Spontaneous and stimulated emission spectra for $^{124}Xe^{35}Cl$ molecules

N.G. Zubrilin, S.M. Baschenko, S.I. Osypov, I.A. Pavlov, M.P. Chernomorets
Institute of Physics, NAS of Ukraine
46, prospect Nauky, 03028 Kyiv, Ukraine,
E-mail: zubrilin@iop.kiev.ua

Abstract. The influence of the isotopic composition of active medium on a lasing spectrum of a XeCl laser has been investigated. Spectra of spontaneous and stimulated emissions for monoisotopic $^{124}Xe^{35}Cl$ molecules were measured. The frequencies in lasing spectrum were determined. The frequencies of vibrational edging in the luminescence spectra of the molecule $^{124}Xe^{35}Cl$ were also measured. We showed that varying the isotopic composition of the active medium one can get the lasing on frequencies different from the lasing ones in the natural XeCl laser.

1. Introduction

The electric discharge XeCl laser is one of the most powerful sources of coherent UV radiation now. This laser has wide applications for different scientific and technological branches. Many applications need for a narrow spectrum, whereas the XeCl laser spectrum is quite wide.

It is well known that, under common lasing conditions and if there are no additional selecting elements, there are four electron-vibrational transitions: 0-0, 0-1, 0-2, and 0-3 in the vicinity of 308 nm. Different schemes were used for narrowing the lasing spectrum. Some papers reported that, under the low pressure of a working medium (0.3–0.5 atm), there is a line structure caused by rotation of molecules [1, 2]. While the frequency is tuned in a laser with the selective resonator, this structure becomes apparent at the high pressure (2-3 atm) [3], which makes the tuning discrete in the tuning range. The identification of the rotational spectrum of the XeCl laser has to be performed with taking into account the great number of overlapping lines from different rotational branches.

One of the ways for simplification of the spectrum structure for its study is usage of mixtures enriched with isotopes [4]. Furthermore, usage of a mixture enriched by isotope, the concentration of which in the natural mixture is low, makes it possible to obtain new lasing lines.

This paper shows spectra of luminescence and lasing for molecules $^{124}Xe^{35}Cl$ ($B{\rightarrow}X$ transition) at a low pressure of the working mixture, and measurements of frequencies for lasing lines and band edgings of the luminescence spectrum were carried out.

2. Equipment and experimental

In this work, we use the electric discharge laser with the self-preionization reported in [5]. External dielectric mirrors form the laser resonator with the reflective index of output mirrors from 55 to 97 %. The rear mirror has reflective index R ~ 100 %. Plane-parallel plates of QU type silica with the thickness $d = 8$ mm were used as the chamber windows. The same laser chamber without external mirrors was used for obtaining the spontaneous spectrum. The chamber windows were inclined at small angle of 3 to 4°. Freon-12 (CF_2Cl_2) and carbon tetrachloride (CCl_4) were used as a donor of chlorine.

The emission spectrum was taken using the spectrograph DFS-8 on RF type film. The reciprocal linear dispersion in the second order of the diffraction grating with 1,800 groove/mm was 0.87 Å/mm. Emission spectrum of an iron hollow cathode lamp was used for the wavelength identification [6]. Line frequencies were determined by computer processing the scanned films (resolution 4000 dpi.) The lines of iron are reproduced with the accuracy better than 0.005 Å.

We obtain microphotograms of emission spectra by computer processing the data from scanned films or by modified microphotometer IFO-451. In the latter case, the analogue signal of photomultiplier was connected to the input of the analogue-to-digit converter of the computer sound card and processed by an applied software.

In this work, we used Xe of the following isotopic compositions

Isotope	^{124}Xe	^{126}Xe	^{128}Xe	^{129}Xe	^{130}Xe	^{131}Xe	^{132}Xe	^{134}Xe	^{136}Xe
^{124}Xe	99.3	0.1	0.1	0.44					
^{136}Xe	–	–	–	–	–	–	0.1		99.9

and the natural Xe mixture as well:

^{124}Xe – 0.096% ^{129}Xe – 26.44% ^{132}Xe – 26.89%

^{126}Xe – 0.090% ^{130}Xe – 4.08% ^{134}Xe – 10.44%

^{128}Xe – 1.92% ^{131}Xe – 21.18% ^{136}Xe – 8.87%

Freon-12 compositions were as follows: $CF_2{}^{35}Cl_2$ – 99.7%, $CF_2{}^{37}Cl_2$ – 0.3%.

3. Results and discussions

Fig. 1 shows the lasing spectrum structure of the molecule ^{124}Xe^{35}Cl at the pressure of working mixture 0.55 atm. In Fig. 1, the intensity scale is essentially nonlinear, especially for the areas of high intensities. For example, for the real spectrum, the intensities of electron-vibrational transitions 0-3 and 0-2 differ from another by several times.

Every electron-vibrational transition shows an internal structure caused by rotation of a molecule. It is well known (see, e.g., [7]) that there are two rotational branches R and P for the molecule XeCl in accordance with the selection rules. Spin splitting of the terms $^2\Sigma^+_{1/2}$ gives four rotational branches, and their superposition forms the obtained structure of the spectrum. Therefore, when changing one isotopic molecule to another, we see, firstly, a small shift of the electron-vibrational bands as a result of changing the vibration quantum, and, secondly, change in the band structure itself resulted from its dependence on the rotational quantum energy.

Fig. 2 shows the part of the lasing spectra of 0-3 transition for the molecules ^{124}Xe^{35}Cl, ^{136}Xe^{35}Cl, and

XeCl of the natural mixture measured at the pressure 1 atm in the same scale. The spectral range is entirely overlapped except one dip near 32,423 cm^{-1}, that results from the absorption line of OH-radical. Therefore, one can expect more entire frequency tuning for the XeCl laser inside the lasing range by using the different isotopic enriched mixtures in this laser.

Table 1 shows frequencies of the lasing lines for the molecule ^{124}Xe^{35}Cl at the pressure 0.55 atm.

The spontaneous emission spectrum of the molecule ^{124}Xe^{35}Cl is shown in Fig. 3. Every vibrational band has a structure caused by molecule rotation, which is similar to the lasing spectrum. Based on [8], we relate the spectral bands to the electron-vibrational transition.

Table 2 shows edging frequencies for electron-vibrational transitions of the molecule ^{124}Xe^{35}Cl.

When determining the edging frequencies, we did not take into account the fact that edging positions are located at some distances to the red from band origins. The estimated calculation shows that this distance for the 0-0 transition is less than 1 cm^{-1}. It is still less for the transitions to higher vibrational levels due to the fact that the first rotational constant decreases while the vibrational quantum number increases.
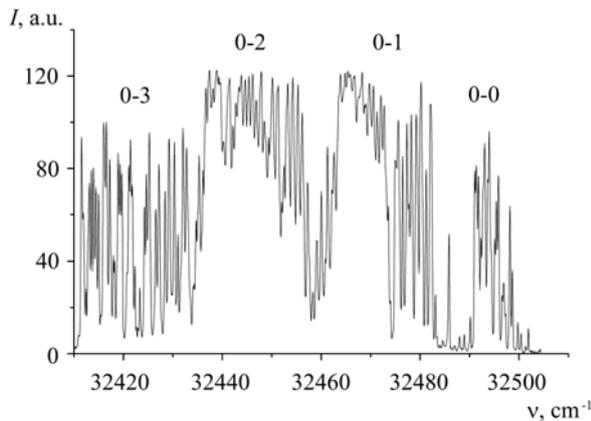
Fig. 1. Generation spectrum of ^{124}Xe^{35}Cl molecule. Upper figures denote the electron-vibration transitions.
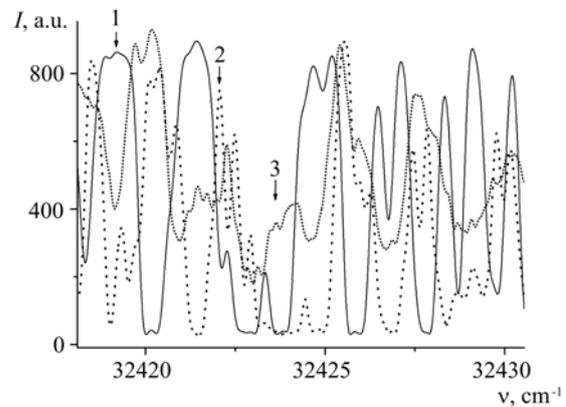
Fig. 2. Section of the 0-3 transition generation spectrum of ^{124}Xe^{35}Cl (1), ^{136}Xe^{35}Cl (2), and XeCl molecules of natural isotopic composition (3).

Table 1. Lasing frequencies of $^{124}Xe^{35}Cl$ at the pressure 0.55 atm.

Band	ν, cm^{-1}	Band	ν, cm^{-1}	Band	ν, cm^{-1}	Band	ν, cm^{-1}	Band	ν, cm^{-1}
0-3	32411.28	0-3	32426.42	0-2	32445.26	0-1	32465.27	0-1	32488.91
0-3	32412.23	0-3	32427.05	0-2	32445.99	0-1	32465.8	0-1	32490.17
0-3	32412.86	0-3	32428.21	0-2	32446.73	0-1	32466.54	0-1	32491.02
0-3	32413.28	0-3	32429.05	0-2	32447.78	0-1	32468.23	0-0	32491.34
0-3	32413.7	0-3	32430.1	0-2	32448.42	0-1	32468.86	0-0	32491.76
0-3	32414.22	0-3	32430.84	0-2	32449.26	0-1	32469.7	0-0	32492.29
0-3	32414.75	0-3	32431.89	0-2	32450	0-1	32470.44	0-0	32493.03
0-3	32415.8	0-3	32432.63	0-2	32451.05	0-1	32471.28	0-0	32493.98
0-3	32416.33	0-3	32434.52	0-2	32451.89	0-1	32472.02	0-0	32495.14
0-3	32417.06	0-3	32435.15	0-2	32452.31	0-1	32472.66	0-0	32495.45
0-3	32417.8	0-3	32435.99	0-2	32453.16	0-1	32473.5	0-0	32495.88
0-3	32418.01	0-2	32436.52	0-2	32454.1	0-1	32474.98	0-0	32496.62
0-3	32418.74	0-2	32437.26	0-2	32455.16	0-1	32475.5	0-0	32496.93
0-3	32419.16	0-2	32437.99	0-2	32456	0-1	32476.45	0-0	32498.2
0-3	32419.48	0-2	32438.73	0-2	32457.16	0-1	32477.3	0-0	32498.62
0-3	32420.95	0-2	32439.15	0-2	32458.21	0-1	32478.14	0-0	32499.79
0-3	32421.27	0-2	32440.2	0-2	32458.95	0-1	32479.2	0-0	32500.42
0-3	32421.58	0-2	32441.36	0-2	32459.9	0-1	32480.15	0-0	32501.79
0-3	32422.11	0-2	32441.99	0-2	32461.16	0-1	32481.2		
0-3	32423.16	0-2	32442.62	0-2	32462.11	0-1	32482.15		
0-3	32424.11	0-2	32443.26	0-2	32462.53	0-1	32483.1		
0-3	32424.42	0-2	32443.68	0-1	32463.8	0-1	32485.74		
0-3	32425.05	0-2	32444.52	0-1	32464.75	0-1	32487.96		

For our observed transitions from higher vibrational levels of upper state (1-0, 2-0), these distances do not increase substantially, due to the fact that the first rotational constant of the upper state does not change significantly at the lower part of the potential curve, where the curve is close to harmonic. As one can not experimentally resolve the edging and origin of bands from the fluorescence spectrum, it should be expected some systematic errors in vibrational constants below [4].

Vibrational constants were determined by the least-squares fitting to the measured frequencies by using Eq.(1) from [8]:

$$\nu_{v'v''} = T_e + \sum_{j=1}^{m} c'_j (v' + \tfrac{1}{2})^j - \sum_{j=1}^{m} c''_j (v' + \tfrac{1}{2})^j , \qquad (1)$$

here, $\nu_{v'v''}$ are measured edging frequencies of vibrational bands, T_e is electron energy, v' and v'' are

Table 2. Frequencies of the measured edgings for electron-vibrational transitions of the molecule $^{124}Xe^{35}Cl$.

Transition	ν, cm^{-1}	Transition	ν, cm^{-1}
0-0	32490.8	1-0	32686.5
0-1	32463.7	1-1	32659.3
0-2	32437.0	1-4	32581.4
0-3	32410.4	1-5	32556.1
0-4	32384.9	1-6	32534.1
0-5	32360.9	2-0	32879.8
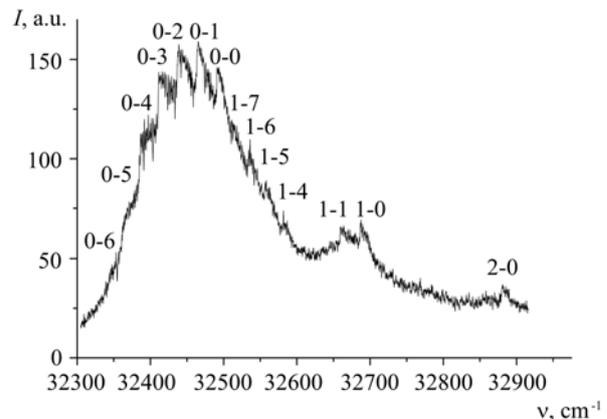
Fig. 3. Spontaneous emission spectrum of $^{124}Xe^{35}Cl$ molecule. Upper figures denote the electron-vibration transitions.

vibrational numbers for upper (B) and lower (X) electronic states, respectively, c'_j and c''_j are vibrational constants for upper and lower states, respectively.

We have got the least squares sum for deviations of measured frequencies from the calculated ones using the obtained constants for $m = 2$ and $n = 3$, but, for $n = 3$, for the lower state, the second and the third unharmonicity constants (c''_2 and c''_3) are very sensitive to the measurement errors. When varying ν_{0-5} over 0.1 cm^{-1} c''_2 varies by 65%, while c''_3 varies more than 10%. This fact resulted from the restricted number of measured bands. Therefore, to determine vibrational constants, we restricted ourselves by a square polynomial when approximating the lower state in Eq. (1).

The resulting vibrational constants for the molecule $^{124}Xe^{35}Cl$ are shown in the column (a) of Table 3. Although the distance between vibrational levels decreases while v″ increases, c''_2 constant is negative, and the decrease of the distance is accounted for the constant c''_3, in accordance with [4, 8, 9]. In our case when vibrational levels of the lower state are described by the square polynomial for the approximation, the decrease of distance is accounted for the constant c''_2.

The mean-square deviation of measured frequencies from those using the constants of Table 1 (a) is 0.12 cm^{-1}.

Column (b) Table 3 shows vibrational constants for the molecule $^{124}Xe^{35}Cl$ obtained by recalculation of data from [4] for the molecule $^{136}Xe^{35}Cl$ by using Eq. (2):

$$^{124}c_n = {}^{136}c_n \cdot \left(\sqrt{\frac{M_1}{M_2}}\right)^n \qquad (2)$$

where $^{124}c_n$ and $^{136}c_n$ are the vibrational constants for the molecules $^{124}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$, respectively, M_1 and M_2 are the reduced masses of the molecules $^{136}Xe^{35}Cl$ and $^{124}Xe^{35}Cl$, respectively.
The mean-square deviation of the measured frequencies from those calculated using Table 1(b) is 0.1 cm^{-1}.

Table 3. Vibrational constants for molecule $^{124}Xe^{35}Cl$ resulted from fitting Eq.(1) to the measured frequencies (column a) and recalculating the data from [4] (column b).

	a	b
ΔT_e	32405.6	32405.8
c'_1	199.26	196.67
c'_2	−1.6	−0.63
c''_1	28.34	26.48
c''_2	−0.39	0.32
c''_3		−0.086
c''_4		−0.00193

4. Conclusions

The frequencies of lasing spectra lines for the monoisotopic molecule $^{124}Xe^{35}Cl$ are measured.

We have shown that when superimposing the lasing spectra of XeCl for different isotope compositions one can get better overlapping the spectral range with lasing lines. Therefore, using laser mixtures with different Xe isotopes one can expect more smooth frequency tuning within the lasing range.

The edging frequencies for 12 electron-vibrational bands for $B \rightarrow X$ transition of the molecule $^{124}Xe^{35}Cl$ are measured, and vibrational constants for this molecule are calculated.

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