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RELAXATION PARAMETERS OF ABSORPTION LINES OF VIBRATIONALLY EXCITED HF MOLECULE

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The design model allowing obtaining authentic values of half-width and shift of line centers of HF molecule of hot and cold strips to dissociation limit has been developed. Calculation results of rotary and oscillatory dependences of relaxation parameters of lines HF-HF were obtained.

1. Introduction

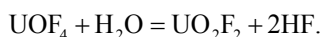
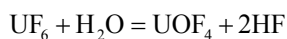
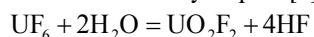
One of the main problems of modern theoretical spectroscopy is the investigation of high molecule vibration state. Reliable values of parameters of molecule absorption lines in gaseous phase are necessary for applications in photochemistry of atmosphere, laser physics developing data bases of spectroscopic information. Here the new model founded on the variant of Korf-Levit-Cherkasov impact broadening theory, energy levels and wave functions of Morse oscillator, computed *ab initio* or semi-empirical functions of multipole moments and polarization of diatomic molecule is given. The proposed model allows studying the influence of intramolecular dynamics of diatomic molecules in conditions of strong vibration excitation on half-width and shift of absorption lines. To check model reliability the half-widths and shifts of line centers of high hot and cold bands of HF molecule were calculated in the article.

Half-widths and shifts of line centers of HF molecule were measured before up to $v=2$ [1–4]. At the present there are no experimental values of half-width and shifts

of line centers formed by transition to higher vibration states of HF molecule. Good fit of half-width and shift of line centers of HF-HF calculated in the paper with measuring results [1–4] confirms as well the reliability of proposed model.

In [5, 6] the results of analysis of dependence of relaxation parameters of line R_0 of diatomic molecules on various factors of intramolecular dynamics are given: change of rotational constant, dipole, quadrupole moments, polarizability. It is shown that significant changes of broadening and shift coefficients depending on intramolecular dynamics are observed for lines of high vibration-rotational (VR) bands of molecules CO HF and. At strong vibration excitation the adiabatic effect connected with energy level shift at collisions should appear as well in half-widths. As it is shown in [7] this effect increases half-widths of H_2O lines in bands conditioned by valence vibration excitation. On the contrary, in H_2O molecule the decrease of half-width of lines in the bands of ν_2 type conditioned by significant rise of rotational constant and anomalous centrifugal effect at excitation of bending vibration is observed [8].

The proposed model may have the following practical applications. Firstly, use of uranium fuel, in particular, UF_6 , UF_4 in atomic power engineering results in air pollution with uranium and hydrocarbon oxyfluorides. Vibrationally excited HF molecules as well as complexes $(\text{HF}+\text{H})$, $(\text{HF}+\text{OH})$ in gaseous state may be formed in the regions of nuclear fuel cycle pass [9]:



Spectroscopic methods allow detecting the places of HF accumulation and its complexes and determining concentration. Secondly, it is necessary to know half-widths and shifts of line centers belonging to high vibration bands of HF for constructing kinetic models of vibrationally excited laser media. At the present chemical HF-lasers are used in different fields of engineering [10]. Thirdly, at the present data bases of spectroscopic information are developed. The given design model allows obtaining reliable spectroscopic information for existing data base.

The detailed numerical analysis of influence of intramolecular dynamics of highly excited VR states on relaxation parameters of absorption lines of diatomic molecules is require. Adiabatic effect occurrence in half-width of HF lines, the influence of changing rotational constant, dipole, quadrupole moments and polarizability on relaxation parameters of absorption lines of hot and cold bands of HF molecule at its strong vibration excitation up to dissociation bound was studied.

2. Theoretical analysis

To determine potential function the model of Morse oscillator was used. Parameters of Morse potential for HF molecule are determined by fit to potential function calculated by *ab initio*. HF molecule has dissociation range 49000 cm^{-1} , Morse potential supports 23 vibration states. Matrix elements of dipole, quadrupole moments, polarizability as well as rotational constant required in broadening theory were numerically determined with wave functions of Morse oscillator. Functions [11–13] of dipole, quadrupole moments and polarizability of HF molecule calculated by *ab initio* and/or determined semi-empirically were used for calculations. Intramolecular dynamics of HF at strong vibration excitation was detailed discussed in [5] therefore, here we stop at vibration dependence of average values of molecular parameters.

The dependence of diagonal matrix elements of dipole moment and polarizability of HF molecule on vibration quantum number v is shown in Fig. 1, *a*, *b*. Difference of matrix elements of polarizability and squares of dipole moment determine adiabatic contribution into half-width and shift of line centers. The calculations showed that this contributions increases 7 times in state $v=20$ in comparison with $v=2$ for HF molecule. Significant changes of half-width and shift of line centers of HF molecule may be expected at increase of vibration quantum number.

The values of rotational energy levels determined by matrix element of rotational constant B_v of optically active molecule depends strongly on the degree of its vibration excitation. The dependence of rotational constant of HF molecule on vibration quantum number v is shown in Fig. 1, *c*. One can find out that strong decrease of vibration constant (7,2 times at increase of v from 0 to 22) takes place.

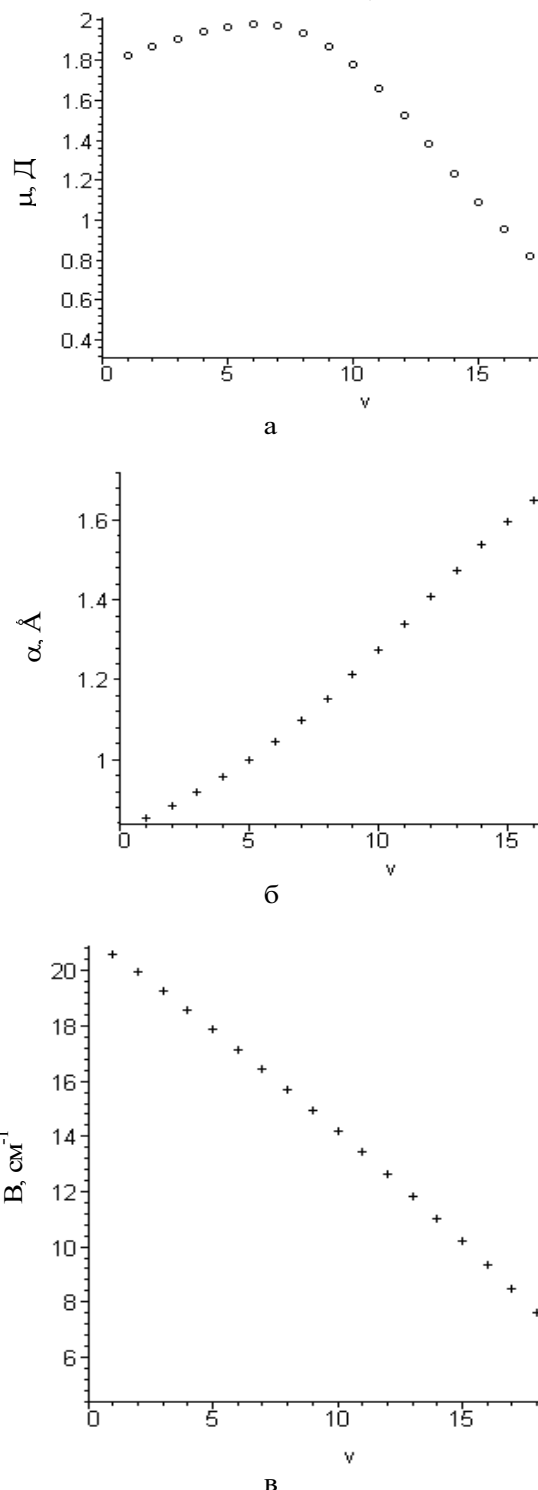


Fig. 1. Dependence of average values of trimolecular characteristics of HF on vibration quantum number: *a*) dipole moment; *b*) polarizability; *c*) rotational constant

Probably, such significant change of rotational constant of HF molecule «compacts» considerably rotational energy spectrum of a molecule in high vibration states close to dissociation bound. Frequencies of rotational transitions determining the value of nonadiabatic contribution into half-width and shift of line centers decrease. It should result in change of half-width and shift of centers of HF-HF lines at increase of rotational quantum number.

3. Results and discussion

Within one of the variants of semiclassical theory of impact broadening [14] in approximation of linear paths and average rate of collisions a half-width $\gamma(i, f)$ and shift $\delta(i, f)$ of line centers are expressed by the formulas:

$$\gamma(i, f) = \frac{mv}{c} \sum_j \rho(j) \int_0^\infty \left[1 - \exp\{-\operatorname{Re} S_2^{\text{outer}}(b)\} \times \right. \\ \left. \times \cos\{S_1(b) + \operatorname{Im} S_2^{\text{outer}}(b)\} \right] b db, \quad (1)$$

$$\delta(i, f) = \frac{mv}{c} \sum_j \rho(j) \int_0^\infty \left[\sin(S_1(b) + \right. \\ \left. + \operatorname{Im} S_2(b)) \exp(-\operatorname{Re} S_2(b)) \right] b db. \quad (2)$$

Here i, f are the quantum numbers of initial and final states of vibration transition; n is the concentration of perturbed particles; v is the relative rate of colliding molecules; $\rho(j)$ is the population of rotational level j of perturbed molecule. Effectiveness function is in a series of theories by decomposition: $S(b) = iS_1(b) + S_2^{\text{outer}}(b) + iS_2^{\text{outer}}(b) + \dots$ $S_1(b)$ is the effectiveness function of the first order determining adiabatic contribution into half-width (1) and shift of center (2) of lines. $\operatorname{Re} S_2(b)$ and $\operatorname{Im} S_2(b)$ are the real and virtual parts of effectiveness function of the second order determining nonadiabatic contribution. Dipole-dipole, dipole-quadrupole, quadrupole-quadrupole and polarization (induction and disperse) interactions were taken into account in intermolecular potential. For short the contributions of dipole-dipole summand into $S_2^{\text{outer}}(b)$ in intermolecular potential are given here:

$$\operatorname{Re} S_2^{\text{outer}}(i, f, b, v) = \frac{4}{9} \frac{1}{(\hbar v b^2)^2} \times \\ \times \sum_{j'} D(jj'|1) \left\{ \sum_{i'} D(ii'|1) \operatorname{Re} \varphi_{11}(k_{jj'ij'}) + \right. \\ \left. + \sum_{f'} D(ff'|1) \operatorname{Re} \varphi_{11}(k_{ff'ij'}) \right\}. \quad (3)$$

Here $\varphi_{11} = \operatorname{Re} \varphi_{11} + i \operatorname{Im} \varphi_{11}$ is the complex resonant function for dipole-dipole interaction. The generalized line force D is determined as a product of square of matrix element of dipole moment μ of absorbing molecule in vibraional state. Force of transition lines depends on diagonal matrix element of dipole moment:

$$D(ii'|1) = |\langle V_i | \mu | V_i \rangle|^2 (j_i 100 | j'_i 0)^2. \quad (4)$$

Here $|V_i\rangle$ are the vibration wave functions of transition initial state; $(j_i 100 | j'_i 0)$ are the coefficients of Klebsch-Gordon [15], $i=0, \dots, 22$. Resonant parameter k in (3) is determined by the difference of rotational level energy in upper or lower vibration states:

$$k_{jj'i} = \frac{2\pi cb}{v} (E_{ji} - E_{j'i} + E_j - E_{j'}) = \\ = \frac{2\pi cb}{v} (\omega_{jj'i} + \omega_{j'i}). \quad (5)$$

Substituting indices j_i, j'_i by j_f, j'_f , the resonant parameter $k_{jj'f}$ in upper vibration state of transition may be obtained. Energy levels $E_{ji}, E_{j'i}$ in (5) are calculated with matrix elements of vibration constant.

Virtual part of effectiveness function is determined by polarization part of intermolecular potential (induction and disperse interaction) and electrostatic interaction. Isotropic part of polarization interaction in Unzold approximation [16] depends on differences of average values of polarizability and dipole moment square in upper and lower state of transition:

$$S_1(i, f, b, v) = \frac{3\pi}{8\hbar v b^5} \left\{ \alpha_2 \{ \langle V_i | \mu_1^2 | V_i \rangle - \langle V_f | \mu_1^2 | V_f \rangle \} + \right. \\ \left. + [\mu_2^2 + \frac{3}{2} \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \alpha_2] \times \right. \\ \left. \times \{ \langle V_i | \alpha_1 | V_i \rangle - \langle V_f | \alpha_1 | V_f \rangle \} \right\}. \quad (6)$$

Here μ_1, μ_2 are the functions of dipole moment; α_1, α_2 is the function of polarizability of absorbing and disturbing molecule; $\varepsilon_1, \varepsilon_2$ are the ionization potentials. In the case of self-broadening $\mu_1 = \mu_2, \alpha_1 = \alpha_2, \varepsilon_1 = \varepsilon_2$ contribution of $S_1(b)$ (6) (adiabatic contribution) into half-width and shift of line centers differ significantly for H_2O molecule: for line half-widths it amounts to about 10 % [7] for shift of line centers it may achieve 75 % in the band $3\nu_1 + \nu_3$ [17].

In the formula for $\operatorname{Im} S_2$ the contribution of just dipole-dipole interaction is given:

$$\operatorname{Im} S_2^{\text{outer}}(i, f, b, v) = \frac{4}{9} \frac{1}{(\hbar v b^2)^2} \times \\ \times \sum_{j'} D(jj'|1) \left\{ \sum_{i'} D(ii'|1) \operatorname{Im} \varphi_{11}(k_{ii'jj'}) - \right. \\ \left. - \sum_{f'} D(ff'|1) \operatorname{Im} \varphi_{11}(k_{ff'jj'}) \right\}. \quad (7)$$

3.1. Vibration and rotational dependences of half-width and shift of HF-HF lines centers of hot and cold bands

To calculate half-widths of HF-HF lines the function of dipole moment from [11], quadrupole moment from [12], polarizability from [13] computed by *ab initio* were used. Some molecular constants are taken from [18]. The required matrix elements of dipole moment, polarizability, rotational constant were determined by numerical integration. It is necessary to mention that the computed values change rather significantly under

the influence of vibration excitation of HF molecule. The computed average dipole moment of the main state equals to 1,80 D (computed value coordinate well with experimentally determined value). The value of rotational constant for the main state computed in this paper $\nu=0$ $B_0=20,617$ cm^{-1} coordinates well with known value $B_0=20,96$ cm^{-1} [18]. Thus, vibration excitation of HF molecule results in significant change of average molecular characteristics as well as significant change of rotational energy spectrum.

Earlier in [5] changes of intramolecular dynamics of HF and CO molecules under the influence of strong vibration excitation were analyzed. To study in detail the influence of vibration excitation on line relaxation parameters the half-width and shift of centers of tens of lines of HF molecule were calculated. Vibration dependence of half-widths of HF-HF lines of cold and hot bands is given in Fig. 2. In the whole half-widths of HF-HF lines reveal weak vibration dependence which is mainly determined by the behavior of dipole moment function. Adiabatic

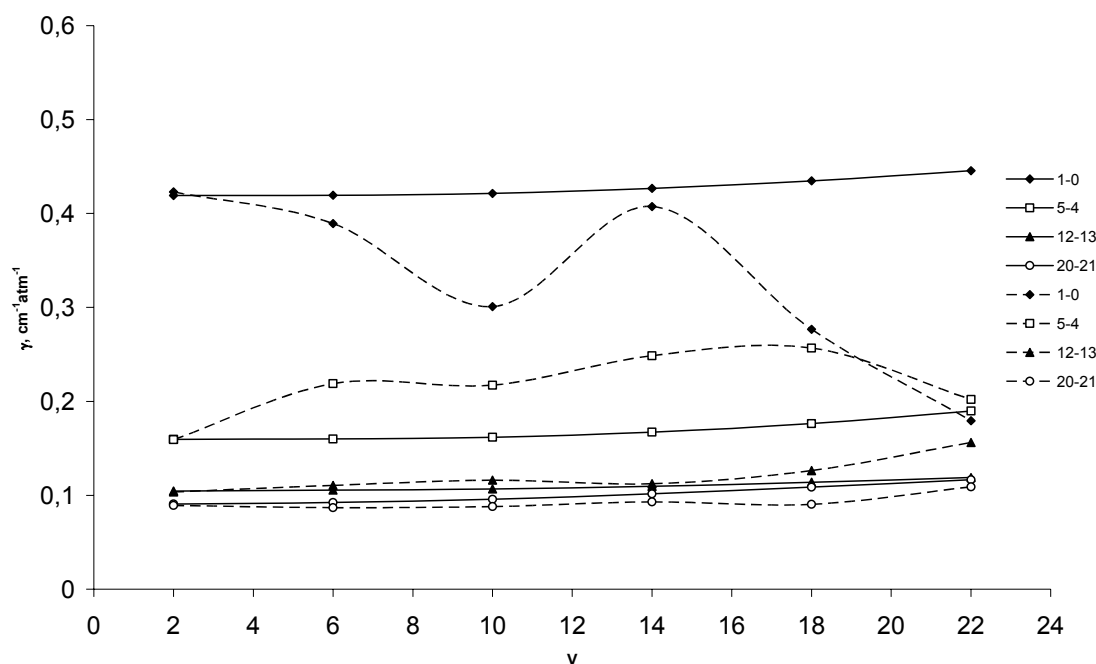


Fig. 2. Dependence of half-width of HF-HF lines on vibration quantum number of upper state; full curves are for cold bands; dashed curve are for hot ones

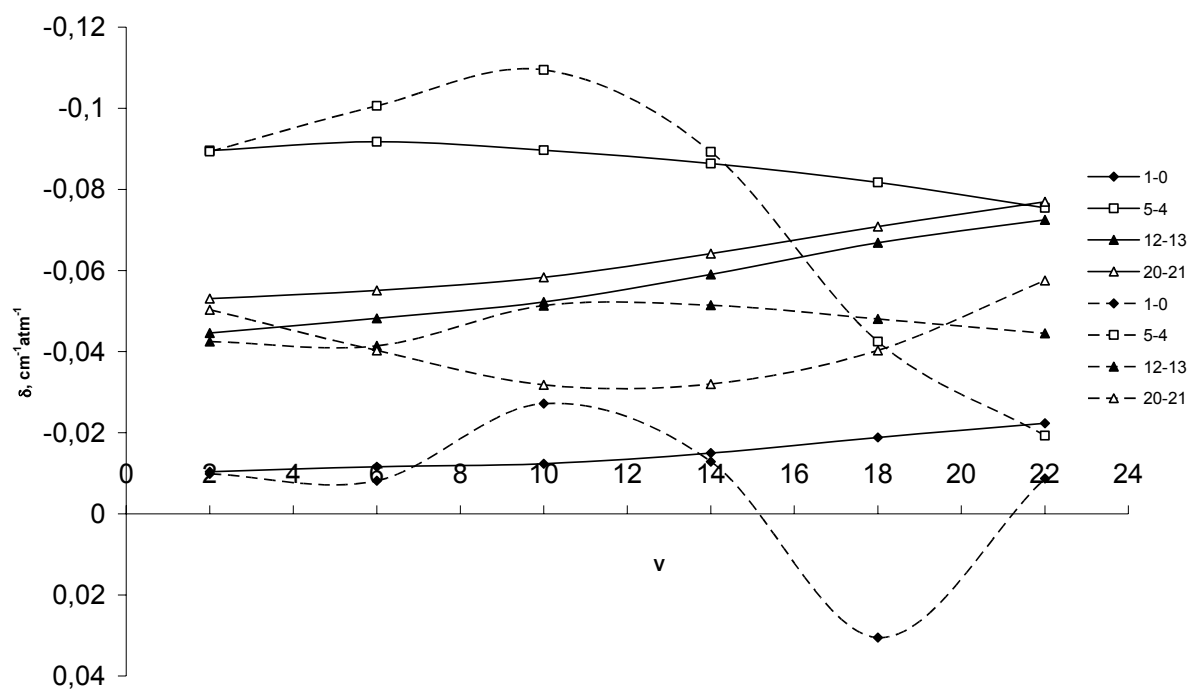


Fig. 3. Dependence of shift of centers of HF-HF lines on vibration quantum number of upper state; full curves are for cold bands; dashed curve are for hot ones

contribution into line half-widths is insignificant. Calculations showed that adiabatic contribution (6) into half-width of HF-HF lines of a band 0–20 does not exceed 10 % at the average. Vibration dependence of line centre shift is given in Fig. 3 for cold and hot bands. Oscillating character of vibration dependence of line center shift

should be noted. The calculations show that vibration dependence of the shift in the whole correlates strongly with the behavior of polarizability function. As a result, negative contribution to line shift increases owing to increase of contribution into center shift from isotropic part of polarization interactions (6) (adiabatic contribution).

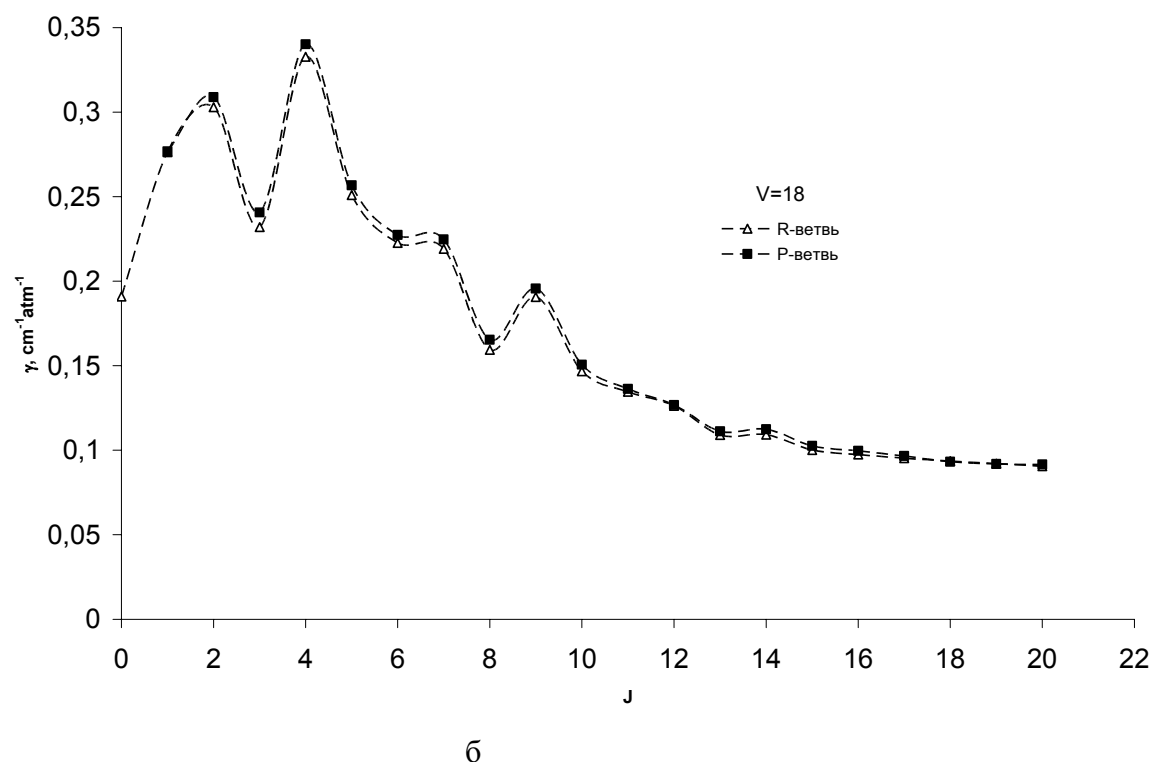
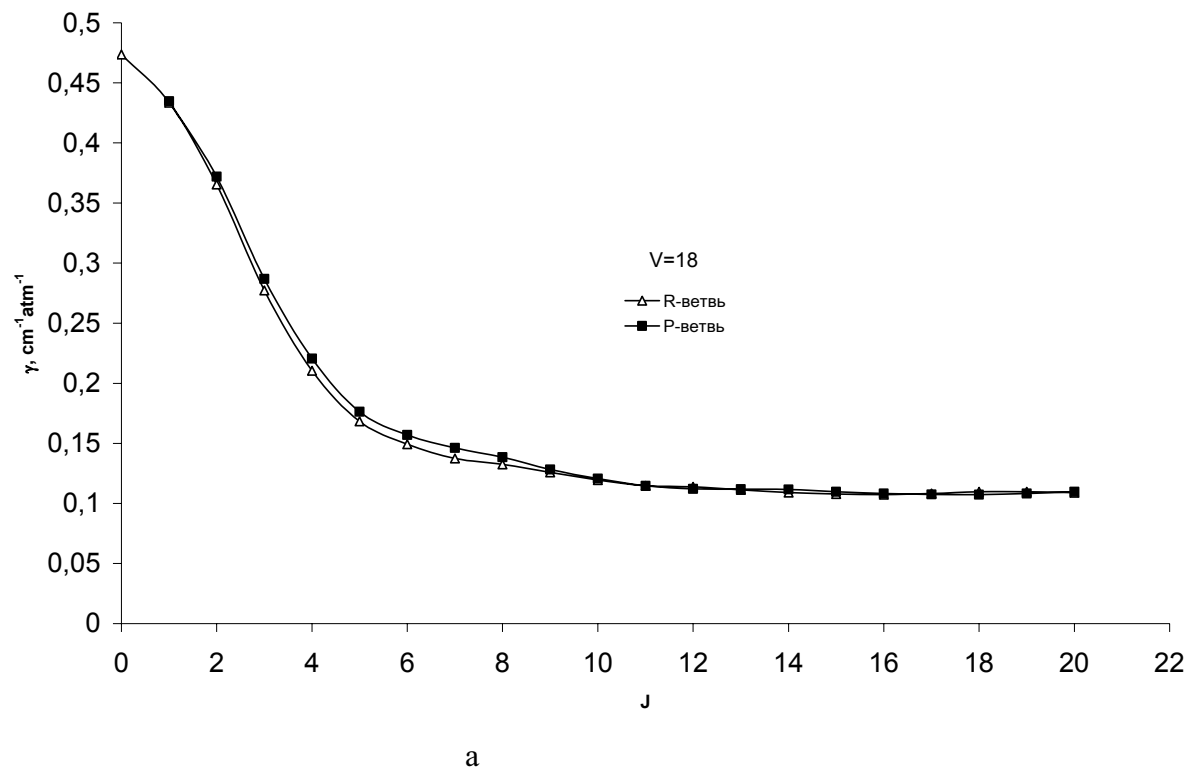


Fig. 4. Dependence of half-widths of HF-HF lines on rotational quantum number of lower state: a) for cold bands; б) for hot bands

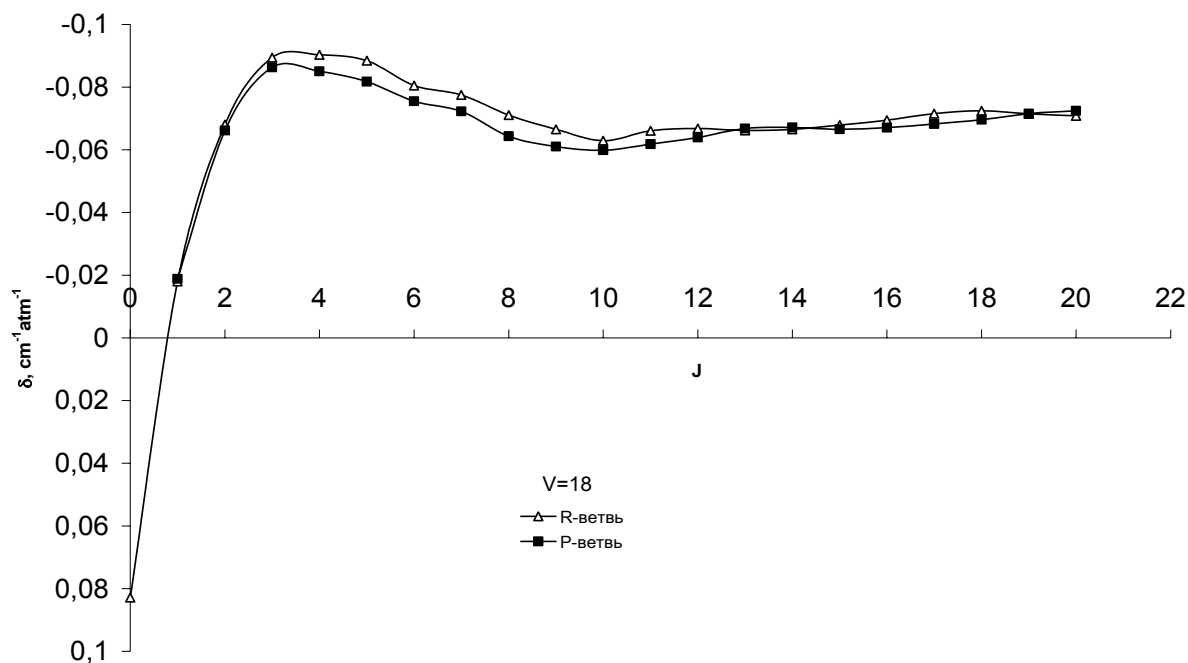
Rotational dependences of line half-widths (vibration quantum number of upper state $\nu=18$) are given in Fig. 4 for cold and hot bands. It is seen that line half-width of cold bands decreases steadily at J increase.

Half-widths of the same lines of hot bands show nonmonotonic dependence on J (Fig. 4, δ). Let us ana-

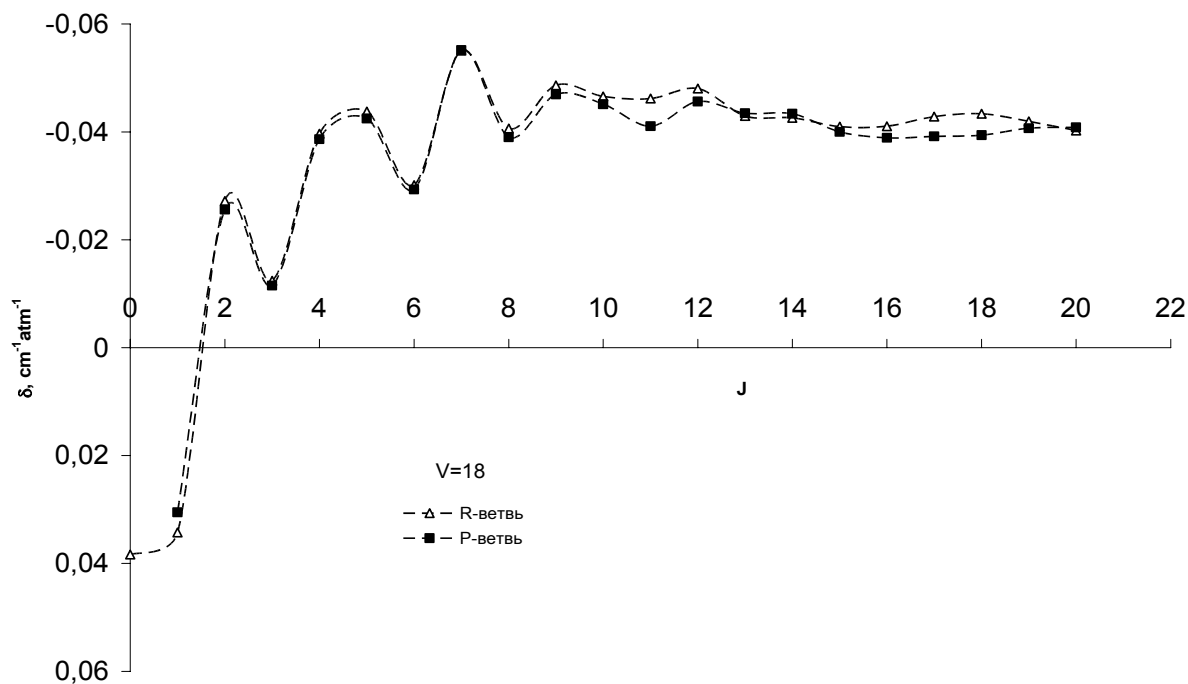
lyze the contributions into half-width from resonant function with frequencies $\omega_{jji'}$, ω_{jff} (5) in upper and lower vibration state:

$$\omega_{jji'} = E_{ji} - E_{j'i} = B_{vi} (j_i^2 + j_i - j_i'^2 - j_i'), \quad (8)$$

$$\omega_{jff} = E_{jf} - E_{j'f} = B_{vf} (j_f^2 + j_f - j_f'^2 - j_f'). \quad (9)$$



a



б

Fig. 5. Dependence of the shift of HF-HF line centers on rotational quantum number of lower state: a) for cold bands; б) for hot bands

HF molecule has large rotational constant $B_v=20,96\text{ cm}^{-1}$ in the ground state and, as a result, high frequencies of rotational transitions in lower vibration state ω_{ji} (8). In vibration state $v=18$ rotational constant $B_v=7,59\text{ cm}^{-1}$ that is 3 times lower. As $B_v \gg B_v$, the main contribution from resonant function into line half-width (3) is determined by frequencies of rotational transitions ω_{ji} (9) in upper vibration state and dependence of half-width on rotational quantum number j for lines of cold bands is steadily decreasing (Fig. 4, a). For the same lines of hot bands (the transition with change of vibration quantum number to 1 is considered) another ratio of rotational constants in lower and upper vibration state is observed. Rotational constants $B_v=8,488\text{ cm}^{-1}$ ($v=17$) and $B_v=7,593\text{ cm}^{-1}$ ($v=18$) differ less than by 1 cm^{-1} , that is $B_v \approx B_v$. Competition of frequencies ω_{ji} (8) and ω_{ji} (9) of rotational transitions is observed. Different contributions from resonant function (3) determine significant difference in line half-widths with adjacent values of rotational quantum number J . As a result, half-width displays nonmonotonic dependence on J (Fig. 4, b).

Rotational dependences of the shift of line centers of cold and hot bands are given in Fig. 5. The change of shift sign especially for hot band lines may be seen (Fig. 5, b). The similar picture of oscillating shifts takes place for the cases broadening of HF molecule line by pressure of polar diatomic molecules [5], H_2O molecule by its own pressure [17].

The analysis of vibration and rotational dependences of relaxation parameters of HF molecule allows drawing the following conclusions:

1. Behavior of functions of multipole moments and polarizability determine the dependence of half-width and shift of line centers on vibration quantum number. Half-widths of HF-HF lines depend weakly on vibration quantum number. Adiabatic contribution into line half-width is calculated; it does not amount to more than 10 % to lines of band 0-20 HF-HF. Shifts of centers of HF-HF lines depends considerably on vibration quantum number, adiabatic contribution into shift of line center is significant.
2. The change of rotational energy spectrum at strong vibration excitation of absorbing molecule conditioned by decrease of rotational constant influences

greatly on line relaxation parameters. As a result, rotational dependences of shifts of centers of HF lines have oscillating character, the change of shift sign is observed. Oscillating shifts have been described before in [5] for HF-HF lines the bands 0-2, for H_2O - H_2O lines the bands $3\nu_1+\nu_3$ [17]. Half-widths of HF-HF lines show nonmonotonic dependence on rotational quantum number.

3. The model given in the article allows obtaining valid values of half-width and shift of line centers of cold and hot bands of HF molecule at strong vibration excitation to dissociation bound.

4. Conclusion

The model is given and half-width and shift of centers of HF-HF lines at strong vibration excitation to dissociation bound are calculated. Adiabatic effect and rearrangement of rotational energy spectrum at strong vibration excitation of HF molecule are studied. Use of *ab initio* or semi-empirically calculated functions of multipole moments, polarizability as initial data ensures the validity of calculation results. The validity of the given model is confirmed as well by coincidence with experimental values of half-width and shift of HF line centers [5-8] of low VR bands. The detailed analysis of vibration and rotational dependences of half-width and shift of line centers was carried out before only for H_2O molecule [8, 17, 19].

It should be noted that the proposed model using the calculated *ab initio* functions of multipole moments and polarizability allows:

- analyzing vibration and rotational dependences of half-width and shift of line centers of high cold and hot bands of HF molecule.
- obtaining valid values of half-width and shift of centers of tens of lines of HF molecule for highly excited vibration states near dissociation bound.

The results of calculations may be used at construction of kinetic models of molecular laser media, in photochemistry of atmosphere, at development of data bases of spectroscopic information.

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HALF-WIDTH AND LINE CENTER SHIFTS FORMED BY TRANSITIONS INTO HIGHLY EXCITED VIBRATION STATES OF CO MOLECULE

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Within the proposed model the half-width and shift of centers of spectral lines formed by transitions on high vibration conditions of CO molecule to dissociation bound have been calculated. The given results allow investigating kinetic processes and characteristics of CO-laser cold plasma.

Introduction

At present much attention is paid to the development of CO-lasers capable of serving as frequency standards. In modern CO-lasers with cascade mechanism of generation the transitions to highly excited vibrational states up to $v=41$ [1], $v=36$, 38 [2, 3] are used. In order to construct laser kinetic models generating at high vibrational-rotational (VR) transitions it is necessary to know relaxation parameters of contour of lines of vibrationally excited working substance. The investigation of vibrational dependence of half-width and shift of centers of CO molecule lines in lasers with optical pumping and cascade generation mechanism gains a special importance [4, 5]. In [4] the properties of plasma of CO-laser with optical pumping were studied and it was ascertained that population of high vibrational states calculated within the bounds of kinetic model does not conform to the measured value (a divergence is almost twice as much). Evidently, the substantial difference of calculation from the experiment is conditioned by ill-posed values of relaxation parameters of high vibrational states of CO molecule.

In [6] the influence of intramolecular dynamics of highly excited vibrational states of diatomic molecules on relaxation parameters of line contour was studied. It was shown that peculiarities of behavior of dipole, qua-

drupole moments, polarizability, rotational constant at strong vibrational excitation may change considerably relaxation parameters of lines of CO molecule belonging to high vibrational states up to $v=50$. In [7] half-width and line center shift of CO molecule formed by cold transitions to low vibrational states to $v=3$ were measured. Measurements of half-widths, line center shifts for transitions with higher value of vibrational quantum number of upper state are absent at present.

The aim of this paper is to develop the model which allows calculating relaxation parameters of lines of CO molecule at strong vibrational excitation up to dissociation bound. The suggested model is based on one of the variants of semiclassical impact theory; on functions of multipole moments and polarizability calculated by *ab initio*; on the model of Morse oscillator. Rotational and vibrational dependence of half-width and line center shift of CO-CO cold and hot bands at change of vibrational quantum number up to $v=65$ were studied as a validity test of the new model. The investigation of cold plasma properties occurring at generation of radiation of CO-laser with optical pumping at high vibrational transitions of working substance; use of relaxation parameters of high vibrational states for constructing kinetic models may be practical application of the results.