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Quasi-Classical Model for Vibrational–Translational and Vibrational–Vibrational Rate Constants

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We present the derivation and the numerical validation of new vibrational rate constants for vibrational–translational and vibrational–vibrational processes in a pure diatomic gas. The approach is based on the quasi-classical representation of the T matrix and the approximation of the multidimensional trajectories. For moderate temperatures, useful analytical formulas are proposed. In the case of high temperatures, a numerical integration has to be performed to compute numerical values of the rate-constants. The rate-constant model proposed here is compared with the forced-harmonic-oscillator rate model in a large temperature range and also with three-dimensional semiclassical trajectory calculations for low temperatures (200 K ≤ T ≤ 8000 K), for nitrogen. The agreement is satisfactory.

Nomenclature

a_{Kq} = coefficients of the intermolecular potential expansion
b_a, b_q, b_r = coefficients a_{Kq} associated with vibrational–translational processes
c_a, c_q, c_r = coefficients a_{Kq} associated with vibrational–vibrational processes
D = Morse potential-well depth
d = Morse potential parameter (softness)
E_{in}, $E_{\mathrm{in}\,1}$, $E_{\mathrm{in}\,2}$, $E_{\mathrm{in}\,1i}$, $E_{\mathrm{in}\,2i}$, $E_{\mathrm{in}\,1f}$, $E_{\mathrm{in}\,2f}$ = internal energies of molecules 1, 2 in initial (i) and final (f) channels
E_m = mean relative translational energy
E_{n_k}, $E_{n_k i}$, $E_{n_k f}$ = vibrational energies
$E_{\mathrm{tr}\,f}$, $E_{\mathrm{tr}\,i}$ = translational energies
f = scattering amplitude
h = Planck's constant, 6.626×10^{-34} J s
$\hbar$ = $h/2\pi$
I = action variable
J_n, J_s = Bessel functions
$K_{i\to f}$ = rate constant of inelastic collisions
K_{n_i,n_f} = vibrational–translational rate constant
$K^{n_{1i},n_{1f}}_{n_{2i},n_{2f}}$ = vibrational–vibrational rate constant
k = Boltzmann's constant, 1.3805×10^{-23} J K^{-1}
m_1, m_2 = molecular masses
N = number density of the gas
$n_i, n_f, n_k, n_{kf}, n_{ki}$ = vibrational quantum levels
P, $P^{\mathrm{sl}}_{\mathrm{VT}}$, $P^{\mathrm{sl}}_{\mathrm{VV}}$ = scattering probabilities
P_{l_1}, P_{l_2} = Legendre polynomials
$\bar{P}$ = average scattering probability
$\bar{P}_{\mathrm{VT}}$, $\bar{P}^{f}_{\mathrm{VT}}$, $\bar{P}^{\mathrm{sl}}_{\mathrm{VT}}$, $\bar{P}^{\mathrm{int}}_{\mathrm{VT}}$ = average scattering probabilities for vibrational–translational processes
$\bar{P}^{\mathrm{sl}}_{\mathrm{VV}}$, $\bar{P}^{f}_{\mathrm{VV}}$ = average scattering probabilities for vibrational–vibrational processes
p_m = mean relative momentum
p_{1i}, p_{2i}, p_{1f}, p_{2f} = momentum
$Q_{1,2}$ = molecular internal coordinates
R = intermolecular distance
R_0 = Morse potential-well minimum position
$r_{e\,1,2}$ = equilibrium interatomic distances
$r_{1,2}$ = interatomic distances
S = classical action increment
T, T_{sl}, T_Δ = temperatures
T_M = T matrix
T_0 = elastic T amplitude
V = intermolecular potential
V_a = attractive part of the potential V
V_r = repulsive part of the potential V
V_0 = isentropic intermolecular potential
V_{0a} = attractive part of the isentropic potential V_0
V_{0r} = repulsive part of the isentropic potential V_0
v_m = mean relative translational velocity
v_1, v_2, v'_1, v'_2 = molecular velocities
x_e = oscillator anharmonicity parameter
Γ = scattering profile
$\Gamma()$ = gamma function
$\gamma_{1,2}$, δ = orientational angles of atoms in a molecule
ε = Lennard–Jones potential parameter
λ_m, λ^-_m, λ^+_m = adiabatic parameters
μ, $\mu_{0\,1,2}$ = reduced masses
σ = cross section
σ_E = elastic cross section
σ_{LJ} = Lennard–Jones potential parameter
τ^{-1} = elastic collision frequency
Φ = angle variables
Ω = solid angle
ω_e, $\omega_{e1,2}$ = oscillator frequencies (spectroscopic constants)
ω_m, ω^-_m, ω^+_m = mean frequencies
ω_{n_k} = oscillation frequency

I. Introduction

THE principal difficulty arising when a high-temperature flow is computed is the simulation of relaxation processes between

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different energy modes. The high-temperature conditions are typical for hypersonic flows around space vehicles at altitudes of ~70 km and higher. A strong nonequilibrium among translational (T), rotational (R), and vibrational (V) modes takes place in the relaxation zone between the bow shock and the body surface. An accurate modeling of energy exchange processes is compulsory for obtaining credible information on space vehicle aerodynamics.

In this paper, we focus on vibrational–translational (VT) and vibrational–vibrational (VV) energy transfers during collisions of diatomic molecules. When a pure diatomic gas that consists of molecules A_2 with discrete vibrational energy is considered, it is necessary to know the rate constants associated with the following VT and VV processes:

$$A_2(n_i) + A_2 \leftrightarrow A_2(n_f) + A_2$$

$$A_2(n_{1i}) + A_2(n_{2i}) \leftrightarrow A_2(n_{1f}) + A_2(n_{2f})$$

where n_i, n_{1i}, n_{2i} and n_f, n_{1f}, n_{2f} are the initial and the final quantum numbers, respectively, that characterize each energy level. Different attempts have been made lately to derive VT and VV rate constants. We mention here exact full quantum calculations,[1] Billing's closed-coupled method,[2] Slavski–Shwarz–Herzfeld (SSH) theory, and also modified forced-harmonic-oscillator (FHO) theory.[3,4]

Here we present new VT and VV rate constants for diatomic molecules. The formulas were obtained with the quasi-classical multidimensional scattering theory for polyatomic gases developed by Bogdanov et al.[5] and Gorbachev et al.[6] In this approach (Sec. II), the calculations are based on the quasi-classical representation of the T operator T_M, on the angle-action variables, and on approximations of multidimensional trajectories. Potentials that include both attractive and repulsive parts are considered. Anharmonicity effects are taken into account. The main modification we introduce here is a mean approximation for the solution of the equations of motion. It may be called a mean frequency or a mean energy approximation.

Our goal is also to analyze numerically different formulas for VT (Sec. III) and VV (Sec. V) rate constants for diatomic nitrogen. We show some of the difficulties in approximating the exact integral formulas and in determining the validity of different approximations. We then give a numerical comparison of the obtained rate constants with the rate constants derived by Adamovich et al.[4] within the framework of the modified FHO theory, and also with the Billing–Fisher three-dimensional trajectory calculations[7–9] (see Sec. IV for VT rate constants and Sec. VI for VV rate constants). In the temperature range within which explicit formulas are not valid, we propose interpolated formulas.

II. Rate Constants for VT Transitions

In this section, we present the VT rate constants derived by Bogdanov et al. from the quasi-classical theory,[5] including the modification corresponding to the mean frequency or the mean energy approximation.

We consider diatomic molecules represented by anharmonic oscillators. In first order, the frequency of oscillations for the quantum level n_k is given by

$$\omega_{n_k} = \omega_e[1 - 2x_e(n_k + 0.5)] \tag{1}$$

and the vibrational energy is written as

$$E_{n_k} = \hbar\omega_e(n_k + 0.5)[1 - x_e(n_k + 0.5)] \tag{2}$$

The model for intermolecular potential-energy surface V of two interacting diatomics, convenient for quasi-classical calculation, was constructed in Ref. 5 (see Sec. VI). In brief, V is, in general, a function of the intermolecular distance R (the norm of the radius vector $\boldsymbol{R}$, connecting the centers of mass of colliding partners), of orientational angles $\gamma_{1,2}$ between vectors $\boldsymbol{r}_{1,2}$ and vector $\boldsymbol{R}$ ($\boldsymbol{r}_{1,2}$ are vectors connecting the atoms in molecules 1 and 2; $r_{1,2}$ are interatomic distances), of δ, the angle that describes the rotation of the plane, spanned by vectors $\boldsymbol{r}_{1,2}$ around the $\boldsymbol{R}$ axis, and of internal coordinates $Q_{1,2}$, which are the deviations of the intermolecular distances $r_{1,2}$ from their equilibrium values $r_{e\,1,2}$:

$$Q_{1,2} = \sqrt{\frac{\mu_{0\,1,2}\omega_{e\,1,2}}{2\hbar}}(r_{1,2} - r_{e\,1,2}) \tag{3}$$

where $\mu_{0\,1,2}$ is the reduced mass of atoms in molecules 1 and 2. The dependence of V on all of these variables is usually written as an expansion in Legendre polynomials $P_l(\cos\gamma)$ and in powers of Q. The coefficients of this expansion are in general functions of R, but usually they are set to be constant. In this case we fail to describe the potential surface within the whole range of intermolecular distance. We suggest that one of the most simple ways to go beyond the constant-coefficient model consists of splitting the intermolecular potential into a repulsive potential V_r and an attractive potential V_a and using two independent sets of expansion coefficients, one for the repulsive potential and another for the attractive potential. Thus if the isotropic potential $V_0(R)$ is split into the parts V_{0r} and V_{0a} mentioned earlier, the discussed expansion of the potential is written as

$$V(R, r_1, \gamma_1, r_2, \gamma_2, \delta) = \sum_{q=r,a} V_{0q}(R)$$
$$\times \sum_{\boldsymbol{K}} a_{\boldsymbol{K}q} P_{l_1}(\cos\gamma_1) P_{l_2}(\cos\gamma_2) \exp(is\delta) Q_1^{k_1} Q_2^{k_2} \tag{4}$$

where $\boldsymbol{K} = (l_1, l_2, s, k_1, k_2)$ is a multiindex and a_{0q} is a constant equal to 1. For the isotropic part V_0, we use the model

$$V_0 = V_{0r} + V_{0a} \tag{5}$$

where

$$V_{0r} = D\exp[-2(R - R_0)/d]$$
$$V_{0a} = -2D\exp[-(R - R_0)/d]$$

that is, the Morse potential. For nitrogen, $D = 1.56 \times 10^{-21}$ J, $d = 1.09 \times 10^{-11}$ m, and $R_0 = 4.67 \times 10^{-10}$ m.

In practice, only the first terms in Eq. (4) are retained, giving nonvanishing probabilities for the processes under consideration. Terms contaning only $P_{l_{1,2}}(\cos\gamma_{1,2})$ are responsible for the so-called RT transitions in molecules 1 and 2; terms containing only $P_{l_1}(\cos\gamma_1)P_{l_2}(\cos\gamma_2)$ are responsible for RRT transitions. Analogously, terms containing $Q_{1,2}$ are responsible for VT transitions in molecules 1 and 2, terms containing Q_1Q_2 are responsible for VVT transitions, and terms containing $P_{l_{1,2}}(\cos\gamma_{1,2})Q_{2,1}$ are responsible for VRT transitions. Usually rotational–vibrational coupling is negligibly small for diatomics, but this is not the case for hydrogen-containing molecules or for highly vibrationally excited ones. These situations were studied in Refs. 10–12.

In this paper, because we consider only VT and VVT transitions, we use the following notation for the coefficients of potential-surface anisotropy: $a_{0,0,0,1,0,q} = b_q$, $a_{0,0,0,1,1,q} = c_q$.

Equilibrium rate constants of inelastic transitions may be written in the form [see Eq. (7.31) in Ref. 5]

$$K_{i\to f} = \frac{(m_1m_2)^{\frac{9}{2}}}{(2\pi)^2(2\pi kT)^3}\int \mathrm{d}v_1\,\mathrm{d}v_2\,\mathrm{d}v_1'\,\mathrm{d}v_2'\delta_{\boldsymbol{p}}\delta_E|T_M|^2$$
$$\times \exp\left(-\frac{m_1v_1^2 + m_2v_2^2}{kT}\right) \tag{6}$$

Here $\delta_{\boldsymbol{p}} = \delta(p_{1i} + p_{2i} - p_{1f} - p_{2f})$ is the δ function of momentum $p_1 + p_2$ conservation and $\delta_E = \delta(E_{\mathrm{tr}\,i} + E_{\mathrm{in}\,1i} + E_{\mathrm{in}\,2i} - E_{\mathrm{tr}\,f} - E_{\mathrm{in}\,1f} + E_{\mathrm{in}\,2f})$ is the δ function of total energy conservation, i.e., the translational energy E_{tr} and the internal energy $E_{\mathrm{in}} = E_{\mathrm{in}\,1} + E_{\mathrm{in}\,2}$, where the subscripts i and f denote initial (precollisional) and final (postcollisional) states. The T matrix[13] is related to the scattering amplitude f by

$$f = -(\mu/2\pi)T_M$$

By using the expression from Ref. 14 for the differential cross section,

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f|^2 \tag{7}$$

and factorizing the T matrix as

$$T_M = T_0\Gamma$$

we can rewrite the cross section in Eq. (7) as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left(\frac{\mu}{2\pi}\right)^2 |T_0|^2 \, |\Gamma|^2 = \frac{\mathrm{d}\sigma_E}{\mathrm{d}\Omega} P \tag{8}$$

Here P is defined as $P = |\Gamma|^2$. The elastic cross section $\mathrm{d}\sigma_E/\mathrm{d}\Omega$ varies slowly with the scattering-angle variation, which allows us to write Eq. (8) as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma_E}{4\pi} P \tag{9}$$

Finally, after integration over the solid angle, we obtain

$$\sigma = \frac{\sigma_E}{2} \int_0^{\pi} P \sin\theta \, \mathrm{d}\theta = \frac{\sigma_E}{2} \bar{P} \tag{10}$$

Fulfilling integrations in Eq. (6) by using the δ functions and taking into account the last expression for $\bar{P}$, we obtain the following equation for inelastic rate constants (see also Sec. 7 in Ref. 5):

$$K_{i \to f} = \frac{\tau^{-1}}{N} \int_{\mathcal{E}^* H(\mathcal{E}^*)}^{\infty} (\mathcal{E}_i \mathcal{E}_f)^{\frac{1}{2}} \bar{P} e^{-\mathcal{E}_i} \, \mathrm{d}\mathcal{E}_i \tag{11}$$

where

$$\mathcal{E}^* = \Delta E / kT, \qquad \Delta E = E_{\mathrm{in}\,f} - E_{\mathrm{in}\,i}, \qquad \mathcal{E}_i = E_{\mathrm{tr}\,i}/kT$$

and H is the unit step function. For purely vibrational transitions, inelastic-scattering probabilities should be averaged over the rotational degrees of freedom. This procedure is described in detail in Ref. 5 and is not reproduced here. As a result, the expression for VT rate constants has the form given by Eq. (11), with $\bar{P}$ replaced with $\bar{P}_{\mathrm{VT}}$.

To specify the average inelastic-scattering probability $\bar{P}_{\mathrm{VT}}$, we introduce first the adiabatic parameter λ_m, defined as

$$\lambda_m = \omega_m d / v_m \tag{12}$$

where d is a characteristic distance related to a potential. In this formula v_m is the relative translational velocity defined by

$$v_m = \sqrt{2E_m/\mu}$$

where E_m is the mean relative translational energy given by

$$E_m = \frac{E_{\mathrm{tr}\,f} + E_{\mathrm{tr}\,i}}{2}$$

and ω_m is the mean frequency given by

$$\omega_m = \frac{\omega_{n_i} + \omega_{n_f}}{2}$$

The collisions are classified into three groups, depending on the adiabatic parameter: fast Collisions ($\lambda_m < \lambda_1 \leq 1$), slow collisions ($1 \leq \lambda_2 < \lambda_m$), and intermediate collisions (all other cases).

Figure 1 shows the dependence of the velocity on the quantum level n corresponding to the reaction $N_2(n) + N_2 \to N_2(n-l) + N_2$ and for different values of the level transition l. To compute the velocity, we used Eq. (12) with the values $\lambda_1 = 1$ for fast collisions and $\lambda_2 = 3.5$ for slow collisions. These values of the adiabatic parameters were also used by Gimelshein et al.[15] and Mallinger and Gimelshein[16] to compute cross sections. We clearly observe the domain of velocities corresponding to each group of collisions. We point out that the value of λ_2 is not strictly defined as we will see when we define the scattering probabilities. We note that the influence of fast collisions increases for high quantum numbers.

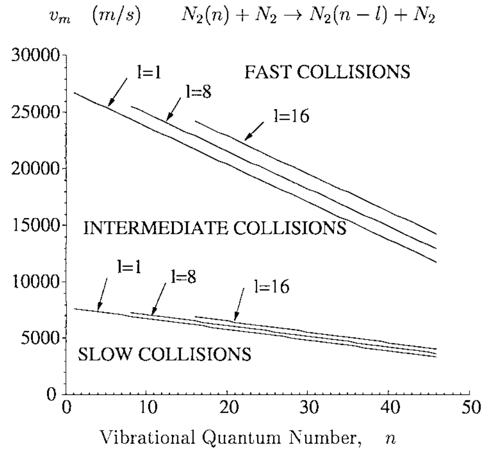

Fig. 1 Velocity v_m computed by the formula $v_m = \omega_m d/\lambda_m$, with $\lambda_m = \lambda_1 = 1$ for fast collisions and $\lambda_m = \lambda_2 = 3.5$ for slow collisions and for different values of the level transition l.

The definition of the average scattering probability depends on the type of collision. For slow collisions, the probability of the transition from energy level n_i to energy level n_f is

$$\bar{P}_{\mathrm{VT}}^{\mathrm{sl}} = \frac{1}{4\pi} \int P_{\mathrm{VT}}^{\mathrm{sl}}(\Omega)\, \mathrm{d}\Omega = \frac{1}{2} \int P_{\mathrm{VT}}^{\mathrm{sl}}(\theta) \sin\theta \, \mathrm{d}\theta \tag{13}$$

under the following definition of the scattering probability: $P_{\mathrm{VT}}^{\mathrm{sl}} = J_{|\Delta n|}^2 (F_{\mathrm{VT}}^{\mathrm{sl}})$, where $J_{|\Delta n|}$ is a Bessel function and $|\Delta n| = |n_f - n_i|$.

The quantity $F_{\mathrm{VT}}^{\mathrm{sl}}$ is part of the classical action increment calculated along the classical trajectory by use of the part of the potential-energy surface of Eq. (4) containing $a_{0,0,0,1,0,q} = b_q$ and the model given by Eq. (5) for the description of the intermolecular distance dependence. Vibrational motion is described in terms of angle-action variables ϕ, $I = \hbar(n + \frac{1}{2})$. By using the relationship $Q = \sqrt{(E_n/\hbar\omega_e)} \cos\phi$, we can rewrite the potential in the form

$$V(R, \phi) = V_0(R) + V_1 \cos\phi \tag{14}$$

and the corresponding action increment will have the following structure:

$$S/\hbar = S_0/\hbar + F_{\mathrm{VT}} \cos\phi \tag{15}$$

Here F_{VT} is an integral of the second term on the right-hand side of Eq. (14) along the classical trajectory. In Ref. 5, the asymptotic procedure for solving the set of motion equations was suggested and the action increment calculated (see Sec. 7 in Ref. 5). In Ref. 10, it was shown that, in the case of slow collisions, the main contribution into F_{VT} is from the a-head trajectories, while in the case of fast collisions the main contribution into F_{VT} is from the straightforward trajectories.

As a result, we obtain the following expression for argument $F_{\mathrm{VT}}^{\mathrm{sl}}$:

$$F_{\mathrm{VT}}^{\mathrm{sl}} = \varepsilon_m^{\frac{1}{2}} \frac{\pi d}{2\hbar} \left[b_r \omega_m \mu d - (2b_a - b_r)(2\mu D)^{\frac{1}{2}} \right] \times \exp\left[-\frac{\omega_m \mu d}{p_m \sin(\theta/2)} \arctan \sqrt{\frac{E_m}{D}} \sin\left(\frac{\theta}{2}\right) \right] \tag{16}$$

Here b_a and b_r are the potential anisotropy parameters, p_m is the momentum of the relative motion $p_m = \mu v_m = \sqrt{(2E_m \mu)}$, and ε_m is defined by $\varepsilon_m = (E_{n_i} + E_{n_f})/2\hbar\omega_e$.

For fast collisions, the probability $\bar{P}_{\mathrm{VT}}^f$ takes the following form (the same intermolecular potential is used):

$$\bar{P}_{\mathrm{VT}}^f = \frac{2\pi d^2}{\sigma_E} \int_{x_0}^{\infty} x \Bigg(1 - \frac{D}{E_m} \exp[-(x - x_{00})] \times \{ \exp[-(x - x_{00})](1 - x) - 2 + x \} \Bigg) J_{|\Delta n|}^2 \left[F_{\mathrm{VT}}^f(x) \right] \mathrm{d}x \tag{17}$$

where x_0 and x_{00} are given by

$$x_0 = x_{00} - \ln\left(1 + \sqrt{1 + E_m/D}\right), \qquad x_{00} = R_0/d \tag{18}$$

and the argument of the Bessel function is given by

$$F^f_{\mathrm{VT}}(x) = (Dd/v_m\hbar)\sqrt{\pi x \varepsilon_m}\exp[-(x - x_{00})] \times \{b_r \exp[-(x - x_{00})] - 2\sqrt{2}b_a\} \tag{19}$$

Furthermore, the elastic cross section,

$$\sigma_E = \pi\sigma^2_{\mathrm{LJ}}\left\{2\left(\frac{5\pi\varepsilon\sigma_{\mathrm{LJ}}}{4\hbar v_m}\right)^{\frac{2}{5}} + 1 + \frac{1}{6}\left[1 + \ln\left(\sqrt{6\pi}\frac{4\varepsilon}{E_m + 4\pi\varepsilon}\right)\right]\right\} \tag{20}$$

has been computed for the Lennard–Jones potential,

$$V(R) = 4\varepsilon\left[(\sigma_{\mathrm{LJ}}/R)^{12} - (\sigma_{\mathrm{LJ}}/R)^6\right] \tag{21}$$

The Lennard–Jones potential is correlated with the Morse potential. Thus the parameters of the Lennard–Jones potential are $\varepsilon = D$ and $\sigma_{\mathrm{LJ}} = R_0/2^{1/6}$.

For intermediate collisions, probabilities are obtained by the interpolation of probabilities for slow and fast collisions in the following way:

$$\bar{P}^{\mathrm{int}}_{\mathrm{VT}} = \exp\left(\frac{\lambda_m - \lambda_2}{\lambda_2 - \lambda_1}\ln\left\{\bar{P}^f_{\mathrm{VT}}[v_m(\lambda_1)]\right\} + \frac{\lambda_1 - \lambda_m}{\lambda_2 - \lambda_1}\ln\left\{\bar{P}^{\mathrm{sl}}_{\mathrm{VT}}[v_m(\lambda_2)]\right\}\right) \tag{22}$$

To ensure the monotonicity of the global probability, we may modify, if necessary, the value of λ_2.

Finally, the elastic collision frequency τ in Eq. (11) is computed with the Lennard–Jones potential[17]:

$$\frac{1}{\tau} = 4N\sigma^2_{\mathrm{LJ}}\left(\pi^{0.9}\Gamma(1, 8)\left(\frac{2kT}{\mu}\right)^{0.3}\left(\frac{5\varepsilon\sigma_{\mathrm{LJ}}}{4\hbar}\right)^{0.4} + \frac{1}{2}\sqrt{\frac{2\pi kT}{\mu}}\left\{1 + \frac{1}{6}\left[1 - \ln\left(\pi + \frac{3}{8}\frac{kT}{\varepsilon}\right)\right]\right\}\right) \tag{23}$$

Before ending this section, we point out that there are at least two possibilities of obtaining information about coefficients $b_{r,a}$ and $c_{r,a}$. The first one consists of the approximation of the potential surface, obtained elsewhere, by the suggested model of Eq. (4) and of the estimation of the coefficients mentioned earlier, which demand a better approximation. The other one consists of the approximation of some scattering characteristics (cross sections, rate constants, etc.) with corresponding values calculated on the basis of our model potential and of the estimation of coefficients that compare this data. In the first case we will meet problems since the potential is a surface in multidimensional space. Although it is known that we should approximate, in the most accurate way, the potential only in the vicinity of the turning point of classical trajectory, it still remains a difficult problem. Therefore we used the second possibility. We determined parameters $b_{r,a}$ and $c_{r,a}$ in such a way that the rate constants for the main transition ($n_i = 1$, $n_f = 0$ for the VT transition and $n_{1i} = 1$, $n_{2i} = 0$, $n_{1f} = 0$, $n_{2f} = 1$, for the VV transition), computed with Eq. (11), are in good agreement with the results obtained for trajectory calculations proposed by Billing and Fisher et al.[7,8] and Capitelli et al.[9] They propose numerical data in the temperature range 200–8000 K that allow us to compute the corresponding rate constants for slow collisions. Here we use a numerical integration to compute the formula of Eq. (11). Figure 2 shows the comparison between rate constants, denoted as K_{VT} and computed by Billing and Fisher[8] and Capitelli et al.[9] and those computed with Eq. (11) with the inelastic-scattering probability given by Eq. (13). The difference is important for low temperatures. As mentioned by Gorbachev and Strelchenya,[6] this difference may be due to the fact that rate constants computed with trajectory calculations are sensitive to the potential-surface method of approximation and the accuracy of calculations decreases with decreasing temperature. The isotropic parameters are chosen to be $b_a = 0.3$ and $b_r = 0.3$. These parameters are fixed for all numerical computations regarding the VT processes.

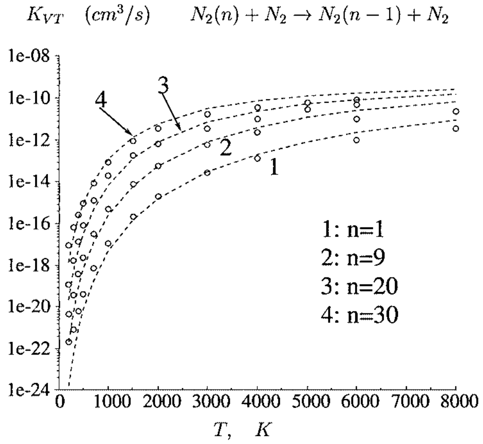

Fig. 2 Comparison of rate constants computed by Billing and Fisher[7] (○) and Eq. (11) (- - - -) with the inelastic-scattering probabilities given by Eq. (13) for different vibrational transitions. In this and subsequent figures, the format 1e (·) indicates ×10(·), e.g., 1e− 08 is $\times 10^{-8}$.

III. Analytical Approximations of VT Rate Constants for Slow Collisions

As can be seen from Eqs. (11), (13), (16), and (17), the probabilities and rate constants for VT transitions are given by complicated integrals. It would be expensive, from a computational time point of view, to use these formulas in direct simulation Monte Carlo or hydrodynamic solvers. The main difficulty in deriving analytical formulas is the Bessel function that appears in the definition of both slow and fast collisions. In the case of fast collisions, this problem is not yet solved and we cannot improve the proposed integral formula. In the case of slow collisions,[5] when $\lambda_m \gg 1$, the argument of the Bessel function is such that $F^{\mathrm{sl}}_{\mathrm{VT}} \ll 1$. As a consequence the Bessel function may be approximated by the first term of its expansion. Thanks to the previous approximation and using the Laplace method of integration, we write the probabilities for VT transitions as

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = A_{\mathrm{VT}}\left[\lambda_m|\Delta_n|\left(\arctan\sqrt{\frac{E_m}{D}} - \frac{\sqrt{DE_m}}{D + E_m}\right)\right]^{-1} \times \exp\left(-2\lambda_m|\Delta_n|\arctan\sqrt{\frac{E_m}{D}}\right) \tag{24}$$

where

$$A_{\mathrm{VT}} = \frac{G_{\mathrm{VT}}}{\Gamma^2(|\Delta n| + 1)}\left\{\frac{\pi d}{4\hbar}\left[b_r\omega_m\mu d - (2b_a - b_r)(2\mu D)^{\frac{1}{2}}\right]\right\}^{2|\Delta n|} \tag{25}$$

with $G_{\mathrm{VT}} = \varepsilon_m^{|\Delta n|}$.

We propose here a second analytical formula, which we derived by using the Laplace method of integration and appropriate approximations, given by

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = J^2_{|\Delta n|}\left(F^{\mathrm{sl}}_{\mathrm{VT}}\right)\left[\lambda_m|\Delta_n|\left(\arctan\sqrt{\frac{E_m}{D}} - \frac{\sqrt{DE_m}}{D + E_m}\right)\right]^{-1} \tag{26}$$

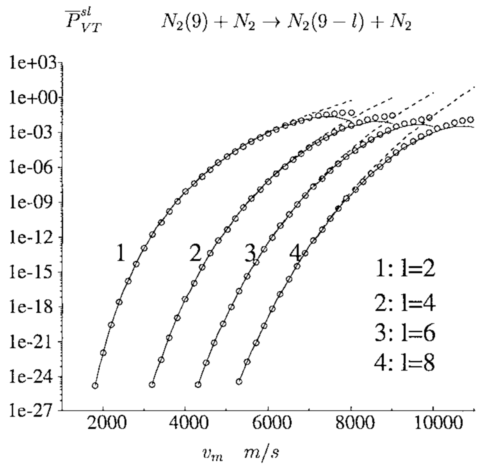

Fig. 3 Comparisons of inelastic-scattering probabilities for slow collisions between Eq. (19) (○), computed with a numerical integration, and the approximate formula of Eq. (24) (- - - -) and Eq. (26) (——).

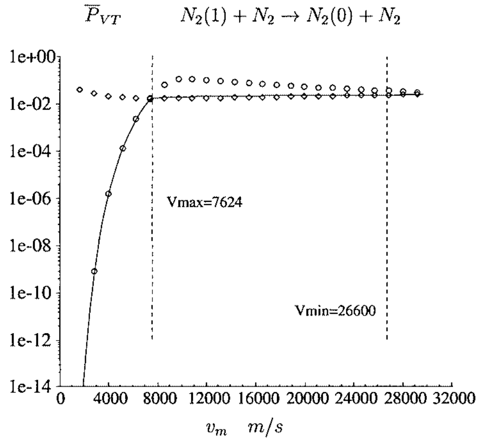

Fig. 4 Comparison of inelastic-scattering probabilities obtained for slow collisions (○) and fast collisions (◇). The solid curve is the interpolated probability obtained according to Eq. (22).

This last formula is more general because we have not made use of any approximation of the Bessel function. The derivation of Eqs. (24) and (26) is detailed in Appendix A.

It is possible to derive a simple approximation for low energies such as $E_m \ll D$. In this case, individual scattering probabilities do not depend on the scattering angle θ in Eq. (16) and integration of Eq. (13) becomes trivial. However, in this paper we do not consider such regimes.

Figure 3 shows comparisons of slow-collision inelastic-scattering probabilities among Eq. (13), computed with a numerical integration, and approximations of Eqs. (24) and (26). The initial vibrational level is assumed to be 9 and the final vibrational levels 1, 3, 5, and 7. The approximation of Eq. (26) is better than that of Eq. (24) as the transition level increases. As an example, Fig. 4 shows a comparison of inelastic-scattering probabilities, computed with a numerical integration, for fast, slow, and intermediate collisions. In the zone of intermediate collisions (the middle zone indicated by dashed lines), the probability is obtained by interpolation of fast and slow collisions according to Eq. (22). The value V max is the maximum velocity for slow collisions and V min the minimum velocity for fast collisions. The velocities V max and V min are defined by Eq. (12), substituting λ_m with λ_2 and λ_1, respectively. As the quantum level increases, the influence of fast collisions becomes stronger.

When $\bar{P}_{\mathrm{VT}}^{\mathrm{sl}}$ is known, it remains to compute the integral in Eq. (11) to determine the VT rate constant for slow collisions. We consider only deexcitation processes corresponding to $\Delta E < 0$. Substituting Eq. (24) into Eq. (11) and using the steepest-descent method of integration (see Appendix B), we write

$$K_{i \to f} = K_{n_i, n_f} = \frac{\tau^{-1}}{N} 4 A_{\mathrm{VT}} \frac{p_0^4}{a_m} \sqrt{\frac{2\pi kT}{g''(p_0)}}$$
$$\times \frac{\left[1 - (\Delta E_{**}/2)^2\right]^{\frac{1}{2}}}{\{\arctan(1/\sqrt{D_{**}}) - [\sqrt{D_{**}}/(1 + D_{**})]\}}$$
$$\times \exp\left[-p_0^2 - \frac{a_m}{p_0\sqrt{kT}} \arctan\left(\frac{1}{\sqrt{D_{**}}}\right) - \frac{\Delta E_*}{2}\right] \tag{27}$$

where the function g is given by

$$g(p) = p^2 + (a_m/p\sqrt{kT}) \arctan\left(p\big/\sqrt{D_*}\right) - \tfrac{1}{2}\log\left(p^2 + \Delta E_*/2\right) \tag{28}$$

and $\Delta E_{**} = \Delta E_*/kTp_0^2$, $D_{**} = D_*/kTp_0^2$, and $a_m = \mathrm{d}\omega_m|\Delta_n| \times \sqrt{(2\mu)}$. Furthermore, g' and g'' denote the first and the second derivatives, respectively, of g, and p_0 is the root of $g' = 0$.

For some asymptotic regimes, it is possible to derive an explicit expression for p_0. Consider the Landau–Teller regime, $E_m \gg D$, $|\Delta E|$, which is equivalent to $p \gg \sqrt{D_*}$, $|\Delta E_*|$; the equation $g' = 0$ may be reduced to

$$2p_{\mathrm{LT}}^2 - \frac{\pi}{2}\frac{a_m}{\sqrt{kT}\,p_{\mathrm{LT}}} = 0 \tag{29}$$

Its solution is

$$p_{\mathrm{LT}} = \left[(\pi/4)\left(a_m\big/\sqrt{kT}\right)\right]^{\frac{1}{3}} \tag{30}$$

It shows that our formula is an extension of the Landau–Teller formula, taking into account an attractive part of molecular interaction and threshold effects.[12] Considering now a first-order solution, we write

$$p_0 = p_{\mathrm{LT}}(1 + x) \tag{31}$$

Substituting this expression into $g' = 0$ and considering the first-order approximation, we obtain

$$p_0 = \left(\frac{\pi a_m}{4\sqrt{kT}}\right)^{\frac{1}{3}} + \frac{4\sqrt{D_*}}{3\pi} - \frac{1}{6}\left(\frac{4\sqrt{kT}}{\pi a_m}\right)^{\frac{1}{3}} \tag{32}$$

From Eq. (30), it is clear that $E_{\mathrm{LT}} = kTp_{\mathrm{LT}}^2$ decreases up to zero while temperature decreases. On the other hand, as follows from the behavior of the function g', $p_0 \geq \sqrt{(-\Delta E_*/2)}$, and we should look for p_0 in the form

$$p_0 = \sqrt{(-\Delta E_*/2)}(1 + y) \tag{33}$$

with $y > 0$, as g' has a singularity at $\sqrt{(-\Delta E_*/2)}$. The first-order approximation gives (again $p \gg \sqrt{D_*}$)

$$p_0 = \sqrt{(-\Delta E_*/2)}(1 - 2/\Delta E_*) \tag{34}$$

This formula is valid for lower temperatures than Eq. (32) is. The critical temperature T_Δ, which separates the two regimes, may be obtained by equating the expressions for p_0 given by Eqs. (31) and (33). After some reductions, T_Δ is written as

$$kT_\Delta = \frac{4}{\pi a_m}\left(\frac{-\Delta E}{2}\right)^{\frac{1}{3}} \left[1 + 7\frac{\sqrt{-\Delta E}}{\pi a_m}\right.$$
$$\left.\times \left(1 + \frac{4a_m\sqrt{D}}{7\Delta E}\right)\bigg/\left(1 - 5\frac{\sqrt{-2\Delta E}}{\pi a_m}\right)\right] \tag{35}$$

Thus, for $T > T_\Delta$, Eq. (32) is valid, and for $T < T_\Delta$, Eq. (34) is valid. In numerical computations, we use only Eq. (32) because T_Δ is always very small.

By using the preceding results, we may derive a characteristic temperature T_{sl} under which the rate constants for slow collisions are valid. To determine T_{sl}, we write

$$\lambda_2 = \frac{a_m}{\sqrt{kT}|\Delta n|p} \tag{36}$$

Substituting p with the Landau–Teller approximation of Eq. (30), we obtain

$$kT_{\text{sl}} = \frac{8\mu(d\omega_m)^2}{\pi|\Delta n|\lambda_2^3} \tag{37}$$

By using the same method of integration, we can write the VT rate constants corresponding to the approximation given by Eq. (26) for inelastic-scattering probabilities as

$$K_{n_i,n_f} = \frac{\tau^{-1}}{N} 4J^2_{|\Delta n|}[F_{\text{VT}}(p_0)]\frac{p_0^4}{a_m}\sqrt{\frac{2\pi kT}{g''(p_0)}}$$
$$\times \left\{\left[1-\left(\frac{\Delta E_{**}}{2}\right)^2\right]^{\frac{1}{2}} \Bigg/ \left[\arctan\left(\frac{1}{\sqrt{D_{**}}}\right) - \frac{\sqrt{D_{**}}}{1+D_{**}}\right]\right\}$$
$$\times \exp\left(-p_0^2 - \frac{\Delta E_*}{2}\right) \tag{38}$$

In Eq. (38), p_0 and $g''(p_0)$ are the same as for the rate constants that correspond to the approximation given by Eq. (27).

We give some numerical results below. Figure 5 shows comparisons of rate constants for slow collisions, computed with a numerical integration (trapezoidal method) and approximations of Eqs. (27) and (38). In all cases, the approximation of Eq. (38) is in better agreement with results obtained by a numerical integration. Furthermore, we note that the agreement is better for low quantum numbers. We recommend therefore the use of the approximate formula of Eq. (38) for computing VT rate constants for slow collisions for temperatures at which the approximate formula of Eq. (27) breaks down.

Figure 6 presents VT rate constants as functions of quantum levels for different temperatures. The dashed curves show the rate constants that correspond to the approximate formula of Eq. (27), with p_0 computed with the approximate formula of Eq. (32) and the solid curves with p_0 computed with the Newton method to obtain the solution of the equation $g' = 0$. The approximate formula of Eq. (32) gives good results for all temperatures. The agreement with the numerical results of Billing and Fisher (circles), obtained with trajectory calculations as mentioned above, is not good for low temperatures and high temperatures with high quantum numbers in the case of $N_2 + N_2$ collisions. For intermediate temperatures the agreement is quite satisfactory. Finally, for temperatures of 1000 and 6000 K, we present the rate constants computed for slow collisions by a numerical integration. For a temperature, of 1000 K, the numerical values obtained with Eqs. (27) and (38) are in a good agreement with the values obtained with the integral formula and do not depend on the quantum level. This is of course true for lower temperatures. Unfortunately, this conclusion is not valid for a temperature of 6000 K and consequently for higher temperatures. In this case, the difference increases when the quantum level increases.

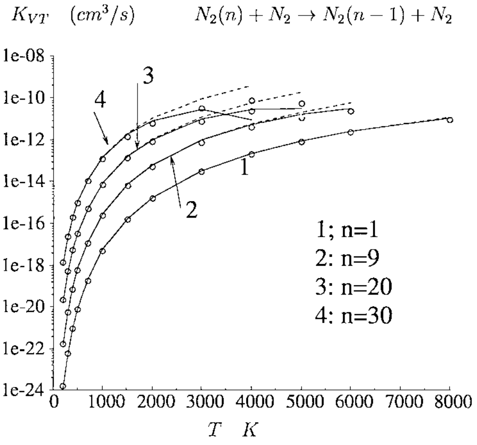

Fig. 5 Comparison of VT rate constants for slow collisions, obtained with the integral formula of Eq. (11) (○) and the approximate formulas of Eq. (27) (- - - -) and Eq. (38) (——).

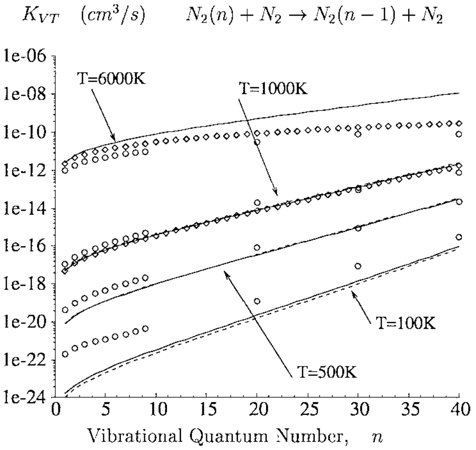

Fig. 6 Comparison of rate constants for slow collisions. The dependence is on a quantum level and concerns only one-level transitions.

Figure 7 shows a comparison among rate constants computed for slow collisions only and those computed for fast, intermediate, and slow collisions. Only one-level transitions were considered. The comparison is good for low temperatures, which was predicted. For high temperatures, the importance of fast collisions is evident. For only slow collisions, the rate constants overpredict vibrational transitions.

IV. Comparison with the VT Model of Adamovich et al.

The rate-constant model developed by Adamovich et al.[4,18,19] for VT and VVT processes is based on the semiclassical nonperturbative analytical theory for a harmonic oscillator acted on by an external exponential force,[3,20] called the forced harmonic oscillator (FHO). This last model takes into account multiquantum processes and also single-quantum processes at high collision velocities and high temperatures, but it neglects the role of vibrational–rotational coupling. Several modifications were introduced by Adamovich et al. to take into account some realistic effects. In particular, a steric factor was introduced to take into account the noncollinear nature of molecular collisions. It has a phenomenological meaning and is determined by comparison with the probability of the essential transition obtained by three-dimensional trajectory calculations.[7–9] Furthermore, to take anharmonicity effects into account, a mean frequency approximation is used. The intermolecular potentiel is the Morse potential. The scattering probabilities for VT transitions involve Bessel functions, and the following approximation is used:

$$J_s(z) = \left(\frac{z}{2}\right)^s \frac{1}{s}\exp\left[-\frac{z^2}{4(s+1)}\right] \tag{39}$$

We obtain the VT rate constants by averaging the scattering probabilities over Maxwellian translational energy distribution and by using the steepest-descent method to evaluate the resulting integral.

In Fig. 8, we compare the VT rate constants for four different single transitions. In the model of Adamovich et al., the steric factor

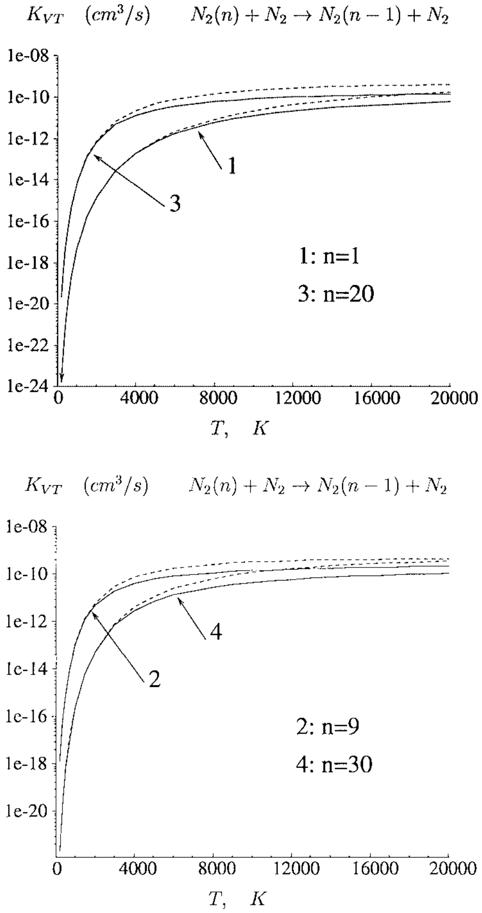

Fig. 7 Comparison of VT rate constants computed for fast, intermediate, and slow collisions (——) and only slow collisions (- - - -). In both cases we have used a numerical integration.

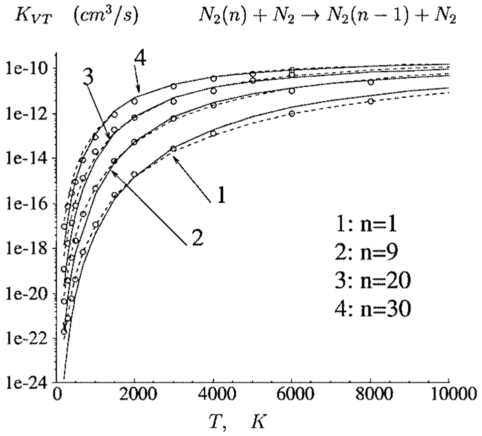

Fig. 8 Comparison of VT rate constants for different one-level transitions, computed with the models of Adamovich et al. (- - - -), Gorbachev (——), and Billing and Fisher (○).

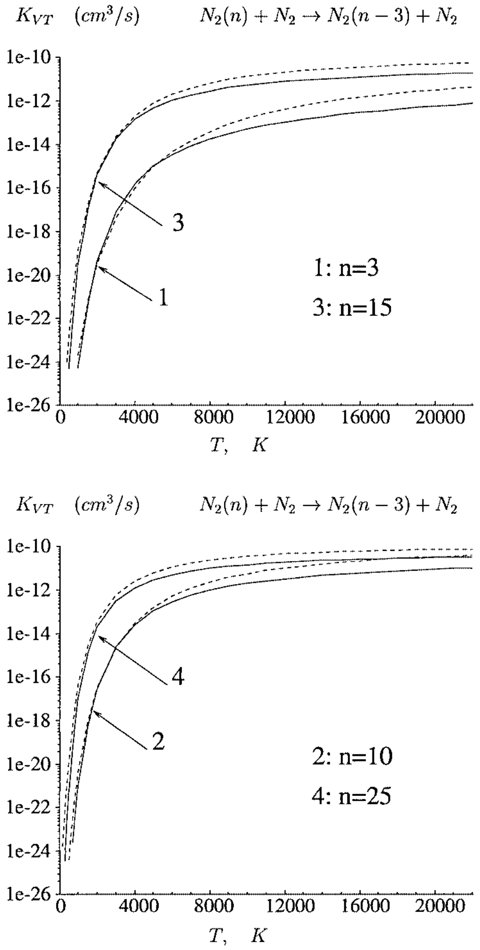

Fig. 9 Comparison of VT rate constants for different three-level transitions, computed with the models of Adamovich et al. (- - - -) and Gorbachev (——).

S_{VT} is equal to $\frac{1}{2}$. The presented VT rate constants have been computed with the integral formula of Eq. (11) with different definitions of the scattering probabilities for slow, intermediate, and fast collisions. Note that the rate constants of Adamovich et al. are in a good agreement with the Billing–Fisher numerical results for low temperatures. We have explained above a possible reason for this difference regarding our model. For high temperatures, both numerical results are in good agreement. This good agreement disappears when the multilevel transition $N_2(n) + N_2 \to N_2(n-j) + N_2$, with $j > 1$, is considered. Figures 9 and 10 show VT rate constants computed for $j = 3$ and 5, respectively. For high temperatures the agreement is bad and the difference increases as j increases. This may be due, in our opinion, to the fact that Gorbachev used three-dimensional collision models and also because of the approximation of Eq. (39), which is not valid for multilevel transitions (large s).

This observation is confirmed by the next numerical results. Figure 11 shows the dependence of the VT rate constants on the quantum level n for the different reactions $N_2(n) + N_2 \to N_2(n-j) + N_2$, $j = 1, 3, 5$, and for different temperatures. The difference between the rate constants of Adamovich et al. and Gorbachev increases again when j increases.

V. Rate Constants for VV Transitions

In this section we consider VV energy exchange processes. From a theoretical point of view, the same approach as that for VT processes is used. Consequently we give only the main formulas of VV scattering probabilities and VV rate constants.

A VV inelastic collision of two diatomic molecules leads to vibration energy exchange between both molecules. The frequencies and the energies are given by Eqs. (1) and (2), respectively. Considering again the mean frequency approximation, we write

$$\omega_m^+ = \frac{\omega_i^+ + \omega_f^+}{2}, \qquad \omega_k^+ = |\omega_{1k} + \omega_{2k}|, \qquad k = i, f$$

$$\omega_m^- = \frac{\omega_i^- + \omega_f^-}{2}, \qquad \omega_k^- = |\omega_{1k} - \omega_{2k}|, \qquad k = i, f$$

where i and f are initial and final channels, respectively.

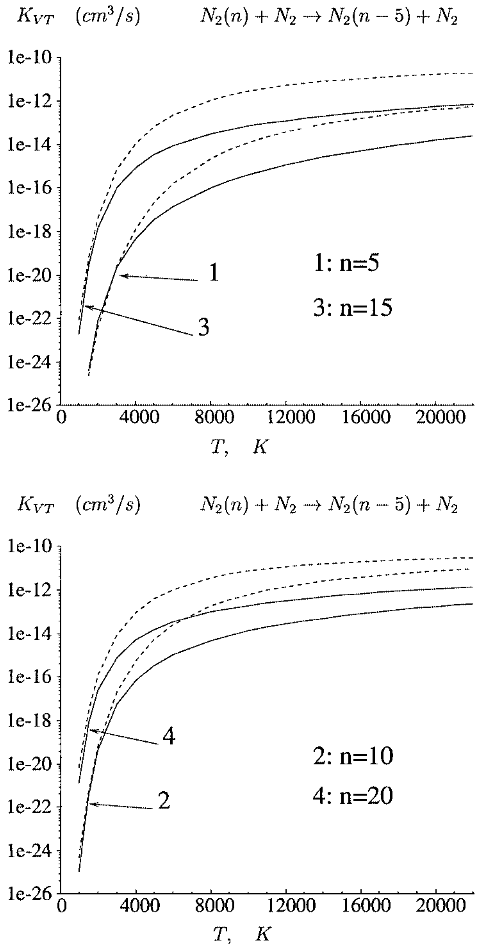

Fig. 10 Comparison of VT rate constants for different five-level transitions, computed with the models of Adamovich et al. (----) and Gorbachev (——).

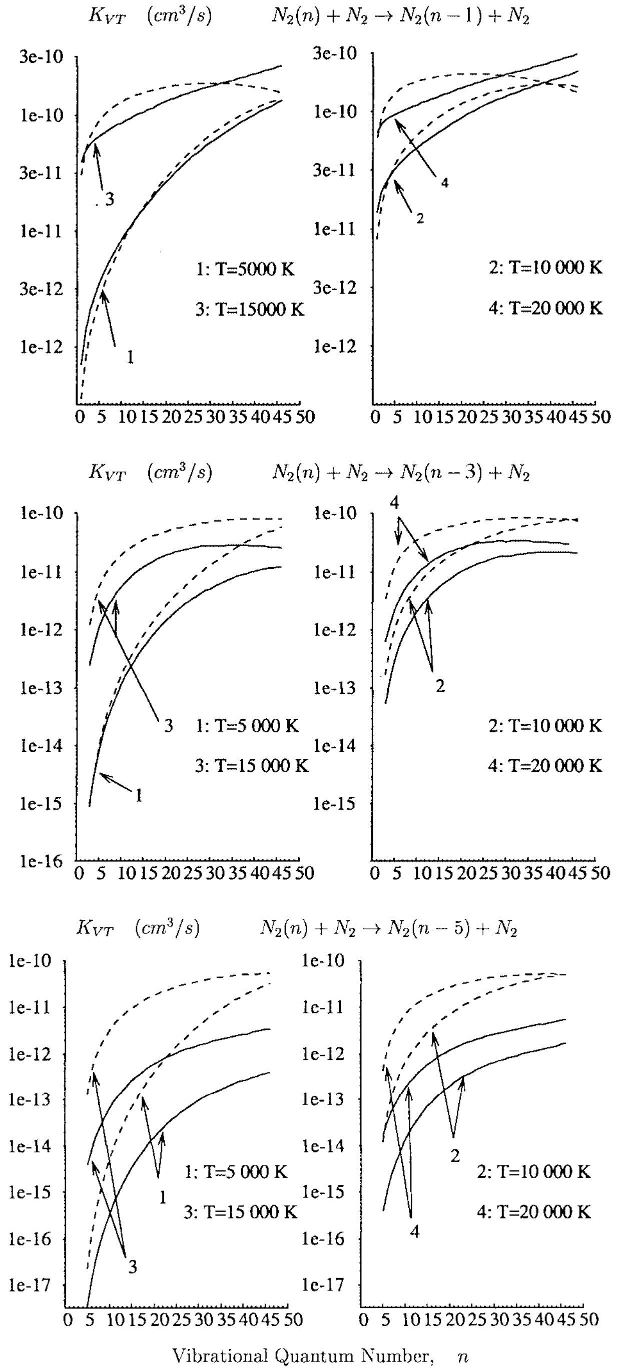

Fig. 11 Comparison of VT rate constants that depend on the initial vibrational level for different multilevel transitions and for different temperatures. The results of Adamovich et al. are represented by dashed curves and the Gorbachev results by solid curves.

As for VT collisions, we define the adiabatic parameters as

$$\lambda_m^{\pm} = \frac{\omega_m^{\pm} d}{v_m}$$

The parameter λ_m^+ is less than 1 only for very high velocities. In our case, we are not interested in such high velocities and we restrict ourselves to the case $\lambda_m^+ > 1$. That means that the collisions are adiabatic: The collision time is greater than one period of the oscillator. Then the adiabatic propensity rules determine the process of energy exchanges.[12] In this case the transitions verify that $\Delta n_1 = -\Delta n_2$, where $\Delta n_k = n_{kf} - n_{ki}$, with $k = 1, 2$.

Depending on the adiabatic parameter λ_m^-, the collisions are classified into three groups: slow collisions ($\lambda_m^- > \lambda_2^- > 1$), fast collisions ($\lambda_m^- < \lambda_1^- < 1$), and intermediate collisions (the other cases).

For slow collisions, the average scattering probabilities are written as

$$\bar{P}_{\mathrm{VV}}^{\mathrm{sl}} = \frac{1}{2} \int_0^{\pi} P_{\mathrm{VV}}^{\mathrm{sl}}(\theta) \sin\theta \, \mathrm{d}\theta \tag{40}$$

where the scattering probabilities are written as $P_{\mathrm{VV}}^{\mathrm{sl}} = J_{\kappa_-}^2 (F_{\mathrm{VV}}^{\mathrm{sl}})$ and

$$F_{\mathrm{VV}}^{\mathrm{sl}} = \varepsilon_{mn}^{\frac{1}{2}} \frac{\pi d}{2\hbar} \Big[c_r \omega_m^- \mu d - (2c_a - c_r)(2\mu D)^{\frac{1}{2}} \Big] \times \exp\left[-\frac{\omega_m^- \mu d}{p_m \sin(\theta/2)} \arctan\sqrt{\frac{E_m}{D}} \sin\left(\frac{\theta}{2}\right) \right]$$

In this formula, we have used the following definitions:

$$\varepsilon_{mn} = \frac{\varepsilon_{n_1 m} \varepsilon_{n_2 m}}{4}, \qquad \varepsilon_{n_q m} = \frac{E_{n_q i} + E_{n_q f}}{2\hbar\omega_e}$$

$$q = 1, 2, \qquad \kappa_- = \frac{|\Delta n_1 - \Delta n_2|}{2}$$

For fast collisions, we write the scattering probabilities as

$$\bar{P}_{\mathrm{VV}}^{f} = \frac{2\pi d^2}{\sigma_E} \int_{x_0}^{\infty} x \left(1 - \frac{D}{E_m} \exp[-(x - x_{00})] \times \{ \exp[-(x - x_{00})](1 - x) - 2 + x \} \right) J_{\kappa_-}^2 \left[F_{\mathrm{VV}}^{f}(x) \right] \mathrm{d}x \tag{41}$$

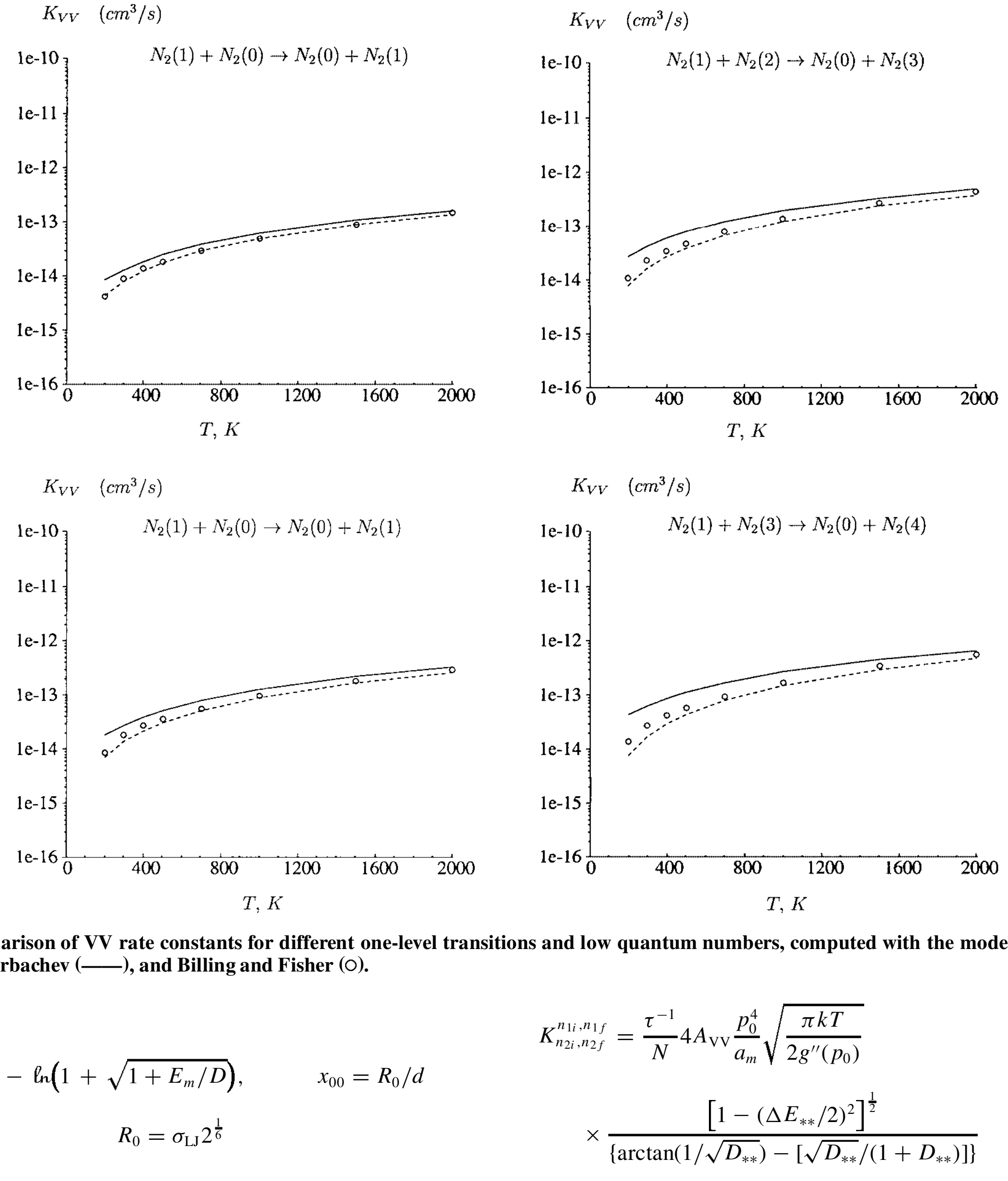

Fig. 12 Comparison of VV rate constants for different one-level transitions and low quantum numbers, computed with the models of Adamovich et al. (- - - -), Gorbachev (——), and Billing and Fisher (○).

where

$$x_0 = x_{00} - \ln\left(1 + \sqrt{1 + E_m/D}\right), \qquad x_{00} = R_0/d$$

$$R_0 = \sigma_{\mathrm{LJ}} 2^{\frac{1}{6}}$$

$$F^f_{\mathrm{VV}}(x) = \frac{Dd}{v_m \hbar}\sqrt{\pi x \varepsilon_{n_1 m}\varepsilon_{n_2 m}}\exp[-(x - x_{00})] \times \left\{c_r \exp[-(x - x_{00})] - 2\sqrt{2}c_a\right\}$$

where σ_E is given by Eq. (20). For intermediate collisions, the scattering probabilities are determined by the interpolation formula of Eq. (22).

For slow collisions, the average VV scattering probabilities can be approximated exactly like averaged VT scattering probabilities. In the case of slow collisions, if we assume that $F^{\mathrm{sl}}_{\mathrm{VV}} \ll 1$, we can again substitute Bessel functions with the first term of their expansions. The result of the integration in Eq. (40), by the Laplace method, is precisely the formula of Eq. (24), where A_{VT} is substituted for A_{VV}, λ_m for λ^-_m, and $|\Delta_n|$ for κ_-. The quantity A_{VV} is defined by

$$A_{\mathrm{VV}} = \frac{G_{\mathrm{VV}}}{\Gamma^2(\kappa_- + 1)}\left\{\frac{\pi d}{4\hbar}\left[c_r \omega^-_m \mu d - (2c_a - c_r)(2\mu D)^{\frac{1}{2}}\right]\right\}^{2\kappa_-}$$

where $G_{\mathrm{VV}} = (\varepsilon_{n_1 m}\varepsilon_{n_2 m}/4)^{\kappa_-}$. By using this approximation for the scattering probabilities, we obtain the VV rate constants by computing the integral of Eq. (11) by using the steepest-descent method. Thus the corresponding VV rate constants are written as ($\Delta E < 0$)

$$K^{n_{1i}, n_{1f}}_{n_{2i}, n_{2f}} = \frac{\tau^{-1}}{N} 4 A_{\mathrm{VV}} \frac{p_0^4}{a_m}\sqrt{\frac{\pi k T}{2g''(p_0)}} \times \frac{\left[1 - (\Delta E_{**}/2)^2\right]^{\frac{1}{2}}}{\{\arctan(1/\sqrt{D_{**}}) - [\sqrt{D_{**}}/(1 + D_{**})]\}} \times \exp\left[-p_0^2 - \frac{a_m}{p_0\sqrt{kT}}\arctan\left(\frac{1}{\sqrt{D_{**}}}\right) - \frac{\Delta E_*}{2}\right] \tag{42}$$

where $a_m = \mathrm{d}\omega^-_m \kappa_- \sqrt{(2\mu)}$,

$$g''(p_0) = 2 + \frac{2a_m}{p_0^3\sqrt{kT}}\left[\arctan\left(\frac{1}{\sqrt{D_{**}}}\right) - \frac{2(1 + D_{**}/2)\sqrt{D_{**}}}{(1 + D_{**})^2}\right] + \frac{1}{p^2}\frac{1 - \Delta E_{**}/2}{\left[1 + (\Delta E_{**}/2)^2\right]^2}$$

D_{**} and E_{**} are defined by $D_{**} = D_*/p_0^2$ and $E_{**} = E_*/p_0^2$, and p_0 is the root of

$$g'(p) = 2p - \frac{a_m}{\sqrt{kT}}\frac{1}{p^2}\arctan\left(\frac{p}{\sqrt{D_*}}\right) + \frac{a_m}{\sqrt{kT}}\frac{1}{p}\frac{\sqrt{D_*}}{p^2 + D_*} - \frac{p}{p^2 + \Delta E_*/2}$$

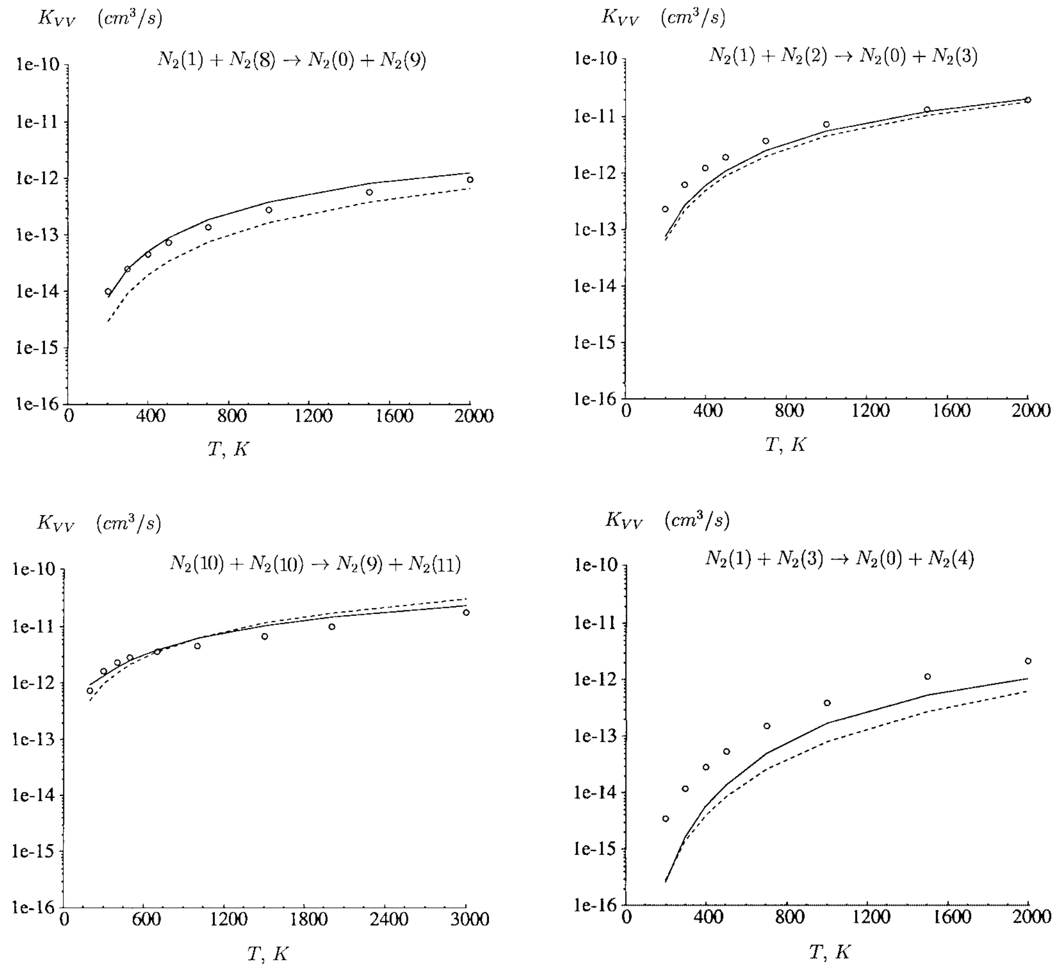

Fig. 13 Comparison of VV rate constants for three different one-level transitions and 1 two-level transition (bottom right), computed with the models of Adamovich et al. (- - - -), Gorbachev (——), and Billing and Fisher (○).

Here again, we may derive a second approximation that is analogous to Eq. (38) for VT rate constants. It is written as

$$K^{n_{1i},n_{1f}}_{n_{2i},n_{2f}} = \frac{\tau^{-1}}{N}4J^2_{\kappa_-}[F_{\mathrm{VV}}(p_0)]\frac{p_0^4}{a_m}\sqrt{\frac{2\pi kT}{g''(p_0)}}$$

$$\times\frac{\left[1-(\Delta E_{**}/2)^2\right]^{\frac{1}{2}}}{\{\arctan(1/\sqrt{D_{**}})-[\sqrt{D_{**}}/(1+D_{**})]\}}$$

$$\times\exp\left(-p_0^2-\frac{\Delta E_*}{2}\right) \tag{43}$$

with the previous definitions for p_0 and $g''(p_0)$.

VI. Comparison with the VV Model of Adamovich et al.

The VV rate constants derived by Adamovich et al. are based on the FHO theory (see Sec. V). The steric factor S_{VV} plays the same role as S_{VT} for VT transitions. This parameter is determined in such a way that the FHO probabilities $P(1,0\to 0,1)$ match the results of Billing and Fisher.[7]

The first numerical results we propose concern comparisons of VV rate constants derived by Adamovich et al., Gorbachev et al., and Billing and Fisher for low temperatures. The VV rate constants of Gorbachev et al. are computed according to Eq. (11) by use of a numerical integration. Furthermore, we have performed the integration over the velocity domain associated with intermediate and fast collisions only, and we have used the corresponding definitions for the scattering probabilities. It appears that slow collisions can be neglected. The following values were used for the boundary adiabatic parameters: $\lambda_1 = 1$, $\lambda_2 = 3.5$, the same as for VT rate-constant computations. The values of the anisotropic parameters are $c_a = 0.0022$ and $c_r = 0.0017$. Figure 12 shows different one-level VV rate constants for low quantum numbers. Results obtained with Gorbachev's model are in a good agreement with those of Billing and Fisher. When the results obtained with the model of Adamovich et al. are compared with those obtained with the Gorbachev model, we note a small overprediction. Figure 13 shows rate constants for one-level VV transitions but for higher quantum numbers. In that case, the results of our model are on the whole in better agreement with the Billing–Fisher results than those of the model of Adamovich et al. The graph on the bottom right of Fig. 13 presents rate constants for a two-level VV transition. In this case the rate constants of both Gorbachev and Adamovich et al. are lower than the Billing–Fisher rate constants. Figures 14 and 15 represent the VV rate constants computed previously but for higher temperatures. Unfortunately, we do not have numerical results for the Billing–Fisher model for this case. We note a good agreement for low temperatures but a significant overprediction of the rate constants of Adamovich et al. for high temperatures. It is difficult to draw any conclusion. We can mention that Gorbachev's model takes into account three-dimensional trajectories, which is not the case of the model of Adamovich et al., as already noted.

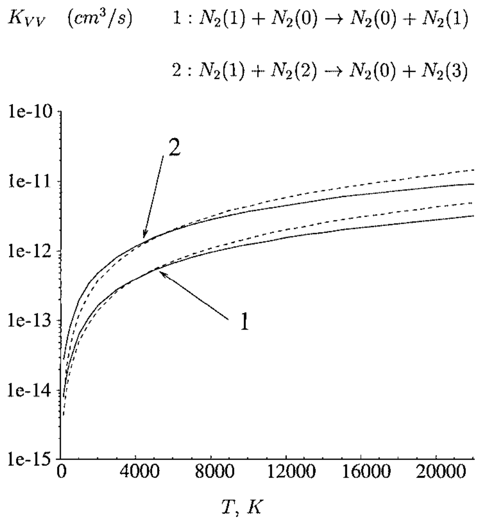

Fig. 14 Comparison of VV rate constants for different one-level transitions, computed with the models of Adamovich et al. (- - - -) and Gorbachev (——).

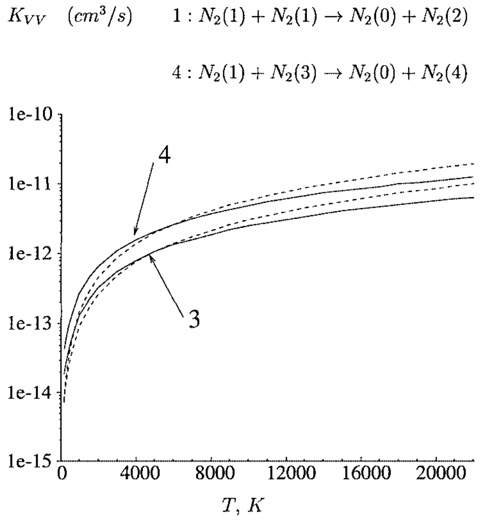

Fig. 15 Comparison of VV rate constants for different one-level transitions, computed with the models of Adamovich et al. (- - - -) and Gorbachev (——).

Before ending this paper, we point out that Adamovich et al.[21] presented an improved model (taking into account three-dimensional trajectories) at the AIAA/ASME 7th Joint Thermophysics and Heat Transfer Conference that was not considered in this paper and will lead to further investigations.

VII. Conclusion

In this paper we have presented new formulas for VT and VV rate constants, based on the quasi-classical multidimensional scattering theory for polyatomic gases. Numerical results computed with these formulas were compared with the models of Adamovich et al. and Billing and Fisher for nitrogen. Some differences exist between these models. Although it is possible to analyze these difference from a theoretical point of view, we regret the lack of experimental data.

Considering computations of master equations for vibrational relaxation, we have proposed a new analytical formula that is valid for low-temperature flows. For high-temperature flows it is necessary to use exact integral formulas by means of an interpolation procedure.

In a subsequent paper, these new VT and VV rate constants will be introduced into a hydrodynamic solver to compute master equations for vibrational relaxation coupled with equations of conservation of momentum and total energy.

Appendix A: Derivation of Eqs. (24) and (26)

We give details here on the derivation of Eqs. (24) and (26) for VT probabilities in the case of slow collisions.

The Bessel function is approximated by the first term of its expansion, that is,

$$J^2_{|\Delta_n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(n)\right] \approx \frac{\left[F^{\mathrm{sl}}_{\mathrm{VT}}(n)/2\right]^{2|\Delta n|}}{\Gamma(|\Delta_n|+1)} \tag{A1}$$

When approximation (A1) is substituted into Eq. (13), the probability for VT transitions is written as

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = \frac{1}{2}\int_0^{\pi} \frac{\left(F^{\mathrm{sl}}_{\mathrm{VT}}/2\right)^{2|\Delta n|}}{\Gamma^2(|\Delta n|+1)} \sin\theta \,\mathrm{d}\theta$$

which we can rewrite, by using Eq. (25), as

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = \frac{A_{\mathrm{VT}}}{2}\int_0^{\pi} \exp\left\{-\frac{2|\Delta n|\lambda_m}{\sin(\theta/2)}\right. \\ \left.\times\left[\arctan\sqrt{\frac{E_m}{D}}\sin\left(\frac{\theta}{2}\right)\right]\right\} \sin\theta\,\mathrm{d}\theta \tag{A2}$$

By using changes of variables, $x = \sin(\theta/2)$ and $y = 1/x$, we rewrite Eq. (A2) as

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = 2A_{\mathrm{VT}}\int_1^{\infty} y^{-3}\exp\left[-2|\Delta n|\lambda_m y \arctan\left(\sqrt{\frac{E_m}{D}}\frac{1}{y}\right)\right]\mathrm{d}y \tag{A3}$$

or

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = 2A_{\mathrm{VT}}\int_1^{\infty} y^{-3}e^{\psi(y)}\,\mathrm{d}y$$

where

$$\psi(y) = -2|\Delta n|\lambda_m y \arctan\left[\sqrt{(E_m/D)}(1/y)\right]$$

Because the main contribution of the integral of Eq. (46) is in the neighborhood of point 1, we expand the function ψ at the first order around this point. The first derivative of ψ is given by

$$\psi' = -2|\Delta n|\lambda_m\left[\arctan\left(\sqrt{\frac{E_m}{D}}\frac{1}{y}\right) - \frac{\sqrt{E_m D}\,y}{y^2 D + E_m}\right]$$

Then the Laplace method leads to the expression of Eq. (24).

Regarding the second approximation for the scattering probability of slow collisions, we start rewriting Eq. (13) as

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = \frac{1}{2}\int_0^{\pi} J^2_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(\theta)\right]\sin(\theta)\,\mathrm{d}\theta \\ = \frac{1}{2}\int_0^{\pi} \exp\left(\log\left\{J^2_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(\theta)\right]\right\}\right)\sin(\theta)\,\mathrm{d}\theta \tag{A4}$$

Using the preceding changes of variables, we can rewrite Eq. (A4) as

$$\bar{P}^{\mathrm{sl}}_{\mathrm{VT}} = 2\int_0^{\infty} y^{-3}\exp\left(2\log\left\{J_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(y)\right]\right\}\right)\mathrm{d}y \\ = 2\int_0^{\infty} y^{-3}e^{\psi(y)}\,\mathrm{d}y$$

where now the function ψ is $\psi = 2\log\{J_{|\Delta n|}[F^{\mathrm{sl}}_{\mathrm{VT}}(y)]\}$. With obvious notation, $F^{\mathrm{sl}}_{\mathrm{VT}}(y)$ can be written as

$$F^{\mathrm{sl}}_{\mathrm{VT}}(y) = A_{\mathrm{F}}\exp\left\{-\lambda_m y \arctan\left[\sqrt{(E_m/D)}(1/y)\right]\right\}$$

Thus the first derivative of ψ is written as

$$\psi'(y) = 2\frac{J'_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(y)\right]}{J_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(y)\right]}F'^{\mathrm{sl}}_{\mathrm{VT}}(y)$$

Knowing that

$$F'^{\mathrm{sl}}_{\mathrm{VT}}(y) = -\lambda_m\left[\arctan\left(\sqrt{\frac{E_m}{D}}\frac{1}{y}\right) - \frac{\sqrt{E_m D}\,y}{y^2D + E_m}\right]F^{\mathrm{sl}}_{\mathrm{VT}}(y)$$

$$J'_{|\Delta n|}(z) = \frac{|\Delta n|}{z}J_{|\Delta n|}(z) - J_{|\Delta n|+1}(z)$$

we deduce the final expression for the first derivative of ψ:

$$\psi'(y) = -2\lambda_m\left[\arctan\left(\sqrt{\frac{E_m}{D}}\frac{1}{y}\right) - \frac{\sqrt{E_m D}y}{y^2D + E_m}\right]F^{\mathrm{sl}}_{\mathrm{VT}}(y)$$

$$\times\left\{\frac{|\Delta n|}{F^{\mathrm{sl}}_{\mathrm{VT}}(y)} - \frac{J_{|\Delta n|+1}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(y)\right]}{J_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(y)\right]}\right\}$$

Because for $F^{\mathrm{sl}}_{\mathrm{VT}} \leq 1$ we have

$$\frac{|\Delta n|}{F^{\mathrm{sl}}_{\mathrm{VT}}(1)} \gg \frac{J_{|\Delta n|+1}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(1)\right]}{J_{|\Delta n|}\left[F^{\mathrm{sl}}_{\mathrm{VT}}(1)\right]}$$

the value of $\psi'(1)$ is

$$\psi'(1) = -2\lambda_m|\Delta n|\left\{\arctan\left(\sqrt{E_m/D}\right) - \left[\sqrt{E_m D}\big/(D + E_m)\right]\right\}$$

Finally, the Laplace method of integration leads to the approximate formula of Eq. (26).

Appendix B: VT Rate Constants—Derivation of Eqs. (27) and (38)

We propose here the details of the procedure used to compute the VT rate constants given by Eqs. (27) and (38).

Substituting $\bar{P}^{\mathrm{sl}}_{\mathrm{VT}}$ with the expression of Eq. (24) into Eq. (11), we write the rate constants as

$$K_{n_i,n_f} = \frac{\tau^{-1}}{N}\frac{A_{\mathrm{VT}}}{(kT)^2}\int_0^\infty (E_{\mathrm{tr}\,i}E_{\mathrm{tr}\,f})^{\frac{1}{2}}$$

$$\times\left[\lambda_m|\Delta_n|\left(\arctan\sqrt{\frac{E_m}{D}} - \frac{\sqrt{DE_m}}{D + E_m}\right)\right]^{-1}$$

$$\times\exp\left(-2\lambda_m|\Delta_n|\arctan\sqrt{\frac{E_m}{D}}\right)\exp\left(-\frac{E_{\mathrm{tr}\,i}}{kT}\right)\mathrm{d}E_{\mathrm{tr}\,i} \tag{B1}$$

We proceed now with an appropriate change of variables. Because of the energy conservation, we have $E_{\mathrm{tr}\,f} = E_{\mathrm{tr}\,i} - \Delta E$. Let us define the variable p as

$$p = \sqrt{\frac{E_m}{kT}} = \sqrt{\frac{E_{\mathrm{tr}\,i}}{kT} - \frac{\Delta E_*}{2}} \tag{B2}$$

where $\Delta E_* = \Delta E/kT$. It follows that

$$E_{\mathrm{tr}\,i} = kT\left(p^2 + \frac{\Delta E_*}{2}\right), \qquad E_{\mathrm{tr}\,f} = kT\left(p^2 - \frac{\Delta E_*}{2}\right)$$

When the change of variables of Eq. (B2) is used, Eq. (B1) becomes

$$K_{n_i,n_f} = \frac{\tau^{-1}}{N}4A_{\mathrm{VT}}\frac{\sqrt{kT}}{a_m}\exp\left(-\frac{\Delta E_*}{2}\right)$$

$$\times\int_{\sqrt{-\Delta E_*/2}}^\infty\sqrt{p^4 - \left(\frac{\Delta E_*}{2}\right)^2}\left[\arctan\left(\frac{p}{\sqrt{D_*}}\right)\right.$$

$$\left.-\frac{p\sqrt{D_*}}{p^2 + D_*}\right]^{-1}\exp\left[-p^2 - \frac{a_m}{p\sqrt{kT}}\arctan\left(\frac{p}{\sqrt{D_*}}\right)\right]p^2\,\mathrm{d}p \tag{B3}$$

where we have used the notation

$$\lambda_m|\Delta n| = a_m/p\sqrt{kT}, \qquad D_* = D/kT$$

We rewrite Eq. (B3) as

$$K_{n_i,n_f} = \frac{\tau^{-1}}{N}2A_{\mathrm{VT}}\frac{\sqrt{kT}}{a_m}\exp\left(-\frac{\Delta E_*}{2}\right)$$

$$\times\int_{\sqrt{-\Delta E_*/2}}^\infty f(p)\exp[-g(p)]\,\mathrm{d}p \tag{B4}$$

where

$$f(p) = \sqrt{p^2 - \frac{\Delta E_*}{2}}\left[\arctan\left(\frac{p}{\sqrt{D_*}}\right) - \frac{p\sqrt{D_*}}{p^2 + D_*}\right]^{-1}p$$

$$g(p) = p^2 + \frac{a_m}{p\sqrt{kT}}\arctan\left(\frac{p}{\sqrt{D_*}}\right) - \frac{1}{2}\log\left(p^2 + \frac{\Delta E_*}{2}\right)$$

After some algebra, we obtain the first and the second derivatives of g, written, respectively, as

$$g'(p) = 2p - \frac{a_m}{\sqrt{kT}}\frac{1}{p^2}\arctan\left(\frac{p}{\sqrt{D_*}}\right)$$

$$+\frac{a_m}{\sqrt{kT}}\frac{1}{p}\frac{\sqrt{D_*}}{p^2 + D_*} - \frac{p}{p^2 + \Delta E_*/2}$$

$$g''(p) = 2 + \frac{2a_m}{p^3\sqrt{kT}}\left[\arctan\left(\frac{p}{\sqrt{D_*}}\right)\right.$$

$$\left.-\frac{2p\left(p^2 + D_*/2\right)\sqrt{D_*}}{\left(p^2 + D_*\right)^2}\right] + \frac{p^2 - \Delta E_*/2}{\left(p^2 + \Delta E_*/2\right)^2}$$

Let us denote the solution of the equation $g' = 0$, that is, the most effective momentum, as p_0. Expanding g in the neighborhood of p_0, we obtain

$$g(p) = g(p_0) + \frac{g''(p_0)}{2}(p - p_0)^2 + \cdots \tag{B5}$$

Substituting Eq. (B5) into Eq. (B4), we obtain

$$K_{n_i,n_f} = \frac{\tau^{-1}}{N}2A_{\mathrm{VT}}\frac{\sqrt{kT}}{a_m}\exp\left[-g(p_0) - \frac{\Delta E_*}{2}\right]f(p_0)$$

$$\times\int\exp\left[-\frac{g''(p_0)}{2}(p - p_0)^2\right]\mathrm{d}p \tag{B6}$$

After integration, the resulting formula is Eq. (27)

Equation (38) is obtained with the same method.

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