DEREMINATION OF POTENTIAL FUNCTION OF AsH$_3$ MOLECULE
ON THE BASIS OF EXPERIMENTAL DATA

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The problem of determination of intramolecular potential function of a molecule of symmetric gyroscope type is considered on the example of arsine molecule AsH$_3$. To solve the given problem the software package in the analytical language MAPLE has been developed. It allows to connent parameters of potential function set through symmetric, natural (invariantrelatively to isotope substitution) and/or normal oscillatory coordinates.

The internal dynamic of a molecule is known to be defined by intramolecular potential function [1]. Therefore, the important condition for understanding the processes taking place in a molecule is to obtain reliable information about it. In this case the interest in qualitative determination of potential function parameters of a molecule is quite understandable.

It should be noted that similar problems have been solved in spectroscopy over some decades. There are two main approaches to solve it. They are application of *ab initio* methods, however the accuracy of such calculations is of 4–5 orders lower than experimental accuracy in determination of those values observed that can be obtained on the basis of information on intramolecular potential function. Another approach is semiempirical methods based on using experimental information about molecular spectra of high resolution of infrared and microwave ranges. As opposed to *ab initio* methods, semiempirical methods provide the information on potential surface parameters with sufficiently higher accuracy.

As for arsine molecule and its potential function in particular, the interest was aroused by several reasons. On the one hand, the study of arsine spectra is important for applied problems of astrophysics, as they are found in the atmospheres of Saturn and Jupiter. [2]. On the other hand, such objects are interesting just from theoretical point of view, as all of them are light pyramidal molecules. Hence, in their vibration-rotation spectra all possible effects and features that could be present in the spectra of other molecules of such type are mostly pronounced. The additional interest in investigation of these molecule spectra was provoked by the fact that they satisfy the so called approximation of local modes [3].

Note that potential function AsH$_3$ was determined only by *ab initio* methods [4], or some parameters (connected with valent oscillations) were determined on the basis of experimental information in the local mode model [5]. Therefore determination of parameters of arsine potential function on the basis of experimental data is an urgent problem nowadays.

In the given work the analysis of centres of vibration-rotation of AsH$_3$ molecules bands has been made, and on this basis the quadratic force parameters of arsine as well as oscillation parameters of anharmonicity and resonance constant permitting to reproduce and predict the centres of vibration-rotation bands with high accuracy have been estimated. The estimations were made on the basis of both experimental information from the literature [6–8], and on that of our data published in the work [9].

It is well known [10], that all spectroscopic parameters of a molecule are parameter functions of molecule equilibrium configuration $r^e_{N\alpha}$ and oscillation form constant $l_{N\alpha\lambda}$. Thus, it becomes clear that the accuracy of all further calculations depends on the accuracy of their determination. That is why on the first stage we determined nuclei equilibrium coordinates and oscillation form constant of AsH$_3$ molecule knowing the equilibrium bond distance r^e and equilibrium angle α^e with high accuracy.

The conditions of coincidence of molecular points of origin with nuclei mass centre of molecule were defined first, the conditions of coincidence of molecular axes with inertia principal axes

$$\sum_N m_N r^e_{N\alpha} = 0, \quad \sum_N m_N r^e_{N\alpha} r^e_{N\beta} = 0, \ \alpha \neq \beta, \quad (1)$$

where N=1, 2, 3, 4 – The number of nuclei in a molecule, AsH$_3$, m_N – mass of a corresponding nucleus, $r^e_{N\alpha}$ – value of nuclei equilibrium coordinates. Notice that for solution simplification of the given equations one should use the properties of molecular symmetry. The solution of combined equations (1) produces

$$r^e_{1x} = r^e \sqrt{\frac{2}{3}(1-\cos\alpha^e)}, \ r^e_{2x} = r^e_{3x} = -r^e\sqrt{\frac{(1-\cos\alpha^e)}{6}}, \ r^e_{4x} = 0;$$

$$r^e_{1y} = 0, \quad r^e_{2y} = -r^e_{3y} = -r^e\sqrt{\frac{(1-\cos\alpha^e)}{2}}, \quad r^e_{4y} = 0;$$

$$r^e_{1z} = r^e_{2z} = r^e_{3z} = -\frac{r^e}{1+\frac{3m_H}{M}}\sqrt{\frac{(1+2\cos\alpha^e)}{3}},$$

$$r^e_{4z} = \frac{r^e}{1+\frac{M}{3m_H}}\sqrt{\frac{(1+2\cos\alpha^e)}{3}},$$

where r^e=1,51101 Å – value of equilibrium bond distance, α^e=92,0690° – equilibrium angle between the bonds [9], m_H, M – masses of hydrogen and arsine nuclei correspondingly.

Knowing the equilibrium nuclei coordinates, then one can find constants of oscillation forms of AsH$_3$ molecule. Notice that from the analysis of only symmetrical molecular properties one can express all $3N(3N-6)=72$ parameters $l_{N\alpha\lambda}$ through 12 constants of oscillation forms. For symmetrical oscillations ($\lambda=1, 2$)

$$l_{3x\lambda} = -l_{3x\lambda} = -\sqrt{3}\,l_{2x\lambda} = -\sqrt{3}\,l_{3x\lambda} = \frac{\sqrt{3}}{2}l_{1x\lambda} = \frac{l_\lambda^{(1)}}{2},$$

$$l_{4x\lambda} = l_{4y\lambda} = l_{1y\lambda} = 0, \quad l_{4z\lambda} = -3\sqrt{\frac{m}{M}}\,l_\lambda^{(2)},$$

$$l_{1z\lambda} = l_{2z\lambda} = l_{3z\lambda} = l_\lambda^{(2)};$$

for doubly disintegrate oscillations ($\lambda=3, 4; s=1, 2$)

$$l_{4x\lambda_2} = l_{1x\lambda_2} = 0, \quad l_{2x\lambda_2} = -l_{3x\lambda_2} = \sqrt{\frac{1}{3}}(l_{1x\lambda_1} - l_{2x\lambda_1}),$$

$$l_{3x\lambda_1} = l_{2x\lambda_1}, \quad l_{4x\lambda_1} = l_{4y\lambda_2} = -\sqrt{\frac{m}{M}}(l_{1x\lambda_1} - l_{2x\lambda_1}),$$

$$3l_{1y\lambda_2} = 4l_{2x\lambda_1} - l_{1x\lambda_1}, \quad \sqrt{3}\,l_{2y\lambda_1} = -\sqrt{3}\,l_{3y\lambda_1}l_{1x\lambda_1} - l_{2x\lambda_1},$$

$$l_{4y\lambda_1} = l_{1y\lambda_1} = 0, \quad 3l_{2y\lambda_1} = 3l_{3y\lambda_2} = 2l_{1x\lambda_1} - l_{2x\lambda_1},$$

$$l_{4z\lambda_2} = l_{4z\lambda_1} = l_{1z\lambda_2} = 0,$$

$$2l_{2z\lambda_1} = 2l_{3z\lambda_1} = 2l_{2z\lambda_2} = -2l_{3z\lambda_2} = -\sqrt{3}\,l_{1z\lambda_1}.$$

For the determination of the latter the system from 12 equations was used obtained from 6 conditions of orthogonality

$$\sum_{N\alpha} l_{N\alpha\lambda}l_{N\alpha\mu} = \delta_{\lambda\mu}, \qquad (2)$$

the first two and the second two Ekkart conditions for doubly disintegrate oscillations

$$\sum_N m_N^{1/2} l_{N\alpha\lambda} = 0, \qquad (3)$$

$$\sum_N m_N^{1/2}(l_{N\alpha\lambda}\,r_{N\beta}^e - l_{N\beta\lambda}\,r_{N\alpha}^e) = 0. \qquad (4)$$

The left parts of these 10 equations present functions from constants of oscillation forms, all coefficients of which are defined in numerical form, but the right parts are equal to 0 or 1. The two missing equations were taken from the cross conditions for the second derivatives from potential function

$$\left(\frac{\partial^2 V}{\partial Q_\lambda \partial Q_\mu}\right)_{Q=0} = 0, \quad \lambda \neq \mu.$$

The left parts of these equations present linear combinations from constants of oscillation forms, that are necessary to define, as well as six quadratic force constants, the latter were taken from [4], but the right parts are equal to zero. Thus, the system of 12 equations was obtained by using the programmes developed in analytical programming language MAPLE. To solve this nonlinear system in numerical form the programme in programming language FORTRAN permitting to solve the given equation system by the method of numerical dif-

ferentiation was created. The constants of oscillation forms obtained as a result of it are presented in table 1.

Table 1. *Nonzero constants of oscillation forms of AsH$_3$ molecule*

$l_{N\alpha\lambda}$	Value	$l_{N\alpha\lambda}$	Value	$l_{N\alpha\lambda}$	Value	$l_{N\alpha\lambda}$	Value
l_{1x1}	0,49427	l_{1z2}	−0,48459	l_{2y31}	0,29956	l_{3z41}	0,16554
l_{1x2}	−0,29837	l_{2x31}	0,16067	l_{2y41}	−0,40033	l_{4x31}	−0,11608
l_{1z1}	−0,29252	l_{2x41}	0,48077	l_{3z31}	0,22123	l_{4x41}	−0,08686

The found in the given stage constants of oscillation forms allow to restore the harmonic frequencies with high accuracy. Hence, all the parameters, such as r^e, α^e, m_N, F_{ij}, $l_{N\alpha\lambda}$ one can use as a zero approximation for further calculations to determine the potential function of arsine. The results of calculations and harmonic frequencies from [4] are shown in table 2.

Table 2. *Harmonic frequencies of AsH$_3$ molecule*

ω_λ	Our results, см$^{-1}$	The results from [4], см$^{-1}$
ω_1	2189,98	2190
ω_2	924,01	924
ω_3	2201,94	2202
ω_4	1014,97	1015

The results obtained were used then to determine the quadratic part of the molecule potential function by means of solving inverse problem. In this case the potential function was taken in symmetrically adapted coordinates [11]:

$$V = V_0 + \frac{1}{2}\sum_{ij} F_{ij} S_i S_j + \frac{1}{6}\sum_{ijk} F_{ijk} S_i S_j S_k + \frac{1}{24}\sum_{ijkl} F_{ijkl} S_i S_j S_k S_l,$$

where F_{ij}, F_{ijk}, F_{ijkl} — force constants; S_i, S_j, S_k, S_l — symmetrical coordinates.

For arsine molecule the symmetrical coordinates are connected with natural coordinates describing the changes in valent bond distances and angels between them in the following way:

$$S_1(A_1) = \frac{r_{41} + r_{42} + r_{43}}{\sqrt{3}}, \quad S_2(A_1) = \frac{\alpha_1 + \alpha_2 + \alpha_3}{\sqrt{3}},$$

$$S_{3a}(E) = \frac{2r_{41} - r_{42} - r_{43}}{\sqrt{6}}, \quad S_{3b}(E) = \frac{r_{42} - r_{43}}{\sqrt{2}},$$

$$S_{4a}(E) = \frac{2\alpha_1 - \alpha_2 - \alpha_3}{\sqrt{6}}, \quad S_{4b}(E) = \frac{\alpha_2 - \alpha_3}{\sqrt{2}},$$

where α_i — change of the angle between r_j and r_k bond, r_{4i} — change of i-bond ($i, j, k=1, 2, 3$).

The quadratic part of potential function in symmetrical coordinates of a molecule of XY$_3$ type of C$_{3v}$ symmetry has the form:

$$V^{(2)} = \frac{1}{2}[F_{11}S_1^2 + F_{22}S_2^2 + 2F_{12}S_1S_2 + F_{33}(S_{3a}^2 + S_{3b}^2)] +$$

$$+ \frac{1}{2}[F_{44}(S_{4a}^2 + S_{4b}^2) + 2F_{34}(S_{3a}S_{4a} + S_{3b}S_{4b})].$$

It should be noted that using symmetrical coordinates in the theoretical formulas appears to be not very convenient, therefore it is important to be able to determine connections between parameters of potential function both in symmetrical coordinates and natural coordinates as using the natural coordinates is more effective in theoretical calculations. The process of transfer from potential function in symmetrical coordinates to potential function in natural coordinates is given, for example, in [12]. Despite the apparent simplicity of the formulas one should point out that realization of this transfer is rather a complex task as further calculations have an intricate form and to make them manually is practically impossible. Therefore we have developed the programmes in the language of analytical programming MAPLE to calculate the necessary analytical formulas by computer.

As a result of the transformations and calculations performed we obtained the quadratic part of potential function of the molecule in the form of linear combination of six quadratic force constants F_{11}, F_{22}, F_{12}, F_{33}, F_{44}, F_{34}, and determined the dependence of harmonic frequencies of the molecule on F_{ij} parameters. The coefficients at F_{ij} are rather complex functions of form oscillation constants of the molecule, atom mass, nuclei equilibrium coordinates. However, it should be mentioned that all these values were found (table 1). In other words, all the coefficients at F_{ij} can be defined in numerical form:

$$\omega_1 = (0,170\cdot10^7 F_{11} + 0,164\cdot10^4 F_{22} + 0,106\cdot10^6 F_{12})^{1/2},$$

$$\omega_2 = (0,453\cdot10^4 F_{11} + 0,147\cdot10^7 F_{22} - 0,163\cdot10^6 F_{12})^{1/2},$$

$$\omega_3 = (0,783\cdot10^2 F_{44} - 0,231\cdot10^5 F_{34} + 0,171\cdot10^7 F_{33})^{1/2}, \quad (5)$$

$$\omega_4 = (0,154\cdot10^7 F_{44} + 0,559\cdot10^5 F_{34} + 0,508\cdot10^3 F_{33})^{1/2}.$$

From the analysis of the equations (5) it follows that the force parameters F_{11} and F_{33} mostly contributed into frequencies ω_1 and ω_3 describing valent oscillations in AsH_3 molecule (as it could be expected) and force parameters F_{22} и F_{44} do into frequencies ω_2 and ω_4, as these oscillations are deformative.

In the first stage of determination of arsine molecule potential function we used the parameters of F_{ij} harmonic part obtained in the work [4] as an initial approximation. As experimental levels used in iterative procedure for determination of potential function parameters, anharmonic parameters of and we used information about 26 centres of bands investigated in the works [6–8] including 4 fundamental bands ν_1 (A_1), ν_2 (A_1), ν_3 (E) and ν_4 (E), all the first overtones $2\nu_1$ (A_1), $2\nu_2$ (A_1), $2\nu_3$ (A_1, E) and $2\nu_4$ (E) (6 bands), doubly exited combinational bands $\nu_2 + \nu_4$ (E) and $\nu_1 + \nu_3$ (E). Six and four threefold and fourfold exited bands, correspondingly, and also two states of five and six fold exited ones. In this case the numerical values of band centres obtained with experimental accuracy (it achieves 0,001...0,003 sm⁻¹ for different bands and different spectral ranges) permit us to determine the values of harmonic frequencies ω_λ, anharmonic constants $x_{\lambda\mu}$ and the most important parameters of resonance interactions correctly. The inverse problem was solved with the

help of Hamiltonian oscillatory matrix considering oscillatory resonance interactions of different types:

$$H^{vibr} = \sum_{\upsilon,\tilde{\upsilon}} |\upsilon\rangle\langle\tilde{\upsilon}| h_{\upsilon\tilde{\upsilon}}.$$

Here the summation is made in all investigated oscillatory states υ, $\tilde{\upsilon}$. Diagonal elements of the matrix have the form:

$$h_{\upsilon\upsilon} = \sum_\lambda \omega_\lambda\left(\upsilon_\lambda + \frac{d_\lambda}{2}\right) + \sum_{\lambda,\mu\geq\lambda} x_{\lambda\mu}\left(\upsilon_\lambda + \frac{d_\lambda}{2}\right)\left(\upsilon_\mu + \frac{d_\lambda}{2}\right) +$$

$$+ \sum_{\lambda,\mu\geq\lambda\nu\geq\mu} y_{\lambda\mu\nu}\left(\upsilon_\lambda + \frac{d_\lambda}{2}\right)\left(\upsilon_\mu + \frac{d_\lambda}{2}\right)\left(\upsilon_\nu + \frac{d_\lambda}{2}\right) + \sum_{\lambda\mu} g_{\lambda\mu}\, l_\lambda\, l_\mu,$$

where ω_λ — value of harmonic frequency; $x_{\lambda\mu}$ and $x_{\lambda\mu\nu}$ — anharmonic constants; $g_{ll'}$ — parameters responsible for splitting oscillatory terms with the same values of quantum number υ_λ, υ_μ, υ_ν; l_λ — oscillatory quantum numbers; d_λ=1 for nondegenerate oscillatory states and d_λ=2 for doubly degenerate states; $l_\lambda=-\upsilon_\lambda, -\upsilon_\lambda+2,...,\upsilon_\lambda-2,\upsilon_\lambda$.

As for nondiagonal matrix elements, their form depends on resonance type, which appears between corresponding oscillatory levels. Solving our problem it is important to take into account two types of resonance interactions. It is Darling-Dennison resonance that appeared between stretching vibrations, if $\Delta\upsilon=\pm2$ and $\Delta l=0$, in this case nondiagonal matrix elements have the following form:

$$h_{\upsilon\tilde{\upsilon}} = -\frac{k_{1133}}{4}[(\upsilon_1+1)(\upsilon_1+2)(\upsilon_3^2-l_3^2)]^{1/2},$$

if $|\upsilon\rangle=(\upsilon_1,...,\upsilon_3,...,l_3,...)$, and $|\tilde{\upsilon}\rangle=(\upsilon_1+2,...,\upsilon_3-2,...,l_3,...)$, i.e.

$$\Delta\upsilon_1 = -2, \quad \Delta\upsilon_3 = +2, \quad \Delta l_3 = 0 \qquad (6)$$

and

$$h_{\upsilon\tilde{\upsilon}} = -\frac{k_{1133}}{4}[\upsilon_1(\upsilon_1-1)((\upsilon_3+2)^2-l_3^2)]^{1/2},$$

,

if $|\upsilon\rangle=(\upsilon_1,...,\upsilon_3,...,l_3,...)$, and $|\tilde{\upsilon}\rangle=(\upsilon_1-2,...,\upsilon_3+2,...,l_3,...)$, i.e.

$$\Delta\upsilon_1 = +2, \quad \Delta\upsilon_3 = -2, \quad \Delta l_3 = 0. \qquad (7)$$

Here the parameter of quadratic part of potential function k_{1333} defines the main contribution of resonance interaction of Darling-Dennison type.

In the case of resonance that appeared between stretching vibrations, if $\Delta\upsilon=\pm1$ and $\Delta l=\pm3$, matrix elements have the following form:

$$h_{\upsilon\tilde{\upsilon}} = \pm\frac{3}{4}k_{1333}[\upsilon_1(\upsilon_3\mp l_3)(\upsilon_3\pm l_3+2)(\upsilon_3\pm l_3+4)]^{1/2},$$

if $|\upsilon\rangle=(\upsilon_1-1,...,\upsilon_3+1,...,l_3\pm3,...)$, and $|\tilde{\upsilon}\rangle=(\upsilon_1,...,\upsilon_3,...,l_3,...)$, i.e.

$$\Delta\upsilon_1 = +1, \quad \Delta\upsilon_3 = -1, \quad \Delta l_3 = \pm3. \qquad (8)$$

and $h_{\upsilon\tilde{\upsilon}} = \mp\frac{3}{4}k_{1333}[(\upsilon_1+1)(\upsilon_3\mp l_3)(\upsilon_3\pm l_3+2)(\upsilon_3\mp l_3-2)]^{1/2},$

if $|\upsilon\rangle=(\upsilon_1+1,...,\upsilon_3-1,...,l_3\pm3,...)$, and $|\tilde{\upsilon}\rangle=(\upsilon_1,...,\upsilon_3,...,l_3,...)$,, i.e.

$$\Delta\upsilon_1 = -1, \quad \Delta\upsilon_3 = +1, \quad \Delta l_3 = \pm3. \qquad (9)$$

Here the parameter of quadratic part of potential function k_{1133} defines the main contribution of resonance interaction of Fermi type.

The quantum numbers and not mentioned in the formulas (6)–(9) have the same value in wave functions $|\upsilon\rangle$ and $|\tilde{\upsilon}\rangle$.

As the result we obtained series of 15 parameters which are presented in column 2 of table 3 and in column 2 and 5 of table 4 with 1σ-confidence interval. The parameters obtained reproduce the experimental values of band centres used in fitting with d_{rms}=0,58 sm^{-1}. In columns 3 and 6 of table 4 the corresponding parameters calculated before with the help of *ab initio* methods [4] are given for comparison. To illustrate the correctness of the obtained results the values of band centres calculated with our parameters, taken from columns 2 and 5 of table 4 are presented in column 3 of table 5. The analysis of the data shows good agreement of experimental and calculated values of band centres. In column 2 of table 5 the values of the same band centres calculated with parameters taken from [4] are presented for comparison.

Table 3. *F_{ij} parameters obtained from experimental data*

Parameter	Our result	Work [4]
F_{11}, aJ·Å^{-2}	2,83771(279)	2,810
F_{12}, aJ·Å^{-1}	0,138*	0,138
F_{22}, aJ	0,58465(315)	0,588
F_{33}, aJ·Å^{-2}	2,88249(190)	2,839
F_{34}, aJ·Å^{-1}	−0,047*	−0,047
F_{44}, aJ	0,67200(257)	0,669
The number of experimental band centres		26
The number of variable parameters		14
rms		0,58 см$^{-1}$

*the value of the parameter is fixed to the value taken from [4]

Table 4. *Oscillatory spectroscopic parameters of AsH$_3$ molecule, sm^{-1}*

Para-meter	Our result	Result from [4]	Para-meter	Our result	Result from [4]
ω_1	2199,29572*	2190	x_{24}	−1,862(987)	0,03
ω_2	921,83883*	924	x_{33}	−20,033(182)	−16,38
ω_3	2218,45970*	2202	x_{34}	−9,46**	−9,46
ω_4	1017,04996*	1015	x_{44}	−2,106(612)	−2,42
x_{11}	−13,205(235)	−10,88	g_{33}	6,290(155)	5,39
x_{12}	−2,06**	−2,06	g_{34}	−0,36**	−0,36
x_{13}	−51,830(330)	−43,28	g_{44}	1,629(204)	2,12
x_{14}	−5,49**	−5,49	–	–	
x_{22}	−3,677(645)	−3,90	k_{1133}	49,689(399)	
x_{23}	−4,84**	−4,84	k_{1333}	−11,9867(481)	

*values did not vary, calculated with F_{ij} parameters from column 2 of table 3,
**parameter value is fixed to the value taken from [4]

It should be pointed out that fitting of potential function fitting of harmonic part was made directly to the experimental values of band centres. Thus, in the course of the problem solving we stated that four parameters F_{11}, F_{22}, F_{33} and F_{44} are defined unambiguously, whereas

parameters F_{12} and F_{34} have more confidence intervals than the values of the parameters themselves. In the given stage of problem solving F_{12} and F_{34} parameters were fixed by the values from the work [4]. Determination of $x_{\lambda\mu}$ and $g_{ll'}$ parameters is conditioned by experimental information. In our case the available data about 26 oscillatory band centres permit us to determine 6 out of 10 parameters of $x_{\lambda\mu}$ and 2 out of 3 parameters of $g_{ll'}$ (table 4). Similarly, as the part of parameters $x_{\lambda\mu}$ failed to be found due to lack of experimental data, their values were fixed to the values of the parameters from the work [4] obtained from *ab initio* calculations. Consideration of the resonance interactions permitted also the two parameters of the quadratic part of k_{1133} and k_{1333}.

Table 5. *Values of band centres of AsH$_3$ molecule, sm^{-1}*

Band	From [4]	Our result	Experiment	Reference
ν_2, A_1	910,797	906,752	906,752	[8]
$2\nu_2$, A_1	1813,79489	1806,14959	1806,14959	[8]
$2\nu_4$, A_1	1985,7889	1990,9811	1990,9811	[7]
ν_1, A_1	2117,824	2115,260	2115,164	[8]
$2\nu_3$, A_1	4205,478	4167,699	4166,772	[8]
$2\nu_1$, A_1	4213,888	4238,046	4237,701	[6]
ν_1+$2\nu_3$, A_1	6177,717	6136,575	6136,316	[6]
$3\nu_1$, A_1	6288,19	6276,00	6275,83	[6]
$3\nu_3$, A_1	6307,59	6365,73	6365,96	[6]
$4\nu_3$, A_1	8027,057	8027,541	8028,977	[6]
$4\nu_1$, A_1	8246,246	8249,19	8249,52	[6]
ν_4, E	997,434	999,225	999,225	[7]
ν_2+ν_4, E	1908,26191	1904,11458	1904,11458	[8]
$2\nu_4$, E	1994,2690	1997,4957	1997,4957	[7]
ν_3, E	2124,509	2126,970	2126,423	[8]
ν_1+ν_3, E	4199,053	4168,188	4167,935	[8]
$2\nu_3$, E	4227,04	4248,64	4247,53	[6]
ν_1+$2\nu_3$, E	6154,94	6136,57	6136,33	[6]
$2\nu_1$+ν_3, E	6258,30	6282,70	6282,36	[6]
$3\nu_3$, E	6264,47	6294,67	6294,71	[6]
ν_1+$3\nu_3$, E	8047,712	8027,547	8028,969	[6]
$2\nu_1$+$2\nu_3$, E	8252,45	8258,13	8258,38	[6]
$5\nu_1$, A_1	9868,4	9841,0	9841,4	[6]
$6\nu_1$, A_1	11272,0	11577,1	11576,3	[6]
$4\nu_1$+ν_3, E	9851,4	9841,0	9841,4	[6]
$5\nu_1$+ν_3, E	11341,5	11577,1	11576,3	[6]

In conclusion it may be said that despite the simplicity of the used model, the results obtained may be used in the future as a reliable basis for correction of potential function parameters of arsine molecule obtained by means of *ab initio* calculations. Besides, the obtained information is iseful for the further spectroscopic analysis of weak highly exited oscillatory states of AsH$_3$ and AsD$_3$ molecules.

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TEMPERATURE OPERATING MODE OF THE CuBr+Ne+H₂(HBr)–LASER AT CHANGE OF PUMPING

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The analysis of a temperature mode of the laser on copper bromide vapour using active additives of hydrogen (bromhydrogen) at change of pumping parameters has been carried out. It is shown that introduction of the optimal additive increases the discharge tube wall temperature from 620 up to 720 °C. The increase of wall temperature 50...60 °C more can occur at change of buffer gas pressure from 3,3 to 13,3 kPa, as well as at increase working capacity twice. It is stated that introduction of the additive raises pressure of working substance vapours in the active media of the laser of average diameter 6,7 Pa more due to interaction of bromine, bromhydrogen with copper atoms settled on the tube wall. The peculiarities of laser thermal mode at high frequencies of pulse sequences (up to 100 kHz) have been considered.

Introduction

Among several modifications of gas copper laser known today the lasers on pure copper vapour (LCV) and lasers on copper bromide vapour (LCBV) have found the widest application in science and engineering. It is conditioned by the possibility of active elements of these radiation sources to operate in the sealed off mode [1–3].

In spite of the fact that LCV durability exceeds that of LCBV [3], the latter attract much attention nowadays. First of all it is explained by the fact that the principle of producing working substance vapour in such a system permits to take nearly a third of the temperature in a gas discharge tube (GDT) in comparison with LCV [4]. It significantly simplifies the construction of the active element and reduces the pumping requirements, it resulting in decrease of power supply size. It affects the cost of the device on the whole. Secondly, LCBV do not yield to

LCV in their characteristics, but in the capacity the former even surmount them [5]. They can also operate at more high frequencies of pulse sequence (FPS) of generation [6], which is very urgent for some applications.

However LCBV operating mode has some peculiarities. It is basically connected with the fact that one needs to control not only the temperature of working channel, but also that of the containers with CuBr vapours. The difference in these temperatures sufficiently depends on pumping conditions. The change of pumping parameters results in change of GDT wall temperature, that influences the temperature of containers with CuBr, hence, the output characteristics of laser.

In recent years H₂, HBr additives are widely used to increase the LCBV energy characteristics [5–7]. Introduction of such admixture into the laser active media change GDT coordination with pumping generator, that also affects the temperature difference mentioned above.