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DEPENDENCE OF MOLECULAR LINE SHIFTS ON THE GAS PRESSURE

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The recent increase in accuracy of spectral measurements brought about an increased number of studies of frequency shifts of the centers of spectral lines as functions of the gas pressure (see, e.g., [1-6]). These studies give information about intramolecular interactions, and are necessary for high-resolution predissociation spectroscopy. At the same time, the number of experimental data in this field is very small, and this makes the theoretical interpretation of the results inconclusive [1]. It is therefore of interest to find a simple law governing the experimental data. At the present time, experimental data are available on the spectral line shifts of symmetric tops [2, 4-6] which will be used in the present work. The authors are grateful to V. P. Kazakov and A. A. Mel'nikov for supplying the data on the spectral line of AsH_3.

Table 1 shows the experimental data on the shift parameter $\Delta\nu_c$ of the spectral line corresponding to transitions $J = 1 \leftarrow 0$ for a number of molecules of the symmetric-top type. The shift is induced by pressure of the same gas whose line shift is measured. A qualitative analysis of the data shows that all shifts have positive signs. This is in agreement with the prediction [3] from the sign of the Stark effect of this transition. A quantitative analysis leads to the conclusion that the most important parameters which affect the magnitude of the shift are the transition frequency ν, and the dipole moment of the molecule μ; these are also given in Table 1. Indeed, in 30-70 cases when the transition frequencies, squares of the dipole moments, and the magnitudes of the shifts took on different values at random, the combination

$$r = \frac{\Delta\nu_c}{\nu\mu^2} \tag{1}$$

had the same value for all transitions, with a root-mean-square error of about 40%. The normalized values of the parameter $r/\bar{r}$ are given in Table 1. This dependence is clearly established for the first time. It should be noted that it is based on data obtained at different times by five research groups (Table 1).

Further analysis of the quantities $r/\bar{r}$ for each molecule makes it possible to make a conclusion about a weaker dependence of the shift on the mass M of the molecule. When the data of Table 1 are approximated by a linear function the root-mean-square deviation of the results decreases to 10%. We note that the order of

TABLE 1

Molecule	Frequency of the line $J = 1 \leftarrow 0$, ν, GHz	Dipole moment of the molecule μ, Debye	Line shift parameter $\Delta\nu_c$, MHz/torr	Ratio $r/\bar{r}$, where $r = \frac{\Delta\nu_c}{\nu\mu^2}$	References
PH_3	266,96	0,57	+0,56	0,60	[4]
CH_3Cl	26,59	1,892	+1	0,98	[6]
AsH_3	224,94	0,22	+0,13	1,11	
$CH_3^{79}Br$	19,14	1,797	+0,85	1,29	[2]
$CH_3^{127}I$	15,00	1,647	+0,70	1,61	[2]
$NH_3(v_2=1)$	466,25	1,2	+3,2*	0,41	[5]

*This result was obtained from [5] under the assumption that the half-width of the line is 7.5 MHz/torr [7].

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TABLE 2

Molecule	Frequency of the lines J = 1←0 ν_0, GHz	Dipole moment of the molecule μ, Debye	Mass of the molecules M, amu	Predicted shift parameter $\Delta\nu_c$, MHz/torr
AsF_3	11,76	2,82	132	+1,6
CH_3CN	18,4	3,92	41	+2,3
CH_3F	51,08	1,79	34	+1,2
CHF_3	20,7	1,64	70	+0,6
NF_3	21,36	0,234	71	+0,01
PF_3	15,64	1,025	88	+0,2

magnitude of these errors coincide with the errors of the experimental determination of the line shifts.

Using these data the authors attempted to predict the shift parameters of the lines J = 1 ← 0 for other symmetric tops whose frequencies and dipole moments were obtained from tables in [7]. The shift parameters were calculated from

$$\Delta\nu_c \ (\text{MHZ/torr}) \approx 1.07 \cdot 10^{-2} \nu\mu^2 f(M), \tag{2}$$

where the frequency ν is measured in gigahertz, the dipole moment μ in Debye, and the dependence on the mass of the molecule f(M) has the form

$$f(M) \approx 1 + 9.3 \cdot 10^{-3} (M - 67), \tag{3}$$

where M is given in atomic mass units. The data of the calculation are shown in Table 2.

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