9. A. E. Bulyshev and N. G. Preobrazhenskii, "Impedance response in an electrodeless HF discharge to optical excitation," Dokl. Akad. Nauk SSSR, 279, No. 6 (1984).
10. L. M. Biberman, V. S. Vorob'ev, and I. T. Yakubov, Nonequilibrium Low-Temperature Plasma Kinetics [in Russian], Nauka, Moscow (1982).
11. W. L. Wiese, M. W. Smith, and B. M. Glennon, "Atomic transition probabilities," NSRDS-NBS, Vol. 4 (1966).
12. J. Hasted, Atomic-Collision Physics [Russian translation], Mir, Moscow (1965).
13. N. K. Zaitsev and N. Ya. Shaparev, Plasma Optoelectric Phenomena [in Russian], Preprint No. 207-209 F, IF SO AN SSSR, Krasnoyarsk (1982).

MOLECULAR-GAS COOLING IN A RESONANT RADIATION FIELD WITH LINE OVERLAP

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Recently, there has been much interest in processes where resonant radiation acts on absorbing or amplifying gas media. The changes in macroscopic parameters (temperature or density) are very important, as they govern the refractive-index changes in the beam. In [1-4], molecular-gas cooling mechanisms on absorption were examined, where the frequency is in resonance with the line center of an absorbing vibrational–rotational transition. This kinetic-cooling intermode transition $00^01 \rightarrow 10^00$, wavelength $\lambda = 10.6$ μm [5], and in CD_4 on absorption in the P branch of a vibrational–rotational transition belonging to the ν_4 mode [6]. The absorption is considered for a solitary spectral line in the absence of overlap with adjacent ones. However, adjacent lines often overlap. The paper discusses molecular-gas cooling mechanisms on light absorption or amplification under these conditions.

Let the gas molecules be rigid rotors, while the frequency ν_I in the beam is almost in resonance with the center frequency ν_0 or the line for a certain vibrational–rotational transition $m(V', j') \rightleftarrows n(V'', j'')$:

$$\nu_I = \frac{E_{V''} - E_{V'} + E_{j''} - E_{j'}}{h} + \Delta\nu. \tag{1}$$

Here $E_{V'}$ and $E_{V''}$ are the vibrational energies of the lower state m and upper state n in the absorbing (amplifying) transition, $E_{j'}$ and $E_{j''}$ are the rotational energies there, h is Planck's constant, and $\Delta\nu$ is the frequency difference.

We neglect thermal conduction and convection (our characteristic times are substantially less than the ones for those processes), and write the equation describing the temperature as

$$\frac{5}{2}\frac{R}{\mu}\rho\frac{dT}{dt} = J, \quad J = k_\nu I - \frac{de_r}{dt} - \frac{de_V}{dt}, \tag{2}$$

where T is the translational temperature; ρ, density; μ, molecular weight; e_V and e_r, vibrational and rotational energies in unit volume; k_ν, absorption coefficient; and I, intensity.

Let the induced-transition time τ_I be substantially longer than the polarization relaxation time τ. We neglect spontaneous decay and derive the changes in the numbers of molecules in the states (V', j') and (V'', j'') that intersect with the radiation from [7, 8]

$$\frac{dN_{j'}}{dt} = -\frac{k_\nu I}{h\nu_I} + J_{RR}^{j'} + J_{RT}^{j'}; \tag{3}$$

$$\frac{dN_{j''}}{dt} = \frac{k_\nu I}{h\nu_I} + J_{RR}^{j''} + J_{RT}^{j''}; \tag{4}$$

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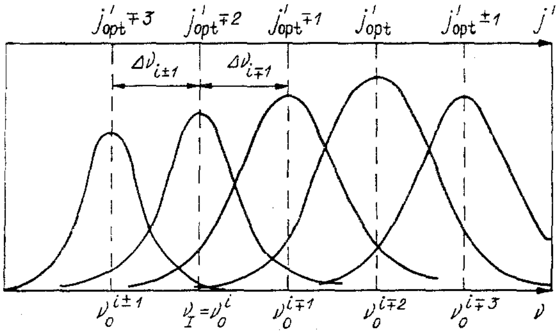

Fig. 1

$$\frac{dN_{V'}}{dt} = -\frac{k_\nu I}{h\nu_I} + J_{VV}^{V'} + J_{VT}^{V'}; \tag{5}$$

$$\frac{dN_{V''}}{dt} = \frac{k_\nu I}{h\nu_I} + J_{VV}^{V''} + J_{VT}^{V''}. \tag{6}$$

Here N_j is the number of molecules excited to the state having rotational quantum number j, and N_V that to the state with vibrational quantum number V; $J_{RR}^j, J_{RT}^j, J_{VV}^V, J_{VT}^V$. are terms defining the population changes in the q(V, j) level on account of R–R, R–T, V–V, and V–T exchange. As $e_V = \sum_V E_V N_V$, while $e_r = \sum_j E_j N_j$, we assume that the interaction occurs only with a finite number of vibrational–rotational lines q ($q_1 < q < q_2$) (line center frequency ν_0^q), so we substitute (3)-(6) with (1) into (2) to get

$$\frac{5}{2}\frac{R}{\mu}\rho\frac{dT}{dt} = \sum_{q=q_1}^{q_2} k_{\nu_I}^q \frac{\Delta\nu_q}{\nu_I} I - \Phi_V - \Phi_R,$$
$$\Phi_V = \sum_k (J_{VV}^k + J_{VT}^k) E_V^k, \quad \Phi_R = \sum_l E_j^l (J_{RR}^l + J_{RT}^l). \tag{7}$$

The summation in the expression for Φ_V or Φ_R is taken over the vibrational or rotational quantum numbers correspondingly, while $\Delta\nu_q = \nu_I - \nu_0^q$.

Let the following condition apply for each line interacting with the radiation:

$$\tau_I < h\Delta\nu_q \min\left(\frac{\tau_R^j}{E_j}\right) < h\Delta\nu_q \min\left(\frac{\tau_V^k}{E_V}\right),$$

where $\tau_R^j = \min\{\tau_{RR}^j, \tau_{RT}^j\}$; $\tau_V^k = \min\{\tau_{VV}^k, \tau_{VT}^k\}$; $\tau_{RT}, \tau_{RR}, \tau_{VT}$ and τ_{VV} are the characteristic times for R–T, R–R, V–T, and V–V exchange.

Then (7) becomes

$$\frac{5}{2}\rho\frac{R}{\mu}\frac{dT}{dt} = \sum_{q=q_1}^{q_2} k_{\nu_I}^q \frac{\Delta\nu_q}{\nu_I} I.$$

Let ν_I be equal to the line-center frequency for a certain vibrational–rotational transition $\nu_0^i(\Delta\nu_i = 0)$. If there is no line overlap, $\Delta\nu_q = 0$ and if $\tau_T < t \leq \tau_I$ (τ_T is the Maxwellian-distribution settling time), the gas temperature will not change. Adjacent-line overlap (e.g., on pressure increase) may alter the translational temperature. For any line satisfying

$$\left| k_{\nu_I}^q I \frac{\nu_I - \nu_0^q}{\nu_I} \right| < \min\left(\frac{E_j N_j}{\tau_R^j}\right) \quad (q_1 < q < q_2), \tag{8}$$

the cooling on absorption will occur if

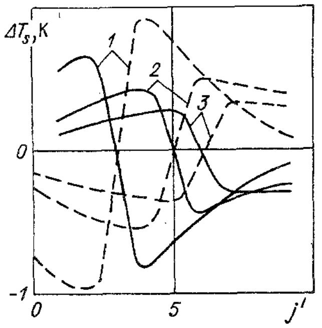

Fig. 2

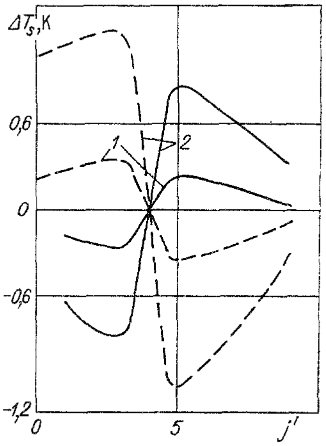

Fig. 3

$$\sum_{q=q_1}^{q_2} k^q_{\nu_I}\Delta\nu_q < 0. \tag{9}$$

The cooling is thus determined by the overall effect from cooling or heating due to adjacent overlapping frequencies near $\nu_I(\nu_0^i)$ and for any line having $\nu_0^q > \nu_0^i$ there will be a contribution to the cooling, while one having $\nu_0^q < \nu_0^i$ produces heating.

The cooling on absorption in a line having $\nu_0^q > \nu_I$ is due to the absorption of a quantum $h(\nu_0^q + \Delta\nu_q)$ exciting a molecule from state m having energy $E_m = E_{V'} + E_{j'}$ to state n having energy $E_n = E_m + h\nu_0^q$. If $\Delta\nu_q < 0$, $E_m < h\nu_I + E_n$, and the energy deficiency $h\Delta\nu_q$ is balanced out by a reduction in the mean kinetic energy in the random translational motion. The gas is cooled, and cooling may also occur if light is amplified by an inverted medium ($k_\nu < 0$) if $\Delta\nu_q > 0$ $(\nu_I > \nu_0^q)$.

We now show that there are cases where (9) applies. We represent the absorption coefficient at a distance $\Delta\nu_q$ $(i - n \leqslant q \leqslant i + n$, n an integer, n < i) from the center of line q as

$$k^q_{\nu_I} = k^q_{\nu_0} H_q(\nu), \tag{10}$$

where $H_q(\nu)$ is a Voigt function and $k^q_{\nu_0}$ is the absorption coefficient at the center of line q for $H_q(\nu) = 1$. Line overlap is usually due to collisional broadening, and then

$$H_q(\nu) = \alpha\frac{p_0^2(b_c^q)^2}{p_0^2(b_c^q)^2 + (\Delta\nu_q)^2}, \quad \alpha = \frac{2\nu_0^q}{c}\sqrt{\frac{2RT_0}{\pi\mu}}.$$

Here b_c^q is the collisional width of line q at half height and p_0 is the pressure.

From (9) and (10),

$$\sum_{q<i} k^q_{\nu_0}\frac{|\Delta\nu_q|}{1+\left(\frac{\Delta\nu_q}{b^q_c p_0}\right)^2} < \sum_{q>i}\frac{k^q_{\nu_0}|\Delta\nu_q|}{1+\left(\frac{\Delta\nu_q}{b^q_c p_0}\right)^2}. \tag{11}$$

Let ν_I be equal to the central frequency for a line having consider saturation in a certain vibrational-translational $\Delta j = j'' - j' = -1$ (P branch); then $\Delta\nu_q = \nu_0^{i+1} - \nu_0^i = -(B_{V''} + B_{V'}) - (2j' + 1)(B_{V'} - B_{V''})$ for adjacent lines in a single vibrational transition (B_V is the rotational constant in state V (V = V', V''). If $j'_i > j_{opt}$, j_{opt} corresponds to the peak in the rotational distribution $\left(j_{opt} = \sqrt{\frac{T}{2B_{V'}}} - \frac{1}{2}\right)$, in which case $k^q_{\nu_0}$. for a line having q < i will be larger than for one having q > i (it is assumed that the Einstein coefficient varies only slightly with j). As the $k^q_{\nu_0}(j)$ dependence is substantially stronger than the $\Delta\nu_q(j)$ or $b_c^q(j)$ one, it is clear that the overlap between adjacent lines at $\nu_I = \nu_0^i$ will mean that (11) is obeyed and the gas cooled. For $j'_i < j_{opt}$, on the other hand, the gas is heated.

On Q-branch absorption $(\Delta j = 0)$ $\Delta\nu_q = -2(j' + 1)\times(B_{V'} - B_{V''})$ and here one gets a complete analogy with absorption in the P branch. For $j'_i > j_{\mathrm{opt}}$ we have cooling, and also heating for $j'_i < j_{\mathrm{opt}}$, but less than for a P branch one $(B_{V'} - B_{V''} \ll 1)$, so the cooling will be very slight.

For R-branch transitions, $(\Delta j = 1)$ $\Delta\nu_q = (2j' + 1)(B_{V''} - B_{V'}) + 3B_{V''} - B_{V'}$. If $j'_i < j_{\mathrm{opt}}$, $k^q_{\nu_0}$ is layer for a line having q > i than for one having q < i, and (11) is obeyed; the gas cools. For $j'_i > j_{\mathrm{opt}}$, the situation reverses and the gas is heated.

P-branch absorption cools the gas for $j'_q > j_{\mathrm{opt}}$, and the same happens for R-branch absorption with $j'_q < j_{\mathrm{opt}}$.

Figure 1 shows these cases, where we show lines having $\nu_0^{i\mp n}$, which correspond to $j' = j_{\mathrm{opt}} \mp (2\mp n)$, with a minus representing the P branch and a plus R $(n = \pm 1, 2, \ldots)$.

If there is amplification on the P branch, (11) is satisfied for $j'_q < j_{\mathrm{opt}}$ and if it occurs on the R branch, for $j'_q > j_{\mathrm{opt}}$ (we envisage that only adjacent lines having identical V' and V" overlap). The overlap cooling is essentially threshold in type and arises at a certain pressure such that $k^q_{\nu_I} > 0$ (or $k^q_{\nu_I} < 0$ on amplification) and satisfies (11).

We now estimate the cooling due to line overlap from above. We consider saturation in a certain vibrational–translational transition whose line center frequency is $\nu_0^q = \nu_I + \Delta\nu_q$, and which occurs for $t = t_I$, while $t_I < \min(\tau^j_R, \tau^k_V)$, and (8) is satisfied only for this transition. We assume for the interaction with only one transition that all the states having $j \neq j', j''$ are populated in accordance with a Boltzmann distribution at temperature T, i.e.,

$$\sum_{j\neq j',j''} E_j \frac{dN_j}{dt} = \frac{R}{\mu}\rho\frac{dT}{dt}. \tag{12}$$

Then we can introduce a rotational reservoir for each vibrational state V' and V'', which have numbers of molecules $N^R_{V'}$ and $N^R_{V''}$ [8].

In the interval $[\tau_T, t_I]$, we have

$$\frac{de_V}{dt} = \frac{k_\nu I}{h\nu_I}(E_{V''} - E_{V'}),\quad \frac{de_r}{dt} = \frac{de_V}{dt}\frac{E_{j''} - E_{j'}}{E_{V''} - E_{V'}}. \tag{13}$$

We integrate (7) with (12) and (13) as

$$\rho\frac{7}{2}\frac{R}{\mu}\Delta T_s = \frac{h\Delta\nu_q}{E^q_{V''} - E^q_{V'}}\left(E^q_{V''}\int_0^{t_I} dN_{V''} + E^q_{V'}\int_0^{t_I} dN_{V'}\right). \tag{14}$$

Here and subsequently, $\Delta T_s = T_s - T_0$, with the subscripts 0 and s corresponding to the parameters for t = 0 and $t = t_I$; (3)-(6) give us that in $[\tau_T, t_I]$

$$N_{V''} + N_{V'} = N^0_{V''} + N^0_{V'}; \tag{15}$$

$$N_{j''} + N_{j'} = N^0_{j'} + N^0_{j''}. \tag{16}$$

However, the saturation condition for the m → n absorbing transition for $t = t_I$ gives

$$N^s_{j''} = \frac{g_n}{g_m}N^s_{j'}. \tag{17}$$

We solve (16) and (17) for $N^s_{j'}$, as

$$N^s_{j'} = \frac{N^0_{j''} + N^0_{j'}}{1 + \dfrac{g_n}{g_m}}. \tag{18}$$

As $N_{V''} = N_{j''} + N^R_{V''}$, $N_{V'} = N_{j'} + N^R_{V'}$ in this rotational-model reservoir and $N^R_{Vs} = N^R_{V0}$, for $t = t_I$ (15) gives

$$N^s_{V'} = N^0_{V'} + N^0_{j''} - N^s_{j'}; \tag{19}$$

$$N^s_{V''} = N^0_{V''} + N^0_{j'} - N^s_{j'}. \tag{20}$$

Integration in (14) with (19) and (20) gives

$$\Delta T_s = \frac{2}{7}\frac{h\Delta\nu_q}{K}\left(x^0_{j'} - x^s_{j'}\right),$$

where $x_j = N_j/N_0$; $N_0 = \rho N_A/\mu$; N_A is Avogadro's number, and K is Boltzmann's constant.

We use (18) with $x^0_{j'} = g_m \frac{N_{V'}}{N_0}\exp\left(-\frac{E_{j'}}{KT_0}\right)\frac{1}{Z_{V'}}$, $x^0_{j''} = g_n \frac{N^0_{V''}}{N_0}\exp\left(-\frac{E_{j''}}{KT_0}\right)\frac{1}{Z_{V''}}$ (Z_V is the statistical sum in state V) to represent the cooling ΔT_s as

$$\Delta T_s = \frac{2}{7}\frac{h\Delta\nu_q}{KZ_{V'}} G_j \frac{N^0_{V'}}{N_0}\exp\left(-\frac{E_{j'}}{KT_0}\right)\left[1 - \frac{N^0_{V''}}{N^0_{V'}}\frac{Z_{V'}}{Z_{V''}}\exp\left(\frac{E_{j'} - E_{j''}}{KT_0}\right)\right],$$
$$G_j = \frac{g_m g_n}{g_m + g_n}. \tag{21}$$

Then (21) shows that the maximal ΔT_s for $N_{V''}/N_{V'} \ll 1$, when only adjacent lines overlap and one considers a linear molecule represented as a rigid rotor, occurs for $T_0 = E_{j'}/K$: $\Delta T_s^{\max} = 0.21\frac{B_{V'}G_j}{Kj'(j'+1)}$. At that T_0, the maximum ΔT_s occurs on absorption in a transition having $j' > j_{opt}$ for the P branch or $j' < j_{opt}$ for the R one if $j' = \text{entier}\left[\frac{1}{2}\sqrt{\frac{B_{V'} + 8KT_0}{B_{V'}}} - 1\right] \mp 1$ (the minus sign corresponds to absorption in the P branch and the plus to R). Then (21) applies for any solitary line having $\nu^q_0 = \nu_I + \Delta\nu_q$. If several lines overlap, the cooling will be determined by the overall cooling or heating effect from each of the lines.

This mechanism for cooling in a resonant field on line overlap applies also for more complicated molecules, such as symmetrical or unsymmetrical tops. However, it has proved impracticable to obtain analytic formulas for ΔT_s in such cases, and the equations must be solved numerically.

We now illustrate that cooling can occur with resonant radiation and line overlap for HCl and CO_2. Figure 2 shows ΔT_s on overlap for HCl on absorption on P-branch transitions $(V' = 0, j' \to V'' = 1, j'')$ (solid lines) and R-branch ones (dashed lines) for various j' and T_0 (T_0 = 300, 900, 1500 K for curves 1-3 correspondingly for j'_{opt} = 3, 5, 6). Parameters I and p_0 chosen to meet (8) only for adjacent lines $(j_q = j' \pm 1)$. The absorption coefficient for λ_I = 3.5 μm (0, j' → 1, j'' transitions in HCl) was calculated from standard formulas. The molecular constants and the collisional widths for HCl were taken from [9, 10]. At p_0 = 1 MPa (the value used in the calculations), the rotational–translational relaxation time for these levels is about 10^{-10} sec and is thus at least 20 times τ_T [11]. The distributions show that the cooling is somewhat larger for the R-branch transitions and can attain 1 K. The maximum occurs only for ΔT_s for T_0 = 300 K for the (0.4 → 1.5) transition; otherwise, $\Delta T_s < \Delta T_s^{\max}$.

We see from (21) that ΔT_s increases with $\Delta\nu$ for example when frequency $\nu^i_0(j_i = j')$ overlaps the line having $j_q = j' \pm l$ $(l = 2, 3, 4)$, but the cooling-existence time is much less than in the case above $(j_q = j' \pm 1)$ because such large $\Delta\nu_q$ are considerably elevated pressures, and $\tau^j_{RT} \sim p_0^{-1}$.

Similar $\Delta T_s = f(j, T_0)$ relations apply for CO_2 on absorbing radiation having λ_I = 10.4-9.4 μm, although there is a much more complicated structure in the spectrum for CO_2 because of close frequency spacing between the lines in the main band for the $10^00\ (02^00) \to 00^01$ transition and for transitions in the band sequences [12]. However, calculations (molecular constants from [12]) show that the cooling here even at the optimum T_0 is no more than 0.08 K, while the contribution from the sequence bands to the change on appropriate line overlap is negligible by comparison with that from the adjacent rotational lines in the main $10^00\ (02^00) \to 00^01$. transition.

Cooling on line overlap is also possible on amplification in an inverted medium, where the cooling increases with the inversion on the amplifying transition. Figure 3 shows the cooling in hydrogen chloride under adjacent-line overlap conditions on amplification on the $(V'', j'' \to V', j')$ transitions in the P and R branches (solid and dashed lines) for various j'. It was assumed that the distribution in the HCl molecules over the vibrational levels corresponded to a Treanor one having T_{V1} = 3000 K (T_{V1} is the effective vibrational temperature for the first level) and T_0 = 300 K. With such T_0 and T_{V1}, there is absolute inversion

$(N_{V''} > N_{V'})$ in HCl for $V > V_*(V_* = 4)$ a distribution having such inversion can arise for example in a discharge. The calculations were performed for the $(V_* + 2) \to (V_* + 1)$ and $(V_* + 3) \to (V_* + 2)$ transitions (curves 1 and 2). Here $j'_{opt} = 4$. The exciting intensity was chosen as in the absorption case. The cooling on amplification occurs in the R branch for $j' < j_{opt}$ and in the P one for $j' > j_{opt}$.

This cooling mechanism with overlap operates also for $t > \tau^j_{RT}$, but in that case there will be a contribution to the translational-temperature change from equilibration between the rotational states that interact with the radiation on the one hand and the translational degrees of freedom on the other. It is necessary to integrate a large number of rotational-kinetic equations to analyze how this mechanism affects the temperature change on line overlap.

LITERATURE CITED

1. A. D. Wood, M. Camac, and F. T. Gerry, "Effects of 10.6 μm induced radiation on the atmospheric refractive index," Appl. Opt., 10, No. 8 (1971).
2. B. F. Gordiets and V. Ya. Panchenko, "Laser-stimulated molecular-gas cooling," Pis'ma Zh. Tekh. Fiz., 4, No. 23 (1978).
3. V. A. Levin, A. A. Sorokin, and A. M. Starik, "Flow of a gas composed of unsymmetrical dipolar molecules in a resonant radiation field," Izv. AN SSSR, Mekh. Zhidk. Gaza, No. 1 (1985).
4. A. M. Starik, "Resonant-radiation cooling for a gas flow composed of diatomic molecules," Zh. Prikl. Mekh. Tekh. Fiz., No. 5 (1984).
5. F. G. Gebhardt and D. C. Smith, "Kinetic cooling of a gas by absorption of CO_2 laser radiation," Appl. Phys. Lett., 20, No. 3 (1972).
6. V. M. Gordienko, A. V. Mikheenko, and V. Ya. Panchenko, "Cooling of selectively excited CD_4 gas during vibrational—vibrational and rotational—translational relaxation," Pis'ma Zh. Tekh. Fiz., 5, No. 8 (1979).
7. A. I. Osipov and V. Ya. Panchenko, Thermal Effects in the Interaction between Laser Beams and Molecular Gases [in Russian], Moscow State Univ. (1983).
8. C. Smith and R. Thomson, Gas-Laser Numerical Simulation [Russian translation], Mir, Moscow (1981).
9. L. V. Gurvich, G. A. Khachkuruzov, V. A. Medvedev, and I. V. Veits, Thermodynamic Parameters of Individual Substances [in Russian], Vol. 1, Izd. Akad. Nauk SSSR, Moscow (1962).
10. A. V. Dem'yanov, I. V. Kochetov, V. G. Pevgov, and V. F. Sharkov, Vibrational Kinetics in Gas Mixtures Containing H_2 and HCl [in Russian], Preprint No. 31576, IAE, Moscow (1979).
11. T. T. Yang and J. A. Blauer, "Analysis of rotational nonequilibrium behavior in hydrogen fluoride/deuterium fluoride systems," J. Appl. Phys., 53, No. 4 (1982).
12. I. P. Kirmusov and A. M. Starik, "A computational study on the absorption and gain spectra of CO_2 at 9.2-10.9 μm," Opt. Spektrosk., 57, No. 3 (1984).