Spatial nonhomogeneity effects in nonequilibrium vibrational kinetics

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Abstract

The paper addresses several problems of kinetics of spatially nonhomogeneous, vibrationally excited gas flows. It is shown that vibrational energy transfer in most diatomic molecules does not affect the transport coefficients of a gas, despite very fast vibration-to-vibration (V-V) rates among high vibrational levels. The influence of diffusion and the vibration-to-electronic (V-E) energy transfer on the vibrational distribution function (VDF) and on the vibrational energy balance is discussed. The diffusion and V-E corrections to the VDF and to the gas heating rate in vibrational relaxation is obtained for the "strong" excitation regime. The effect of the non-local diagnostics on the VDF is considered. It is shown that the spatial integration may significantly influence the inferred distribution function, as has been previously reported in experiments. A new approach for kinetic modeling of nonhomogeneous, vibrationally nonequilibrium flows is suggested. A two-dimensional kinetic model is developed which combines vibrational and translational energy balance and gas motion equations with the analytical theory of anharmonic oscillators. The comparison of the model calculations with both 1D and 2D experiments shows reasonable agreement within the applicability of the gas flow model.

1. Introduction

Nonequilibrium molecular vibrational mode distributions, maintained by the processes of excitation of molecular vibrations, vibration-to-vibration (V-V) and vibration-to-translation (V-T) collisional energy exchange in gases, have been widely studied for various species (see ref. [1] and references therein). These processes are of great interest due to their applications to the problem of environmental clean-up in gas discharges, plasma chemical reactors, molecular laser development, high-enthalpy gas dynamic flows and upper atmosphere chemistry.

For diatomic molecules, an analytical theory of vibrational relaxation of anharmonic oscillators, based on the modified Schwarz, Slawsky, and Herzfeld (SSH) [2,3] and Sharma–Brau [4] theories of the V-T and V-V rates, as well as many numerical models, have been developed in 60s and 70s (see ref. [5] and references therein). These theoretical models considered only the motion of the molecules in the space of vibrational energy (such motion occurs by excitation of vibrations, V-T and V-V exchange, radiation, chemical reactions and so on). However, in a real nonequilibrium gas flow, there is always a presence of some spatial nonhomogeneity in such parameters as gas velocity, temperature, vibrational energy, and concentrations of chemical species. This nonhomogeneity produces diffusion fluxes of mass, of momentum, and of the different modes of molecular energy. If the diffusion flux is comparable or greater than the flux of vibrational quanta in the vibrational energy space due to energy exchange...
in inelastic collisions, it may well affect the vibrational kinetic processes in a gas. Therefore, correct interpretation of the nonequilibrium effects in gas flows requires simultaneous consideration of kinetics and diffusion.

One type of experimental evidence of the correlation between the spatial nonhomogeneity and vibrational kinetics can be seen from the comparison of vibrational distribution functions (VDF) of CO, measured in different experiments, with the well-known theoretical predictions. The VDF is a direct measurement of the populations of each vibrational quantum state existing in the gas. Fig. 1 shows four different measurements of the CO VDF (points): (a) by Farrenq et al. [6], in a CO–N₂–He glow discharge; (b, c, d) by Rich et al. [7], by Adamovich et al. [8], and by Martin and Piar [9], respectively, in an optically pumped CO–Ar–He gas flow. Curves in all four graphs show the Treanor distribution

\[ f_v = f_0 \exp\left(-\frac{E_v}{T_v} + \frac{\Delta E \, v(v-1)}{T}\right), \]  

where \( f_v \) is the relative population of the \( v \)th vibrational quantum level of a diatomic molecule, \( E_v = \omega_v (1 - 2x_v) \), \( \Delta E = \omega_v x_v \), \( T \) is the translational/rotational temperature, and \( T_v = E_v / \ln(f_0/f_i) \) is the vibrational temperature of the
first level. All Treanor distributions are plotted at $T$ and $T_e$ inferred from the experiments. One can see that in cases (a) and (b) the decreasing branch of the Treanor distribution, closely fits the experimental distribution function, from $v = 0$ to its minimum at

$$v_0 = \frac{1}{2} + \frac{T}{2\chi_e T_e}.$$ (2)

The gently sloping plateau in the VDF starts from the Treanor minimum, where the distribution has the value

$$f_{\text{TR}} = \exp(-v_0^2 \Delta E/T) \sim \exp(-E_i T/4\chi_e T_e^2),$$ (3)

as is predicted by the analytical theory of anharmonic oscillators in the "strong" excitation regime, when the near-resonance V–V exchange

$$AB(v) + AB(w-1) \rightleftharpoons AB(v-1) + AB(w), \quad v \approx w \gg 1$$ (4)

dominates (see refs. [5,10,11]). These two cases (a, b) represent the experiments wherein the spatial nonhomogeneity is made not very significant: in case (a) [6], the infrared signal was collected along the axially uniform positive column of a glow discharge, and in case (b) [7], an unfocused gas dynamic laser beam with a uniform power distribution across the beam filled the entire optical absorption cell, with no substantial spatial gradients being present.

However, cases (c, d) demonstrate a considerable deviation from the predicted behavior. Here the well-pronounced plateau starts much earlier than the Treanor minimum, and the plateau height, given by the theory [5], $f_{\text{plateau}}/f_0 \approx f_{\text{TR}}$, is much lower (up to an order of magnitude) than in the experiment. In addition, numerical simulation using the one-dimensional master equation (see ref. [12]) shows that the measured VDF cannot be fit by the calculated curve for any conceivable V–V and V–T rates. Note that the measurements (c, d) have been made in a strongly nonhomogeneous environment, where CO in an absorption cell was excited by a focused CO laser beam. A similar effect has been reported in measurements by De Benedictis and Cramarossa [13] in a decaying CO–N$_2$ RF afterglow. The anomaly observed in these cases is fairly obvious due to the spatial nonhomogeneity.

So far, little attempt has been made to simulate the coupling of the spatial gradients and vibrational energy transfer at strong vibrational disequilibrium. One may mention papers by Osgood, Sackett and Javan [14], where the "vibrational temperature" diffusion has been experimentally observed and discussed; by Likalter and Naidis [10], who investigated the influence of diffusion on the VDF; by Dobkin and Son [15], where they studied the influence of the V–V and V–T processes on the heat conductivity; and a book by Rusanov and Fridman [16], where some issues of nonhomogeneous vibrational kinetics have been discussed qualitatively.

The present paper addresses the following aspects of nonequilibrium vibrational kinetics in nonhomogeneous gas flows: transport coefficient dependencies on vibrational excitation; mutual interaction of the vibrational energy diffusion and the VDF; the influence of the non-local diagnostics by emission or absorption spectroscopy on the observed signal and its interpretation. Finally, the problem of developing a kinetic model, which takes into account the relevant kinetic processes and the diffusion, will be also discussed.

2. Results and discussion

2.1. Vibrational excitation and transport coefficients

A thorough analysis of the influence of the vibrational energy exchange, as an inelastic process, on the heat conductivity and on the translational and vibrational energy fluxes, has been made by Dobkin and Son [15], on the basis of the Wang Chang–Uhlenbeck kinetic equations. It was concluded that at low and moderate temperatures, $100 < T < 700$ K, in diatomic gases as N$_2$, O$_2$, CO, NO, etc., where the rate constant of the V–V exchange
\[ AB(1) + AB(0) \rightarrow AB(0) + AB(1) , \]  
(5)

\( Q_{10} \) is much smaller than the gas dynamic collision frequency \( Z \) (at \( T < 1000 \text{K}, Q_{10}/Z < 10^{-2} \) for CO, and \( < 10^{-4} \) for \( N_2 \)), the influence is negligible. In other words, both translational and vibrational mode energies diffuse with approximately the same diffusion coefficient \( D \), given by the Chapman–Enskog theory, and the two energy fluxes can be written as follows:

\[ q_v = -\rho D \nabla E_v = -\rho c_p D \nabla T = -\lambda \nabla T , \quad q_{vib} = -\rho D \nabla E_{vib} = -\rho D y_\alpha \sum E_v \nabla f_v , \]

(6)

where \( \lambda = \rho c_p D \), and

\[ E_v = (R_0/\mu) \omega_\alpha v [1 - x_\alpha(v + 1)] , \]

(7)

and \( x_\alpha = \frac{N_v}{N} < 1 \) is the mole fraction of vibrationally excited species \( \alpha \) (\( N_2 \), CO, NO etc.) in an inert diluent, such as Ar or He. The authors then expressed the vibrational energy flux in terms of translational and vibrational temperature gradients, rather than the gradient of vibrational energy in Eq. (6),

\[ q_{vib} = -\lambda_v \nabla T - \lambda_{vv} \nabla T_v , \]

(8)

where

\[ \lambda_v = \rho D y_\alpha \sum E_v \frac{\partial f_v}{\partial T} , \quad \lambda_{vv} = \rho D y_\alpha \sum E_v \frac{\partial f_v}{\partial T_v} . \]

(9)

They found that \( \lambda_v \) and \( \lambda_{vv} \) for anharmonic oscillators in the "strong" excitation regime can exceed the usual thermal conductivity coefficient \( \lambda \) by two orders of magnitude. We note that this merely reflects the strong nonlinear dependence of vibrational energy \( E_{vib} \) on \( T \) and \( T_v \), but by no means the influence of vibrational energy transfer in the inelastic collisions on the vibrational mode energy diffusion. This also shows that the use of the expression \( q_{vib} = -\lambda \nabla T_v \) for the vibrational energy flux at strong vibrational disequilibrium would be totally erroneous.

The results by Dobkin and Son can be also obtained by the less formal, but more illustrative method of comparison of the characteristic time for elastic collisions, \( \tau_{TT} \sim 1/NZ \), with the time for VDF change due to the V–V processes, \( \tau_{vv} \). For low vibrational levels, it is enough to note that one has a small parameter, which is the ratio of \( \tau_{TT} \) and the characteristic time of non-resonance V–V exchange

\[ AB(v) + AB(w - 1) \rightarrow AB(v - 1) + AB(w) , \quad w \gg v \sim 1 , \]

\( 4' \)

\[ \tau_{vv}^N \sim 1/(NQ_{10}y_\alpha) , \text{ such as } \]

\[ \tau_{TT}/\tau_{vv} \sim Q_{10}y_\alpha/Z \ll 1 , \]

(10)

which makes impossible any diffusion–vibration coupling. This informal comparison particularly gives insight into the case of large inelastic transition probabilities. We can understand qualitatively, why even near-resonance V–V exchange at high vibrational levels, where V–V rates may become equal to or greater than the gas kinetic frequency (see ref. [17]), still has no effect on the transport coefficients. For the higher levels (plateau region in the "strong" excitation regime), the characteristic time of the VDF change is determined by the simultaneous action of the two fast energy transfer processes (forward and reverse processes of Eq. (4)). This results in the slow vibrational quanta flow upward along the vibrational energy axis [5,10,11]. The flux of quanta \( \Phi_0 \) in \( \text{cm}^3/\text{s} \), is given by

\[ \Phi_0 = \frac{6 \varepsilon Q_{10} \Delta E}{cTB_{vv}^3} (v_0 + 1)^2 f_\text{TR}^2 = v(v_0 + 1)^2 f_\text{TR}^2 , \]

(11)

where \( \nu \) (in \( \text{cm}^3/\text{s} \)) is the vibrational quanta diffusion coefficient, and

\[ \xi = 1 + \frac{\delta_{vv}^3}{12 \Delta_{vv}} (\pi/\Delta_{vv})^{1/2} Q_{10}/Q_{10}^5 . \]

(12)
In Eqs. (11, 12), $Q_{10}^S$, $Q_{10}^B$, $\delta_{VV}$, and $\Delta_{VV}$ are parameters in the expression for the V–V rates (see Eqs. (4, 4'),

$$Q_{v+1,v}^{S, B} = (v+1)(w+1)\left\{Q_{10}^S \exp(-\delta_{VV})[v-w]\right\} \times \left[\frac{1}{2} - \frac{1}{2} \exp(-\delta_{VV}[v-w]) + Q_{10}^B \exp(-\Delta_{VV}(v-w)^2)\right],$$

where $Q_{10}^S$ and $Q_{10}^B$ are the rates of the process (5) calculated taking into account only short-range repulsive forces and long-range dipole–multipole interaction, respectively. Then the characteristic time for VDF change due to the V–V processes is

$$\tau_{VV}^S \sim \frac{y_{_S} \sum E_f f_0}{E_i \Phi_0 N_Y^2} \approx \frac{1}{Q_{10}^S N_Y^2},$$

which is much smaller than the time of near-resonance V–V exchange, $\sim 1/Q_{10}^S N_Y^2$. For typical experimental conditions in strongly pumped CO, at $T \approx 100$–$800$ K, $T_e \approx 2000$–$4000$ K, one has $\tau_0 \sim 5$–$10$, $f_{TR} \sim 10^{-2}$–$10^{-3}$, $\delta_{VV} \sim 6.0$ $T^{-1/2}$–$0.2$–$0.3$, $Q_{10}^S \sim 10^{-12}$ cm$^3$/s, $\xi = 1$–$10$, and the ratio $\tau_{TR}/\tau_{VV}^S \sim 10^{-5}$–$10^{-7}$. This means that the VDF is actually frozen in the elastic collision timescale, despite the fact that the V–V exchange may occur at nearly the gas kinetic rate. This again includes the possibility of diffusion–vibration coupling.

Note that Eq. (11) is not valid in the “moderate” excitation regime, when non-resonance V–V exchange with the low levels is faster than the near-resonance processes. However, in this case one obviously has $\tau_{VV}^B \geq \tau_{VV}^S$, and we come back to Eq. (10). Finally, the V–T relaxation in most diatomic gases at moderate temperatures is so slow (except for high levels) that $\tau_{VV}^T$ is always much greater than $\tau_{VV}^S$.

Thus, one may say that diffusion of the vibrationally excited diatomic molecules may be described using a common diffusion coefficient $D$ for all vibrational levels. The only dependence of $D$ on the vibrational energy is due to the change of the elastic collision cross section with vibrational state, which is a weak dependence. A strong effect of vibrational energy transfer on the transport coefficient only exists for molecules having a large dipole moment, and therefore having large $Q_{10} \sim Z$ (such as CO$_2$ and N$_2$O), and this case requires detailed calculations using the approach of ref. [15].

2.2. Diffusion and vibrational distribution function

It is easy to show that for the Treanor part of the VDF the influence of diffusion is always small except for the very low pressures; comparing the characteristic times for diffusion over a radius $R$, $\tau_{diff} \sim R^2/D$, and the nonresonance V–V exchange, $\tau_{VV}^S$, one has

$$R \sim \left(\frac{D}{Q_{10}^S N_Y^2}\right)^{1/2} \sim \left(\frac{D_{00} N_0}{Q_{10}^S N_Y^2}\right)^{1/2},$$

where the subscript 0 refers to a “normal pressure”, $P = 1$ atm. For example, for pure CO at $T \approx 300$ K this correction is important only if $R \leq 10^{18}$/N cm, or $R \leq 1$ mm even at 1 Torr total pressure.

An analysis of the diffusion flux influences on the plateau part of the VDF for the “strong” excitation regime was first made by Likalter and Naidis [10]. The VDF perturbation by diffusion was calculated as a first-order correction to the analytical solution for the “homogeneous” VDF (ref. [5]),

$$f_n = \frac{N_v}{N} = \frac{1}{v+1} - \frac{P_{10}}{\xi Q_{10}^S N_Y^2} \frac{T}{12 \Delta E} \frac{\delta_{VV} \exp(\delta_{VT} v)}{v+1} - \frac{A_{10}}{\xi Q_{10}^S N_Y^2} \frac{T}{12 \Delta E} \frac{\delta_{VV}^3}{\delta_{VT} v+1},$$

Here $P_{10}$, $\delta_{VT}$ and $A_{10}$ are parameters in the expressions for the V–T and spontaneous radiation rates,

$$P_{v+1,v} = P_{10}(v+1) \exp(\delta_{VT} v), \quad A_{v+1,v} = A_{10}(v+1),$$

(17)
and \( \Gamma \) is to be found from matching of the distribution (1) and (16) at the Trenor minimum \( v_0, \Gamma = f_{TR}(v_0 + 1) \) at \( P_{10}, A_{10} \approx Q_{10} \). In Eq. (16), the first term on the right-hand side describes the plateau in the VDF, created by the nearly constant flow of quanta \( \Phi_0 \) (see Eq. (11)) due to near-resonance V–V exchange, and the other two terms describe the plateau cutoff due to the V–T relaxation and radiation, respectively. According to ref. [10], diffusion adds the following correction to the right-hand side of Eq. (16),

\[
\text{Diff} \approx \frac{L(v) - L(v_0)}{v + 1} \frac{D}{2 \Phi_0 N^2 y_v} \frac{d^2 (IN)}{dx^2},
\]

(18)

where

\[
L(v) = v \left[ \ln \left( \frac{v_1}{v} \right) + 1 \right],
\]

(19)

and \( v_1 \) is the coordinate of the VDF cutoff due to some sink such as V–T relaxation, radiation, diffusion or chemical reactions. For a first estimate, \( v_1 \) can be found by equating \( f_{v_1} \) in Eq. (16) to 0. One finds that the diffusion correction becomes important when

\[
R \approx \left( \frac{v_0 v_1 D}{2 \Phi_0} \right)^{1/2},
\]

(20)

which for typical conditions in nonequilibrium CO environments (see section 2.1) gives \( R \approx (10^{16} - 10^{17})/N \text{ cm}, \) or \( R \approx 0.1 - 1 \text{ mm} \) at \( P \approx 100 \text{ Torr} \). This is a characteristic scale of spatial nonhomogeneity in focused laser beams [12] and in gas discharges with a contracted current channel [18]. Note that, if the condition (20) holds, the diffusion flux exceeds the vibrational quanta flow due to V–V exchange, \( \Phi_0 \). In the non-steady-state flows, this may strongly affect the rise and decay time for characterizing the population and depopulation of the high vibrational levels of diatomic species. Measurements of these characteristic times have been previously used for the inference of the V–V and V–T rates in the time-resolved optical pumping experiments in CO [17,19] and NO in ref. [20]. Eq. (20) indicates that the time-resolved data can be adequately used for this purpose only if the inequality is reversed, which can happen only at high pressures.

Strong vibrational excitation may also lead to occurrence of different vibrationally stimulated chemical reactions with high activation energies (see refs. [5,16]), which, in turn, may affect the VDF. For a chemical reaction faster than resonance V–V exchange, i.e. reactions for which

\[
A \gg Q_{10} v_a^2 f_{v_a}^2,
\]

(21)

where \( A \) is the preexponential factor in the chemical reaction rate expression, \( k = A \exp(-E_a/T) \), and \( v_a \sim E_a/\omega_a \) is the vibrational energy activation level, the plateau distribution has been found by Macheret [21]:

\[
f_v = \frac{\Gamma}{v + 1} \left( \frac{v_a - v}{v_a - v_0} \right)^{1/2}.
\]

(22)

The solution (22), which is independent of the nature of the chemical reaction and of its rate, should replace the first term on the right-hand side of Eq. (16). It is important, for example, to use this correction for simulation of the VDF in the presence of the fast collisional near-resonance vibration-to-electronic (V–E) energy transfer, such as

\[
\text{CO}(X^1\Sigma, v \approx 40) + M \rightarrow \text{CO}(A^1\Pi) + M,
\]

(23)

which has an estimated rate of \( k_{ve} \sim 10^{-12} \text{ cm}^3/\text{s} \) [17,22]. The process (23) is presumably responsible for the experimentally measured [6–9] fall-off of the CO VDF at level \( v \approx 40 \). In fact, there are no experimental measurements where CO has been found to be pumped higher than this level, even at cryogenic temperatures, when the V–T relaxation rates dramatically drop (see Fig. 1a and ref. [6]). Another process which may possibly lead to the VDF cutoff at \( v \approx 40 \), is the two-quantum near-resonance V–V exchange, such as
CO\((v = 0) + \text{CO}(v = 41) \rightarrow \text{CO}(v = 1) + \text{CO}(v = 39)\), \(\Delta E \approx 70\, \text{K}\),

which has been theoretically discussed in refs. [23,24]. Note that for the process (24) to influence the VDF, its rate should also be \(\approx 10^{-12}\, \text{cm}^3/\text{s}\), or comparable to that of the exact resonance one quantum process (5), \(Q_{10} = 2 \times 10^{-12}\, \text{cm}^3/\text{s}\), which seems unlikely.

If one takes into account the plateau shape of Eq. (22) instead of \(P'(v + 1)\) in Eq. (16), the diffusion correction (18) remains valid, but with a different quantum number function \(L(v)\),

\[
L(v) = -L(v) = \frac{1}{2(v_a - v_y)} \int_{v_y}^{v} \left[ -2(v_a - v')^{1/2} + \sqrt{v_a} \ln \left( \frac{\sqrt{v_a} - \sqrt{v_a' - v'}}{\sqrt{v_a} + \sqrt{v_a' - v'}} \right) \right]^{1/2} dv'.
\]

Eq. (19') has been obtained here by integration of the master equation with a diffusion term in the regime of the “strong” excitation (see also ref. [5]). Fig. 2 plots the function \(L(v)\) obtained by Likalter and Naidis [10] (Eq. (19)) and by us (Eq. (19')), for a typical Treanor number \(v_0 = 10\) and plateau cutoff level \(v_1 = v_a = 42\). One can see that the present diffusion correction (18), (19'), is by about factor of 2 smaller than what has been obtained in ref. [10]. The reason is that the number of available vibrational quanta per molecule decreases with vibrational quantum number due to V–E sink, which also reduces the diffusion flux.

Thus, the approximate analytical solution of the master equation (Eqs. (1) and (16) with corrections (18) and (22)) may be used for simulation and analysis of the quasi-steady-state vibrational distribution functions of diatomic molecules, created by the V–V and V–T relaxation, diffusion, and fast V–E energy transfer.

2.3. Spatial integration

As we have shown in section 2.2, the perturbation of the Treanor distribution by diffusion is a minor effect in cases of practical interest. However, the experimental data (see Fig. 1) show that the observed perturbation is much stronger. Note that in an actual experimental setup, the collected signal comes from an extended volume in space, and one observes only the integrated signal intensity,

\[
I_v = \int_{v_1}^{v_2} A_v N(x) f_v(y) dy = A_v \bar{f_v} \int_{v_1}^{v_2} N(y) dy.
\]

In Eq. (25), \(A_v\) is the Einstein coefficient, \(N(y)\) and \(f_v(y)\) are the total concentration of molecules and the relative population of the level \(v\) at point \(y\), respectively, and \(\bar{f_v}\) is the inferred “observed” population. Note that even if in
the experiment the optics are focused at some particular point in space, Eq. (25) is still valid, since the decrease of the radiating volume towards the focal point is exactly compensated by its greater steradiancy.

For the VDF of diatomic molecules, neglecting the influence of the V–T relaxation, radiation and diffusion, this gives (see Eqs. (1) and (16))

\[
\tilde f_v = \int_{\gamma_1}^{\gamma_2} f_0(y) \exp\left(-\frac{E_1}{T_v(y)} + \frac{\Delta E}{T(y)} \nu - 1\right) \frac{dy}{T(y)}
\]

(26)

for the Treanor part of the VDF and

\[
\tilde f_v = \frac{1}{\nu + 1} \left(\frac{v_a - v}{v_a - v_0}\right)^{1/2} \int_{\gamma_1}^{\gamma_2} [v_0(y) + 1] \exp[-v_0(y) \Delta E/T] \frac{dy}{T(y)}
\]

(27)

for the plateau. The observed rotational population of the vibrational band 1 → 0,

\[
\tilde f_{j,1} = \int_{\gamma_1}^{\gamma_2} \frac{B_1}{T(y)} (2j + 1) \exp\left(-\frac{B_1 j(j + 1)}{T(y)}\right) f_0(y) \frac{dy}{T(y)} \exp\left(-\frac{E_1}{T_v(y)}\right)
\]

(28)

can be used for the inference of the common “rotational/translational” temperature \(\tilde T_{r,1} \approx T\), which gives the best fit between the measured rotational spectrum of the thermally nonhomogeneous gas volume, \(\tilde f_{j,1}\), and the single rotational temperature synthetic spectrum

\[
\tilde f_{j,1} = \frac{B_1}{\tilde T_{r,1}} (2j + 1) \exp\left(-\frac{B_1 j(j + 1)}{\tilde T_{r,1}}\right).
\]

(29)

Now we show that in spatially nonhomogeneous media the integration substantially perturbs the Treanor part of the VDF. If one fits the measured VDF by the theoretical “local” distribution function, then for \(\nu = 1\) one obtains

\[
\tilde f_1 \sim \exp\left(-\frac{E_1}{T_v}\right),
\]

(30)

while for any vibrational level in the plateau one has

\[
\tilde f_v \approx \frac{1}{\nu + 1} \left(\frac{v_a - v}{v_a - v_0}\right)^{1/2} \left(\frac{1}{2x_0 T_v^{**}} + \frac{3}{2x_0 \tilde T_{r,1}}\right) \exp\left(-\frac{E_1 \tilde T_{r,1}}{4x_0 T_v^{**}}\right).
\]

(31)

In the simplest case when \(T(x) = \tilde T_{r,1} \approx \) const., which can be realized if \(y_a \ll 1\), when the gas heating is not substantial due to thermal inertia provided by an inert diluent, and assuming that \(T_v\) changes linearly,

\[
T_v(y) = T_v + \frac{T_{v,2} - T_{v,1}}{y_2 - y_1} y,
\]

(32)

we calculate the effective vibrational temperature of the first level, \(T_v^{**}\), and that of the plateau, \(T_v^{**}\), as a function of the minimum and maximum vibrational temperatures \(T_{v,1}, T_{v,2}\), and \(T\) (see Fig. 3). One can see that \(T_v^{**}\) is always greater than \(T_v\), and the difference \(T_v^{**} - T_v\) increases with the spatial nonhomogeneity \(\Delta T_v\) and temperature. In other words, the observed plateau in the VDF corresponds to higher \(T_v\) than the low vibrational levels (see Fig. 4), as has been previously reported and qualitatively explained in ref. [8]. It has been noted that the signal corresponding to the plateau part of the VDF comes from the most excited part of the gas volume with very high \(T_v\), which is localized near the excitation source. At the same time, there is a considerable contribution of the signal from the much less excited region to the Treanor part of the VDF, which decreases its “observed” vibrational temperature,
Fig. 3. Effective vibrational temperatures of the first level, $T^*_v$, and of the plateau, $T^*_{v_p}$. Eqs. (30) and (31) as functions of the spatial nonhomogeneity $\Delta T_v = T_v - T_e$ and temperature.

Fig. 4. Integrated VDF (solid line) and Treamor distributions with two effective vibrational temperatures (dashed lines).

$T^*_v$. A simple estimate of the ratio of the two characteristic distances at which the population of some plateau level $v_p$, and the population of the level $v = 1$, drop e times, gives

$$\frac{L(v = v_p)}{L(v = 1)} \sim \frac{1}{v_0} \left(1 + \frac{T_e}{E_1}\right) \sim \frac{2}{v_0} \sim \frac{4\lambda T_e}{T} \sim 0.2 - 0.3$$

for the typical CO experiments. This estimate also shows that in the measured VDF, the plateau population in the most excited region is underestimated by several times, compared with the population of the Treamor part of the VDF, due to normalization on the same space area, $\sim L(v = 1)$. This may bring a substantial uncertainty in the inference of kinetic rates from the steady-state VDF measurements, which has been done in ref. [8] for the rate of vibrationally induced ionization in CO.

2.4. Two-dimensional kinetic model of vibrationally nonequilibrium gas flows

The analysis of the influence of diffusion and non-local diagnostics on the VDF measurements, made in sections 2.2 and 2.3, shows that the correct interpretation of experimental results requires two-dimensional kinetic modeling. The complete kinetic model for the simulation of spatially nonhomogeneous, vibrationally nonequilibrium gas flows has to include the following equations:

- gas mixture equations of motion;
- translational energy equation with the terms describing the presence of direct heating sources and energy exchange between the translational and vibrational modes;
- a system of the partial differential kinetic equations (PDE) for the population of each vibrational level of each diatomic species (master equation with diffusion),

$$\frac{1}{N} \frac{dN}{dT} f_{v} + \frac{df_{v}}{dr} = \text{div}(D \text{ grad}(f_{v})) + (\text{Exc})_{v} + (V-T)_{v} + (V-V'_{v})_{v} + (V-V')_{v} + (V-E)_{v} + (\text{Rad})_{v} + (\text{Chem})_{v}, \quad v = 0, v_{\text{max}},$$

where $(\text{Exc})_{v}$, $(\text{Rad})_{v}$, $(\text{Chem})_{v}$ and $(V-V')$ are the terms responsible for the excitation of vibrations, infrared radiation, chemical reactions and the vibrational energy transfer between the excited species, respectively.

The solution of such a large number of PDEs $(v_{\text{max}} \sim 50)$ requires extensive computer resources and this has not been attempted here. Even if one neglects diffusion on the right-hand side of Eq. (34), one has $\sim N_{e}^{\gamma}$ ordinary
differential equations, where \( N_g \) is the total number of the grid nodes, which is also unacceptable. However, if the vibrational kinetics are uncoupled from the gas flow field, that is if the characteristic time for the VDF to reach the steady-state, \( \tau_{\text{VDF}} \), is much less than the residence gas dynamic time, \( \tau_{\text{G}} \), the problem may be reduced to the solution of vibrational and translational mode energy balance equations. In this quasi-steady-state case, the system of Eqs. (34) can be replaced by just one equation for the average vibrational energy per molecule of each diatomic species, \( E_{\text{vib}} = \sum E_{v} f_{v} \), where \( E_{v} \) is given by Eq. (7). For now, we confine ourselves by the case of just one diatomic species in an inert diluent, and therefore do not consider V–V' exchange, which can be incorporated later (see ref. [5]).

This energy equation may be obtained directly from Eq. (34) and the continuity equation. In the boundary layer approximation one has

\[
\rho u \frac{\partial E_{\text{vib}}}{\partial x} + \rho u \frac{\partial E_{\text{vib}}}{\partial y} = \frac{1}{y'} \frac{\partial}{\partial y} \left( y' \rho D \frac{\partial E_{\text{vib}}}{\partial y} \right) + \sum E_{v}(\text{Exc})_{v} - (\text{Vib})^{-} .
\]

(35)

Here \( u \) and \( v \) are gas velocity components, \( i = 0, 1 \) for the planar and cylindrical geometries, respectively, and \((\text{Vib})^{-}\) is the vibrational energy loss in V–T, V–V, V–E processes, radiation and diffusion. For the two practically important cases of vibrational excitation by a laser beam and by electron impact, the excitation term can be written as

\[
(\text{Exc})_{v} = T_{v+1,0} f_{v+1} - T_{v,0} f_{v} + T_{v-1,0} f_{v-1} - T_{v,0} f_{v} ,
\]

(36)

where, for example,

\[
T_{v+1,0} = \sum \frac{A_{v} B_{v}}{8 \pi c k T} \left( \frac{2}{\nu} \right) I_{v} \theta \exp \left( - \frac{B_{v} j(j+1)}{T} \right) f_{v} ,
\]

(37)

and

\[
\sum E_{v}(\text{Exc})_{v} \approx \eta_{\text{vib}} iE/N = e y_{e} \nu \mu E^{2} ,
\]

(38)

respectively. In Eqs. (37) and (38), \( A_{v} \) is the Einstein coefficient, \( B_{v} \) is the rotational constant, \( \nu \) is the laser line frequency, \( I_{v} \) is the laser power density on this line in W/cm², \( \theta \) is the absorption line shape factor, \( S_{j} \sim j \) is the Hönig–London factor, \( i \) is the discharge current density, \( E \) is the electric field, \( y_{e} \) is the ionization fraction, \( \mu \) is the electron mobility, and \( \eta_{\text{vib}} \) is the energy fraction of the discharge going into vibration.

In a discharge, one also has to supply equations for concentrations of charged species (electrons and ions), as well as the equation for the electric field (Poisson equation), which, for example, for the positive column of the glow discharge gives \( E = \text{const} \). In addition, the direct heating of the gas by electron impact,

\[
(\text{Dir. heat.}) = (1 - \eta_{\text{vib}}) iE/N ,
\]

(39)

has to be taken into account in the translational energy equation. Parameter \( \eta_{\text{vib}} \) can be found from the solution of the Boltzmann equation for the electron energy distribution function (see ref. [18]).

In the quasi-steady-state “strong” excitation regime, when the vibrational energy loss due to the V–T relaxation on the low levels is negligible, the term \((\text{Vib})^{-}\) in Eq. (35), can be expressed in terms of vibrational quanta flow \( \Phi_{0} \),

\[
(\text{Vib})^{-} \approx \Phi_{0} (R_{0} / \mu) E_{1} (1 - 2 \chi_{v} v_{0}) N y_{e}^{2} \sim \text{const.} \frac{\gamma_{T}}{\gamma_{R}} (v_{0} + 1)^{2} (1 - 2 \chi_{v} v_{0}) .
\]

(40)

According to this result, first obtained by Gordiets and Mamedov [25], the total vibrational energy relaxation rate does not depend on the V–T, V–E, chemical reaction rates, diffusion, and is also independent of the VDF shape above the Treanor minimum \( v_{0} \). The comparison of the formula (40) with the master equation numerical calculations, performed by us, shows good agreement within 20%. For example, Fig. 5 shows the vibrational quanta diffusion coefficient \( \nu \), given by Eq. (11), and calculated using master equation [12].
The vibrational distribution function $f_v$, which still can be present in the excitation term of Eq. (33), is to be determined using the approximate analytical solution ((11), (16), (18), (22)) for the steady-state VDF, where $T_v(x, y, z)$ becomes a parametric function to be found from the normalization conditions

$$\sum f_v(T, T_v, x, y, z) = 1, \quad \sum E_v f_v(T, T_v, x, y, z) = E_{vb}(x, y, z).$$

(41)

The translational energy equation at low Mach numbers can be written as

$$\rho c_p u \frac{\partial T}{\partial x} + \rho c_p v \frac{\partial T}{\partial y} = \frac{1}{y'} \frac{\partial}{\partial y} \left( \lambda' \frac{\partial T}{\partial y} \right) + (\text{Trans})^+ + (\text{Dir. heat.}).$$

(42)

Here the term $(\text{Trans})^+$ describes the gas heating in different relaxation processes. The local vibrational energy loss in relaxation, $(\text{Vib})^-$, is not necessarily equal to the local translational energy gain, $(\text{Trans})^+$. The vibrational energy can be lost from the volume by diffusion or by $V\!\!E$ energy transfer (if existent), followed by the fast radiative deactivation of the excited electronic state ($V\!\!E$/radiation sink). For example, the radiative lifetime of the CO(A $^1\Pi$) state, prepared in the $V\!\!E$ process (23), is $\tau = 10$ ns. The relative energy fractions removed from the vibrational mode by $V\!\!V$, $V\!\!E$/radiation, $V\!\!T$ energy transfer and by diffusion can be easily calculated by differentiation the energy flux along the vibrational axis, $\Psi = \Phi(v) E_v (1 - 2x_v)$,

$$\frac{1}{\Psi_v} \frac{d\Psi}{dv} = \frac{1}{\Phi_v (1 - 2x_v)} \frac{d}{dv} \left[ \Phi(v) (1 - 2x_v) \right] = - \frac{\Phi(v)}{\Phi_v} \frac{2x_v}{1 - 2x_v v_0} - \frac{1}{\Phi_v} \frac{d\Phi(v)}{dv} \frac{1 - 2x_v}{1 - 2x_v v_0}.$$

(43)

Here the first term on the right-hand side describes the energy loss due to the decrease of the vibrational quanta toward the high vibrational levels ($V\!\!V$ exchange), while the second term is the energy loss due to decrease of the number of quanta per molecule (diffusion and/or $V\!\!E$ transfer). Taking into account the vibrational quanta flow change towards the higher levels due to $V\!\!E$ energy transfer and diffusion, one obtains (see also Eqs. (11), (18), (22)),

$$\Phi(v) \approx \alpha v^2 \approx \Phi_{V\!\!E}(v) + \Phi_0(v) = \Phi_0 \frac{v_s - v}{v_s - v_0} + \left[ L(v) - L(v_0) \right] \frac{D}{T_0^2 N \gamma_a} \frac{d^2 (IN)}{dx^2},$$

(44)

where $L(v)$ is given by Eq. (19'). If $V\!\!E$ transfer is not present ($v_s \gg v, v_0$), then the plateau in the VDF is truncated by $V\!\!T$ relaxation, and the first term in Eq. (44) becomes equal to a constant $\Phi_0$, while the diffusion correction is given by Eq. (19).

For the plateau, controlled by $V\!\!T$ relaxation (see Eq. (16)), integration of Eq. (43) gives the relative energy fractions going into $V\!\!V$, $V\!\!T$ processes and diffusion,
\[(V-V) \approx \frac{2x_e(u_1-u_0)}{1-2x_e u_0}, \quad (\text{45})\]

\[(\text{Diff}) = \frac{D}{\Phi_0 \Gamma^2 N^2 \gamma_a} \frac{d^2}{dx^2} \left( (N) \frac{(v_1-v_0)}{1-\frac{1}{2}x_e(v_1+v_0)} - v_0 \ln(v_1/v_0)(1-x_e u_0) \right), \quad (V-T) = 1 - (V-V) - (\text{Diff}). \quad (\text{47})\]

For the plateau, controlled by V-E transfer (see Eq. (22)), when the V-T losses are negligible at any vibrational level, the energy dissipation in V-V processes becomes smaller than that given by Eq. (45), by a factor of 2. The V-E/radiation loss is

\[(V-E) \approx \frac{1-x_e(u_0+u_0)}{1-2x_e u_0}. \quad (\text{48})\]

The expression for vibrational energy loss in diffusion is too long, and we leave it here as an integral

\[(\text{Diff}) = \frac{1}{\Phi_0 (1-2x_e u_0)} \int_{u_0}^{u_0} \frac{d\Phi_q(v)}{dv} (1-2x_e u) \, dv, \quad (\text{49})\]

where \(\Phi_q(v)\) is given by Eq. (44) with \(L(v)\) from Eq. (19'). In one-dimensional flow, a simple estimate for typical values of \(v_0 \lesssim 10, v_1 \lesssim 40, x_e \sim 6 \times 10^{-7}\), and for the plateau controlled by V-T relaxation, gives \((V-V) \sim 40\%, (V-T) \sim 60\%\). For the case of the V-E transfer domination one has \((V-V) \sim 20\%, (V-E) \sim 80\%\). Of course, the energy fraction removed by V-E transfer, may strongly vary with pressure (or collisional deactivation time of the excited electronic state) and the optical density of a gas.

The two energy equations (35) and (42) have to be supplemented by the momentum and continuity equations,

\[
\begin{align*}
\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} & = 1 \frac{\partial}{\partial y} \left( y' \eta \frac{\partial \alpha}{\partial y} \right) - \frac{\partial P}{\partial x}, \quad (\text{50})
\end{align*}
\]

\[
\frac{\partial (\rho u y')}{\partial x} + \frac{\partial (\rho v y')}{\partial y} = 0. \quad (\text{51})
\]

The natural boundary conditions are

\[
\begin{align*}
\left. \frac{\partial u}{\partial y} \right|_{y=0} = \left. \frac{\partial T}{\partial y} \right|_{y=0} = \left. \frac{\partial E_{\text{vib}}}{\partial y} \right|_{y=0} = 0, \quad (\text{52})
\end{align*}
\]

\[
\left. u \right|_{\text{wall}} = \left. v \right|_{r=0} = 0, \quad \left. T \right|_{\text{wall}} \approx T_w(x), \quad \gamma v_e T_{\text{wall}} + D \frac{\partial E_{\text{vib}}}{\partial y} \right|_{\text{wall}} = 0,
\]

where \(\gamma\) is the probability of heterogeneous vibrational relaxation on the wall, \(v_e\) is the average molecular velocity, and \(T_w(\gamma)\) is determined by the cooling regime of the laser absorption cell or the discharge tube.

Thus, we obtain the complete system of equations \(((35), (42), (50)-(51))\), where the VDF is given by Eqs. (1), (16), (18) and (22), which allow simulation of 2D vibrationally nonequilibrium, quasi-steady state gas flows in the boundary layer approximation. Note that, beside its affordability, this model has one additional important advantage, since it depends only on a few kinetic rates. We also note that the shape of the VDF, except the cutoff coordinate \(v_1\), depends on the oscillator matrix elements.

The model can be generalized for non-steady-state problems using the time-dependent analytical theory of anharmonic oscillators, developed in refs. [11,26].
2.5. Results of calculations and discussion

First, the model developed in section 2.4 has been tested in calculations of quasi-1D CO–Ar–He flow in a laser absorption cell used in experiments of Rich et al. [7] (see also section 1). In these experiments, an absorption cell of 25 cm length and 0.95 cm in diameter was nearly filled by a 200 W gas dynamic CO laser beam directed along the flow axis, the gas flow velocity being 9.0–9.8 m/s at 1 atm total pressure. The quasi-steady-state condition was satisfied at $\tau_{\text{OD}} \approx 30$ ms and $\tau_{\text{PV}} \approx 1$ ms. No substantial spatial gradients were present because of the uniform laser power distribution across the beam, which removes the diffusion effects.

Necessary kinetic data used in the model, such as $Q_{\text{CO-Ar-He}}^{\delta}$, $Q_{\text{Ar-CO}}^{\delta}$, $\Delta_{\text{PV}}$, $\Delta_{\text{V}}$, $P_{\text{CO-Ar}}$, $P_{\text{Ar-CO}}$, and $P_{\text{He}}$ were taken from ref. [12]. Note that the values of these parameters are not those recommended by SSH and Sharma–Braun theories; they have been inferred from the experiments [7, 17], where theoretical relations (13) and (17) for $V-V$ and $V-T$ rates have been used only a convenient parameterizations.

Since at this high pressure the collisional deactivation time of the CO(A $^1\Pi$) state is $\approx 0.1$ ns, while its radiative lifetime is $\approx 10$ ns, it has been assumed that all the energy going into the singlet state came back to the vibrational mode of the CO ground electronic state in collisions.

Fig. 6 presents the comparison of the model calculations of the VDF (curves) with the experimental data of ref. [7] (points), at a distance of 4 cm from the cell inlet, for three different gas mixtures. One can see that the results are in good agreement. The vibrational temperature obtained in the calculations from the energy balance equations (35) and (42), fits its experimental value, $T_v = 2600$ K. The plateau slope, given by Eq. (22), is consistent with the assumption of the presence of a strong vibrational energy sink at the level $v \approx 40$ of CO. The decrease in relative populations of the high levels with the increase of He concentration is due to the faster CO $V-V$ relaxation on He atoms, which has also been reported in ref. [8].

The absorbed laser power, obtained in the calculations, also agrees well with the experimental value of 40 W (the experimental laser spectrum was one of the input parameters of the computer code). The calculated temperature increase of $\Delta T \approx 60$ K at the outlet of the cell agrees with the calculations using a 1D master equation within 20%.

Next, the 2D model has been used for the simulation of the glow discharge experiments [6]. Here, a gas mixture CO:N$_2$:He = 0.2:0.7:5.2 at a total pressure of 6.1 Torr was flowing through a discharge tube of 120 cm length and 1.34 cm in diameter, cooled by liquid nitrogen. The 2-arm discharge voltage and current were $V = 6.6$ kV and $I = 14$ mA, respectively, at an interelectrode distance of $L = 54$ cm, which gives a power loading of $Q \approx 1.7$ W/cm in the positive column. At present, our 2D kinetic model does not incorporate the simulation of a discharge. For this reason, the electron concentration distribution across the tube was taken to be the Shottky distribution

$$n_e(y) \sim J_0(2.4 y/R),$$

(53)
where \(J_0\) is Bessel function, normalized to the total discharge current \(I\). The distribution (53) assumes that the ionization rate across the discharge tube is constant and the loss of electrons is by diffusion, which is a reasonable approximation for low-pressure glow discharges [18]. The electric field has been assumed to be constant in the entire discharge area, \(E = V / L\). Finally, the discharge energy fraction going into vibrations was assumed to be \(\eta_{\text{vib}} \approx 1\), which is a good approximation for CO: \(N_2: \text{He}\) mixtures at the reduced electric field \(E/N \approx 1 \times 10^{-16} \text{ V cm}^{-2}\) (see ref. [16]). These assumptions allowed simple calculation of the vibrational excitation term (38) in the vibrational energy equation (35).

We also assumed that nitrogen in the mixture does not contribute in the vibrational energy balance, despite its effective vibrational excitation by electron impact. In the steady-state, the vibrational temperatures of CO and \(N_2\) are related as follows (see ref. [27]):

\[
\frac{D_{v}^{N_2}}{T_{v}^{N_2}} - \frac{E_{v}^{\text{CO}}}{T_{v}^{\text{CO}}} = \frac{E_{v}^{N_2} - E_{v}^{\text{CO}}}{T},
\]

which for experimental values of \(T = 125 \text{ K}\) and \(T_{v}^{\text{CO}} = 1975 \text{ K}\) gives \(T_{v}^{N_2} = 900 \text{ K}\). Simple estimates then show that the vibrational energy stored in nitrogen is several orders of magnitude less than that in CO, and therefore it has been neglected. The V–V and V–T data for CO–CO and CO–He were extrapolated down to \(\approx 100 \text{ K}\) from the results of trajectory calculations by Billing [28], which are available for \(T \geq 200 \text{ K}\).

At these experimental conditions the collisional and radiative lifetimes of CO(A \(^1\Pi\)) state are comparable. For this reason, it is not clear what part of the discharge energy is being lost by the ultraviolet radiation, and how much energy is going into the gas heating. We made two limiting calculations, assuming zero and 100% efficiency of the V–E/radiation mechanism.

Fig. 7 shows the results of comparison of the experimental CO VDF [6] (points) with the 2D calculations (curves). Here the "observed" VDF and temperature were calculated using Eqs. (25) and (28), with a substitution \(dy \rightarrow dy\), since in the experiments [6] the IR signal has been collected along the discharge tube. The solid and the dashed curves correspond to the assumptions of zero and 100% energy loss by radiation, respectively. One can see that in both cases the agreement of the calculated VDF with the experiment is reasonable (both curves are close to each other since the vibrational energy relaxation rate is approximately the same). However, the calculated average temperature at zero radiative energy loss, \(T = 123 \text{ K}\), is much closer to its experimental value \(T = 125 \pm 3 \text{ K}\), than the temperature, corresponding to the second assumption, \(T = 94 \text{ K}\). Better understanding of the role of CO(A \(^1\Pi\)) radiation in the energy balance of vibrationally excited CO requires additional experimental measurements of absolute intensities of the CO 4th positive emission bands in optical pumping experiments.
The "dimple" in the VDF at the level \( v \approx 25 \), which may be seen more clearly in the original work \([6]\), is presumably due to the near-resonance V–E transfer

\[
\text{CO}(X \ ^1\Sigma, v \sim 25) + M \approx \text{CO}(a \ ^3\Pi) + M,
\]

which has not been considered by the model.

The influence of diffusion on the VDF has been found to be weak (\( \leq 10\% \)), and therefore is not shown in Fig. 7. The reason is that at these discharge parameters, the spatial nonhomogeneity is not very strong, and, in addition, the radial profiles of \( T \) and \( T_v \) are similar (see Fig. 8), which leads to a weak change of the expression \( IN \) in the diffusion correction (18),

\[
IN = \nu_0 f_{TR} N \sim \frac{1}{T} \frac{T}{\nu_x T_v} \exp(-E_i T/4 \nu_x T_v^2)
\]

and makes the correction negligible.

Both quasi-1D and 2D calculations for the conditions \([6,7]\) have shown that the diffusion energy flux to the wall consists almost entirely of the translational energy, due to the small probability of vibrational excitation quenching on the wall \( \gamma \). Measurements of vibrational quenching of \( \text{H}_2, \text{D}_2, \) and \( \text{N}_2 \) on quartz, steel and aluminum give \( \gamma = 6 \times 10^{-4} - 5 \times 10^{-3} \) at room temperature (see ref. \([29]\)). Variation of \( \gamma \) in the range \( 10^{-2} - 10^{-4} \) did not substantially affect the energy balance, integrated VDF and temperature for both experimental conditions \([6,7]\).

The question of applicability of the 2D kinetic model to the optical pumping experiments \([8,9]\) needs careful analysis. In ref. \([8]\), the CO–Ar–He mixture at a total pressure of \( P = 100 \) Torr was flowing in a six-arm cross absorption cell of 35 mm inner diameter and 12 cm total length (see the details and the schematic of the cell in refs. \([8,12]\)). As one can see, the cell length is comparable to its diameter. In addition, the diameter of the focused laser beam, \( d_L \approx 2.5 \) mm, was much less than the cell diameter, to provide higher power density (the focal area size was estimated to be \( d_f \approx 1 \) mm).

In this situation, the gas flow in the near-axis region of the cell is a circular jet, which accelerates due to the axial pressure gradient

\[
\frac{\partial P}{\partial x} \sim \rho u \left( \frac{\partial T}{\partial x} - \frac{1}{A} \frac{\partial A}{\partial x} \right),
\]
resulting from the fast intensive gas heating in vibrational relaxation processes. In Eq. (57), $A$ is the effective cross-section of the jet, $A \sim \chi / R_e$, for the laminar jet. Since $A$ is much smaller than the cross section of the cell, this axial gradient is not constant across the cell (or radial and axial velocity components are comparable), and the boundary layer approximation is not valid. Calculations performed using the boundary layer flow code have shown that the model gives substantially underestimated values of the observed VDFs (up to an order of magnitude) and translational temperatures (up to two times) compared to the experiments. Qualitatively, this can be explained by the effect of suction of the ambient gas by the accelerating jet, which is created by the positive radial pressure gradient, $\partial P / \partial y \sim - \partial P / \partial x$. This suction reduces the effect of diffusion towards the cell walls, and actually "locks" the energy in the near-axis area, which increases the integrated $T$ and $T_e$.

In experiments [9], the CO–Ar–He mixture was injected in the cell from a 4 mm tube, perpendicular the focused laser beam axis, and extracted through a similar tube placed 8 mm downstream (see the cell schematic in ref. [12]). Obviously, the characteristic size of the excitation region along the gas flow is comparable to its size across the jet, and therefore the axial and radial gradients of temperature and vibrational energy are also comparable. For this reason, again, the boundary layer approach cannot be used.

As one can see, the influence of the flow field on the spatial distributions of temperature and vibrational energy, and therefore on the measured $T$ and VDF, cannot be neglected. Simulation of the nonequilibrium gas flows [8,9] can be performed using the same approach described in section 2.4, and the full 2D Navier–Stokes equations. The kinetic model based on the Navier–Stokes flow code, is currently being developed.

3. Summary

The influence of spatial nonhomogeneity on the vibrational kinetics of anharmonic oscillators has been analyzed. It has been found that for the diatomic molecules with $Q_{10} / Z \ll 1$, vibrational energy relaxation has no effect on the heat conductivity of a gas, despite the very high probabilities of V–V processes at the high vibrational levels. Analytical correction for V–E transfer and diffusion influence on the VDF and on the gas heating rate in vibrational relaxation has been obtained. It has been shown that non-local diagnostics of spatially inhomogeneous, vibrationally nonequilibrium flows leads to a substantial deviation of the observed VDF from the theoretical predictions. A 2D kinetic model based on the vibrational and translational mode energy balance equations, on an analytical VDF of the diatomic species and on a boundary layer flow code, has been developed. The comparison of the model with the experiments has shown good agreement within the limits of the boundary layer approximation applicability. A more advanced model based on the same semi-analytical approach and the Navier–Stokes flow code is being developed.

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