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On the determination of the vibrational temperature by Optical Emission Spectroscopy

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Abstract.

Over the years, until the present days, a persistent mistake has been found in the literature: the use of the “vibrational temperature” of an emitting electronic state as somewhat representative of the vibrational temperature of the gas in the discharge. Such a temperature is determined by fitting the spectra measured by optical emission spectroscopy. Besides the misuse of the word *temperature*, the results of such fittings are ambiguously named “vibrational temperature” and sometimes used to argue about the vibrational non-equilibrium and its variation with discharge conditions. What has this *temperature* to do with the vibrational excitation of the molecules’ ground state, i.e. of the large majority of gas components? It is well established that the connection between the vibrational population of the excited and the ground state exists through the excitation process, the collisional quenching, and the vibrational relaxation in the manifold of the excited state. Nevertheless, this is very often ignored in the literature. In this note, we discuss this subject with the example of the “vibrational temperature” of the $N_2(C,v)$ manifold, showing how much all the mentioned parameters can drive to incorrect deductions from an anyway conceptually wrong measurement.

Keywords: plasma diagnostics, optical emission spectroscopy, gas discharges.

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1. Introduction

The vibrational excitation of molecules in gas discharges is of great interest in the kinetics of gas phase processing. An actual issue is, for example, its importance in promoting the dissociation of CO₂ with high efficiency. The experimental determination of the vibrational distribution function, VDF, or, more simply, of the vibrational temperature, is then an attractive issue. It is clear that, from the point of view of the discharge kinetics and processing, we are speaking of the vibrational excitation of ground state neutral molecules, which are by orders of magnitude the most abundant species in the system; except for highly energy intensive discharges, with very high ionization degrees, where electronically excited states have a role in the overall kinetics [1]. The measurement of the VDF with an adequate time resolution requires laser Raman techniques like the Linear (spontaneous), CARS and absorption spectroscopy (for an overview of VDF measurement techniques, see [2] and references therein).

Optical emission spectroscopy (OES), i.e. the measurement and analysis of spectra from electronically excited states, nowadays benefits of the availability of high performance and easy to use spectrographs. Bands systems can be measured with high time resolution, and the vibrational population of electronically excited states can be inferred using simulation codes available for free. Is it possible to infer the VDF from OES data? It is well known that a connection between the vibrational population of the excited state and that of the ground state can exist through the excitation process and the collisional processes in the manifold of the excited state. In other words, a collision-radiative model (CR) should, in principle, allow inferring information on the VDF from OES measurements, provided, first of all, that the excitation has something to do with the ground state, and, second, that the collision processes are all quantitatively established. Electron impact excitation is the elective process for such a possibility to be feasible. Luminescence from recombination or energy transfer between excited states must be discarded. This procedure, although obvious, is not always adopted. Over the years, until the present days, a persistent mistake has been found in the literature: the use of the “vibrational temperature” of an emitting electronic state as somewhat representative of the vibrational temperature (T_v) of the gas in the discharge. Besides the misuse of the word *temperature*, the result of such fittings is an ambiguous “vibrational temperature” that, unfortunately, is sometimes used to

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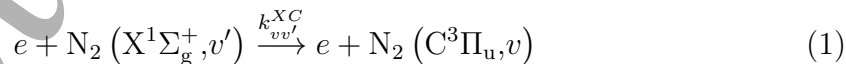
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argue about the vibrational non-equilibrium, its variation with discharge conditions and time in pulsed discharges. In the present note, we discuss this subject with the example of the “vibrational temperature” of the $N_2(C,v)$ manifold, T_v^C from now on, showing how much all the mentioned parameters can drive to incorrect deductions from an anyway conceptually wrong measurement. The $N_2(C,v)$ manifold is by far the best characterized one, with decent knowledge of the electron impact excitation cross-sections and of the collisional rate constants [3, 4]. Using the collisional-radiative model of [5], we have calculated how much the ratio T_v^C/T_v can change on changing the collisional conditions by varying the gas pressure or the gas composition. Although the $N_2(C)$ state might be peculiar, its example shows the kind of misinterpretations that can be found in the literature. The present paper is mainly a warning against this widespread mistake, and an attempt to fix the state of the arts of using OES to determine the VDF of the molecule ground state; with a digression on the meaning and criteria for a condition of partial equilibrium in the ro-vibrational manifold of an electronic state.

For a correct reading of the paper we would like to specify two points. The use of a vibrational temperature for the ground state is often an oversimplification or an approximation in highly non-equilibrium systems like gas discharges ([2, 6]). We are using it for demonstrative purposes only. In addition, we shall show the dependence of experimental outcomes on changing one parameter at a time, for the sake of the discussion clarity. The parameters can change simultaneously in real discharge conditions, making it even more challenging to avoid misinterpretations.

2. Model for $N_2(C,v)$ population

The $N_2(C^3\Pi_u)$, which decays radiatively emitting the Second Positive System (SPS) bands, is produced in a discharge mostly by electron impact on the ground state:



whose rate constant depends on the electron energy distribution function. Here we restrict to this case only, where there is a connection between the VDF of the ground state and the vibrational population of the excited state that emits radiation. Other processes not involving the ground state, like the Pooling reaction $N_2(A) + N_2(A) \longrightarrow N_2(C) + N_2(X)$, produce a completely different vibrational population

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of the C state [7]. Their presence would pollute the analysis that follows. In an experiment, one should ascertain that they are negligible.

The equation for the time evolution of the population C_v of the vibrational level $N_2(C,v)$ can be written:

$$\frac{dC_v}{dt} = n_e \sum_{v'=0}^{10} k_{vv'}^{XC} X_{v'} - (k_v^{QE} X + A_v) C_v - X \sum_{w \neq v} k_{vw} C_w + X \sum_{w \neq v} k_{wv} C_w \quad (2)$$

that, at the stationary state, becomes:

$$n_e \sum_{j=0}^{10} k_{vj}^{XC} X_j = (k_v^{QE} X + A_v) C_v + X \sum_{w \neq v} k_{vw} C_w - X \sum_{w \neq v} k_{wv} C_w \quad (3)$$

where n_e is the electron density; X_v and X are the populations of the vibrational level $N_2(X,v)$ and of the whole ground state $N_2(X)$, respectively; k_v^{QE} the electronic quenching rate constant; A_v the radiative rate of the $N_2(C,v)$ state; k_{vw} the vibrational energy transfer rate constant. The quantitative knowledge of excitation and collision processes in these equations requires a short discussion.

Electron impact cross-sections. In our simulation, we set a Boltzmann VDF with temperature T_v , and use the first 11 v' levels only. The cross-sections for electron impact from $(X, v' = 0)$ are reasonably well known. Here, as in [5], we use the choice made in [3] and based on the cross-sections of Zubek [8,9]. The extension to other v' values is made by scaling the $v' = 0$ cross-sections values according to the Franck-Condon Factors of the transition, and by shifting the threshold according by the vibrational energy of levels v' . For a discussion on the cross-sections choice and scaling procedure, we defer the reader to paragraph 2.2 of [3].

Collisional data. Rate constants for total quenching, k_v^Q and for vibrational energy transfer (VET) k_{vw} for $w - v = \Delta v < 0$ § were measured in [4], with pure N_2 as collider gas, at a gas temperature T_{gas} close to room temperature. They are shown in fig. 1. The electronic quenching increases strongly with v . This is perhaps a peculiarity of nitrogen collider. Known cases with H_2 , H_2O and O_2 colliders show much higher rate constants almost independent on v [10]. The O_2 case is also shown in the figure. In the conditions of the measurements, VET rate constants for $\Delta v > 0$, with a positive energy gap, were negligible, and did not modify the data analysis.

§ Here we label as v the initial and w the final vibrational states of the VET transfer

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Analogously, VET with $\Delta v > 0$ were discarded in [5], in which experimental spectra of a DBD discharge at low gas temperature were analyzed. Here, since we want to explore also conditions of high gas temperature and vibrational excitation (of the ground state), we insert them in the simulations, so that, from the data of [4], we calculate the pure electronic quenching rate coefficient, i.e. the quenching out of the whole $N_2(C,v)$ manifold as:

$$k_v^{QE} = k_v^Q - \sum_{w < v} k_{vw} \quad (4)$$

For $\Delta v > 0$, a discussion is necessary. As a matter of fact, our knowledge on electronic quenching and VET is limited to the rate coefficients of energy loss, while the details on where the excess energy is accommodated are missing. In addition to energy transfer to translational energy, many routes might be available for the transfer of the excess energy to internal energy of the colliding molecule. In the specific case of our VET collisions with N_2 collider, we can have VT transfers:

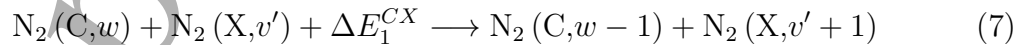


In this case, we can use the detailed balance to calculate the $\Delta v > 0$ rate coefficient as:

$$k_{vw} = k_{wv} \exp\left(-\frac{\Delta E_{vw}}{k_B T_{gas}}\right) \quad (6)$$

where: ΔE_{vw} is the energy difference between state w and v ; k_B the Boltzmann constant. This relation holds in the hypothesis that the k_{wv} is entirely due to the VT process 5

Among the possible transfers into internal energy of the collider N_2 molecule, we consider only the transfer that can have a role in the equilibrium between T_v^C and T_v , i.e. a kind of hybrid VV transfer:



here for simplicity we show only one-quantum transitions, the most probable ones in VV transfers in the ground state. The energy defect is quite small, $\Delta E_1^{CX} \approx 0.04eV$, and of the order of kT_{gas} also at low gas temperatures. The hybrid VV can then be considered as a quasi-resonant process. Again for simplicity,

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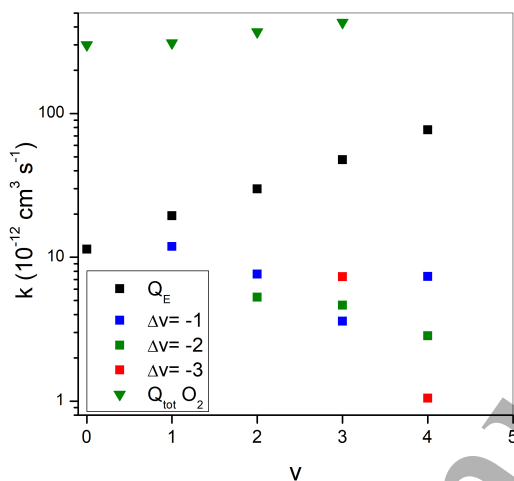


Figure 1. Rate constants of the collision processes in the $N_2(C,v)$ manifold measured in [4] for N_2 collider: black - $k_v^{Q_E}$; colored - k_{vw} for $\Delta v = -1, -2, -3$. The green triangles are the total quenching by O_2 collider.

we consider all the possible combinations of vibrational levels as quasi-resonant, and approximate the $\Delta v > 0$ rate coefficient by detailed balance:

$$k_{vw} = k_{vw} \exp\left(-\frac{\Delta E_{vw}}{k_B T_v}\right) \quad (8)$$

which holds if the hybrid VV is the dominant VET process, as in the VT case. Using formula 6 or 8 in equation 3 will then represent calculations with upper limit values of VT or hybrid VV rate coefficients of $\Delta v > 0$ VET processes. This will be sufficient for our discussion.

3. Simulations with variable parameters

To underline the effect of parameters changes, and how these affect the (C,v) populations without any relationship with T_v , we proceed as follows. We show both populations plots, normalized to that of $(C,v = 0)$, and T_v^C plots, as a function of parameters changes. T_v^C is obtained by the exponential fit of the populations of $v = 0, 1, 2$, to mimic “vibrational temperature” measurements by OES. We shall

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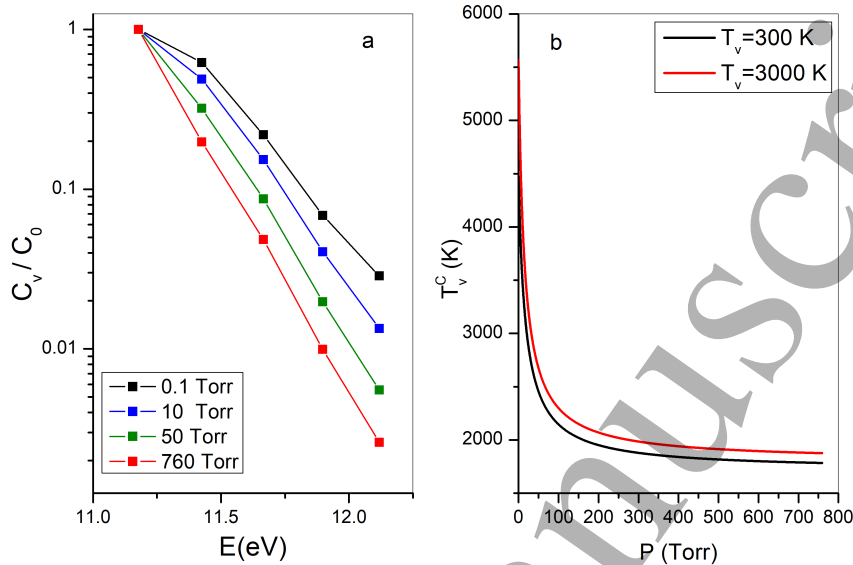


Figure 2. Simulation of the pressure dependence - at fixed $T_{gas} = 400$ K, $T_e = 3$ eV - of: (a) populations of $N_2(C, v = 0 \dots 4)$ normalized to that of $v=0$, $T_v = 1000$ K; (b) T_v^C at two values of T_v . In (a) the populations of the five v -levels are plotted as a function of the energy of the (C, v) state.

examine pressure, T_v , T_e and T_{gas} parameters changes, obtained by varying one parameter only and keeping the other three at a fixed value. We shall outline what wrong, plausible deductions can be done for each case, if T_v^C is taken as being representative of the T_v value or even only of its trend with the changing parameters. We shall also outline the actual dependence on the parameters, which can be seen in the details of the $N_2(C, v = 0 \dots 4)$ populations.

3.1. Pressure dependence

The dramatic change of T_v^C on increasing the pressure can be appreciated in fig. 2. **Wrong plausible deduction:** *The VDF (or T_v) is strongly deactivated as an effect of the increasing frequency of collision processes.*

The correct explanation is that the strong v -dependence of the collision quenching imposes its footprint on the shape of the $N_2(C, v)$ relative populations, as the collision frequency progressively overcomes and dominates the radiative rates.

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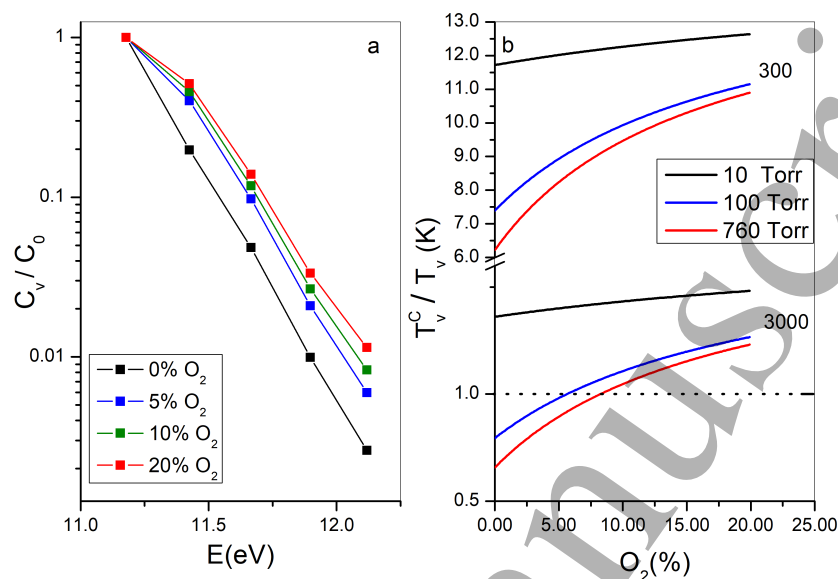


Figure 3. Simulation of the gas composition dependence, with addition of oxygen to nitrogen - at fixed, $T_{gas} = 400$ K, $T_e = 3$ eV - of: (a) populations of $N_2(C, v = 0 \dots 4)$ normalized to that of $v=0$, $T_v = 1000$ K; (b) T_v^C/T_v at two values of T_v and three pressures.

Since the v -dependence of the collision quenching is peculiar to the N_2 collider, one might think that in other cases the effect of the pressure would not be that important. The point is that we can exclude a trend like that of figure 2 only if we reasonably know the v -dependence of collision quenching.

3.2. Gas composition dependence

By adding O_2 to N_2 , T_v^C increases, as shown in figure 3. At any pressure and T_v values. To better appreciate the distance from the condition $T_v^C = T_v$, we have plotted the ratio of the two temperatures in figure 3(b). **Wrong plausible deduction:** *The vibrational excitation of nitrogen is increased by adding oxygen.* This is followed by searching for the kinetic mechanisms responsible for such an occurrence.

The correct explanation is that the strong v -dependence of the nitrogen collision quenching is drastically smoothed by the presence of oxygen, whose quenching rate

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coefficients are much larger and with a “flat” dependence on v . A similar behaviour is observed on addition of H_2 and H_2O , and perhaps with other molecular colliders, the collisional data of which are unfortunately not known. Note that the calculations with O_2 are somewhat incomplete, since we do not know the VET rate coefficients for this collider.

3.3. T_v dependence

So far, we have analyzed the enormous influence of collision processes on the population distribution of C-state vibrational levels. But, once collisions are properly accounted for, can we use the SPS bands to infer information on the VDF? The answer is yes, but with the due care. Looking at figure 4(b), we observe that the value of T_v^C is dramatically different from T_v , but a correlation, although non-linear, exists, since T_v^C is an increasing function of T_v . Looking into the details of C_v values in figure 4(a), we readily see that the relative population of levels $v \geq 2$ is fairly sensitive to T_v . Accurate measurements of the bands relevant to these vibrational states can then provide insights into the VDF. Although this is indirect information since we do not know the details of the VDF. Here, we have simply assumed a Boltzmann VDF, but deviations from it will have a role in populating (C,v) states. A global trend of the VDF can anyway be deduced. It is also reasonable to think that “ T_v^C increasing function of T_v ” is a universal statement that can be applied to any molecule, although semi-quantitative deductions can be made only if all the relevant parameters are well known, as in the present case.

3.4. T_e dependence

Having turned for the moment our attention to what can be “measured ” by the analysis bands emissions, the other interesting parameter is the electron temperature. The effects of T_e variations are shown in figure 5. As it is easily understandable, the influence of the electron temperature gets smaller and smaller as long as T_e becomes larger than the energy spacing between v -levels. The trend is similar to that with increasing T_v . The chance of discriminating between T_e and T_v in the measured populations is given by the different shape of the population distribution impressed by the increase of T_v , especially for $v \geq 2$.

The low sensitivity of the vibrational populations on T_e at high electron temperatures is an obvious consequence of the small energy spacing between the

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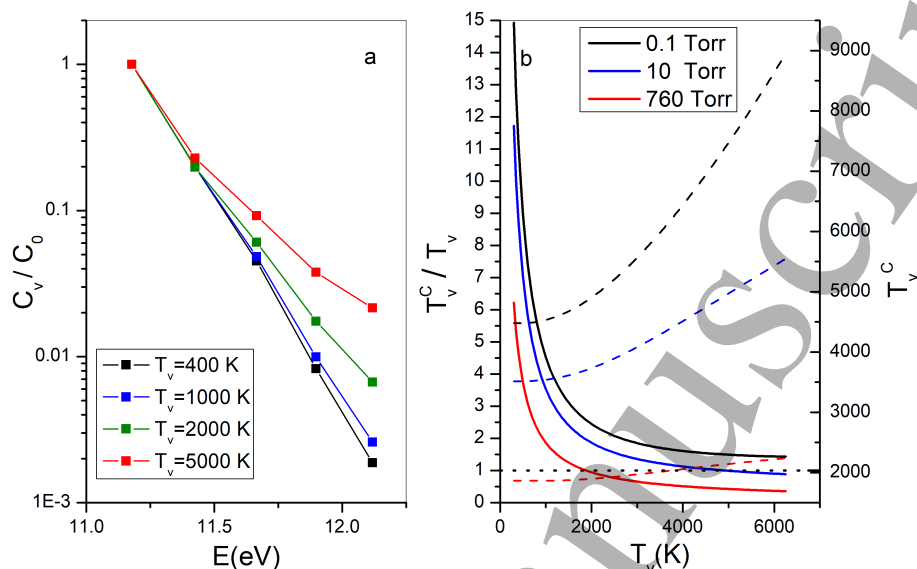


Figure 4. Simulation of the dependence on ground-state vibrational temperature T_v - at fixed $P = 760$ Torr, $T_{gas} = 400$ K, $T_e = 3$ eV - of: (a) populations of $N_2(C, v = 0 \dots 4)$ normalized to that of $v=0$; (b) T_v^C/T_v (continuous) and T_v^C (dashed) at three pressure values.

vibrational levels. Therefore, the analysis of $N_2(C, v)$ populations is not the best way to measure T_e . One can employ the well known method of the FNS/SPS bands ratio (see, for example [11] and references therein.), where FNS, the First Negative System, is the emission from the $N_2^+(B)$ state. In this case, the ratio is extremely sensitive to T_e , since the excitation thresholds differ by a large amount of about 7.7 eV. The measurement is also easy, since the strongest (0,0) band of the FNS falls around 390 nm, and can be collected in a single spectral window together with the whole $\Delta v = -3$ bands sequence of the SPS. Once T_e is determined with the aid of the FNS bands, we can use the $N_2(C, v)$ simulation to estimate the vibrational temperature T_v of the ground state. Note that we have up to now used a Maxwellian EEDF for simplicity. A better simulation can be obtained using a Boltzmann solver like BOLSIG+ [12] to calculate the EEDF and, then, the electron-impact rate coefficients. In this case, the free parameter will be the reduced electric field, E/N , instead of the electron temperature.

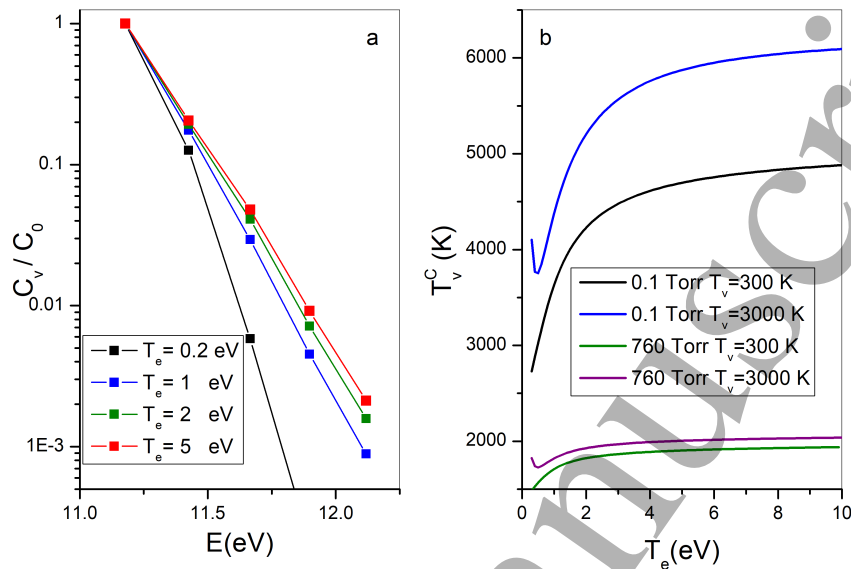


Figure 5. Simulation of the dependence on the electron temperature T_e - $T_{gas} = 400$ K - of: (a) populations of $N_2(C, v = 0 \dots 4)$ normalized to that of $v=0, T_v = 1000$ K; (b) T_v^C at two T_v and pressure values.

4. Route to equilibrium in the $N_2(C, v)$ manifold

So far we have analyzed the dependence on T_v from the point of view of the excitation mechanism only, and discarded the influence of the gas temperature. Now we address the existence of a route to (partial) equilibrium in the $N_2(C, v)$ manifold, due to collisions within the manifold. We start with the eventual equilibrium with the gas kinetic temperature, T_{gas} , since it is connected with another mistake found in the literature, i.e. the comparison of T_v^C and T_{gas} as a marker of a disequilibrium in the discharge. In turn, T_{gas} is measured from the rotational temperature T_{rot}^C of emission bands (we shall return on this point later).

The first big mistake in this kind of reasoning is to think that the vibrational population of the radiative state can reach an equilibrium with the gas temperature. What happens on increasing the gas temperature is shown in figure 6. The main actors of the T_{gas} dependence are the $\Delta v > 0$ VET transfers. In the calculations we use using the upper limit of their rate coefficients, formula 6, which corresponds,

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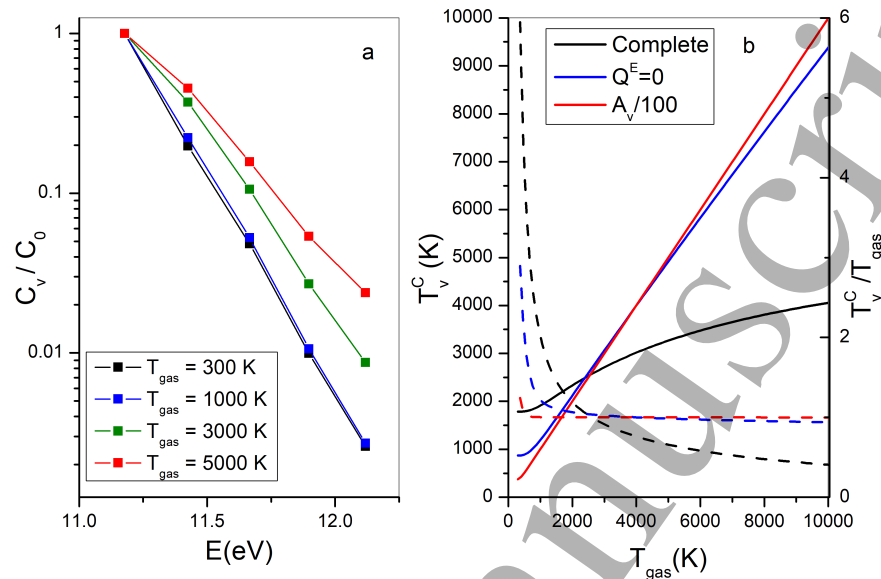


Figure 6. Simulation of the dependence on the gas temperature T_{gas} - $T_e = 3$ eV, $T_v = 1000$ K $P = 760$ Torr - of: (a) populations of $N_2(C, v = 0 \dots 4)$ normalized to that of $v=0$; ; (b) T_v^C (continuous) and T_v^C/T_v (dashed) and pressure values. In (b) three cases of quenching data sets are reported: the complete set, without electronic quenching, with radiative rates divided by 100.

as already said, to the hypothesis of VET transfers dominated by VT processes 5. The relative C_v/C_0 populations increase, and T_v^C as well, but equilibrium is never achieved. The reason is that there is no time available for reaching equilibrium since the lifetime of the excited state is too short. Gaining equilibrium depends on the $K_{vw}/(K_{QE} + A)$ ratio, where $K = Xk$ is the collisional frequency. This ratio increases with T_{gas} , because of the exponential factor in expression 6, but it always remains substantially lower than 1, making equilibrium impossible. To see how equilibrium might be achieved, we have done two more simulations, in which the lifetime of the state has been progressively increased by putting to zero the electronic quenching and then dividing by 100 the radiative rate. As expected, increasing the ratio $K_{vw}/(K_{QE} + A)$ at values well above 1, equilibrium ($T_v^C = T_{gas}$) is also reached at low gas temperatures. This is unrealistic case for $N_2(C)$ state. Might it be real for other molecular emitting states? Unfortunately, the knowledge

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of VET rate coefficients is rather poor. The only known case is $\text{OH}(\text{A}^2\Sigma^+, v = 0, 1)$, which emits the strong 3064 Å bands system [13, 14]. VET rate coefficients are lower than electronic quenching ones for most colliders, with the only, notable exception of N_2 . This might be a case in which, at high temperature, equilibrium might be approached in the $\text{OH}(\text{A}, v)$ manifold. Other cases are not known. But even in the case the emitting state reaches the $T_v^C = T_{gas}$ equilibrium, we come to the second conceptual mistake: to argue that the discharge is evolving towards an equilibrium between vibrational and kinetic degrees of freedom. As we have seen, almost always, and by a large amount, $T_v^C \neq T_v$. One might argue that anyway a interesting equilibrium condition for the vibrational temperature of an excited state is observed. However, this equilibrium is irrelevant since electronically excited states have negligible populations, and do not influence the global kinetics and the energy balance of a discharge. An exception to this argument is that of discharges with very high ionization degrees, like nanosecond scale spark discharges, where excited states can contribute to the macroscopic kinetics [1].

This discussion can be repeated identically if we consider the hybrid VV process 7 as the dominant VET mechanism, and substitute T_{gas} with T_v . We then conclude that also an equilibrium with the vibrational temperature by VET collisions cannot be even approached. The lack of knowledge on the VET processes may affect the correct use of equation 3. In conditions of high vibrational temperature and strong disequilibrium with T_{gas} , we do not know, as a matter of fact, which temperature should be used in the detailed balance relationships. The existence of further energy exchange processes might made things even more complicated. We then argue that the conclusions of sections 3.3 and 3.4 should be considered safe roughly in conditions of $kT_{gas}, kT_v < \Delta E_{vw}$.

Last but not least, a remark on the relationship $T_{rot} = T_{gas}$. This topic has been widely discussed and clarified in [15]. Basically, all the emissions from electronic states produced by energy transfers or recombination processes must be discarded, also at high pressure. The reason is that, the product nascent rotational excitation in a exothermic process is generally supra-thermal. This issue is often misjudged with the justification that “sub-nanosecond rotational-translational relaxation” ensures rotational equilibration at high pressure. However, this argument is almost always wrong. It can be true only in gas mixture with a buffer noble gas and small quantities of molecular gas.

It is a matter of facts that the rotational energy transfer frequency K_{RET}

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can be sub-nanosecond. Nevertheless, to reach the $T_{rot} = T_{gas}$ equilibrium, a sufficient number of RET collisions must occur *within the state's effective lifetime*. In other words, the frequency of RET must be larger than the total quenching rate ($K_{RET} \gg (K_Q + A)$). This is not always verified, as in the case for OH(A) state. For a striking evidence of non-relaxed nascent rotational distributions, see [14,16].

5. Concluding remarks

In this paper, we have underlined the incorrect deductions that can be found in the literature about the vibrational analysis of emission bands by OES. The syllogism “ $T_v^C = T_{rot}$ ($T_v^C \neq T_{rot}$) implies $T_v = T_{gas}$ ($T_v \neq T_{gas}$)” is wrong and can even be the sum of two errors that may combine and lead to false conclusions. We hope that, through the $N_2(C, v)$ example, we could define the boundaries for a correct interpretation of the OES data. Also, we have underlined the need for collisional data for electronic states to enrich the portfolio of band emissions useful for diagnostic purposes, especially in atmospheric pressure discharges.

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OES and vibrational temperature

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