Study of Microwave Pressure Lineshifts: Dynamic and Isotopic Dependences

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The study of pressure lineshifts and line broadenings initiated earlier (*J. Mol. Spectrosc.* **94,** 264–282 (1982)) is extended to some other perturbing gases and to isotopic species. New dependences of the lineshifts on the molecular parameters are found. One of them is the dependence of the sign of the shift of the "test" lines on the type of perturbing gas. This dependence, as well as the proportionality of the lineshift to the line frequency found before is explained in terms of a "dynamic Stark effect" model. The dependence of the lineshifts on the isotopic composition of the absorbing molecule is also reported. One of the main results of the study is the demonstration of higher sensitivity of lineshifts to the characteristics of molecular interactions as compared to the corresponding line broadening.

INTRODUCTION

In a previous paper (*1*) we investigated microwave molecular pressure lineshifts induced by polar symmetric top perturbing gases and found some principal dependences of the shifts on the molecular parameters. In the present paper, investigations of the lineshifts (mainly of the same lines as in Ref. (*1*)) are extended to other polar perturbing gases. Experimental studies were performed in the submillimeter wave region by a RAD spectrometer (*2*) using the methods described in Ref. (*1*). These studies permitted us to observed new shift dependences on molecular parameters, in particular, the dependence of the sign of the shift on the type of perturbing molecules. Consideration of this dependence as well as the proportionality of the shift to the transition frequency found before (*1*) can be interpreted by a simple "dynamic Stark effect" model that is a natural extension of the "Stark shift" model used in Ref. (*1*). A more detailed investigation of the lineshifts of different isotopic species by the same perturbing gases also revealed a weaker but definite dependence of the magnitude of the shift on the isotopic composition of the absorbing molecule.

EXPERIMENTAL DETAILS

To investigate the dependence of the shift on the type of perturbing gas, we used as "test" lines of the absorbing molecules the lines of the rotational transition $J = 1 \leftarrow 0$ of the ammonia molecule $^{14}NH_3$ and the transition $1_{10} \leftarrow 1_{01}$ of the water molecule $H_2^{18}O$ (in natural abundance). For perturbing gases we used H_2O, N_2O, PH_3, OCS, NH_3, C_6H_5Cl, and C_3H_7ON for the ammonia transition and H_2O, HCl, H_2S, and NH_3 for the water transition. The results obtained for the experimental dependences of these two transition frequencies on the perturbing gas pressure are

shown in Figs. 1 and 2, and the corresponding shift parameters obtained using the method of least squares are presented in Tables I and II.[1] It may be noted that the shift parameter obtained for ammonia perturbed by C_3H_7ON (equal to $+14.3(6)$ MHz/Torr, Table I) is, probably, the largest of those measured so far.

The most typical feature of the results obtained is the dependence of both the value and the sign of the lineshift on the perturbing gas type. It should be noted that both transitions investigated showed (as in Ref. (1)) uniform behavior in this regard. More detailed consideration of the results allows us to conclude, that shifts of both investigated lines by heavy (i.e., those with large moments of inertia) linear and asymmetric top molecules as well as shifts by symmetric tops have a positive sign, while shifts of the same lines by light (i.e., those with small moments of inertia) linear or asymmetric top molecules have a negative sign. Since we considered this to be a new and interesting result, we tried to obtain additional information. One result was kindly presented to us by E. N. Karyakin, to whom the authors express their gratitude. While investigating the submillimeter wave spectrum of water vapor, Karyakin measured the shift and broadening of the analogous transition $1_{10} \leftarrow 1_{01}$ of the excited state $v_2 = 1$ of the $H_2{}^{16}O$ molecule by water vapor pressure; both shift and broadening parameters are close to the results of our measurements of the corresponding shift and broadening of the $H_2{}^{18}O$ ground state. To obtain additional experimental information, we measured lineshifts of the $1_{10} \leftarrow 1_{01}$ transition of the water molecule $H_2{}^{16}O$ in the ground state induced by heavier polar molecules, namely $(C_2H_5)_3SiH$ and $(C_2H_5)_3GeH$. The resultant frequency dependences, displayed in Fig. 3, also agree well with the above results. The shift and broadening parameters obtained by least squares for this case are presented in Table III.

One experimental detail connected with measurements of the shifts produced by relatively large molecules as perturbers appears to be worth noting. These molecules have, as a rule, a very dense spectrum in the neighborhood of the investigated line of the absorbing molecule. An example of such a situation is shown in Fig. 4 where a portion of the C_3H_7OH spectrum near the $J = 1 \leftarrow 0$ of $^{14}NH_3$ line is presented. Thus, when observing the spectrum of the mixture (absorber + perturber) one can measure together with the true pressure shift of the absorber line an apparent shift of the absorber line center produced simply by the wings of neighboring lines of the perturbing gas. To minimize this effect, it is important to use a sufficiently strong line of the absorbing molecule whose intensity significantly exceeds that of the perturber lines. Experimental dependences in Figs. 1–3 are close to linear ones, thus veryifying the validity of this conclusion. This criterion allows one to include a rather wide class of large polar molecules in investigations of the shift and broadening of "test" lines.

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[1] Note the peculiarities in the behavior of the line frequency dependences on foreign gas pressure in the low pressure region. While in the case of a self-shift, the extrapolation of the linear dependence to zero pressures gives the nonshifted line frequency v_0, and in the case of lineshift by a foreign gas it can be easily shown that when extrapolating to zero pressures the line crosses the frequency axis at the point $v_0 + (\Delta v_{ss} - \Delta v_{sf})p_0$ where Δv_{ss} is the self-shift parameter for investigated line, Δv_{sf} is the same for the foreign gas, and p_0 is the initial pressure of the investigated gas. In the case when Δv_{ss} and Δv_{sf} have different signs, the deviation of the intersection point from v_0 is the largest. This effect, for example, is clearly observed in Fig. 2.
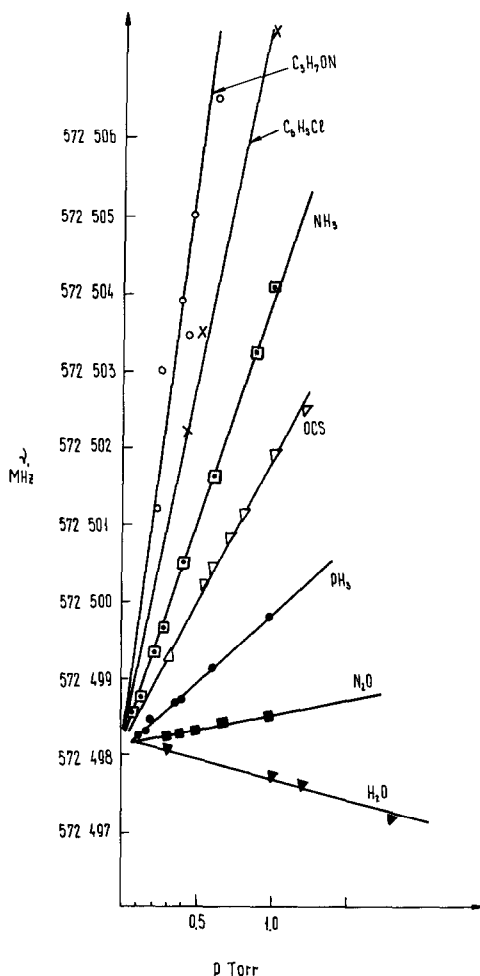
FIG. 1. The frequency dependence of the $s(1.0) \leftarrow a(0.0)$ transition of the ammonia $^{14}NH_3$ molecule on the pressure of various perturbing gases. Perturbing gases are labeled in the figure. The nonshifted transition frequency is determined as $\nu_0 = 572\ 497.99(4)$ MHz.

The experiments described above and given in Ref. (1) were aimed at investigating the main (strongest) dependences of lineshifts on molecular parameters. Of course, by necessity (since the interaction of such complex objects as molecules is a rather complicated process) both the measured dependences and the model describing the main features of the phenomenon were somewhat qualitative. However, experimental possibilities at present significantly exceed the accuracy necessary for investigation of those "first-order" effects. One may hope that, after their having been described with sufficient accuracy, it is now possible to study weaker dependences, i.e., "second-order" effects. As an example of such an experimental investigation, we performed a detailed comparative study of the shift and broadening of the lower rotational transitions $J = 1 \leftarrow 0$ of ammonia $^{14}NH_3$ and $^{15}NH_3$, where we discovered a slight
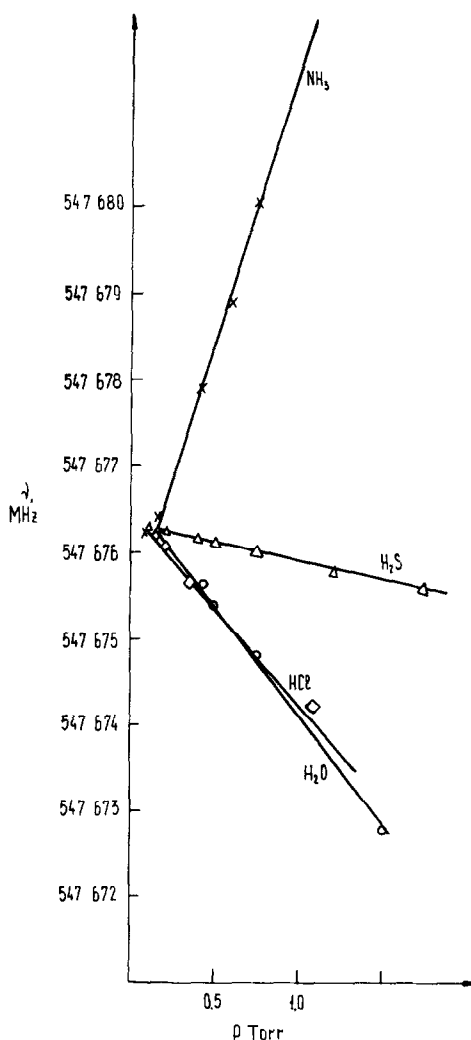
FIG. 2. The frequency dependence of the $1_{10} \leftarrow 1_{01}$ transition of the water $H_2{}^{18}O$ molecule on the pressure of various perturbing gases. Perturbing gases are labeled in the figure. The nonshifted transition frequency is determined as $\nu_0 = 547\ 676.66(5)$ MHz.

but sufficiently definite difference of the line shift and broadening of these molecules by different gases. We will now describe this investigation.

To study the rotation–inversion transitions $s(1.0) \leftarrow a(0.0)$ of ammonia $^{14}NH_3$ and $^{15}NH_3$ we adopted the following procedure to increase the accuracy of the measurements. The value of the frequency deviation chosen for modulation of a submillimeter frequency synthesizer was essentially smaller than the linewidth, so that a signal at the RAD spectrometer output corresponded more closely to the first derivative of the absorption line shape. An experimental record of the isotopic $^{15}NH_3$ ammonia line in natural abundance ($\sim0.36\%$) is presented in Fig. 5. In the experiments, we measured both the line center frequency (at pressure p) ν_{0p} and the frequencies of

TABLE I

Values of Pressure Lineshift and Broadening Parameters for the $s(1, 0) \leftarrow a(0, 0)$ Transition
of Ammonia $^{14}NH_3$ Molecule and Various Perturbing Gases

Perturbing molecule	Measured shift parameter $\Delta\nu_s$ (MHz/Torr)	Measured broadening (HWHM) parameter $\Delta\nu_B$ (MHz/Torr)	Estimated shift parameter $\Delta\nu_s^c$ (MHz/Torr)
C_3H_7ON	+14.3(6)	30(2)	+74
C_6H_5Cl	+9.2(5)	15(1)	+23
NH_3	+6.10(7)	14.4(10)	+3.4
PH_3	+1.86(8)	5.85(30)	+0.84
OCS	+3.72(9)	8.3(8)	+4.6
N_2O	+0.56(3)	5.4(5)	+0.29
H_2O	−0.62(6)	13.4(10)	−1.5

extrema ν_{min} and ν_{max} which, on the assumption of a Lorentzian line profile and small optical depth of the gas, are related to the line halfwidth (HWHM at pressure p) by the known relation $\Delta\nu = \sqrt{3}/2 \, (\nu_{max} - \nu_{min})$. Pressure in the cell was measured by means of a membrane pressure gauge with an accuracy of ±0.005 Torr in the region 0.01–1.0 Torr; this gauge was calibrated at two points: the pressure of water vapor above melting ice (assumed to be equal to 4.579 Torr (5)), and high vacuum ($P \leqslant 10^{-5}$ Torr). The absorption cell was filled with ammonia and pressure measurements in it were performed before and after the experiment. As a rule, these pressure values differed by no more than 2–3% and accordingly we took the mean value of these two measurements for the pressure value in the cell. Due to the strength of the $s(1.0) \leftarrow a(0.0)$ line of ordinary ammonia $^{14}NH_3$ ($\gamma_{max} \simeq 0.37$ cm^{-1}) measurements with it were performed in a short ($l = 1.3$ cm) absorption cell. In experiments with phosphine and nitrous oxide we used an ammonia sample enriched by the ^{15}N isotope up to 75%. In other experiments we used high purity ammonia with natural isotopic abundances and "chemically pure" phosphine. Examples of the experimental dependences on pressure of the line center frequency ν_{0p} and frequencies ν_{min}, ν_{max}, are presented in Figs. 6 and 7, respectively. The dependences obtained are

TABLE II

Values of Pressure Lineshift and Broadening Parameters for the $1_{10} \leftarrow 1_{01}$ Transition
of Water $H_2^{18}O$ Molecule and Various Perturbing Gases

Perturbing molecule	Measured shift parameter $\Delta\nu_s$ (MHz/Torr)	Measured broadening (HWHM) parameter $\Delta\nu_B$ (MHz/Torr)	Estimated shift parameter $\Delta\nu_s^c$ (MHz/Torr)
NH_3	+6.35(25)	19.7(20)	+13.4
H_2S	−0.70(7)	13.6(10)	−3.0
HCl	−2.04(7)	—	−2.4[a]
H_2O	−2.56(7)	17.5(15)	−4.7

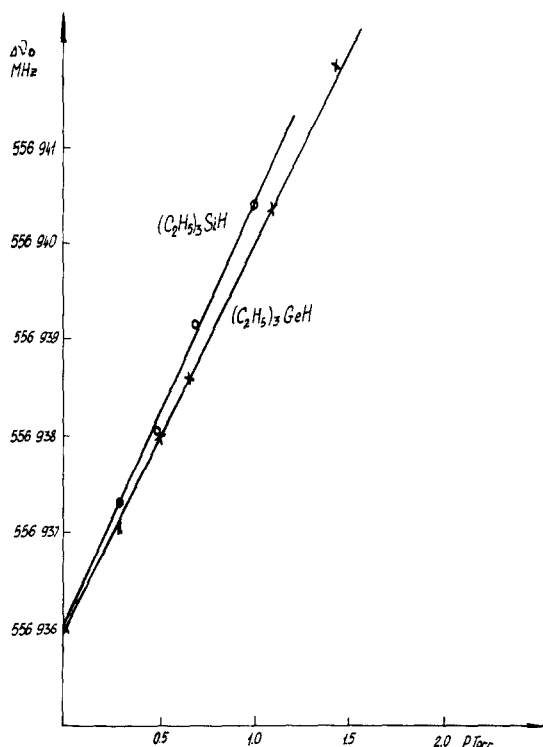[a] In calculations the broadening parameter was assumed to be equal to $\Delta\nu_B = 15$ MHz/Torr.

FIG. 3. The frequency dependence of the $1_{10} \leftarrow 1_{01}$ transition of the water $H_2^{16}O$ molecule on the pressure of triethylsilane $(C_2H_5)_3SiH$ (O) and triethylgermane $(C_2H_5)_3GeH$ (X).

close to linear ones. Consideration of the dependences in Figs. 6 and 7 and similar ones obtained for other perturbing gases enable us to conclude that the spread of experimental points when measuring the line center frequency ν_{0p} is essentially smaller than that when measuring the frequencies of extrema ν_{min}, ν_{max}; consequently, the accuracy of determination of the pressure lineshift parameter in our experiments exceeds the accuracy of determination of the pressure line broadening parameter. This conclusion is also confirmed by examining Table IV containing experimental values for the line shift and broadening parameters obtained by least squares criteria. When obtaining the broadening parameter, we took into account the influence of

TABLE III

Measured Values of Pressure Lineshift and Broadening Parameters for the $1_{10} \leftarrow 1_{01}$ Transition of Water $H_2^{16}O$ Molecule and Triethylsilane and Triethylgermane as Perturbing Gases

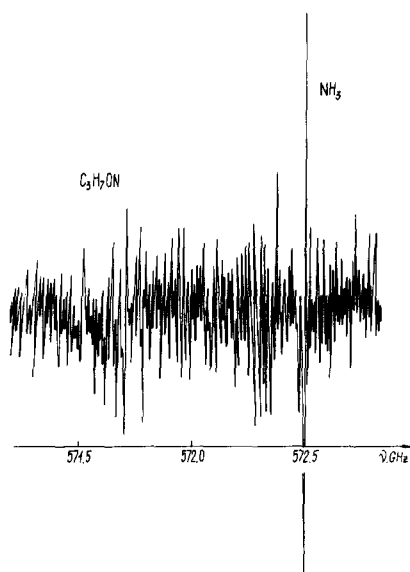| Foreign gas	Measured shift parameter $\Delta\nu_s$ (MHz/Torr)	Measured broadening (HWHM) parameter $\Delta\nu_B$ (MHz/Torr)
$(C_2H_5)_3SiH$	+4.4	9.0
$(C_2H_5)_3GeH$	+4.0	9.5

FIG. 4. A part of the spectrum of C_3H_7ON recorded near the $s(1.0) \leftarrow a(0.0)$ transition of the ammonia $^{14}NH_3$ molecule. Pressure of C_3H_7ON is $p \simeq 0.34$ Torr, and the $^{14}NH_3$ line seen in the picture is produced by a small admixture of ammonia.

finite optical depth of the gas in the cell. Therefore, higher accuracy of the measurements and an "additional degree of freedom" make the pressure lineshift a very attractive source of information on molecular interaction that significantly supplements the data from pressure broadening of lines.

Figure 8 displays the experimental results for the shifts of the line centers of the $S(1.0) \leftarrow a(0.0)$ transitions in $^{14}NH_3$ and $^{15}NH_3$ induced by ammonia, phosphine, and nitrous oxide. Consideration of Fig. 8 and Table IV indicates that there is a systematic difference in shift parameters for these similar and closely located molecular transitions for the different isotopes which are outside of the experimental error limits.[2] This difference in lineshifts varying from 6 to 20% depending on the type of the perturbing gas cannot be explained only by the difference in relative velocities of the isotopic molecules, as this difference does not exceed 2%. The most essential (nondynamical) difference between these molecules that can possibly affect the value of the shift parameter for these transitions is the presence of a quadrupole splitting of the energy levels of the $^{14}NH_3$ molecule caused by the spin $I = 1$ of the ^{14}N nucleus; for the $^{15}NH_3$ molecule a quadrupolar splitting is known to be absent. However, the existing shift theories do not at present take into account such fine details of the interactions, and the results obtained must be interpreted accordingly.[3] We hope that

[2] The difference in self-shift parameters of these transitions was noted earlier by us in Ref. (1) (that was the primary reason for the present, more thorough investigation); however, it was difficult at that time to decide this effect definitely. A similar tendency can be noted for line broadening in the case of the ammonia–ammonia interaction; in other cases the difference in broadening parameters does not exceed experimental errors.

[3] Another example may be interactions of "right–right," and "right–left" stereoisomers, molecules with known differences in quadrupolar moments, etc.
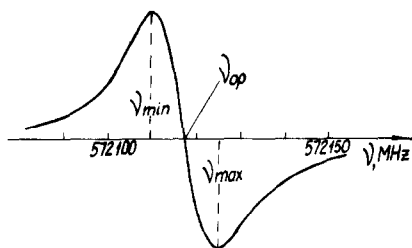
FIG. 5. An example of the record of the $s(1.0) \leftarrow a(0.0)$ line of the ammonia $^{15}NH_3$ molecule obtained by a RAD spectrometer and a submillimeter frequency synthesizer. Ammonia pressure is $p \simeq 1$ Torr, and the line is recorded as first derivative of the absorption profile; the measured frequencies ν_{min}, ν_{0p}, ν_{max} are shown in the figure.

the number of such experimental data providing information on the finer details of the molecular interaction will increase as further investigations by the methods previously described (3) are carried out.

THEORY

In paper (1) as a simple "heuristic" approach for the description of molecular lineshifts by gas pressure we applied a "Stark" shift mechanism, that led to a systematic description of the lineshifts observed. Fully understanding the necessity of a more rigorous pressure lineshift theory, we believe, however, that at the present stage of investigation it might again prove useful to keep the approach for the description of the fundamental dependences of the lineshifts on the parameters of the interacting molecules as simple as possible. Ascertaining simple analytic dependences relating lineshifts and average molecular parameters can, in our opinion, help determine quickly the main features necessary for a more exact theory and also suggest the most interesting directions for further experimental investigations.

The dependences observed in the present paper for the lineshift on the type of perturbing molecule can be, in our opinion, simply explained within the framework of a dynamical Stark shift mechanism, naturally extending the approach applied in Ref (1). This mechanism is quite similar to the "light shifts" that have been invoked to describe optical pumping experiments (see, for instance Ref. (7)).

The expression for the mean energy level shift of a transition $\overline{\Delta E_n}$ induced by an alternating electric field of the perturbing molecule can be calculated within the binary collision approximation using second order perturbation theory (6) and has the form

$$\overline{\Delta E_n} = -\frac{\varkappa}{h} \Sigma' |\mu_{mn}^{(z)}|^2 \int_{-\infty}^{\infty} \frac{|G(\nu)|^2}{\nu_{mn} - \nu} \, d\nu. \tag{1}$$

In this expression, $\mu_{mn}^{(z)}$ is the matrix element of the dipole moment component along the perturbing field $\mathscr{E}(t)$, $\varkappa = 2\pi n\nu\rho d\rho$ is the number of collisions per unit time, n is the density of perturbing molecules, v is the mean velocity of relative motion of the colliding molecules ρ is the impact parameter, and $G(\nu)$ is the perturbing field spectrum, $\nu_{mn} = (E_m - E_n)/h$. Detailed calculations will be given by us elsewhere; here we confine ourselves mainly to qualitative considerations and estimates of the
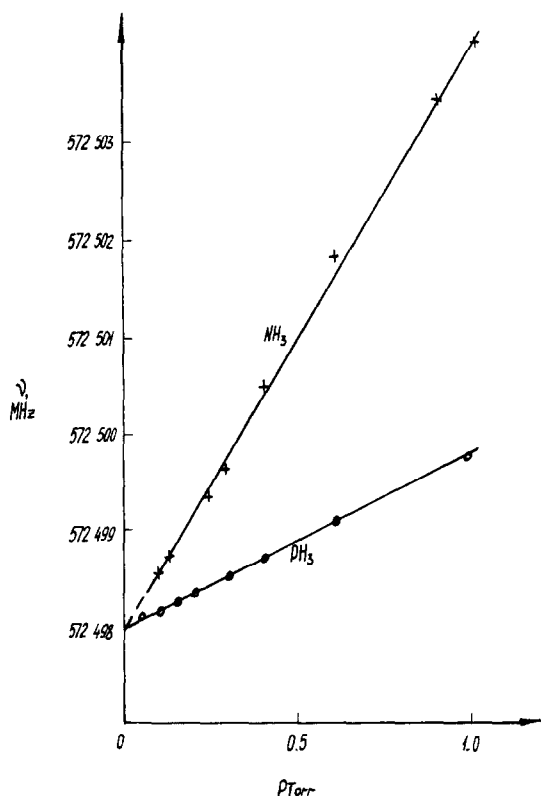
FIG. 6. The frequency dependence of the $s(1.0) \leftarrow a(0.0)$ transition of the ammonia $^{14}NH_3$ molecule on the pressure of ammonia (+) and phosphine (O). Measurements were carried out in the absorption cell with a length $l = 1.3$ cm for ammonia and $l = 10$ cm for phosphine as perturbers.

orders of magnitude of the effect. For the transition $J = 1 \leftarrow 0$ taking into account only the (prevailing) shift of the lower ($J = 0$) level it follows from Eq. (1) that

$$\Delta\nu_s(\rho) = -\frac{\overline{\Delta E_0}}{h\rho} = \frac{2\pi|\mu_{01}^{(z)}|^2 v\rho d\rho}{h^2 kT} \int_{-\infty}^{\infty} \frac{|G(\nu)|^2}{\nu_0 - \nu} \, d\nu \tag{2}$$

where $p = nkT$ is the perturbing gas pressure, and ν_0 is the frequency of the transition. It can be seen from expressions (1) and (2) that the sign of the shift can be determined by the mechanism considered if various perturbing molecules have different "mean" perturbation spectra. Consider the qualitative form of the perturbation spectrum for various types of molecules investigated by us, taking for simplicity the perturbing gas molecule in the "most probable" state. The difference in the perturbation spectrum can be associated with the behavior of the perturbing molecule during the collision duration $\tau \simeq \rho/v$ and amplitude $\mathcal{E}_0 \simeq \mu/\rho^3$. A simplified spectrum of such perturbation molecule, the perturbing field pulse will have the form of a "video pulse" with a duration $\tau \simeq \rho/v$ and amplitude $\mathcal{E}_0 \simeq \mu\rho^3$. A simplified spectrum of such perturbation is shown in Fig. 9a. From this point of view, it is not essential to determine whether the slowly rotating molecule is a linear, symmetric, or asymmetric top. For molecules
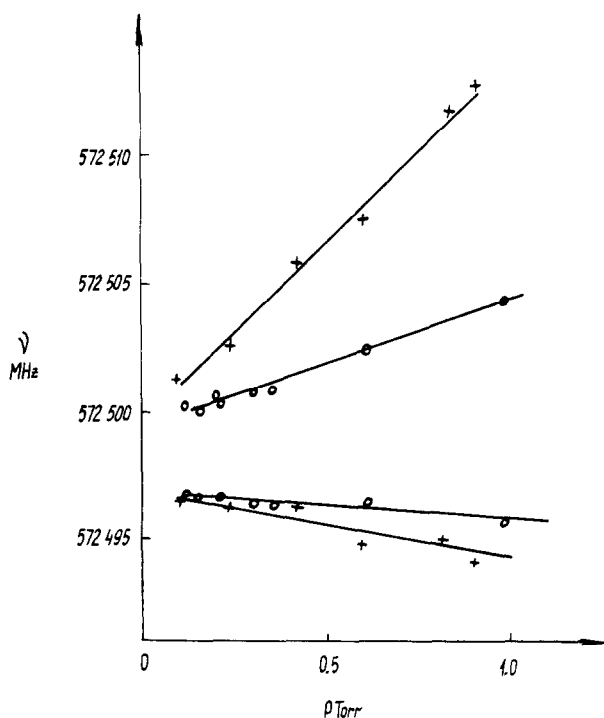
FIG. 7. The frequency dependence of the extrema ν_{min} and ν_{max} of the absorption profile derivative of the $s(1.0) \leftarrow a(0.0)$ line of ammonia $^{14}NH_3$ on pressure of ammonia NH_3 (+) and phosphine PH_3 (O).

of the symmetric top type, the "mean" perturbation will also possess a large component of the form 9a independently of the speed of rotation (4); its amplitude will be of the order of $\mathscr{E}_0 \simeq \mu_{eff}/\rho^3$, where μ_{eff} is the effective dipole moment introduced in Ref. (1) and is equal for a light symmetric top with rotational constants A, B to $\mu_{eff} \simeq \mu B^{1/2}/(A^{1/2} + B^{1/2})$. The situation is qualitatively different for rapidly rotating linear or asymmetric top polar molecules. If such molecules make several turns during the collision time, the perturbing field pulse will have the form of the "pulse filled

TABLE IV

Measured Values of Pressure Lineshift and Broadening Parameters for the $J = 1 \leftarrow 0$ Transitions of Ammonia $^{14}NH_3$ and $^{15}NH_3$ Molecules by Pressure of Ammonia, Phosphine, and Nitrous Oxide as Perturbing Gases

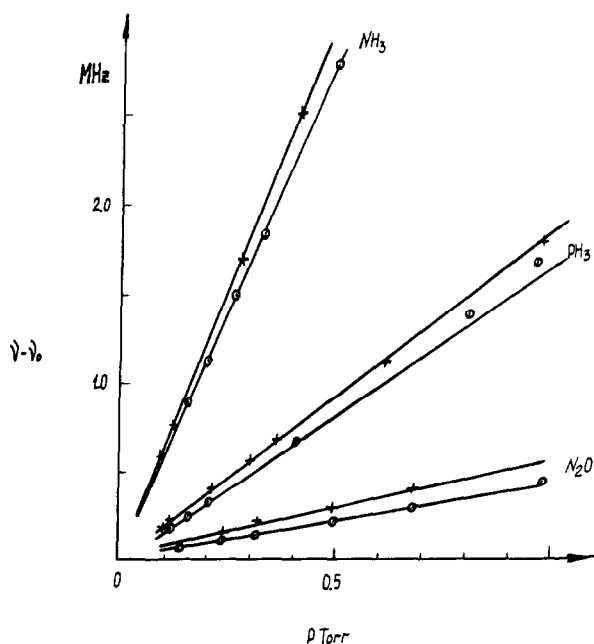| Absorbing molecule	$^{14}NH_3$		$^{15}NH_3$	
Perturbing gas	Measured shift parameter $\Delta\nu_s$ (MHz/Torr)	Measured broadening (HWHM) parameter $\Delta\nu_B$ (MHz/Torr)	Measured shift parameter $\Delta\nu_s$ (MHz/Torr)	Measured broadening (HWHM) parameter $\Delta\nu_B$ (MHz/Torr)
NH_3	6.10(7)	14.40(40)	5.71(10)	11.90(50)
PH_3	1.86(8)	5.85(30)	1.67(7)	5.55(30)
N_2O	0.56(3)	5.43(50)	0.44(3)	5.31(50)

FIG. 8. The dependence of the shift of the frequencies of the $s(1.0) \leftarrow a(0.0)$ transitions of ammonia $^{14}NH_3$ (+) and $^{15}NH_3$ (O) on pressure of NH_3, PH_3, and N_2O.

by carrier rotation frequency" whose field amplitude is again equal to $\mathscr{E}_0 \simeq \mu/\rho^3$ and the simplified form of the spectrum is given in Fig. 9b. For rough estimations, the rotational frequency of a "mean" linear molecule can be assumed to be equal to $\nu_{rot} \simeq 2BJ_{max}$, where B is the rotational constant, $J_{max} \simeq (kT/2hB)^{1/2}$ is the rotational quantum number corresponding to the maximum of population of rotational levels (4). In the case of a strongly asymmetric top, one can use for the same estimates (as for the calculation of the rotational partition sum) the geometric mean of three
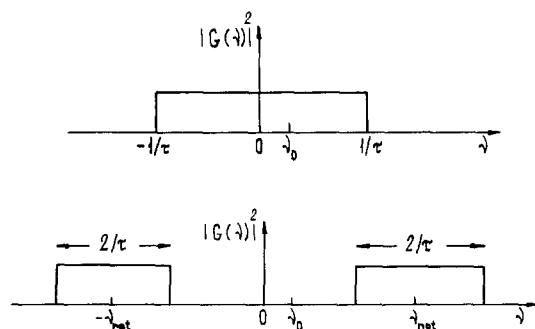

FIG. 9. The idealized shape of the perturbation spectra $|G(\nu)|^2$ produced by a polar perturbing molecule passing near an absorbing one for the cases (a) permanent space component of the dipole moment during the collision time, and (b) rapidly (compared with the collision time) rotating dipole moment. In the picture, ν_0 is the transition frequency of absorbing molecule, ν_{rot} the rotational frequency of perturbing molecule, and τ the collision time.

rotational constants. The "number of turns during the collision time" estimated with these assumptions for the light molecules presented in Tables I and II lies within 2 to 3 and the type of the spectrum in Fig. 9b is possible for them. In both cases the order of magnitude of $|G(\nu)|$ in Fig. 9 is equal to $\mathscr{E}_0\tau$ and after integration in Eq. (2) with the assumptions $\nu_0 \ll 1/\tau$ we have

$$\Delta\nu_s = \frac{4\pi\nu_0|\mu_{01}^{(z)}|^2\mu_{eff}^2}{h^2kTv^2\rho_0} \qquad \text{for case (a)} \qquad (3)$$

and

$$\Delta\nu_s = -\frac{8\pi\nu_0|\mu_{01}^{(z)}|^2\mu^2}{3h^2kTv_{rot}^2\rho_0^3} \qquad \text{for case (b)} \qquad (4)$$

where ρ_0 is the minimal impact parameter which can be estimated as in Ref. (1) from the line broadening parameter $\Delta\nu_B$ as $\rho_0 \simeq [2kT\Delta\nu_B/v]^{1/2}$. The resulting estimates of the shift parameter for the cases investigated at $T = 300$ K are given in Tables I and II; for the $1_{10} \leftarrow 1_{01}$ water transition, the shift was calculated in the approximation of a pair of isolated levels that lead to doubling of the values calculated through Eqs. (3) and (4). As can be seen, these very rough estimations nevertheless give the correct signs and, in most cases, even the order of magnitude of pressure lineshift parameters (8).[4]

Perhaps the most interesting result of the above consideration is the proportionality of shifts to the transition frequency ν_0 as evident in formulas (3) and (4). Such a proportionality was discovered by us empirically (for the same $J = 1 \leftarrow 0$ transitions of symmetric tops) earlier (1) but was not explained at that time. At that time we only mentioned the probable dynamic character of this dependence and expressed the hope of explaining it in future on the basis of a dynamical Stark effect model. This dependence arising naturally in the present work is further confirmation of the agreement between our qualitative theoretical model and the main features of the observed shift phenomenon.

Therefore, in conclusion, the investigations of pressure shifts of some lines of polar molecules commenced by us in Ref. (1) have been extended in the present paper to a considerably broader class of perturbing gases. We have succeeded in generalizing and extending the simple "Stark" approach for the description of pressure lineshifts. In the future, we plan to extend these investigations to more complicated cases of lineshifts.

[4] *Note added in proof.* Calculations analogous to those presented in Table I, except for the $\nu_0\tau \gg 1$ condition, give estimated shifts values (in the same order as in Table I and omitting H_2O case) of $+13$; $+7.2$; $+2.4$; $+0.99$; $+3$; $+0.33$ MHz/Torr.

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