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INVESTIGATION OF MOLECULAR LINE SHIFT BY PRESSURE OF INERT GAS

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Frequency shifts of the $J=1 \leftarrow 0$ rotational line of PH_3 at a frequency of 267 GHz as a result of pressure of the inert gases He, Ne, Ar, Xe are investigated. The calculated values of the shifts are in good agreement with experiments.

Earlier the authors offered an interpretation of the experimentally measured shifts of spectral lines by gas pressure for $J=1 \leftarrow 0$ transitions of molecules of symmetrical-top type [1]. The line shift was interpreted in terms of Stark displacement of the levels between which the transition occurs, in the field of other molecules. It is definitely of interest to extend calculations of the shift both to other molecular transitions and to mixtures of gases.

In this paper we will calculate the shifts of rotational molecular lines as a result of pressure of inert gases; the results are compared with experiments conducted by the authors, and also with literature data. This case is both of practical interest (in conjunction with the use of inert gases as "buffers") and of theoretical interest — from the standpoint of verifying the fruitfulness of the "Stark" approach.

1. The frequency shift of a spectral line is determined as the result of Stark displacement of the energy levels of the molecular transition under consideration upon interaction ("collision") with another molecule. Collisions are assumed to be pair collisions, a valid assumption for pressures up to atmospheric values [2]. The necessary calculations of the Stark displacement of the energy levels in strong fields were made in [3]. The fact that, to compute the shift, we are in effect interested in the displacement of the level as averaged over the quantum numbers M makes it possible to greatly simplify the calculations. Specifically, it turns out that the displacement of the levels as averaged over M , for the case $K=0$ under consideration, can be well approximated by the following power-law relation:

$$\varepsilon = -az^b, \quad (1)$$

where ε and z are, respectively, the level displacement and the Stark interaction parameter, expressed in units of hB : $\varepsilon = W/hB$, $z = \mu\mathcal{E}/hB$ (B and μ are the rotational constant and dipole moment of the molecule; W , energy of the level; and \mathcal{E} , electric field strength); the constants a and b , which depend on the quantum numbers, are given in Table 1. As in [1], we will assume that when molecules approach to a distance less than some R_0 , the molecule under consideration changes its quantum state, and thus the region $R < R_0$ need not be taken into account in calculating the line shift. As in [1], R_0 is determined from the condition

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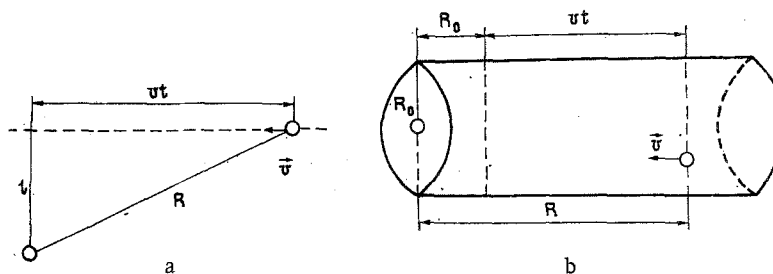


Fig. 1

TABLE 1

J	0	1	2	3
a	0,2131	0,0242	0,002	$4,68 \cdot 10^{-5}$
b	1,5	2	2,486	3,33
z_0	4,45	12,85	25,04	37,28

that the Stark perturbation becomes equal to the distance to the nearest higher energy level.* Thus, for $J = 0$ the value of ϵ is -2 in this case; for $J = 1$ we have $\epsilon = -4$; for $J = 2$ $\epsilon = -6$, and so forth; Table 1 gives the corresponding values of z_0 as computed from (1).

For the first rotational transitions, when R_0 is much larger than the dimensions of the molecule ("radiospectroscopic collisions" [2]), we can confine ourselves to the dipole approximation for the field of the perturbing molecule. When a polar molecule collides with an atom of inert gas, the field of the latter, determined by the induced dipole moment, is equal to the following (to within a coefficient of order unit):

$$\mathcal{E} = \alpha \mu / R^6, \quad (2)$$

where α is the polarizability of the atom; R is the distance between the atom and molecule. In this case the parameter z is

$$z = \alpha \mu^2 / \hbar B R^6. \quad (3)$$

Let us compare the averaged shift of the line frequency. Figure 1 shows a scheme of pair collision of molecules. Weak "radiospectroscopic" collisions do not alter the trajectory of the molecule, and it is convenient to make calculations in two stages: for $l > R_0$ (Fig. 1a) and for $l \leq R_0$ (Fig. 1b). For case a), if τ is the mean time between collisions, then the number of collisions per second with impact parameter from l to $l + dl$ and with relative velocity from v to $v + dv$ is

$$1/\tau = 2\pi n l v F(v) dl dv, \quad (4)$$

where n is the concentration of atoms involved in the collisions under consideration; $F(v)$ is the relative-velocity distribution function. The time-average displacement of the energy level of a molecule in collisions with these atoms, in the paired-collision approximation, is

$$1/\tau \int_{-\infty}^{\infty} \epsilon(t) dt = - \frac{2aD}{v \tau l^{6b-1}} \left(\frac{\alpha \mu^2}{\hbar B} \right)^b, \quad (5)$$

where $D = \int_0^{\pi/2} \sin^{6b-2} \varphi d\varphi = \frac{\Gamma(3/2)\Gamma(3b-1/2)}{\Gamma(3b)}$; Γ is a gamma function. Substituting (4) into

(5) and integrating with respect to l from R_0 to ∞ and with respect to v from 0 to ∞ , we can obtain the displacement of the energy level:

$$\epsilon_1 = - \frac{4\pi n \mu \sqrt{\alpha} a D z_0^{b-1/2}}{3\sqrt{\hbar B} (2b-1)} \quad (6)$$

[here R_0 is expressed in terms of z_0 from (3)]. Correspondingly, for case b),

$$1/\tau = \pi R_0^2 n v F(v) dv, \quad (7)$$

*We should note that this estimate for R_0 is of course arbitrary to some extent.

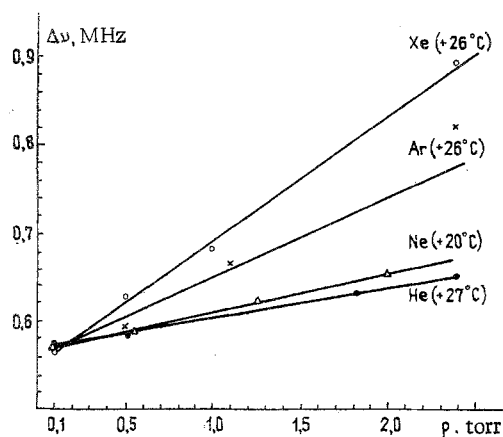


Fig. 2

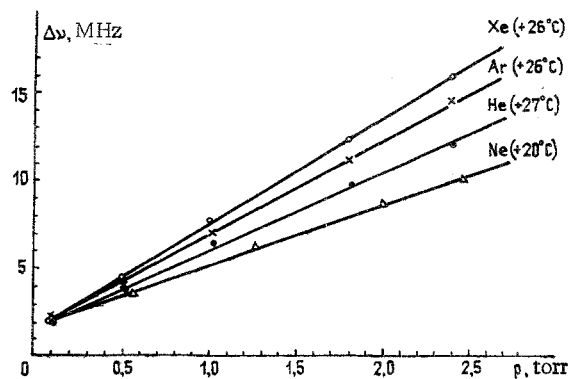


Fig. 3

Fig. 2. Experimental behavior of displacement of center of $J=1 \leftarrow 0$ of PH_3 molecule as a result of inert gas pressure.

Fig. 3. Experimental behavior of total width of $J=1 \leftarrow 0$ line of PH_3 molecule (with respect to half-intensity level) as a function of inert gas pressure.

TABLE 2

Transition	$P_l - P_u$
$J = 1 \leftarrow 0$	0,347
$J = 2 \leftarrow 1$	0,234
$J = 3 \leftarrow 2$	0,172

and similar calculations yield

$$\varepsilon_2 = - \frac{\pi n \mu \sqrt{\alpha} a z_0^{b-1/2}}{\sqrt{hB}(6b-1)} \quad (8)$$

Thus, the total displacement of the level is

$$\varepsilon = \varepsilon_1 + \varepsilon_2 = - \frac{\pi n \mu \sqrt{\alpha}}{\sqrt{hB}} P, \quad (9)$$

where $P = a z_0^{b-1/2} \left[\frac{1}{6b-1} + \frac{4D}{3(2b-1)} \right]$. The line frequency shift is

$$\Delta \nu = (\varepsilon_u - \varepsilon_l) B = \frac{\pi n \mu \sqrt{\alpha B}}{\sqrt{h}} (P_l - P_u), \quad (10)$$

where l and u denote the lower and upper levels, respectively, while P_l and P_u are computed for the smallest of the z_0 levels which determines the change in the quantum state of the molecule (in our case the z_0 lowest levels); values of $(P_l - P_u)$ are given in Table 2. The shift parameter is determined in the customary fashion:

$$\Delta \nu_c = \frac{\Delta \nu}{P} = \frac{\pi \mu \sqrt{\alpha B}}{k T \sqrt{h}} (P_l - P_u), \quad (11)$$

and the final working formula is

$$\Delta \nu_c = 11.8 \gamma \frac{\mu \sqrt{\alpha B}}{T} (P_l - P_u) \text{ (MHz/torr)}, \quad (12)$$

where B is expressed in gigahertz, μ in Debye units, α in angstroms cubed and γ is a numerical factor of order unit that takes account of the approximate nature of the calculations and is determined empirically.

TABLE 3

Molecule	Rotational transition	Rotational constant B, GHz	Shifting gas	Expt. shift parameter $\Delta\nu_c^e$, MHz/torr	Calc. shift parameter $\Delta\nu_c$, MHz/torr	Reference
PH ₃	1 ← 0	133,48	He	+0,039 (20)	+0,036	
PH ₃	1 ← 0	133,48	Ar	+0,109 (30)	+0,102	
PH ₃	1 ← 0	133,48	Xe	+0,142 (50)	+0,160	
PH ₃	1 ← 0	133,48	Ne	+0,045 (20)	+0,051	
H ₂ CO	2 ₀₂ ← 1 ₀₁	36,4 †	He	+0,01 (4)	+0,053	[5]
H ₂ CO	3 ₀₃ ← 2 ₀₂	36,4 †	He	+0,02 (2)	+0,039	[5]
HCl	1 ← 0	312,95	Ar	+1,03	+0,564	[7]*
HCl	2 ← 1	312,95	Ar	+0,39	+0,38	[7]*
HCl	3 ← 2	312,95	Ar	+0,35	+0,28	[7]*

*These results were obtained by infrared spectroscopy.

†B + C/2.

2. Experimental investigations of line shift and broadening were conducted using an RAD submillimeter microwave spectrometer with a precise frequency measurement system [4]. We investigated the shift and broadening of the $J=1 \leftarrow 0$ spectral line of the phosphine molecule, PH₃, at a frequency $\nu_0 \approx 267$ GHz as a result of pressure of the inert gases He, Ne, Ar, Xe. The gas pressure was monitored by a membrane vacuum gauge. The following procedure was employed to eliminate "self-shift" of the PH₃ line by the pressure. At the beginning of each trial, phosphine was admitted into the evacuated absorption cell of pressure $p \approx 0.1$ torr, and the frequency of the center of the $J=1 \leftarrow 0$ line was measured; this then provided the reference point for the given trial. Then inert gas was added to the cell at pressures $p \approx (0.5-2.5)$ torr, and the center frequency of the line was again measured. The resultant data were used to determine the shift parameter of the molecular line resulting from nonpolar gas pressure. The spectral line width was measured in each trial simultaneously with the frequency.

Figures 2 and 3 and Table 3 present the experimental findings.

3. Table 3 gives experimental values of the parameters of the line shift as a result of inert gas pressure obtained by us and in [5, 7], as well as calculated values of the shift parameters. The polarizabilities of the inert gas atoms were computed from the indices of refraction [6] and are (in units of angstromscubed 0.207; 0.396; 1.68 and 4.154 for helium, neon, argon, and xenon, respectively; the value $\gamma = 0.874$ was employed in calculations using (12).

Examination of the results reveals that, for different molecules, different quantum transitions, and different inert gases, the calculated shift values obtained using the same value of the empirical factor γ differ from the experimental ones within the limits of statistical indeterminacy. This evidently provides some solid support for the "Stark" approach to the explanation of molecular line shifts in the case under consideration.

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