = \frac{1}{2} (\alpha_{\text{N}_2-\text{N}_2} + \alpha_{\text{O}_2-\text{O}_2}).$$



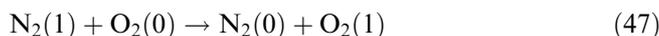
**Fig. 4.** The dependence of the sum of rate coefficients for the VV-processes  $\text{O}_2(n) + \text{O}_2(0) \rightarrow \text{O}_2(n-1) + \text{O}_2(1)$  and for the VT-processes  $\text{O}_2(n) + \text{O}_2(0) \rightarrow \text{O}_2(n-1) + \text{O}_2(0)$  on vibrational level  $n$ : dashed line, our calculation; solid line, semiclassical trajectory calculation of Billing and Kolesnick (1992); crosses, experimental data of Park and Slanger (1994)

The formula means that the radius of the overall exchange potential is the sum of short range potential radii of colliding molecules (Nikitin *et al.*, 1989). So the calculated rate coefficient is

$$k_{VV'}^{\text{N}_2-\text{O}_2} = P_{st}^{\text{N}_2} P_{st}^{\text{O}_2} f_{at} f_{sh} 5.74 \cdot 10^{-17} T^{3/2} \frac{1}{2} \left[ 3 - \exp\left(-\frac{2\gamma}{3}\right) \right] \exp\left(-\frac{2\gamma}{3} + \frac{557}{T}\right),$$

$$\gamma = \frac{326}{\sqrt{T}}, \quad (46)$$

for the VV'-process

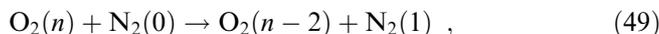


and

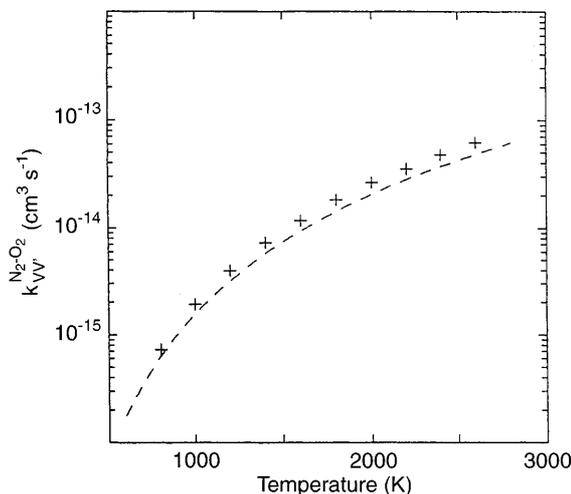
$$k_{VV'}^{\text{O}_2-\text{N}_2} = \frac{n(n-1)}{524} P_{st}^{\text{N}_2} P_{st}^{\text{O}_2} f_{at} f_{sh} 5.74 \cdot 10^{-17} T^{3/2} \frac{1}{2} \left[ 3 - \exp\left(-\frac{2\gamma}{3}\right) \right] \exp\left(-\frac{2\gamma}{3} - \frac{34.6(n-18.5)}{T}\right),$$

$$\gamma = \frac{20.2 \cdot |n-18.5|}{\sqrt{T}}, \quad (48)$$

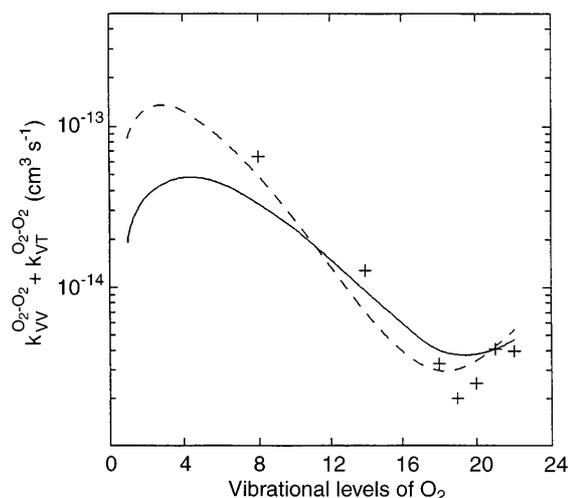
for the other VV'-process



where in the calculation of vibrational factor we have used a formula for the matrix element of multiquantum transfer obtained by Herman and Shuler (1953) for Morse potential approximation. The results of the calculation according to Eqs. (46) and (48) are compared with the experimental data of Gilmore *et al.* (1969) and Park and Slanger (1994) in Figs. 5 and 6. There is seen good agreement of the calculations and experimental data for both kinds of VV'-energy transfer in the collision of molecular nitrogen and oxygen.



**Fig. 5.** The temperature dependence of the rate coefficient for the VV'-process  $\text{N}_2(1) + \text{O}_2(0) \rightarrow \text{N}_2(0) + \text{O}_2(1)$ : dashed line, our calculation; crosses, experimental data of Gilmore *et al.* (1969)



**Fig. 6.** The dependence of rate coefficients for the VV'-processes  $O_2(n) + N_2(0) \rightarrow O_2(n-2) + N_2(1)$  on vibrational level  $n$ : *dashed line*, our calculation; *solid line*, semiclassical trajectory calculation of Billing (1994); *crosses*, experimental data of Park and Slanger (1994)

The semiclassical trajectory calculation of Billing (1994) for the process (49) is also presented in Fig. 6. As in the case of  $N_2-N_2$  collision there is some overestimation by our calculations of the trajectory results. The large difference of our and trajectory calculations can be explained not only by the different approximate methods. The theoretical calculations for VV-exchange in molecular nitrogen using the integral quasiclassical representation method (Zhuk and Klopovsky, 1988) have shown the sensitivity of the results to chosen potential surface. As can be seen from their calculation, the rate constants obtained with different potential surfaces differ by factors of 5–7 but the temperature dependence is similar.

## Conclusions

The FOPA was one of the first methods to have been applied in the calculation of vibrational energy transfer in the collisions involving vibrationally excited molecules. The simplicity of analytical expressions for the rate coefficients of vibrational-translational and vibrational-vibrational processes has allowed us to use effectively the results of the FOPA calculation in an interpretation of experimental data of the vibrational energy relaxation. But sometimes the disagreement of theoretical estimations based on the approximation with the results of experimental measurement has led to the suggestion that the application of the simple method is not correct in the calculation of the rates of vibrational energy transfer processes.

Nikitin (1974a, b), Nikitin and Osipov (1977), Nikitin *et al.* (1989) have pointed out some factors of atom-molecular collision which are to be taken into account in the calculations according to the FOPA. We have used the FOPA to obtain the analytical expressions of the rate coefficients of TV, VT, VV and VV'-energy transfer in molecular collisions of the main atmospheric compo-

nents. The factors of molecular attraction, oscillator frequency change, anharmonicity, 3-dimensionality and quasiclassical motion have been considered in the approximation. We have normalized the presented analytical expressions on the experimental data of VT-relaxation times in  $N_2$  and  $O_2$  to obtain the steric factors and the extents of repulsive exchange potentials in the collisions  $N_2-N_2$  and  $O_2-O_2$ . The obtained values of exchange potential radii are in good agreement with recent quantum-mechanical calculations.

The approach was applied to calculate the rate coefficients of vibrational-vibrational energy transfer in the collisions  $N_2-N_2$ ,  $O_2-O_2$  and  $N_2-O_2$ . It is shown that there is good agreement of our calculations with experimental data for all considered cases of the energy transfer. The disagreement with the results of semiclassical trajectory calculation can be explained both by the difference of applied approximate methods and by the sensitivity of semiclassical trajectory calculation to the chosen potential surface.

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