The Effect of Fluorine and Hydrogen Concentrations on the Chain Reaction of HF Chemical Laser

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Abstract:

A numerical investigation has been performed to examine the effect of fluorine concentration on the chain reaction mechanisms and parameters of hydrogen fluoride (HF) chemical laser. The practical difficulties associated with this type of lasers impose that an alternative route might be quite useful. Thus, particular attention was paid to develop a computer program to investigate various processes. The results of this computer simulation program proved their credibility when compared with the little published data. This computer program is called Reaction Rate Simulation Model (RRSM). An entirely new approach to emulate the reaction mechanisms has been followed. The effectiveness of reaction rates in the processes of HF laser production has been investigated. This simulation program dealt with the percentages of the forward and reverse reactions, when a large number of reactions have been considered. In addition a large number of species have been taken into account in these reactions. From the computer program (RRSM), some valuable results could be predicted with regard to the hydrogen fluoride chemical laser.

1. Introduction

The physical approach of simulation model requires studying the rate equations in order to analyze and predict the kinetic behavior of the chemical laser systems. These are complex non-equilibrium molecular systems; the complexity arises from the large number of significantly populated levels and active transitions. The multitude of rate processes sets a limitation on this approach, commonly known as kinetic modeling. A more technical difficulty is associated with the numerical solution of large sets of nonlinear rate equations. This problem can be gradually overcome by producing fast computers, and approximation technique helps in overcoming the numerical difficulties.

The development of a computer model that includes the most important physico-chemical kinetics features under the assumption of rotational-translational equilibrium makes it possible to calculate the specific energy of coherent radiation, pulse duration, and population and concentrations variation of each species present in the reaction system. With the aid of a computer model, many factors can be studied i.e. the effect of mixture composition, spectral conditions of stimulated emission of radiation, and initiation intensity on laser output. For neutral atom and ion gas lasers, the departure from Maxwellian distribution is not far.

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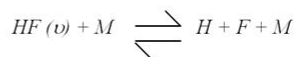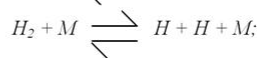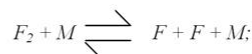* **Scientific Researcher, Environment Ministry

Chemical lasers have many attractive features, they produce the high output power per unite weight. In general, chemical reactions excite vibrational levels and thus the output wavelength is always in the infrared (1 µ m to 12 µ m). 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). This laser belongs to the family of high power chemical gas lasers. Principle of chemical lasers is that they efficiently convert energy derived from chemical bonds and reactions into excited states of atoms or molecules and then into the laser beam. These chemical reactions usually take place in gaseous media. Very huge advantage of the chemical lasers is then the high quality of the beam. This is due to the homogeneity of the lasing media in a resonator (usually low pressure gas)(Pickova et al,2006)

2. Model Formulation

Initially, the active medium is assumed to be a homogeneous mixture of F_2, H_2, F, H and diluents. Relative concentrations of F/F_2 and H/H_2 are chosen to simulate initiation by an external source. The dominant reactions of the chemical system are (see for example, Gross and Bott 1976):

a.   Photodissociation of F_2:
$$F_2 + h\nu \rightarrow 2F$$
$$H_2 + h\nu \rightarrow 2H$$
b.   The $H_2 + F_2$ chain:
$$F + H_2 \rightarrow HF(\upsilon) + H \qquad \upsilon = 0, 1, 2, 3$$
$$H + F_2 \rightarrow HF(\upsilon) + F \qquad \upsilon = 0, 1,...., 8$$
where υ is the vibrational quantum number
c.   Vibration-   Translation   (VT) deactivation:
$$HF(\upsilon) + M \rightarrow HF(\upsilon-1) + M$$
where M is the catalytic species
d.   Vibration – Vibration (VV) transfer:
$$HF(\upsilon) + HF(\upsilon') \rightarrow HF(\upsilon-1) + HF(\upsilon'+1)$$
$$HF(\upsilon) + H_2(\upsilon') \rightarrow HF(\upsilon-1) + H_2(\upsilon'+1)$$

e.   Dissociation- Recombination:

$$F_2 + M \rightleftharpoons F + F + M;$$

$$H_2 + M \rightleftharpoons H + H + M;$$

$$HF(\upsilon) + M \rightleftharpoons H + F + M$$

where M is the catalytic species

The chemical reaction is given by

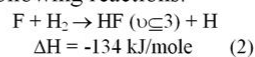$$\sum_i \alpha_{ri}[N_i] \rightleftharpoons \sum_i \beta_{ri}[N_i] \qquad (1)$$

where
$[N_i]$ = molar concentration for the ith species in reaction r,
α_{ri} , β_{ri} are stoichiometric coefficients of reaction r,
k_r, k_{-r} = forward and backward rate coefficients for the rth reaction, and the summation is over all species including any catalytic ones.

3. Chemical Pumping Reaction

The operation principle of the hydrogen fluoride chemical laser is based on the high rate constant and exothermicity of the chemical reaction. The chemical reaction produces HF in the vibrational excited states; it is highly exothermic and a large quantity of chemical energy is released. This excess energy is the equivalent pumping energy for this chemical laser. It is to be noted that this chemical energy is enormous compared to the other forms of pumping energy (Das 1991). Therefore, population inversion occurs between the vibrational – rotational states of the HF molecules that are produced by the following reactions:
$$F + H_2 \rightarrow HF(\upsilon \leq 3) + H$$
$$\Delta H = -134 \text{ kJ/mole} \qquad (2)$$
And
$$H + F_2 \rightarrow HF(\upsilon \subseteq 8) + F$$

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$\Delta H = -406 \text{ kJ/mole}$ (3)

Since the heat ΔH of these two reactions is 134 and 406 kJ/mole, respectively, the vibrational levels of the HF molecule, which becomes excited.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). The highest vibrational level, in which vibrationally excited HF (υ) molecules are formed is determined by the total energy available via equations (2) and (3). This total energy is the sum of the reaction enthalpy ΔH, activation energy E_a, and thermal energy $(5/2)\ RT$, which generally is small (Theodoropoulos et al 1999). It should be noted that because of larger exothermicity of the hot reaction much higher vibrational levels of HF are populated, there has been considerable interest in utilization of the hot reaction to increase laser power (Detweiler and Sentman, 2005). The inversion occurs because some of the reaction rates are faster for higher vibrational quantum numbers than for lower ones.

4. The program processes In setting the RRSM computer program several matters have been considered. The chemical processe included ninety-six reactions, which covered many reactions that have not been investigated by many authors. For this matter one may see Cohen (1972), and Sojka and Kerber (1986). These ninety-six reactions would take place in the chain reaction of the $H_2 - F_2$ chemical system. There are thirty-one species present in this system. For convenience, the concentration of the various species has been given a code number in the program statements. Table (1) reveals the code numbers for the concentration and the corresponding species. It is assumed that the reacting mixture is homogeneous and confined within a laser cavity. Each of the computational series has been performed at a fixed ratio of the initial gas mixture constituents (i.e. H_2: F_2: He). The initiation of the reaction has been assumed to take place by a constant number of photons in each of the computational series. The number of photons differs from one series to another in order to investigate their effect. Variations in these assumptions cause variations in the species concentration

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Table (1) Code number for the concentration of the corresponding species

Concentration Number	Species Name	Definition
Conc(1)	F_2	Fluorine molecule
Conc(2)	$h\nu$	Initiation photons
Conc(3)	F	Fluorine atom
Conc(4)	$H_2(0)$	Hydrogen molecule at ground state
Conc(5)	$H_2(1)$	Hydrogen molecule at first excited state
Conc(6)	$H_2(2)$	Hydrogen molecule at second excited state
Conc(7)	H	Hydrogen atom
Conc(8)	He	Helium atom
Conc(9)	HF(0)	Hydrogen fluoride at ground state
Conc(10)	HF(1)	Hydrogen fluoride at first excited state
Conc(11)	HF(2)	Hydrogen fluoride at second excited state
Conc(12)	HF(3)	Hydrogen fluoride at third excited state
Conc(13)	HF(4)	Hydrogen fluoride at fourth excited state
Conc(14)	HF(5)	Hydrogen fluoride at fifth excited state
Conc(15)	HF(6)	Hydrogen fluoride at sixth excited state
Conc(16)	HF(7)	Hydrogen fluoride at seventh excited state
Conc(17)	HF(8)	Hydrogen fluoride at eighth excited state
Conc(18)	HF total	Total hydrogen fluoride molecules
Conc(19)	F_2+H_2	Summation of fluorine and hydrogen
Conc(20)	All except H, H_2	All species except hydrogen atoms and hydro molecules
Conc(21)	$H + H_2$	Summation of hydrogen atoms andhydrogen molecules
Conc(22)	HF $h\nu(1\rightarrow0)$	Photon energy due to transition from $1\rightarrow0$
Conc(23)	HF $h\nu(2\rightarrow1)$	Photon energy due to transition from $2\rightarrow1$
Conc(24)	HF $h\nu(3\rightarrow2)$	Photon energy due to transition from $3\rightarrow2$
Conc(25)	HF $h\nu(4\rightarrow3)$	Photon energy due to transition from $4\rightarrow3$
Conc(26)	HF $h\nu(5\rightarrow4)$	Photon energy due to transition from $5\rightarrow4$
Conc(27)	HF $h\nu(6\rightarrow5)$	Photon energy due to transition from $6\rightarrow5$
Conc(28)	HF $h\nu(7\rightarrow6)$	Photon energy due to transition from $7\rightarrow6$
Conc(29)	HF $h\nu(8\rightarrow7)$	Photon energy due to transition from $8\rightarrow7$
Conc(30)	$H_2 h\nu(1\rightarrow0)$	Photon energy due to transition from $1\rightarrow0$
Conc(31)	$H_2 h\nu(2\rightarrow1)$	Photon energy due to transition from $2\rightarrow1$

The following equation gives the time evolution of the population, which is based on the classical rate law with its typical limitations (see for example, Levine 1988).

$$\Delta c/\Delta t = - k_1 [c_1]^{n1} [c_2]^{n2} [c_3]^{n3}$$
$$(4)$$

where

$\Delta c/\Delta t$ is the rate of change of concentration, Δt being very short time interval,

k_1 is the reaction rate constant,

c_1, c_2, c_3, ------- represent the concentration of species 1, 2, 3, ----

n_1, n_2, n_3, ------- are integers where each one represents the number of species that each constituent participate in the

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considered reaction. Equation (4) may be written in the following form,

$$\Delta c = - k_1 \Delta t [c_1]^{n1} [c_2]^{n2} [c_3]^{n3} \quad (5)$$

or,

$$Conc_{new} - Concn_{old} = - k_1 \Delta t [c_1]^{n1} [c_2]^{n2} [c_3]^{n3} \quad (6)$$

$$Conc_{new} = Concn_{old} - k_1 \Delta t [c_1]^{n1} [c_2]^{n2} [c_3]^{n3} \quad (7)$$

where

$Conc_{new}$ is the new concentration of each species,

$Concn_{old}$ is the old concentration of each species.

Due to the (a) high rate constants, and (b) high exothermicity of the H_2 - F_2 chain reaction shown in equation (3), the population inversion occurs between the vibrational states of the HF species produced by the reactions. To find the population of each species at various vibrational levels, a Boltzmann distribution is assumed. The population of vibrational levels depends on the ratio ΔE_υ / kT and on the quantum, number υ. Therefore, to determine the distribution of species among a vibrational state the following formula has been used (see for example, Levine 1988),

$$\frac{N_2}{N_1} = e^{-\Delta E/kT} \quad (8)$$

where $\Delta E = h\nu = E_2 - E_1$, E_1 and E_2 being the energy of states 1 and 2 respectively, N_1 is the number of molecules in the state 1, and N_2 is the number of molecules in the state 2. If E_2 is greater than E_1, then ΔE is positive and Equation (8) says that N_2 is less than N_1. The number of molecules in a state decreases with increasing energy of the state.
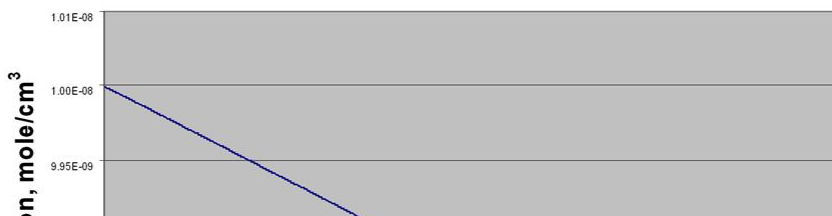
5.Result and Discussion

The mixture of H_2, F_2, and He gases leads to the chain reaction. The reaction lasts some time during which the concentration of the various species changes with increasing time. In the following chain reactions it has been assumed that the rate of composition equals the rate of decomposition. Variation of concentration with time depends on the type of species. For instance, the concentration of F_2 falls linearly and steeply with time at a negative slope from 1×10^{-8} mole/cm^3 to 9.75×10^{-9} mole/cm^3 over a period of about 1.9×10^{-6} s as shown in Figure (1). On the other hand, the F concentration increases linearly with time. It is seen that within a period of 1.6×10^{-6}s the concentration of F becomes 5.5×10^{-16} mole/cm^3 as shown in Figure (2). This increase in F atoms concentration is due to the dissociation of the F_2 molecules that decrease with time as indicated by Figure (1). The rate of decrease of F_2 molecules is 7.94375×10^{-2} mole/cm^3/s while the rate of increase of F atoms is 3.478×10^{-10} mole/cm^3/s. The H_2 concentration decreases with time where after about 0.4×10^{-6} s its concentration remains constant ($\sim 4 \times 10^{-12}$ mole/cm^3) for the rest of the reaction period as shown in Figure (3).

The H concentration increases sharply with the increase of the reaction time within a period of about 0.2×10^{-6} s as shown in Figure (4). It then reaches its highest constant value of 1.097×10^{-9} mole/cm^3 within the remaining period of the reaction. The dissociation of H_2 produces two H atoms, one is involved in the hot reaction and the other causes the build up of H concentration.
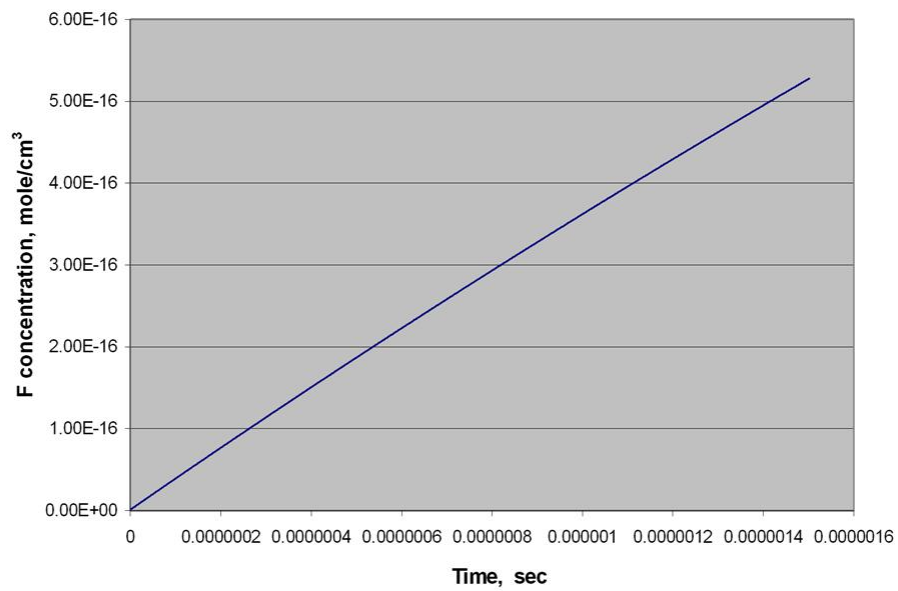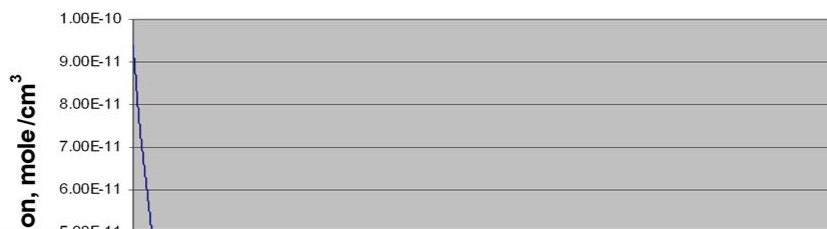
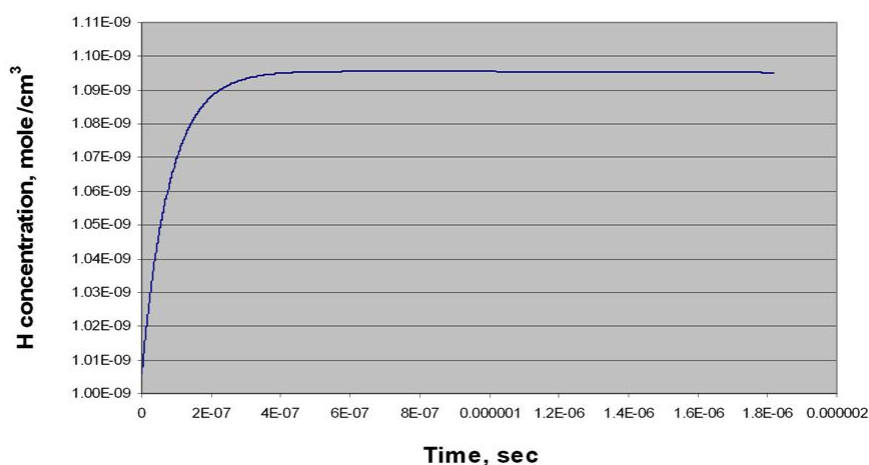Figure (2) Concentration of F atoms as a function of time.

Figure (4) Concentration of H as a function of time.

The variation of the HF species concentration with reaction time is shown in Figure (5). It is seen that the species have an initial concentration of 1×10^{-9} mole/cm^3 and increases rather rapidly within 10^{-6}s. Then, the concentration increases linearly with .

reaction time. Figure (5) represents the population inversion of the HF molecules at different vibrational levels. These molecules have been produced as a result of the high exothermicity of the chain reaction
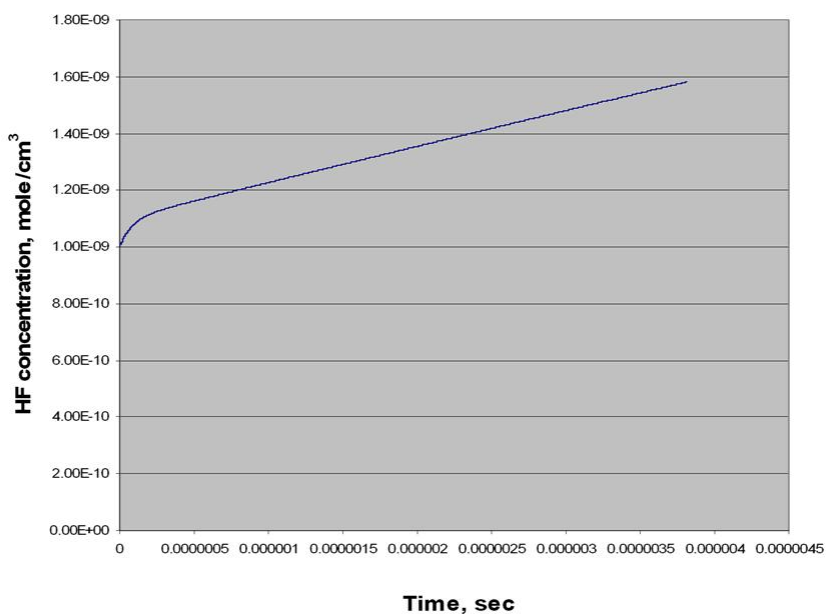
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Figure (5) Concentration of HF as a function of time.

6. Conclusions

The computer program RRSM (Reaction Rate Simulation Model) is found to have many advantages. It reduces the computational efforts in performing the simulation without affecting the reliability of the results. Instead of dealing with a large number of differential equations as in the case of the rate equation computer program, one has to deal with a large number of reaction mechanisms that might be present in the chemical reaction system. Thus the present investigation has dealt with a new number of reaction mechanisms where ninety-six reactions and thirty-one species that are directly involved in the $H_2 - F_2$ chain reaction have been taken into consideration. The validity and usefulness of RRSM lies in the accuracy of the rate constants that have been used. Usually these constants are available for forward reactions only. However, this simulation model deals with the percentages of the forward and reverse reactions.

The virtues of the proposed program include their approach in dealing with the chemical reactions of HF laser and little requirements. Although the full potentialities of the program is not yet fully practically assessed but it is already clear from these computations that they could bring about new developments which could be difficult with the present requirements.

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تأتير تراكيز الفلورين والهايدروجين على التفاعل المتسلسل في ليزر فلوريد الهيدروجين

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الخلاصة

تم أجراء نمذجه حاسوبيه لمعرفة تأثير تركيز الفلورين على آلية التفاعل المتسلسل لليزر فلوريد الهيدروجين (HF) الكيمياوي. أن المصاعب العملية الملازمة لهذا النوع من الليزرات يفرض الى اقتراح أسلوب بديل قد يكون اكثر فائدة. لذا تم التركيز على تطوير برنامج حاسوبي لمحاكاة عمليات متنوعة. وقد أثبتت نتائج برنامج المحاكاة الحاسوبي مصداقيتها عند مقارنتها مع النتائج القليلة المنشورة. أن البرنامج RRSM الخاص بنمذجة محاكاة معدل التفاعل قد اتبع أسلوبا جديدا لمحاكاة آليات التفاعل المتبعة وتمت دراسة فاعلية معدلات التفاعل على عمليات انتاج الليزر. وقد تعامل برنامج الماكاة هذا مع النسب المئوية للتفاعلات الامامية والمعكوسة حيث تم الاهتمام بعدد كبير من التفاعلات التي قد تظهر خلال عمليات انتاج ليزر HF. بالاضافة الى أنه تمت دراسة عدد كبير من مكونات التفاعل ومن الممكن توقع بعض النتائج القيمة من برنامج RRSM ، لذا فأن بالإمكان تجنب المخاطر العملية التي تواجه عادة مع ليزر فلوريد الهيدروجين.

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