

INTERPRETATION OF THE SHIFT OF FREQUENCIES OF MOLECULAR LINES BY GAS PRESSURE

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For the $J = 1 \leftarrow 0$ transition in symmetric-top molecules, using all currently available data, we find that the ratio of the measured value of the self-shift of the line frequency to the calculated value depends smoothly on the relative interaction time of the molecules. These dependences are satisfied by nearly all known shifts of these lines by the pressure of extraneous gas of polar symmetric-top molecules, and also by the self-shifts of the frequencies of lines of a number of inversion transitions in ammonia.

The recently obtained experimental data on the frequency shifts of lines of the lowest rotational transitions ($J = 1 \leftarrow 0$) of symmetric-top molecules by gas pressure brought about the discovery of some experimental dependences which relate these shifts to the parameters of the molecules [1]. A successful, although knowingly simplified, interpretation of these data was given in [2, 3]. A further accumulation of experimental data confirmed and improved, on the one hand, the observed laws using twice the number of spectral lines. It also made it possible to obtain analogous dependences for the transitions between pairs of isolated levels and for line shifts by extraneous gases [4]. On the other hand, the experimental shifts for molecules CF_3H [5], CH_3CCH [6] and CH_3CN^* differ by a considerable factor from the quantitative value of the shift parameter† if one assumes that the sign and order of magnitude of the shift obtained from the Stark effect [8] and empirical dependences [1, 4] remain valid. All this indicated an advancement of the investigation and explanation of the shift of lines by pressure, as well as the inadequacy of the approximate description which agrees with only a part of the observed phenomena. In the present work, we obtain more accurate functional dependences of the shifts on the molecular parameters which, in combination with theory, make it possible to describe well all currently available experimental data on the self-shifts of the transitions $J = 1 \leftarrow 0$ of polar symmetric tops and inversion transitions of ammonia, and also some shifts of lines by the pressure of extraneous gas. We show a relationship between the dependences obtained in the present work and those obtained in [1, 4].

For the theoretical estimate of the magnitude of the shift parameter we shall confine ourselves to the known approximation of collision broadening and line shift for a classical oscillator. Following [9] we shall assume that the line shift (in the mono-velocity approximation) is equal to

$$\Delta\nu = (1/2\pi)Nv\sigma'' \quad (1)$$

or the shift parameter (i.e., the shift per unit pressure) is

$$\Delta\nu_c = (\Delta\nu/p) = (v\sigma''/2\pi kT), \quad (2)$$

where N is the density of molecules; v , relative velocity; $p = NkT$, gas pressure;

$$\sigma'' = 2\pi \int_0^\infty \sin \eta \rho d\rho; \quad (3)$$

η , increment of phase of the transition as a result of a collision with the perturbing molecule; and ρ , impact parameter.

If a perturbing molecule at a distance R from the molecule under study causes the frequency shift

$$\kappa = C_n R^{-n}, \quad (4)$$

then, following [9], one can obtain that

*The data on the shift parameter of this molecule were kindly made available to us by R. Shvendeman.

†For a comparison one can note that the calculated value of the shift parameter for the transition $J = 1 \leftarrow 0$ in molecules CH_3CCH [5] differs from the experimental value even in the sign of the shift.

$$\Delta\nu_c = \frac{1}{2kT} \Gamma\left(\frac{n-3}{n-1}\right) \left[\frac{\sqrt{\pi} \Gamma((n-1)/2)}{\Gamma(n/2)} C_n \right]^{2/(n-1)} v^{(n-3)/(n-1)} \sin \frac{\pi}{n-1} \quad (5)$$

(for $0 < 2/(n-1) < 1$), where Γ is the gamma function.

We shall assume that the dependence (4) is determined by the Stark effect of the levels participating in the transition in the field of the perturbing molecule [8]:

$$\kappa = 2\pi\epsilon B, \quad (6)$$

where ϵ is the magnitude of the shift of the energy levels averaged over the quantum numbers M , which will be approximated by the power dependence [3]

$$\epsilon = az^b. \quad (7)$$

The change of energy ϵ is expressed in the units of hB (where B is the rotational constant of the molecule and h is Planck's constant), and $z = \mu \mathcal{E} / hB$ (where μ is the dipole moment of the molecule and \mathcal{E} is the field intensity). For the perturbing field of a symmetric-top molecule we shall use the dipole approximation

$$\mathcal{E} = \mu_{\text{eff}} / R^3, \quad (8)$$

where μ_{eff} is the effective dipole moment of the molecule, equal to the average value of the projection of the dipole moment on the direction of the angular momentum of the molecule J :

$$\mu_{\text{eff}} = \langle \mu [K / \sqrt{J(J+1)}] \rangle. \quad (9)$$

It can be shown that after averaging over the rotational states we obtain for a symmetric-top molecule

$$\mu_{\text{eff}} \simeq \mu B^{1/2} / (A^{1/2} + B^{1/2}), \quad (10)$$

where A and B (C and B for an oblate top) are rotational constants of the molecule.

For the transitions $J = 1 \leftarrow 0$ of a symmetric top, $a = 0.174$ and $b = 1.65$. These values were found from the data of [19].* For the inversion transitions of ammonia, the calculations were carried out as for a pair of close levels. The data on the shifts of these transitions for $J = K$ can be found in [10]. Here, $b = 1.5$, and the value of a varies from 0.21 to 0.3 for $J = K$ from 1 to 5. The results of the calculation, together with the experimental data, are shown in Table 1 for those lines for which the experimental values of the shift and broadening parameters were available.

It is seen from Table 1 that the agreement of theory with experiment is not good. However, a further investigation makes it possible to observe an order in the data which includes in a natural way the experimental results which did not fit into the earlier empirical dependences [1, 4].

We introduce the relative interaction time of the molecules (the interaction time expressed in terms of the periods of the oscillation which corresponds to the frequency of the transition in question):

$$\tau = (R_0/v)/T_0 = R_0 v/v. \quad (11)$$

The value of R_0 is determined from the experimental broadening of the corresponding lines ($\Delta\nu_y$ is the half-width of the line per unit pressure) according to [11]:

$$R_0 = (2kT\Delta\nu_y/v)^{1/2}. \quad (12)$$

We now consider the ratio of the experimental shift to the calculated one $\Delta\nu_c^e/\Delta\nu_c$, as a function of the inverse interaction time introduced above (Fig. 1). The obtained points lie on a surprisingly smooth curve. In particular, even the points for CH_3CN , CH_3CCH , and CF_3H which did not fit earlier lie on this curve as well as the remaining points. The total number of points which include all shifts of the transitions $J = 1 \leftarrow 0$ of symmetric tops which have been measured up till now is 15. It is significant that these data were obtained at different times by more than ten groups of investigators. The observation of the functional dependence shown in Fig. 1 clearly indicates that all the currently available data can be described well, and that the methods used for the description of the line shifts by gas pressure must be corrected. It is possible that the reason why in some cases the calculation gives a too high magnitude of the shift for a short relative interaction time is due to the dependence of the Stark level shift on the duration of the interaction with the field. It is known that if the duration of the interaction with the field is smaller than the period of the oscillation which corresponds to the transition frequency, the Stark effect of the transition is considerably reduced [12]. This dependence agrees qualitatively with that obtained in Fig. 1. At the present time, clearly, one can only discuss the presence of yet another, more general, dependence which relates the spectral line shifts by gas pressure to the molecular parameters of the gas. This is the main aim of the present work.

*The shift of the $J = 1$ level is small and was neglected.

TABLE 1. Theoretical ($\Delta\nu_c$) and Experimental ($\Delta\nu_c^e$) Line Shifts by Gas Pressure

Molecule	Line	$\Delta\nu_c$, MHz/torr	$\Delta\nu_c^e$, MHz/torr	$\Delta\nu_y$, MHz/torr	$1/\tau$	$\Delta\nu_c^e/\Delta\nu_c$	Literature
PH ₃	$J = 1 \leftarrow 0$	1,77	0,56	5,3	3,04	0,32	[4]
AsH ₃	$J = 1 \leftarrow 0$	0,30	0,15	3,5	2,38	0,49	[4, 15]
NH ₃ *	$J = 1 \leftarrow 0$	8,14	5,85	13,5	1,32	0,72	[4]
CF ₃ H	$J = 1 \leftarrow 0$	22,2	2,28	34,0	8,91	0,10	[5, 13]
CH ₃ Cl	$J = 1 \leftarrow 0$	12,9	1	21,8	11,3	0,079	[6]
CH ₃ Br	$J = 1 \leftarrow 0$	10,1	0,85	17,2	11,0	0,083	[14]
CH ₃ I	$J = 1 \leftarrow 0$	7,93	0,7	14,0	11,4	0,087	[14]
CH ₃ CN	$J = 1 \leftarrow 0$	45,6	4,6	94,2	9,3	0,10	[20]
CH ₃ CCH	$J = 1 \leftarrow 0$	3,19	0,01	10,0	31,4	0,0032	[6]
NH ₃ *	$J = 1 \leftarrow 0$	8,44	5,75	13,5	1,48	0,68	[4]
PH ₃ †	$J = 1 \leftarrow 0$	1,80	0,56	5,3	3,17	0,31	[4]
NH ₃	$J = K = 4$	30,4	0,24	24	26,1	0,0079	[10, 16]
NH ₃	$J = K = 2$	28,4	0,29	22,3	28,1	0,010	[10, 20]
NH ₃	$J = K = 3$	29,7	0,33	24,8	26,4	0,011	[10, 16]
NH ₃	$J = K = 5$	30,9	0,24	24,7	25,8	0,0079	[10, 16]

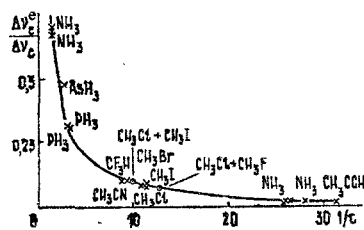
* $v_3 = 1$.† $v_2 = 1$.

Fig. 1

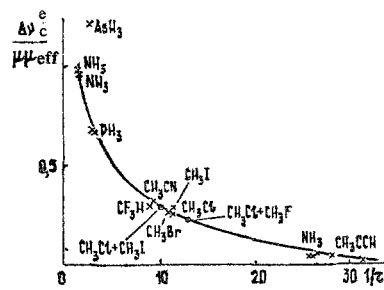


Fig. 2

Fig. 1. Ratio of the experimental value of the shift parameter of a spectral line by gas pressure $\Delta\nu_c^e$ to the calculated value $\Delta\nu_c$ according to [5], as a function of the inverse relative interaction time between the molecules τ [11]. The crosses show the corresponding self-shifts of molecules shown in Table 1. The circles show the corresponding line shifts by extraneous gases whose molecules are also polar symmetric tops.

Fig. 2. Ratio of the experimental value of the shift parameter of a spectral line by gas pressure $\Delta\nu_c^e$ and the product of the dipole moment of the molecule μ and the effective dipole moment μ_{eff} of the molecule (in relative units), as a function of the inverse interaction time of the molecules τ [11]. The transitions of the molecules and other notation are analogous to that of Fig. 1.

It is interesting to analyze now the relationship of the obtained results with the empirical laws obtained earlier. This will be done also for other cases of line shifts. We introduce, as we did in [3], the minimum impact parameter ρ_0 which is determined from the equality of the quantity ϵ to the magnitude of energy of the quantum of the transition. It is natural to assume that for $\rho < \rho_0$, the quantum state of the molecule is changed. Then in (3) one should integrate within the limits from ρ_0 to infinity. If $\eta(\rho_0) \ll 1$, $\sin \eta \approx \eta$, the obtained expression for the shift parameter $\Delta\nu_c$ coincides completely with the result of the calculation under identical assumptions, according to the method developed in [3]. The calculated formula has the form

$$\Delta\nu_c = (G/T)\mu\mu_{\text{eff}} \quad (13)$$

where G is a proportionality constant. On the other hand, it is known [9] that in the calculation of σ'' , the main contribution comes from collisions with the impact parameters $\rho \geq \rho_W$ (ρ_W is the Weisskopf radius determined from the condition that for $\rho = \rho_W$, the phase increment in one collision $\eta = 1$). It is interesting to note that ρ_W and ρ_0 do not differ by more than 12% for nearly all molecules considered here.

The values of $\Delta\nu_c$ calculated from (13) differ markedly from the experimental values but, again, if one constructs the functional dependence of $\Delta\nu_c^e/\mu\mu_{\text{eff}}$ on $1/\tau$, a smooth curve is obtained which is shown (in relative units) in Fig. 2. It is seen from Fig. 2 that only the point for the least polar molecule AsH_3 falls out somewhat, but even here the disagreement is less than 25%. The numerical values of a and b which are obtained in the approximation of the Stark shift of levels (7) affect only the magnitude of the coefficient G but do not distort the general form of the functional dependence in Fig. 2. If this functional dependence is approximated by a hyperbola, i.e.,

$$\Delta\nu_c^e/\mu\mu_{\text{eff}} \sim \tau, \quad (14)$$

one obtains the expression

$$\Delta\nu_c^e \sim \nu\mu\mu_{\text{eff}} M^{1/2} \quad (15)$$

which coincides with the form of the empirical dependence [1, 4] if the quantity R_0 is assumed constant and the dependence of μ_{eff} on the rotational constants is neglected. In principle, R_0 and μ_{eff} are different for different molecules but this dependence would be difficult to "guess" in the determination of empirical laws. However, even the approximation (14) is crude, and the main aim of this investigation is to demonstrate the relationship between the functional dependences obtained in the present work and those obtained earlier in [1, 4]. The use of the obtained results makes it possible, in particular, to correct the predictions of [1] for the shift parameters of lines $J = 1 \leftarrow 0$ of molecules CH_3F and PF_3 whose broadening parameters can be found in [20]. The corrected quantities are equal to +1.94 MHz/torr for CH_3F and +0.52 MHz/torr for PF_3 , independently of the choice of curves in Fig. 1 or Fig. 2.

We consider also the possibility of generalization of the obtained results to other shifts of molecular lines by gas pressure. It is natural to expect, in particular, that an argument analogous to the one above can be applied to the shift of the same lines by the pressure of an extraneous gas whose molecules are also of the polar symmetric-top type. Unfortunately, the available data here are few and partly contradictory. MacGillivray [18] gives data on the shift and broadening of the transition $J = 1 \leftarrow 0$ in CH_3Cl by the pressure of CH_3F and CH_3I . The calculations carried out for this case by the above method give results which agree well with the dependences obtained for the self-shift. For the pair $\text{CH}_3\text{Cl} + \text{CH}_3\text{F}$ the quantity $1/\tau = 12.8$, and the quantity $\Delta\nu_c^e/\Delta\nu_c = 0.07$. For the pair $\text{CH}_3\text{Cl} + \text{CH}_3\text{I}$ $1/\tau = 9.8$ and $\Delta\nu_c^e/\Delta\nu_c = 0.09$. These points are shown in Figs. 1 and 2. In a good agreement with the obtained dependences are the results of analysis of the shift and broadening [7] of the same transition $J = 1 \leftarrow 0$ in CH_3Cl by the molecules of CH_3Br . For this case $1/\tau = 10.1$ and $\Delta\nu_c^e/\Delta\nu_c = 0.11$ (the point is not shown in order not to obstruct the clarity of the graph). The signs and order of magnitude of the data on the shift of the transition $I_{01} - I_{10}$ of water H_2^{16}O , H_2^{17}O and H_2^{18}O by the pressure of ammonia NH_3 , which are given in [4] and are equal to +6.0 MHz/torr, +6.3 MHz/torr and +6.0 MHz/torr, respectively, also agree with the obtained dependences. However, the absence of data on broadening makes it impossible to analyze these data accurately and quantitatively by the above method. These data are contrasted by the information about the large negative shifts of the inversion lines of ammonia (with $J = K$) by the pressure of CH_3Cl , given in [17]. At the present time, we have no explanation of this result. Thus, one can conclude that the majority of the currently available data on the shift of lines by extraneous gases which were studied here, and whose molecules are polar symmetric tops, also agree with the laws obtained above from the data on self-shifts. It is desirable, however, to investigate this problem further.

The classification of the increasingly large volume of data on the shift of molecular lines by gas pressure makes it possible to display general laws for the shifts and indicates, in particular, the usefulness of the "Stark" approach to the interpretation of molecular lines by gas pressure, which was suggested in [8] and developed further in [1-4].

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CORRELATION CHARACTERISTICS OF SOUND IN A WAVEGUIDE WITH A STATISTICALLY ROUGH WALL

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A system of differential equations is derived for the amplitude correlation functions of the normal modes of the scalar field in a waveguide with a statistically rough wall. The correlation properties of the field in space and time variables are discussed.

A closed system of equations has been obtained previously [1] for the second moments of the amplitudes of the normal modes of a monochromatic field in a waveguide with a statistically rough wall. We now extend the results of [1] to the case in which the roughness heights depend not only on the spatial coordinates, but also on the time. The derived equations are used to analyze the behavior of the coherence function of the field with respect to the space and time variables.

Let us consider a waveguide formed by a perfectly compliant statistically rough surface $z = \zeta(x, y, t)$, where x, y, z are Cartesian coordinates and $\zeta(x, y, t)$ is a centered stochastic function homogeneous and isotropic with respect to the space variables, and by a perfectly rigid surface $z = D$. We assume that the sound velocity $c = c(z)$ depends on the coordinate z in the general case.

The scalar field $\Phi(x, y, z, t)$ satisfies the wave equation and the boundary conditions

$$(\partial/\partial z)\Phi(x, y, z, t)|_{z=D} = 0; \quad (1a)$$

$$\Phi(x, y, z, t)|_{z=\zeta(x, y, t)} = 0. \quad (1b)$$

Instead of the exact condition (1b) we apply to the centroidal plane $z = 0$ an approximate boundary condition valid for roughness heights that vary smoothly in space and time and are small in comparison with any characteristic space scales of the field $\Phi(x, y, z, t)$ [2]:

$$\left[\Phi(x, y, z, t) + \zeta(x, y, t) \frac{\partial}{\partial z} \Phi(x, y, z, t) \right]_{z=0} = 0. \quad (1c)$$

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