RELAXATION OF THE SYMMETRIC VIBRATION MODE OF THE CO_2 MOLECULE

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The applicability of the Landau–Teller energy-relaxation equation of a harmonic oscillator is verified for the CO_2 molecule in which there is Fermi resonance. It is shown that the distribution over the split levels of the symmetric mode formed by vibrational exchange processes and transitions within multiplets is analogous to the Treanore distribution for a single-mode anharmonic oscillator.

1. INTRODUCTION

The description of the kinetics of vibrational–translational exchange (VT) for symmetric longitudinal and bending vibrations of the CO_2 molecule is of considerable interest for CO_2 lasers (since the lower 10^00 and 02^00 lasing levels belong to these modes) and for other problems in which the vibrational relaxation of CO_2 is substantial.

The Landau–Teller form of the energy-relaxation equation of a harmonic oscillator [1] is ordinarily used. To derive this equation, it is essential that the harmonic-oscillator spectrum be equidistant, and hence, the exponential factors in the transition probabilities, which originate because of the adiabaticity of the vibrational–translational exchange, are identical for all transitions between adjacent levels. The dependence of the one-quantum transition probabilities on the vibrational number is given by the square of the matrix element of the oscillator coordinate. However, a relatively small deviation of the spectrum from an equidistant one already results in the fact that the adiabatic factors for different one-quantum transitions differ radically. This circumstance is well known and should be taken into account for diatomic molecules if the vibrational temperature is sufficiently high so that the levels would be populated with noticeable anharmonicity [2]. However, the anharmonicity is substantial at the very lowest-lying vibrational levels (Fermi resonance) for CO_2 molecules, and should perhaps be taken into account if only the levels 10^00, 02^00, 02^20 are populated sufficiently. In a number of cases, the Landau–Teller form of the energy-relaxation equation can remain satisfactory.

Herzfeld [3] and Seeber [4] evaluated the probability of a number of vibrational transitions for CO_2 collisions with CO_2 on the basis of the Schwartz–Slavsky–Herzfeld theory with Fermi resonance taken into account. However, the influence of the Fermi resonance on the form of the quasistationary vibrational distribution and on the energy-relaxation equation for symmetric vibrations has not been discussed in the literature. The examination of these questions is the purpose of the present paper.

2. VIBRATIONAL STATES OF THE SYMMETRIC CO_2 MODE

Symmetric vibrations of the CO_2 molecule consist of longitudinal (mode 1) and bending (mode 2) vibrations. A two-dimensional oscillator corresponds to the latter in the vibrational spectrum of CO_2. The wave functions [5]

$$\Psi_{vl}=\Phi_l(\varphi)\, R_{vl}(\rho)$$

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TABLE 1

v	Energy shift	State
0	0	$(00^0v_3) = \|00^0v_3\rangle$
1	0	$(01^1v_3) = \|01^1v_3\rangle$
2	$\|\langle 10^0v_3\| V_\Phi \|02^0v_5\rangle\|$ $-\|\langle 10^0v_3\| V_\Phi \|02^0v_3\|$ 0	$(10^0v_3) = \frac{1}{\sqrt{2}}(\|10^0v_3\rangle + \|02^0v_3\rangle)$ $(02^0v_3) = \frac{1}{\sqrt{2}}(\|10^0v_3\rangle - \|02^0v_3\rangle)$ $(02^0v_3) = \|02^2v_3\rangle$
3	$\|\langle 11^1v_3\| V_\Phi \|03^1v_3\rangle\|$ $-\|\langle 11^1v_3\| V_\Phi \|03^1v_3\rangle\|$ 0	$(11^1v_3) = \frac{1}{\sqrt{2}}(\|11^1v_3\rangle + \|03^1v_3\rangle)$ $(03^1v_3) = \frac{1}{\sqrt{2}}(\|11^1v_3\rangle - \|03^1v_3\rangle)$ $(0^3v_3) = \|03^3v_3\rangle$
4	$\sqrt{\|\langle 20^0v_3\| V_\Phi \|12^0v_3\rangle\|^2 + \|\langle 12^0v_3\| V_\Phi \|04^0v_3\rangle\|^2}$ 0 $-\sqrt{\|\langle 20^0v_3\| V_\Phi \|12^0v_3\rangle\|^2 + \|\langle 12^0v_3\| V_\Phi\, 04^0v_3\rangle\|^2}$ $\|\langle 12^0v_3\| V_\Phi \|04^2v_3\rangle\|$ $-\|\langle 12^2v_3\| V_\Phi \|04^2v_3\rangle\|$ 0	$(20^0v_3) = \frac{1}{\sqrt{6}}(\|20^0v_3\rangle + \sqrt{3}\|12^0v_3\rangle + \sqrt{2}\|04^0v_3\rangle)$ $(12^0v_3) = \frac{1}{\sqrt{3}}(\sqrt{2}\|20^0v_3\rangle - \|04^0v_3\rangle)$ $(04^0v_3) = \frac{1}{\sqrt{6}}(\|20^0v_3\rangle - \sqrt{3}\|12^0v_3\rangle + \sqrt{2}\|04^0v_3\rangle)$ $(12^2v_3) = \frac{1}{\sqrt{2}}(\|12^2v_3\rangle + \|04^2v_3\rangle)$ $(04^2v_3) - \frac{1}{\sqrt{2}}(\|12^2v_3\rangle - \|04^2v_3\rangle)$ $(04^4v_3) = \|04^4v_3\rangle$

with angular part

$$\Phi_l = \frac{1}{\sqrt{2\pi}} e^{il\varphi}$$

and radial part

$$R_{\nu l} = \left(\frac{m_2\omega_2}{\hbar}\right)^{1/2} \sqrt{\frac{2\nu!}{(\nu + |l|)!}}\, e^{-\frac{\rho^2}{2}} \rho^{|l|} L_\nu^{(|l|)}(\rho^2),$$

correspond to its states with a definite moment of momentum, where φ is the angle of rotation relative to the molecule axis, $\rho = \sqrt{(m_2\omega_2/\hbar)}r$ is the dimensionless radius (r is the transverse dimension of the bent molecule), $m_2 = 2m_0m_C/m_{CO_2}$ is the reduced oscillator mass, ω_2 is a frequency, and $L_\nu^{(|l|)}(\rho^2)$ are Laguerre polynomials of the square of the dimensionless radius. The parameter ν is related to the vibrational number v_2 by the relationship $2\nu = v_2 - l$. The vibrational moment l takes on the values $-\nu_2, -\nu_2 + 2, \ldots \nu_2$.

The nonzero perturbation matrix elements of the form φ equal

$$\langle v_2^{|l|} |\rho \cos\varphi| (v_2 + 1)^{|l|+1}\rangle = \sqrt{\frac{v_2 + |l| + 2}{8}};\qquad (2.1)$$
$$\langle v_2^{|l|} |\rho \cos\varphi| (v_2 + 1)^{|l|-1}\rangle = \sqrt{\frac{v_2 - |l| + 2}{8}}.$$

The specifics of the CO_2 vibrational spectrum are that a quantum of the symmetrical longitudinal vibrations is a multiple of the quantum of the bending vibrations ($\hbar\omega_1 = 2\hbar\omega_2$). Consequently, the symmetrical vibrations actually form one mode. The symmetric mode levels are characterized by the vibrational number $v = 2v_1 + v_2$ and degenerate, in a harmonic approximation, with the multiplicity

$$g_v = \begin{cases} (v+2)^2/4, & \text{if } v - \text{is even} \\ (v+1)(v+3)/4, & \text{if } v - \text{is odd}. \end{cases}$$

The anharmonic term in the vibrational Hamiltonian of the molecule $V_\Phi = Az_1\rho^2$, where z_1 is the dimensionless normal coordinate of the longitudinal symmetric vibrations, results in splitting of the symmetric mode levels (Fermi resonance) [5]. According to perturbation theory for a degenerate level, linear combinations of those initial wave functions for which the nondiagonal matrix elements of the anharmonic perturbation differ from zero correspond to its split components. Since a perturbation with the symmetry of the molecule is independent of the angle φ, then wave functions of states with identical vibrational momentum are combined. The nonzero matrix elements equal

$$|\langle v_1 v_2^l v_3 | A z_1 \rho^2 | (v_1-1), (v_2+2)^l, v_3 \rangle| = \frac{W_0}{2}\sqrt{v_1[(v_2+2)^2-l^2]}, \quad (2.2)$$

where $W_0 \simeq 51\ \text{cm}^{-1}$ is the Fermi resonance constant. The level shifts and the coefficients are derived from perturbation theory in linear combinations of the initial wave functions, which are expressed in terms of the matrix elements (2.2).

The vibrational states corresponding to the components of the first four multiplets are presented in Table 1. The angular brackets denote the initial states and the parentheses, the correct states. Table 1 has been composed by neglecting second-order terms in perturbation theory and the anharmonic terms different from Fermi resonance. This affords sufficient accuracy for our purpose in the spectrum range under consideration. It is seen from Table 1 that transitions are possible between all components of adjacent multiplets with vibrational momentum differing by one, which are subject to a perturbation originating during a collision and proportional to the coordinate of the plane-polarized bending vibration ($\rho\cos\varphi$). This also refers to the 10^00, 20^00 levels which are traditionally longitudinal symmetric vibrations. Transitions subjected to a perturbation proportional to $\rho^2\cos^2\varphi$ are possible between components of the very same multiplet. According to [4], the velocities of transitions between Fermi-resonant levels are hence of the same order as between the levels not related to Fermi resonance.

3. QUASISTATIONARY VIBRATIONAL DISTRIBUTION

Let us clarify the form of the level distribution in the case when the frequencies of the V−T transitions between adjacent multiplets are small compared to the frequencies of the vibrational exchange and the transitions between components of the very same multiplet. This distribution is the solution of the kinetic problem including V−V transition between components of adjacent multiplets and transitions between components of one multiplet and hence containing a large number of different velocity constants. Let us show that a universal distribution independent of the velocity constants (a Treanore-type distribution) exists.

TABLE 2

	Transition	$\lvert(m\lvert\rho\cos\varphi\rvert n)\rvert^2$	$\sum_{m,n}\lvert(m\lvert\rho\cos\varphi\rvert n)\rvert^2$	He $\frac{f_{mn}}{f_{01}}$	He $\sum_{m,n}\frac{f_{mn}}{f_{01}}\lvert(m\lvert\rho\cos\varphi\rvert n)\rvert^2$	CO$_2$ $\frac{f_{mn}}{f_{01}}$	CO$_2$ $\sum_{m,n}\frac{f_{mn}}{f_{01}}\lvert(m\lvert\rho\cos\varphi\rvert n)\rvert^2$
0—1	00^00-01^10	1/2	1/2	1	1/2	1	1/2
1—2	01^10-02^00	1/4	3/2	1,8	1,7	3	2
	01^10-02^20	1		1,1		1,2	
	01^10-10^00	1/4		0,55		0,33	
2—3	02^00-03^10	$(\sqrt{2}+1)^2/8$	7/2	1,2	3,6	1,5	4
	02^00-03^30	0		0,55		0,33	
	02^00-11^10	$(\sqrt{2}-1)^2/8$		0,27		0,1	
	02^20-03^10	1/4		2		3,7	
	02^20-03^30	3/2		0,9		0,82	
	02^20-11^10	1/4		0,45		0,22	
	10^00-03^10	$(\sqrt{2}-1)^2/8$		3,7		11	
	10^00-03^30	0		1,5		2	
	10^00-11^10	$(\sqrt{2}+1)^2/8$		0,82		0,74	

The desired distribution should cancel the total V−V current (i.e., the difference between the number of direct and reverse transitions per unit volume per unit time) between adjacent multiplets. Hence, let us seek the distribution cancelling all elementary V−V currents. Let us introduce a two-subscript notation for the populations of the separate components $n_{v\beta}$, where the first subscript is the vibrational number of the multiplet to which the level belongs, and the second is a formal subscript making the level within the multiplet specific. The condition of zero elementary V−V current is

$$Q_{(v\beta),(v'\beta')}^{(v+1,\lambda),(v'-1,\lambda')}\left(n_{v\beta}n_{v'\beta'}-n_{v+1,\lambda}n_{v'-1,\lambda'}e^{-\frac{\Delta E}{T}}\frac{g_{v\beta}g_{v'\beta'}}{g_{v+1,\lambda}g_{v'-1,\lambda'}}\right)=0, \tag{3.1}$$

where $Q_{(v\beta),(v'\beta')}^{(v+1,\lambda),(v'-1,\lambda')}$ is the velocity constant of the process for which one of the colliding molecules makes the transition from the state $v\beta$ into $v + 1$, λ, while the other goes from the state $v'\beta'$ into $v' - 1$, λ'; ΔE is the defect in transition vibrational energy. Since (3.1) is an equation of the detailed balance for the elementary process, it is satisfied for the Boltzmann distribution $n_{v\beta} \sim g_{v\beta}e^{E_{v\beta}/T}$. Because of the presence of the integral of V−V collision, the sum of vibrational numbers of the multiplets, a more general solution of (3.1) of the form

$$n_{v\beta} \sim g_{v\beta}e^{\gamma v-\frac{E_{v\beta}}{T}}, \tag{3.2}$$

exists, which corresponds to the energy of a mode different from the equilibrium value at the gas temperature. Let us now note that the distribution (3.2) cancels not only all V−V currents (including the two-quanta currents) but also all currents within the multiplets [since v has been fixed within one multiplet and (3.2) reduces to a Boltzmann distribution with the gas temperature]. Hence, the distribution (3.2) is quasistationary, i.e., is stationary to the accuracy of taking into account the V−T exchange resulting in a slow change in the parameter γ. This distribution is completely analogous to the Treanore distribution for a single-mode anharmonic oscillator [6].

Applying the Boltzmann H-theorem, it can be shown that the currents in the system damp out with time for the set of processes under consideration (V−V processes and transitions between multiplet components), and an arbitrary initial distribution goes over into a Treanore-type distribution (3.2) (see the Appendix).

The parameter γ governs the effective vibrational temperature T_V, i.e., the temperature originating during the transition to the equidistant spectrum:

$$\frac{1}{T_V}=\frac{1}{T}-\frac{\gamma}{\hbar\omega}.$$

It is interesting to note that for a sufficiently high vibrational temperature and a low gas temperature the distribution over the symmetric mode levels is a sawtooth, i.e., the origination of population inversions between adjacent multiplet components is possible. In particular, the populations of levels (referred to the statistic weights) $v\beta$ and $v + 1$, λ belonging to adjacent multiplets are compared for

$$\frac{T_V}{T}=\frac{1}{1-\frac{E_{v+1,\lambda}-E_{v\beta}}{\hbar\omega}}$$

(this occurs for $T_V/T \approx 5$ for the 10^00 and 03^10 levels, for example).

If the gas temperature is high compared to the splitting into multiplets and the deviations of their centers from equidistant separation, then the Treanore-type distribution is transformed into a Boltzmann distribution with a vibrational temperature governed by the parameter γ. The multiplet population is hence distributed over its components in proportion to its statistical weights.

Let us emphasize that sums of the numbers v_1 and v_2 are not conserved separately for the V−V collisions, but a distribution of the form

$$n_{v_1v_2^l0} \sim g_le^{\gamma_1v_1+\gamma_2v_2-\frac{E_{v_1v_2^l0}}{T}}$$

with $\gamma_1 \neq \gamma_2$ will already not be quasistationary. Hence, it is meaningless to introduce different vibrational temperatures of the longitudinal symmetric and bending modes: if these temperatures exist, they are identical.

A quasistationary vibrational distribution for both CO_2 modes which exist if the transition frequencies between the symmetric and antisymmetric modes and the V–T transition frequencies are small compared to the V–V transition frequencies in the modes, has the form

$$n_{v_1 v_2^l v_3} = n_{00^0 0} g_l \, e^{\gamma_S(2v_1+v_2)+\gamma_a v_3 - \frac{E_{v_1 v_2^l v_3}}{T}}, \tag{3.3}$$

where $g_l = 1$ if $l = 0$ and $g_l = 2$ if $l \neq 0$; γ_S and γ_a are related to the vibrational temperatures of the symmetric and antisymmetric modes.

The vibrational levels form a square lattice on the vv_3 plane. The distribution (3.3) exists only in some neighborhood of the ground level in which V–V processes predominate. As the vibrational numbers grow, the role of the intermodal transitions (VV') portrayed by diagonals in the lattice will increase. Apparently the transitions $vv_3 \rightarrow v+4, v_3-1$ hence play the main role in the domain adjacent to the v_3 axis, and the transitions $vv_3 \rightarrow v+3, v_3-1$, in the domain adjacent to the v axis (this is related to the onset of resonance at the appropriate transitions which originate because an antisymmetric mode quantum diminishes as the vibrational number of the symmetric mode increases). The sum $4v_3 + v$ is conserved for V–V' collisions of the first kind and the sum $3v_3 + v$, for the second kind. Hence, the quasistationary distribution in the domain where V–V' processes predominate over all others is

$$n_{v_1 v_2^l v_3} \sim e^{\gamma_r(2v_1+v_2+rv_3) - \frac{E_{v_1 v_2^l v_3}}{T}},$$

where $r = 4$ near the v_3 axis and $r = 3$ near the v axis. Finally, the distribution is evidently Boltzmannian with the gas temperature in the domain where V–T processes predominate.

4. ENERGY-RELAXATION EQUATION

Since there is no success in obtaining a compact equation for the energy relaxation with splitting in the symmetric mode and with the adiabatic factors originating because of this difference taken into account, let us clarify the possibility of applying the ordinary relaxation equation by using a numerical confirmation. For this purpose, let us establish the dependence of the transition probabilities between adjacent multiplets on the vibrational number of the multiplet within the framework of Landau–Teller theory. The transition probability between multiplets is obtained by summation over the final states and averaging over the initial states of the transition probabilities between individual components, each of which is proportional to the square of the absolute value of the perturbation matrix element and the adiabatic factor dependent on the transition energy. Given in Table 2 are the squares of the absolute values of the perturbation matrix elements proportional to $\rho \cos \varphi$, evaluated for the states represented in Table 1 by using (2.1), and the relative values of the adiabatic factors

$$f_{mn} \sim \exp\left[-3\left(\frac{\pi^2 \mu \omega_{mn}^2}{2\alpha^2 T}\right)^{1/3}\right].$$

(where μ is the reduced mass of the colliding molecules, ω_{mn} is the transition frequency, and $1/\alpha$ is the characteristic length of the change in potential). Considered are the cases of practical interest of quenching by helium and CO_2 molecules at a comparatively low temperature T = 300°K, when the effect of anharmonicity should be large. Only the main exponential Landau–Teller factor was taken into account in evaluating the adiabatic factor, which is sufficient for a qualitative description. The characteristic length of the potential change was taken equal to $0.2 \cdot 10^{-8}$ cm [3]. For simplification, it is assumed that the populations of the multiplet components are referred to as their statistical weights.

It is seen from Table 2 that the relative change in the adiabatic factors reaches 3 in the case of quenching by helium and 10 in the case of quenching by CO_2 molecules. At the same time, the sums of the squares of matrix elements with weight f_{mn}/f_{01} agree with the sums of squares for quenching by helium to ~15% accuracy and for quenching by CO_2 molecules to ~30% accuracy. This is explained partially by the fact that the multiplet centers are almost equidistant and the greatest matrix elements correspond to transitions between them, and partially by cancellations originating during the summation. The cancellation is improved as the number v increases because of the increase in the number of components in the multiplets. If the deviation of the sum of the weighted squares of the matrix elements from the sum of the squares is neglected, then it is possible to arrive at an energy-relaxation equation in the Landau–Teller form. This is done most simply by noting that the sum of the squares of the absolute values of the transition matrix elements between two sets of states does not change when the initial states in each set are replaced by their linear combinations. Let us use a representation originating during selection of bending vibrations as basis states with plane polarization for the sum of the squares. Equating the time derivative of the symmetric mode energy, equal to the sum of the energies of modes 1 and 2, to the energy transmitted to the translational degrees of freedom per unit time during the transitions between adjacent multiplets, we obtain

$$\frac{d}{dt}(E_1+E_2) = -\hbar\omega_2 \sum_v \left(n_v P_v^{v+1} - n_{v+1} P_{v+1}^{v}\right),$$

where P_v^{v+1} is the frequency of transitions between the multiplet v and v + 1, and n_v is the multiplet population $\left(n_v = \sum_{v_3} n_{vv_3}\right)$.

Using the representation

$$P_{v+1}^{v} = P_1^0 \frac{2}{g_{v+1}} \sum_{\substack{v_1, v_{2x}, v_{2y} \\ 2v_1+v_{2x}+v_{2y}=v}} (v_{2x}+1),$$

where g_{v+1} is the statistical weight of the multiplet and v_{2x} and v_{2y} are the vibrational numbers of the bending vibrations polarized in the xz and yz planes, the equation ordinarily used,

$$\frac{d}{dt}(E_1+E_2) = -P_1^0(1-\alpha)(E_2 - E_2(T)),$$

can be obtained, where $\alpha = e^{-\hbar\omega_2/T}$.

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APPENDIX. PROOF OF THE UNIQUENESS AND CONVERGENCE TO A TREANORE-TYPE DISTRIBUTION

Let us introduce the potential relative to a Boltzmann distribution with the gas temperature

$$\varphi_{v\beta} = \frac{n_{v\beta}}{G_{v\beta}},$$

where

$$G_{v\beta} = g_{v\beta} n_{00} e^{-E_{v\beta}/T}.$$

According to the definition, the ground-state potential is $\varphi_{00} = 1$. In the new notation, the expression for the V–V current $v\beta + v'\beta' \to v + k_1\lambda + v' - k_1\lambda'$ (k = 0, 1, 2) is

$$\sigma_{(v\beta),(v'\beta')}^{(v+k_1\lambda),(v'-k_1\lambda')} \left(\varphi_{v\beta}\varphi_{v'\beta'} - \varphi_{v+k_1\lambda}\varphi_{v'-k_1\lambda'}\right), \tag{A.1}$$

where the conductivity equals

$$\sigma_{(v\beta),(v'\beta')}^{(v+k_1\lambda),(v'-k_1\lambda')} = Q_{(v\beta),(v'\beta')}^{(v+k_1\lambda),(v'-k_1\lambda')} G_{v\beta} G_{v'\beta'}.$$

The current between the multiplet components is

$$\sigma_{(v\beta)}^{(v\lambda)} \left(\varphi_{v\beta} - \varphi_{v\lambda}\right), \tag{A.2}$$

where the conductivity is

$$\sigma^{(v\lambda)}_{(v\beta)} = P^{(v\lambda)}_{(v\beta)} G_{v\beta}$$

($P^{(v\lambda)}_{(v\beta)}$ is the frequency of the transitions $v\beta \rightarrow v\lambda$).

The conductivities are invariant relative to replacement of the initial by the final states and relative to commutation of the collision partners in the initial and final states. Let us note that the current (A.2) can be written in the form (A.1) for k = 0 and by a change in the indices from primes to zeros (since $\varphi_{00} = 1$).

For simplicity, let us henceforth denote the level by a single subscript. The balance equations for the population levels are written as

$$\frac{dn_k}{dt} = -\sum_{l,m,n} \sigma^{mn}_{kl} (\varphi_k \varphi_l - \varphi_m \varphi_n), \tag{A.3}$$

where k, l, m, n take on all values from the very same set. The system (A.3) is analogous to a Boltzmann kinetic equation, for which the H-theorem can hence be proved [7].

Let us introduce the functional

$$H = \sum_k n_k \ln \varphi_k$$

and let us evaluate the time derivative,

$$\frac{dH}{dt} = \sum_k (1 + \ln \varphi_k) \frac{dn_k}{dt}. \tag{A.4}$$

It follows from this last equation that a necessary condition for stationarity of the population $dn_k/dt = 0$ is that the derivative dH/dt vanish. Substituting (A.3) into (A.4) and symmetrizing with respect to the subscripts, we obtain

$$\frac{dH}{dt} = -\frac{1}{4} \sum_{k,l,m,n} \ln \frac{\varphi_k \varphi_l}{\varphi_m \varphi_n} \sigma^{mn}_{kl} (\varphi_k \varphi_l - \varphi_m \varphi_n). \tag{A.5}$$

Since the terms in the sum (A.5) are nonnegative, then

$$\frac{dH}{dt} \leqslant 0. \tag{A.6}$$

Equality is possible in (A.6) only in the case

$$\varphi_k \varphi_l - \varphi_m \varphi_n = 0 \tag{A.7}$$

for $\sigma^{mn}_{kl} \neq 0$. The system (A.7) agrees with the condition that all the elementary currents vanish. Therefore, cancellation of all the elementary currents for the system under consideration is a necessary and sufficient condition for stationarity of the populations. Since H is bounded, then it follows from (A.6) that the currents damp out with time and an arbitrary initial distribution tends to a stationary distribution.

Returning to the two-subscript notation for the levels in (A.7) and recalling that the sum of the vibrational numbers of the multiplets is retained in all the processes under consideration, we find

$$\alpha_{v\beta} = e^{\gamma v}$$

(we also took account of the normalization $\varphi_{00} = 1$). We obtain for the populations

$$n_{v\beta} = G_{v\beta} \varphi_{v\beta} = n_{00} g_{v\beta} e^{\gamma v - \frac{E_{v\beta}}{T}},$$

which agrees with (3.2). This distribution can be considered as partial equilibrium, possible if the velocities of the V−T processes are low (in the same sense as the state of a gas with a nonequilibrium chemical composition if the chemical reaction rates are low). In conclusion, let us emphasize that the proof presented refers to some neighborhood of the ground level in which the influence of the V−T processes (both direct and indirect, associated with taking account of the boundary conditions for large vibrational numbers) is negligible.

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