

The Study of Microwave Pressure Lineshifts

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The results of experimental investigations of pressure shifts and broadening of spectral lines of polar molecules performed in the submillimeter region by a microwave spectrometer RAD are reported. About 30 measurements were made of self-shift and foreign gas shift parameters of the lines of NH_3 , PH_3 , AsH_3 , and H_2O molecules including lineshifts in excited vibrational states, lineshifts of transitions connected by common levels, lines with various values of J and K quantum numbers, and the "forbidden" $|\Delta K| = 3$ lines. On the basis of the data obtained in this work and data available in the literature, new experimental dependences of lineshifts on molecular parameters are found. The results are well described by a simple "Stark effect" model of lineshifts. Some new directions of investigations are outlined.

The present paper describes some studies of pressure lineshifts of polar molecules carried out in the Institute of Applied Physics, Academy of Sciences of the USSR, Gorky. As noted in Refs. (1, 2) the number of experimental studies of pressure lineshifts carried out by microwave spectroscopy methods is not large and the results are in some cases contradictory; this creates some difficulties in theoretical treatment of this phenomenon. Our study was directed toward obtaining a greater amount of experimental data and to a search for some regularities connecting lineshifts to molecular parameters. The lineshifts were investigated by using the submillimeter microwave spectrometer RAD (3, 4). The absence of interference troubles, a wide range and high accuracy of frequency measurements, as well as the possibility of operations in a considerably broad pressure range, make RAD a very convenient technique for the study of pressure lineshifts. The method of investigating the lineshifts by the RAD is described, for instance, in Ref. (5). An example of experimental dependence of the spectral line frequency on pressure measured by using the RAD spectrometer is given in Fig. 1. Figure 2 displays a similar dependence of linewidth for the same transition.

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The study began by pointing out the coincidence in many cases of the measured sign of pressure self-shifts for some lines of polar molecules and the calculated sign of the Stark shift of the centers of the same lines (6). Examples of this may be, for instance, the positive (toward higher frequencies) pressure lineshifts of the transitions $J = 1 \leftarrow 0$ of polar symmetric tops (7-11) and the positive shifts of ammonia inversion transitions (12). The Stark effect, as is known, also shifts the line centers corresponding to the transitions $J = 1 \leftarrow 0$ and those between two close

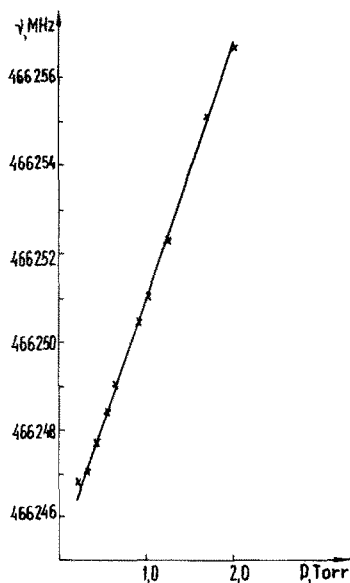


FIG. 1. Dependence of the measured frequency of the transition $a(0, 0) \leftarrow s(1, 0)$ in the state $v_2 = 1$ of $^{14}\text{NH}_3$ on ammonia pressure. The nonshifted frequency $\nu_0 = 466\,245.6$ MHz, the pressure lineshift parameter $\Delta\nu_s^p = +5.65$ MHz/Torr.

isolated levels toward higher frequencies (see, for example, Ref. (13)). An agreement between the signs of the Stark shift and pressure lineshifts can be more clearly illustrated by our measurements of both positive and negative self-shifts of the system of successive submillimeter transitions between rotational-inversion levels of the ammonia molecule $^{14}\text{NH}_3$ in the excited vibrational state $v_2 = 1$. The scheme of the transitions investigated is shown in Fig. 3 together with signs and values of measured self-shift parameters (lineshifts per pressure unit). The majority of shifts given in Fig. 3 can be simply understood using the "Stark" interaction model. Thus, the signs of shifts in the system of successive transitions $a(2, 1) \leftarrow s(2, 1) \leftarrow a(1, 1) \leftarrow s(1, 1)$ can be understood as a result of predominant "pushing apart" by Stark effect of closely situated levels $a(1, 1)$ and $s(2, 1)$, etc. Of course, more or less accurate calculation of shift parameters in the "Stark interaction model" during molecular collisions shifting the lines presents difficulties due to the proper choice of the averaged field strength for each molecular state (and, consequently, order of the Stark interaction), due to the averaging procedure over the quantum number M , due to the probable partial nonadditivity of shifts (see below), etc. It should be noted, however, that for at least several lower levels at constant K , accounting for the "simplest" second-order Stark effect on the assumption of the same field value for each level and use of common averaging procedure of matrix elements of the transition dipole moment over M (13) permits us to obtain the correct qualitative (and partially quantitative) picture of pressure lineshifts. In this way, we obtain, in particular, correct lineshift signs—positive for $a(0, 0) \leftarrow s(1, 0)$, $s(3, 0) \leftarrow a(2, 0)$, $s(2, 1) \leftarrow a(2, 1)$, $a(2, 2) \leftarrow s(2, 2)$ and negative for $a(1, 1) \leftarrow s(1,$

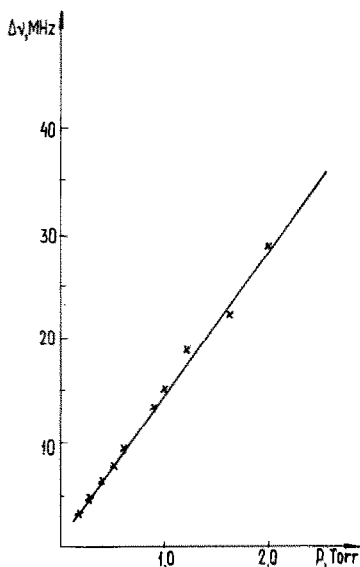


FIG. 2. Dependence of the linewidth (HWHM) of the transition $a(0, 0) \leftarrow s(1, 0)$ in the state $v_2 = 1$ of $^{14}\text{NH}_3$ on ammonia pressure. The broadening parameter $\Delta\nu_0 = 13.75 \text{ MHz/Torr}$.

1), $a(2, 1) \leftarrow s(2, 1)$, and $s(3, 2) \leftarrow a(2, 2)$ as well as the correct relation between values of lineshift parameters for some values of K . These results initiated attempts to search for some simple and possibly general dependences of parameters of lineshifts on molecular parameters and constituted the basis of a simple "Stark" working model of lineshifts, which permitted us to predict and describe in a simple way some cases of molecular pressure lineshifts. Such an approximate description served, of course, as simple heuristic "guidance to action" for obtaining facts for a more rigorous lineshift theory.

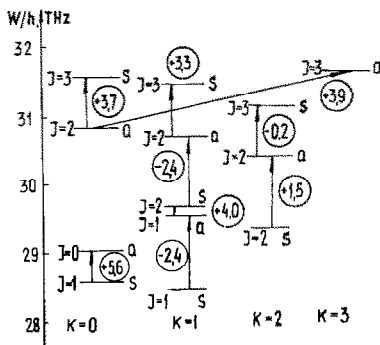


FIG. 3. A display of lower rotational-inversion levels of the state $v_2 = 1$ of $^{14}\text{NH}_3$. The observed transitions are shown by arrows. The values of measured parameters of ammonia pressure line self-shifts in MHz/Torr are given in circles. The sign + corresponds to a lineshift toward higher frequency.

TABLE I

The Relation between Self-Shift Parameters and Molecular Parameters
for Transitions $J = 1 \leftarrow 0$ of Polar Symmetric Tops

Mole- cule	Vibr. state	Transition frequency ν , GHz	Dipole moment μ Deb.	Shift parameter $\Delta\nu_s^e$ MHz/Torr	Mol. weight m a.m.u.	$r' = \frac{\Delta\nu_s^e}{\nu\mu^2m^{1/2}}$	References
$^{14}\text{NH}_3$	ground	572.49	1.459	+ 6.1	17	0.91	this work
$^{15}\text{NH}_3$	ground	572.11	1.459	+ 5.5	18	0.80	- " -
$^{14}\text{NH}_3$	$\nu_4 = 1$	645.74	1.459	+ 5.85	17	0.78	- " -
$^{14}\text{NH}_3$	$\nu_4 = 1$	577.33	1.459	+ 5.75	17	0.85	- " -
$^{14}\text{NH}_3$	$\nu_2 = 1$	466.25	1.250	+ 5.65	17	1.41	- " -
PH_3	ground	266.96	0.570	+ 0.56	34	0.83	[11]
PH_3	$\nu_2 = 1$	256.27	0.57	+ 0.56	34	0.87	[11]
AsH_3	ground	224.95	0.22	+ 0.15	78	1.17	[24]
CH_3Cl	ground	26.59	1.89	+ 1.0	50	1.12	[7]
CH_3Br	ground	19.14	1.80	+ 0.85	94	1.06	[9]
CH_3I	ground	15.00	1.65	+ 0.70	142	1.08	[9]

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The next stage was the analysis of experimental data on pressure lineshifts of the same lower rotational transitions $J = 1 \leftarrow 0$ in different polar symmetric tops (14) presented in Table I. Consideration of the data of Table I containing shifts of both submillimeter transitions measured by us and centimeter transitions of various molecules given in the literature showed that all of them can be described in a rough approximation by the simple empirical dependence:

$$\Delta\nu_s^e \approx r'\nu\mu^2m^{1/2}, \quad (1)$$

where ν is the transition frequency, μ^2 is the squared molecular dipole moment, m is the molecular weight, and r' is some coefficient. The value r' remains constant for all molecules in Table I within 20%, though the values ν , μ , and m are sometimes very different. It seems improbable that such a coincidence is only accidental. Certainly, the empirical dependence (1) must be considered as an approximate one and probably as not accounting for a number of smaller effects. Thus, later we will have to know experimental parameters of the self-shifts of the same lines of molecules CF_3H (15), CH_3CCH (7), and CH_3CN (16) which also preserved the positive

sign but were up to several times different from the values predicted by the use of Eq. (1). We shall discuss this point somewhat later.

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To interpret the empirical dependence (1) and obtain the theoretical estimations of the self-shift parameters we made an attempt to use the known collisional broadening and shift approximation of the classical oscillator (17) with "Stark" perturbation. The lineshift according to Ref. (17) in the monovelocity approximation equals

$$\Delta\nu = Nv \int_0^\infty \sin \eta \cdot \rho d\rho \quad (2)$$

or the shift parameter

$$\Delta\nu_s = \frac{\Delta\nu}{p} = \frac{v}{kT} \int_0^\infty \sin \eta \cdot \rho d\rho, \quad (3)$$

where N is the molecular density, v is the relative velocity, $p = NkT$ is the gas pressure, η is the phase change of the transition frequency resulting from collision with a perturbing molecule, and ρ is the impact parameter. If the perturbing molecule, being at the distance R from the absorbing molecule, shifts the frequency transition of the latter as

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

then according to Ref. (17) one obtains for $0 < 2/(n-1) < 1$:

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

where Γ is the gamma function.

Assume that the dependence (4) is determined by the Stark shift of transition levels in the field of the perturbing molecule

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

where B is the rotational constant, ϵ is the resulting shift of energy levels expressed in hB units and averaged over quantum numbers M , which can be obtained from Ref. (18) and approximated by the dependence

$$\epsilon = az^b, \quad z = \frac{\mu E}{hB}, \quad (7)$$

where E is the electric field intensity. For the transitions $J = 1 \leftarrow 0$ in symmetric tops under consideration $a = 0.174$ and $b = 1.65$; here we took into account only the larger shift of the lower level $J = 0$, while the shift of the level $J = 1$ was neglected due to its relative smallness. For the perturbing field of a symmetric-top molecule in the dipole approximation

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

where μ_{eff} is the effective dipole moment of the perturbing molecule equal to the mean dipole moment projection on the direction of momentum J ; for a symmetric-

TABLE II

Calculated $\Delta\nu_s^c$ and Experimental $\Delta\nu_s^e$ Parameters of Pressure Self-Shifts of the Molecular Lines

Molecule	Line	$\Delta\nu_s^c \frac{\text{MHz}}{\text{Torr}}$	$\Delta\nu_s^e \frac{\text{MHz}}{\text{Torr}}$	$\Delta\nu_s^c \frac{\text{MHz}}{\text{Torr}}$	$1/\tau$	$\frac{\Delta\nu_s^e}{\Delta\nu_s^c}$	References
$^{14}\text{NH}_3$	J=1-0	+8.50	+6.1	16	1.37	0.72	this work
PH_3	J=1-0	+1.77	+0.56	5.3	3.04	0.32	[11]
AsH_3	J=1-0	+0.30	+0.15	3.5	2.38	0.49	[24]
$^{15}\text{NH}_3$	J=1-0	+8.51	+5.6	13.5	1.50	0.65	this work
$^{14}\text{NH}_3^a$	J=1-0	+8.14	+5.85	13.5	1.32	0.72	- " -
CF_3H	J=1-0	+22.2	+2.28	34.0	8.91	0.10	[8,15]
CH_3Cl	J=1-0	+12.9	+1.0	21.8	11.3	0.079	[7]
CH_3Br	J=1-0	+10.1	+0.85	17.2	11.0	0.083	[9]
CH_3I	J=1-0	+7.93	+0.70	14.0	11.4	0.087	[9]
CH_3CN	J=1-0	+45.6	+4.60	94.2	9.30	0.10	[16,1]
CH_3CCH	J=1-0	+3.19	+0.01	10.0	31.4	0.0032	[7]
$^{14}\text{NH}_3^a$	J=1-0	+8.44	+5.75	13.5	1.48	0.68	this work
PH_3^b	J=1-0	+1.80	+0.56	5.3	3.17	0.31	[11]
$^{14}\text{NH}_3$	J=K=4	+30.4	+0.24	24.0	26.1	0.0079	[12,26]
$^{14}\text{NH}_3$	J=K=2	+28.4	+0.29	22.3	28.1	0.010	[12,1]
$^{14}\text{NH}_3$	J=K=3	+29.7	+0.33	24.8	26.4	0.011	[12,26]
$^{14}\text{NH}_3$	J=K=5	+30.9	+0.24	24.7	25.8	0.0079	[12,26]

^a $v_4 = 1$ ^b $v_2 = 1$

top molecule after averaging over rotational states

$$\mu_{\text{eff}} = \left\langle \mu \frac{|K|}{(J(J+1))^{1/2}} \right\rangle \cong \mu \frac{B^{1/2}}{A^{1/2} + B^{1/2}}, \quad (9)$$

where A and B (C and B for an oblate top) are rotational constants of the molecule.¹ The results of calculating the lineshifts of transitions, for which experimental parameters of shift and broadening were available, are given in Table II.

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Table II shows the absence (apart from sign of shifts) of any good agreement, in general, between calculated and experimental values of the shift parameters.

¹ It particularly appeared that the use of μ_{eff} in the case of symmetric tops permitted us to describe experimental results more accurately. Molecules of other types need further consideration.

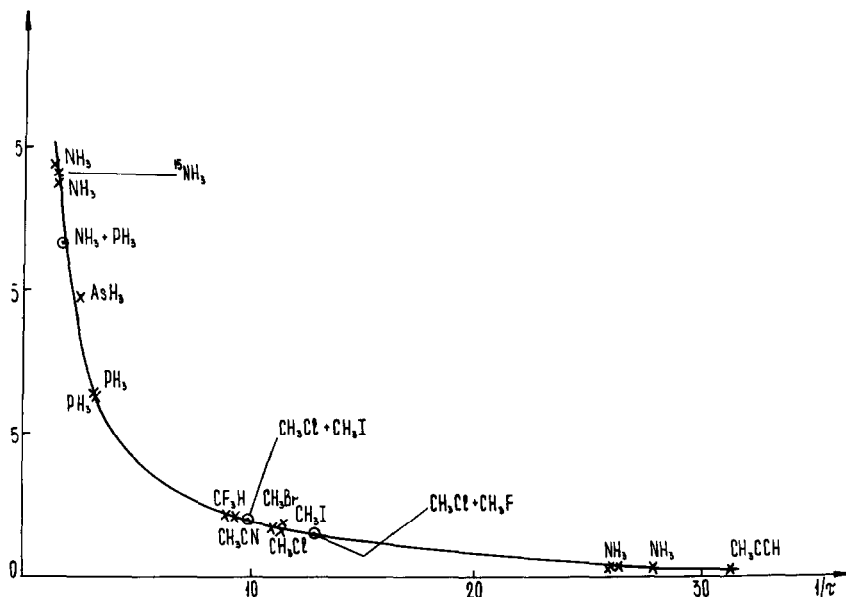


FIG. 4. Dependence of the ratio $\Delta\nu_S^e/\Delta\nu_S^c$ of the experimental value of pressure lineshift $\Delta\nu_S^e$ to the calculated value $\Delta\nu_S^c$ (from Eq. (5)) on the inverse of the relative interaction time of the molecules τ (10); \times , points corresponding to the molecular line self-shifts presented in Table II; \circ , are points corresponding to lineshifts by foreign gases also belonging to polar symmetric tops.

However, further consideration permits to find some regularities in the results obtained, including also the data of Refs. (7, 15, 16). Let us introduce in the usual way the relative time of molecular interaction expressed in corresponding transition frequency periods as

$$\tau = R_0 \nu v^{-1}, \quad (10)$$

R_0 is determined here from the experimentally measured broadening parameter $\Delta\nu_B^e$ of the corresponding lines ($\Delta\nu_B^e$ is the half-width of the line at the half-intensity level per pressure unit) according to Ref. (13) as

$$R_0 = \left(\frac{2kT\Delta\nu_B^e}{v} \right)^{1/2}. \quad (11)$$

The dependence of the ratio of measured to calculated shift parameters $\Delta\nu_S^e/\Delta\nu_S^c$ on the inverse value of the relative time of interaction introduced earlier is plotted in Fig. 4. One can see that the points obtained fall well on an unexpectedly smooth curve also displayed in Fig. 4; in particular, the points corresponding to the lineshifts of CF_3H , CH_3CCH , and CH_3CN , poorly described earlier by Eq. (1), also fall well on the same curve as others. The total number of points including all the shifts of the transitions $J = 1 \leftarrow 0$ of symmetric tops measured to this time are 12; note that the experimental data were obtained at different times by different investigators. The dependence given in Fig. 4 indicates, apparently, the possibility of a

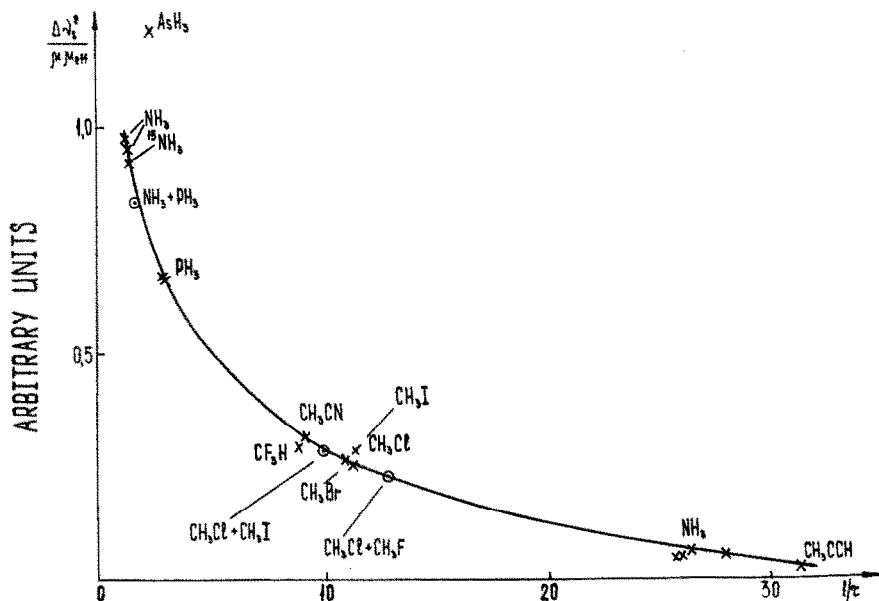


FIG. 5. Dependence of the ratio $\Delta\nu_S^0/\mu\mu_{\text{eff}}$ of the experimental value of the shift parameter $\Delta\nu_S^0$ to the product of the dipole moment of the absorber molecule μ with the effective dipole moment of the perturber molecule μ_{eff} (9) on the inverse of the relative interaction time of the molecules τ (10). Other symbols are analogous to those given in Fig. 4.

good description of pressure lineshifts by corrected calculation methods. It is possible that the situation, when calculation gives overestimated shift values for short relative interaction times, is associated with the dependence of Stark shift of levels on the time of interaction with the field.² It is known, that for an interaction time less than the transition frequency period, the Stark effect significantly decreases (19). This agrees at least qualitatively with the dependence in Fig. 4.

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It is interesting to outline the relation between the results obtained in the preceding section and the empirical dependence Eq. (1) formulated earlier. For demonstration purposes it is convenient to introduce some simplifications, namely: we shall integrate in Eq. (3) from some ρ_0 and assume (roughly) that for the region $\rho > \rho_0$, $\sin \eta \simeq \eta$. The value ρ_0 in Ref. (20) was determined by us from the condition that at $\rho = \rho_0$, ϵ is equal to the energy of the quantum of transition investigated (it seems natural to assume that at $\rho < \rho_0$ the quantum state of the molecule changes). Note that the values of ρ_0 obtained in such a way for nearly all molecules considered coincide closely (within the limits of 12%) with the Weisskopf radius ρ_w determined, as is known, from the condition that at $\rho = \rho_w$ the phase change

² Another reason can be a change of the relation between the number of elastic and inelastic collisions of molecules.

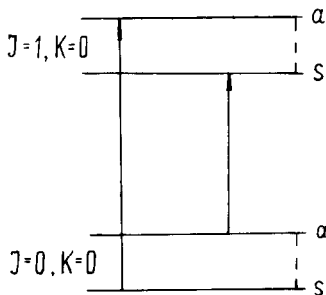


FIG. 6. A display of energy levels of $^{14}\text{NH}_3$ in the degenerate vibrational state $v_4 = 1$ for inversion-rotational transitions $^a_s(1, 0) \leftarrow ^s_a(0, 0)$.

in collision $\eta = 1$. The resulting formula has the form

$$\Delta\nu_S^c = \frac{G}{T} \mu\mu_{\text{eff}}, \quad (12)$$

where G is some coefficient. The values $\Delta\nu_S^c$ calculated according to Eq. (12) also differ strongly from the measured ones, but again, when constructing the dependence $\Delta\nu_S^c/\mu\mu_{\text{eff}}$ on τ^{-1} , we obtain a smooth curve plotted (in relative units) in Fig. 5. This figure shows that only one point falls off the curve, namely, that for AsH_3 molecule, having the smallest dipole moment. Nevertheless the difference from the smooth curve amounts to no more than 25%. The numerical values of a and b obtained with the approximations of Eq. (7) affect only the coefficient G but not the general appearance of the curve in Fig. 5.

If we approximate now the dependence given in Fig. 5 by a hyperbola, i.e.,

$$\Delta\nu_S^c/\mu\mu_{\text{eff}} \sim \tau, \quad (13)$$

then, on the assumption that R_0 is constant and the dependence of μ_{eff} on rotational constants is not taken into account, the expression for $\Delta\nu_S^c$ coincides with the empirical dependence in Eq. (1). Actually μ_{eff} and R_0 are different for different molecules, but it was difficult to "guess" this dependence empirically.

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At the next stages of investigation we made some attempts to apply the results obtained to other cases of pressure lineshifts and conducted corresponding experimental investigations, the results of which are described below.

(A) The relations mentioned above agree with the self-shifts of inversion transitions of the ground vibrational state of the ammonia molecule at $J = K$ measured in Ref. (12). Constants in Eq. (7) calculated in the approximation of a pair of isolated levels are: $b = 1.5$ and a from 0.21 to 0.3 for $J = K$ from 1 to 5. The obtained values $\Delta\nu_S^c/\Delta\nu_S^c$ and $\Delta\nu_S^c/\mu\mu_{\text{eff}}$ for the transitions studied in Ref. (12) are also given in Table II and displayed in Figs. 4 and 5. Both calculated and measured signs of shifts are positive and their values agree well with the dependences obtained earlier, in particular, with the empirical one of Eq. (1). Moreover, the experiments

performed by us show the absence of an appreciable mutual pressure shift for a pair of close levels, if the matrix element of the dipole moment of the transition between them is equal to zero. The scheme of the levels used for such an experiment is shown in Fig. 6. These levels are $J = 1$, $K = 0$, and $J = K = 0$ of the ammonia molecule $^{14}\text{NH}_3$ in the excited vibrational state $\nu_4 = 1$. In the degenerate vibrational state ν_4 at $K = 0$ both inversion levels a and s are present, but purely inversion transitions between them (shown in Fig. 6 by a dotted line) are forbidden, since the matrix element of the dipole moment for them at $K = 0$ turns out to be zero. We observed pressure shifts of the inversion-rotational transitions shown in Fig. 6 by solid arrows. The results of our measurements are presented as circles in Fig. 6. The difference between the shifts of these transitions must be equal to the sum of pressure shifts of the inversion splitting levels. At the same time the measured shift of both inversion-rotational transitions coincide within the limits of experimental errors: $\Delta\nu_s^c = +5.85 \pm 0.15$ MHz/Torr for $a(1, 0) \leftarrow s(0, 0)$ and $\Delta\nu_s^c = +5.75 \pm 0.25$ MHz/Torr for $s(1, 0) \leftarrow a(0, 0)$, i.e., the resulting shift of both inversion transitions is $+(0.1 \pm 0.3)$ MHz/Torr. The results obtained agree well with the "Stark" model of pressure lineshifts where the transitions only slightly displaced by the Stark effect must also be weakly shifted by gas pressure independent of the form of the perturbing molecules.

(B) It was natural to expect within the "Stark" model approach, that dependences analogous to those obtained for self-shifts of the lines of polar symmetric tops must exist also for the same lineshifts by foreign gas pressure, if molecules of the perturber are also polar symmetric tops. In this case in Eq. (12) and similar expressions, μ will correspond to the dipole moment of the absorbing molecule, and μ_{eff} to the perturbing one. To perform the analysis we used experimental data on shift and broadening of the transition $J = 1 \leftarrow 0$ of CH_3Cl by pressure of CH_3F , CH_3Br , CH_3I given in Refs. (21, 22), and measured shifts and broadening of the transitions $J = 1 \leftarrow 0$ in molecules $^{14}\text{NH}_3$, $^{15}\text{NH}_3$ by pressurizing with ammonia (NH_3) and phosphine (PH_3). The results of measurements and calculations are given in Table III. Points for the pairs $\text{CH}_3\text{Cl} + \text{CH}_3\text{F}$, $\text{CH}_3\text{Cl} + \text{CH}_3\text{I}$, $^{15}\text{NH}_3$

TABLE III

Calculated $\Delta\nu_s^c$ and Experimental $\Delta\nu_s^c$ Shift Parameters of Transitions $J = 1 \leftarrow 0$ of Symmetric Tops by the Pressure of Foreign Gas, Molecules of Which Also Belong to Polar Symmetric Tops

Invert. molecule	Line	Foreign gas	$\Delta\nu_s^c$ MHz/Torr	$\Delta\nu_s^e$ MHz/Torr	$\Delta\nu_b^e$ MHz/Torr	$1/\tau$	$\frac{\Delta\nu_s^e}{\Delta\nu_s^c}$	References
CH_3Cl	$J=1 \leftarrow 0$	CH_3F	+ 16.6	+ 1.14	24.4	12.8	0.069	[21]
CH_3Cl	$J=1 \leftarrow 0$	CH_3I	+ 8.75	+ 0.79	16.9	9.8	0.090	[21]
CH_3Cl	$J=1 \leftarrow 0$	CH_3Br	+ 10.5	+ 1.1	19.1	10.1	0.105	[22]
$^{14}\text{NH}_3$	$J=1 \leftarrow 0$	PH_3	+ 3.40	+ 1.86	7.6	1.65	0.55	this work
$^{15}\text{NH}_3$	$J=1 \leftarrow 0$	PH_3	+ 3.40	+ 1.67	6.3	1.81	0.49	- " -

TABLE IV

Experimental Values of Shift Parameters of Transitions $1_{01} \leftarrow 1_{10}$ of Water H_2^{16}O and H_2^{18}O by Ammonia and Phosphine Pressure

Molecule	Transition	Frequency (GHz)	$\Delta\nu_S^e(\text{NH}_3)$ (MHz/Torr)	$\Delta\nu_S^e(\text{PH}_3)$ (MHz/Torr)	$\frac{\Delta\nu_S^e(\text{NH}_3)}{\Delta\nu_S^e(\text{PH}_3)}$
H_2^{16}O	$1_{01} \leftarrow 1_{10}$	556.9	+5.9	+1.6	3.7
H_2^{18}O	$1_{01} \leftarrow 1_{10}$	547.7	+6.1	+1.4	4.4

+ NH_3 , $^{15}\text{NH}_3$ + PH_3 are also represented in Figs. 4 and 5; the point for CH_3Cl + CH_3Br is not plotted because of lack of space. It is seen that these results agree well with those obtained earlier for the case of the self-shift of polar symmetric-top lines.

To increase the amount of experimental data in this field we analyzed also the data measured by us earlier on water vapor when it was present as an impurity during the investigations of the ammonia and phosphine spectra. These data together with measurements of Ref. (23) permitted us to determine the shift values of lines $1_{1,0} \leftarrow 1_{0,1}$ of the molecules H_2^{16}O and H_2^{18}O by perturbed ammonia and phosphine, and are given in Table IV. These lineshift data are certainly less accurate and data on broadening of these lines are absent; thus a complete analysis is impossible. However, both the sign and the values of the shifts agree well with the empirical dependence Eq. (1) modified for foreign gas shifting (27) and the ratio of lineshifts by ammonia and phosphine is close to the ratio of the effective dipole moments of these molecules. We believe that the results obtained contribute also to reliability of the approximate model of pressure lineshifts used in the present paper.

(C) We investigated pressure self-shifts of separate components of the quadrupole hyperfine structure of the arsine transition $J = 1 \leftarrow 0$ at a frequency ~ 225 GHz (24). The quadrupole structure is due to the ^{75}As nucleus having a spin $I = 3/2$. The results of measurements given in Table V show that within the ex-

TABLE V

Experimental Values of Self-Shift Parameters of Separate Components of the Quadrupole Structure of the AsH_3 , $J = 1 \leftarrow 0$ Transition

Transition $F' \leftarrow F$	Frequency of center of nonshifted line ν_0 , MHz	Pressure shift parameter $\Delta\nu_S^e$, MHz/Torr
$3/2 \leftarrow 3/2$	224896.866	+ 0.149(20)
$5/2 \leftarrow 3/2$	224937.787	+ 0.150(20)
$1/2 \leftarrow 3/2$	224969.860	+ 0.154(20)

TABLE VI

Parameters of Lineshift and Line Broadening of PH_3 $J = 1 \leftarrow 0$ Transition by Pressure of Inert Gases. $\Delta\nu_s^e$ and $\Delta\nu_b^e$ are Experimental Values, $\Delta\nu_s^c$ are Calculated Values

Foreign gas	$\Delta\nu_b^e$ MHz/Torr	$\Delta\nu_s^e$ MHz/Torr	$\Delta\nu_s^c$ MHz/Torr	$1/\tau$	$\frac{\Delta\nu_s^e}{\Delta\nu_s^c}$
He	2.9(3)	+0.039(20)	+0.15	13.6	0.26
Ne	2.6(3)	+0.045(20)	+0.12	5.6	0.38
Ar	3.4(3)	+0.109(30)	+0.17	3.7	0.63
Xe	3.8(3)	+0.142(50)	+0.21	2.6	0.68

perimental errors, the shifts are equal for all three line components. This result seems also natural, since molecular interactions leading to the shifts must be strong in comparison with the quadrupole splitting, and in this case Stark energy values are the same as those in the case of absence of hyperfine quadrupole structure. Indirect proofs of the shift independence (in the first approximation) of the hyperfine structure of the lines are also the close coincidence of the shift parameters for the transitions $J = 1 \leftarrow 0$ of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ by phosphine pressure and the self-shift parameters of an analogous transition of the same molecules in both the ground and excited $v_2 = 1$ vibrational states.

(D) We investigated the pressure shift of the transition $J = 1 \leftarrow 0$ of the phosphine molecule, PH_3 , at a frequency ~ 267 GHz by pressure of various inert gases—He, Ne, Ar, Xe (20). In this case, the field producing the shifts of the levels in the Stark model must be created by the dipole moment induced by a polar molecule in an inert gas atom and one can expect that the sign of the lineshift must remain the same as in the self-shift case, while the shift parameter decreases; greater values of the polarizability of an inert gas atom must correspond to greater pressure shifts. To measure smaller shift values we used the following method. At the beginning of each experiment we filled an evacuated absorbing cell with phosphine (absorber) to some pressure $p \cong 0.1$ Torr which was the initial pressure for this experiment and measured the frequency of the transition $J = 1 \leftarrow 0$. Then we added an inert gas (perturber) within a pressure interval up to 2.5 Torr and again measured the phosphine transition frequency. Such a method permitted us to exclude the line self-shift contribution due to phosphine, since the partial pressure of the latter did not vary during one experiment and allowed us to determine the shift parameter due to inert gas pressure only. The data obtained are given in Table VI together with shift parameters calculated according to Eq. (5). Figure 7 displays the dependence $\Delta\nu_s^e/\Delta\nu_s^c$ on τ^{-1} for this case, which resembles those given in Figs. 4 and 5. It can be seen that the general behavior of the calculated values of the lineshifts agrees qualitatively (but not quantitatively) with the experimental one.

(E) One more direction of our study was the investigation of the dependence

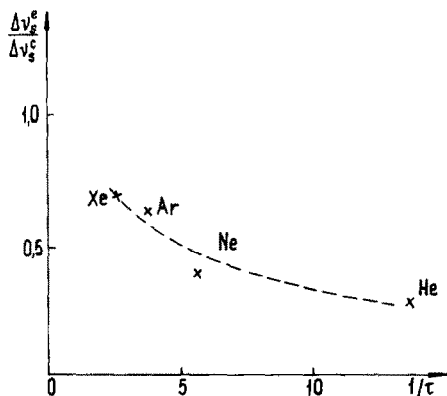


FIG. 7. Dependence of the ratio of the measured shift $\Delta\nu_s^e$ of the line $J = 1 \leftarrow 0$ of PH_3 caused by pressure of inert gases to its calculated value $\Delta\nu_s^c$ on the inverse of the relative interaction time τ (10). Points corresponding to various gases (Xe, Ar, Ne, He) are marked in the figure.

of pressure shifts of rotational lines of polar symmetric tops on values of the J and K quantum numbers. Due to a wide frequency range of the spectrometer RAD we obtained systematic experimental data on self-shifts of rotational lines of PH_3 and AsH_3 corresponding to transitions from $J = 1 \leftarrow 0$ to $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$, and to various values of K including $K = 0$ and $K = J$. The greater intensity of PH_3 lines permitted us to obtain a greater accuracy of measurements, while a smaller value of the rotational constant B for AsH_3 permitted us to perform measurements in a greater interval of J quantum numbers. Figure 8 represents the measured values of self-shift parameters for transitions $J + 1 \leftarrow J$, $K = 0$ of AsH_3 normalized to the self-shift parameter for the transition $J = 1 \leftarrow 0$ which is equal

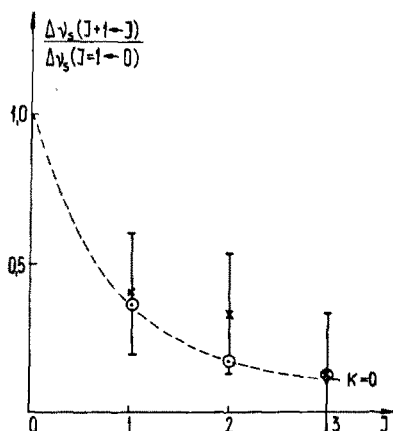


FIG. 8. Dependence of the normalized parameter of pressure spectral line self-shift on the quantum number J for transitions $J + 1 \leftarrow J$, $K \leftarrow K = 0$ of AsH_3 . \times , Experimental points; \circ , points calculated in the "Stark" shift model. Dotted lines mean "continuous" approximations of calculated dependences on J . The experimental errors are indicated in the figure.

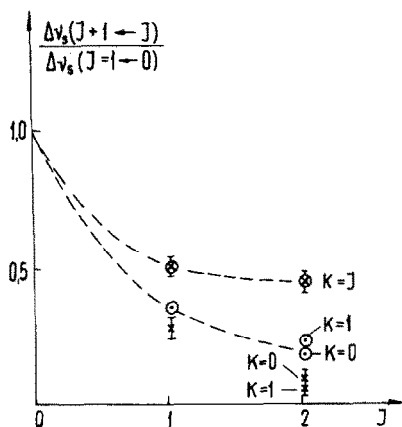


FIG. 9. Dependence of the normalized parameter of pressure spectral line self-shift on the quantum number J for transitions $J + 1 \leftarrow J$, $K \leftarrow K$ of PH_3 . \times , Experimental points; \circ , points calculated in the "Stark" shift model. Dotted lines mean "continuous" approximations of calculated dependences on J for the cases $K = 0$ and $K = J$. The experimental errors are indicated in the figure.

to $+0.15$ MHz/Torr. Figure 9 also shows the normalized line self-shift values for transitions $J + 1 \leftarrow J$, $K \leftarrow K$ of the phosphine molecule. Absolute values of the self-shift parameters for these transitions of PH_3 are given in Table VII.

The results of measurements show that for the polar symmetric-top molecules: (a) the self-shift sign remains positive, while the shift value greatly decreases with increase of J at least within the interval of J quantum numbers from 0 to 3 and (b) the self-shift values for transitions with $K = 0$ decrease with increase of J more rapidly than for transitions with $J = K$. Positive signs of shifts and the tendency of shifts to decrease with increase of J are also in agreement with results of Ref. (8), obtained for transitions $J = 1 \leftarrow 0$ and $J = 2 \leftarrow 1$ of CH_3I . However, our

TABLE VII

Experimental Values of Pressure Line Self-Shift Parameters for Transitions $J + 1 \leftarrow J$, $K \leftarrow K$ of the PH_3 Molecule

Transition		Shift parameter
$J+1 \leftarrow J$	K	$\Delta \nu_s^e$, KHz/Torr
1 \leftarrow 0	0	+ 560 /15/
2 \leftarrow 1	0	+ 147 /15/
2 \leftarrow 1	1	+ 275 /15/
3 \leftarrow 2	0	+ 42 /15/
3 \leftarrow 2	1	+ 38 /15/
3 \leftarrow 2	2	+ 245 /15/

TABLE VIII

Experimental Values of Nonshifted Frequencies ν_0 , Self-Shift Parameters $\Delta\nu_S^0$, and Self-Broadening Parameters $\Delta\nu_B^0$ of Allowed $s(3, 0) \leftarrow a(3, 0)$ and "Forbidden" $a(3, 3) \leftarrow a(2, 0)$ Transitions in the State $v_2 = 1$ of the $^{14}\text{NH}_3$ Molecule

Transition	Frequency ν_0 (MHz)	$\Delta\nu_S^0$ (MHz/Torr)	$\Delta\nu_B^0$ (MHz/Torr)
$s(3, 0) \leftarrow a(2, 0)$	769,710.1	$+3.69 \pm 0.1$	11.8 ± 0.5
$a(3, 3) \leftarrow a(2, 0)$	772,593.6	$+3.86 \pm 0.15$	10.9 ± 1.0

results do not agree with the experimental data of Ref. (8) which showed a greater value of the shift parameter for the transition $J = 2 \leftarrow 1, K = 0$ compared with the shift parameter for the transition $J = 2 \leftarrow 1, K = 1$ nor with the calculated data of Ref. (8) which predicted a greater value of the shift parameter for the transition $J = 2 \leftarrow 1, K = 1$ as compared to the shift parameter for the transition $J = 1 \leftarrow 0, K = 0$.

Of interest is a comparison of experimental data with estimations obtained with the "Stark" model. Consider first a qualitative picture. In the case of line self-shift of the lines of the same molecule differing only by quantum numbers J and K , a number of parameters affecting the shift values are constant and shift differences should be determined mainly by the differences in the Stark shifts of levels during molecular interaction. Note at once that a first-order Stark effect does not shift line centers and should not be taken into account (6). Moreover, a second-order Stark effect does not shift line centers either for levels with $K = 0$ with the exception of the lowest $J = K = 0$ level (13) and it is necessary to take into account higher orders of perturbation for them. As is known (13), Stark effect decreases with increase of J conserving "on average" the character of "pushing centers of levels apart," i.e., a positive sign of lineshifts. An absolutely highest shift value should belong here to the lowest rotational transition $J = 1 \leftarrow 0, K = 0$. The lowest transitions in level groups with the same $K \neq 0$ are of the form $J + 1 \leftarrow J, K \leftarrow K = J$, for which the greatest shifts for given K values can be expected, and for which shifts also decrease with increase of J . All these qualitative dependences agree well with experimental data of Table VIII.

Calculation of shift parameters for transitions $J + 1 \leftarrow J, \Delta K = 0$ of the PH_3 and AsH_3 molecules gives a complete qualitative and in the majority of cases quantitative agreement with experiment. The calculated values of shift parameters normalized to the shift parameter of the transition $J = 1 \leftarrow 0$ are also represented in Figs. 8 and 9. The calculation was carried out by formula (5); an approximation of the form (7) was performed according to the calculations of Ref. (19); to simplify calculations it was assumed in each case that the Stark shift of the upper level in the transition averaged over quantum numbers M can be neglected to a first approximation compared with the lower-level shift. As can be seen from Figs. 8 and 9, calculated and measured values for transitions of AsH_3 with $K = 0$ agree within experimental errors; they also agree well for PH_3 transitions with $K = J$. There is some difference only for PH_3 transitions with $K = 0$ and $K = 1$ for $J = 2$ whose

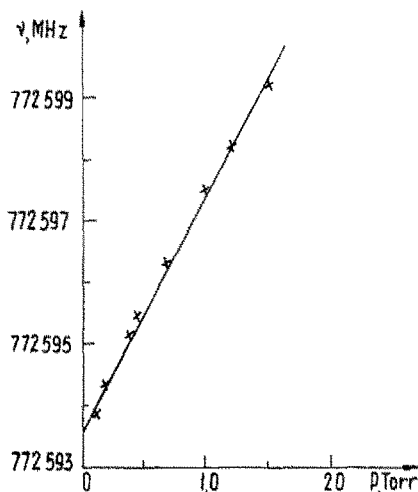


FIG. 10. Experimental dependence of the frequency of the "forbidden" transition $a(3, 3) \leftarrow a(2, 0)$ of $^{14}\text{NH}_3$ in the state $v_2 = 1$ on ammonia pressure. The nonshifted transition frequency value is $\nu_0 = 772\,593.6$ MHz.

experimental values are somewhat lower than the calculated ones. In general, the "Stark" approach in this case leads also to results which reasonably agree with experiment.

7

At present some new directions of investigation of molecular absorption pressure lineshifts become possible. Three of them are described below.

(a) As far as we know, we performed the first pressure lineshift measurements for "forbidden" $|\Delta K| = 3$ transition in a symmetric-top type molecule. The self-shift of the transition $a(3, 3) \leftarrow a(2, 0)$ of the ammonia molecule $^{14}\text{NH}_3$ in the $v_2 = 1$ vibrational state was investigated (for the level scheme see Fig. 3). The transition frequency was near 772.5 GHz. The results of measuring the dependence of this transition frequency on pressure are given in Fig. 10. For comparison we also measured the self-shift parameter of the allowed transition $s(3, 0) \leftarrow a(2, 0)$ sharing the same lower level with the forbidden one (see also Fig. 3) and located nearly 2.8 GHz lower. A record of this part of the ammonia spectrum obtained by RAD and containing the lines mentioned is given in Ref. (5). Frequencies and parameters of self-shift and self-broadening measured for both lines are presented in Table VIII. It can be expected that similar to the fact that measurements of "forbidden" transition frequencies significantly increased the information on molecules, measurements of forbidden transition lineshifts can supply additional information on details of molecular interactions at collisions. In particular, such measurements permit us to determine the relative shifts of energy levels with various K , which are not practically connected by an electric dipole interaction; in earlier work such information was either obtained indirectly or absent altogether. The data of Table VIII indicate the absence of a considerable relative shift of levels $s(3, 0)$ and $a(3, 3)$ by pressure of ammonia.

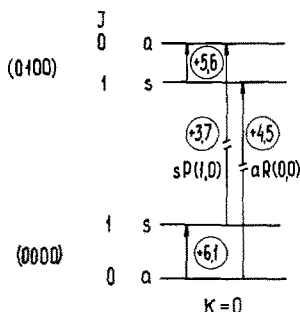


FIG. 11. A display of energy levels $J = 0, 1$; $K = 0$ of $^{14}\text{NH}_3$ in the ground and $\nu_2 = 1$ excited vibrational states. Arrows show inversion-rotational and vibration-inversion-rotational transitions for which self-shift parameters are measured. Experimental self-shift parameters in MHz/Torr are given in circles.

(b) Obtaining data on shifts of successive transitions having common levels (examples can be seen in Fig. 3) permits us to study the question on shift additivity. Thus, for example, measurement of the pressure shift of the transition $a(2, 1) \leftarrow s(1, 1)$, closing the chain of transitions $a(2, 1) \leftarrow s(2, 1) \leftarrow a(1, 1) \leftarrow s(1, 1)$, could answer the question of whether or not this transition lineshift equals the sum of transition lineshifts in the chain. Unfortunately, the frequency of the transition $a(2, 1) \leftarrow s(1, 1)$ lies in the far infrared region and cannot be measured by RAD yet. However, such measurements can be made using other molecules, in particular, asymmetric tops.

(c) One more interesting direction of investigations is a joint analysis of ir and microwave data on the pressure shifts of lines with common levels which is possible now due to extension of microwave pressure shift measurements to absorption lines of molecules in excited vibrational states and increase of accuracy of measurements of lineshifts in the ir region. Consider the scheme of energy levels for the ammonia molecule, $^{14}\text{NH}_3$, displayed in Fig. 11. We measured pressure self-shift parameters of transitions $s(1, 0) \leftarrow a(0, 0)$ and $a(0, 0) \leftarrow s(1, 0)$ in the ground and excited $\nu_2 = 1$ vibrational states of ammonia by RAD spectrometer. Pressure lineshifts of ν_2 band lines $aR(0, 0)$ and $sP(1, 0)$ were also measured recently by a diode laser spectrometer (25). All the transitions in Fig. 11 obey the selection rule $|\Delta J| = 1$. On the assumption of shift additivity they can be analyzed by the method of combination differences. In particular the identity

$$\Delta\nu_s[aR(0, 0)] + \Delta\nu_s[a(0, 0) \leftarrow S(1, 0)] \\ \equiv \Delta\nu_s[S(1, 0) \leftarrow a(0, 0)] + \Delta\nu_s[sP(1, 0)] \quad (14)$$

should be fulfilled. It can be seen that the results of measurements of lineshifts given (in circles) in Fig. 11 satisfy identity (14) with an accuracy $\sim 3\%$, which is better than the accuracy quoted in the experiments.

It is of interest to compare measured and calculated shift parameters in this more complicated system of transitions including vibrational ones. We performed our calculation with the simplification that only a quadratic Stark effect was taken

TABLE IX

Experimental $\Delta\nu_s^e$ and Calculated $\Delta\nu_s^c$ values of Pressure Lineshift Parameters of Rotational and Rotational-Vibrational Transition of Ammonia Molecule in the Fig. 11 Scheme of Levels

Transition	$\Delta\nu_s^e$ MHz/Torr	$\Delta\nu_s^c$ MHz/Torr	References
s/1,0/ \leftrightarrow a/0,0/ ground state	+ 6.1	+ 5.9	this work
a/0,0/ \leftrightarrow s/1,0/ $v_2 = 1$	+ 5.6	+ 6.5	this work
aR/0,0/, v_2 -band	+ 4.5	+ 4.7	[25]
sP/1,0/, v_2 -band	+ 3.7	+ 5.5	[25]

into account as a second-order correction for the energies of the levels. In this approach, evidently, the contribution of terms including vibrational transitions is negligibly small. The nonzero average shift of the $J = 1, K = 0$ level in a second-order Stark effect approximation is associated in this case with a perturbation of the rotational structure of the symmetric-top levels due to inversion splitting. Results of the calculations together with the experimental data are given in Table IX. Their comparison shows that even this simplified calculation in the "Stark effect" lineshift model gives, nevertheless, the right signs of shift parameters and calculated values agree with experimental ones with accuracy from 3 to 50%. Note, that identity (14) for calculated values is fulfilled also with accuracy 2%. These results demonstrate, apparently, that for description of the shifts of vibrational-rotational transitions in this case, it is enough to take into account only "rotational" shifts. Of course, at this time this conclusion is a result of a single experiment and further investigations are desirable.

Calculation in the "Stark" model permits us to determine also absolute values of averaged shifts of energy levels per pressure unit. Thus, the calculation shows that the shift of the $J = 1$ level in the ground state is small compared with shifts of other levels in Fig. 11. This enables us (using, for example, experimental data for lineshift parameters) to determine the following absolute values of averaged level shift parameters (Fig. 11) caused by collisions: in the ground state for $J = 0$, $\Delta W/h \cong -6.1$ MHz/Torr and for $J = 1$, $\Delta W/h \cong 0$; in the excited state ($v_2 = 1$) for $J = 0$, $\Delta W/h \cong 3.7$ MHz/Torr and for $J = 1$, $\Delta W/h \cong -1.6$ MHz/Torr. Some ambiguity of these values is caused by the possibility of using various combinations of experimental parameters of lineshifts for a level shift determination.

As a summary, investigations of microwave pressure lineshifts described in the present paper considerably increase the number of experimental data on lineshifts, discover new empirical dependences of lineshifts on molecular parameters, demonstrate on the basis of a rough working model the possibility of a unified description of pressure shifts of some spectral lines of polar molecules, and outline some new directions of investigations in this field. An essential narrowing of limits of the expected shift parameters of lines of polar molecules is achieved in some cases in this work, i.e., an increase of prediction power and reliability of estimations. The

increase of experimental basis as well as prediction power of methods should, in our opinion, be useful for further investigations in this field.

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