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## A quasi-classical model for VT and VV rate constants.

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Thème 4 — Simulation et optimisation  
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**Abstract:** We present in this report vibrational rate constants for VT and VV process in a pure diatomic gas, based on the quasi-classical theory. Different approximations are derived for moderate temperatures flows. Numerical results are proposed for diatomic nitrogen ( $N_2$ ), and compared with Adamovich et als and Billing-Fisher models.

**Key-words:** Vibrational relaxation, VT, VV, pur diatomic gas, quasi-classical theory.

*(Résumé : tsvp)*

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<sup>†</sup> INRIA, Domaine de Voluceau, B.P. 105, F 78153 Le Chesnay Cedex, France *email:* mallinger@inria.fr, The work was done during a visit of the François Mallinger to the Institute IHPCDB of St Petersburg, in the framework on a joined research project on Rarefied Gas Dynamics and High Speed Flows supported by the Liapunov Institute.

## Un modèle de taux de relaxation VT et VV déduit de la théorie quasi-classique.

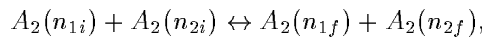
**Résumé :** Nous présentons dans ce rapport un modèle de taux de relaxation vibrationnelle pour les processus VT et VV dans un gaz diatomique pur, basé sur la théorie quasi-classique. Différentes approximations sont dérivées pour des écoulements à températures modérées. Des résultats numériques sont proposés pour un gaz d'azote ( $N_2$ ), et comparés aux résultats numériques obtenus pour les modèles d'Adamovich et al. et de Billing-Fisher.

**Mots-clé :** Relaxation vibrationnelle, VT, VV, gaz pur diatomique, théorie quasi-classique.

## 1 Introduction

The principal difficulty arising when computing a high-temperature flow is the simulation of relaxation processes between different energy modes. The high-temperature conditions are typical for hypersonic flows around space vehicles at altitudes of about 70km and higher. A strong nonequilibrium between translational, rotational and vibrational modes takes place in the relaxation zone between the bow shock and body surface. An accurate modeling of energy exchange processes is compulsory for obtaining credible information on space vehicle's aerodynamics.

In this paper, we focus on Vibrational-Translational (VT) and Vibrational-Vibrational (VV) energy transfer during collisions of diatomic molecules. Considering a pure diatomic gas that consist of molecules  $A_2$  with discrete vibrational energy, it is necessary to know the rate constants associated with the following VT and VV processes respectively



where  $n_i, n_{1i}, n_{2i}$  and  $n_f, n_{1f}, n_{2f}$  are initial and final quantum numbers that characterise each energy level. Different attempts have been made lately to derive VT and VV rate constants. We mention here exact fully quantum calculations [20], Billing closed coupled method [8], SHH theory, and also modified FHO theory [21], [1].

Here, we present new VT and VV rate constants for diatomic molecules. The formulas were obtained using the quasiclassical multidimensional scattering theory for polyatomic gases developed by Gorbachev et al. [9],[15]. In this approach the calculations are based on the quasiclassical representation of  $T$  operator in the angle-action variables and on approximations of multi-dimensional trajectories. Potentials that includes both attractive and repulsive part are considered. Anharmonicity effects are taken into account. The main modification we introduce here is a mean approximation for the solution of equations of motion. It may be called as mean frequency or mean energy approximation.

Our goal is also to analyze numerically different formulas for VT and VV rate constants for diatomic nitrogen. We show some difficulties of approximating the exact integral formulas and determining the validity of different approximations. We give then a numerical comparison of the obtained rate constants with the rate constants derived by Adamovich et al. [1] in the framework of modified FHO theory, and also with Billing-Fisher's 3D trajectory calculations [4], [6], [12]. In the temperature range where explicit formulas are not valid, we propose interpolated formulas.

## 2 The rate constants for VT transitions

In this section, we present the VT rate constants derived by Gorbachev et al. from the quasiclassical theory [9].

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

$$(1) \quad \omega_{n_k} = \omega_e(1 - 2x_e(n_k + 0.5)),$$

where  $\omega_e$  is the oscillator frequency and  $x_e$  is the anharmonicity parameter, and vibrational energy is written as

$$(2) \quad E_{n_k} = \omega_e(n_k + 0.5)(1 - x_e(n_k + 0.5)).$$

The energy exchange between relative translational energy and vibrational energy of one of collided particles takes place in an inelastic collision. If we denote by  $E_i$  and  $E_f$  the translational energy of the relative motion before and after the collision respectively, and  $(E_{n_i}, E_{n_f})$  the vibrational energy of a particle whose internal structure is modified, the conservation of total energy may be written as

$$(3) \quad E_i + E_{n_i} = E_f + E_{n_f}.$$

Collisions which lead to vibrational-translational energy exchanges promote the relaxation of gas towards vibrational equilibrium. At the macroscopic level, the process of vibrational relaxation is partially described by the VT rate constant.

The integral formula for VT rate constants is written as

$$(4) \quad K_{n_i, n_f} = \frac{\tau^{-1}}{N} \int_{\mathcal{E}^* H(\mathcal{E}^*)}^{\infty} (\mathcal{E}_i \mathcal{E}_f)^{1/2} \bar{P}_{VT} \exp(-\mathcal{E}_i) d\mathcal{E}_i,$$

where

$$(5) \quad \mathcal{E}^* = \frac{\Delta E}{kT}, \quad \Delta E = E_{n_f} - E_{n_i}, \quad \mathcal{E}_i = \frac{E_i}{kT},$$

and  $H$  is the unit step function.

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

$$(6) \quad \lambda_m = \frac{\omega_m d}{v_m},$$

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

$$(7) \quad v_m = \sqrt{\frac{2E_m}{\mu}},$$

where  $E_m$  is the mean relative translational energy

$$(8) \quad E_m = \frac{E_f + E_i}{2},$$

and  $\omega_m$  is the mean frequency

$$(9) \quad \omega_m = (\omega_{n_i} + \omega_{n_f})/2.$$

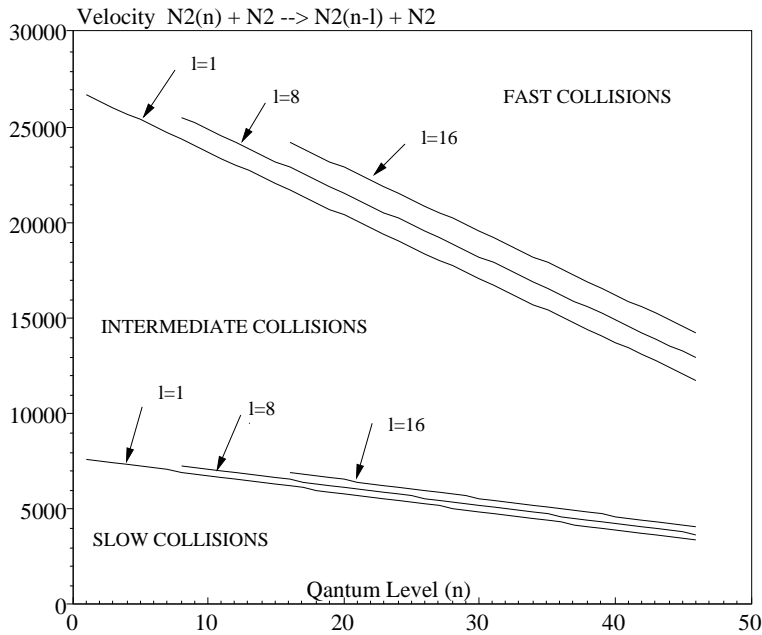
The collisions are classified into three groups depending on the the adiabatic parameter:

Fast collisions:  $\lambda_m < \lambda_1 \leq 1$ ,

Slow collisions:  $1 \leq \lambda_2 < \lambda_m$ ,

Intermediate collisions: all other cases.

The following figure shows the dependence of the adiabatic parameter upon the quantum level  $n$  corresponding to the reaction  $N_2(n) + N_2 \rightarrow N_2(n-l) + N_2$  and for different values of the level transition  $l$ . The values  $\lambda_1 = 1$ , for fast collisions, and  $\lambda_2 = 3.5$  were used by Gimelshein et al. [13], [18] to compute some cross sections. The value of  $\lambda_2$  is not strictly defined as we will see when we will define the scattering probabilities. We note that the influence of fast collisions increases for high quantum numbers.



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

$$(10) \quad \bar{P}_{VT}^{sl} = \frac{1}{4\pi} \int P_{VT}^{sl}(\Omega) d\Omega = \frac{1}{2} \int P_{VT}^{sl}(\theta) \sin\theta d\theta,$$

where the scattering probability is defined by ( $J_{|\Delta n|}$  is a Bessel function)

$$(11) \quad P_{VT}^{sl} = J_{|\Delta n|}^2(F_{VT}^{sl}).$$



Choosing the Morse potential

$$(12) \quad V(R) = D\{\exp[-2(R - R_0)/d] - 2\exp[-(R - R_0)/d]\},$$

( $D$  is the well depth,  $d$  and  $R_0$  are parameters) for describing the intermolecular interactions, one obtains the following expression for argument  $F_{VT}^{sl}$

$$(13) \quad \begin{aligned} F_{VT}^{sl} &= \varepsilon_m^{1/2} \frac{\pi d}{2\hbar} \left[ b_r \omega_m \mu d - (2b_a - b_r)(2\mu D)^{1/2} \right] \times \\ &\times \exp \left( -\frac{\omega_m \mu d}{p_m \sin(\theta/2)} \arctan \sqrt{\frac{E_m}{D}} \sin(\theta/2) \right). \end{aligned}$$

Here  $b_a$  and  $b_r$  are the potential anisotropy parameters,  $p_m$  is the momentum of the relative motion

$$(14) \quad p_m = \mu v_m = \sqrt{\frac{2E_m}{\mu}},$$

and  $\varepsilon_m$  is defined by

$$(15) \quad \varepsilon_m = \frac{E_{n_i} + E_{n_f}}{2\hbar\omega_e}.$$

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

$$(16) \quad \bar{P}_{VT}^f = \frac{2\pi d^2}{\sigma_E} \int_{x_0}^{\infty} x \left[ 1 - \frac{D}{E_m} e^{-(x-x_{00})} (e^{-(x-x_{00})} (1-x) - 2+x) \right] J_{|\Delta n|}^2(F_{VT}^f(x)) dx,$$

where  $x_0$  and  $x_{00}$  are given by

$$(17) \quad x_0 = x_{00} - \ln(1 + \sqrt{1 + E_m/D}), \quad x_{00} = R_0/d,$$

and the argument of the Bessel function by

$$(18) \quad F_{VT}^f(x) = \frac{Dd}{v_m \hbar} \sqrt{\pi x \varepsilon_m} e^{-(x-x_{00})} (b_r e^{-(x-x_{00})} - 2\sqrt{2}b_a).$$

Furthermore, the elastic cross section

$$(19) \quad \sigma_E = \pi \sigma^2 \left( 2 \left( \frac{5\pi \varepsilon \sigma}{4\hbar v_m} \right)^{2/5} + 1 + \frac{1}{6} \left[ 1 + \ln \left( \sqrt{6\pi} \frac{4\varepsilon}{E_m + 4\pi\varepsilon} \right) \right] \right),$$

have been computed for the Lennard-Jones potential

$$(20) \quad V(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right].$$

The Lennard-Jones potential is correlated with Morse potential. Thus, parameters of the Lennard-Jones potential are:  $\varepsilon = D$  and  $\sigma = R_0/2^{1/6}$ , where  $D$  and  $R_0$  are the parameters of the Morse potential.

For intermediate collisions the probability is obtained by the interpolation of probabilities for slow and fast collisions in the following way

$$(21) \quad \bar{P}_{VT}^{int} = \exp \left[ \frac{\lambda_m - \lambda_2}{\lambda_2 - \lambda_1} \ln(\bar{P}_{VT}^f(v_m(\lambda_1))) + \frac{\lambda_1 - \lambda_m}{\lambda_2 - \lambda_1} \ln(\bar{P}_{VT}^s(v_m(\lambda_2))) \right].$$

To ensure the monotonicity of the global probability, we may modify, if it is necessary, the value of  $\lambda_2$ .

Finally, the elastic collision frequency  $\tau$  in formula (4), is computed with the Lennard-Jones potential [11]

$$(22) \quad \tau^{-1} = 4N\sigma^2 \left[ \pi^{0.9} \Gamma(1, 8) \left( \frac{2kT}{\mu} \right)^{0.3} \left( \frac{5\varepsilon\sigma}{4h} \right)^{0.4} + \frac{1}{2} \sqrt{\frac{2\pi kT}{\mu}} \left( 1 + \frac{1}{6} \left( 1 - \ln \left( \pi + \frac{3kT}{8\varepsilon} \right) \right) \right) \right].$$

**Remark 2.1** In the previous formulas,  $F_{VT}$  is a part of the classical action increment that is calculated along the classical trajectory. For the potential

$$V(R, \phi) = V_0(R) + V_1(R) \cos \phi$$

where  $\phi$  is the oscillator phase, the action increment may be written in the form

$$\frac{S}{\hbar} = \frac{S_0}{\hbar} + F_{VT} \cos \phi$$

Here  $\hbar F_{VT}$  is an integral of  $V_1$  along the classical trajectory. For slow collisions the a-head trajectories are responsible for  $F_{VT}$ , while for fast ones the straightforward trajectories are responsible for  $F_{VT}$ .

**Remark 2.2** In this remark, we show the relation between the scattering probability and the cross-section.

The cross-section  $\sigma$  may be written as [17]

$$(23) \quad \frac{d\sigma}{d\Omega} = |f|^2,$$

where the scattering amplitude  $f$  is related to the  $T$ -matrix [19] by the following equation

$$(24) \quad f = -\frac{\mu}{2\pi} T.$$

Factorizing the  $T$ -matrix such as

$$(25) \quad T = T_0 \Gamma,$$

where  $T_0$  and  $\Gamma$  are elastic and inelastic contribution, respectively, the cross-section is written [10]

$$(26) \quad \frac{d\sigma}{d\Omega} = \left(\frac{\mu}{2\pi}\right)^2 |T_0|^2 |\Gamma|^2 = \frac{d\sigma_E}{d\Omega} P.$$

In the last equality,  $P$  is the scattering probability, defined as  $P = |\Gamma|^2$ . The elastic cross-section  $d\sigma_E/d\Omega$  varies slowly compared with  $P$ , which allows to write the last equation as

$$(27) \quad \frac{d\sigma}{d\Omega} = \frac{\sigma_E}{4\pi} P.$$

Finally, after integration we obtain

$$(28) \quad \sigma = \frac{\sigma_E}{2} \int_0^\pi P \sin\theta d\theta = \frac{\sigma_E}{2} \bar{P}.$$

Before ending this section, we want to point out that, due to the lack of information about the part of the intermolecular potential responsible for the inelastic collisions, parameters  $b_a$  and  $b_r$  in formulas (10) and (16) may be used as two fitting parameters. We determine these parameters in such a way that the rate constants, for the essential transition, computed with formula (4) are in good agreement with the results obtained for trajectory calculations by Billing-Fisher et als. [4] [6] [12]. They propose numerical data in the temperature range 200-8000K, which allow us to compute the corresponding rate constants for slow collisions. Here, we use a numerical integration to compute formula (4). Figures (1-A-...-D) show the comparison between rate constants computed by Billing-Fisher [6] [12] and those computed with formula (4) with the inelastic scattering probability given by (10). The difference is important for low temperatures. As mentioned by Gorbachev et al. [15], rate constants computed using trajectory calculations are sensitive to the method of approximation of potential surface and accuracy of calculations falls down with decreasing temperature. The isotropic parameters are chosen to be  $b_a = 0.3$  and  $b_r = 0.3$ . These parameters will be fixed for all numerical computations.

### 3 Analytical approximations of VT transition probabilities for slow collisions

As it can be seen from formulas (4), (10) and (16), 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 DSMC or hydrodynamic solvers. The main difficulty in deriving some analytical formulas is the Bessel function which appears in the definition of both slow and fast collisions. In the case of slow collisions [9], when  $\lambda_m \gg 1$ , the

argument of Bessel function is such that  $F_{VT}^{sl} \ll 1$ . As a consequence we can approximate Bessel function by the first term of its expansion. Thus we write

$$(29) \quad J_{|\Delta n|}^2(F_{VT}^{sl}(n)) \approx \frac{1}{\Gamma(|\Delta n| + 1)} \left( \frac{F_{VT}^{sl}(n)}{2} \right)^{2|\Delta n|}.$$

Substituting expression (29) in (10), we write

$$(30) \quad \bar{P}_{VT}^{sl} = \frac{1}{2} \int_0^\pi \left( \frac{F_{VT}^{sl}}{2} \right)^{2|\Delta n|} \frac{1}{\Gamma^2(|\Delta n| + 1)} \sin\theta d\theta.$$

In order to simplify the preceding expression, we introduce the following notations

$$(31) \quad A_{VT} = \frac{G_{VT}}{\Gamma^2(|\Delta n| + 1)} \left( \frac{\pi d}{4\hbar} \left[ b_r \omega_m \mu d - (2b_a - b_r)(2\mu D)^{1/2} \right] \right)^{2|\Delta n|},$$

where

$$(32) \quad G_{VT} = \varepsilon_m^{|\Delta n|}.$$

Thus (30) becomes

$$(33) \quad \bar{P}_{VT}^{sl} = \frac{A_{VT}}{2} \int_0^\pi \exp \left( -\frac{2|\Delta n| \lambda_m}{\sin(\theta/2)} \left( \arctan \sqrt{\frac{E_m}{D}} \sin(\theta/2) \right) \right) \sin\theta d\theta.$$

As it was done by Gorbachev et al [11] for similar expressions, we use the Laplace method to integrate formula (33). Using the changes of variables  $x = \sin(\theta/2)$  and  $y = 1/x$ , we rewrite formula (33) as

$$(34) \quad \bar{P}_{VT}^{sl} = 2A_{VT} \int_1^\infty y^{-3} \exp \left( -2|\Delta n| \lambda_m y \arctan \left( \sqrt{\frac{E_m}{D}} \frac{1}{y} \right) \right) dy,$$

or

$$(35) \quad \bar{P}_{VT}^{sl} = 2A_{VT} \int_1^\infty y^{-3} e^{\psi(y)} dy,$$

where

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

As the main contribution of integral (34) is in a neighbourhood of the point 1, we expand the function  $\psi$  at the first order around this point. The first derivative of  $\psi$  is given by

$$(36) \quad \psi' = -2|\Delta n| \lambda_m \left[ \arctan \left( \sqrt{\frac{E_m}{D}} \frac{1}{y} \right) - \frac{\sqrt{E_m D} y}{y^2 D + E_m} \right].$$

The Laplace method leads to the following final expression of integral (34)

$$(37) \quad \bar{P}_{VT}^{sl} = -\frac{2A_{VT}e^{\psi(1)}}{\psi'(1)},$$

$$(38) \quad \begin{aligned} \bar{P}_{VT}^{sl} &= A_{VT} \left[ \lambda_m |\Delta_n| \left( \arctan \sqrt{\frac{E_m}{D}} - \frac{\sqrt{DE_m}}{D + E_m} \right) \right]^{-1} \times \\ &\times \exp \left( -2\lambda_m |\Delta_n| \arctan \sqrt{\frac{E_m}{D}} \right). \end{aligned}$$

We give now a second approximation for the scattering probability for slow collisions. We start from rewriting exact formula (10) as

$$(39) \quad \begin{aligned} \bar{P}_{VT}^{sl} &= \frac{1}{2} \int_0^\pi J_{|\Delta_n|}^2(F_{VT}^{sl}(\theta)) \sin(\theta) d\theta, \\ &= \frac{1}{2} \int_0^\pi \exp \left( \log(J_{|\Delta_n|}^2(F_{VT}^{sl}(\theta))) \right) \sin(\theta) d\theta. \end{aligned}$$

Using the previous changes of variables, equation (39) can be written

$$(40) \quad \bar{P}_{VT}^{sl} = 2 \int_0^\infty y^{-3} \exp(2 \log(J_{|\Delta_n|}(F_{VT}^{sl}(y)))) dy = 2 \int_0^\infty y^{-3} e^{\psi(y)} dy,$$

where, now, the function  $\psi$  is

$$(41) \quad \psi = 2 \log(J_{|\Delta_n|}(F_{VT}^{sl}(y))).$$

With obvious notations,  $F_{VT}^{sl}(y)$  can be written as

$$(42) \quad F_{VT}^{sl}(y) = A_F \exp \left( -\lambda_m y \arctan \left( \sqrt{\frac{E_m}{D}} \frac{1}{y} \right) \right).$$

Thus, the first derivative of  $\psi$  is written

$$(43) \quad \psi'(y) = 2 \frac{J'_{|\Delta_n|}(F_{VT}^{sl}(y))}{J_{|\Delta_n|}(F_{VT}^{sl}(y))} F_{VT}^{sl}(y).$$

Knowing that

$$(44) \quad F_{VT}^{sl}(y) = -\lambda_m \left[ \arctan \left( \sqrt{\frac{E_m}{D}} \frac{1}{y} \right) - \frac{\sqrt{E_m D} y}{y^2 D + E_m} \right] F_{VT}^{sl}(y),$$

and

$$(45) \quad J'_{|\Delta n|}(z) = \frac{|\Delta n|}{z} J_{|\Delta n|}(z) - J_{|\Delta n|+1}(z),$$

we deduce the final expression for the first derivative of  $\psi$

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

Since for  $F_{VT}^{sl} \leq 1$ , we have

$$\frac{|\Delta n|}{F_{VT}^{sl}(1)} \gg \frac{J_{|\Delta n|+1}(F_{VT}^{sl}(1))}{J_{|\Delta n|}(F_{VT}^{sl}(1))},$$

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

$$(46) \quad \psi'(1) = -2\lambda_m |\Delta n| \left[ \arctan \left( \sqrt{\frac{E_m}{D}} \right) - \frac{\sqrt{E_m D}}{D + E_m} \right].$$

Finally, the Laplace method of integration leads to the following approximation for  $\bar{P}_{VT}^{sl}$

$$(47) \quad \bar{P}_{VT}^{sl} = J_{|\Delta n|}^2(F_{VT}^{sl}) \left[ \lambda_m |\Delta n| \left( \arctan \sqrt{\frac{E_m}{D}} - \frac{\sqrt{D E_m}}{D + E_m} \right) \right]^{-1}.$$

We will refer to this approximation as approximation A2.

It is possible to derive a simple approximation for low energies such as  $E_m \ll D$ . In this case individual scattering probabilities don't depend on scattering angle  $\theta$  in formula (13) and integration (10) becomes trivial. But in this paper we don't consider such regime.

Figures (2A-...-D) show comparisons of inelastic scattering probability for slow collisions, computed with formula (4) using a numerical integration, for approximations A1 and A2. We have considered different one level transitions. We notice that approximation A2 is not really better. On figure (3A-...-D), we consider the same comparison for 2-4-6 and 8 level transitions. In this case, approximation A2 is better than A1 as the transition level increases. Finally, figure (4a-...-D) represents a comparison of inelastic scattering probability, computed with a numerical integration, for fast, slow and intermediate collisions. In the zone of intermediate collisions (the middle zone delimited by dashed lines) the probability is obtained by interpolation of fast and slow collisions according to formula (21). 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 formula (6) substituting  $\lambda_m$  by  $\lambda_2$  and  $\lambda_1$  respectively. As the quantum level increases the influence of fast collisions becomes stronger.

## 4 Analytical approximations of VT rate constants for slow collisions

In this section we derive analytical formulas for rate constants of slow collisions using the steepest descent method [9]. Here, we will consider only de-excitation processes, when  $\Delta E < 0$ . Now, introducing a first approximation for transition probability (38) in (4), the rate constants are written as

$$(48) \quad K_{n_i, n_f} = \frac{\tau^{-1} A_{VT}}{N (kT)^2} \int_0^\infty (E_i E_f)^{1/2} \left[ \lambda_m |\Delta_n| \left( \arctg \sqrt{\frac{E_m}{D}} - \frac{\sqrt{D E_m}}{D + E_m} \right) \right]^{-1} \times \\ \times \exp \left( -2 \lambda_m |\Delta_n| \arctg \sqrt{\frac{E_m}{D}} \right) \exp \left( -\frac{E_i}{kT} \right) dE_i,$$

We proceed now with an appropriate change of variables. Due to the energy conservation one has

$$(49) \quad E_f = E_i - \Delta E.$$

Let's define the variable  $p$  as

$$(50) \quad p = \sqrt{\frac{E_m}{kT}} = \sqrt{\frac{E_i}{kT} - \frac{\Delta E_*}{2}},$$

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

$$(51) \quad E_i = kT \left( p^2 + \frac{\Delta E_*}{2} \right), \quad E_f = kT \left( p^2 - \frac{\Delta E_*}{2} \right).$$

Using the change of variables (50), equation (48) becomes

$$(52) \quad K_{n_i, n_f} = \frac{\tau^{-1} A_{VT} \sqrt{kT}}{N a_m} e^{-\Delta E_*/2} \int_{\sqrt{-\Delta E_*/2}}^\infty \sqrt{p^4 - (\Delta E_*/2)^2} \times \\ \times \left( \arctan \left( \frac{p}{\sqrt{D_*}} \right) - \frac{p \sqrt{D_*}}{p^2 + D_*} \right)^{-1} \exp \left[ -p^2 - \frac{a_m}{p \sqrt{kT}} \arctan \left( \frac{p}{\sqrt{D_*}} \right) \right] p^2 dp,$$

where we have used the notations

$$(53) \quad \lambda_m |\Delta_n| = \frac{a_m}{p \sqrt{kT}}, \quad a_m = d\omega_m |\Delta_n| \sqrt{2\mu}, \quad D_* = \frac{D}{kT}.$$

We rewrite formula (52) as

$$(54) \quad K_{n_i, n_f} = \frac{\tau^{-1}}{N} 2A_{VT} \frac{\sqrt{kT}}{a_m} e^{-\Delta E_*/2} \int_{\sqrt{-\Delta E_*/2}}^{\infty} f(p) \exp(-g(p)) dp,$$

where

$$(55) \quad f(p) = \sqrt{p^2 - \Delta E_*/2} \left( \arctan \left( \frac{p}{\sqrt{D_*}} \right) - \frac{p\sqrt{D_*}}{p^2 + D_*} \right)^{-1} p,$$

and

$$(56) \quad g(p) = p^2 + \frac{a_m}{p\sqrt{kT}} \arctan \left( \frac{p}{\sqrt{D_*}} \right) - \frac{1}{2} \log (p^2 + \Delta E_*/2).$$

After a simple algebra we obtain the first and second derivative of  $g$ , written as

$$(57) \quad g'(p) = 2p - \frac{a_m}{\sqrt{kT}} \frac{1}{p^2} \arctan \left( \frac{p}{\sqrt{D_*}} \right) + \frac{a_m}{\sqrt{kT}} \frac{1}{p} \frac{\sqrt{D_*}}{p^2 + D_*} - \frac{p}{p^2 + \frac{\Delta E_*}{2}},$$

and

$$(58) \quad g''(p) = 2 + \frac{2a_m}{p^3\sqrt{kT}} \left( \arctan \left( \frac{p}{\sqrt{D_*}} \right) - \frac{2p(p^2 + D_*/2)\sqrt{D_*}}{(p^2 + D_*)^2} \right) + \frac{p^2 - \Delta E_*/2}{(p^2 + \Delta E_*/2)^2}.$$

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

$$(59) \quad g(p) = g(p_0) + \frac{g''(p_0)}{2}(p - p_0)^2 + \dots$$

Substituting (59) in (54) one gets

$$(60) \quad K_{n_i, n_f} = \frac{\tau^{-1}}{N} 2A_{VT} \frac{\sqrt{kT}}{a_m} e^{-g(p_0) - \Delta E_*/2} f(p_0) \int \exp \left( -\frac{g''(p_0)}{2}(p - p_0)^2 \right) dp.$$

After the integration, this formula may be written as

$$(61) \quad K_{n_i, n_f} = \frac{\tau^{-1}}{N} 4A_{VT} \frac{p_0^4}{a_m} \sqrt{\frac{2\pi kT}{g''(p_0)}} \frac{(1 - (\Delta E_{**}/2)^2)^{1/2}}{\left( \arctan(1/\sqrt{D_{**}}) - \frac{\sqrt{D_{**}}}{1 + D_{**}} \right)} \times \\ \times \exp \left[ -p_0^2 - \frac{a_m}{p_0\sqrt{kT}} \arctan \left( \frac{1}{\sqrt{D_{**}}} \right) - \Delta E_*/2 \right],$$



where  $\Delta E_{**} = \Delta E_*/p_0^2$  and  $D_{**} = D_*/p_0^2$ .

For some asymptotic regimes, it is possible to derive an explicit expression for  $p_0$ .

Considering the Landau-Teller regime:  $E_m \gg D$ ,  $|\Delta E|$  which is equivalent to  $p \gg \sqrt{D_*}$ ,  $|\Delta E_*|$ , equation  $g' = 0$ , with LHS from (57), may be reduced to the following equation

$$(62) \quad 2p_{LT}^2 - \frac{\pi}{2} \frac{a_m}{\sqrt{kT} p_{LT}} = 0.$$

Its solution is

$$(63) \quad p_{LT} = \left( \frac{\pi}{4} \frac{a_m}{\sqrt{kT}} \right)^{1/3}.$$

It shows that our formula is an extension of Landau-Teller formula taking into account an attractive part of molecular interaction and threshold effects (see [14]). Considering a first order solution,  $p_0$  is written as

$$(64) \quad p_0 = p_{LT}(1 + x).$$

Substituting this expression in (57) and considering the first order approximation, one has

$$(65) \quad p_0 = \left( \frac{\pi a_m}{4\sqrt{kT}} \right)^{1/3} + \frac{4\sqrt{D_*}}{3\pi} - \frac{1}{6} \left( \frac{4\sqrt{kT}}{\pi a_m} \right)^{1/3}.$$

From equation (63), it is clear that  $E_{LT} = kT p_{LT}^2$  decreases up to zero while temperature decreases. On the other hand, as it 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

$$(66) \quad p_0 = \sqrt{\frac{-\Delta E_*}{2}} (1 + y),$$

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

$$(67) \quad p_0 = \sqrt{\frac{-\Delta E_*}{2}} \left( 1 - \frac{2}{\Delta E_*} \right).$$

This formula is valid for lower temperatures than formula (65). The critical temperature  $T_\Delta$ , that separates this two regimes, may be obtained by equating expressions for  $p_0$  (64) and (66). After some reductions  $T_\Delta$  is written as

$$(68) \quad kT_\Delta = \frac{4}{\pi a_m} \left( \frac{-\Delta E}{2} \right)^{1/3} \left( 1 + 7 \frac{\sqrt{-\Delta E}}{\pi a_m} \frac{1 + \frac{4a_m\sqrt{D}}{7\Delta E}}{1 - 5 \frac{\sqrt{-2\Delta E}}{\pi a_m}} \right).$$

Thus, for  $T > T_\Delta$ , formula (65) is valid and for  $T < T_\Delta$  formula (67). In numerical computations, we use only formula (65) because  $T_\Delta$  is always very small.

Using the previous results, we may derive a characteristic temperature  $T_{sl}$  under which the rate constants for slow collisions are valid. In order to determine  $T_{sl}$ , we write

$$(69) \quad \lambda_2 = \frac{a_m}{\sqrt{kT}|\Delta n|p}.$$

Substituting  $p$  by the Landau-Teller approximation (63), one obtains

$$(70) \quad kT_{sl} = \frac{8\mu(d\omega_m)^2}{\pi|\Delta n|\lambda_2^3}.$$

Using the same method of integration, the VT rate constants corresponding to approximation A2 for inelastic scattering probability may be written as

$$(71) \quad K_{n_i, n_f} = \frac{\tau^{-1}}{N} 4J_{|\Delta n|}^2(F_{VT}(p_0)) \frac{p_0^4}{a_m} \sqrt{\frac{2\pi kT}{g''(p_0)}} \frac{\left(1 - \left(\frac{\Delta E_{**}}{2}\right)^2\right)^{1/2}}{\left(\arctan\left(\frac{1}{\sqrt{D_{**}}}\right) - \frac{\sqrt{D_{**}}}{1 + D_{**}}\right)} \times \\ \times \exp\left(-p_0^2 - \frac{\Delta E_*}{2}\right).$$

In the previous formula,  $p_0$  and  $g''(p_0)$  are the same as for the rate constants corresponding to approximation A1.

We give below some numerical results. Figure (5A-...-D) shows a comparison of rate constants for slow collisions computed with a numerical integration (trapezoidal method) and approximation A1 (61) and A2 (71). In all cases, approximation A2 is in better agreement with result obtained by numerical integration. Furthermore, we notice that the comparison is better for low quantum numbers. We recommend therefore to use approximation A2 for computing VT rate constants for slow collisions for temperatures where approximation A1 breaks down.

Figure (6) presents VT rate constants as function of quantum level for different temperatures. The dashed lines show the rate constants corresponding to approximation A1 with  $p_0$  computed with the approximate formula (65), and the continuous line with  $p_0$  computed using the Newton method for the solution of equation (57). The approximate formula (65) gives good results for all temperatures. The agreement with Billing-Fisher's numerical results (circles) obtained using trajectory calculations, as already mentioned, 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 1000K and 6000K, we present the rate constants computed for slow collisions using a numerical integration. For the temperature 1000K, the numerical values obtained with approximations A1 and A2 are in a good agreement with the values obtained with the integral formula and does not depend on the quantum level. This is of course true for lower

temperatures. Unfortunately, this conclusion is not valid for the temperature of 6000K, and consequently for higher temperatures. In this case, the difference increases when the quantum level increases.

Figure (7A-...-D) shows a comparison between rate constants computed with slow collisions only and fast, intermediate and slow collisions. Only one-level transitions were considered. The comparison is good for low temperatures what was predictable. For high temperatures, the importance of fast collisions is evident. Considering only slow collisions, rate constants overpredicts vibrational transitions.

## 5 Comparison with Adamovich's VT model

In this section, we present the VT rate constants derived by Adamovich et al. [1], [2], [3] using the results of paper [1]. We give also some numerical comparisons with VT rate constants derived by Gorbachev et al..

The theory used by Adamovich et al. is the Forced Harmonic Oscillator theory [16], [21] (FHO). This is a semiclassical non-perturbative analytical method for one dimensional problem. Several modifications were introduced in order to take into account some realistic effects such as non-collinear collisions and anharmonicity. The approximate scattering probabilities for VT transition from level  $n_i$  to final level  $n_f$  may be written as [1]:

$$(72) \quad P_{VT}(n_i \rightarrow n_f, \varepsilon) = J_s^2 \left[ 2(n_s \varepsilon)^{1/2} \right],$$

where

$$s = |n_i - n_f|, \quad n_s = \max \left( \frac{i!}{f!}, \frac{f!}{i!} \right),$$

and  $\varepsilon$  is a function dependent on the frequency, the arithmetic average of initial and final collision velocities and the steric factor  $S_{VT}$  (which is a constant). This steric factor was introduced to take into account the non-collinear nature of molecular collisions. It has a phenomenological meaning and is determined by comparison with the probability of the essential transition obtained by 3D trajectory calculations [4] [6] [12].

Averaging the probabilities (72) over Maxwellian translational energy distribution and using the steepest descent method to evaluate the resulting integral, the VT rate constant is written as

$$(73) \quad K_{n_i, n_f} = \text{Zexp} \left( \frac{\theta s}{2T} \right) C_{VT} \left( S_{VT} \frac{\theta'}{|\theta|} \right)^s \left( \frac{\theta'}{T} \right)^{1/6} n_s \left( \frac{2\pi}{\delta} \right)^{1/2} \frac{s^{1/3}}{(s!)^2} \\ \exp \left[ -s^{2/3} \left( \frac{\theta'}{T} \right)^{1/3} \left( 1 - \frac{2}{\pi} \arctan(\phi) \right)^2 \left( \frac{C_{VT}^2}{2} + \frac{1}{C_{vt}} \right) - s(1 - C_{VT}^3) \right],$$

where

$$V_{mo} = \left( \frac{2\pi\omega s k T}{\alpha\mu} \right)^{1/3},$$

$$\begin{aligned}\theta' &= \frac{4\pi\omega^2\mu}{\alpha^2k}, & \theta &= \frac{\Delta E}{sk}, & \Delta E &= \varepsilon_{n_i} - \varepsilon_{n_f}, \\ \delta &= 3 + \frac{1 - C_{VT}^3}{C_{VT}^3} \times \frac{2\pi\omega}{\alpha V_{mo} C_{VT}}, \\ \phi &= \sqrt{\frac{2Dk}{\mu V_{mo}^2}},\end{aligned}$$

and

$$(74) \quad C_{VT} = \left[ 1 - \frac{S_{VT}}{s} \frac{\theta'}{|\theta|} \left( \frac{2n_s^{1/s}}{s+1} + 1 \right) \exp\left(-\frac{2\pi\omega}{\alpha V_{mo} C_{VT}}\right) - \frac{2}{s(s+2)} \left[ \frac{n_s^{1/s}}{s+1} S_{VT} \frac{\theta'}{|\theta|} \right]^2 \exp\left(-\frac{4\pi\omega}{\alpha V_{mo} C_{VT}}\right) \right]^{1/3}.$$

In these formulas,  $V_{mo}$  is the Landau-Teller most effective velocity,  $\alpha$  and  $D$  are the exponential repulsive parameter and the well depth of the Morse potential, respectively, and  $\mu = m_{N_2}/2$  is the reduced mass of colliding particles. Finally  $Z$  is the ratio of an elastic frequency and the number density. The dimension of the forward rate coefficient is *meter<sup>3</sup>/second*.

To take into account anharmonicity effects, the following mean frequency approximation is used

$$(75) \quad \omega = \begin{cases} \frac{\Delta E}{\hbar s} & \text{if } s \neq 0, \\ \frac{\Delta E}{\hbar} & \text{if } s = 0. \end{cases}$$

It should be noted that the following approximation for Bessel functions was used to compute the integral formula for VT rate constants

$$(76) \quad J_s(z) = \left(\frac{z}{2}\right)^s \frac{1}{s} \exp\left(-\frac{z^2}{4(s+1)}\right).$$

The importance of this approximation can be observed on the following numerical results.

First, we have computed the VT rate constants for one-level transitions  $N_2(L) + N_2 \rightarrow N_2(L-1) + N_2$  (fig (8)) with  $L = 1$  (A),  $L = 9$  (B),  $L = 20$  (C) and  $L = 30$  (D). The VT rate constant is a function of the temperature. Note that Adamovich's rate constants are in a good agreement with Billing-Fisher's numerical results for low temperatures. This good result is because of an appropriate choice of the steric factor  $S_{VT} = 1/2$ . Gorbachev's VT rate constants have been computed using the integral formula (4) with different definitions of the scattering probabilities for slow, intermediate and fast collisions. For high temperatures, both numerical results are comparable.

This good agreement disappears when considering multi-level transition  $N_2(L) + N_2 \rightarrow N_2(L-j) + N_2$  with  $j > 1$ . Figures (9,A-B) show VT rate constants computed for  $j = 3$  and

$j = 5$  respectively. For high temperatures the agreement is bad and the difference increases as  $j$  increases. This may be due to the fact that Gorbachev uses 3D collision models, and also because the approximation (76) which is not valid for multi-level transitions (large  $s$ ).

This observation is confirmed by the next numerical results. Figure (10) shows the dependence of the VT rate constants upon quantum level  $L$ , for the different reactions  $N_2(L) + N_2 \rightarrow N_2(L - j) + N_2$  for  $j = 1, 3, 5$  and for different temperatures. The difference between Adamovich's and Gorbachev's rate constants increases again when  $j$  increases.

## 6 The rate constants for VV transitions

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

A VV inelastic collision of two diatomic molecules leads to vibration energy exchange between both molecules. If we denote by  $E_{n_{1i}}$ ,  $E_{n_{2i}}$ , and  $E_{n_{1f}}$ ,  $E_{n_{2f}}$  the energy of particles 1 and 2 before and after a collision respectively, the energy conservation law is written

$$(77) \quad E_{n_{1i}} + E_{n_{2i}} = E_{n_{1f}} + E_{n_{2f}}.$$

The frequency and energy are given by formulas (1) and (2) respectively. Considering again the mean frequency approximation, we write

$$(78) \quad \begin{aligned} \omega_m^+ &= \frac{\omega_i^+ + \omega_f^+}{2}; & \omega_k^+ &= |\omega_{1k} + \omega_{2k}|, & k &= i, f, \\ \omega_m^- &= \frac{\omega_i^- + \omega_f^-}{2}; & \omega_k^- &= |\omega_{1k} - \omega_{2k}|, & k &= i, f, \end{aligned}$$

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

As for VT collisions, we define adiabatic parameters

$$(79) \quad \lambda_m^\pm = \frac{\omega_m^\pm d}{v_m}.$$

The parameter  $\lambda_m^+$  is less to 1 only for very high velocities. In our case, we are not interested in such high velocities and we will restrict ourself 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 [14]. In this case the transitions verify

$$(80) \quad \Delta n_1 = -\Delta n_2,$$

where  $\Delta n_k = n_{kf} - n_{ki}$  with  $k = 1, 2$ .

Depending on the adiabatic parameter  $\lambda_m^-$ , the collisions are classified in three groups

Slow collisions:  $\lambda_m^- > \lambda_2^- > 1$ ,

Fast collisions:  $\lambda_m < \lambda_1^- < 1$ ,

Intermediate collisions: the other cases.

For slow collisions, the average scattering probabilities are written

$$(81) \quad \bar{P}_{VV}^{sl} = \frac{1}{2} \int_0^\pi P_{VV}^{sl}(\theta) \sin\theta d\theta.$$

The scattering probabilities are written as

$$(82) \quad P_{VV}^{sl} = J_{\kappa_-}^2(F_{VV}^{sl}),$$

where

$$(83) \quad \begin{aligned} F_{VV}^{sl} &= \varepsilon_{mn}^{1/2} \frac{\pi d}{2\hbar} \left[ c_r \omega_m^- \mu d - (2c_a - c_r)(2\mu D)^{1/2} \right] \times \\ &\times \exp\left( -\frac{\omega_m^- \mu d}{p_m \sin(\theta/2)} \arctan \sqrt{\frac{E_m}{D}} \sin(\theta/2) \right). \end{aligned}$$

In this formula, we have used the following definitions,

$$(84) \quad \varepsilon_{mn} = \frac{\varepsilon_{n_1 m} \varepsilon_{n_2 m}}{4},$$

$$(85) \quad \varepsilon_{n_q m} = \frac{E_{n_q i} + E_{n_q f}}{2\hbar\omega_e}; \quad q = 1, 2,$$

$$(86) \quad \kappa_- = \frac{|\Delta n_1 - \Delta n_2|}{2}.$$

For fast collisions, we write the scattering probabilities as

$$(87) \quad \bar{P}_{VV}^f = \frac{2\pi d^2}{\sigma_E} \int_{x_0}^{\infty} x \left[ 1 - \frac{D}{E_m} e^{-(x-x_{00})} (e^{-(x-x_{00})} (1-x) - 2+x) \right] J_{\kappa_-}^2(F_{VV}^f(x)) dx,$$

where  $x_0$  and  $x_{00}$  are given by

$$(88) \quad x_0 = x_{00} - \ln(1 + \sqrt{1 + E_m/D}), \quad x_{00} = R_0/d, \quad R_0 = \sigma_0 2^{1/6},$$

$$(89) \quad F_{VV}^f(x) = \frac{Dd}{v_m \hbar} \sqrt{\pi x \varepsilon_{n_1 m} \varepsilon_{n_2 m}} e^{-(x-x_{00})} (c_r e^{-(x-x_{00})} - 2\sqrt{2}c_a),$$

where  $\sigma_E$  is given by (19). For intermediate collisions, the scattering probabilities are determined by the interpolation formula (21).

For slow collisions, the average VV scattering probabilities can be approximate exactly as averaged VT scattering probabilities. In the case of slow collisions, we suppose that

$F_{VV}^{sl} \ll 1$  which allows us to replace Bessel functions by the first term of their expansion. The result of integration of (81), using the Laplace method, is formula (38), where  $A_{VT}$  should be replaced by  $A_{VV}$ ,  $\lambda_m$  by  $\lambda_m^-$  and  $|\Delta_n|$  by  $\kappa_-$ .  $A_{VV}$  is defined by

$$(90) \quad A_{VV} = \frac{G_{VV}}{\Gamma^2(\kappa_- + 1)} \left( \frac{\pi d}{4\hbar} \left[ c_r \omega_m^- \mu d - (2c_a - c_r)(2\mu D)^{1/2} \right] \right)^{2\kappa_-},$$

with

$$(91) \quad G_{VV} = \left( \frac{\varepsilon_{n_1 m} \varepsilon_{n_2 m}}{4} \right)^{\kappa_-}.$$

Using this approximation for the scattering probabilities, the VV rate constants are obtained by computing integral (4) by the steepest descent method. Thus VV rate constants corresponding to approximation A1, are written as ( $\Delta E < 0$ )

$$(92) \quad K_{n_{2i}, n_{2f}}^{n_{1i}, n_{1f}} = \frac{\tau^{-1}}{N} 4 A_{VV} \frac{p_0^4}{a_m} \sqrt{\frac{\pi k T}{2g''(p_0)}} \frac{(1 - (\Delta E_{**}/2)^2)^{1/2}}{\left( \arctan(1/\sqrt{D_{**}}) - \frac{\sqrt{D_{**}}}{1 + D_{**}} \right)} \times \\ \times \exp \left[ -p_0^2 - \frac{a_m}{p_0 \sqrt{kT}} \arctan \left( \frac{1}{\sqrt{D_{**}}} \right) - \Delta E_*/2 \right],$$

where

$$(93) \quad a_m = d \omega_m^- \kappa_- \sqrt{2\mu},$$

$$(94) \quad g''(p_0) = 2 + \frac{2a_m}{p_0^3 \sqrt{kT}} \left( \arctan \left( \frac{1}{\sqrt{D_{**}}} \right) - \frac{2(1 + D_{**}/2)\sqrt{D_{**}}}{(1 + D_{**})^2} \right) + \\ + \frac{1}{p^2} \frac{1 - \Delta E_{**}/2}{(1 + (\Delta E_{**}/2)^2)^2},$$

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

$$(95) \quad g'(p) = 2p - \frac{a_m}{\sqrt{kT}} \frac{1}{p^2} \arctan \left( \frac{p}{\sqrt{D_*}} \right) + \frac{a_m}{\sqrt{kT}} \frac{1}{p} \frac{\sqrt{D_*}}{p^2 + D_*} - \frac{p}{p^2 + \frac{\Delta E_*}{2}}.$$

Considering approximation A2, we may compute the following VV rate constants formula

$$(96) \quad K_{n_{2i}, n_{2f}}^{n_{1i}, n_{1f}} = \frac{\tau^{-1}}{N} 4 J_{\kappa_-}^2 (F_{VV}(p_0)) \frac{p_0^4}{a_m} \sqrt{\frac{2\pi k T}{g''(p_0)}} \frac{(1 - (\Delta E_{**}/2)^2)^{1/2}}{\left( \arctan(1/\sqrt{D_{**}}) - \frac{\sqrt{D_{**}}}{1 + D_{**}} \right)} \\ \exp(-p_0^2 - \Delta E_*/2),$$

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

## 7 Comparison with Adamovich's VV model

The VV rate constants derived by Adamovich et al. are based on the FHO theory (see section 5). They are written as follows

$$(97) \quad K_{n_{2i}, n_{2f}}^{n_{1i}, n_{1f}} = Z \frac{n_{s1} n_{s2}}{s!} \langle P_{1 \rightarrow 0}^{0 \rightarrow 1} \rangle^s \left[ 1 + 2 \frac{n_{s1}^{1/s} n_{s2}^{1/s}}{s+1} \langle P_{1 \rightarrow 0}^{0 \rightarrow 1} \rangle \right]^{-(s+1)} \frac{C(3-C)}{2},$$

where

$$n_{s1} = \max \left( \frac{i_1!}{f_1!}, \frac{f_1!}{i_1!} \right), \quad n_{s2} = \max \left( \frac{i_2!}{f_2!}, \frac{f_2!}{i_2!} \right),$$

$$s = |i_1 - f_1|$$

$$\langle P_{1 \rightarrow 0}^{0 \rightarrow 1} \rangle = \frac{S_{VV} \alpha^2 k T}{2 \omega^2 \mu},$$

$$\theta' = \frac{4 \pi^2 \mu \omega^2}{\alpha^2 k},$$

$$C = \exp \left( -\frac{4}{9} \left( \frac{\theta'}{T} \right) \frac{|\Delta E|}{2 \sqrt{2} E_m s} \right),$$

$$\Delta E = \varepsilon_{i1} + \varepsilon_{i2} - \varepsilon_{f1} - \varepsilon_{f2},$$

$$E_m = \frac{1}{2s} (|\varepsilon_{i1} - \varepsilon_{f1}| + |\varepsilon_{i2} - \varepsilon_{f2}|).$$

The frequency of the harmonic oscillator is replaced by the

$$\omega = \frac{\omega_1 + \omega_2}{2},$$

with

$$\omega_{1,2} = \begin{cases} \frac{|\varepsilon_{i1,2} - \varepsilon_{f1,2}|}{|i-f| \hbar}, & i \neq f \\ \frac{|\varepsilon_{i+11,2} - \varepsilon_{i1,2}|}{\hbar}. \end{cases}$$

The steric factor  $S_{VV}$  play the same role as  $S_{VT}$  for VT transitions. This parameter is determined in such a way that the FHO probabilities  $P(1, 0 \rightarrow 0, 1)$  match with the results of Billing-Fisher [4].

The first numerical results we give concern comparisons of VV rate constants derived by Adamovich et al., by Gorbachev et al., and Billing-Fisher, for low temperatures. Gorbachev's VV rate constants are computed with formula (4) using a numerical integration. Furthermore, we have performed the integration over the velocity domain associated to intermediate and fast collisions only and 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 constants computations. The values of the anisotropic parameters are:  $c_a = 0.0022$  and  $c_r = 0.0017$ . Figure (11) shows different one-level VV rate constants for low quantum numbers. Results obtained with Gorbachev's model is in a good agreement with Billing-Fisher. Compared with results obtained with Adamovich's model we note a small overprediction. Figure (12A-B-C) shows rate constants for one-level VV transitions but for higher quantum numbers. Gorbachev's and Adamovich's results are quite similar and in a good agreement with Billing-Fisher results. Figure (12D) presents rate constants for a two-level VV transitions. In this case both Gorbachev's and Adamovich's rate constants are lower than Billing-Fisher rate constants.

Figures (13) and (14) represent the VV rate constants computed previously but for higher temperatures. Unfortunately, we don't have numerical results for Billing-Fisher's model for this cases. We note a good agreement for low temperatures but a significant overprediction of Adamovich's rate constants for high temperatures. It is difficult to draw any conclusion. We can mention that Gorbachev's model take into account 3D trajectories which is not the case of Adamovich's model as already noted.

## 8 Implementation in an hydrodynamic code

We have shown in the previous sections the difficulty of derivation of a general analytical formula for VT and VV rate constants, valid for a large temperature range. The main difficulty is due to the impossibility to obtain a good approximation for the Bessel functions. Analytical formulas we have derived can only be applied for low-temperature regimes.

For high-temperature regimes no analytical formula exists. This is a major problem to compute master equations modeling vibrational relaxation. It is obvious that the use of integral formulas to compute VT and VV rate constants in master equations would lead, for any numerical method, to an excessive time of computation.

We suggest here the following approach for VT rate constants. For each transition from initial level  $n_i$  to final level  $n_f$ , the rate constant  $K_{n_i, n_f}(T)$  is computed for different temperatures. Then, the numerical values of  $K_{n_i, n_f}(T)$  (more precisely  $\ln(K_{n_i, n_f}(T))$ ) are interpolated using a 1D polynomial interpolation of order  $n$ . Finally, the  $(n + 1)$  coefficients which give the analytical approximation formula for the rate  $K_{n_i, n_f}(T)$  are stored. Repeating this procedure for appropriate VT transitions, we have a 3D array  $K(n_i, n_f, C_k)$ , where  $C_k$  are the coefficients of the interpolated formula for  $K_{n_i, n_f}$ .

Only the de-excitation rate constants ( $n_i > n_f$ ) have to be computed. Excitation rate constants ( $n_i < n_f$ ) are computed such that

$$(98) \quad K_{n_i, n_f} = K_{n_f, n_i} \exp\left(-\frac{\varepsilon_{n_f} - \varepsilon_{n_i}}{kT}\right),$$

which guarantees a perfect detailed balance.

To compute master equations, the array  $K(n_i, n_f, C_k)$  is read during initialization step, and analytical formulas resulting of interpolation are used to compute VT rate constants during time integration.

Concerning the polynomial interpolation, it is possible to use Tchebychev polynomials up to order the  $n = 9$ .

The same procedure may be applied to VV rate constants.

## 9 Conclusion

In this paper we have presented new formulas for VT and VV rate constants, based on the quasiclassical multidimensional scattering theory for polyatomic gases. The results of computation obtained with these formulas were compared with those of Adamovich and Billing-Fisher model for Nitrogen. Some difference exists between these models. Although if it is possible to analyze these difference from a theoretical point of view, we may regret the lack of experimental data.

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

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

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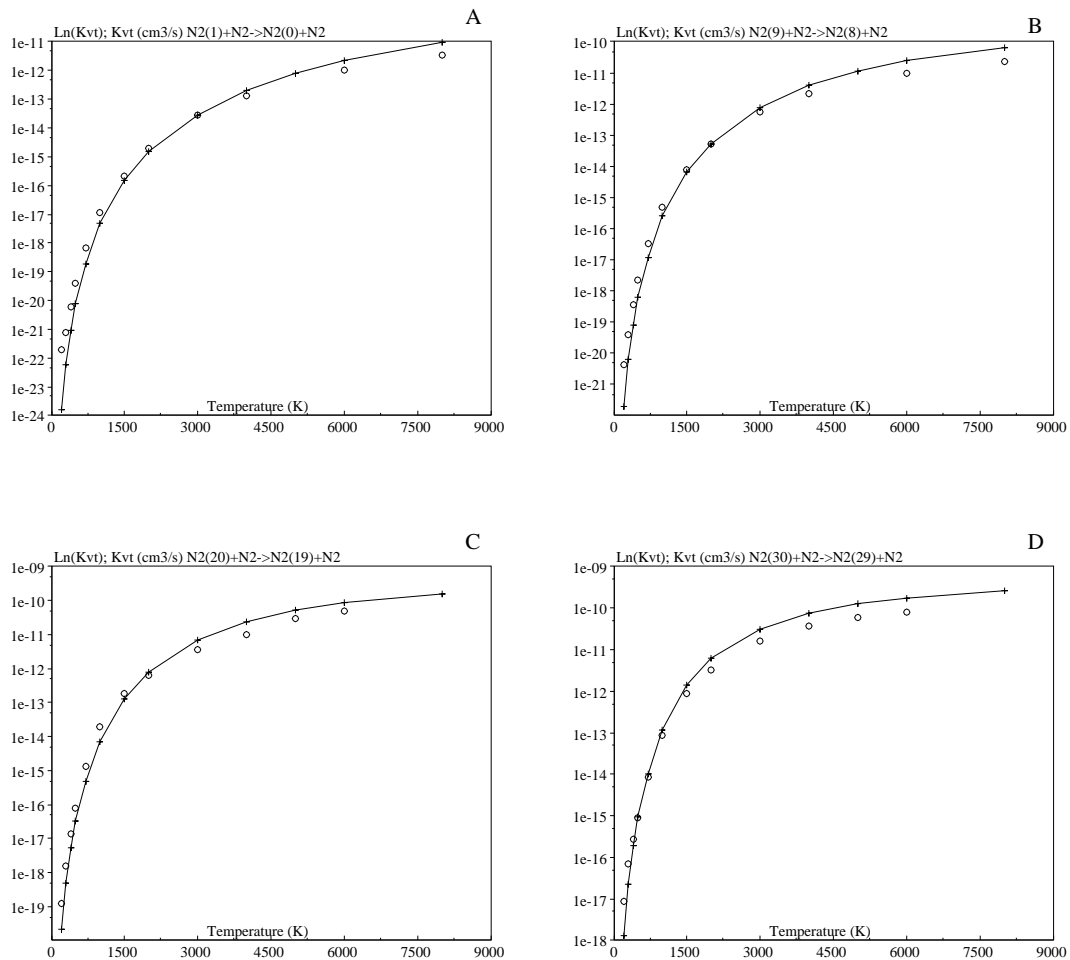


Figure 1: Comparison of rate constants computed by Billing-Fisher (circles) and formula (4) (crosses) with inelastic scattering probability given by (10) for different vibrational transitions.

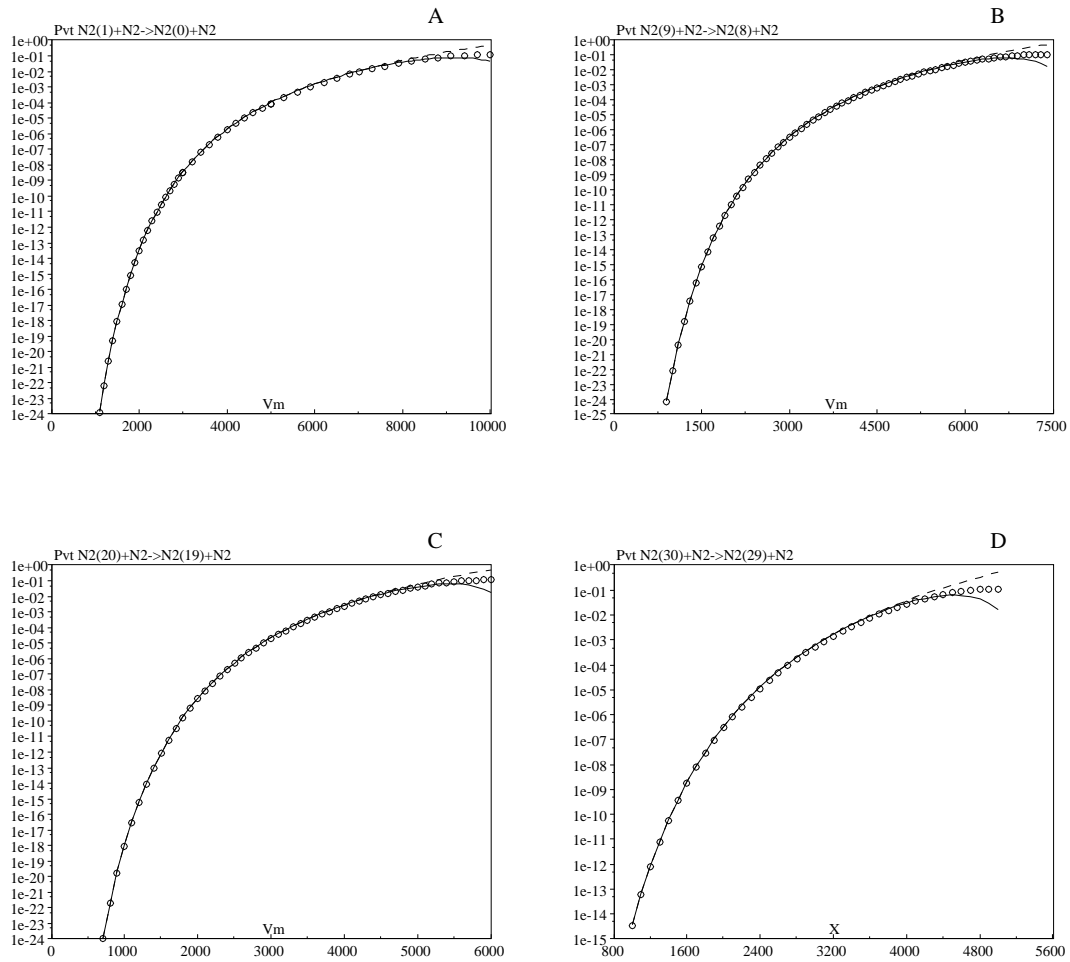


Figure 2: Comparison of inelastic scattering probability for slow collisions computed by formula (10) (circles) using a numerical integration and that by approximations A1 (dashed lines) and A2 (continuous line).

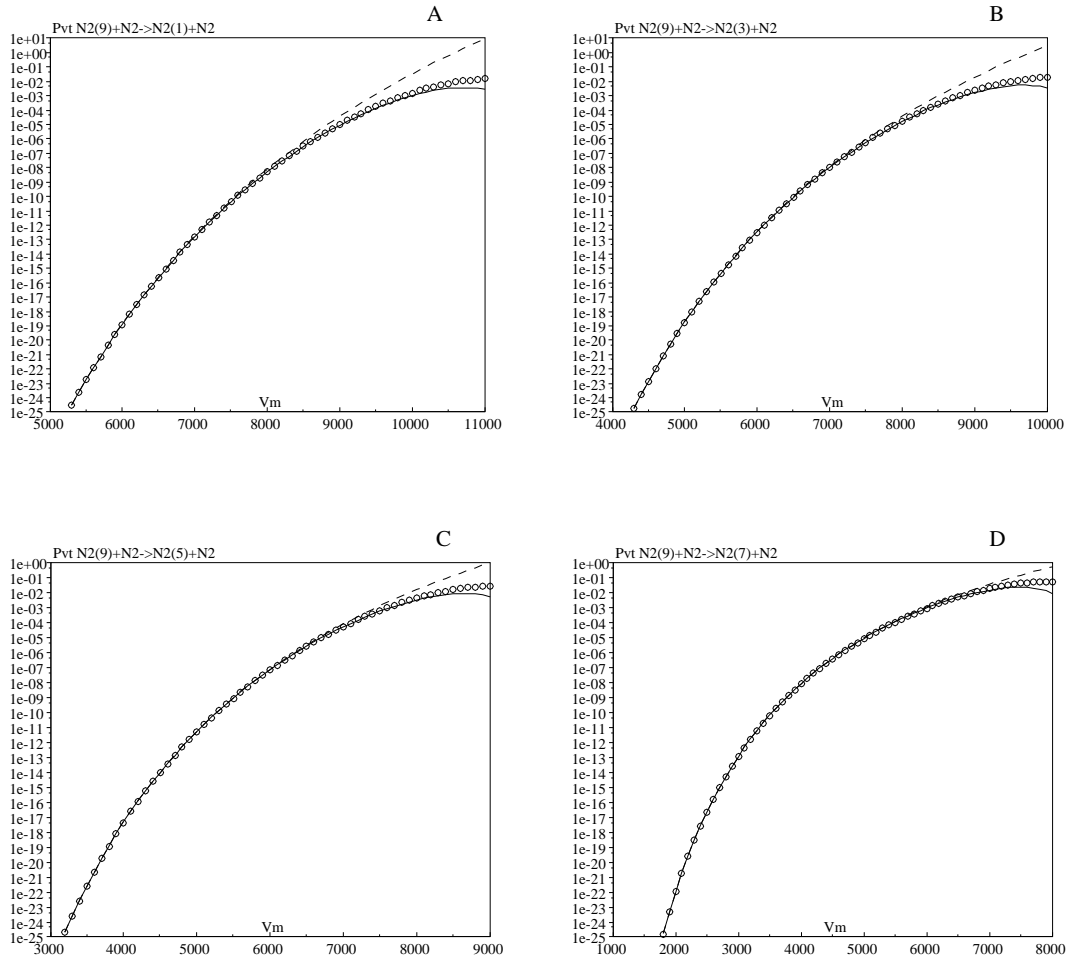


Figure 3: Comparisons of inelastic scattering probability for slows collisions computed by formula (10) (circles), using a numerical integration and that by approximations A1 (dashed lines) and A2 (continuous line).

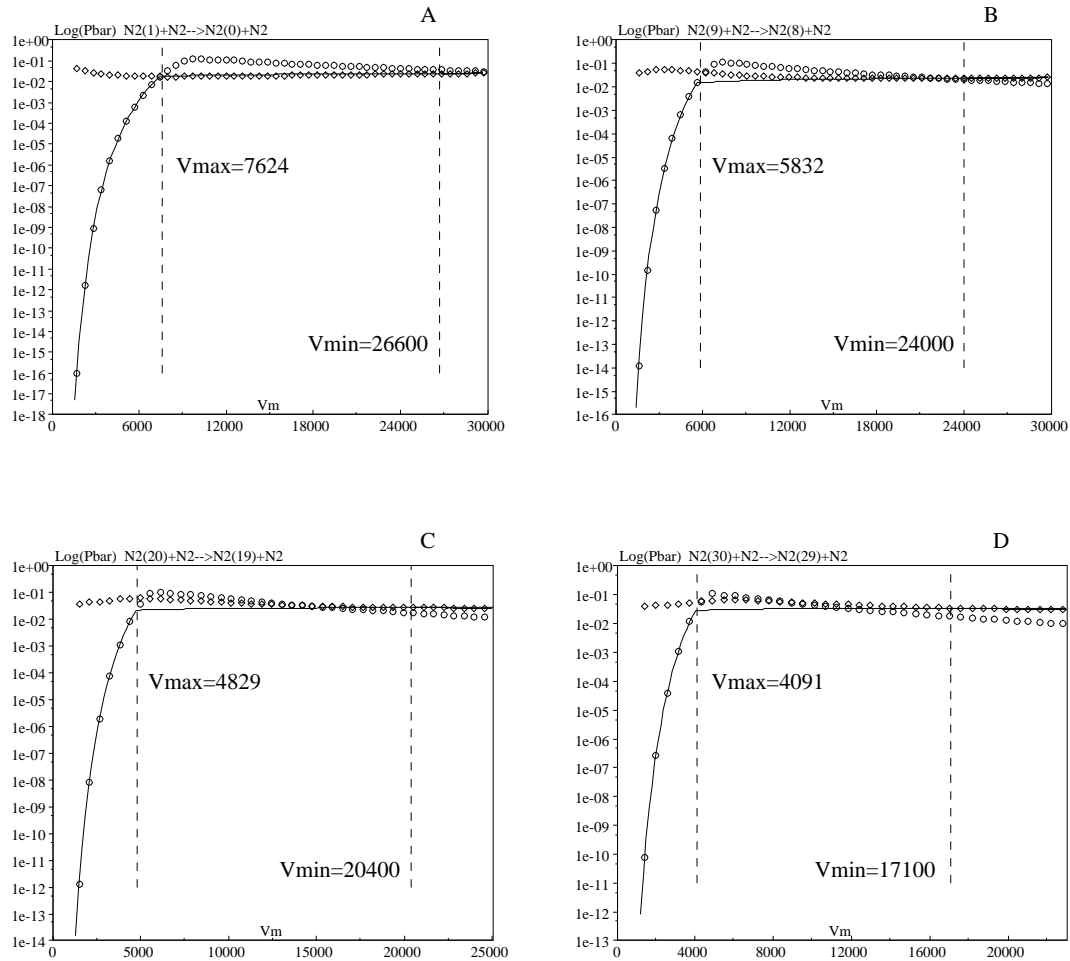


Figure 4: Comparison of inelastic scattering probability obtained for slow (circles) and fast (rhombuses) collisions. The solid lines are the interpolated probabilities.

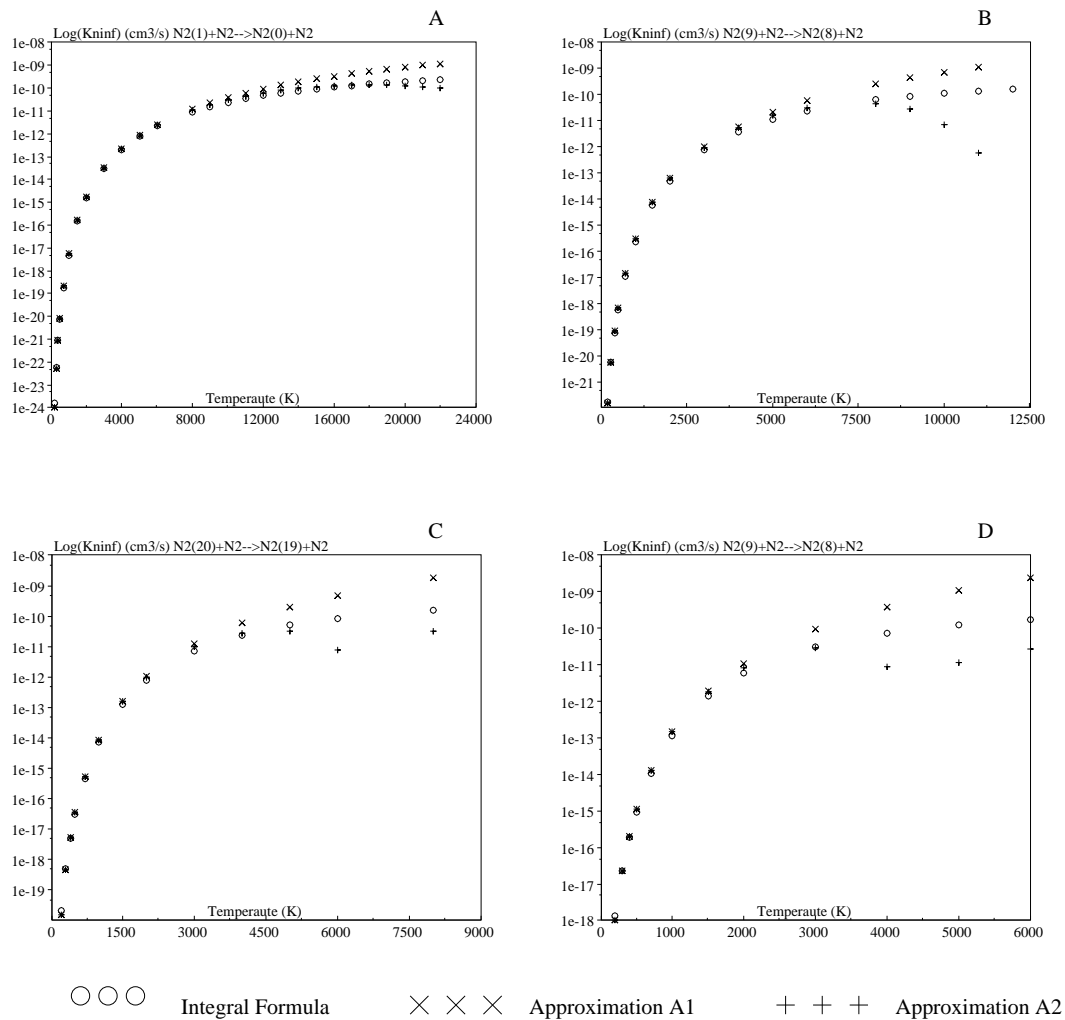
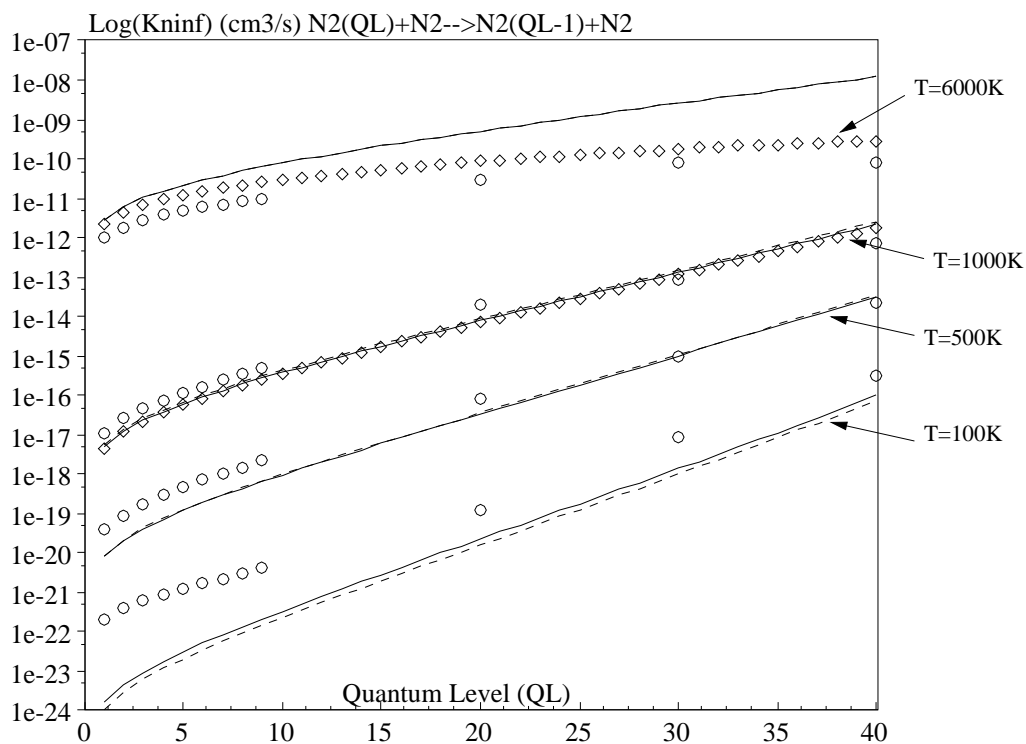


Figure 5: Comparison of VT rate constants for slow collisions obtained using integral formula and approximations A1 and A2. The rate constants are given as functions of the temperature.





○ Billing-Fisher

◇ Numerical Integration for slow collisions

Approximation A1: ——— Po computed with formula 53  
 - - - - - Po computed using Newton method

Figure 6: Comparison of rate constants for slow collisions. The dependence is upon a quantum level and concerns only one level transitions.

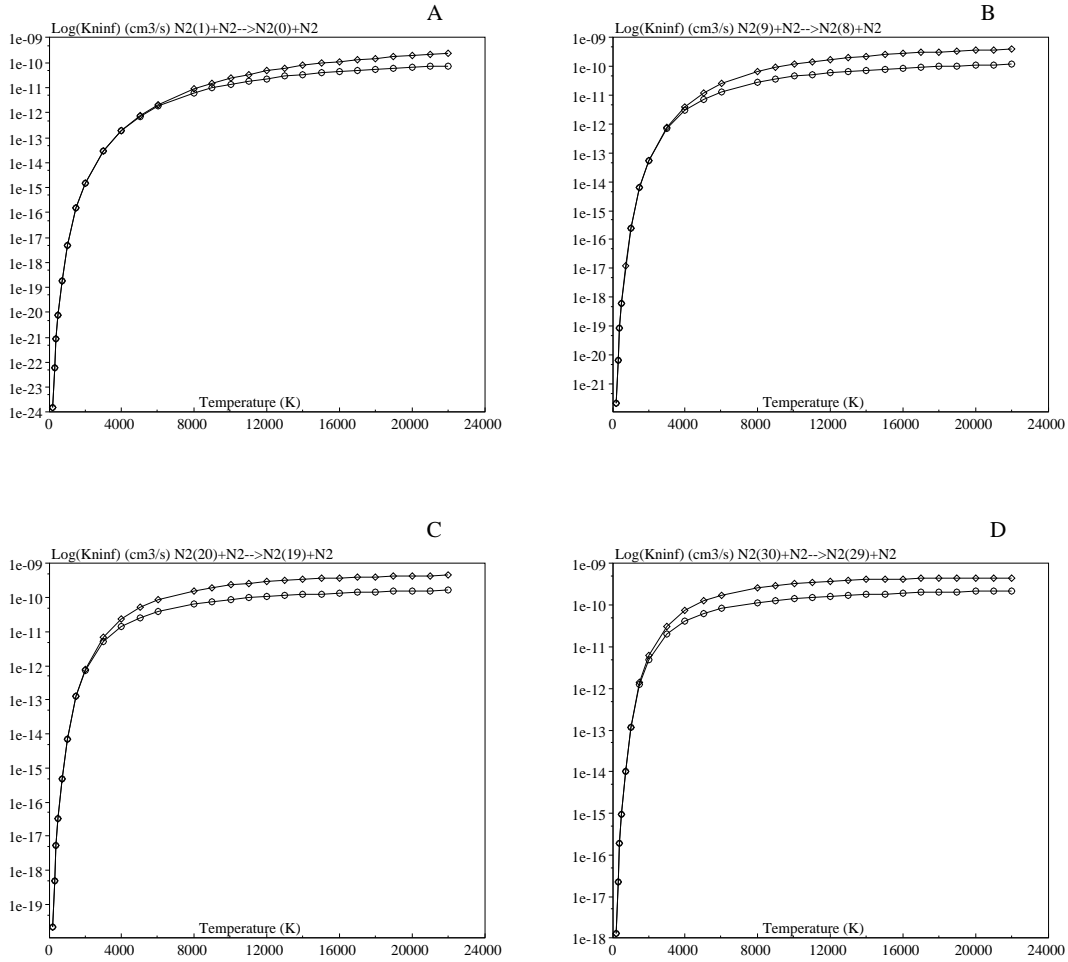


Figure 7: Comparison of VT rate constants computed for fast-intermediate-slow collisions (circles) and only slow collisions (rhombuses). In both cases we have used a numerical integration. The rate constants are given as function of the temperature.

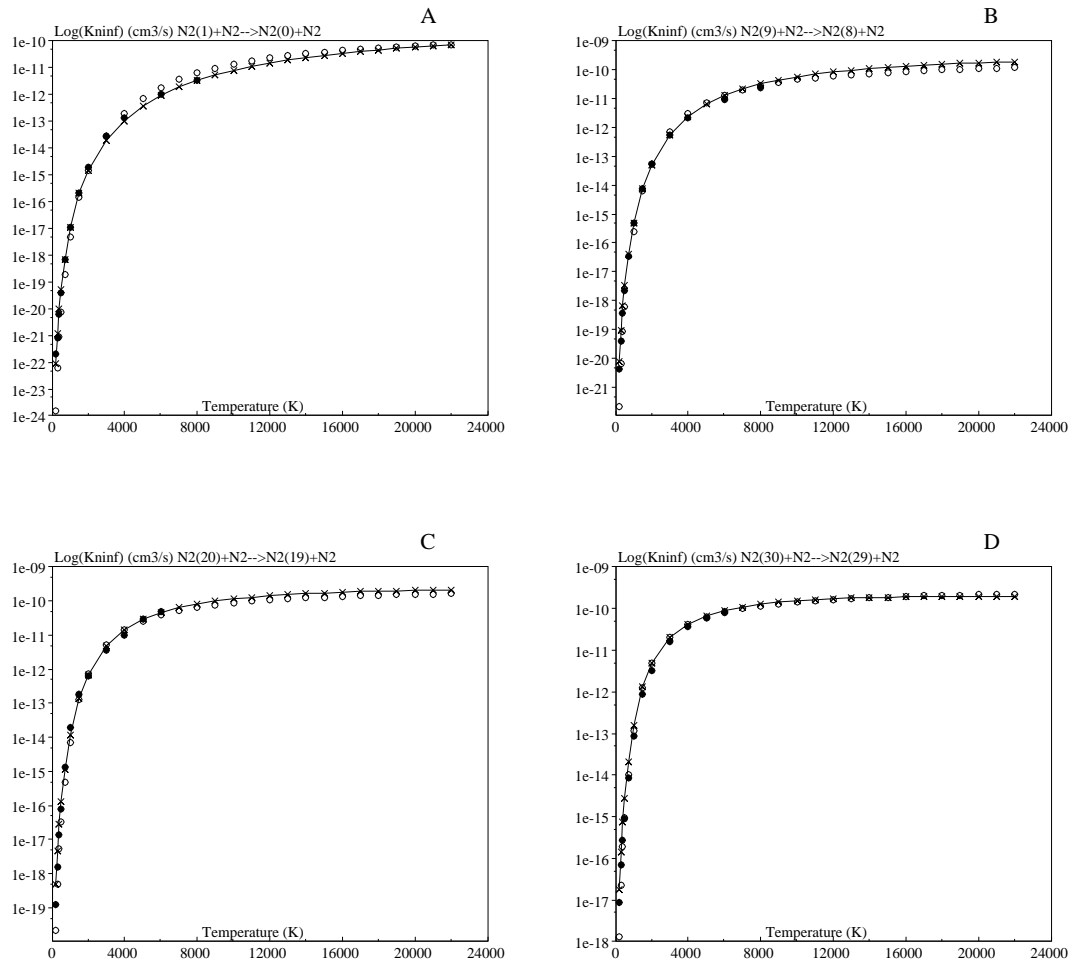


Figure 8: Comparison of VT rate constants, for different one-level transitions, computed with Adamovich model (crosses), Gorbachev model (white circles) and by Billing-Fisher model (black points).

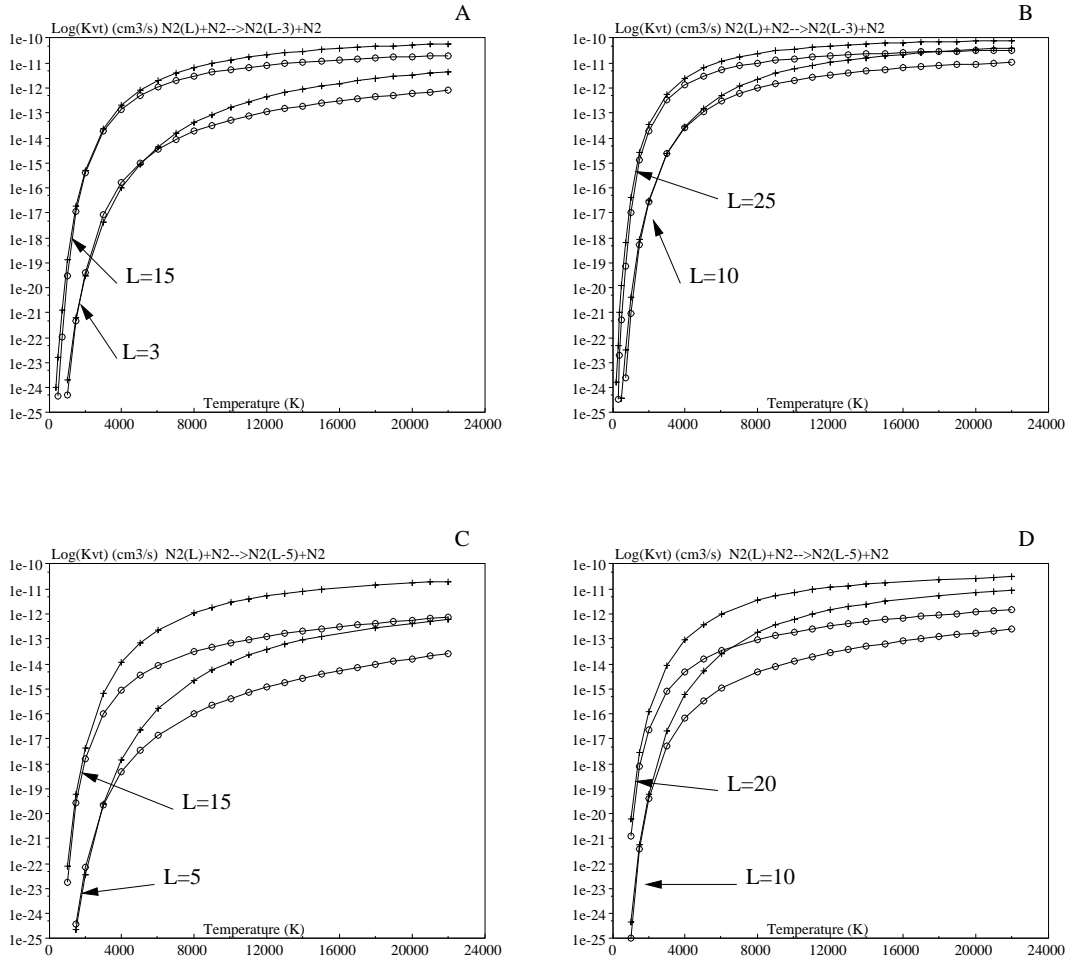


Figure 9: Comparison of VT rate constants, for different 3 and 5 level transitions, computed with Adamovich model (crosses) and Gorbachev model (white circles).

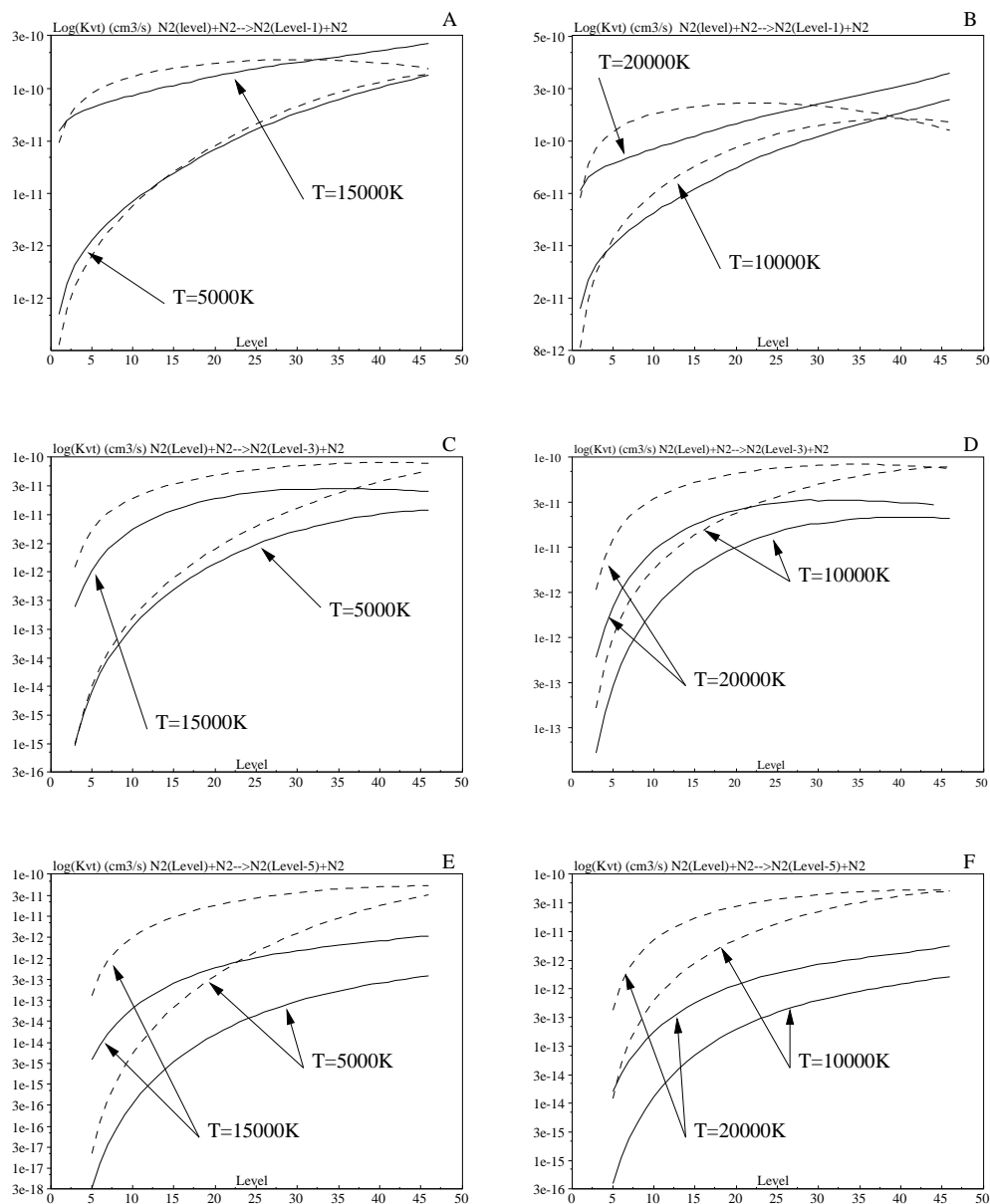


Figure 10: Comparison of VT rate constants depending on the initial vibrational level for different multi-level transitions, and for different temperatures. Adamovich results are represented by dashed line and Gorbachev results by continuous line.

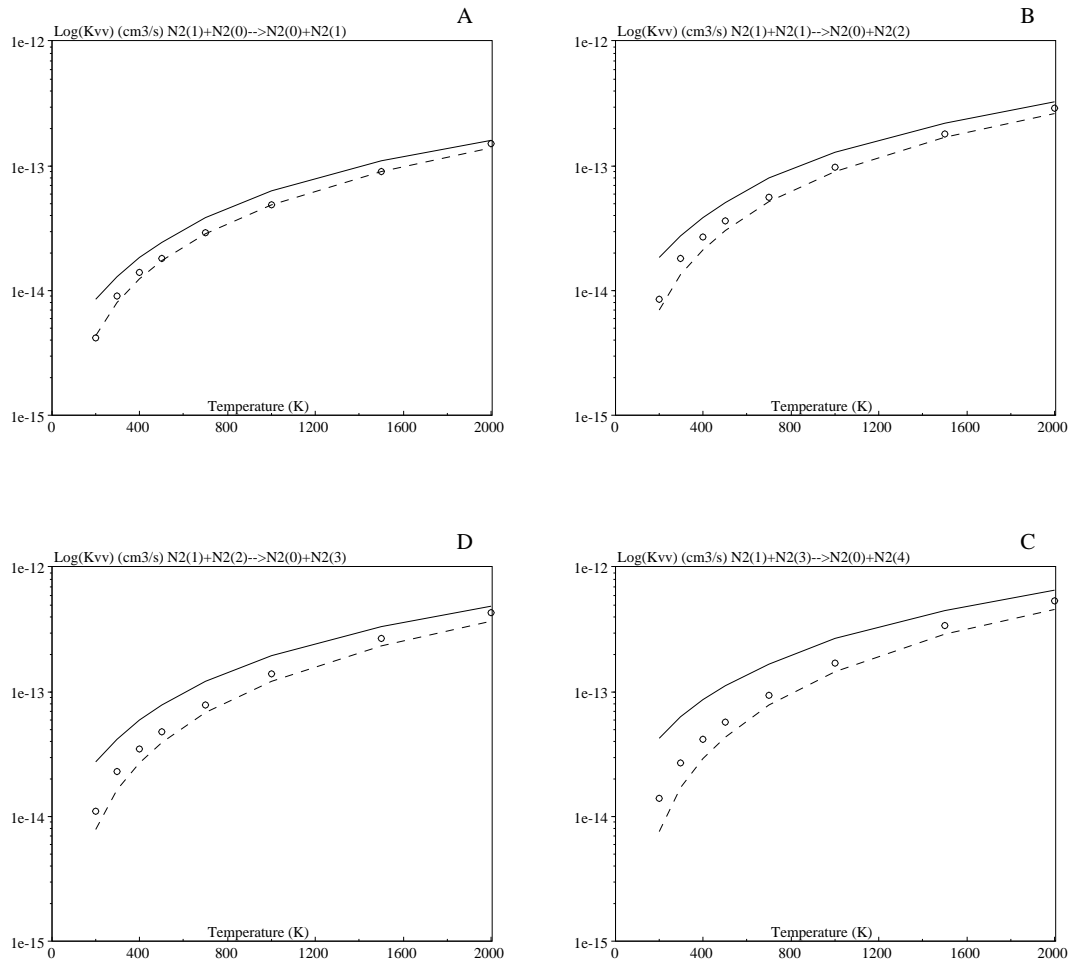


Figure 11: Comparison of VV rate constants, for different one-level transitions, computed with Adamovich model (dashed lines), Gorbachev model (solid lines) and by Billing-Fisher model (circles).

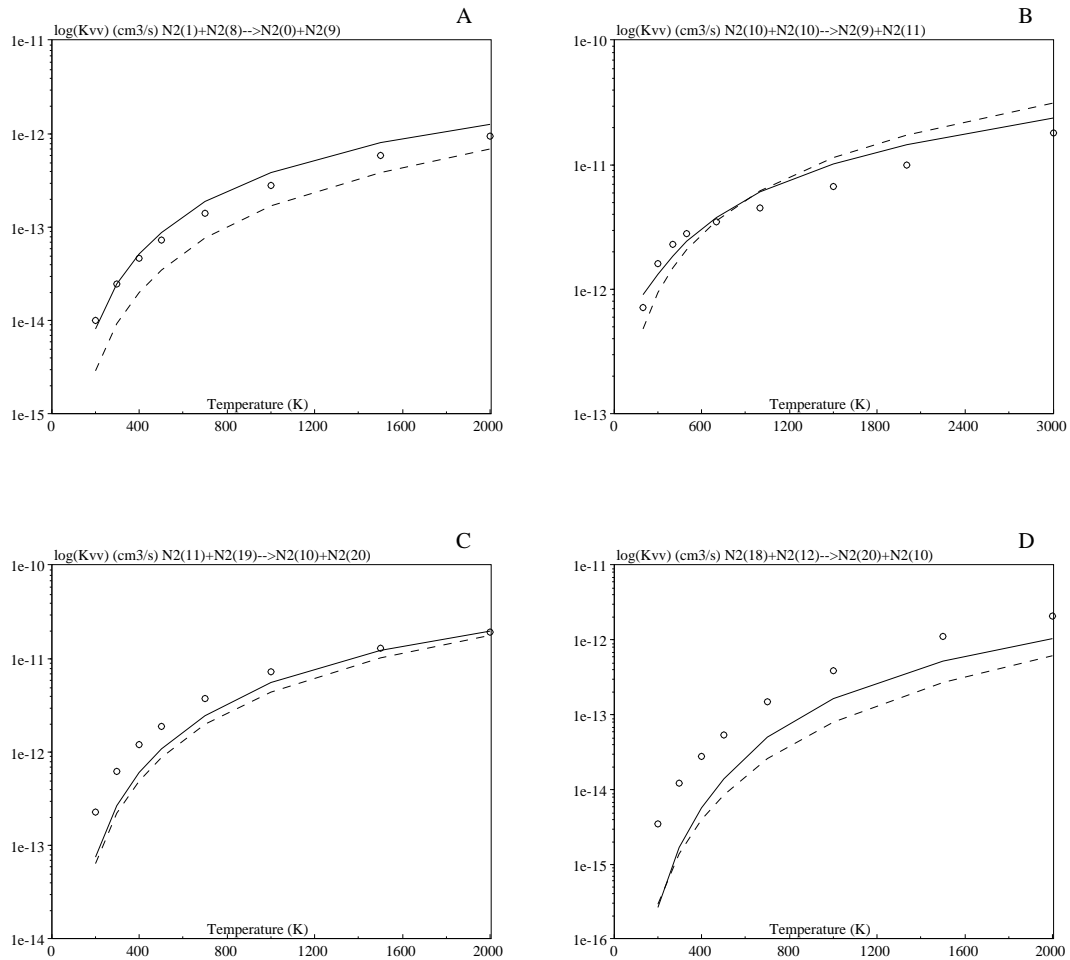


Figure 12: Comparison of VV rate constants, for different one-level transitions (A-B-C) and two-level transition (D), computed with Adamovich model (dashed lines), Gorbachev model (solid lines) and by Billing-Fisher model (circles).

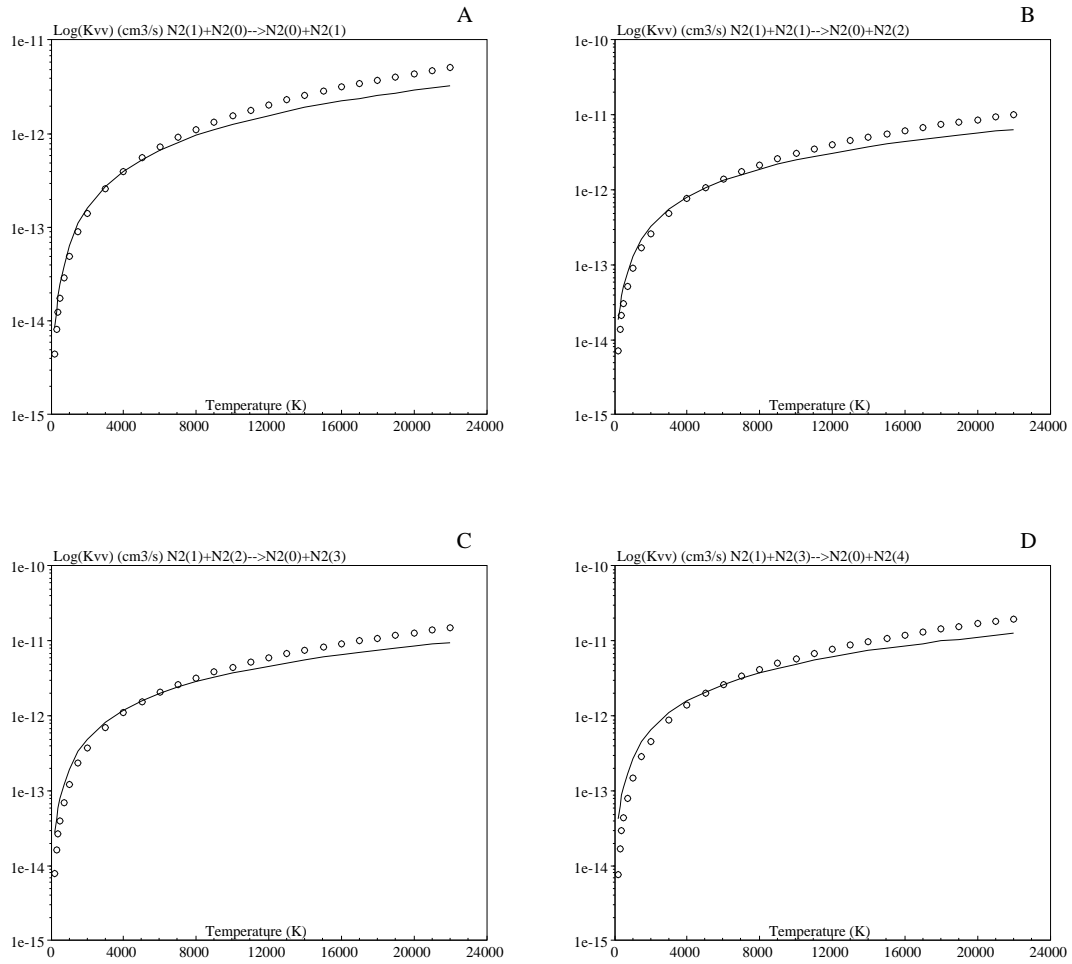


Figure 13: Comparison of VV rate constants, for different one-level transitions, computed with Adamovich model (cercles), Gorbachev model (solid lines).



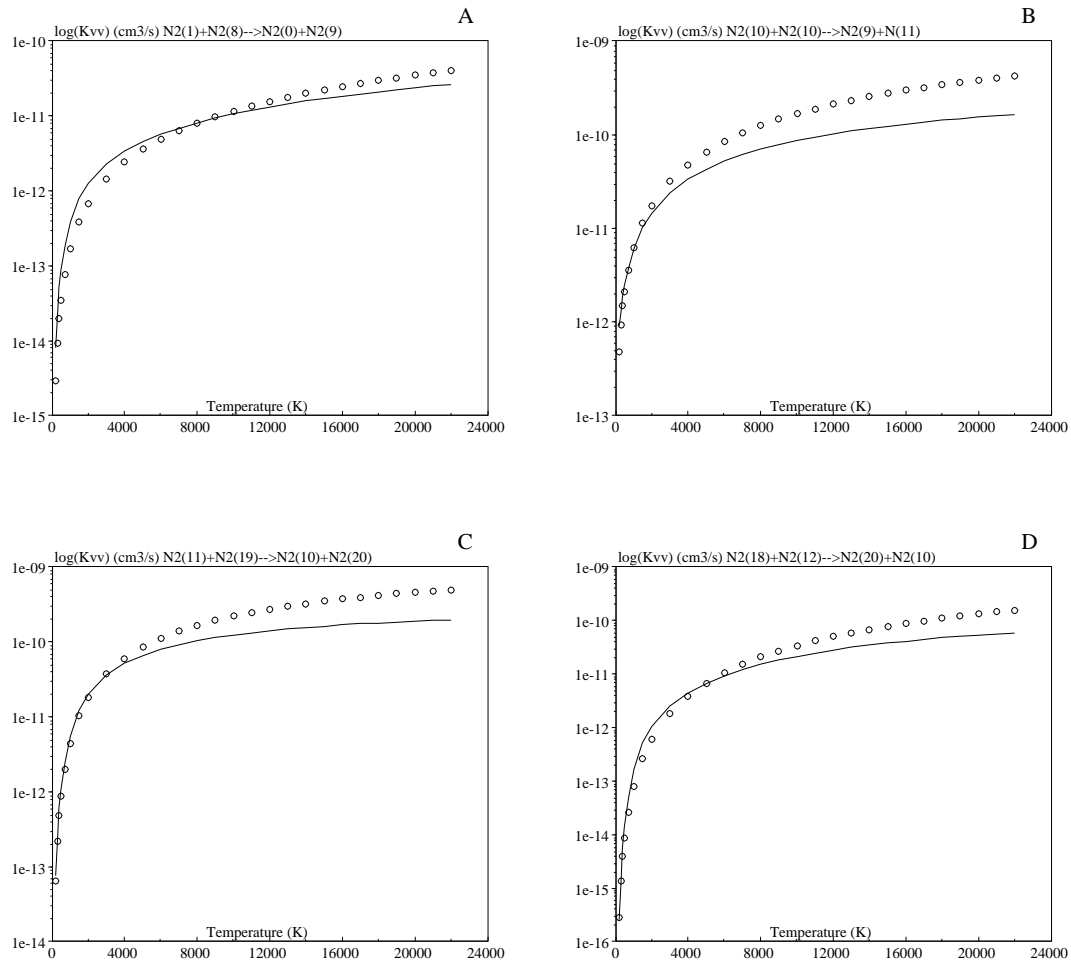


Figure 14: Comparison of VV rate constants, for different one-level transitions (A-B-C) and two-level transition (D), computed with Adamovich model (cercles), Gorbachev model (solid lines) .



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