Semiconductor Physics, Quantum Electronics & Optoelectronics, 2009. V. 12, N 1. P. 17-22.

PACS 33.20.Lg, 42.55.Lt, 42.62.Fi

Influence of the isotopic composition on emission spectra of XeCl molecules

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Abstract. A mechanism of the origin of the fine structure inherent to XeCl molecules is computer simulated. The wavelengths of the fine structure in the lasing spectra for single isotope molecules $^{129}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$ are presented. The edges of electron-oscillating bands of the molecules $^{124}Xe^{35}Cl$, $^{129}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$ are characterized and some principle constants of XeCl molecule are determined.

Keywords: excimer laser, isotopic composition, emission spectra, fine structure.

Manuscript received 23.10.08; accepted for publication 18.12.08;

1. Introduction

It is well-known that the most of the excimer emission spectra molecules of noble gas halides display the wide structure less broad bands resulted in bound-free transitions from excited to the base (dissociable) state. However, some of them (e.g. XeCl) are typical to create a weak chemical bond in the base state, which causes the more or less defined structure of emission spectrum. For the first time, the fine structure of the lasing spectrum XeCl for the laser with electron beam pumping under the total pressure 0.6 atm was reported in [1]. The possible origins of the fine structure in the lasing spectrum were discussed in [2-4]. The main origin of the fine structure in the lasing spectrum of XeCl is appearance of a rotational structure of the molecule, and it was reported in [5]. The influence of isotopic composition of the operating gas mixture in a XeCl laser on the fine structure in the spectrum was investigated in [6]. It was shown that varying the mixture composition one could achieve denser filling of spectral lasing range with lasing lines, and in some cases the spectrum became continuous. To ascertain the origin of this fine structure and its behaviour under lasing conditions is important for both fundamental and applied researches. This paper concerns the influence of isotopic mixture composition on lasing spectra of the XeCl molecule based on the computer simulation. The emission frequencies for the fine structure in experimental lasing spectra of single isotopic molecules $^{129}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$ are characterized. The frequencies of edges for bands of electron-oscillation transitions for molecules $^{124}Xe^{35}Cl$, $^{129}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$ are also characterized and some fundamental oscillation constants of some single isotopic molecules are concurrently computed from the experimental spectroscopic data by using the least-squares method.

2. Equipment and experiments

We used an electric discharge laser with self-preionization. The dimensions of discharge chamber were 30×1.8×0.8 cm. The inter-electrode distance was 1.8 cm. The optical resonator consisted of two external dielectric mirrors. The reflectivity for output mirror varied between 55 to 97 %. The rear mirror reflection R was close to 100 %. Windows of the discharge chamber were parallel-sided plates from fused quartz KU-1 type with the thickness $d = 8$ mm. To characterize spontaneous emission spectra, we used the same laser discharge chamber without external mirrors, and the windows of chamber were declined at a small angle (3° to 4°). Freon-12 (CF_2Cl_2) and tetrachloride (CCl_4) were used as chlorine donors.

The emission spectra were recorded using the X-ray film of the RF type with DFS-8 spectrograph. We used a diffraction grid 1800 groove/mm in the second order of diffraction; the reciprocal linear dispersion was 0.87 Å/mm. We used an iron lamp with the hollow cathode to identify wavelengths [7]. Frequencies were characterized by computer image processing of scanned films. The iron lines playback accuracy was close to 0.005 Å.

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					
^{129}Xe	–	–	–	99.9	–	< 0.1	< 0.1	–	–
^{136}Xe	–	–	–	–	–	–	0.1		99.9

Freon-12 was of the following composition: $CF_2{}^{35}Cl_2$ – 99.7 %, $CF_2{}^{37}Cl_2$ – 0.3 %.

3. Computer simulation

Our computer model is based on the algorithms described in [8, 9]. This model takes into account only bound-bound transitions. We use spectral constants of $^{136}Xe^{35}Cl$ from [8] to calculate these constants for an investigated isotope. Then positions of the rotational frequencies for each of electron-oscillation transition and each rotational frequency were defined by the Lorenz curve with the associated half-height width. The final spectrum resulted from summation of intensities for each rotational transition in the overall spectral range. The population of molecules between the rotational levels for the specified temperature of gas discharge was also taken into account. Issuing from the efficiency and consumed power of our laser, gas temperature in the discharge for our experiments was estimated as 400 to 700 K.

Fig. 1 shows the computed and experimental emission spectra of $^{136}Xe^{35}Cl$ molecule. Numbers of the electron-oscillational transition are shown above. Lasing spectra were recorded under the total pressure of the mixture 0.5 atm. The half-height width of the Lorenz curve for each rotational transition was 0.4 cm^{-1}.

Fig. 2 shows the appearance of the fine structure in the spectral range 0-3 of the electron-oscillational transition. Points display rotational frequencies for different electron-oscillational transitions. Four rotational branches of 0-3 transition and rotational frequencies of 0-4 and 0-5 transitions imposed on the 0-3 transition are shown. The lines of the fine structure appear in the ranges with the higher density of rotational frequencies in electron-rotational transitions.

This model was used for simulation of the influence of the isotopic composition on the fine structure of the emission spectra for the molecule XeCl. Fig. 3 shows the isotopic shift of the rotational frequencies and variations of the spectrum fine structure after substitution the molecule $^{136}Xe^{35}Cl$ (solid line in the spectrum and filled circles) by the molecule $^{124}Xe^{35}Cl$ (dashed line in the spectrum and clear circles). In the figure, arrows display the isotopic shift for some rotational frequencies. The large mass of the molecule XeCl leads to a rather small isotopic shift, even if the heaviest isotope Xe (136) substitutes the lightest Xe (124). The high density of frequencies also resulted from the high molecular mass. However, the value of isotopic shifts is almost the same as difference between frequencies forming the fine structure. As a result, the relative structure of the rotational frequencies varies as the isotopic composition. This fact causes significant variations in the fine structure of the spectrum and the appearance of new lasing lines.

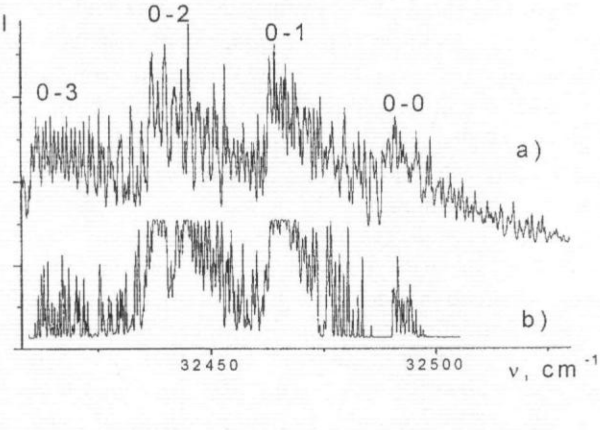

Fig. 1. Computed luminescence spectrum (a) and experimental lasing (b) of $^{136}Xe^{35}Cl$.

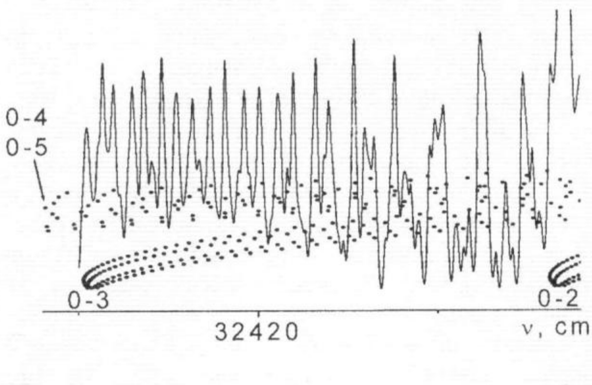

Fig. 2. A part of the computed spectrum and Fortr diagrams for 0–3 electron-oscillational transition of the molecule $^{136}Xe^{35}Cl$.

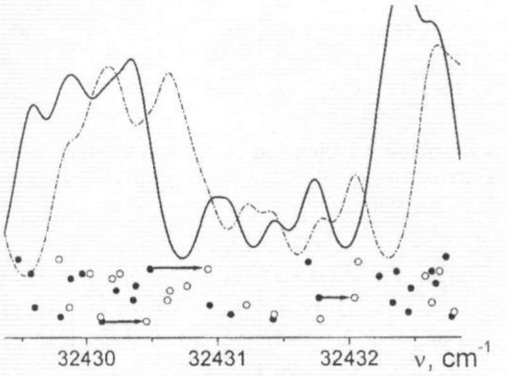

Fig. 3. A part of the spectrum of 0-3 transition and the rotational frequencies for the molecules $^{136}Xe^{35}Cl$ and $^{124}Xe^{35}Cl$.

We estimated the value of the collisional line broadening factor for the XeCl molecule basing on the fact that the density of visible lines in the fine structure of experimental and simulated spectra in the fixed spectral range weakly depend on the isotopic composition of the molecule (it only shifts the position of the fine structure), but strongly depends only on the total pressure of the work mixture (or the width of the Lorenz curve for a simulated spectrum). The width of the Lorenz curve in simulated spectra for different isotopes was fitted to obtain the same number of lines in the fixed range on the fine structure as in the experimental spectra. The obtained line width dependence on the pressure for the separated rotational transition is shown in Fig. 4.

The dependence in Fig. 4 could be expressed by the following expression:

$$\Delta\nu(p) = 0.23 + 0.48 \cdot p, \tag{1}$$

where $\Delta\nu$ is the half-height width of the lasing line for the separated electron-oscillational transition in cm^{-1}, p – pressure of the operating mixture in atmospheres.

Fig. 5 shows the simulated luminescence spectra of $^{136}Xe^{35}Cl$ with the fixed Lorenz curve half-height width 0.67 cm^{-1} (a) and 0.4 cm^{-1} (b), which simulate operation pressures 3 and 5 atm in the dependence (1). The numbers for electron-oscillational transitions are shown above.

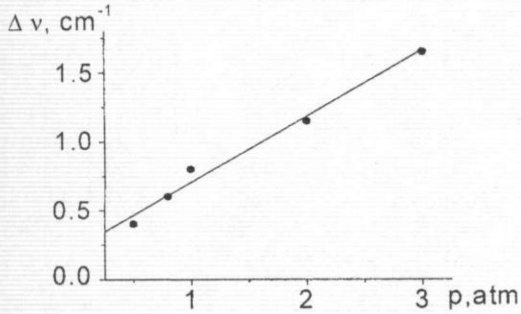

Fig. 4. Line width dependence on the pressure for the separated rotational transition of the single isotopic molecule XeCl.

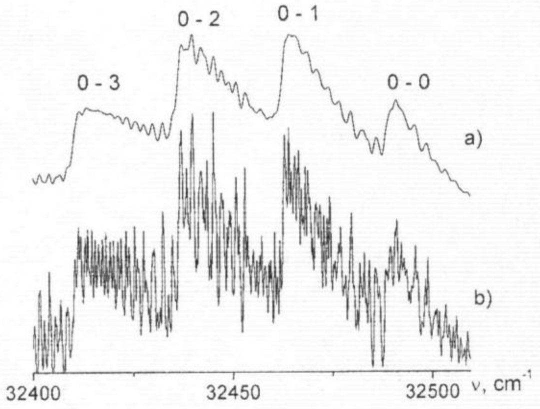

Fig. 5. Luminescence spectra of the molecule $^{136}Xe^{35}Cl$ calculated for different half-height width of the Lorenz curve for the separated electron-oscillational-rotational transition: a) 1.67 cm^{-1}, b) 0.4 cm^{-1}.

4. Experimental research

4.1. Lasing spectra

We should point out that our analysis is only qualitative because of the usage of the rotational constants for the molecule $^{136}Xe^{35}Cl$ obtained by approximate methods from positions of fine structure lines [8] and are not real. Variation of the isotopic composition in the operation mixture causes appearance of new lasing lines, and the position of these lines could not be calculated. That is why the frequencies of the fine structure lasing lines for the molecule XeCl with different isotopic compositions were characterized in our experiments. Frequencies for the fine structure lines for the molecule $^{124}Xe^{35}Cl$ under the pressure 0.5 atm were reported in [6].

Figs 6 and 7 show lasing spectra for the molecules $^{129}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$ registered under the pressure of the operation mixture 0.5 atm. Lines of the fine structure numbered from the left to the right. Each tenth line is marked by the vertical dash. The emission wavelengths in air and the frequencies of the fine structure spectra are shown in Figs 6 and 7 and listed in Tables 1 and 2.

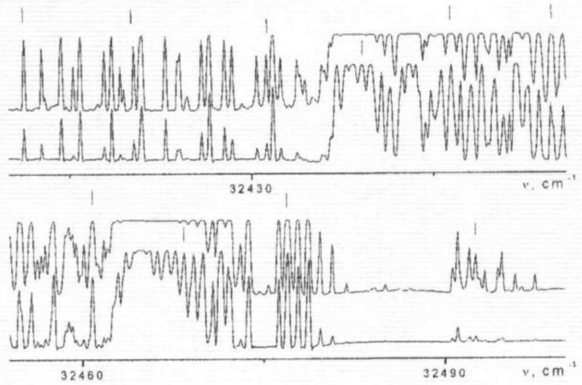

Fig. 6. Lasing spectrum for the molecule $^{129}Xe^{35}Cl$.

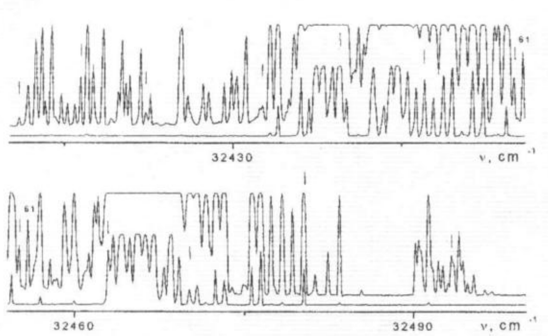

Fig. 7. Lasing spectrum for the molecule $^{136}Xe^{35}Cl$.

Table 1. Emission wavelengths in air and the frequencies of the fine structure spectra for the lasing spectrum of the molecule $^{129}Xe^{35}Cl$.

Line #	λ, Å	ν, cm^{-1}	Line #	λ, Å	ν, cm^{-1}
1	3084.45	32411.28	49	3080.41	32453.79
2	3084.31	32412.75	50	3080.32	32454.74
3	3084.16	32414.33	51	3080.22	32455.79
4	3084.07	32415.27	52	3080.17	32456.32
5	3084.01	32415.91	53	3080.14	32456.63
6	3083.82	32417.9	54	3080.11	32456.95
7	3083.76	32418.53	55	3080.05	32457.58
8	3083.7	32419.16	56	3079.93	32458.84
9	3083.67	32419.48	57	3079.9	32459.16
10	3083.59	32420.32	58	3079.87	32459.48
11	3083.53	32420.95	59	3079.81	32460.11
12	3083.34	32422.95	60	3079.74	32460.85
13	3083.24	32424	61	3079.65	32461.8
14	3083.17	32424.74	62	3079.54	32462.96
15	3083.06	32425.89	63	3079.48	32463.59
16	3083	32426.52	64	3079.42	32464.22
17	3082.88	32427.79	65	3079.36	32464.85
18	3082.82	32428.42	66	3079.29	32465.59
19	3082.62	32430.52	67	3079.23	32466.22
20	3082.55	32431.26	68	3079.16	32466.96
21	3082.5	32431.78	69	3079.09	32467.7
22	3082.44	32432.42	70	3079.03	32468.33
23	3082.31	32433.78	71	3078.95	32469.18
24	3082.25	32434.41	72	3078.88	32469.91
25	3082.12	32435.78	73	3078.8	32470.76
26	3082.05	32436.52	74	3078.74	32471.39
27	3082	32437.05	75	3078.68	32472.02
28	3081.92	32437.89	76	3078.58	32473.08
29	3081.87	32438.41	77	3078.52	32473.71
30	3081.8	32439.15	78	3078.36	32475.4
31	3081.73	32439.89	79	3078.28	32476.24
32	3081.65	32440.73	80	3078.21	32476.98
33	3081.58	32441.47	81	3078.13	32477.83
34	3081.48	32442.52	82	3078.05	32478.67
35	3081.43	32443.05	83	3077.96	32479.62
36	3081.38	32443.57	84	3077.86	32480.67
37	3081.3	32444.41	85	3077.75	32481.83
38	3081.26	32444.83	86	3077.44	32485.11
39	3081.18	32445.68	87	3076.92	32490.6
40	3081.1	32446.52	88	3076.88	32491.02
41	3081.03	32447.26	89	3076.79	32491.97
42	3080.95	32448.1	90	3076.74	32492.5
43	3080.86	32449.05	91	3076.67	32493.24
44	3080.76	32450.1	92	3076.56	32494.4

45	3080.69	32450.84	93	3076.53	32494.72
46	3080.65	32451.26	94	3076.43	32495.77
47	3080.59	32451.89	95	3076.38	32496.3
48	3080.5	32452.84	96	3076.27	32497.46

Table 2. Emission wavelengths in air and the frequencies of the fine structure spectra for the lasing spectrum of the molecule $^{136}Xe^{35}Cl$.

Line #	λ, Å	ν, cm^{-1}	Line #	λ, Å	ν, cm^{-1}
1	3084.48	32410.97	54	3080.73	32450.42
2	3084.41	32411.7	55	3080.64	32451.36
3	3084.34	32412.44	56	3080.55	32452.31
4	3084.29	32412.96	57	3080.46	32453.26
5	3084.26	32413.28	58	3080.42	32453.68
6	3084.21	32413.8	59	3080.36	32454.31
7	3084.13	32414.64	60	3080.29	32455.05
8	3084.07	32415.27	61	3080.22	32455.79
9	3084.01	32415.91	62	3080.11	32456.95
10	3083.96	32416.43	63	3080.03	32457.79
11	3083.91	32416.96	64	3079.99	32458.21
12	3083.85	32417.59	65	3079.9	32459.16
13	3083.77	32418.43	66	3079.82	32460
14	3083.7	32419.16	67	3079.7	32461.27
15	3083.64	32419.79	68	3079.65	32461.8
16	3083.61	32420.11	69	3079.62	32462.11
17	3083.57	32420.53	70	3079.53	32463.06
18	3083.54	32420.85	71	3079.5	32463.38
19	3083.45	32421.79	72	3079.43	32464.11
20	3083.41	32422.21	73	3079.36	32464.85
21	3083.37	32422.63	74	3079.29	32465.59
22	3083.11	32425.37	75	3079.23	32466.22
23	3083.05	32426	76	3079.16	32466.96
24	3082.92	32427.37	77	3079.07	32467.91
25	3082.88	32427.79	78	3079.02	32468.44
26	3082.75	32429.15	79	3078.94	32469.28
27	3082.69	32429.79	80	3078.86	32470.12
28	3082.64	32430.31	81	3078.79	32470.86
29	3082.56	32431.15	82	3078.72	32471.6
30	3082.42	32432.63	83	3078.64	32472.45
31	3082.36	32433.26	84	3078.57	32473.18
32	3082.29	32433.99	85	3078.34	32475.61
33	3082.2	32434.94	86	3078.26	32476.45
34	3082.16	32435.36	87	3078.17	32477.4
35	3082.1	32435.99	88	3078.08	32478.35
36	3082.03	32436.73	89	3078	32479.2
37	3081.97	32437.36	90	3077.9	32480.25
38	3081.91	32437.99	91	3077.8	32481.31
39	3081.83	32438.83	92	3077.7	32482.36
40	3081.77	32439.47	93	3077.6	32483.42
41	3081.71	32440.1	94	3077.42	32485.32
42	3081.61	32441.15	95	3076.96	32490.17
43	3081.57	32441.57	96	3076.93	32490.49
44	3081.49	32442.41	97	3076.85	32491.34
45	3081.39	32443.47	98	3076.77	32492.18
46	3081.33	32444.1	99	3076.73	32492.6
47	3081.28	32444.62	100	3076.66	32493.34
48	3081.19	32445.57	101	3076.6	32493.98
49	3081.12	32446.31	102	3076.56	32494.4
50	3081.05	32447.05	103	3076.52	32494.82
51	3080.97	32447.89	104	3076.47	32495.35
52	3080.89	32448.73	105	3076.38	32496.3
53	3080.82	32449.47	106	3076.32	32496.93

The playback accuracy for the values of the line wavelengths in the fine structure inherent to the same isotope under the same pressure is close to 0.009 Å.

4.2. Spontaneous emission spectra

For the first time, the oscillation constants for the single isotope molecule $^{136}Xe^{35}Cl$ were obtained in [8]. The overlapping of rotational branches for different electro-oscillational transitions causes blurring the edges of the oscillational transitions bands. This fact leads to slowing down the accuracy in the edge position. In this paper, we get oscillational constants for the molecule XeCl by the analysis of spontaneous emission spectra for some single isotopic molecules concurrently.

Table 3 listed frequencies for the edges of electron-oscillational transition bands for the molecules $^{124}Xe^{35}Cl$, $^{129}Xe^{35}Cl$ and $^{136}Xe^{35}Cl$.

Table 3. Frequencies of the edges inherent to electron-oscillational bands in spontaneous emission spectra of the molecules $^{136}Xe^{35}Cl$ (a), $^{129}Xe^{35}Cl$ (b) and $^{124}Xe^{35}Cl$ (c).

a		b		c	
Transition	ν, cm^{-1}	Transition	ν, cm^{-1}	Transition	ν, cm^{-1}
0-0	32490.2	0-0	32490.54	0-0	32490.8
0-1	32463.1	0-1	32463.57	0-1	32463.7
0-2	32436.8	0-2	32436.94	0-2	32437.0
0-3	32411.0	0-3	32410.7	0-3	32410.4
0-4	32386.0	0-4	32385.5	0-4	32384.9
0-5	32360.9	0-5	32361.1	0-5	32360.9
1-0	32683.6	1-0	32684.68	1-0	32686.5
1-1	32656.8	1-1	32657.85	1-1	32659.3
1-4	32579.3	1-4	32579.78	1-4	32581.4
1-5	32554.6	1-5	32556.08	1-5	32556.1
1-6	32532.5	1-6	32533	1-6	32534.1
2-0	32875.6	2-0	32878.02	2-0	32879.8

The mean-square deviation for our data and the frequencies edges data for the molecule $^{136}Xe^{35}Cl$ from [8] are close to 0.2 cm^{-1}.

We obtain the oscillational constants by using the least-squares method fitting to the measured data on frequency edges of three molecules concurrently from the expression

$$k_{V_{v'v''}} = \Delta T_e + \sum_{j=1}^{m} (\rho_k^j)^{136} c'_j \cdot (v' + 1/2)^j - \sum_{j=1}^{n} (\rho_k^j)^{136} c''_j \cdot (v'' + 1/2)^i, \tag{2}$$

where k – Xe isotope mass (124. 129 or 136), $^{136}c'_j$ – j-th constant for the molecule $^{136}Xe^{35}Cl$, ρ_k – square root of the ratio of reduced masses for the molecules $^{136}Xe^{35}Cl$ and $^{k}Xe^{35}Cl$. For the molecule $^{136}Xe^{3}Cl$ ρ_k equals to 1.

The calculated, in this way, oscillational constants for the molecule $^{136}Xe^{35}Cl$ are listed in Table 4.

Table 4. Oscillational constants for the molecule $^{136}Xe^{35}Cl$ obtained by the least-squares method fitting to the experimental spectral data for three single isotopic molecules concurrently.

Constant	Value, cm^{-1}
ΔT_e	32405.8
c'_1	195.3
c'_2	–0.86
c''_1	26.5
c''_2	0.18
c''_3	–0.056

5. Conclusion

The fine structure in lasing spectra of the XeCl molecule (transition $B^2\Sigma^+_{1/2} \to X^2\Sigma^+_{1/2}$) is determined by the molecule rotation and complicated by the presence of several isotopes of Xe and two isotopes of Cl.

The obtained collisional line broadening for the XeCl molecule from our simulation and experimental researches equals 0.48 cm^{-1}/atm, which is rather differs from the earlier data (see e.g. [9]).

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