Emission of a pulsed purely rotational transition chemical $H_2 - F_2$ laser

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Abstract. **The possibility of obtaining efficient emission at purely rotational transitions of HF molecules in a pulsed chemical hydrogen fluoride laser is studied theoretically. The operation of a $H_2 - F_2$ laser with a gas pressure of 1.1 atm emitting at the v, $j \to v$, $j - 1$ ($v = 1 - 6$, $j = 10 - 14$) transitions is simulated taking into account resonance VR processes. The total specific laser energy release calculated over all the vibrational levels is 5.5 J L^{-1} on purely rotational transitions at $\lambda \sim 17$ μm ($j = 14$), 3.5 J L^{-1} at $\lambda \sim 18.5$ μm ($j = 13$), and 2.5 J L^{-1} at $\lambda \sim 20$ μm ($j = 12$).**

At present visible and IR lasers are well studied and widely used for different applications. The development of lasers emitting in a longer-wavelength range ($\lambda \geqslant 15$ μm) proceeds much slower, although the scope of their applications is quite broad and includes various biochemical, spectroscopic, and plasma diagnostics investigations, isotope separation, remote atmospheric sounding, and studies of semiconductor materials. In [1 – 4], a new pumping scheme was proposed for far-IR lasers emitting at the rotational transitions in hydrogen halides by exciting preliminarily their vibrational states. This excitation scheme takes into account that the vibrational relaxation of a number of diatomic hydrogen-containing molecules is governed by the vibrational – rotational (VRT) mechanism [5 – 9]. The specific feature of this mechanism is the resonance transfer of the energy stored in molecular vibrations to excite the high-lying rotational states of the same molecule. It is assumed that such a relaxation mechanism is inherent in hydrogen halides. For example, in the HF molecule these rotational states correspond to levels with quantum numbers $j \geqslant 14$. Under certain conditions, such excitation performed from 'above', taking into account the slower thermal relaxation of the upper rotational levels compared to the lower levels, can produce the inverse population of

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rotational states. The equilibrium population of the rotational states is limited by energies $\sim k_B T$, where T is the gas temperature. Because the rotational quantum numbers of these energy levels at room temperature are $j_{eq} \ll 14$, it is possible to produce inversion on the cascade of rotational states with $j_{eq} \leqslant j \leqslant 14$.

In [1, 2], thermal excitation of the vibrational levels of HF molecules followed by the gas cooling during its rapid expansion in vacuum was considered. According to calculations, the inverse population at the rotational levels of HF was $\sim 10^{14}$ cm^{-3}. In [4], the same inverse population was obtained in the calculation of an electroionisation discharge in a mixture containing HF molecules. In [10], a chemical $H_2 - F_2$ laser based on the $F : F_2 : H_2 : He = 0.02 : 0.99 : 1 : 20$ mixture ($T = 300$ K, $p = 2700$ Pa) was simulated numerically. The calculation showed that, if the VRT relaxation dominates over the VR relaxation, laser action can be obtained at rotational transitions in a chemical $H_2 - F_2$ laser with the specific output energy ~ 0.1 J L^{-1}. Such lasing was observed in experiments described in [11 – 20] and many other papers. For example, an atmospheric pressure chemical laser based on the $F_2 : H_2 : He = 0.1 : 0.1 : 0.9$ mixture was studied in [11]. It was found that $\sim 10 \%$ of the output radiation energy was emitted in the long-wavelength region ($\lambda > 15$ μm) corresponding to purely rotational transitions. In [14 – 17], laser action was obtained at rotational transitions in hydrogen-containing molecules OH, OD, NH, and HF in mixtures where the dominating role of the VRT relaxation was theoretically established. Lasing at the transitions from high rotational levels of hydrogen halides HF, HCl, and HBr excited by an electric discharge was reported in [12, 13]. The only explanation of strong rotational excitation is the direct excitation of the rotational states during VRT relaxation.

The aim of this paper is to study theoretically the possibility of obtaining efficient generation at purely rotational transitions in a pulsed chemical hydrogen fluoride laser. Earlier in [21], the multilevel model of a pulsed chemical $H_2 - F_2$ laser was developed which can be used to investigate lasing at individual vibrational – rotational v, $j - 1 \to v - 1$, j transitions, taking into account the non-equilibrium population of the rotational sublevels of HF molecules. This model was employed for calculating the spectral, temporal, and energy parameters of radiation of the vibrational – rotational $H_2 - F_2$ laser, which well agrees with experimental data obtained at the 'Applied Chemistry' Federal State Unitary Enterprise [21]. In this paper, we use the modified version of this model taking into account the VRT relaxation mechanism of HF molecules.

Consider a pulsed chemical H$_2$–F$_2$ laser emitting at the $v, j \to v, j - 1$ ($v = 1 - 6$) purely rotational transitions. Let us write equations for the populations of rotational sublevels of HF molecules, which are similar to equations for the medium of a vibrational–rotational hydrogen fluoride laser [21]:

$$\frac{dn_v^{(j)}}{dt} = -\frac{\alpha_{v,j} I_{v,j}}{h v_{v,j}} + \frac{\alpha_{v,j+1} I_{v,j+1}}{h v_{v,j+1}}$$

$$+ \frac{n_v - n_v^{(j)}}{M_{v,j} \tau_{v,j}} - \frac{n_v^{(j)}}{\tau_{v,j}} + R_{v,j} + S_{v,j}. \qquad (1)$$

Here, $n_v^{(j)}$ is the concentration of HF molecules at the vibrational–rotational level v, j; n_v is the total population of the vth vibrational level of HF; $\alpha_{v,j} = \sigma_{v,j}[n_v^{(j)} - n_v^{(j-1)} \times (2j + 1)/(2j - 1)]$; $\sigma_{v,j}$ is the cross section for induced radiation at the $v, j \to v, j - 1$ transition; $I_{v,j}$ is the intensity of intracavity laser radiation at this transition; $v_{v,j}$ is the corresponding radiation frequency; $\tau_{v,j}$ is the characteristic rotational relaxation time in the rotational reservoir model [22]; $M_{v,j} = (2j + 1)^{-1}(T/Q_v) \times \exp[j(j+1)Q_v/T] - 1$; Q_v is the characteristic rotational temperature for the vth vibrational level in the HF molecule; $R_{v,j}$ is the term describing the resonance VTR process: HF$(v + 1, j')$ + M $\to$ HF(v, j) + M; $S_{v,j}$ is the decay probability for the v, j level per unit time due to superluminescence. It was assumed that $S_{v,j} = A_{v,v-1} g_s(L \alpha_{v,v-1})$, where $A_{v,v-1}$ is the Einstein coefficient for spontaneous emission at the $v, j \to v - 1, j + 1$ vibrational–rotational transition; $\alpha_{v,v-1}$ is the gain at this transition; and L is the length of the active laser medium; the expression for the function $g_s(x)$ was taken from paper [23]. The rotational relaxation time $\tau_{v,j}$ is related to the rate constants $k_v^M(j \to j')$ of the RT processes HF(v, j) + M $\to$ HF(v, j') + M by the expression

$$\frac{1}{\tau_{v,j}} = \sum_{j',M} k_v^M(j \to j') N_M, \qquad (2)$$

where N_M is the concentration of the M component of the laser mixture. The time dependence of the radiation intensity $I_{v,j}$ is described by the rate equations

$$\frac{dI_{v,j}}{dt} = c(\alpha_{v,j} - g)I_{v,j} + V_{v,j}. \qquad (3)$$

Here, g is the threshold gain for radiation at purely rotational transitions in HF and $V_{v,j}$ is the term describing spontaneous radiation. It was assumed in calculations that the radiation intensity of vibrational–rotational transitions in HF is considerably lower than $I_{v,j}$. This can be achieved by using a selective resonator and the active medium of length not exceeding a threshold value of 20–50 cm [24]. Equations (3) should be solved together with equations (1) and equations for the population n_v of the vibrational levels of the HF molecule ($v = 0 - 7$), chemical kinetics equations, equations for the mean storage of vibrational quanta of H$_2$ and the gas medium temperature. Chemical processes proceeding in the H$_2$–F$_2$–O$_2$–He mixture, the corresponding rate constants and other parameters considered in calculations are presented in [25].

Calculations were performed for the H$_2$:F$_2$:O$_2$:He = 1:3:0.3:7 ($p = 1.1$ atm) mixture at the initiation level specified by the initial concentration $N_a = 3 \times 10^{16}$ cm^{-3} of free fluorine atoms. The rate constants $k_v^M(j \to j')$ of RT

processes were described by expressions with the exponential dependence of $k_v^M(j \to j')$ on the rotational energy with the same numerical coefficients as in [21].

For simplicity, we considered in calculations only the following one-quantum ($\Delta v = 1$) resonance VR processes: HF$(v, 3)$ + M $\to$ HF$(v - 1, 14)$ + M, where $v = 2 - 7$ and M = HF, H$_2$. The rate constants of these processes were assumed equal to the corresponding rate constants of vibrational–translational relaxation of HF molecules in collisions with HF and H$_2$ molecules [25]. In this case, lasing on purely rotational transitions in HF is possible in the cascade of the $v, 14 \to v, 13$; $v, 13 \to v, 12$; $v, 12 \to v, 11$ ($v = 1 - 6$) transitions, etc. at the wavelengths ~ 17, ~ 18.5, ~ 20 μm, respectively, etc. Due to the absence of experimental values of the induced radiation cross sections for the $v, j \to v, j - 1$ transitions in HF molecules for $v = 1 - 6$ and $j = 10 - 14$, their values were varied in calculations from 10^{-15} to 10^{-14} cm^2. Note that the laser energy releases calculated for these purely rotational transitions for $\sigma_{v,j} = 10^{-15}$ cm^2 ($g = 10^{-3}$ cm^{-1}) and 10^{-14} cm^2 ($g = 10^{-2}$ cm^{-1}) were almost the same.

Table 1. Specific laser energy release ε_j calculated for the $v, j \to v, j - 1$ transition.

v	ε_{14}/J L^{-1}	ε_{13}/J L^{-1}	ε_{12}/J L^{-1}	ε_{11}/J L^{-1}	ε_{10}/J L^{-1}
1	0.7	0.4	0.3	0.15	0.05
2	1.4	0.9	0.5	0.3	0.1
3	1.3	0.9	0.6	0.3	0.15
4	1.1	0.7	0.5	0.3	0.15
5	0.7	0.5	0.4	0.25	0.15
6	0.3	0.2	0.15	0.1	0.06

Table 1 presents the specific output energy calculated for a H$_2$–F$_2$ laser emitting at purely rotational $v, j \to v, j - 1$ ($v = 1 - 6$, $j = 14 - 10$) transitions for $\sigma_{v,j} = 10^{-14}$ cm^2 and $g = 10^{-2}$ cm^{-1}. One can see that the specific output energy at the $v, j \to v, j - 1$ transitions for $v = 2 - 4$ and $j = 14$ can exceed 1 J L^{-1}, while the total energy output over all the vibrational levels at purely rotational transitions at ~ 17 μm achieves 5.5 J L^{-1}. The calculated time dependences on the laser radiation intensity emitted at the rotational transitions of HF molecules ($v = 3$) are presented in Fig. 1.
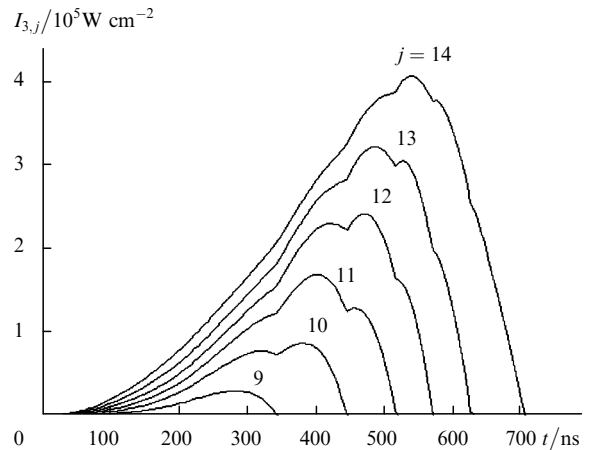

Figure 1. Calculated time dependences of the intracavity radiation intensity emitted at the purely rotational $v = 3, j \to v = 3, j - 1$ transitions in HF molecules. The threshold gain is $g = 10^{-2}$ cm^{-1}.

Thus, we have simulated the operation of a pulsed chemical hydrogen fluoride laser emitting at purely rotational transitions in HF. Calculations performed for the $H_2 - F_2$ laser mixture at a total pressure of 1 atm and the initiation level 3×10^{16} cm^{-3} have shown that efficient lasing can occur at the $v, j \rightarrow v, j - 1$ transitions with $v = 1 - 6$ and $j = 10 - 14$. The specific laser energy release at purely rotational transitions calculated over all the vibrational levels achieves 5.5 J L^{-1} at $\lambda \sim 17$ μm ($j = 14$), 3.5 J L^{-1} at 18.5 μm ($j = 13$), and 2.5 J L^{-1} at $\lambda \sim 20$ μm ($j = 12$).

Note in conclusion that there exists a hypothesis about the important role of multiphoton VR transitions [6–9] resulting in excitation of higher rotational levels (for example, for the HF molecule for $\Delta v = 5$ for resonance transitions, rotational levels with $\Delta j \sim 30$ are excited). In this case, the spectral range of emission at purely rotational transitions can be considerably expanded to the blue.

References

1. Igoshin V.I., Molevich N.E., Oraevsky A.N. *Kvantovaya Elektron.*, **10**, 748 (1983) [*Sov. J. Quantum Electron.*, **13**, 463 (1983)].
2. Igoshin V.I., Molevich N.E., Oraevskyi A.N. *Int. J. Infrared and Millimeter Waves*, **5**, 403 (1984).
3. Molevich N.E., Oraevsky A.N. *Kvantovaya Elektron.*, **11**, 1515 (1984) [*Sov. J. Quantum Electron.*, **14**, 1024 (1984)].
4. Kogan E.Ya., Molevich N.E., Oraevsky A.N., Soroka A.N., Shcherglov V.A. *Khim. Fiz.*, **6**, 41 (1987).
5. Molevich N.E., Oraevsky A.N. *Khim. Vys. Energ.*, **21**, 3 (1987).
6. Wilkins R.L. *J. Chem. Phys.*, **67**, 5838 (1977).
7. Wilkins R.L. *J. Chem. Phys.*, **70**, 2700 (1979).
8. Wilkins R.L., Kwok M.A. *J. Chem. Phys.*, **73**, 3198 (1980).
9. Wilkins R.L., Kwok M.A. *J. Chem. Phys.*, **70**, 1705 (1979).
10. Kerber R.L., Brown R.C., Emery K.A. *Appl. Opt.*, **19**, 293 (1980).
11. Chen H.L. et al. *J. Chem. Phys.*, **61**, 306 (1974).
12. Deutsch F. *Appl. Phys. Lett.*, **11**, 18 (1967).
13. Akkit D.P., Yardley J.T. *IEEE J. Quantum Electron.*, **6**, 113 (1970).
14. Downey G.D. et al. *J. Chem. Phys.*, **66**, 1685 (1977).
15. Smith J.H., Robinson D.W. *J. Chem. Phys.*, **68**, 5474 (1978).
16. Smith J.H., Robinson D.W. *J. Chem. Phys.*, **71**, 271 (1979).
17. Smith J.H., Robinson D.W. *J. Chem. Phys.*, **74**, 5111 (1981).
18. Krogh O.D., Pimentel G.C. *J. Chem. Phys.*, **67**, 2993 (1977).
19. Cuellar E., Pimentel G.C. *J. Chem. Phys.*, **71**, 1385 (1979).
20. Rice W.W., Oldenborg R.C. *IEEE J. Quantum Electron.*, **13**, 86 (1977).
21. Azarov M.A., Igoshin V.I., Pichugin S.Yu., Troshchinenko G.A. *Kvantovaya Elektron.*, **29**, 21 (1999) [*Quantum Electron.*, **29**, 859 (1999)].
22. Bashkin A.S., Kurdoglyan M.S., Oraevsky A.N. *Trudy FIAN*, **194**, 45 (1989).
23. Basov N.G., Bashkin A.S., Igoshin V.I., Nikitin V.Yu., Oraevsky A.N. Preprint FIAN, No. 44 (Moscow, 1976).
24. Igoshin V.I., Pichugin S.Yu. *Kvantovaya Elektron.*, **24**, 477 (1997) [*Quantum Electron.*, **27**, 465 (1997)].
25. Igoshin V.I., Pichugin S.Yu. *Kvantovaya Elektron.*, **21**, 417 (1994) [*Quantum Electron.*, **24**, 384 (1994)].