

Analysis of halfwidths and shifts of diatomic molecule line centers due to transitions to highly excited vibrational states

A.D. Bykov and V.N. Stroinoва*

*Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
* Tomsk Polytechnic University*

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Halfwidths and shifts of HF–HF R_0 line centers belonging to high vibrational bands lying near the dissociation threshold have been estimated in the case of self-broadening for the first time. A considerable narrowing (up to 25 percent) was found for the lines of 0–22 HF band compared to the rotational band. The decrease in halfwidths is explained by the fact that the mean dipole moment and the absorption constant of the molecule strongly change as the molecule is vibrationally excited. It has been found that the line shifts increase due to increase of the absorbing molecule polarizability upon its vibrational excitation.

Introduction

Halfwidths and line center shifts of molecular gases are important spectroscopic parameters in data banks, used for solution of various problems of atmospheric optics, astrophysics, and laser physics. To calculate these line profile parameters, it is necessary to know energy levels and wave functions, trajectories of relative motion, as well as mean values of dipole and quadrupole moments, polarizability, and other molecular characteristics, determining the intermolecular interaction in a given vibrational state.

The vibrational excitation changes mean molecular characteristics and can lead to a significant change in line profile parameters. Thus, for example, it was shown^{1,2} that intramolecular interactions (Δk -effect, change in the mean dipole moment and polarizability), accompanying a strong vibrational excitation of the H₂O molecule, lead to 39 percent decrease in the halfwidth,¹ more than 70 percent change in the line shift, and alternation of its sign.²

In this paper, we analyze the effect of strong vibrational excitation on the halfwidth and shift of HF molecular lines formed by transitions to highly excited vibrational states, whose energy is close to the dissociation threshold. Earlier, the halfwidths and shifts of HF spectral lines were studied^{3,4} for transitions to the low vibrational states $v < 2$. The relaxation parameters of the HF molecule absorption line profile, caused by transitions to the vibrational states $v > 2$, have not been studied yet.

The aim of this work is to estimate the influence of changes in the mean dipole moment, polarizability, and rotational constant in the upper vibrational state upon a strong vibrational excitation of the molecule (up to $v = 22$) on the HF line halfwidths and shifts in the case of self-broadening.

The traditional method of determining the rotational-vibrational energy levels and wave functions involves an application of the perturbation theory (in the general case, in the form of the method of effective rotational Hamiltonian). The main assumption of the perturbation method is a smallness of intramolecular interactions in comparison with the zero-approximation energy. The zero approximation is usually chosen in the form of the system of independent harmonic oscillators, and such characteristics as the dipole moment, potential energy function, or moments of inertia are represented as expansions into the Taylor series near the linear configuration of the molecule. Mean values of molecular characteristics are also represented as power expansions in terms of a small parameter.

For low vibrational states, the wave functions are located in a close vicinity near the equilibrium configuration of the molecule. As a consequence, the mean values of the dipole and quadrupole moments and polarizability, which determine the intermolecular potential, vary only slightly upon the excitation of one or several vibrational quanta. The variation of mean values of the multipole moments, as well as the rotational energy spectrum, rotational and centrifugal distortion constants can be easily taken into account in the framework of the perturbation theory.

Quite a different situation should be expected in the case of strong vibrational excitation at transitions to the vibrational states lying near the dissociation threshold. As an example, Fig. 1 shows the potential energy function of the HF molecule, energy levels and wave functions of the ground ($v = 0$) and several high-excited ($v = 5, 10, 15$) vibrational states and the dipole moment function. It can be seen that the wave function of the ground state is located near the equilibrium value of the bond length, but wave functions of the

high-excited vibrational states ($v = 10, 15$) occupy a wide region, covering the whole range of variability of the dipole moment.

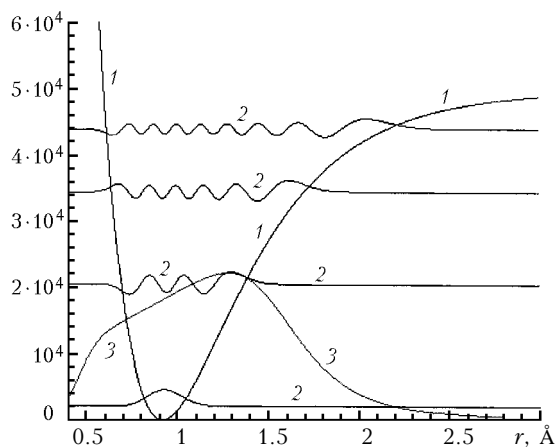


Fig. 1. Potential energy (in cm^{-1}) (curve 1), wave functions ($\times 10^3$) (curves 2), and dipole moment function ($\times 10^4$ D) (curve 3) of the HF molecule.

It should be obviously expected that the mean dipole moment represented as a perturbation series would diverge. In addition, the mean dipole moment changes quite widely. In this case, it is desirable to calculate wave functions and matrix elements of the dipole moment using some alternative methods: variational method⁵ or specialized methods for summation of series.^{6,7} Note that the variational methods are now widely used^{8,9} for non-rigid molecules like H_2O .

This paper analyzes the halfwidth and shift of HF lines due to transitions to high-excited vibrational states up to $v = 22$.

1. Theoretical analysis

Within the framework of the theory of impact broadening, the line halfwidth γ_{if} and shift δ_{if} are expressed as

$$\gamma_{if} + i\delta_{if} = \frac{n}{c} \sum_j \rho(j) \int_0^\infty v F(v) dv \int_0^\infty b S(b, v) db. \quad (1)$$

Here i, f are the indices, numbering the initial and final ro-vibrational levels of the absorbing molecule, respectively; j is the index, numbering the states of the perturbing molecule; n is the concentration of buffer gas particles; c is the speed of light; $\rho(j)$ is the density matrix, determining the population of energy levels of the perturbing molecule; $F(v)$ is the Maxwell distribution for the relative velocity of colliding particles; $S(b, v)$ is the efficiency function of collision with the impact distance b and velocity v . In the general case, $S(b) = \text{Re}S(b) + \text{Im}S(b)$; the real and imaginary parts can be represented in the second order of the perturbation theory as¹⁰:

$$\begin{aligned} \text{Re}S(b) &= \\ &= 1 - \exp\{-\text{Re}S_2^{\text{outer}}(b)\} \cos\{\text{Im}S_2^{\text{outer}}(b) + S_1(b)\}; \\ \text{Im}S(b) &= \\ &= \exp\{-\text{Re}S_2^{\text{outer}}(b)\} \sin\{\text{Im}S_2^{\text{outer}}(b) + S_1(b)\}, \quad (2) \end{aligned}$$

where $S_1(b)$, $S_2(b)$ are the well-known first- and second-order interruption functions of the Anderson theory. If polar molecules collide, the main contributor to $S_2(b)$ is the dipole–dipole interaction, and the interruption function $S_2(b)$ can be represented as follows:

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

Here φ_{11} is the resonance function for the dipole–dipole interaction; $D(ii'|1)$, $D(ff'|1)$ are the generalized line strengths, determined as squares of reduced matrix elements of the dipole moment operator μ_1 of the absorbing molecule in the ro-vibrational states i and f . For diatomic molecules

$$D(ii'|1) = \langle V_i | \mu_1 | V_i \rangle^2 (j_i 100 | j_i' 0)^2. \quad (4)$$

In Eq. (4), V_i are vibrational wave functions of the initial state; $(j_i 100 | j_i' 0)$ are the Clebsch–Gordan coefficients; the adiabatic parameter k in Eq. (3) is determined by the energy balance in transitions between rotational levels in the upper or lower vibrational states:

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

Let us introduce the approximation of the transition mean frequency, analogous to the full resonance approximation $k_{ii'j'} = k_{ff'j'} = 0$, known from the theory of broadening. Within the framework of this approximation, the contribution from the resonant function to the halfwidth is maximal, and the shift is minimal: $\text{Re}\varphi_{11} = 1$, $\text{Im}\varphi_{11} = 0$. Let $\bar{\omega}_{ii'}$, $\bar{\omega}_{jj'}$, $\bar{\omega}_{ff'}$ be the mean frequencies of virtual transitions in Eq. (5). We use the frequency mean values for determination of the function $S_2^{\text{outer}}(b)$ (3). Then the resonance function for the dipole–dipole interaction, calculated in the ordinary way, is approximately equal to:

$$\text{Re}\varphi_{11}(\bar{\omega}_{ii'} + \bar{\omega}_{jj'}) = C_i,$$

$$\text{Re}\varphi_{11}(\bar{\omega}_{ff'} + \bar{\omega}_{jj'}) = C_f;$$

$$\text{Im}\varphi_{11}(\bar{\omega}_{ii'} + \bar{\omega}_{jj'}) = \text{Im}\varphi_{11}(\bar{\omega}_{ff'} + \bar{\omega}_{jj'}) = 0. \quad (6)$$

If Eq. (6) is used for calculation of the interruption function (3), the summation over i' , f' , j' is reduced to the square dipole moment of the absorbing or

perturbing molecule. As a result, we obtain a simple approximation for $S_2^{\text{outer}}(b)$:

$$\tilde{S}_2^{\text{outer}} = \frac{4}{9} \frac{1}{(\hbar v b^2)^2} \mu_0^2 \{ \mu_i^2 C_i + \mu_f^2 C_f \}, \quad (7)$$

where

$$\mu_0^2 = |\langle 0 | \mu_0 | 0 \rangle|^2, \quad \mu_i^2 = |\langle i | \mu_i | i \rangle|^2, \quad \mu_f^2 = |\langle f | \mu_f | f \rangle|^2.$$

Equation (7) accounts for the influence of the change in the mean dipole moment and rotational constant due to increase of the amplitude of atomic vibrations in the absorbing molecule in the excited states.

The mean frequencies of virtual transitions in Eq. (6) were calculated by the equation

$$\bar{\omega}_{ff'} + \bar{\omega}_{j'j} = 2B_f j + 2B_0 j_{\text{max}}. \quad (8)$$

Here B_f is the rotational constant of the absorbing molecule in the upper vibrational state of the transition; j_{max} is the rotational quantum number of the most populated level of the perturbing molecule (for the HF molecule $j_{\text{max}} = 4$, as shown by the calculations of the density matrix $\rho(j)$). This choice of mean frequencies of transitions corresponds to the R_0 line. Further calculations of the halfwidth were carried out with the interruption function $\tilde{S}_2^{\text{outer}}(b)$ (7). In the calculations of line halfwidths and shifts, the approximation of the mean frequency of transition (6)–(8) accounts for the change in the rotational constant B , which in the literature is referred to as Δk -effect.

The first-order interruption function $S_1(b)$ is determined by the isotropic part of the intermolecular potential, i.e., by the contributions of induction and dispersion interactions:

$$S_1(b) = \frac{3\pi}{8\hbar v b^5} \times \left\{ \alpha_2 \left\{ \langle V_i | \mu_1^2 | V_i \rangle - \langle V_f | \mu_1^2 | V_f \rangle \right\} + \left[\mu_2^2 + \frac{3}{2} \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \alpha_2 \right] \left\{ \langle V_i | \alpha_1 | V_i \rangle - \langle V_f | \alpha_1 | V_f \rangle \right\} \right\}, \quad (9)$$

where μ_1 , μ_2 are the dipole moment operators of the absorbing and perturbing molecules; α_1 , α_2 are the polarizability functions of the absorbing and perturbing molecules; ε_1 , ε_2 are the ionization potentials. In the case of self-broadening, $\mu_1 = \mu_2$, $\alpha_1 = \alpha_2$, $\varepsilon_1 = \varepsilon_2$.

2. Results and discussion

To calculate the halfwidth and shift of HF–HF lines, we used the calculated *ab initio* dipole function¹¹ and the parameters of the Morse potential function,¹² where they are determined so that to reconstruct best the data of *ab initio* calculations. The HF molecule polarizability was determined only for several lower vibrational states,¹³ and therefore in this paper it was approximated by a second-order polynomial. The

needed dipole-moment matrix elements $\mu(r)$ and rotational constants $B(r) = b_e/r^2$ were determined from a numerical simulation. The obtained values are shown in Figs. 2–4. It should be noted that the calculated parameters vary quite widely under the effect of vibrational excitation of the HF molecule. For example, the mean dipole moment of the ground state, calculated by us, is equal to 1.8 D (the calculated value is in a good agreement with the experimental one), and in the vibrational state $v = 22$ it is equal to 0.11 D, that is, 16 times lower. The polarizability of the HF molecule increases fast, achieving 4.2 \AA^3 for the state $v = 22$, which is almost 5 times higher than in the ground state (0.86 \AA^3). The vibrational excitation of the HF molecule leads to a strong increase of the moment of inertia due to increase of the amplitude of atomic vibrations, which leads to a significant decrease of the rotational constant (7 times in the state $v = 22$ as compared to the state $v = 0$). The rotational constant, calculated by us for the ground state $v = 0$, $B_0 = 20.617 \text{ cm}^{-1}$ agrees well with the known value $B_0 = 20.96 \text{ cm}^{-1}$ [Ref. 12].

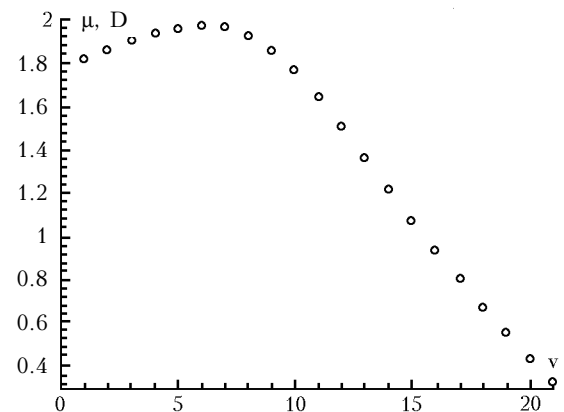


Fig. 2. Mean dipole moment as a function of the vibrational quantum number.

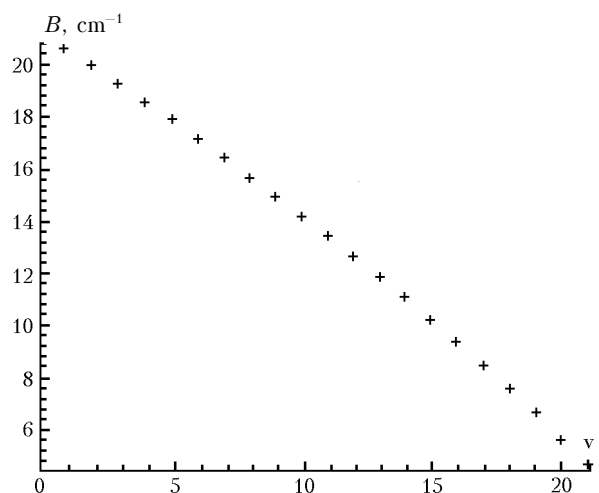


Fig. 3. Rotational constant B as a function of the vibrational quantum number.

Thus, the vibrational excitation of the HF molecule leads to a strong change of mean molecular

characteristics and the rotational energy spectrum. These factors obviously affect the halfwidths and shifts in different ways. For example, the decrease of the mean dipole moment leads to a decrease of line halfwidths, while the decrease of the rotational constant leads to their increase.

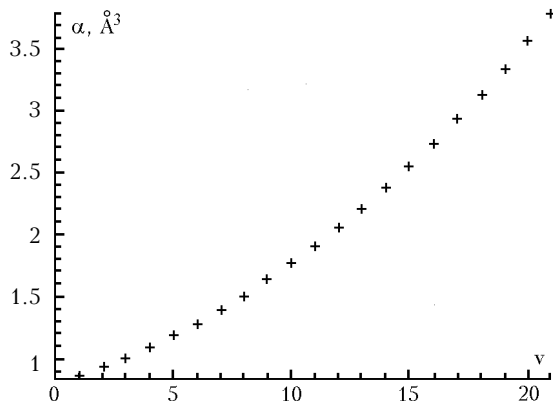


Fig. 4. Polarizability as a function of the vibrational quantum number.

To determine the total effect of vibrational excitation, we have calculated line halfwidths and shifts by Eqs. (1), (2), and (6)–(8). The results obtained for the bands $0 \rightarrow v_n$, $v_n = 1, \dots, 22$, and hot bands $v_n \rightarrow v_n + 1$, $v_n = 1, \dots, 21$, are shown, respectively, in Figs. 5, 6 and 7, 8.

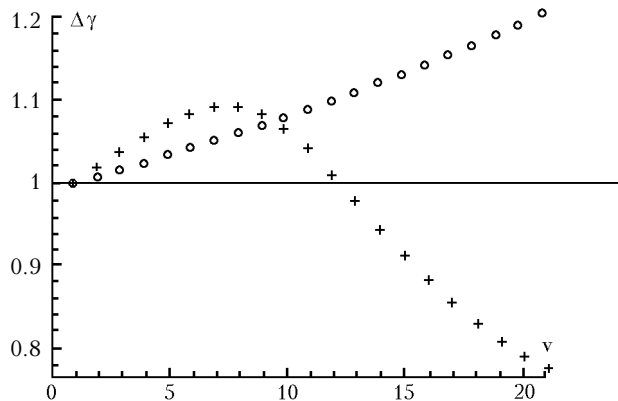


Fig. 5. Relative change of R_0 line halfwidth $\Delta\gamma$ vs. the vibrational quantum number.

Figure 5 depicts the relative change of the line halfwidths with all factors taken into account (crosses) and with regard for the change of only the rotational constant (circles). The calculations show that the vibrational dependence of the halfwidths is rather complicated: for $v = 0, \dots, 6$ the halfwidth somewhat increases (up to 8 percent), and with further increase of the transition energy the lines narrow by 25 percent as compared to the rotational band lines. This narrowing is caused by a fast decrease of the mean dipole moment (more than 10 times for $v = 22$), while the change of the rotational constant leads to the 22 percent increase in the line halfwidth.

Note that the Doppler halfwidth for the considered transitions is an order of magnitude smaller than the collisional halfwidth. We have also estimated the contributions to the line broadening from the dipole-quadrupole and quadrupole-quadrupole interactions in the repulsive part of the potential.

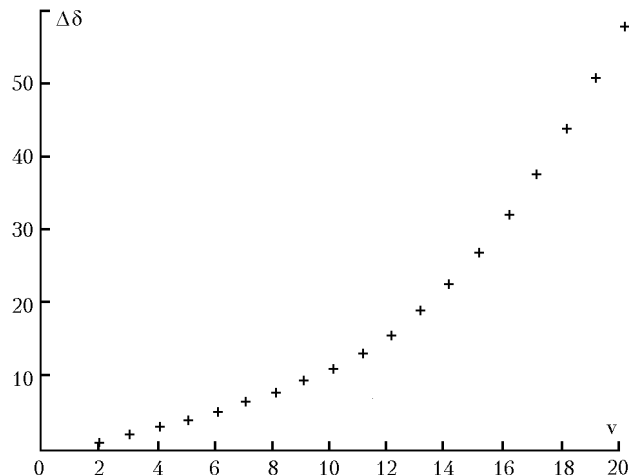


Fig. 6. Relative change of R_0 line shift $\Delta\delta$ vs. the vibrational quantum number.

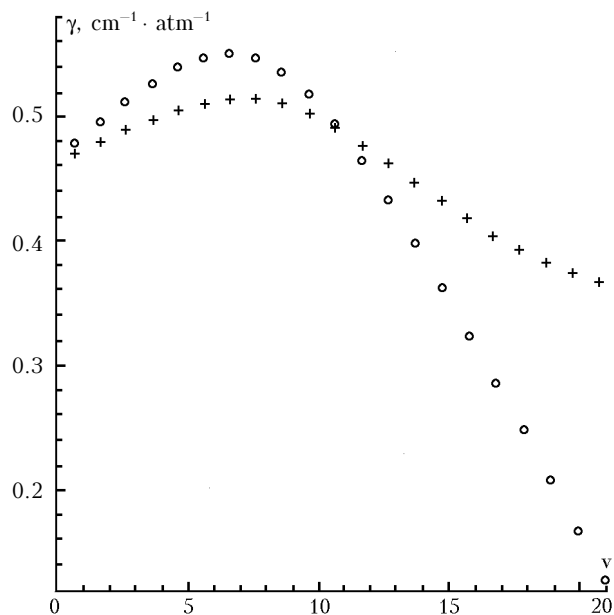


Fig. 7. R_0 line halfwidth for hot (circles) and cold (crosses) bands vs. the vibrational quantum number.

These contributions appeared to be less than 1 percent for all considered bands. The results obtained are in agreement with calculations of halfwidths for H_2O-N_2 [Ref. 1], in which the narrowing of H_2O absorption lines achieved 39 percent for some lines in the $5v_2$ band as compared to the same lines in the rotational band.

We have also estimated the shift of HF–HF lines taking into account the dipole-dipole and polarization (induction and dispersion) interactions in the approximation of the mean frequency (see Fig. 6).

The mean polarizability of the first six vibrational states of HF was taken from Ref. 13 (*ab initio* calculation), for other vibrational states up to $v = 22$ the mean polarizability was approximated by the quadratic polynomial (see Fig. 4). The function $S_1(b)$ calculated by Eq. (9) is shown in Fig. 9.

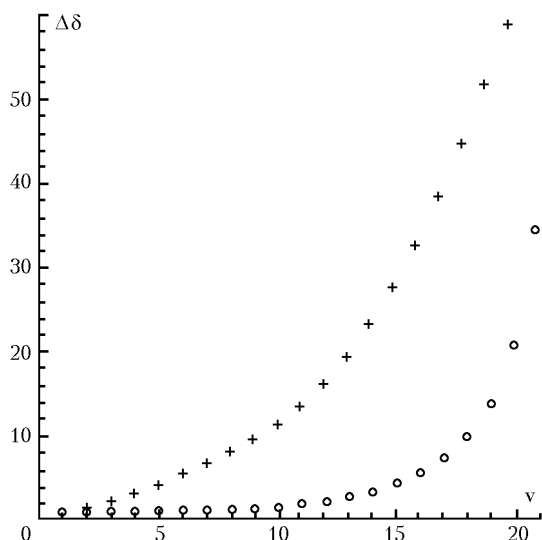


Fig. 8. Relative change of line shift $\Delta\delta$ for hot (circles) and cold (crosses) bands vs. the vibrational quantum number.

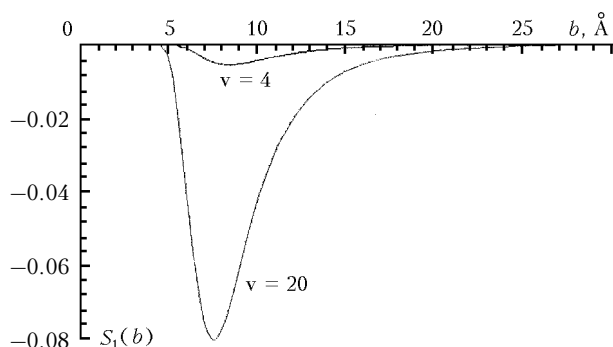


Fig. 9. Imaginary part of the efficiency function $S_{if}(b, v)$ for the R_0 transition and $v = 4, 20$ as a function of the impact distance.

It can be seen that the contribution to the line shift from $S_1(b)$ increases two orders of magnitude in the state $v = 20$ as compared to the state $v = 4$. The negative sign of the line shift is determined by the increase of polarizability α_f in the upper vibrational state of the transition (the function $S_1(b)$ given by Eq. (9) has the negative sign). This is in agreement with the measurements^{3,4} for the band 0–2. The estimates of the ratio of the line shift in the 0– v bands to the shift in the 0–2 band show that the shift increases 5 times in the 0–5 band (see Fig. 6). The shift estimates for higher vibrational bands cannot be considered as realistic, because the mean polarizability was calculated up to $v = 5$ and then extrapolated to higher vibrational states. In general, the change in the line shift (see Fig. 6) copies the increase of the mean polarizability (see Fig. 4). The line shift appears to be rather sensitive to variations

of the mean polarizability with the increase of the vibrational excitation of the absorbing molecule. This is in agreement with calculations and measurements for the shift of H_2O lines.²

The calculated data on the line halfwidth and shift for the hot transitions (circles) are shown in Figs. 7 and 8 in comparison with the data for the cold bands (crosses). It can be seen that the narrowing effect is even more pronounced: the halfwidths of higher bands decrease more than 5 times. The situation for line shifts is quite opposite: for the hot bands, the shifts do not change so strongly. This is obviously attributed to a smaller polarizability difference $\alpha_f - \alpha_i$ in S_1 [Ref. 9].

Conclusions

In this paper, we have estimated, for the first time, the changes of halfwidths and shifts of HF–HF lines due to a strong vibrational excitation of the molecule up to the dissociation threshold. The calculations have been carried out in the approximation, taking into account all main factors: change of the mean dipole moment and the strength of the dipole-dipole interaction, polarizability of the absorbing molecule, the adiabatic effect, and change of the rotational energy spectrum. It should be emphasized that we used the results of the *ab initio* calculations as initial data. Since the HF molecule has a high constant dipole moment, the main contributor is the dipole-dipole interaction, while the contributions of other interactions can be neglected. We have considered the case of self-broadening of the R_0 line (the mean frequencies (8) were taken just for this line, when the resonant energy exchange between the colliding molecules is observed).

The calculations have shown that the lines caused by transitions to high-excited vibrational states of the absorbing molecule, narrow due to the mean dipole moment decrease. The narrowing achieves 25 percent in the 0–22 band as compared to the 0–2 band. It should be expected that the changes in line halfwidths of other hydrogen halides would have some close values, because the dipole moment function changes similarly.⁷

In addition, this paper presents the estimates of changes in the HF–HF line shifts in the mean frequency approximation for high vibrational bands. The significant change in the shift is caused by the strong increase of the mean polarizability in high-excited vibrational states. The calculations show that the shift increases five times for the lines of the 0–5 band as compared to the 0–2 band.

The vibrational dependence of the halfwidth and shift has been estimated for the lines of the hot bands as well.

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