

PRESSURE SHIFT OF MOLECULAR LINES: DEPENDENCE OF THE SIGN OF  
THE SHIFT ON THE SPECIES OF PERTURBING GAS

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We have experimentally investigated how the lines of the  $J = 1 \leftarrow 0$  transition of the molecule  $^{14}\text{NH}_3$  and the  $1_{10} \leftarrow 1_{01}$  transition of the  $\text{H}_2^{18}\text{O}$  molecule shift and broaden under the influence of the pressure of various gases. We have discovered how the sign of the shift depends on the species of perturbing gas. We discuss the mechanism for this dependence and carry out numerical estimates. Our results can be explained on the basis of a model of the dynamical Stark shift of the levels.

Shifts of molecular lines by gas pressure are a manifestation intermolecular interactions. Another aspect of these interactions is the broadening of molecular lines by the gas pressure. However, these phenomena have not been studied to the same extent. Despite the fact that the broadening has been actively investigated only by microwave spectroscopy for more than 30 years [1], the first measurements of microwave molecular line shifts which were subsequently confirmed were only performed in the 1970s [2, 3]. In traditional microwave spectrometers with traditional receivers for the radiation, pressure line shifts are difficult to investigate experimentally, basically because of interference effects. When lines are observed on the slopes of the frequency characteristics, this causes the observed position of line center to depend on pressure in a way which is indistinguishable from the true line shift. In the infrared range, shifts are difficult to observe basically because the line frequency cannot be measured with great precision. The submillimeter microwave spectrometer RAD [4] is practically free from the harmful effects of interference, and line frequencies are measured with high precision. With the creation of RAD, it became possible to investigate the phenomena of molecular spectral line shifts by gas pressure in a systematic way for the first time.

We have investigated [5-16] the shifts of a series of molecular lines by gas pressure, measuring shifts from 0.15 to 6.1 MHz/torr. We have discovered certain laws which govern how the pressure shifts of the lines are related to the parameters of the interacting molecules. In particular, we discovered that if the perturbing molecules belong to the species of polar symmetric tops, the experimental signs of the pressure shifts of a series of lines agree with the signs of the displacements of the centers of these lines computed according to the Stark effect. This result was used to create a simple model for the molecular interaction in this case, and we were successful in explaining and predicting a number of cases of pressure line shifts.

In the present paper, we also use the RAD spectrometer to investigate the gas pressure shifts of some of the molecular lines which were studied in [5-16], but in this case, we use molecules which belong to different species. For our investigation, we took the  $J = 1 \leftarrow 0$  transition of the ground state of the ammonia molecule  $^{14}\text{NH}_3$ , and the  $1_{10} \leftarrow 1_{01}$  transition of the ground state of the water molecule  $\text{H}_2^{18}\text{O}$ , at frequencies of around 572 and 547 GHz, respectively. The line of  $\text{H}_2^{18}\text{O}$  was observed in its natural concentration. A major portion of the dependences which we obtained earlier were established precisely for transitions of these kinds: low rotational transitions of symmetric tops (the  $J = 1 \leftarrow 0$  transition of ammonia belongs to this kind), and transitions between a pair of levels which are quite far from other levels (the  $1_{10} \leftarrow 1_{01}$  transition of water is like this). Fifteen cases of  $J = 1 \leftarrow 0$  transitions in symmetric tops, with perturbing molecules belonging to a species of polar symmetric tops, have been investigated in the earlier work [14-16]. In all 15 cases, we found that the

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TABLE 1. Shift and Broadening of the  $J = 1 \leftarrow 0$  Transition of the Ammonia Molecule  $^{14}\text{NH}_3$  Due to the Pressure of Various Gases

Perturbing gas	$\Delta\nu_{\text{sh}}$ (experiment) MHz/torr	$\Delta\nu_{\text{br}}$ MHz/torr	$\Delta\nu_{\text{sh}}$ (calculated) MHz/torr	Literature
$\text{NH}_3$ $\text{H}_2\text{O}$	+6,1 -0,62	14,4 13,4	+3,4 -1,5	[10] Present work

**Note:** The broadening parameter  $\Delta\nu_{\text{br}}$  is determined from the half-width of the line at the half-intensity level, referred to unit pressure.

TABLE 2. Shift and Broadening of the  $1_{10}-1_{01}$  Transition of the Water Molecule  $\text{H}_2^{18}\text{O}$  Due to the Pressure of Various Gases

Perturbing gas	$\Delta\nu_{\text{sh}}$ (experimental) MHz/torr	$\Delta\nu_{\text{br}}$ MHz/torr	$\Delta\nu_{\text{sh}}$ (calculated) MHz/torr	Literature
$\text{NH}_3$ $\text{H}_2\text{S}$ $\text{HCl}$ $\text{H}_2\text{O}$	+6,53 -0,70 -2,04 -2,56	17,9 13,6 — 17,5	+13,4 -3,0 -2,4* -4,7	[10] and present work Present work — —

**Note:** The broadening parameter  $\Delta\nu_{\text{br}}$  is determined as in Table 1.

\*For the calculation of  $\Delta\nu_{\text{sh}}$  we assume  $\Delta\nu_{\text{br}} = 15$  MHz/torr.

sign of the frequency pressure shift was positive. In particular, we obtained a positive shift for the transition which is under investigation in the present paper, the  $J = 1 \leftarrow 0$  transition in ammonia, when the shift is caused by ammonia molecules. It was also established in [14-16] that the gas pressure shift in the frequency of the  $1_{10} \leftarrow 1_{01}$  transition of the water molecule has a positive sign when the perturbing molecules belong to a species of polar symmetric tops. This latter result was established in four experiments, corresponding to observations of the shifts of these lines from each of the isotopic variants of water,  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$ , and for cases in which the perturbing gas was ammonia and phosphine.

In the present work, we have studied  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{O}$  as the perturbing gases. The  $\text{HCl}$  molecule belongs to the species of light linear polar molecules, while the  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  molecules belong to the species of light asymmetric polar tops.

The technique of using RAD for investigating line shifts and broadening was described in [10]. In Figs. 1 and 2, we show how the line frequencies depend on pressure.\* The small amount of scatter among the experimental points indicates that the measurements are quite precise. The values of the line shift parameters determined from Figs. 1 and 2 are assembled in Tables 1 and 2. For comparison, we also present in the tables the shift parameters for lines which have been investigated for pressure shifts in ammonia.

The results of the present work show that for both of the lines which have been investigated, the sign of the shift of these lines due to pressure effects in  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{O}$  is negative, i.e., it is opposite to the sign of the shift of the same lines due to pressure effects in ammonia,  $\text{NH}_3$ . Since this result was unexpected, we carried out some control experiments. In one of these, we repeated the measurement of the line shift of  $1_{10} \leftarrow 1_{01}$   $\text{H}_2^{18}\text{O}$  due to ammonia pressure, which had been made previously in another apparatus. The results

\*We note the peculiarities in the behavior of the line frequency dependence on pressure at low gas pressures. Just as in the case of self-shifting, extrapolation of the graph to zero pressure gives the frequency of the undisplaced line  $\nu_0$ , so in the case when another gas causes the material under investigation to undergo a line shift, it is easy to show that the extrapolated graph intersects the zero-pressure axis at a point  $\nu_0 + (\Delta\nu_{\text{sh}1} - \Delta\nu_{\text{sh}2})P_0$ . Here,  $\Delta\nu_{\text{sh}1}$  is the self-shift parameter for the line under investigation,  $\Delta\nu_{\text{sh}2}$  is a parameter which characterizes the shift of the line under investigation as a result of the presence of the other gas, and  $P_0$  is the initial pressure of the gas under investigation. In this case, when  $\Delta\nu_{\text{sh}1}$  and  $\Delta\nu_{\text{sh}2}$  have different signs, the point of intersection deviates from  $\nu_0$  by a smaller amount. This effect can be clearly observed in Figs. 1 and 2, where arrows denote the values  $\nu_0(\text{NH}_3) = 572\,497.99$  MHz and  $\nu_0(\text{H}_2^{18}\text{O}) = 547\,676.44$  MHz.

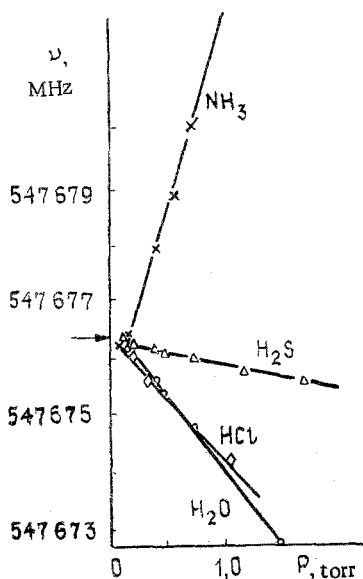


Fig. 1

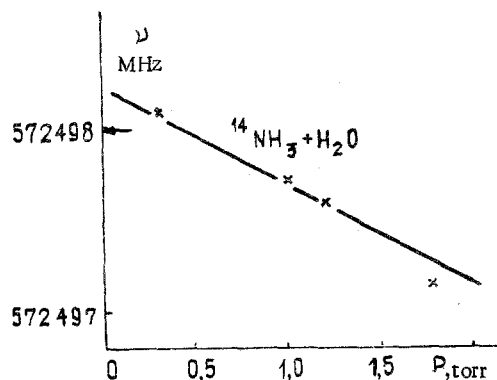


Fig. 2

Fig. 1. Frequency of line center of the transition  $1_{10} \leftarrow 1_{01}$  in the  $\text{H}_2^{18}\text{O}$  molecule as a function of pressure of ammonia  $\text{NH}_3$ , pressure of hydrogen sulfide  $\text{H}_2\text{S}$ , pressure of hydrogen chloride  $\text{HCl}$ , and pressure of water vapor  $\text{H}_2\text{O}$ .

Fig. 2. Frequency of line center of the transition  $J = 1 \leftarrow 0$  in the  $^{14}\text{NH}_3$  molecule as a function of the pressure of water vapor  $\text{H}_2\text{O}$ . The arrow denotes the frequency of the unshifted line.

which we obtained agree with those which were previously published [14-16]. This is noted in Table 1. The material for the other control experiment was placed at my disposal by E. N. Karyakin, to whom I am grateful. While he was investigating the submillimeter spectrum of water vapor, he measured the shift and the broadening of the analogous transition  $1_{10} \leftarrow 1_{01}$  in the  $\nu_2 = 1$  excited state of the  $\text{H}_2^{16}\text{O}$  molecule due to the pressure of water vapor. These measurements are nearly coincident with the results for the shift and broadening of the line in the ground state of  $\text{H}_2^{18}\text{O}$  water. Previous authors [5-16] have remarked that the shift parameters for the ground and excited states of molecules are similar in the case where the level schemes are similar. They have also remarked that the shift parameters for molecules in which isotopes have been substituted are similar. Hence, as far as we are concerned, this control experiment has confirmed the results of the present work.

The change in the sign of the pressure shifts of certain molecular lines as the perturbing molecular gas is changed (this is the sign change which we have discovered in our work) can be explained in terms of the Stark mechanism also. In this case, however, the mechanism of the line shift is a dynamical one. It is not difficult to obtain (following [17]) an expression for the mean displacement of an energy level of an observed transition  $\overline{\Delta E_n}$  in the variable electric field of a perturbing molecule. In the approximation of binary collisions with impact parameter  $\rho$ , we have

$$\overline{\Delta E_n} = -\frac{x}{h} \sum_m' |\mu_{nm}^{(z)}|^2 \int_{-\infty}^{\infty} \frac{|G(\nu)|^2}{\nu_{mn} - \nu} d\nu. \quad (1)$$

Here,  $\mu_{nm}$  is the matrix element of the component of the dipole moment along the perturbing field  $\epsilon(t)$ ;  $x = 2\pi n v \rho d \rho$  is the number of collisions per unit time; ( $n$  is the density of perturbing molecules, and  $v$  is the mean speed of the relative motion of the colliding molecules);  $G(\nu)$  is the spectrum of the perturbing field; and  $\nu_{mn} = (E_m - E_n)/h$ . In view of the complicated nature of the perturbation itself, and in view of the large number of averages which are required, detailed calculations need to be considered separately. We will undertake calculations in subsequent papers.

Here, we confine ourselves to calculating an estimate of the shift parameter for the  $J = 1 \leftarrow 0$  transition, allowing for the displacement of only one lower level. (This is partly

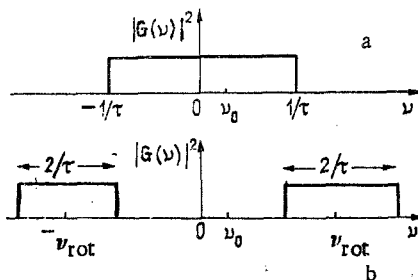


Fig. 3

justified for the following reason: in a statistical field, the displacement of levels with  $J \neq 0$  is equal to zero in second-order perturbation theory, when the displacement is averaged over the quantum number  $M$  [1].) In this case, it follows from (1) that

$$\Delta\nu_{sh}(\rho) = -\frac{\overline{\Delta E_0}}{h\rho} = \frac{2\pi|\mu_{01}^{(2)}|^2 v\rho d\rho}{h^2 kT} \int_{-\infty}^{\infty} \frac{|G(v)|^2}{v_0 - v} dv, \quad (2)$$

where  $p = nkT$  is the pressure of the perturbing gas, and  $v_0$  is the frequency of the  $J = 1 \leftarrow 0$  transition.

In this particular case, the most essential physical difference between the light polar perturbing molecules which we have investigated seems to be that the  $\text{NH}_3$  molecule belongs to the symmetric top species of molecules, while the molecules  $\text{HCl}$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{S}$  belong to linear molecules and to the asymptotic top species of molecules, respectively. It is known [1] that polar molecules in the symmetric top species have a dipole moment component which is constant with respect to spatial orientation, whereas neither linear molecules nor molecules of the asymmetric top species have such a component. It is natural to conjecture that this difference may play a role in the observed effect, i.e., a change in sign of the line shift. In this regard, we need to take into consideration of course that in our case, the conservation of constant spatial orientation of the molecule is important only at the time of collision. Hence, if we allow for the fact that the collision time is short, we expect that in the first instance, colliding molecules of different species ought to behave differently if the molecules are rotating rapidly. On the average, light molecules (i.e., those with small moment of inertia) will be observed to be rotating faster. Heavy molecules, on the other hand, ought to behave identically as perturbers (within the framework of our conjectures) independently of whether the molecules are symmetric, asymmetric, or linear.

For simplicity, we will consider that the perturbing object is a gas molecule in its "most probable" state. Then as the perturbing molecule passes near the molecule under investigation, the impulse field which acts on the latter will have the form of a "videoimpulse" of duration  $\tau \approx \rho/v$  and amplitude  $\varepsilon_0 \approx \mu_{\text{eff}}/\rho^3$  for symmetric and/or slowly rotating molecules. For slowly rotating molecules, the effective dipole moment  $\mu_{\text{eff}}$  is equal to the total dipole moment of the perturbing molecule,  $\mu$ , while for a light symmetric top with rotational constants  $A$  and  $B$ ,  $\mu_{\text{eff}} = \mu\sqrt{B}/(\sqrt{A} + \sqrt{B})$ . (In this case,  $\mu_{\text{eff}}$  is equal to the projection of the dipole moment onto the axis of rotation of the top.) A simplified spectrum of such a perturbation is shown in Fig. 3a. For rapidly rotating linear and asymmetric molecules, the impulse field has the form of an "impulse with filling in," with a field amplitude of  $\varepsilon_0 \approx \mu/\rho^3$ , and a simplified spectrum as shown in Fig. 3b. The frequency of the variable field where the "filling in" occurs is determined by the rotational frequency of the molecule. For linear molecules,  $\nu_{\text{rot}} \approx 2BJ_{\text{max}}$ , where  $B$  is the rotational constant, and  $J_{\text{max}} = (kT/2hB)^{1/2}$  is the rotational quantum number corresponding to the rotational level with maximum population [1]. In the case of a strongly asymmetric top, we can use the geometric mean of the three rotational constants for rough estimates. Within the framework of these conjectures, the estimated number of revolutions of the light molecules listed in Tables 1 and 2 during the time of a collision lies between two and three [i.e.,  $\nu_{\text{rot}} = (2-3)\tau^{-1}$ ]. The following condition is usually fulfilled:  $v_0 \ll 1/\tau$  ( $v_0 \sim 10^{10}-10^{11}$  Hz,  $1/\tau \sim 10^{12}$  Hz [1]). When this is fulfilled, the integral in (2) can be calculated easily for perturbations which have the properties shown in Fig. 3. The integral is equal to  $2q^2\tau v_0$  in case (a) and  $4q^2\nu_0/\tau\nu_{\text{rot}}^2$  in case (b). Assuming for purposes of these estimates that  $q \sim \varepsilon_0\tau$ , and carrying out the integration over  $\rho$  in (2), we obtain

$$\Delta\nu_{sh} = \frac{4\pi\nu_0 |\mu_{01}^{(z)}|^2 \mu_{eff}^2}{h^2 k T v^3 \rho_0} \quad \text{for case (a);} \quad (3)$$

$$\Delta\nu_{sh} = - \frac{8\pi\nu_0 |\mu_{01}^{(z)}|^2 \mu^2}{3h^2 k T v_{rot}^2 \rho_0^3} \quad \text{for case (b).} \quad (4)$$

Here,  $\rho_0$  is the minimum impact parameter, which may be estimated from the line broadening parameter  $\Delta\nu_{br}$  as follows:  $\rho_0 = [(2kT\Delta\nu_{br})/v]^{1/2}$ . In Tables 1 and 2 we give results of calculating the shift parameter at  $T = 300^\circ\text{K}$  according to relations (3) and (4).<sup>\*</sup> It is obvious that the calculated signs and order of magnitude of  $\Delta\nu_{sh}$  agree with the experimental values. A noteworthy result of the treatment presented above is that the theoretical formulas (3) and (4) which we have obtained show that the shifts are proportional to the transition frequency  $\nu_0$ . This had been discovered in the earlier experimental work [7, 8].

Hence, the essentially dynamical dependence of the line shifts on pressure which we have discovered in the present work and in [7, 8] can actually be explained in a unified manner on the basis of the dynamical Stark effect. In our opinion, our investigations now enable us to start calculating the phenomenon of pressure shifts of lines quantitatively, as well as the temperature dependences of the shifts, etc. It should be noticed in particular that in a number of cases, the shift turns out to be much more sensitive to the details of the intermolecular interactions than the line width. (This is obvious from the data in Tables 1 and 2.) And yet it is the line width which has been used almost exclusively so far for investigating these interactions.

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<sup>\*</sup>In calculating  $\Delta\nu_{sh}$  for the  $1_{10} \leftarrow 1_{01}$  transition of the water molecule, we allowed for the interaction of this pair of levels only. Therefore, the value of the shift obtained from (3) and (4) was increased by a factor of two.