Comparison of HF and HCl Chemical Laser Parameters by using Mathematical Model

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Abstract:

A simplified theoretical comparison of the hydrogen chloride (HCl) and hydrogen fluoride (HF) chemical lasers is presented by using computer program. The program is able to predict quantitative variations of the laser characteristics as a function of rotational and vibrational quantum number. Lasing is assumed to occur in a Fabry-Perot cavity on vibration-rotation transitions between two vibrational levels of hypothetical diatomic molecule. This study include a comprehensive parametric analysis that indicates that the large rotational constant of HF laser in comparison with HCl laser makes it relatively easy to satisfy the partial inversion criterion. The results of this computer program proved their credibility when compared with the little published data.

Introduction:

Although the first chemical laser was an HCl laser reported by Kasper and Pimental (1965), the HCl laser has received relatively little attention. Investigations on chemical fluorine + hydrogen chain-reaction lasers peaked in 1970s and 1980s, meanwhile the chain chemical reaction is now more studied than the conventional oxygen-hydrogen one (Bravy,1996). The use of the hydrogen fluorination chain reaction chain reaction for which the rate of the chain chemical pumping process is much higher than that of deactivation processes has helped to make certain progress in this direction is that the number of vibrationally excited molecules produced in its course is much greater than that of the priming atoms formed during initiation (Basov and et al,1990).

To compare H_2+Cl_2 with the H_2+F_2 chain reaction chemical systems. The combination of: (i) IR spectral range suitable for molecular vibrations attack as well as for transmittance in atmosphere, (ii) large number of lines, and (iii) high peak power, makes HCl laser very promising tool (Gordon and et al, 1997). But its short coming, in comparison with HF laser, was a low efficiency, arising from the absence in H_2+Cl_2 system of fast chain reaction inherent to H_2+F_2 one. The HF pulsed chemical laser on a chain H_2+F_2 are indisputable leader among the pulsed lasers. The chemical reaction is initiated for example by F atoms photolytical formation $F_2 + h\nu \rightarrow 2F$, followed by fast chain reaction. The reaction of H_2 and F_2 to form excited HF takes place in two steps: the "cold reaction":

$$F + H_2 \rightarrow HF^{*} + H \quad \Delta H = -134 kJ/mole \quad \ldots (1)$$

And the "hot reaction":

$$H + F_2 \rightarrow HF^{*} + F \quad \Delta H = -406 kJ/mole \ldots (2)$$

where vibrationally excited HF*, molecules appear in both links of the chain.

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Since the hot reaction releases more energy and populates higher vibrational bands of HF than the cold reaction, there has been considerable interest in utilization of the hot reaction to increase laser power (Detweiler and Sentman, 2005).

The above reaction (1) known as pumping reaction, of fluorine (oxidizer) and hydrogen (fuel) produces about 14.7 kJ/g of fluorine with approximately 60% of the energy going into excited vibrational states of HF molecule (Wisniewski, 2003). This energy distribution allows for the creation of population inversion required for lasing. Excited state of HF can be deactivated by collision with other species inside laser cavity at rates as fast as the pumping reaction. Due to this, the fuel and oxidizer are kept separately until they reach the optical cavity (Palekar, 2004).

In most respects HF and HCl are quite similar; the main difference in the chemistry of the two systems lies in the lower bond energy of HCl (4.43 eV) while the HF bond energy (5.86 eV) (Eletskii, 1981).resulting generally in lower reaction exothermicities for HCl – forming reactions. In particular, in the H_2 – Cl_2 chain reaction, only the reaction

$H+Cl_2 \rightarrow HCl^* + Cl \quad \Delta H = -189 kJ/mole$ … (3)

leads to vibrational excitation. The reaction

$Cl+H_2 \rightarrow HCl^* + Cl \quad \Delta H = +4 kJ/mole$ … (4)

produces only HCl in the ground state. Thus, although the H_2 + Cl_2 chain reaction has been used for flash lamp pumped HCl lasers, the system is inherently inefficient (Stitch, 1979).

It can be shown that HCl molecules appear in the zero vibrational state (E_0 = 0) in the reaction (4), and only 0.015% of the HCl molecules formed occupy the v = 6 level corresponding to an energy of 189kJ/mole .The small fraction of HCl molecules carrying away a large amount of vibrational energy at the moment of their formation, as well as the high probability of vibrational and rotational energy dissipation by molecular collisions.

Things are different for a similar reaction between fluorine and hydrogen (reaction 2), where the heat of reaction is 2.5 times higher than the endothermicity of the fluorine molecule dissociation. Thus it may be assumed that the number of excited HF molecules with energy sufficient to dissociate F_2 on collision will be considerably higher than in the case of HCl.

Chemical lasers have many attractive features, they produce the highest output power per unite volume and per unite weight. In general, chemical reactions excite vibrational levels and thus the output wavelength is always in the infrared (1 μm to 12 μm). If one – shot large power is needed as, for example, in a star wars scenario, chemical lasers can produce large amounts of destructive energy without any electrical power (Das, 1991).

In the present work, theoretical studies of HF and HCl chemical lasers were performed in order to determine the effect of some parameters in the laser production.

Model Formulation

Formulation of the chemical laser model using Matlab computer programs, laser vibration-rotation state populations N (v, J) are computed from the kinetic reactions, with the effect of lasing, absorption, and spontaneous emission taken into account. The gain coefficient is $\alpha(v,J) = \frac{hN_A}{4\pi}\omega_c(v,J)\phi_c B(v,J) \times \left[\frac{g_l}{g_u} n_v - n_l\right]$ …(5)

where v and J are quantum numbers of the transition's lower level, h is Planck's constant, and N_A is the Avogadro's number. ω_c (v, J)is the wave number of the transition, B(v, J) is an Einstein coefficient, g_u and g_l are upper and lower state degeneracies. The wave number for P-branch transition into level (v, J) is taken as Kerber and Whittier (1976),

$$\omega_c (v, J) = \omega_v - (2 * J / 1.4388) * \theta_r(v) \quad \ldots(6)$$

where v= 0, 1, 2, 3……. And J = 1, 2, 3…... θ_r (v) is the characteristic rotational temperature which is approximated by θ_r (v) = (30- v) kelvin, and the constant 1.4388 is hc/k (where h is Planck's constant, c is speed of light and k is Boltzman constant).

Both Doppler and pressure broadening are considered through use of the Voigt profile ϕ_c, evaluated at line center is given by

$$\phi_c = (1.0921 * 10^6 / \omega_c) (W / T)^{1/2} \quad ...(7)$$

where W is the molecular weight of the diatomic molecule(for HF = 20 g/mole and for HCl = 36 g/mole) the constant $1.0921 * 10^6$ is $[c^2 \ln 2 / (2\pi * 10^7 N_A k)]1/2$, T is the absolute temperature, c is the speed of light, , and k is the Boltzmann constant. The Einstein isotropic absorption coefficient given by

$$B (v, J) = 6.282 * 10^{50}(J / 2J+1) | M_{v+1, v}|^2 \quad ...(8)$$

where M= the matrix element of the electric dipole moment,
and

$$| M_{v+1, v}=(v +1)^{1/2} * [(0.988*10^{-19}*(1 + 2.66*10^{-2} J)] \quad \ldots (9)$$

The rotational partition function where calculated taking into account the approximations that had been put forward by Kerber and Whittier (1975), the rotational temperature θ_r(v) in kelvin has been computed as a function of the vibrational quantum number v with the aid of the following relation (as given above),

$$\theta_r(v) = 30 - v \ldots(10)$$

The results of the calculated θ_r have been applied in the computations of the rotational partition function Q_r(v). For the vibrational level v, Q_r may be computed from the following formula (Emanuel 1971),

$$Q_r = \frac{1}{\sigma}\left(\frac{T}{\theta_r}\right) \quad \ldots (11)$$

where T is the absolute temperature in kelvin and σ is a symmetry factor; it equals to 1 for heteronuclear and 2 for homonuclear molecules.

The HF and HCl lasers action were assumed operating from three vibrationally excited levels on single vibrational-rotational transition having maximum gain coefficient for each pair of levels. The rotational distributions within a vibrational level were assumed to be in thermal equilibrium. Maximum gain vibrational-rotational transition always lies within the P-branch and its rotational quantum number may change in time being dependent on gas mixture temperature.

Results and Discussion

The certain Mathlab computer model was developed to simulate some parameters of the HF and HCl chemical lasers. The model can overpredicted performance of the chain reaction in both types of lasers. These parameters were calculated by using computer modeling. Based on the values of (ω_v) which were given for both HF and HCl of the band energy level spacing, the wave number (ωv,J) in cm^{-1} for P-branch has been calculated using equation (6) and the results plotted in Figure (1) as a function of rotational quantum number (J) for both HF and HCl lasers. As it appears, the increases in J will cause a linear decrease in ω with a negative slope. It can be seen from the figure that the decreases in wave number with J for HF is more clearly than for HCl, this probably due the higher value of the band origin of HCl in comparison with HF.

Figure (2) shows the variation of the matrix element dipole moment (MEDM) denoted by $|M_{v+1,v}|$ at various rotational quantum numbers for both HF and HCl lasers. It is seen that MEDM increases with increasing in J particularly at higher values of J. At J=0, the matrix element dipole moment has a certain value, as one would except from Equation (9). This linear variation of $M_{v+1,v}$ with J is identical to that published by Emanuel (1971) for HF laser. The highest values of MEDM for HCl are due to the large values of the constants that make it relatively easy to satisfy the partial inversion criterion. However, it can be seen that the increases of MEDM with J is faster than that for HCl. As a result of that, the HF laser is experimentally one of the easiest systems to get going.

Figure (3) shows the variation of rotational partition function (Q_r) as a function of the temperature at three vibrational states of transition for both HF and HCl. These plots are in agreement with those published by Emanuel (1971). It is seen that Q_r increases with increasing temperature and v, particularly at high temperatures and the values for the three states of v are nearly the same for HF. However, within room temperature, Q_r = 10 for HF and for HCl are independent of v and it has different values for different v

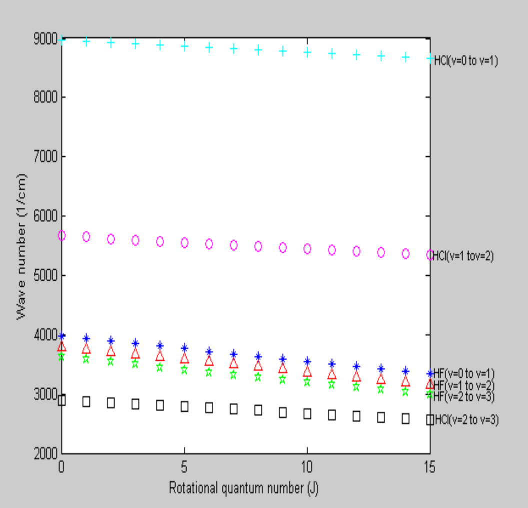

Figure (1) Wave number for HF and HCl molecules as a function of rotational quantum number (J)

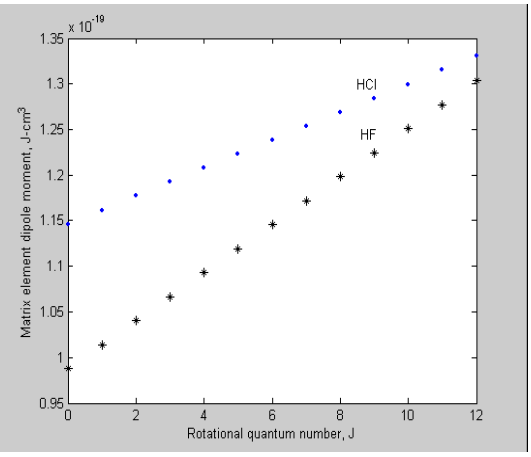

Figure (2) Matrix element dipole moment of HF and HCl molecules as a function of rotational quantum number (J)

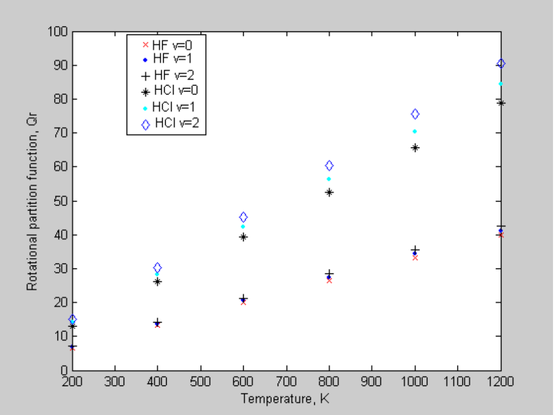

Figure (3) Rotational partition function for HFand HCl as a function of temperature at various values of the vibrational quantum number v.

CONCLUSION:

In this study is presented a model by which the laser parameters pulsed chemical laser can be followed. The main difference between the model discussed here and the ones found in the literature for HF laser only, is that the handling the rotational distribution.

The great advantages of this model are in reducing the computational efforts in performing simulation without affecting the reliability of the results. Instead of dealing with thirty or more differential equations (one equation for each rotational state) per vibration one has to deal with few equations only. This can reduce the total number of equations in a model which follows the development in time of radiation from each vibrational state separately. As a final point to refer to the preliminary study of HCl laser. Although no detailed study has been performed it is my belief that the result is acceptable in comparison with the available HF chemical laser results.

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مقارنة بعض معلمات ليزر فلوريد الهايدروجين (HF) وليزر كلوريد الهيدروجين(HCl) الكيمياوي باستخدام برنامج رياضي

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الخلاصة:

في هذا البحث تمت مقارنة بعض معلمات ليزر فلوريد الهيدروجين HF وليزر كلوريد الهيدروجين HCl باستخدام البرنامج الرياضي (Matlab) . أن هذا البرنامج يحتوي على ألاف البرامج الفرعية ومنها البرنامج الخاص بالمعادلة الخطيةالمستخدمة في متن البحث حيث أن للبرنامج القابلية على استنتاج التغيرات الكمية في خصائص الليزر كدالة للأعداد الكمية والدورانية الاهتزازية على فرض أن الانبعاث الليزري يحدث في فجوة فابري – بيرو وللانتقالات الدورانية- الاهتزازية بين مستويين اهتزازيين للجزئية الثنائية. هذه الدراسة تضمنت تحليل المعلمات التي تدل على أن القيمة العالية لثابت الدوران بالنسبة الى ليزر فلوريد الهيدروجين HF بالمقارنة مع ليزر كلوريد الهيدروجين HCl تساعد على تحقيق معايير انقلاب التعداد بسهولة. هذه النتائج للبرنامج الرياضي برهنت على مصداقية النتائج عند مقارنتها مع المنشورات العالمية المتوفرة.