Simulations of CO$_2$ multi-temperature vibrational kinetics on the basis of new relaxation time models

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Abstract. Vibrational relaxation of a single-component carbon dioxide in adiabatic thermal bath is studied in multi-temperature approaches using several models for the vibrational relaxation time. The energy production terms in two- and three-temperature vibrational energy relaxation equations are written in the frame of the common Landau–Teller model as well using corrections based on introducing multi-temperature relaxation times for various vibrational energy exchanges within and between CO$_2$ modes. For the relaxation time evaluation, two theoretical models for the transition probabilities are implemented: the first-order perturbation theory and the forced harmonic oscillator model; several experimental data sets are also assessed. It is shown that the forced harmonic oscillator model provides satisfactory agreement with experimental relaxation times in a wide temperature range. Solutions obtained using the two theoretical models for the transition probabilities show essentially different trends, incubation time and relaxation rate.

1. Introduction
Modeling of vibrational kinetics in carbon dioxide flows is of vital importance for Mars exploration and Earth environmental programs. Although state-to-state simulations became a powerful tool for studying different vibrational relaxation mechanisms [1, 2, 3], multi-temperature models [4, 5, 6] are still preferable in engineering applications due to their comparative computational efficiency. There are two main directions in improving the accuracy of multi-temperature models in polyatomic gases: increasing the model complexity by introducing vibrational temperatures of all vibrational modes [6], and development of reliable models for vibrational relaxation times, taking into account various relaxation channels [7, 8]. Since experimental data on the relaxation time are obtained in limited temperature ranges [9, 10, 11], theoretical approaches based on the high precision data for the cross sections of vibrational energy transitions are rather relevant.

Recently we have developed a kinetic-theory model for the evaluation of relaxation times in carbon dioxide [5, 7, 8]. The model is based on averaging the vibrational energy variation during different transitions with one-temperature or multi-temperature vibrational distribution functions; the transition probabilities are calculated using either the first-order perturbation SSH [12] or forced harmonic oscillator (FHO) [13, 14] models. The main feature of the model is that it defines an effective relaxation time for each kind of energy exchange, whereas in experiments, relaxation times of only vibrational-translational transitions in the bending mode (VT$_2$) or inter-mode exchange between bending and asymmetric modes (VV$_{2-3}$) are measured. Moreover, the theoretical relaxation times depend on the gas temperature and vibrational temperatures of
the modes involved to the transition, and therefore can be used under strongly non-equilibrium conditions.

The objective of this study is to assess the theoretical model developed in [7, 8] in the adiabatic thermal bath simulations of CO$_2$ kinetics, and to compare solutions obtained in the frame of two- and three-temperature approaches with those obtained using available experimental data.

2. Vibrational relaxation models

In the present study, we consider a single-component gas without chemical reactions. Two multi-temperature models: three-temperature (3T) and two-temperature (2T) are assessed. The 3T model is based on the assumption of rapid vibrational-vibrational (VV) energy exchange within three CO$_2$ modes (1 – symmetric, 2 – bending and 3 – asymmetric), and inter-mode VV transitions between symmetric and bending vibrations. Such a relation between the rates of vibrational exchanges allows one to introduce the temperatures $T_{12}$ and $T_3$ of coupled symmetric-bending and asymmetric modes, respectively [15]. For harmonic oscillators, the Boltzmann vibrational distributions with temperatures $T_{12}$ and $T_3$ are established during the fast relaxation stage; during the slow stage, $T_{12}$ and $T_3$ attain the equilibrium value corresponding to the gas temperature $T$.

The set of equations for the description of vibrational relaxation of a single-component CO$_2$ under adiabatic thermal bath conditions includes relaxation equations for the specific energies of the coupled mode $E_{12}$, asymmetric mode $E_3$, and total energy $E$ conservation equation:

$$
\rho \frac{dE_{12}}{dt} = R_{12} = R_{12}^{VT} + R_{12}^{VV_{2-3}} + R_{12}^{VV_{1-2-3}},
$$

$$
\rho \frac{dE_3}{dt} = R_3 = R_3^{VV_{2-3}} + R_3^{VV_{1-2-3}},
$$

$$
E = \text{const}.
$$

Here, $\rho$ is the gas density, $E$ includes translational, rotational and total vibrational energy, $R_{12}$, $R_3$ are the relaxation terms for the coupled and asymmetric modes including contributions of VT$_2$ vibrational-translational transitions in the bending mode and VV$_{2-3}$ inter-mode transitions. The last process is equivalent to the VV$_{1-2-3}$ transitions between all modes since the energy variations in both processes are almost equal. VT$_3$ transitions in the asymmetric mode occur much slower than other processes [15, 3] and thus neglected in the present study.

The energy production terms in the relaxation equations are usually calculated by the Landau–Teller (LT) formulas:

$$
R_{12} = \rho \sum_{\gamma} \frac{E_{12}^{\gamma}(T) - E_{12}(T_{12})}{\tau_{\gamma}}, \quad \gamma = VT_2, VV_{2-3}, VV_{1-2-3},
$$

$$
R_3 = \rho \sum_{\gamma} \frac{E_3^{\gamma}(T) - E_3(T_3)}{\tau_{\gamma}}, \quad \gamma = VV_{2-3}, VV_{1-2-3}
$$

with different relaxation times $\tau_{\gamma}$. The range of applicability of this approach is rather limited, since it uses one-temperature relaxation times measured experimentally under specific temperature and pressure conditions.

A possible way to improve the accuracy of the Landau–Teller equations for CO$_2$ is to introduce multi-temperature vibrational relaxation times and use correction factors that depend on the temperature ratios [7]. Thus, for VT$_2$ transitions in the combined symmetric-bending mode, the
correction factor has the form \( T/T_{12} \), and the expression for the corresponding relaxation term takes the form:

\[
R_{12}^{\text{VT}} = \rho \frac{E_{12}(T) - E_{12}(T_{12})}{\tau_{12}^{\text{VT}}(T, T_{12})} \frac{T}{T_{12}}. \tag{4}
\]

Note that in this case, \( \tau_{12}^{\text{VT}} \) is the effective time of VT \(_2\) relaxation in the coupled mode depending on both \( T \) and \( T_{12} \).

The two-temperature model is based on the assumption of rapid inter-mode transitions which allows one to introduce a single vibrational temperature \( T_v \); the slow process is the VT relaxation of the total vibrational energy \( E_{\text{vibr}} \). In this case, Eqs. (1) and (2) reduce to the single relaxation equation for \( E_{\text{vibr}} \) with the relaxation term \( R \) specified by VT transitions.

3. Relaxation times

We consider one-temperature and multi temperature approaches for relaxation time calculations. Details on the derivation can be found in \[8\]. An effective relaxation time in the \( M \)th mode due to the process \( \lambda \), \( \tau_\lambda^M(T, T_{12}, T_3) \) (\( \lambda \) is the transition type: VT, VV\(_2\)\(_{-3}\) and VV\(_1\)\(_{-2}\)\(_{-3}\); \( M = 12 \) for the coupled symmetric-bending mode, \( M = 3 \) for the asymmetric mode), and overall relaxation time \( \tau_\lambda(T) \) of this process can be obtained in the form

\[
\frac{1}{\tau_M^\lambda(T, T_{12}, T_3)} = \frac{2\pi k}{m c_M} \left( \frac{\Delta \varepsilon_M^\lambda}{kT} \right)^2 \sum_{i_1, i_2, i_3} n_{i_1, i_2, i_3}(T_{12}, T_3) \kappa_{i_1, f}^\lambda(T), \tag{5}
\]

\[
\frac{1}{\tau_\lambda(T)} = \frac{2\pi k}{m c_{\text{vibr}}} \left( \frac{\Delta \varepsilon_\lambda}{kT} \right)^2 \sum_{i_1, i_2, i_3} n_{i_1, i_2, i_3}(T) \kappa_{i_1, f}^\lambda(T). \tag{6}
\]

Here \( k \) is the Boltzmann constant, \( m \) is the molecule mass, \( n_{i_1, i_2, i_3} \) are populations of vibrational states \( i_1, i_2, i_3 \) of symmetric, bending and asymmetric modes (we use the multi-temperature or one-temperature Boltzmann distributions), \( c_M, c_{\text{vibr}} \) are corresponding specific heats

\[
c_M = \frac{\partial E_M}{\partial T_M}, \quad c_{\text{vibr}} = \frac{\partial E_{\text{vibr}}}{\partial T}.
\]

\( i = (i_1, i_2, i_3), f = (f_1, f_2, f_3) \) are the initial and final quantum numbers of \( \text{CO}_2 \), \( \Delta \varepsilon_M^\lambda \) are energy variations in the \( M \)th mode due to the process \( \lambda \), \( \Delta \varepsilon_\lambda = \Delta \varepsilon_{12}^\lambda + \Delta \varepsilon_{3}^\lambda \). The state-resolved rate coefficient for the process \( \lambda \) is introduced by the expression

\[
k_{i_1, f}^\lambda(T) = 8 \left( \frac{kT}{\pi m} \right)^{1/2} \int_0^\infty \exp(-g_0^2) g_0^3 \sigma_{\text{VHS}}(g) P_{i_1, f}^\lambda(g) \, dg_0, \tag{8}
\]

\( g_0 \) is the dimensionless relative velocity, \( \sigma_{\text{VHS}} \) is the cross section for the variable hard sphere model, which is assumed independent of the rotational state and internal state of the collision partner, \( P_{i_1, f}^\lambda \) is the probability of the corresponding transition.

The critical point in the time evaluation is the choice of a model for probabilities of corresponding vibrational transitions. In the present study, we use the first-order perturbation SSH theory \[12\] and a more advanced and accurate forced harmonic oscillator (FHO) model \[13, 14\] for the transition probabilities. The results were compared with the relaxation times of different processes (VT, VV\(_{m-k}\)) obtained from experimental data \[11, 10\] as well as with the overall vibrational relaxation time \( \tau_{\text{vibr}} \) measured in \[9\]. A comparison for VT\(_2\) transitions is presented in Figure 1. One can see poor agreement of the relaxation time predicted using the SSH theory in the low- and moderate temperature range. In the same range, using the
Figure 1. One temperature VT$_2$ relaxation times as functions of $T^{-1/3}$ for pressure $p = 1$ atm. FHO and SSH models for the transition probabilities. Comparison with experimental data.

FHO model yields rather good agreement with all measurements. It has to be mentioned that extrapolating experimental data of [10] for temperatures higher than 3000 K is not justified since they are measured at $T < 2500$ K. On the other hand, data of [11] are suitable for higher temperatures; it is seen that the agreement of the relaxation times obtained using the FHO model with these data is satisfactory.

4. Results and discussions

The series of simulations with different relaxation terms representation was conducted for the assessment of the relaxation model. Additional calculation with using averaged state-to-state (STTS) relaxation terms is considered in the 3T approximation based on the results of [3] where the SSH theory is employed for the transition rate coefficients. Although the state-to-state approach yields slightly different results with respect to multi-temperature ones, the general time distributions of temperatures are similar; this allows to compare qualitatively the results obtained using the SSH and FHO models for the vibrational energy transitions. The notations for various model sets are given in Table 1. Several types of initial conditions are considered corresponding to moderate deviation from equilibrium (TC1, TC2) and weak deviation from equilibrium (TC3, TC4), see Table 2.

Comparison of the temperature profiles obtained in the two-temperature approach using different overall one-temperature relaxation time models is presented in Figure 2. Assuming the results obtained using the experimental data of [11] as reference, we can notice that the FHO model gives satisfactory agreement for the temperature profiles in the case TC1 of an initially heated gas, the differences do not exceed 7%. The discrepancy between the temperature values in the TC2 is about 14%, which is rather high and nearly the same as the difference between solutions obtained with the Losev [11] and Achasov [10] data. At the same time, the discrepancies between the results calculated with the relaxation times according to [10] reach 11% and 16% for the cases TC1 and TC2, respectively. The trends of temperature profiles obtained using different one-temperature relaxation times directly corresponds to the VT$_2$ relaxation time relation in Figure 1, and deviation of $\tau$ evaluated according to the FHO model from the Losev data [11] correlates with calculated temperature distributions.
### Table 1. Set of models used in simulations

| Notation | Model |
|----------|-------|
| LT (1T) Losev | Landau–Teller formulation with one-temperature relaxation time calculated according to [11] |
| LT (1T) Achasov | Landau–Teller formulation with one-temperature relaxation time calculated according to [10] |
| LT (1T) FHO | Landau–Teller formulation with one-temperature relaxation time calculated using the FHO model [7, 8] |
| LT (MT) FHO | modified Landau–Teller formulation with multi-temperature relaxation time calculated using the FHO model [7, 8] |
| (aver. STS) SSH | averaged state-to-state relaxation terms [3] calculated using the SSH theory [12] |

### Table 2. Test cases

| TC1 | \( T(0) = 3000 \text{ K}, \ T_v(0) = 1000 \text{ K}, \ p = 100 \text{ Pa} \) |
| TC2 | \( T(0) = 1000 \text{ K}, \ T_v(0) = 3000 \text{ K}, \ p = 100 \text{ Pa} \) |
| TC3 | \( T(0) = 2000 \text{ K}, \ T_v(0) = 1800 \text{ K}, \ p = 100 \text{ Pa} \) |
| TC4 | \( T(0) = 1800 \text{ K}, \ T_v(0) = 2000 \text{ K}, \ p = 80 \text{ Pa} \) |

**Figure 2.** Temperature distributions as functions of time for different initial conditions: TC1 (left); TC2 (right). Two-temperature model. Solid lines correspond to the gas temperature, dashed lines correspond to the vibrational temperatures.

Applying a more accurate 3T approach leads to visible differences in the results obtained using different relaxation time models (see Figure 3). The gas temperatures obtained using the
Figure 3. Temperature distributions as functions of time for different initial conditions: TC1 (left); TC2 (right). Three-temperature model.

FHO model are in good agreement with those obtained with the times from [11], the discrepancy does not exceed 5%, whereas using the time from [10] yields a shift in the temperature profiles, and equilibrium is established much faster.

Figure 4. Temperature distributions as functions of time for different initial conditions: TC3 (left); TC4(right).

The test cases corresponding to weak deviations from equilibrium are also considered in this study (TC3 and TC4). Under such conditions, more accurate modified Landau–Teller expressions with multi-temperature relaxation times can be used. The latter expressions are not applicable under strongly non-equilibrium conditions since they are obtained by linearizing the exact kinetic-theory energy production terms with respect to the relative differences in the vibrational and gas temperatures [7]. Comparison of the gas temperature profiles given in Figure 4 shows that the refinement of the kinetic model for the relaxation terms (MT FHO) leads to closer results when compared with simulations based on the Losev relaxation times [11],
and the values of $T$ almost coincide (the difference is less than 1%).

![Figure 5. Temperature distributions as functions of time for different initial conditions: TC1 (left); TC2 (right). Three-temperature model, comparison of SSH and FHO models.](image)

Finally the comparison of temperature profiles obtained in the three-temperature approach using the 1T FHO relaxation time \cite{7} and using averaged state-to-state relaxation terms \cite{3} calculated via SSH theory \cite{12} is presented in Figure 5. Such comparison is qualitative since more detailed representation of the energy production terms using averaged STS relaxation terms can lead to differences in temperature profiles; nevertheless, it can be used for preliminary estimations. It is clearly seen that the characteristic times of processes differ by one–two orders of magnitude which leads to completely dissimilar behaviour of temperatures, incubation time and overall time of relaxation. In the case of the SSH model, vibrational relaxation in the symmetric and bending modes starts much faster due to high rates of VT$_2$ exchange. On the other hand, relaxation in the asymmetric mode is rather slow, which is caused by under-predicted values of the VV$_{2-3}$ and VV$_{1-2-3}$ rate coefficients calculated in the frame of the SSH model \cite{7}. For the FHO model, the vibrational temperatures are located close to each other because of the strong influence of the VV exchanges which occur at the same time scale as VT$_2$ process according the model (see \cite{8}). Thus, applying the FHO and SSH model yields qualitatively different relaxation mechanisms in carbon dioxide.

5. Conclusions

Several models for the vibrational relaxation times are assessed in a problem of spatially homogeneous multi-temperature kinetics of carbon dioxide. Theoretical models are based on the effective relaxation times introduced for each mode and type of energy exchange; these times are obtained by averaging the state-resolved transition rate coefficients and depend on both translational and vibrational temperatures, contrarily to commonly used analytical models and experimental results. The SSH and FHO transition probabilities are implemented for the relaxation times calculation; whereas the FHO models provides good agreement with experimental data in a wide temperature range, the SSH model yields much faster VT relaxation in the bending mode.

The equations of vibrational relaxation are written in the form of original and generalized Landau–Teller formulas in the three-temperature and two-temperature approaches. Relaxation processes in four test cases with various initial conditions are simulated, and temperature profiles are compared. The best agreement to the solution obtained on the basis of the
Losev’s experiments for relaxation times is obtained when the multi-temperature FHO relaxation times are used. For the FHO model and experimental times, temperatures of the coupled and asymmetric modes are hardly distinguishable whereas for the SSH theory, relaxation in the asymmetric mode proceeds significantly slower due to under-predicted rates of inter-mode vibrational transitions. Thus, using the FHO and SSH models leads to different mechanisms of vibrational relaxation.

Acknowledgments
The reported study was funded by a grant of the President of the Russian Federation MK-1243.2020.1.

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