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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_2 and O_2 to obtain the steric factors and the extent of repulsive exchange potentials in collisions N_2-N_2 and O_2-O_2. 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 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).

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

$$O + N_2 \rightarrow NO + N \tag{1}$$

$$N + O_2 \rightarrow NO + O \tag{2}$$

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^+ 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^+ losses and the decrease of electron concentration. The collisions of excited N_2 with thermal ionospheric electrons promote the heating of the electron gas and, under conditions of enhanced F region electron densities, N_2 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

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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_2-N_2, O_2-O_2, N_2-O_2 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 ω, 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:

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

(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 $m_A m_B/(m_A + m_B)$, μ 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 α are constants determining the amplitude and the range of intermolec-
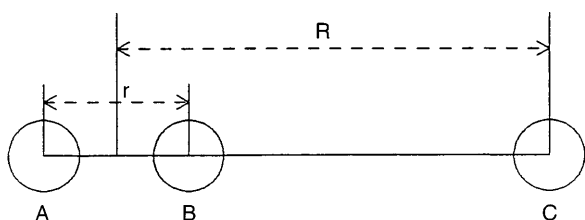

A   B   C

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

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

(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:

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

(5)

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

(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

$$\exp(-z) = E_z \, \text{sech}^2\left(\sqrt{\frac{E_z}{2}}\tau \right)$$

(7)

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

(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

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

(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,

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

(10)

where Ψ_n, Ψ_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 $0 \leftrightarrow 1$:

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

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

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

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:

$$\Re = \exp(1.685m) \quad . \tag{12}$$

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 $(1 - m + \ldots)$.

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)):

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

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

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

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

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

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

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

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):

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

where the solution of homogeneous Eq. (12) is

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

and

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

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

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

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

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

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

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

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

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

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:

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

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 τ'', τ' with and without the attraction, respectively, following Nikitin (1974a):

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

where E is the relative energy of the molecule and the particle at infinite separation before collision and ε 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):

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

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:

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

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 θ 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:

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

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

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

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:

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

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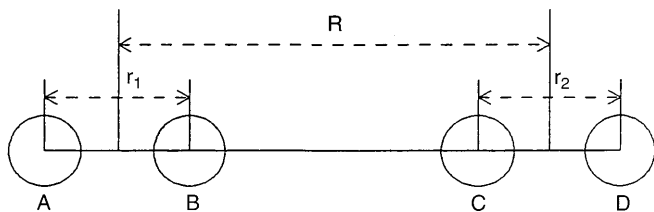
Fig. 2. The collinear collision of the molecules AB and CD

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

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,

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

μ 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

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

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:

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

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

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

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

$$\frac{\Delta E_{VV}^{CL}}{E_0} = \lim_{\tau\to\infty} \frac{m}{2}\frac{B^2}{4}$$

$$\left\{\left|\int_{-\infty}^{\tau} \exp[-z(s)]\sin(\tau - s)\cos\left(\frac{\omega_2}{\omega_1}s + \delta\right)ds\right|^2\right.$$

$$\left. + \left|\int_{-\infty}^{\tau} \exp[-z(s)]\cos(\tau - s)\cos\left(\frac{\omega_2}{\omega_1}s + \delta\right)ds\right|^2\right\}$$

$$\approx mB^2 E_z[\pi\xi \cdot \operatorname{csch}(\pi\xi)]^2 \quad , \tag{32}$$

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:

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

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

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

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

Here the vibrational factors are

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 θ_1 and θ_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 ε 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 $\gamma < (\pi/4)^{3/2}$.
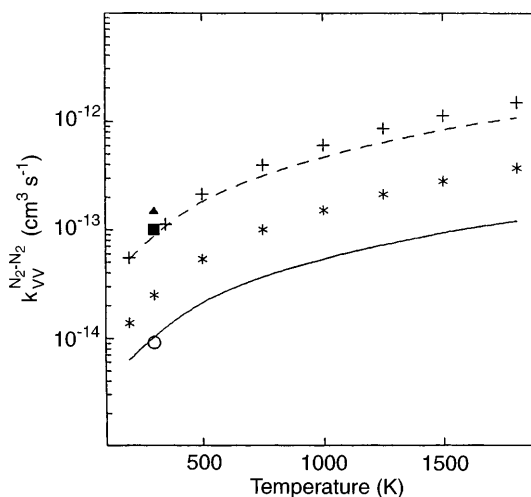
In the calculation of the rate coefficient for the resonant process

$$N_2(1) + N_2(0) \to N_2(0) + N_2(1) \qquad (41)$$
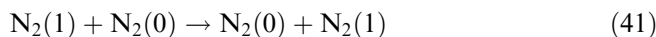
we have used $\alpha_{N_2-N_2} = 39\,nm^{-1}$. The formula obtained for the process (41) is the following:

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

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 $N_2(1) + N_2(0) \to N_2(1) + N_2(0)$: *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.

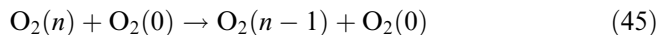In the calculation of the rate coefficient for the process

$$O_2(n) + O_2(0) \rightarrow O_2(n-1) + O_2(1) \quad (43)$$
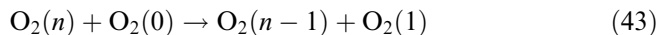
we have used $\alpha_{O_2-O_2} = 45 \ nm^{-1}$. The formula obtained for the process (43) is the following:

$$k_{VV}^{O_2-O_2} = \frac{n}{1 - \frac{n-1}{66}} P_{st}^{O_2} P_{st}^{O_2} f_{at} f_{sh} 8.4 \cdot 10^{-17} T^{3/2}$$
$$\frac{1}{2} \left[3 - \exp\left(-\frac{2\gamma}{3}\right) \right] \exp\left(-\frac{2\gamma}{3} - \frac{17.3(n-1)}{T}\right) ,$$
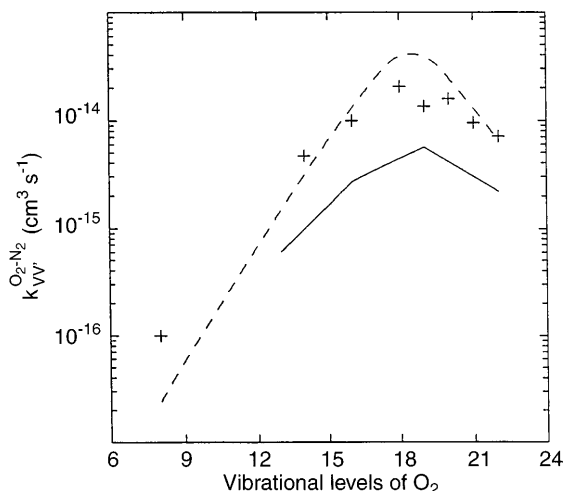$$\gamma = \frac{9.76(n-1)}{\sqrt{T}} \quad . \quad (44)$$

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

$$O_2(n) + O_2(0) \rightarrow O_2(n-1) + O_2(0) \quad (45)$$

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 N_2-O_2 collisions we suppose from Billing (1994)

$$\alpha_{N_2-O_2} = \frac{1}{2}(\alpha_{N_2-N_2} + \alpha_{O_2-O_2}) \quad .$$

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

$$k_{VV'}^{N_2-O_2} = P_{st}^{N_2} P_{st}^{O_2} f_{at} f_{sh} 5.74 \cdot 10^{-17} T^{3/2}$$
$$\frac{1}{2} \left[3 - \exp\left(-\frac{2\gamma}{3}\right) \right] \exp\left(-\frac{2\gamma}{3} + \frac{557}{T}\right) ,$$
$$\gamma = \frac{326}{\sqrt{T}} \quad , \quad (46)$$

for the VV′-process

$$N_2(1) + O_2(0) \rightarrow N_2(0) + O_2(1) \quad (47)$$
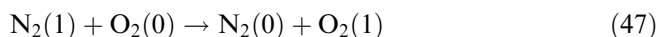
and

$$k_{VV'}^{O_2-N_2} = \frac{n(n-1)}{524} P_{st}^{N_2} P_{st}^{O_2} f_{at} f_{sh} 5.74 \cdot 10^{-17} T^{3/2}$$
$$\frac{1}{2} \left[3 - \exp\left(-\frac{2\gamma}{3}\right) \right]$$
$$\exp\left(-\frac{2\gamma}{3} - \frac{34.6(n-18.5)}{T}\right) ,$$
$$\gamma = \frac{20.2 \cdot |n-18.5|}{\sqrt{T}} \quad , \quad (48)$$

for the other VV′-process

$$O_2(n) + N_2(0) \rightarrow O_2(n-2) + N_2(1) \quad , \quad (49)$$
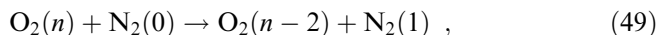
where in the calculation of vibrational factor we have used a formula for the matrix element of multiquantum transfer obtained by Herman and Shuler (1953) for Morse potential approximation. The results of the calculation according to Eqs. (46) and (48) are compared with the experimental data of Gilmore *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.

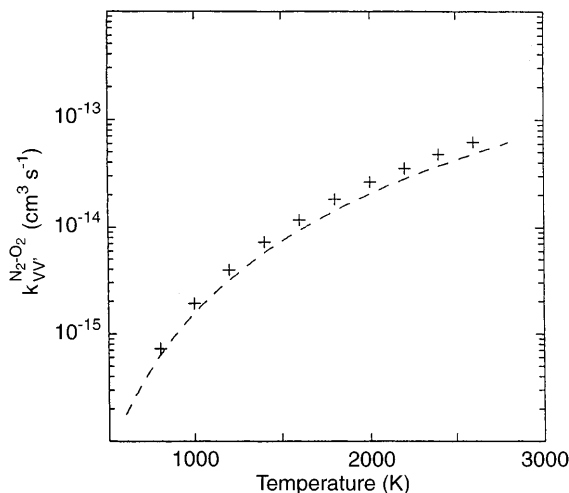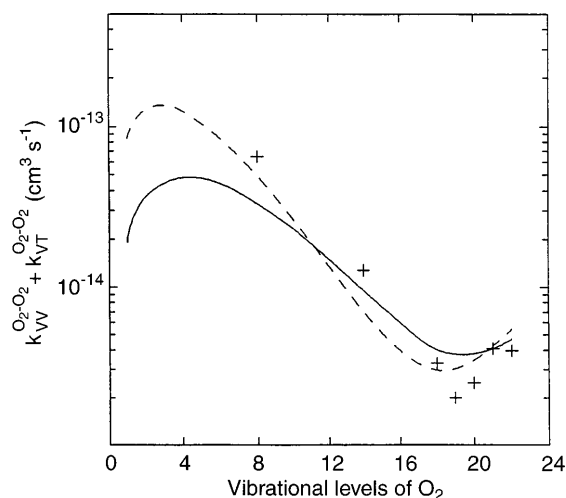**Fig. 4.** The dependence of the sum of rate coefficients for the VV-processes $O_2(n) + O_2(0) \rightarrow O_2(n-1) + O_2(1)$ and for the VT-processes $O_2(n) + O_2(0) \rightarrow O_2(n-1) + O_2(0)$ on vibrational level n: *dashed line*, our calculation: *solid line*, semiclassical trajectory calculation of Billing and Kolesnick (1992): *crosses*, experimental data of Park and Slanger (1994)

Fig. 5. The temperature dependence of the rate coefficient for the VV′-process $N_2(1) + O_2(0) \rightarrow N_2(0) + O_2(1)$: *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 atommolecular 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.

References

Akishev, Y. S., A. V. Demyanov, I. V. Kochetov, A. P. Napartovich, S. V. Pashkin, V. V. Ponomarenko, V. G. Pevgov, and V. B. Podobedov, Determination of constants of vibrational exchange in N_2 from the heating of the gas, *Heatphys. High Temp.*, **20**, 818–827, in Russian, 1982.

Aladjev, G. A., and A. S. Kirillov, Vibrational kinetics of molecular nitrogen and its role in the composition of the polar thermosphere, *Adv. Space Res.*, **16**, (1)109–(1)112, 1995.

Aladjev, G. A., and A. S. Kirillov, Vibrational kinetics of N_2 and O_2 in the high-latitude upper atmosphere, *Cosmic Res.*, **35**, 227–234, in Russian, 1997.

Baz, A. I., Ya. B. Zeldovich, and A. M. Perelomov, *The scattering, reactions and disintegrations in non-relativistic quantum mechanics.* Moscow, Nauka, in Russian, 1971.

Billing, G. D., Vibration-vibration and vibration-translation energy transfer, including multiquantum transitions in atom-diatom and diatom-diatom collisions, in *Nonequilibrium vibrational kinetics*, Ed. M. Capitelli, Berlin, Springer, 104–136, 1986.

Billing, G. D., VV and VT rates in N_2-O_2 collisions, *Chem. Phys.*, **179**, 463–467, 1994

Billing, G. D., and E. R. Fisher, VV and VT rate coefficients in N_2 by a quantum-classical model, *Chem. Phys.*, **43**, 395–401, 1979.

Billing, G. D., and R. E. Kolesnick, Vibrational relaxation of oxygen. State to state rate constants, *Chem. Phys. Lett.*, **200**, 382–386, 1992.

Calvert, J. M., and R. C. Amme, Three-dimensional Morsepotential calculation of vibrational energy transfer: application to diatomic molecules. *J. Chem. Phys.*, **45**, 4710–4715, 1966.

Camak, M., O_2 vibration relaxation in oxygen-argon mixtures, *J. Chem. Phys.*, **34**, 448–459, 1961.

Eyring, H., S. H. Lin, and S. M. Lin, *Basic chemical kinetics.* Wiley, New York, 1980.

Gilmore, F. R., E. Bouer, and McGowan, A review of atomic and molecular excitation mechanisms in nonequilibrium gases, *J. Quant. Spectr. Radiat. Trans.*, **9**, 157–183, 1969.

Gordeev, O. A., and V. A. Shahatov, Determination of rate constant of VV-exchange in glow discharge of nitrogen using the method of CARS spectroscopy, *J. Tech. Phys.*, **65,** 40–51, in Russian, 1995.

Hansen, C. F., and W. E. Pearson, Three-dimensional model of collision-induced vibrational transitions in homonuclear diatomic molecules, *J. Chem. Phys.*, **53,** 3557–3567, 1970.

Herman, R. C., and K. E. Shuler, Intensities of vibration-rotation bands, *J. Chem. Phys.*, **21,** 373–374, 1953.

Kelley, J. D., and M. Wolfsberg, Comparison of approximate translational-vibrational energy-transfer formulas with exact classical calculations, *J. Chem. Phys.*, **44,** 324–338, 1966.

Kirillov, A. S., The rates of plasma-chemical processes involving vibrationally excited molecules, *Cosmic Res.*, **35,** 155–163, in Russian, 1997.

Landau, L. D., and E. M. Lifshitz, *Quantum mechanics: non-relativistic theory*. Pergamon, Oxford, 1965.

Mies, F. H., Effects of anharmonicity on vibrational energy transfer, *J. Chem. Phys.*, **40,** 523–531, 1964.

Millikan, R. C., and D. R. White, Systematics of vibrational relaxation, *J. Chem. Phys.*, **39,** 3209–3213, 1963.

Mishin, E. V., Y. Y. Ruzhin, and V. A. Telegin, *Interaction of electron fluxes with the ionospheric plasma*. Leningrad, Gidrometeoizdat, in Russian, 1989.

Nikitin, E. E., *Theory of elementary atomic and molecular processes in gases*. Oxford, Clarendon, 1974a.

Nikitin, E. E., *Theory of elementary atomic and molecular reactions. Part 2*. Novosibirsk, Novosibirsk University, in Russian, 1974b.

Nikitin, E. E., and A. I. Osipov, Vibrational relaxation in gases, in *INT. Kinetics and catalice*, **4,** Moscow, VINITI, in Russian, 1977.

Nikitin, E. E., A. I. Osipov, and S. J. Umanskii, Vibrational-translational energy exchange in collisions of homonuclear diatomic molecules, *Chem. Plasma*, **15,** 3–44, in Russian, 1989.

Park, H., and T. G. Slanger, $O_2(X, v = 8–22)$ 300 K quenching rate coefficients for O_2 and N_2, and $O_2(X)$ vibrational distribution from 248 nm O_3 photodissosiation, *J. Chem. Phys.*, **100,** 287–300, 1994.

Polak, L. S., P. A. Sergeev, and D. I. Slovetskii, A calculation of vibrational distribution in the state $X^1 \sum_{g^+}$ of molecule N_2 in the discharge, *Chem. High Ener.*, **7,** 387–393, in Russian, 1973.

Radzig, A. A., and B. V. Smirnov, *The reference book in atomic and molecular physics*, Moscow, Atomizdat, in Russian, 1980.

Rapp, D., and T. Kassal, The theory of vibrational energy transfer between simple molecules in nonreactive collisions, *Chem. Rev.*, **69,** 61–102, 1969.

Richards, P. G., and D. G. Torr, A factor of 2 reduction in theoretical F2 peak electron density due to enhanced vibrational excitation of N_2 in summer at solar maximum, *J. Geophys. Res.*, **91,** 11331–11336, 1986.

Richards, P. G., D. G. Torr, and W. A. Abdou, Effects of vibrational enhancement of N_2 on the cooling rate of ionospheric thermal electrons, *J. Geophys. Res.*, **91,** 304–310, 1986.

Rusanov, V. D., and A. A. Fridman, *Physics of chemically active plasma*, Moscow, Nauka, in Russian, 1984.

Schwartz, R. N., and K. F. Herzfeld, Vibrational relaxation times in gases (three-dimensional treatment), *J. Chem. Phys.*, **22,** 767–773, 1954.

Secrest, D., and B. R. Johnson, Exact quantum-mechanical calculation of a collinear collision of a particle with a harmonic oscillator, *J. Chem. Phys.*, **45,** 4556–4570, 1966.

Smith, I. W. M., Vibrational energy transfer in collisions involving free radicals, in *Nonequilibrium vibrational kinetics*, Ed. M. Capitelli, Springer, Berlin, 113–157, 1986.

Suchkov, A. F., and Y. N. Shebeko, Kinetics of vibrational exchange in the nonequilibrium nitrogen. Comparison of the theory with experiment, *Chem. High Ener.*, **15,** 279–283, in Russian, 1981.

Valyanskii, S. I., K. A. Vereshchagin, W. Wernke, A. Y. Volkov, P. P. Pashinin, V. V. Smirnov, V. I. Fabelinskii, and P. L. Tshapovskii, The investigation of the kinetics of vibrational and rotational distribution function of nitrogen excited by impulse discharge, *Quant. Elect.*, **11,** 1833–1836, in Russian, 1984.

Valyanskii, S. I., K. A. Vereshchagin, A. Y. Volkov, P. P. Pashinin, V. V. Smirnov, V. I. Fabelinskii, and L. Holtz, The measurement of rate coefficient of VV-exchange in nitrogen under biharmonic excitation, *Quant. Elect.*, **11,** 1836–1839, in Russian, 1984.

van der Avoird, A., P. E. S. Wormer, and A. P. J. Jansen, An improved intermolecular potential for nitrogen, *J. Chem. Phys.*, **84,** 1629–1635, 1986.

Vlasov, M. N., and T. M. Izakova, Nonlinear theory of production of main ionospheric maximum, *Chem. Phys.*, **8,** 612–618, in Russian, 1989.

Wormer, P. E. S., and A. van der Avoird, Heisenberg exchange and electrostatic interactions between O_2 molecules: an ab initio study, *J. Chem. Phys.*, **81,** 1929–1939, 1984.

Zabelinskii, I. E., O. E. Krivonosova, and O. V. Shatalov, Vibrational excitation of molecular oxygen in collisions O_2-O_2, *Chem. Phys.*, **4,** 42–45, in Russian, 1985.

Zhuk, Y. N., and K. S. Klopovsky, Quasiclassical calculations of the rate constants for V-V exchange in nitrogen, *Chem. Phys. Lett.*, **153,** 181–184, 1988.