EFFECTS OF QUANTUM FLUX ON THE RELAXATION OF PAIRED MODES OF THE CO_2 MOLECULE

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The basic features have been elucidated [1] for the quasistationary distribution of CO_2 molecules over the paired-mode levels related to Fermi resonance. The discussion is within the framework of Treanor's model for the vibrational kinetics in the approximation of zero quantum flux through the multiplets. Further analysis [2] for a two-mode system of anharmonic oscillators has shown that this approximation is permissible only when the vibrations are slightly overexcited. In [3], a solution was found to the relaxation problem for anharmonic oscillators that incorporates the quantum flux excited by V-V exchange under nonequilibrium conditions.

Here we make a more detailed study of the vibrational kinetics of paired CO_2 modes using the method of [3]. This example is of interest not only in relation to the specific features of anharmonicity in vibrational systems with Fermi resonance but also from the practical viewpoint, as it has a bearing on the production of gasdynamic lasers GDL using transitions between levels of the paired modes of CO_2 [4-6].

1. The name paired is given to the symmetrical longitudinal vibration ν_1 and the doubly degenerate bending vibration ν_2 in the CO_2 molecule. In the harmonic approximation, the frequencies are $\omega_1 = 2\omega_2$, so they form a single symmetrical mode whose energy levels $E_V = v\omega$ are degenerate and have weights $g_V = (v + a)(v + b)/4$, where $\omega = \omega_2$ and $v = 2v_1 + v_2$ (the subscript indicates the type of vibration) and $a = b = 2$ if v is even and $a = 1$ but $b = 3$ if v is odd. Anharmonicitiy produces splitting in the accidentally degenerate $(v_1 v_2^{\prime} 0)$ levels with identical vibrational momentum l (Fermi resonance). As a result, there is a multiplet structure in the levels for the paired modes of CO_2. The multiplet splitting energy ΔE_V is dependent on v and in the lower part of the spectrum, which is of the main interest, with v = 2-5, it is 1-3 W, where $W = 51\ cm^{-1}$ is the Fermi interaction constant. As $\omega = 667\ cm^{-1}$ is large by comparison with ΔE_V (this is not the only reason), the characteristic rates of nonresonance V-V exchange and internal V-T transition in the multiplets are much higher than that corresponding to the external V-T transitions between adjacent multiplets. This scale of rates for the V-T and V-V processes means that the Treanor model for the level populations can be used for the group of lower multiplets [7, 8]. In the quasiequilibrium approximation, this corresponds to the following form for the distribution of the CO_2 molecules over the levels of the paired modes [1]:

$$N_{v\beta} = g_\beta \exp[-v\omega/T_1 - (E_{v\beta} - \omega v)/T], \tag{1.1}$$

where $N_{V\beta}$ is the relative population, $E_{V\beta}$ is energy, and $g\beta$ is the statistical weight of the level $(v\beta) \equiv (v_1 v_2^{\prime} 0)$ or else of the β component of the multiplet with vibrational number $v = 2v_1 + v_2$, and $g_\beta = 1$ if $l = 0$ but $g_\beta = 2$ if $l \neq 0$, with T_1 the vibrational temperature.

This distribution is an analog of the Treanor one for single-mode anharmonic oscillators, but in form it is substantially different from the latter in having a nonmonotone distribution of the molecules over the paired CO_2 mode levels on account of the displacements of the components differing in sign and magnitude relative to the centers of the multiplets. For the same reason, there is here no single division of the spectrum into subcritical and supercritical regions for anharmonic oscillators that correspond to the descending and ascending branches of the Treanor distribution. The distinction can be made only in relation to the distribution of the molecules over the multiplets as a whole, with the critical value v_* defined as the vibration number at which there is a minimum in the reduced populations of the multiplets per unit statistical weight $\bar{N}_v = \sum_{\beta \equiv v} N_{v\beta}/g_v$; in Fig. 1 (T_1 = 1200°K, T = 75°K), the points and the kinked line show the form of the quasiequilibrium distribution of

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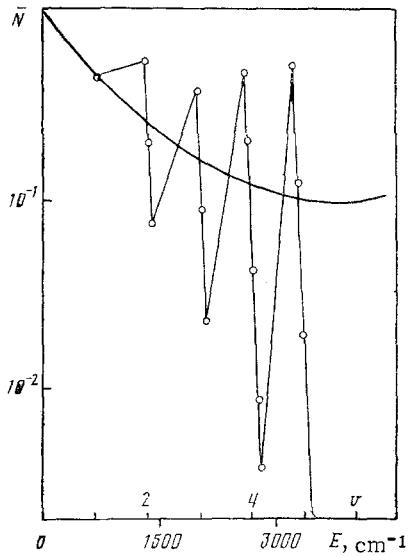

Fig. 1

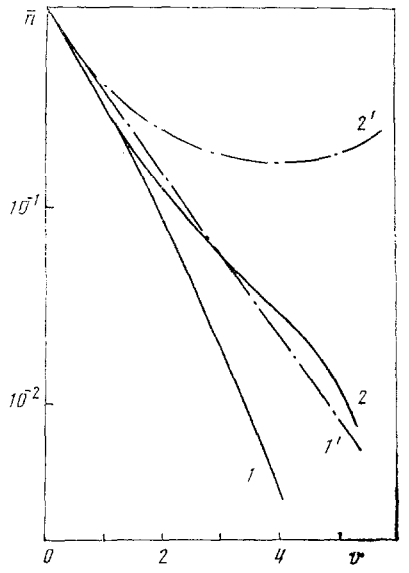

Fig. 2

the reduced populations of the individual levels $\bar{N}_{V\beta} = N_{V\beta}/g_\beta$, while the smooth solid line is that for the multiplets $\bar{N}_V$ in the symmetrical mode. An important point is that the distribution for $\bar{N}_V$ has an ascending branch and corresponds to the Treanor distribution when there is Fermi-resonance multiplet splitting [7]:

$$N_v^T = \exp\left[-v\omega/T_1 - (\bar{E}_v - \omega v)/T\right]$$

for the symmetrical mode with $\bar{E}_V = \bar{E}_V = \omega v - \bar{\varkappa}_v \omega v^2$ and the anharmonicity constant

$$\bar{\varkappa}_v = \frac{T}{\omega v^2} \ln \sum_{\beta \equiv v} \frac{g_\beta}{g_v} \exp\left(-\frac{E_{v\beta} - \omega v}{T}\right),$$

which is dependent on the gas temperature. Here the value of $\bar{\varkappa}_v$ is almost the same for all the multiplets in the lower part of the spectrum (apart from the first $\bar{\varkappa}_1 = 0$) and constitutes for example $\bar{\varkappa} = 0.0041$ at 100°K and 0.0066 at 50°K. Qualitatively, the correspondence can be explained on the observation that a large fraction of the molecules will be in the lower states of the multiplets when there is vibrational quasiequilibrium. As the multiplet splitting increases with v, the Fermi resonance naturally influences the $\bar{N}_V$ in the same way as anharmonicity influences the vibrational distribution in a one-mode oscillator.

2. The presence of a rising branch in $\bar{N}_V$ indicates that there may be a flux of quanta into the upper levels. This arises in a nonequilibrium anharmonic-oscillator system on

account of preferential passage of quanta from the lower levels to the higher ones in V-V exchange and the loss of these in the upper part of the spectrum, where V-T processes predominate. It has been shown [3] that the V-V flux leads to instability in the rising branch of the Treanor distribution. Allowance for the effects of this in the case of paired CO_2 modes requires a kinetic description of the Treanor model, which in principle should be based on equations for the balance of the populations $n_{v\beta}$ for each level $(v\beta)$ and therefore will include not only V-V processes but also V-T transitions within the multiplets. However, the task is simplified if one bears in mind that the internal V-T processes do not alter the flux of quanta through the multiplets and belong to the group of fast processes. Then

$$n_{v\beta} = g_\beta x_v \exp[-(E_{v\beta} - \omega v)/T]$$

and the kinetic description amounts to the balance equations only for the multiplet populations n_V:

$$dn_v/dt = I_v - I_{v+1},\ I_v = x_{v-1}R_{v-1,\,v} - x_vR_{v,\,v-1}, \tag{2.1}$$

where

$$R_{vv'} = \frac{Z}{F}\sum_{u\lambda,\lambda',\mu,\mu'} g_{\lambda'}g_{\mu'}n_{u\lambda}\left(\frac{n_{v\mu}}{x_v}\right)Q^{u\lambda,u'\lambda'}_{v\mu,v'\mu'},\quad F = \sum_{u\lambda} n_{u\lambda}; \tag{2.2}$$

with $Q^{u\lambda,\ u'\lambda'}_{v\mu,\ v'\mu'}$ the probability of V-V exchange accompanied by the transition of one molecule from state $u\lambda$ to $u'\lambda'$ and the other from $v\mu$ to $v'\mu'$, with $u' - u = v - v' = \pm 1$, while Z is the collisional frequency. In writing Eqs. (2.1)-(2.2) we have neglected V-T transitions between adjacent multiplets in accordance with the Treanor model. It was assumed that they resemble other processes that produce dissipation of the quanta in the paired modes in being important only at high levels in the region $v \geqslant v_0$; then Eq. (2.1) can be considered as the equation of continuity for the quantum flux through the multiplets $v = 1 - v_0$, where I_V is the total flux and n_V is the quantum concentration in the $v - 1 \to v$ transition. The solution to equations of this type in the stationary-flux approximation

$$I_v = I \neq 0\ (v = 1, 2, \ldots v_0) \tag{2.3}$$

is familiar for example from nucleation theory [9, 10]; it is readily found by the pivot method from the recurrence relation for x_V implied by Eqs. (2.1) and (2.3), and it has the form

$$\frac{x_v}{X_v} = 1 - \frac{I}{J_{v-1}}, \tag{2.4}$$

$$X_v = \prod_{m=1}^{v}\frac{R_{m-1,m}}{R_{m,m-1}},\quad J_v^{-1} = \sum_{m=0}^{v}(X_mR_{m,m+1})^{-1},\quad I = J_{v_0}.$$

In deriving Eq. (2.4) allowance has been made for the fact that the quanta that attain the limiting $v_0 + 1$ multiplet are rapidly removed from the system and therefore $x_{V_0+1} = 0$ (boundary condition).

3. The solution of Eq. (2.4) defines the stationary flux distribution between the centers of the multiplets in the region $v = 1 - v_0$; this distribution becomes a Boltzmann one $x_V = X_V \equiv \exp(-v\omega/T_1)$ for $I = 0$ with the vibrational temperature in general different from the gas temperature. This quasiequilibrium approximation was used in [1] in considering the relaxation kinetics. The approach is justified only in the case of weak disequilibrium [2].

Figure 2 shows calculations on the effects of the V-V flux on the distribution of the CO_2 molecules over the paired-mode levels when there is strong disequilibrium for $T_1 = 1000°K$, $T = 50°K$ ($v^* = 4$); curves 1 and 2 correspond to the flux distribution of the quantities x_V, n_V, while 1' and 2' correspond to the quasiequilibrium X_V, $\bar{N}_V$. A calculation was performed from Eq. (2.4) with $v_0 = 6$ by iteration. The initial values for J_V were the values of the rates $R_{VV'}$ calculated on the assumption that long-range V-V exchange is dominant, i.e., V-V transitions involving the lower (01^11) state. Then a correction was made to $R_{VV'}$ for each of the contributions from the multiplets with $v = 2$-5. The energy shift $\Delta E_{V\beta} = E_{V\beta} - \omega v$ and the correct wave functions for the vibrational states $(v\beta) = \sum_{\beta \equiv v} C_\beta |v\beta\rangle$

TABLE 1

v	State $(v\beta)=\Sigma C_\beta \lvert v\beta\rangle$	$E_{v\beta}-\omega v$, W
1	$01^10=\lvert 01^10\rangle$	0
2	$02^00,100=0{,}707\lvert 100\rangle\mp 0{,}707\lvert 02^00\rangle$ $02^20=\lvert 02^20\rangle$	∓ 1 0
3	$03^10,11^10=0{,}707\lvert 11^10\rangle\mp 0{,}707\lvert 03^10\rangle$ $03^30=\lvert 03^30\rangle$	$\mp 1{,}41$ 0
4	$04^00,200=0{,}408\lvert 200\rangle\mp 0{,}707\lvert 12^00\rangle+0{,}577\lvert 04^00\rangle$ $04^20,12^20=0{,}707\lvert 12^20\rangle\mp 0{,}707\lvert 04^20\rangle$ $12^00=0{,}816\lvert 200\rangle-0{,}577\lvert 0,4^00\rangle$ $04^40=\lvert 04^40\rangle$	$\mp 2{,}45$ $\mp 1{,}73$ 0 0
5	$05^10,21^10=0{,}447\lvert 21^10\rangle\mp 0{,}707\lvert 13^10\rangle+0{,}547\lvert 05^10\rangle$ $05^30,13^30=0{,}707\lvert 0,5^30\rangle\mp 0{,}707\lvert 13^30\rangle$ $13^10=-0{,}774\lvert 21^10\rangle+0{,}632\lvert 05^10\rangle$ $05^50=\lvert 05^50\rangle$	$\mp 3{,}16$ ∓ 2 0 0
6	$06^00,300=0{,}213\lvert 300\rangle\mp 0{,}529\lvert 22^00\rangle+0{,}674\lvert 14^00\rangle\mp 0{,}47\lvert 06^00\rangle$ $06^20,14^20=0{,}463\lvert 22^20\rangle\mp 0{,}707\lvert 14^20\rangle+0{,}535\lvert 06^20\rangle$ $06^40,14^40=0{,}707\lvert 06^40\rangle\mp 0{,}707\lvert 14^40\rangle$ $14^00,22^00=0{,}682\lvert 300\rangle\mp 0{,}48\lvert 22^00\rangle-0{,}208\lvert 14^00\rangle\pm 0{,}512\lvert 06^00\rangle$ $22^20=-0{,}756\lvert 22^20\rangle+0{,}654\lvert 06^20\rangle$ $06^60=\lvert 06^60\rangle$	$\mp 4{,}3$ $\mp 3{,}74$ $\mp 2{,}23$ $\mp 1{,}22$ 0 0

were calculated as in [1] in the first order of perturbation theory by neglecting the anharmonic terms different from the Fermi-resonance ones. Table 1 gives the results from this calculation for v = 1-6. The values of $\Delta E_{v\beta}$ obtained in this way agree within 3% with experimental values [11]. The following equation [8] was used for the V-V exchange probabilities:

$$Q^{u\lambda,u-1\lambda'}_{v-1\mu,v\mu'}=V^2_{v-1\mu,v\mu'}V^2_{u\lambda,u-1\lambda'}Q^{10}_{01}\exp\left(-\bar{\delta}\left|\Delta E^{\lambda\lambda'}_{\mu\mu'}\right|+\frac{\Delta E^{\lambda\lambda'}_{\mu\mu'}}{2T}\right),$$

where $\Delta E^{\lambda\lambda'}_{\mu\mu'}=E_{u\lambda}-E_{u-1\lambda'}-E_{v\mu'}+E_{v-1\mu}$ is the resonance defect and $\bar{\delta}$ is the adiabatic factor for the V-V exchange. Then the matrix elements for the transitions

$$V_{v-1\mu,v\mu'}=\sum_{\mu\mu'}C_\mu C_{\mu'}\langle v-1\mu\,|\,V\,|\,v\mu'\rangle$$

were calculated in the dipole approximation, with

$$\langle v_1v_2^{|l|}\,|\,V\,|\,v_1\,(v_2+1)^{|l|\pm1}\rangle=\sqrt{\frac{1}{8}(v_2\pm|l|+2)}$$

the nonzero terms.

Figure 2 shows that when there is strong disequilibrium the flux distribution over the centers of the multiplets may deviate appreciably from a Boltzmann one with temperature T_1 even in the lower part of the spectrum. It is characterized by the vibrational temperatures of the multiplets $T_v=\omega/\ln(x_{v-1}/x_v)$, which decreases as v increases. On account of this cooling of the paired modes by the V-V flux, the stationary distribution for n_v does not have an ascending branch and falls fairly rapidly in the region $v > v_*$. This provides finiteness in the statistical sum F and, an important point, closeness to the corresponding harmonic approximation for the paired CO_2 modes. The latter is usually assumed a priori in making calculations on the vibrational kinetics of a CO_2 GDL in the Treanor model [4, 6, 12]. If F is calculated from the quasiequilibrium distribution of Eq. (1.1) and no suitable constraint is imposed on the summation limit in $v(v \leqslant v_*)$, it is possible to produce a large error in the final results. An example of this is provided by [5, 13], where incorrect normalization of the vibrational distribution was performed by direct summation of Eq. (1.1) up to v = 8, which gave rise to considerable underestimates of the inversion and the gain in a CO_2 GDL employing paired modes.

4. In conclusion, we consider the effects of the V-V flux on the rate of energy relaxation in the paired CO_2 modes when there is strong disequilibrium. There are two possible

reasons [2, 3] for the loss of vibrational energy in anharmonic oscillators with a V-V flux; loss of quanta from the higher levels in V-T processes in the region $v > v_0$ and direct nonresonant V-V exchange. In the first case, the rate of the energy relaxation flux is $\Gamma = d\varepsilon/dt$, or rather the component is determined as $\Gamma_{(1)} = \omega_{v_0+1} I$; in the second, it is $\Gamma_{(2)} = \sum_{v=1}^{v_0} \Delta\bar{\omega}_v I$, where $\omega_v = E_v - E_{v-1}$ is the quantum energy and $\Delta\bar{\omega}_v$ is the mean value of the resonance defect for V-V exchange that excites the flux of quanta in the $v - 1 \to v$ transition. On account of the level splitting in the paired modes, there is here also energy loss in internal V-T processes in the multiplets in the region $v \leqslant v_0$.

Estimates show that the vibrational-relaxation channels for the paired CO_2 modes resemble those for anharmonic oscillators in being very effective at low temperatures. For example, at T = 50°K, T_1 = 1000°K calculations indicate that the relaxation of the vibrational energy ε through the upper levels for $Q_{01}^{10} = 0.01$ is just as rapid (per collision) as is ordinary V-T relaxation of the paired modes in carbon dioxide at a temperature T = 600-1000°K and is characterized by the probability $P = \Gamma_{(1)}/Z\varepsilon \sim 10^{-4}$. As regards the other energy-loss channels related to a kind of friction in the V-V flux, the performance of these under these conditions is substantially less. In fact, the main contribution to the V-V flux is produced by close V-V exchange at low temperatures when the paired modes are strongly excited, this involving the participation of the lower components of the multiplets similar in shift. Therefore, the mean resonance defect $\Delta\bar{\omega}_v$ characterizing the V-V flux is small not only by comparison with ω but also with the splitting energy ΔE_v and is 0.1-0.3 W. The V-V flux occurs mainly via the lower components of the multiplets, so an equally small value should apply to the mean energy $\Delta\bar{E}_v$ lost by molecules by V-T transition within the multiplets. This can be estimated from the anharmonicity constant $\bar{\varkappa}$ for the symmetrical mode, $\Delta\bar{E}_v \simeq 2\bar{\varkappa}\omega \sim 0.1-0.2$ W, which also implies that the energy of the quanta carried by the V-V flux into the region where they are lost in internal and external V-T processes should be close to ω. In addition, there is the relative narrowness of the flux region $v = 1 - v_0$ due to the rapid overlap and closing up of the multiplet spectrum at $v \sim 8$-10, which means that the energy losses by the internal V-T channels and the nonresonance V-V ones are unimportant: $\Gamma_{(2,3)}/\Gamma_{(1)} \simeq 2\bar{\varkappa}v_0 \sim 10^{-1}$. As the vibrational excitation of the paired modes decreases, the proportion of energy lost in the friction increases, and in the limit of weak disequilibrium, where the V-V flux is excited by distant V-V exchange, it is estimated as $\Delta\bar{\omega}_v \sim \Delta\bar{E}_v \simeq 2\bar{\varkappa}\omega v$ and $\Gamma_{(2,3)} \simeq \bar{\varkappa}\omega v_0^2 I$, these values being comparable with the corresponding rates for loss of quanta in the upper levels.

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STATIONARY MODE OF EXPANSION OF A VAPOR HEATED BY RADIATION OR A FAST-PARTICLE FLUX

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A high-power radiation or fast-particle flux will evaporate the surface of an obstacle and will heat the vapor to high temperatures, the vapor then expanding with high velocity. A high pressure is set up at the obstacle. These phenomena have recently attracted attention in relation to pulsed controlled fusion CF. The energy sources are mainly lasers and electron beams. Considerable progress has been made recently [1-7] in producing high-power ion beams. Flux densities of the order of 1 GW/cm^2 have been attained with pulse lengths of 0.01-1 μsec [7]. Estimates have been made of the parameters needed to attain the conditions of CF using ion beams [7-10]. There is also a discussion [11] on the scope for using a high-power radiation continuum for this purpose, this being emitted by strong shock waves generated for example by shells accelerated by particle beams.

The interaction of radiation and particle fluxes with obstacles is of interest not only in relation to CF but also in simulating the collisions of micrometeorites with obstacles, the acceleration of microscopic objects to very high speeds, research on the optical properties and equations of state for materials under extreme conditions, diagnosis of radiation beams and sources, and many other scientific and engineering purposes. The heating and motion of the vapor in general constitute very complicated nonstationary processes, which sometimes are two-dimensional. It is desirable to have a simple model on the other hand that enables one to elucidate the trends in the major parameters with the source parameters and the target characteristics.

Estimates have been made [12] on the plasma parameters attained on exposing a target to a proton pulse for the case where the vapor has planar geometry. If the irradiation is sufficiently prolonged, the vapor thickness will be greater than the radius of the spot or radius of curvature of the target. The expansion becomes two-dimensional and the vapor density falls more rapidly than in the planar case. The peripheral vapor layers become transparent to the incident particles, which penetrate to deeper layers. The energy is deposited mainly at distances $r > r_0$, where r_0 is the target radius. A quasistationary plasma corona is produced. The evaporation rate in the target is much less than the plasma expansion speed, and the main part near the target is played by heating by absorption, while far away cooling predominates as a result of the expansion, while there is ongoing acceleration and passage through the speed of sound. This picture has been described in [13, 14] for laser radiation, and the parameters of the moving radially symmetrical plasma were derived for the case of all-round heating due to the inverse bremsstrahlung of the photoelectric effect. In [15] a study was made of the parameters of the stationary corona when laser radiation is absorbed in a layer with a concentration close to critical, while the energy is transferred to deeper layers by electron thermal conduction.

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