Two-modes approach to the state-to-state vibrational kinetics of CO$_2$

Vladislav Kotov

Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung-Plasmaphysik (IEK-4), 52425 Jülich, Germany

E-mail: v.kotov@fz-juelich.de

Received 5 March 2020, revised 11 May 2020
Accepted for publication 15 June 2020
Published 13 July 2020

Abstract

Two-modes (symmetric–asymmetric) reduction of the CO$_2$ vibrational kinetics has been introduced systematically for the purpose of state-to-state modeling. The two-modes approach is known from multi-temperature models. Its basic assumption is that vibrational energy of the CO$_2$ molecule which depends on 4 quantum numbers can be approximated by a function of only 2 numbers. Subsequently, vibrational states of CO$_2$ with the same quantum numbers of the effective symmetric and asymmetric mode can be grouped into one combined state. The paper presents the calculation of the average probabilities of transitions between combined states based on the Schwartz–Slawsky–Herzfeld theory. Closed analytical formulas are derived for vibrational–translational and vibrational–vibrational transitions.

Keywords: CO$_2$, vibrational kinetics, state-to-state model, transition probabilities

(Some figures may appear in colour only in the online journal)

1. Introduction

Conversion of CO$_2$ into CO in microwave gas discharges is extensively studied at present due to its potential significance for production of synthetic fuels and electrification of chemical industry [1]. It is expected that transitions between vibrational states of CO$_2$ play a decisive role in the conversion processes [2, 3]. The most straightforward and common way of numerical modeling of the complex multi-step chemical processes is the state-to-state kinetics which treats excited states as separate species. Within this approach the chemical system is described by a set of particle balance equations for each individual species—the master equations.

The CO$_2$ molecules have 3 modes of oscillations: symmetric stretching, symmetric bending and asymmetric stretching [4]. The double degenerate bending mode is a ro-vibrational mode which possesses rotational moment. Subsequently, the vibrationally excited state is described by 4 quantum numbers. The total number of different vibrational states of CO$_2$ with energies below the dissociation limit $E_{\text{diss}} = 5.5$ eV is estimated to be $\approx 10^5$. Thus, the state-to-state approach in its direct form cannot be applied in practice even to 0D problems of the CO$_2$ plasma conversion because of too high computational costs.

One possible solution of this issue is offered by the model proposed in [5–7] where vibrational states are combined into effective asymmetric states with equilibrium (Boltzmann) distribution of symmetric modes. That is, only 21 vibrationally excited CO$_2$ species have to be taken into account. This model has already found wide application and serves as a basis for creating models with further reduced number of species suitable for 2D/3D flow calculations. Such as the reductions based on the principal components analysis [8] and on combining the asymmetric levels into ‘lumped states’ [9]. Automatic algorithms of grouping the energy states into bins are developed as well [10]. Further optimization of the computational performance is achieved in the models with assumed shape of the vibrational distribution function [11] and with continuum energy spectrum approximations. Examples of those lat-
ter are diffusion equation in the vibrational energy space [12] and the recently proposed method based on the Fokker–Plank equation [13, 14].

Nevertheless, the computationally fast reduced and continuum spectrum models rely on the detailed state-to-state calculations which serve as benchmarks for verification and calibration. The state-to-state approach remains a tool which can revive internal mechanisms of vibrational kinetics otherwise not accessible by other methods.

A serious drawback of all the models of the CO$_2$ chemical conversion process listed above—starting from [5]—is that they focus on the kinetics of asymmetric modes. The non-equilibrium dynamics of the symmetric modes is neglected on assumption of their fast thermal equilibration. This assumption is, however, cannot be verified by the models themselves.

Both symmetric and the asymmetric vibrational modes of CO$_2$ are taken into account in the state-to-state model [15] developed for the spacecraft atmospheric entry simulations. In this model the ro-vibrational bending modes are combined into one effective state described by 3 quantum numbers instead of 4. This yields $\approx 10^8$ model species with vibrational energies smaller than $E_{\text{disc}}$. Solving a set of master equations of that size turned out to be still too computationally demanding. In practical applications of that model the number of effective states had to be reduced down to 1224 (states with vibrational energy smaller than 3 eV) [15, 16].

It is possible to devise a model which can be placed in the middle between the model of [5, 6] and the one of [15, 16]. The vibrational energy of CO$_2$ can be approximated as being a function of only two numbers—the mode numbers of symmetric ($v_s$) and asymmetric ($v_a$) vibrations [3]. This two-modes approximation which goes back to the multi-temperature models of the CO$_2$ vibrational spectrum [2, 3] allows to combine the states with same $v_s$, $v_a$ into one effective state. The total number of such ‘combined states’ with vibrational energies below $E_{\text{disc}}$ is around 900. That is, the state-to-state description in this approximation is computationally feasible at least in 0D/1D simulations. At the same time, the assumption of thermal equilibrium is applied here only within the groups of symmetric vibrations with close energies. The populations of such groups represented by the combined states are calculated by the model itself. In particular, the pump up of vibrational energy due to vibrational–vibrational exchange between the symmetric modes can be investigated. This is the main difference between the two-modes approximation and the model of [5, 6].

The two-modes state-to-state model is technically not difficult to implement in a computer code. The main difficulty was found to be the absence of readily available formulas for the probabilities of transitions between the combined symmetric–asymmetric states. The present paper intends to close this gap. The calculation of those transition probabilities is the main subject of this paper. Same as in [5, 6, 15, 16] the consideration is based on the Schwartz–Slawsky–Herzfeld (SSH) theory [17, 18, 20]. This is an approximate first order perturbation theory based on the assumption that the short-range interaction dominates. This model gained wide popularity because it leads to simple analytic expressions for transition probabilities. At the same time, the model was found to be sufficiently accurate for vibrational–translational processes [19, 20]. Moreover, the rate coefficients [21] calculated using the SSH formulas as scaling relations were recently applied in [22] for modeling the CO$_2$ kinetics in a glow discharge, and a good agreement with experiment was obtained.

The arguments above speak in favor of the SSH model that it can be used as a reasonable first approximation which is valid at least qualitatively. It will be shown here that two extra assumptions lead to simple analytic formulas for the effective probabilities of transitions between combined states as well. Those are: (i) the linear oscillator approximation for calculation of matrix elements; (ii) the assumption that vibrational energy is exactly a function of $v_s$, $v_a$ only. This latter assumption, when it holds, also allows not to take into account the Fermi resonance (between symmetric vibrations) explicitly.

The validity of those assumptions is expected to deteriorate for large $v_s$, $v_a$ due to anharmonicity and subsequent smearing of the energy levels gathered into combined states. The picture of discrete levels can still be formally applied, but the transition probabilities, strictly speaking, may differ from those derived here. For high vibrational energies a near resonance collisionless energy exchange between symmetric and asymmetric modes leads to an effect similar to broadening of spectral lines which affects the probabilities of the vibrational–translational processes [12]. Also the justification used here for neglecting the Fermi resonance would not apply anymore. All those non-harmonic effects are very difficult to quantify and this is not attempted in the present paper. This difficulty is not to last extent due to the lack of exact knowledge of the CO$_2$ vibrational energy dependence from the quantum numbers. A further brief discussion of this subject will be given in the conclusions.

Although the SSH theory is considered to be well known its individual pieces are scattered over a number of publications the reader might not be familiar with. Therefore, the paper starts from an overview and a summary of the theory in sections 2–4. Section 2 address the derivation of the basic equations. In section 3 the application of the SSH theory specifically to CO$_2$ is described. The resulting formulas for vibrational transitions are summarized in section 4. Sections 5 and 6 present the original contribution of the present work. The two-modes approach and general equations for the probabilities of transitions between combined states are introduced in section 5. In section 6 selection of the most relevant processes is made, and formulas for the corresponding transition probabilities are derived. The last section concludes the paper and address some outstanding issues of the model.

2. Overview of the SSH theory

2.1. Zener’s method

The basis of the SSH model is the Zener’s method [23]. In his original paper Zener considered a co-linear collision of a
Approximation of the 1st order is obtained by substituting $Q_{v=0} = U^{v=0}, Q_{v \neq 0} = 0$ into the right-hand sides of (3) which are then solved for $Q_v$. The resulting solution has the following asymptotic form at $r \to +\infty$:

$$
\Psi (x, r) = \frac{\exp \left( \frac{-i p_0 r}{\sqrt{2 \pi \mu} p_0} \right)}{\sqrt{2 \pi \mu p_0}} + \sum_u a_u^e \frac{\exp \left( \frac{i p_0 r}{\sqrt{2 \pi \mu} p_0} \right)}{\sqrt{2 \pi \mu p_0}} \Psi_u (x).
$$

The term $\frac{\exp \left( \frac{-i p_0 r}{\sqrt{2 \pi \mu} p_0} \right)}{\sqrt{2 \pi \mu p_0}}$ describes an incoming wave—free particles which move toward each other, the term $\frac{\exp \left( \frac{i p_0 r}{\sqrt{2 \pi \mu} p_0} \right)}{\sqrt{2 \pi \mu p_0}}$, subsequently, an outgoing wave. See e.g., [24], section 21. That is, the first term stands for the quantum state of the system before the encounter, the terms in the sum stand for the states after the encounter. According to the general rules of quantum mechanics, see e.g., [24], section 3, squares of the coefficients $a_u^e$ then determine the probability of each state after the encounter $w_{v=0}$ which equals to [23]:

$$
w_{v=0} = |a_v^e|^2 = 4 \pi^2 \int_{-\infty}^{+\infty} U^v (r) V_v^e (r) U^v (r) \, dr.
$$

2.2. Generalization of Schwartz, Slawsky and Herzfeld. Translational part of the transition probability

Schwartz, Slawsky and Herzfeld [17] generalized the Zener’s method to the co-linear collisions of poly-atomic molecules. For them the equation (2) is replaced by a more sophisticated wave equation written in terms of the normal coordinates of molecular oscillations. Here for clarity the particle $\Lambda$ is still taken as a structureless object without oscillations. Generalization for the case when both colliding particles can change their vibrational states is straightforward and will be shown below in section 4.

The interaction energy is in general a function $V (x_\nu, r)$ of all normal coordinates of the molecule $x_\nu$ and of the parameter $r$ which characterizes the motion of the centers of masses of the colliding particles relative to each other. As this latter the distance between $A$ and the closest atom of the molecule is usually taken, see section 3.2 below. Displacements of the oscillating atoms from their equilibrium positions can be assumed to be much smaller than $r$ which allows to factorize the interaction term (an example will be shown in section 3.2):

$$
V (x_\nu, r) = V (x_\nu) \cdot V (r).
$$

When (7) holds the integral (6) is separated as follows:

$$
w_{v=0} = R_v^a \cdot |V_v^a|^2
$$

$$
R_v^a = 4 \pi^2 \left[ \int_{-\infty}^{+\infty} U^v (r) V (r) U^v (r) \, dr \right]^2
$$

$$
|V_v^a|^2 = \left[ \int_{-\infty}^{+\infty} \Psi_v (x_\nu) V (x_\nu) \Psi_v (x_\nu) \, dx_\nu \right]^2
$$

where $R_v^a$ is called ‘the translational part’ of the transition probability, and $|V_v^a|^2$ is ‘the oscillatory part’—square of the matrix element of the oscillating molecule; $v$ stands for the
values of its vibrational quantum numbers before collision, $u$—after collision. In this way the equation for molecular vibrations (2) and equation for the motion of the centers of masses (5) are completely separated from each other.

Equation (5) was solved analytically by Jackson and Mott for a special shape of the potential function $V(r) = C e^{-ar}$, where $C$ and $a$ are given constants [25]. The functions $U^{\alpha\beta}(r)$ which fulfill the required boundary conditions do not depend on $C$, the analytic expression for the integral (8b) reads:

$$R_v^u = \frac{(\theta_u^2 - \theta_v^2) \sqrt{\sinh \theta_u \sinh \theta_v}}{4\pi^2 (cosh \theta_u - cosh \theta_v)}$$

$$\theta_{v,u} = \frac{2\pi}{\hbar a} \sqrt{2\mu E_{kin,v,u}}$$

(9)

here $E_{kin}$ is the sum of the translational kinetic energies of the colliding particles before ($\theta_v$) and after ($\theta_u$) the interaction.

In [17] an extra assumption is made to apply the expression (9) to the realistic Lennard-Jones interaction potential. It is assumed that the transitions mainly take place due to short-range interaction near the distance of the closest approach. The Lennard-Jones potential in the vicinity of this point is fitted into the exponential function. A procedure was elaborated to calculate the parameter $a$ from the viscosity data [17, 18].

To get the transition probability as a function of (translational) temperature, equation (9) has to be integrated over Maxwellian velocity distribution of the colliding molecules. In [17] the integral over Maxwellian distribution is calculated (approximately) for co-linear collisions, in the later paper [18] the theory was generalized to realistic 3D collisions. The assumption that the transition is most probable in the vicinity of the distance of closest approach leads to similar mathematical treatment as for the co-linear collisions. Also, the period of rotation is assumed to be large compared to both the period of oscillations and the fly-by time. The final relation for the temperature dependent translational part of transition probability derived in [18] reads (for $|\Delta E| > 0$):

$$R_v^u = Z(\Delta E, T) \exp \left( \frac{\Delta E}{2T} \right)$$

$$Z(\Delta E, T) = 64 \pi \frac{\mu T}{3 (\hbar a)^2} \sigma^{1/3} \exp \left( -3\sigma^{2/3} \right)$$

(10)

$$\sigma = \frac{\pi}{\hbar a} \sqrt{\frac{\mu}{2T} |\Delta E|}, \quad \Delta E = E_v - E_u$$

(11)

here $T$ is translational-rotational temperature of the gas in the units of energy. $Z(\Delta E, T)$ in the present paper corresponds to $Z^{-1}$ in [20, 21]. Equation for $Z(\Delta E, T)$ in [18–21] also contains a factor which does not deviate much from 1 and is omitted here. Note also that there is a factor 4 missing in the expressions for transition probability in [17, 18]. This mistake which goes back to the very fist paper [23] was later recognized and corrected in [19, section 62, p 299].

3. Application of the SSH model to CO$_2$  

3.1. Modes of oscillations and wave functions

CO$_2$ is known to be a linear symmetric molecule [4]. It has three modes of vibrations: (1) symmetric stretching; (2) symmetric bending; (3) asymmetric stretching. The bending mode is double degenerate and possesses rotational momentum. The whole vibrationally excited state is described by 4 quantum numbers, in Herzberg notation [4]: $(v_1, v_3, v_2)$. To find the wave functions required to calculate the matrix elements (8c) the simplest linear oscillator model is applied. The oscillations are described by independent equations for the stretching modes 1, 3 and the degenerate mode 2:

$$\frac{\hbar^2}{2m_{1,3}} \frac{\partial^2}{\partial v_{1,3}^2} + m_{1,3} \omega_{1,3}^2 v_{1,3}^2 - E_{1,3} \Psi_{1,3}(v_{1,3}) = 0$$

(12)

$$\frac{\hbar^2}{2m_2} \left( \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} \right) + m_2 \omega_2^2 (x_2^2 + y_2^2) - E_2 \Psi_{2}(x_2, y_2) = 0$$

(13)

here $m$ are the masses ascribed to the modes (see below), and $\omega$ are the measurable oscillation frequencies. It is convenient to transform (13) into polar coordinates $x_2 = \rho \cos \phi$, $y_2 = \rho \sin \phi$, and look for the solution in the form $\Psi_{2}(\rho \phi)$, while the angular part $\Psi_{\phi}(\phi) = e^{\pm i\phi}/\sqrt{2\pi}$ is readily calculated, see e.g. [24, section 27]. Here $l$ is the projection of the rotational angular momentum to the axis of the unperturbed molecule. Equation for the radial part $\Psi_{\rho}(\rho)$ then reads:

$$\frac{\hbar^2}{2m_2} \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + m_2 \omega_2^2 \rho^2 \frac{\partial^2}{\partial \rho^2} + \left( E_2 - \frac{\hbar^2 l^2}{2m_2 \rho^2} \right) \Psi_{\rho}(\rho) = 0.$$  

(14)

The full wave function is the product of the individual modes:

$$\Psi_{v_1,v_3,v_2} = \Psi_{v_1}(z_1) \Psi_{v_3}(z_3) \Psi_{\rho}(\rho) \frac{e^{\pm i\phi}}{\sqrt{2\pi}}.$$  

(15)

A well known non-harmonic effect which occurs when the energy terms of the order higher than 2 omitted in equations (12), (13) are included is the Fermi resonance. It takes place in CO$_2$ due to the fact the fundamental frequency $\omega_1$ is almost exactly twice as large as $\omega_2$. Solutions of higher order obtained by solving the so called secular equations (secular determinant), see [24, section 39] and [26] take a form of the linear combinations of the eigenfunctions (15). In the subsequent discussion the Fermi resonance is not taken into account. Later in section 5.4 it will be shown that as long as the assumptions of the two-modes approach, section 5.1, hold, and the states in Fermi resonance are orthogonal to each other it is not required to explicitly take this effect into account.

3.2. Interaction potential as a function of normal coordinates

Specifically for CO$_2$ the problem of expressing the interaction potential as a function of normal coordinates $(z_1, z_3, x_2, y_2)$
was solved by Herzfeld in [20]. The geometry of the collision is sketched in figure 2. An interaction between structureless atom M and the atom A of the molecule closest to M is considered, influence of other atoms of the molecule is neglected. \( \tilde{x}, \tilde{y}, \tilde{z} \) are the displacements of the atom A from its equilibrium position in the Cartesian system with zero placed in the position of M. Under assumption of small displacements \( \tilde{x}, \tilde{y}, \tilde{z} \approx r \) the instant distance between A and M is:

\[
\tilde{r} = \sqrt{\tilde{x}^2 + \tilde{y}^2 + (r + \tilde{z})^2} \approx r + \tilde{z},
\]

(16)

The coordinates \( x, y, z \) are defined in another coordinate system with axis \( z \) directed along the unperturbed axis of the molecule, and the origin placed into the unperturbed position of A. An exponential interaction potential is transformed as:

\[
V(\tilde{r}) = V_0 e^{-a\tilde{r}} \approx V_0 e^{-ar} e^{i2\pi\cos\theta}\sin\theta.
\]

(17)

This is the factorization assumed in (7).

Following [20] the geometrical displacements are written as linear combinations of the normal coordinates:

\[
\begin{align*}
\epsilon_{(C,O)} &= \alpha_{1(C,O)} z_1 + \alpha_{3(C,O)} z_3, \\
x_{(C,O)} &= \alpha_{2(C,O)} x_2, \\
y_{(C,O)} &= \alpha_{2(C,O)} y_2.
\end{align*}
\]

(18)

The procedure of finding the coefficients \( \alpha \) elaborated in [20] is based on the requirement that the momentum and energy balance is fulfilled for each individual mode separately—this follows from the orthogonality of non-degenerate normal vibrations, see [4, section 2.11]. The procedure assumes free molecular oscillations—that is, the influence of the interaction with M is neglected. Assignment of the mode masses in (12) can be done arbitrary. In the final results only ratios \( \alpha^2/m \) appear, and \( \alpha^2 \) depends on the chosen \( m \) so that the mass cancels out. In the present work the assignment made in [20] is used. Although \( \alpha \) for O and C atoms are substantially different, Herzfeld [20] suggests for modes 1 and 3 to always use \( \alpha_{1,3} = \alpha_{1,3}^{(0)} \). For mode 2 an arithmetic mean of \( \alpha_{2}^{(0)} \) and \( \alpha_{2}^{(C)} \) is suggested. The masses \( m \) and corresponding coefficient \( \alpha \) from [20] are reproduced in table 1 below.

Substituting (18) into (17) yields:

\[
V(z_1, z_2, x_2, y_2) = e^{i2\pi\cos\theta}\sin\theta \\
\approx (1 + a\cos\theta_{1,2,3}) (1 + a\sin\theta_{2,3,2}).
\]

(19)

The linearization is justified by smallness of the displacements, \( \alpha_{1,2,3,2,3} \ll a^{-1} \).

### Table 1. Input quantities for equation (26).

| \( i \) | 1 | 2 | 3 |
|---|---|---|---|
| \( m_i \) | \( m_O \) | \( 2m_O m_C \) | \( 2m_O m_C \) |
| \( \alpha_i^2/m_i \) | \( \frac{1}{4} \) | \( \frac{1}{4} \) | \( \frac{1}{4} \) |
| \( \alpha_i^2 \) | \( \frac{1}{4} a^2 \) | \( \frac{1}{4} a^2 \) | \( \frac{1}{4} a^2 \) |
| \( \hbar \omega_i (eV) \) | 0.1679 | 0.08342 | 0.2971 |

#### 3.3. Matrix elements

To find the oscillatory part of the transition probability equations (15) and (19) are substituted into (8c). By doing so the integral in (8c) is separated into three independent integrals for each mode of oscillations. For a transition from CO2 (\( v_1, v_2, v_3 \)) to CO2 (\( u_1, u_2, u_3 \)) this integral can be then written as:

\[
V_{v_1,v_2,v_3}^{u_1,u_2,u_3} = \int \Psi_{v_1,v_2,v_3}^{*} (\alpha_{v_1,v_2,v_3}) \Psi_{u_1,u_2,u_3} (\alpha_{u_1,u_2,u_3}) dz_{v_1,v_2,v_3}
\]

(20)

Since the interaction takes place mainly in the vicinity of the closest approach and the rotation is sufficiently slow it is assumed that the angle \( \theta \) is not changed during the interaction, and can be taken out of the integral.

Expressions for the non-zero matrix elements (\( v_1, v_2, v_3 | u_1, u_2, u_3 \)) of the coordinate of a linear oscillator are readily available, see e.g. [24] section 23:

\[
\langle v | z | v - 1 \rangle^2 = \frac{\hbar v}{2mv^2}.
\]

(21)

Calculation of the matrix element of a double degenerate oscillator was addressed in [27]. The integral is transformed into polar coordinates:

\[
V_{v_1}^{u_1} = \int_{0}^{2\pi} \int_{-\infty}^{\infty} \Psi_{v_1} (\rho) \frac{e^{i\theta}}{\sqrt{2\pi}} (1 + a\cos\theta \sin\theta) \Psi_{u_1} (\rho) e^{-i\phi} \frac{\rho \sin\theta}{\sqrt{2\pi}} dp d\phi.
\]

(22)

Integration over \( \phi \) is performed applying the relation \( \int_{-\infty}^{\infty} e^{\mp i\phi} dp = 2\pi \delta (\alpha) \) (see [24, section 15, equation (15.7)]). The first term of the sum equals to:

\[
\int_{-\infty}^{\infty} \int_{0}^{2\pi} \Psi_{v_1} (\rho) \frac{e^{i\theta}}{\sqrt{2\pi}} \Psi_{u_1} (\rho) e^{-i\phi} \frac{\rho \sin\theta}{\sqrt{2\pi}} dp d\phi
\]

\[
= \delta_{v_1}^{u_1} \int_{0}^{2\pi} \Psi_{v_1} (\rho) \Psi_{u_1} (\rho) \rho dp d\phi = \delta_{v_1}^{u_1} \delta_{\rho}^{2\pi}.
\]

The analytic solution of the Schrödinger equation (14) is expressed in terms of the associate Laguerre polynomials (see...
and the integration over \( \rho \) above follows from the properties of those polynomials and from the normalization. In order to integrate the second term the \( v_2 \) is replaced by \( v_2 = \rho \sin \phi = \rho \frac{v_2}{2} \). This yields finally:
\[
V_{v_2}^{(l)} = \frac{\delta_{\phi}^{\alpha} g_{v_2}}{2i} \alpha_2 \sin \theta \delta_{\phi_1}^{\alpha} \langle v_2' | \rho | \rho_2^{(l)} \rangle - \frac{1}{2i} \alpha_2 \sin \theta \delta_{\phi_2}^{\alpha} \langle v_2' | \rho | \rho_2^{(l)} \rangle.
\]
(23)

The angular momentum \( l \) is always changed by \( \pm 1 \) when the quantum number \( v_2 \) is changed. The non-zero matrix elements of the double-degenerate linear oscillator found in [27] read:
\[
\begin{align*}
&\langle v^l | \rho | (v + 1) (l) \rangle^2 = \frac{\hbar}{2m\omega} (v - l + 2) \\
&\langle v^l | \rho | (v + 1) (l+1) \rangle^2 = \frac{\hbar}{2m\omega} (v + l + 2) \\
&\langle v^l | \rho | (v - 1) (l) \rangle^2 = \frac{\hbar}{2m\omega} (v + l) \\
&\langle v^l | \rho | (v - 1) (l+1) \rangle^2 = \frac{\hbar}{2m\omega} (v + l - 1)
\end{align*}
\]
(24)

Transformation of the original notation of [27] into equations (24) is explained in appendix A. Transitions \( v2 \rightarrow v2 - 1 \), \( l \rightarrow v2 \rightarrow [l] + 1 \) are not possible because the state \( v2 - 1 \) cannot have rotational quantum \( l = v2 + 1 \), see equation (36) below. (24) automatically give the correct value 0 for the matrix elements of such transitions.

4. Probabilities of the elementary vibrational transitions in CO\(_2\): a summary

Combining (20), (21), (23), (24) the resulting squares of the matrix elements of the individual modes can be expressed as follows:
\[
\begin{align*}
|V_{v1}^{(l)}|^2 &= |V_{v1}^{(l)}|^2 = \frac{\hbar}{2m\omega} (v - l + 2) \\
|V_{v1}^{(l+1)}|^2 &= \cos^2 \theta A_1 \alpha_1^\nu \|_{v1}^{(l+1)} \\
|V_{v1}^{(l-1)}|^2 &= \cos^2 \theta A_1 \alpha_1^\nu \|_{v1}^{(l-1)} \\
|V_{v2}^{(l+1)}|^2 &= \frac{\hbar}{4} \sin^2 \theta A_2 \alpha_2^\nu \|_{v2}^{(l+1)} \|_{v2}^{(l+1)}
\end{align*}
\]
(25)

where:
\[
A_i = a_i^x a_i^y \hbar^2 = \frac{1}{2m_i \omega_i} \frac{1}{2} \cdot 1.820 \cdot 10^{-3} \left( \frac{\alpha^2}{m} \right) \frac{a^2}{\hbar \omega_i}
\]
(26)

and \( X \) are the normalized matrix elements of linear oscillators:
\[
\begin{align*}
X_{v_{1,3}}^{(l)} &= v_{1,3}, & X_{v_{1,3}}^{(l+1)} &= v_{1,3} + 1 \\
X_{v_{2,1}}^{(l)} &= v_{2,1}, & X_{v_{2,1}}^{(l+1)} &= v_{2,1} + 1 \\
X_{v_{2,1}}^{(l)} &= v_{2,2} + l, & X_{v_{2,2}}^{(l+1)} &= v_{2,2} + l \\
X_{v_{2,3}}^{(l)} &= v_{2,3} + 2, & X_{v_{2,3}}^{(l+1)} &= v_{2,3} + 2 + 1.
\end{align*}
\]
(27)

### Table 2. Theoretical values of steric factors.

| End state \( v_{11}^a, v_{12}^a, v_{21}^a \) | Steric factor value |
|----------------------------------------|---------------------|
| \( v_{11}^a, v_{12}^a, v_{21}^a \)     | \( S_{11} = \cos^2 \theta \) 1/3 |
| \( v_{11}^b, v_{12}^b, v_{21}^b \)     | \( S_{12} = \sin^2 \theta \) 1/6 |
| \( v_{11}^c, v_{12}^c, v_{21}^c \)     | \( S_{13} = \cos^2 \theta \) 1/3 |
| \( v_{11}^d, v_{12}^d, v_{21}^d \)     | \( S_{14} = \sin^2 \theta \) 1/6 |
| \( v_{11}^e, v_{12}^e, v_{21}^e \)     | \( S_{15} = \cos^2 \theta \) 1/3 |
| \( v_{11}^f, v_{12}^f, v_{21}^f \)     | \( S_{16} = \sin^2 \theta \) 1/6 |

\*The initial state is CO\(_2\) \( v_{11}, v_{12}, v_{21} \).

In equation (26) with numerical factor \( \hbar \omega_i \) in eV, \( \alpha \) is in \( \AA^{-1} \). \( \langle \frac{\alpha^2}{m} \rangle \) is in (a.m.u.)\(^{-1} \). \( A_i \) itself is dimensionless. The quantities required for calculation of the factors \( A_i \) are put together in table 1. Definitions of \( \alpha_i \) and the corresponding coefficients \( \alpha_i^\nu \) are taken from [20] (same \( \alpha_i \) and \( \alpha_i^\nu \) were used in [21]). \( \hbar \omega_i \) are from [28]. Numerical values of the factors \( \langle \frac{\alpha^2}{m} \rangle \) are calculated assuming the carbon atom mass \( m_c = 12 \) and the oxygen atom mass \( m_o = 16 \), \( m_{CO_2} = 2m_o + m_c \).

The total probability \( P \) of a transition from CO\(_2\) \( v_{11}, v_{12}, v_{21} \) to CO\(_2\) \( v_{11}, v_{12}, v_{21} \) is obtained by combining the oscillatory and translatory parts, see (8a), and averaging over the angle \( \theta \):
\[
P_{v_{11},v_{12},v_{21}} = S \cdot A \cdot X \cdot Z \cdot (|\Delta E|, T) \exp \left( \frac{\Delta E}{RT} \right)
\]
(28)

\[
|\Delta E| = E_{v_{11},v_{12},v_{21}} - E_{a_i a_i a_i a_i}
\]
(29)

Here \( E \) are vibrational energies of the corresponding states, \( A \) and \( X \) are the products of \( A_i \), table 1, and the normalized matrix elements (27) of the modes which are changed in the transition. \( S \) is a ‘steric’ factor obtained by averaging the product of the angular terms of (25) over \( \theta \). Factors \( S \) for all transitions considered in the present work are given in table 2. Following [20] the calculation of \( S \) is done on assumption of a homogeneous distribution of \( \theta \), the distribution function is \( f(\theta) \) \( d\theta = \frac{1}{2} \sin \theta \) \( d\theta \).

The function \( Z (|\Delta E|, T) \) defined by (10) can only be used when \( \sigma > 1 \). Instead of this formula in practical calculations, see e.g. [5], a fit proposed in [32] is applied:
\[
Z (|\Delta E|, T) = \frac{4\mu T}{(\hbar a)^2} \left[ 3 - \exp \left( -\frac{2\sigma}{3} \right) \right] \exp \left( -\frac{2\sigma}{3} \right)
\]
(30)

This equation matches (10) when \( \sigma \to \infty \), and gives a correct asymptotic value for \( |\Delta E| = 0 \) as well, see figure 3. For \( \sigma \) it is convenient to re-write equation (11) in a more vivid form:
\[
\sigma = \frac{|\Delta E|}{E_{\sigma}}, \quad E_{\sigma} = E_{\sigma}^{300K} \sqrt{\frac{T}{300K}}, \quad E_{\sigma}^{300K} = \frac{\hbar a}{\pi} \sqrt{\frac{2 \cdot 300K}{\mu}}
\]
(31)

Parameter \( E_{\sigma}^{300K} \) calculated for different collision partners which may occur in CO\(_2\) plasma is given in table 3. Parameter \( a \) is calculated with the formula proposed in [17] as \( a = 2 \cdot 18.5/\left( r_{0}^A + r_{0}^B \right) \), where \( r_{0}^A, r_{0}^B \) are parameters of the Lennard-Jones potential of the colliding molecules. Values of \( r_{0} \) applied here are same as in [5]: \( r_{0}^{CO}_A = 3.94 \AA, r_{0}^{CO}_B = 3.69 \AA, \)
\[ r_0^{O_2} = 3.47 \, \text{Å}. \] In the equation for \( a \) the original coefficient 17.5 is replaced by 18.5 as suggested in [19, table 39.1, method B].

Generalization of the theory to the case where both colliding particles change their vibrational states appears to be straightforward. In order to do that the oscillations of the atom \( M \) have to be added to (16) in addition to oscillations of \( A \). Linearization will then lead to the expression \( \tilde{r} = r + \tilde{z} + \tilde{z}_M \), where \( \tilde{z}_M \) is the displacement of \( M \) from the equilibrium position in its molecule. Subsequently, (17) receives one more multiplier \( e^{i\omega t} \), and the transition probability (8a) will be multiplied by another term (8c) calculated for the molecule to which the atom \( M \) belongs.

The final result will be expressed by the same equation (28), only factors \( X \) and \( A \) have to include multipliers related to the elementary quantum jumps in the second molecule. If the directions of the colliding molecules can be taken as completely independent, then their steric factors \( S \) are calculated independently as well, and multiplied with each other. \( \Delta E \) in (28) and (30) is actually the difference of translational kinetic energies before and after the collision. Therefore, in the general case it must include the total change of vibrational energy in both molecules. That is, for inelastic collision of \( \text{CO}_2 \) molecules of the kind:

\[
\text{CO}_2 \left( v_1, v_2, v_3 \right) + \text{CO}_2 \left( u_1, u_2, u_3 \right) \\
\rightarrow \text{CO}_2 \left( \gamma_1, \gamma_2, \gamma_3 \right) + \text{CO}_2 \left( v_1, v_2, v_3 \right)
\]

equation (29) must be replaced by:

\[
\Delta E = E_{v_1, v_2, v_3} + E_{u_1, u_2, u_3} - E_{\gamma_1, \gamma_2, \gamma_3} - E_{v_1, v_2, v_3}.
\]

5. Two-modes approach

5.1. Combined states

In \( \text{CO}_2 \) the fundamental frequency \( \omega_1 \) is very close to \( 2\omega_2 \), see table 1. Therefore, neglecting terms of higher order over \( v_1, v_2, v_3 \) and \( I \), the vibrational energy \( E_v \) of a \( \text{CO}_2 \) molecule can be approximately written as:

\[
E_v \approx h\omega_2 \left( v_3 + 1 \right) + h\omega_3 \left( v_2 + \frac{1}{2} \right)
\]

(33)

where

\[
v_3 = 2v_1 + v_2, \quad v_5 = v_3
\]

(34)

\( v_5 \) describes both symmetric modes and is called 'the symmetric quantum number'.

The most basic assumption of the two-modes approach to describing the vibrational kinetics of \( \text{CO}_2 \) is that vibrational energy depends only on \( v_5 \), \( v_5 \). It is not critical that exactly expression (33) must hold, but the critical assumption on which all analytic derivations are based is that states with \( (v_1, v_2, v_3) \) which have same \( v_5 \) and \( v_5 \) all have exactly same vibrational energy. Such states can be gathered into one 'combined state' \( [v_5, v_5] \). Subsequently, \( (v_1, v_2, v_3) \) which belong to \( [v_5, v_5] \) are called the 'sub-states' of this combined state. Further, very fast equilibration of the sub-states populations is assumed which, together with the assumption of equal energy, implies that the populations of the sub-states are equal as well. In practical calculations as the energy of a combined state \( E_{v_5,v_5} \) the average vibrational energy of all its sub-states is taken. Those latter are calculated applying expressions more accurate than (33), see [28–31], which include terms of higher order.

From (34) one can see that if the symmetric quantum number is even, \( v_5 = 2n \), then \( v_5 = 2 \left( n - v_1 \right) \). Condition \( v_5 \geq 0 \) is fulfilled by all \( v_1 \geq 0 \) which run from 0 to \( n \). For the odd symmetric number \( v_5 = 2n + 1 \), \( v_5 = 2 \left( n - v_1 \right) + 1 \). The condition \( v_5 \geq 0 \) is again fulfilled by all \( v_1 \) from 0 to \( n \). The full set of the combinations \( (v_1, v_2) \) which belong to one \( v_5 \) state can be written as follows:

\[
v_5 = 2n \quad \text{or} \quad 2n + 1
\]

\[
v_1 = i, \quad v_2 = v_5 - 2i, \quad i = 0..n.
\]

(35)

As shown in [27] the values which can be assumed by the angular momentum \( I \) depend on \( v_2 \):

\[
I = -v_2, -v_2 + 2 \ldots 0 \quad \text{or} \quad 1 \ldots v_2 - 2, \quad v_2
\]

(36)

\( v_2 + 1 \) states in total.

The total number of sub-states in a combined state—the effective degeneracy of the state \( [v_5, v_5] \)—equals to:

\[
N_{v_5} = \sum_{i=0}^{n} \sum_{l=0}^{v_2+1} \frac{(v_2+1)}{n} (v_5 - 2i + 1)
\]

(37)
5.2. Average probabilities of transitions between combined states

Let us first consider a general case where the sub-states have different energies \( E_{v_1', v_2', l} \), and their populations are distributed according to Boltzmann formula. Relaxation of a combined state in a collision with unchanging particle M:

\[
\text{CO}_2 [v_1, v_2] + M \rightarrow \text{CO}_2 [u_1, u_2] + M
\]
is realized by the elementary transitions between its sub-states:

\[
\text{CO}_2 (v_1, v_2', v_3) + M \rightarrow \text{CO}_2 (u_1, u_2', u_3) + M.
\]
The probability of the transition between combined states is obtained by averaging over the elementary transitions:

\[
P_{v_1, v_2}^{u_1, u_2} = \frac{\sum_{v_1', v_2', v_3} \sum_{v_1, v_2} p_{v_1', v_2', v_3}^{v_1' v_2' v_3} \exp \left( -\frac{E_{v_1', v_2', v_3}}{T} \right)}{\sum_{v_1', v_2', v_3} \exp \left( -\frac{E_{v_1', v_2', v_3}}{T} \right)}.
\]

The probability \( p_{v_1', v_2', v_3}^{v_1' v_2' v_3} \) is defined by (28) with \( \Delta E \) defined by (29). The sum \( \sum_{v_1', v_2', v_3} \) is taken over all sub-states of the state \([v_1, v_2]\), the sum \( \sum_{v_1, v_2} \) represents all possible changes of \( l \) in the transition:

\[
\sum_{l_{-m}} = \sum_{l -l_{+1}} \quad \text{or} \quad \sum_{l_{-m}} = \sum_{l -l_{a} -1}.
\]
By applying the basic two-modes assumption that \( E_{v_1', v_2, l} = E_{v_1, v_2, l} \), \( E_{a, v_3} = E_{a, v_3} \), \( (38) \) is simplified as follows:

\[
P_{v_1, v_2}^{u_1, u_2} = (SA)^{u_1 u_2} X_{u_1}^{v_1} Y_{u_2}^{v_2} Z \left( |\Delta E|, T \right) \exp \left( \frac{\Delta E}{2T} \right)
\]

\[
Y_{u_2} = \frac{\sum_{v_1} \sum_{v_2} X_{v_1}^{v_1} Y_{v_2}^{v_2}}{\sum_{v_2} Y_{v_2}^{v_2}}
\]

\[
M_{u_2}^{v_2} = \frac{\sum_{v_1} \sum_{v_2} X_{v_1}^{v_1} Y_{v_2}^{v_2}}{\sum_{v_2} Y_{v_2}^{v_2}}
\]

\( N_{v_2} \) is determined by equation (37), \( X_{v_2}^{u_2} \) stands for the normalized matrix element of the asymmetric mode transitions, see (27):

\[
X_{v_2}^{v_2} = 1, \quad X_{v_2}^{v_2 - 1} = v_2, \quad X_{v_2}^{v_2 + 1} = v_2 + 1
\]
\( X_{v_1}^{v_1} \) is the remaining product of the matrix elements for the transitions between symmetric modes (or 1 if those modes are not changed).

For vibrational–vibrational relaxation between the combined states:

\[
\text{CO}_2 [v_1, v_2] + \text{CO}_2 [u_1, u_2] \rightarrow \text{CO}_2 [\gamma_1, \gamma_2] + \text{CO}_2 [v_1, v_2].
\]
realized by the elementary transitions where both molecules change their states:

\[
\text{CO}_2 (v_1, v_2', v_3) + \text{CO}_2 (u_1, u_2', u_3) \rightarrow \text{CO}_2 (\gamma_1, \gamma_2', \gamma_3) + \text{CO}_2 (v_1, v_2', v_3)
\]
an equation similar to (38) can be written for the average transition probability:

\[
P_{\gamma_1, \gamma_2}^{v_1, v_2} = \frac{\sum_{v_1', v_2', v_3} \sum_{v_1, v_2} p_{v_1', v_2', v_3}^{v_1' v_2' v_3} \exp \left( -\frac{E_{v_1', v_2', v_3}}{T} \right)}{\sum_{v_1', v_2', v_3} \exp \left( -\frac{E_{v_1', v_2', v_3}}{T} \right)}
\]

where, extending (28):

\[
P = P \left( \gamma_1, \gamma_2, \gamma_3 \right) \left( v_1, v_2' \right) \left( u_1, u_2' \right)
\]

\[
= (SA)_{v_1, v_2} \left( SA \right)_{u_1, u_2} X_{v_1, v_2} \left( \gamma_1, \gamma_2, \gamma_3 \right) Y_{u_1, u_2} \left( \gamma_1, \gamma_2, \gamma_3 \right)
\]

\[
\times Z \left( |\Delta E|, T \right) \exp \left( \frac{\Delta E}{2T} \right)
\]

\[\Delta E \] is defined by (32), \( Y_{u_2}^{v_2} \) are defined by (40).

5.3. Detailed balance

It can be shown that fulfillment of the condition:

\[
M_{v_1}^{v_1} = M_{u_2}^{u_2}
\]

is sufficient for the detailed balance relations to be valid for the probabilities of direct and reverse transitions between combined states defined by equations (39) and (44).

From equation (42) it is readily seen that \( X_{v_2}^{v_2} = X_{v_2}^{v_2} \). Therefore, if (45) holds for the transition probability defined by (39), then one can write:

\[
P_{v_1, v_2}^{u_1, u_2} N_{v_2} = (SA)_{v_1, v_2}^{u_1, u_2} X_{v_1, v_2}^{u_1, u_2} M_{u_2}^{v_2} Z \left( |\Delta E|, T \right) \exp \left( \frac{\Delta E}{2T} \right)
\]

\[
= (SA)_{v_1, v_2}^{u_1, u_2} X_{v_1, v_2}^{u_1, u_2} M_{u_2}^{v_2} Z \left( -|\Delta E|, T \right)
\]

\[
\times \exp \left( -\frac{\Delta E}{2T} \right) \exp \left( \frac{\Delta E}{T} \right)
\]

\[
= P_{u_1, u_2}^{v_1, v_2} N_{u_2} \exp \left( \frac{E_{v_1, v_2}}{T} \right)
\]

\[
\text{see (29) for } \Delta E. \text{ Or:}
\]

\[
P_{v_1, v_2}^{u_1, u_2} N_{v_2} \exp \left( -\frac{E_{v_1, v_2}}{T} \right) = P_{u_1, u_2}^{v_1, v_2} N_{u_2} \exp \left( -\frac{E_{u_2, u_2}}{T} \right).
\]
For the transition probability defined by (44):

\[
p_{\gamma_{a}s_{a}\gamma_{b}s_{b}}[z_{a}z_{b}]}N_{s_{a}}N_{s_{b}} = \frac{(SA)^{s_{a}}_{a}s_{a}}{N_{s_{a}}} N_{s_{a}} X^{s_{a}}_{a}s_{a} M^{s_{b}}_{b} M^{s_{b}}_{b} \times Z(\pm \Delta E/T) \exp \left( \pm \Delta E/T \right) \]

\[
= \frac{(SA)^{s_{a}}_{a}s_{a}}{N_{s_{a}}} N_{s_{a}} X^{s_{a}}_{a}s_{a} M^{s_{b}}_{b} M^{s_{b}}_{b} \times Z(\pm \Delta E/T) \exp \left( -\Delta E/T \right) \exp \left( \pm \Delta E/T \right) \]

\[
= p_{\gamma_{a}s_{a}\gamma_{b}s_{b}}[z_{a}z_{b}]}N_{s_{a}}N_{s_{b}} \exp \left( -\Delta E/T \right) \exp \left( \pm \Delta E/T \right).
\]

Or, making use of equation (32):

\[
p_{\gamma_{a}s_{a}\gamma_{b}s_{b}}[z_{a}z_{b}]}N_{s_{a}}N_{s_{b}} \exp \left( -E_{\gamma_{a}s_{a}} + E_{\gamma_{a}s_{a}} \right) = p_{\gamma_{a}s_{a}\gamma_{b}s_{b}}[z_{a}z_{b}]}N_{s_{a}}N_{s_{b}} \exp \left( -E_{\gamma_{a}s_{a}} + E_{\gamma_{a}s_{a}} \right).
\]

Equations (46) and (47) which are valid when (45) is fulfilled are indeed the detailed balance relations between the probabilities of the forward and backward transitions.

5.4. Fermi resonance

Wave functions of the states in Fermi resonance \(\Psi_{a}\) are linear combinations of the eigenfunctions (15) denoted here as \(\Psi_{i}(z)\) (\(X_{a}\) is denoted as \(z\))

\[
\Psi_{a}(z) = \sum_{i} a_{i} \Psi_{i}(z).
\]

The total number of functions \(\Psi_{a}\) equals the number of terms in the sum. The orthogonality condition\(^2\) reads:

\[
\int_{-\infty}^{+\infty} \Psi_{a}(z) \bar{\Psi}_{a}(z) dz = \delta_{a}^{m}.
\]

Substituting (48) yields:

\[
\int_{-\infty}^{+\infty} \left[ \sum_{i} a_{i} \Psi_{i}(z) \right] \left[ \sum_{j} a_{j} \Psi_{j}(z) \right] dz = \sum_{i} a_{i} a_{i}^{*} = \delta_{a}^{m},
\]

or, in a matrix form:

\[
\sum_{i} a_{i} a_{i}^{*} = \sum_{i} a_{i} a_{i}^{*} = \delta_{a}^{m} \Rightarrow AA^{*} = I.
\]

(I is a unit matrix). From this equation it readily follows that:

\[
(AA^{*})^{T} = A^{*} A^{*} = I
\]

\[
A = (AA^{*}) A = A (A^{*} A) \Rightarrow A^{*} A = I.
\]

That is:

\[
\sum_{i} a_{i} a_{i}^{*} = \sum_{i} a_{i} a_{i}^{*} = \delta_{a}^{m}.
\]

\(^2\) The author has to admit that although all examples found in the literature fulfill this condition he could not find a formal proof of that property.

The matrix element \(V_{a}^{b}\) of the transition between two Fermi states \(a\) and \(b\) is calculated as:

\[
u = u(z_{1}, z_{3}, \rho, \phi) = (1 + \alpha \rho z_{1} \cos \theta)(1 + \alpha \rho z_{3} \cos \theta)
\]

\[
\times (1 + \alpha \rho y z_{3} \sin \theta)
\]

\[
V_{a}^{b} = \int_{0}^{\infty} \int_{-\infty}^{+\infty} \Psi_{a}(z_{1}, z_{3}, \rho, \phi) u(z_{1}, z_{3}, \rho, \phi) \Psi_{a}^{*}(z_{1}, z_{3}, \rho, \phi) \rho d\rho d\phi dz_{1} dz_{3}
\]

\[
= \int_{-\infty}^{+\infty} \left[ \sum_{i} a_{i} \Psi_{i} \right] u \left( \sum_{j} b_{j}^{*} \Psi_{j} \right) \rho d\rho d\phi dz_{1} dz_{3}
\]

\[
= \sum_{i} \sum_{j} a_{i} b_{j}^{*} \int_{-\infty}^{+\infty} \Psi_{i} a \Psi_{j} r d\rho d\phi dz_{1} dz_{3}
\]

\[
= \sum_{i} \sum_{j} a_{i} b_{j}^{*} V_{j}^{i}
\]

where \(V_{j}^{i} = V_{a}^{m} V_{j}^{b} \), is the product of matrix elements (20) and (23). Square of the matrix element of the transition \(a \rightarrow b\):

\[
|V_{a}^{b}|^{2} = \left( \sum_{i} \sum_{j} a_{i} b_{j}^{*} V_{j}^{i} \right) \left( \sum_{i} \sum_{j} a_{i} b_{j}^{*} V_{j}^{i} \right)^{*}
\]

\[
= \sum_{i} \sum_{j} \sum_{l} a_{i} b_{j}^{*} a_{l}^{*} b_{l}^{*} V_{j}^{i} V_{l}^{i}.
\]

Integration of (51) over angle \(\theta\) yields:

\[
\int_{0}^{2\pi} \sum_{i,j,k} a_{i} b_{j}^{*} a_{l}^{*} b_{l}^{*} V_{j}^{i} (V_{l}^{i})^{*} d\theta
\]

\[
= SA \sum_{i,j,k} a_{i} b_{j}^{*} a_{l}^{*} b_{l}^{*} \sqrt{X_{i}^{j}} (\sqrt{X_{l}^{i}})^{*}.
\]

See (28). Let \(n\) are all states \(a\) which are described by the linear combinations (48) of the same states \(\Psi_{i}\), belonging to one combined state. Subsequently, \(m\) are all states \(b\) in Fermi resonance belonging to another combined state. Statistical factors \(Y\) in (39) and (44) written for the transition between those combined states will contain sums of the squares of matrix elements for all possible transitions between states \(n\) and \(m\).

Making use of (50) those sums can be transformed as follows:

\[
\sum_{n} \sum_{m} \left| X_{i}^{j} \right| = \sum_{k,l,i,j} \sum_{n} \sum_{m} a_{kl} a_{n} b_{m} b_{nl} \sqrt{X_{i}^{j}} (\sqrt{X_{l}^{i}})^{*}
\]

\[
= \sum_{k,l,i,j} \sqrt{X_{i}^{j}} (\sqrt{X_{l}^{i}})^{*} \sum_{n} \sum_{m} a_{kl} a_{n} b_{m} b_{nl}
\]

\[
= \sum_{k,l} \sum_{i,j} \sqrt{X_{i}^{j}} (\sqrt{X_{l}^{i}})^{*} \delta_{j}^{l} \delta_{j}^{l}
\]

\[
= \sum_{k} \sum_{l} \sqrt{X_{i}^{j}} (\sqrt{X_{l}^{i}})^{*} = \sum_{k} \sum_{l} X_{k}^{j}.
\]
This result implies that the sum taken for transitions between vibrational states described by the single eigenfunctions leads to exactly same result as when the orthogonal linear combinations of the eigenfunctions are taken into account explicitly. That is, in frame of the assumptions of the two-modes approximation and as long as the states in Fermi resonance are orthogonal there is no need to take them into account explicitly.

6. Calculation of the two-modes transition probabilities

6.1. Selection of relevant processes

The assumption that oscillating molecule is represented as a set of linear oscillators limits the allowed elementary transitions to one-quantum jumps only. Nevertheless, the total number of all logically possible transitions is very large. At the same time, a limited number of the most relevant processes can be defined based on the simple considerations which will be presented below. This pre-selected set of transitions is shown in table 4. In this table the column ‘combined’ denotes the end state of the molecules after the collision written it terms of combined states, and the ‘sub-state’ are the corresponding sub-states after the collision. The initial states are assumed to be:

\[ \text{CO}_2 [v_1, v_3] + M \text{ or } \text{CO}_2 [v_1, v_3] + \text{CO}_2 [u_s, u_a] \]

and

\[ \text{CO}_2 (v_1, v_1', v_3) + M \text{ or } \text{CO}_2 (v_1, v_1', v_3) + \text{CO}_2 (u_1, u_2', u_3) \]

respectively, where \( M \) is a particle which is not changed in the collision. Parameter (SA) in the last column is calculated assuming \( \alpha^{-1} = 0.2 \text{ Å} \) — last row of table 1. This coefficient, see (39) and (44), helps to sort out the processes whose probabilities can be expected to be negligibly small. Another parameter which helps to reject the likely irrelevant processes is \( |\Delta E| \) since the transition probability is rapidly decreased with increased \( |\Delta E| \), see figure 3.

Let us first consider collisions of the kind \( \text{CO}_2 [v_1, v_3] + M \) where only one particle is changed. Processes (1)…(4) in table 4 are all possible transitions of that kind where only one of the two modes—\( v_1 \) or \( v_3 \)—is modified. Those processes represent vibrational–translational (VT) energy exchange. Energy exchange between the modes \( v_1 \) and \( v_3 \) takes place in processes (5)…(7). Transitions which involve quantum jumps of the same modes as (5)…(7), but with both symmetric and asymmetric quantu changed in the same direction would represent another VT-channel. It can be immediately seen that they can be neglected compared to the processes (1)…(4). The (SA) of those latter is larger, and their \( |\Delta E| \) is smaller.

In processes (8)…(11) which describe vibrational–vibrational (VV) exchange only symmetric or only asymmetric mode is changed. The same transitions where the mode numbers are changed in the same direction would be VT-processes competing with (1)…(4). Applying the same argument as in the previous paragraph leads to the same conclusion that this VT-channel can be neglected compared to (1)…(4).

Collisions where both particles can change the symmetric and asymmetric modes simultaneously lead either to VT or VV-transfer or to the inter-mode exchange of vibrational energy. That is, only those of them shall be taken into account which can compete with processes (1)…(11). Same as above, VT-processes (1)…(4) and VV-processes (8)…(11) are always faster due to both larger (SA) and smaller \( |\Delta E| \). Hence, only inter-mode transitions which can compete with (5)…(7) should be left—those are processes (12)…(16).

In (12)…(16) the asymmetric mode of only one molecule is changed. Taking into account that \( h\omega_3 = 3.56 h\omega_2 \), table 1, the only process where \( v_3 \) of both molecules are changed, and which could be competitive with (12)…(16) is the one with smallest \( |\Delta E| \):

\[
\text{CO}_2 [v_1, v_3] + \text{CO}_2 [u_s, u_a] \rightarrow \text{CO}_2 [v_1 \pm 3, v_3 = 1] + \text{CO}_2 [u_s \pm 3, u_a = 1].
\]

The factor (SA) of this transition is very small, (SA) = \((S_{123}A_1A_2A_3)^2 = 2 \times 10^{-17}\), and this process can be neglected compared to (12)…(16).

The list of pre-selected processes, table 4, can be further refined. First of all, the alternative elementary pathways of the processes (2), (5), (9) marked with * can be immediately neglected because their (SA) is orders of magnitude smaller, and \( |\Delta E| \) is exactly same. Second, among the VT-processes (1)...(4) only the process (2) with smallest \( |\Delta E| \) must be taken into account, since (SA) of the processes (1), (3), (4) is same or smaller than that of (2). Due to the same reason process (5) can be neglected compared to (6). At the same time, (7) cannot be sorted out on the basis of purely qualitative considerations. Although for this process (SA) is much smaller than that of (6) its \( |\Delta E| \) is also smaller.

Since for vibrational–vibrational processes (8)...(11) \( |\Delta E| \) is very small, the magnitude of their probabilities is determined entirely by (SA). Thus, the process (11) can be neglected compared to (9) and (10). Processes (12)...(16) have close (SA) and (15) and (16) can be applied which takes away the processes (15) and (16).

The outcome of the selection procedure is presented in the first column of table 4 where only the processes selected for further consideration are numbered.

6.2. Transition probabilities

In table 5 all relevant processes picked up from table 4 are listed, together with statistical factors (40) required for the calculation of their probabilities. There are in total 15 processes (including direct and reverse transitions), but only 6 statistical factors \( Y \) listed in table 6 are required. To calculate the denominators of (40) equation (41) is reduced using definitions (35):

\[
M_{n_{1}}^{\nu_{2}} = \sum_{i=0}^{n} \sum_{j=0}^{\nu_2} X_{v_1, v_2}^{u_1, u_2} = \sum_{i=0}^{n} X_{v_1, v_2}^{u_1, u_2}(\nu_2 + 1). \tag{52}
\]

The quantities \( X_{v_1, v_2}^{u_1, u_2} \) are given in the last column of table 6. For transitions where \( v_2 \) is not changed \( X_{v_1, v_2}^{u_1, u_2} = X_{v_1, v_2}^{u_1, u_2} \). for
transitions where \( v_2 \) is changed:

\[
X_{v_1, u_1}^{v_2, u_2} = X_{v_1, u_1}^{v_2, u_1} + X_{v_1, u_1}^{v_2, u_2}.
\]

6.3. Calculation of statistical factors \( Y \)

Substituting \( X_{v_1, v_2}^{u_1, u_2} \) from table 6 into \((52)\) and replacing \( v_1, v_2 \) by applying \((35)\) yields:

\[
\frac{1}{2}M_{v_2}^{n+3} = \sum_{i=0}^{n} (v_1 + 1) (v_2 + 2) (v_2 + 1),
\]

The sums can be calculated analytically applying the known formulas \( \sum_{i=0}^{n} i^2 = n (n + 1) (2n + 1) / 6 \) and \( \sum_{i=0}^{n} i^3 = n^2 (n + 1)^2 / 4 \) which can be found e.g. in [33] (section 2.3.3 there). The resulting equations for \( M_{v_2}^{n} \) are different for odd and even \( v_2 \):

\[
M_{v_2}^{n-2} = \frac{1}{6} n (n + 1) (2n + 1)
\]

\[
M_{v_2}^{n-2} = \frac{1}{3} n (n + 1) (n + 2)
\]

\[
M_{v_2}^{n+2} = \frac{1}{6} (n + 1) (n + 2) (2n + 3)
\]

\[
M_{v_2}^{n+2} = \frac{1}{3} (n + 1) (n + 2) (n + 3)
\]

\[
M_{v_2}^{n+1} = \frac{2}{3} n (n + 1) (4n + 5)
\]
are linked by the detailed balance relation (45). It can be proven that the for the sums above the symmetry condition (45) is fulfilled. That is, the probabilities of the direct and reverse processes calculated in two-modes approximation are linked by the detailed balance relation (46) or (47).

| 2-modes transition | Statistical factor Y Matrix element $X_{v_0}^{v_1}$ |
|---------------------|-----------------------------------------------|
| $[v_i - 1, v_j]$    | $Y_{v_i}^{-1}$                              |
| $[v_i + 1, v_j]$    | $Y_{v_i}^{+1}$                              |
| $[v_i + 2, v_j - 1]$| $Y_{v_i}^{+2}$                              |
| $[v_i - 2, v_j + 1]$| $Y_{v_i}^{-2}$                              |
| $[v_i + 3, v_j - 1]$| $Y_{v_i}^{+3}$                              |
| $[v_i - 3, v_j + 1]$| $Y_{v_i}^{-3}$                              |

Table 5. List of relevant transitions obtained by taking out slower processes from table 4. The indices in the first column correspond to the first column in table 4.

| Elementary transition | $X_{v_1}^{v_0}^{a_1}$ | $X_{v_1}^{v_0}^{a_2}$ |
|-----------------------|------------------------|------------------------|
| $Y_{v_i}^{-1}$ $(v_i, v_j') \rightarrow (v_i + 1, v_j')$ | $v_1 + 1$ | $v_1 + 1$ |
| $Y_{v_i}^{+1}$ $(v_i, v_j') \rightarrow (v_i - 1, v_j')$ | $v_1$ | $v_1$ |
| $Y_{v_i}^{+1}$ $(v_i, v_j') \rightarrow (v_i, (v_j + 1)^{(+1)}$ | $v_2 + l + 2$ | $2(v_2 + 2)$ |
| $Y_{v_i}^{+1}$ $(v_i, v_j') \rightarrow (v_i, (v_j + 1)^{(-1)}$ | $v_2 - l + 2$ | $2v_2$ |
| $Y_{v_i}^{-1}$ $(v_i, v_j') \rightarrow (v_i - 1, (v_j - 1)^{(-1)}$ | $v_2 + l$ | $2v_2$ |
| $Y_{v_i}^{+1}$ $(v_i, v_j') \rightarrow (v_i + 1, (v_j + 1)^{(+1)}$ | $(v_1 + 1)(v_2 + l + 2)$ | $2(v_1 + 1)(v_2 + 2)$ |
| $Y_{v_i}^{+1}$ $(v_i, v_j') \rightarrow (v_i + 1, (v_j + 1)^{(-1)}$ | $(v_1 + 1)(v_2 - l + 2)$ | $2v_1 v_2$ |
| $Y_{v_i}^{-1}$ $(v_i, v_j') \rightarrow (v_i - 1, (v_j - 1)^{(-1)}$ | $v_1 (v_2 - l)$ | $2v_1 v_2$ |
| $Y_{v_i}^{+1}$ $(v_i, v_j') \rightarrow (v_i + 1, (v_j - 1)^{(-1)}$ | $v_1 (v_2 + l)$ | $2v_1 v_2$ |

Table 6. Statistical factors.

The final formulas for the factors $Y$ listed in table 6 read:

$$M_{v_i=2n+1}^{-1} = \frac{2}{3} (n + 1)(n + 2)(4n + 3)$$

$$M_{v_i=2n}^{+1} = \frac{2}{3} (n + 1)(n + 2)(4n + 3)$$

$$M_{v_i=2n+1}^{+1} = \frac{2}{3} (n + 1)(n + 2)(4n + 9)$$

$$M_{v_i=2n}^{-3} = \frac{2}{3} n(n + 1) + 1$$

$$M_{v_i=2n+1}^{-3} = \frac{2}{3} n^2(n + 1)(n + 2)$$

$$M_{v_i=2n}^{+3} = \frac{2}{3} (n + 1)^2(n + 2)(4n + 3)$$

$$M_{v_i=2n+1}^{+3} = \frac{2}{3} (n + 1)(n + 2)(n + 3)^2.$$ 

In the present paper the average probabilities of transitions have been derived between groups of vibrational states of CO$_2$ combined on assumption that their energy is a function of the effective symmetric $v_s$ and the asymmetric $v_a$ quantum...
numbers only. The final analytic formulas are expressed by equations (39), (44) and the equations for statistical factors $Y$ in section 6.3. It has been shown that the derived relations fulfill the detailed balance, and that the Fermi resonance must not be taken into account explicitly within the assumptions of the model.

Inaccuracies which may be introduced in the model by the harmonic oscillator approximation have been already briefly discussed in the introduction. The assumption that vibrational energy is strictly a function of only the two quantum numbers $v_1$ and $v_2$ which led to the simple algebraic expressions (39), (44) apparently introduces a further inaccuracy. This fact on its own does not discard the derived expressions and does not preclude their use. The theoretical formulas are commonly applied not to find the absolute values of the transition probabilities, but as scaling laws to find the rates of transitions for which no experimental data are available. See [5, 21]. That is, the final rate coefficients always contain uncertainties related to the experimental data, and those uncertainties can be large. The review paper [34] suggests typically a factor of 3 and even larger differences for the rate coefficients taken from different sources. The extra error introduced when proceeding from equations (38), (43) to (39), (44) is not of practical relevance if it is below the inaccuracies of the underlying experimental data. To estimate this error equations (39), (44) can be compared directly with the results obtained by applying (38), (43).

There is a difficulty which makes this estimate not straightforward. Namely the lack of an accurate model for vibrational energy which would be valid at large quantum numbers. Several expressions for the CO$_2$ vibrational energy can be found in the literature. The equation from [28] which keeps terms up to second order in quantum numbers $v_1$, $v_2$, $v_3$, $l$ was used in the present work. This expression was obtained by fitting the spectroscopic data for $v_1$ up to 3, $v_2$ up to 7 and $v_3$ up to 5. That is, applying this expression to $v_2$ significantly larger than 7 is already a wide extrapolation. In the more recent paper [29] an expression with terms up to third order is proposed, states with $v_3$ up to 9 were used for the fit. This expression which is thought to be more accurate than [28] produces much stronger scattering of the energies of sub-states belonging to one combined state for high $v_2$. This scattering can very likely be an artifact of the polynomial extrapolation of higher order. Furthermore, the effect mostly comes from the terms proportional to $l^2$. In a later paper [30] the data set of [29] was refined, and it was shown that a good fit can be obtained even with those terms set to zero. Extrapolation to large $v_3$ with the equation from [30] leads to much smaller scattering than both [28, 29]. That is, the basic assumption of the two-modes approximation would be fulfilled with much higher precision. Expression for vibrational energy from [31] which was used in [15] does not have the $l^2$-dependence as well.

It should be also reminded about another two known issues with the SSH theory itself. The first is that when the SSH expressions are formally applied to high excited states the resulting probabilities may become larger than one. This is a genuine problem of the method of perturbations (Zener’s method). This limitation can manifest itself especially at high temperatures. The second issue is related to the assumption of the dominance of short-range interactions. This assumption is known to be incorrect for vibrational–vibrational exchange between asymmetric vibrations with small $|\Delta E|$ [35, 36]. If dipole–dipole interactions do not affect the transitions between symmetric states (the CO$_2$ is a symmetric molecule with zero dipole moment in ground state), than this latter problem does not affect the derivations of the present paper. It only affects the process 4 in table 5 where a term which takes into account the long-range interaction has to be added, see e.g. [37].

**Appendix A. Translation of the results from [27]**

Formulas for the matrix elements of a double degenerate oscillator applied here were taken from the review paper [27]. According to table 4 there $(\rho_{Sh})$ is variable $\rho$ in [27]):

$$
\frac{\langle v' | \rho_{Sh}^l | (v + 1)^{l-1} \rangle^2}{\langle v' | \rho_{Sh}^l | (v + 1)^{l+1} \rangle^2} = \frac{v + l}{2} + 1
$$

(A.1)

It can be easily shown that (A.1) stay valid when $|l|$ is replaced by $l$. For $l \geq 0$, this statement is obvious. For $l < 0$, $|l| = -l$:

$$
\frac{\langle v' | \rho_{Sh}^l | (v + 1)^{l+1} \rangle^2}{\langle v' | \rho_{Sh}^l | (v + 1)^{l-1} \rangle^2} = \frac{v - l}{2} + 1
$$

To reconstruct the absolute values of the matrix elements implied in [27] it is noticed that $\rho_{Sh}^l$ is connected to $\rho$ in the present paper as:

$$
\frac{1}{\rho_{Sh}^l} = \frac{\rho_{Sh}}{\sqrt{2\pi mc\omega_{Sh}}} \text{, } \rho
$$

(A.2)
This follows from equation for $\xi_{1,2}$ in [27], section 3.1, definition of $r$ ($r_{SB}$) in section 3.2 there, and the definition of $\rho$ ($\rho_{SB}$) after equation (2). The frequency $\omega_{SB}$ is defined in [27], section 3.1, as:

$$\omega_{SB} = \frac{f}{c} = \frac{\omega}{2\pi c} \Rightarrow 2\pi c \omega_{SB} = \omega$$

where $\omega$ is the fundamental frequency as defined in the present paper. Substituting $\omega_{SB}$ into (A.2) yields:

$$\rho = \sqrt{\frac{\hbar}{m\omega \rho_{SB}}}.$$ 

Therefore, the squares of matrix elements (A.1) must be multiplied by $\frac{\hbar}{m\omega}$ to give the matrix elements in terms of $\rho$ of the present paper. This translation factor coincides with the matrix elements of linear oscillators given in [27], table 1:

$$\langle v | q | v - 1 \rangle^2 = \frac{v}{2} \langle v | q | v + 1 \rangle^2 = \frac{v + 1}{2}.$$ 

Multiplied by $\frac{\hbar}{m\omega}$ those formulas yield exactly (21).

Equation (A.1) multiplied by $\frac{\hbar}{m\omega}$, with $\frac{\rho_{SB}}{\rho}$ replaced by $\rho$ and $|l|$ replaced by $l$ give (24).

**ORCID iDs**

Vladislav Kotov © https://orcid.org/0000-0003-3832-4257

**References**

[1] van Rooij G J, Akse H N, Bongers W A and van de Sanden M C M 2018 Plasma Phys. Control. Fusion 60 014019
[2] Rusanov V D, Fridman A A and Sholin G V 1981 Sov. Phys. - Usp. 24 447
[3] Fridman A A 2008 Plasma Chemistry (Cambridge: Cambridge University Press)
[4] Herzberg G 1945 Infrared and Raman Spectra of Polyatomic Molecules (New York: van Nostrand)
[5] Kozak T and Bogaerts A 2014 Plasma Sources Sci. Technol. 23 045004
[6] Kozak T and Bogaerts A 2015 Plasma Sources Sci. Technol. 24 015024
[7] Koelman P et al 2017 Plasma Processes Polym. 14 1600155
[8] Peerenboom K, Parente A, Kozak T, Bogaerts A and Degrez G 2015 Plasma Sources Sci. Technol. 24 025004
[9] Berthelot A and Bogaerts A 2016 Plasma Sources Sci. Technol. 25 045022
[10] Sahai A, Lopez B, Johnston C O and Panesi M 2017 J. Chem. Phys. 147 054107
[11] de la Fuente J F, Moreno S H, Stankewicz A I and Stefanidis G D 2016 React. Chem. Eng. 1 540
[12] Rusanov V D, Fridman A A and Sholin G V 1986 Vibrational kinetics and reactions of polyatomic molecules in nonequilibrium systems Nonequilibrium Vibrational Kinetics ed M Capitelli (Berlin: Springer)
[13] Diomede P, van de Sanden M C M and Longo S 2018 J. Phys. Chem. A 122 7918
[14] Viegas P, van de Sanden M C M, Longo S and Diomede P 2019 J. Phys. Chem. C 123 22823
[15] Armenise I and Kustova E V 2013 Chem. Phys. 415 269
[16] Armenise I and Kustova E V 2018 J. Phys. Chem. A 122 5107
[17] Schwartz R N, Slawsky Z I and Herzfeld K F 1952 J. Chem. Phys. 20 1591
[18] Herzfeld K F and Litovitz T A 1959 Absorption and Dispersion of Ultrasonic Waves (New York: Academic)
[19] Schwartz R N and Herzfeld K F 1954 J. Chem. Phys. 22 767
[20] Herzfeld K F 1967 J. Chem. Phys. 47 743
[21] Ultrasystems Inc., Blauer J A and Nickerson G R 1973 Technical Report AFRL-TR-73-57
[22] Silva T et al 2018 Plasma Sources Sci. Technol. 27 015019
[23] Zener C 1931 Phys. Rev. 37 556
[24] Landau L and Lifshitz M 1965 Quantum Mechanics (Course of Theoretical Physics vol 3) (Oxford: Pergamon Press)
[25] Jackson J M and Mott N F 1932 Proc. R. Soc. A 137 703
[26] Fermi E 1931 Z. Phys. 71 250
[27] Shaffer W H 1944 Rev. Mod. Phys. 16 245
[28] Suzuki I 1968 J. Mol. Spectrosc. 25 479
[29] Chedin A 1979 J. Mol. Spectrosc. 76 430
[30] Teffo J-L, Sulakshina O N and Perevalov V I 1992 J. Mol. Spectrosc. 156 48
[31] Billing G D 1979 Chem. Phys. 41 11
[32] Keck J and Carrier G 1965 J. Chem. Phys. 43 2284
[33] Bronstein I N and Semendjaev K A 1991 Taschenbuch der Mathematik (Leipzig: Teubner)
[34] Joly V and Robin A 1999 Aerosp. Sci. Technol. 3 229
[35] Sharma R D and Brau C A 1967 Phys. Rev. Lett. 19 1273
[36] Sharma R D and Brau C A 1969 J. Chem. Phys. 50 924
[37] Jeffers W Q and Kelley J D 1971 J. Chem. Phys. 55 4433