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Experimental Nonadditivity of Pressure Lineshifts in the System of Transitions of the Ammonia Molecule

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Experimental evidence of inequality of algebraic sums of pressure lineshift parameters of transitions along different paths connecting the same initial and final energy levels in the spectrum of the ammonia molecule is demonstrated. Though such a possibility follows, e.g., from different values of parameters of nearest approach of perturbing molecules $\mathbf{b}_0$ for different transitions in Anderson-type theories (and similar effects in other theories), up to now it lacked experimental evidence. Some consequences of the phenomenon and further studies are discussed.

Often initial and final levels in the system of energy levels of a molecule can be connected via different sets of transitions which form different paths in the energy level scheme. With the appearance of precise measurements of pressure lineshift parameters it is of interest to compare the algebraic sums of the experimental lineshift parameters along different paths.

During the past thirteen years only three full sets of pressure lineshift parameters have been measured; these involve the lowest J and K levels of the ammonia molecule, in its ground and $v_2 = 1$ states. The first example of two different closed paths connecting the same states was found in the lowest transitions of ammonia (*1*), between levels with $K = 0$ and $J = 0$ and 1; it showed coincidence between the two sums of measured lineshifts to within 3%, i.e., well within the quoted accuracy limits. This scheme was later discussed theoretically in Ref. (*2*), where the calculated sums of lineshifts coincided to within 5%.

However, the second example of closed chains of transitions, found in (*3*) for $K = 2$ and $J = 2$ and 3, also involving ground and $v_2 = 1$ states of ammonia, showed evidence of nonadditivity.

Combination of our measurements with recent IR measurements (*4, 5*) made it possible to find a third combination for $K = 1$, $J = 1$ and 2 also involving ground and $v_2 = 1$ states of ammonia, which also showed nonadditivity of the lineshifts, which is the subject of the present short communication.

For completeness let us consider here both cases of nonadditivity that were found. The transitions of the ammonia molecule involved, with their pressure self-shift parameters and their errors, are collected in Table 1.

In Fig. 1, the first scheme of transitions, with $K = 2$, involving the ground and $v_2 = 1$ states of ammonia molecule together with experimental pressure self-shift parameters, is shown (*3*). As can be seen, the results of summing pressure self-shift parameters along two paths do not coincide and the error limits of results of summing do not overlap.

In Fig. 2, the second scheme of transitions, with $K = 1$, also involving ground and $v_2 = 1$ states of ammonia molecule together with experimental pressure self-shift parameters, is presented. Again, results of summing pressure self-shift parameters along two paths do not coincide; the difference between two sums is 0.97 MHz/Torr.

Unfortunately, for some of the lineshift parameters included in the chain no error limits were directly mentioned in numbers, so for them some estimates were made. These shift parameters were measured in (*1, 8, 11*). For one of them (marked in Table 1 by an asterisk) estimates of error were obtained from the experimental dependence of this transition frequency on ammonia pressure presented in Fig. 1 of Ref. (*8*) and gave an error limit of a few (no more than 5) percent. For another (marked in Table 1 by two asterisks) belonging to the same series of measurements from figures and numbers in Refs. (*1, 8, 11, 12*), the same 5% upper level of error was assumed.[1]

Comparison of the sums of measured lineshift parameters along two paths in Fig. 2 showed significant difference between them, and estimated error limits did not overlap (Table 1 and Fig. 2). It is worth noting that for this case, also, calculated lineshift parameters are available for all transitions involved (Table 1), which permits combinations of calculated values of lineshifts to be compared; the difference of two sums of calculated lineshift

[1] For six ammonia lines self-shifts of which were measured in this series, in the references aforementioned, the error of the lineshift parameters varied from 1.1% for $J = 1–0$ transitions of $^{14}NH_3$ and 1.8% for $^{15}NH_3$ ammonia to 3.9% for the forbidden transition $a(3, 3) \leftarrow a(2, 0)$ in the $v_2 = 1$ state and 2.5 and 4% for the pair of $J = 1–0$ transitions in the high-lying $v_4 = 1$ state. The same series of measurements produced lineshift parameters for the scheme (1) which showed coincidence between the two sums mentioned within 3%.

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TABLE 1
Transitions of the Ammonia Molecule and Their Experimental and Calculated Pressure Self-Shift Parameters Involved in the Schemes of Figs. 1 and 2

Ammonia Transitions Involved	Frequencies/ Wavenumbers Of Transitions	Measured Self – Shifts MHz/Torr	Errors Quoted MHz/Torr	Calculated Self – Shifts MHz/Torr	References
aQ(2,2), $v_2 = 1 \leftarrow 0$	931.33 cm^{-1}	– 1.11	0.02	– 1.4	(4) , (6)
a(2,2) ← s(2,2), $v_2 = 1$	1 067.7 GHz	+ 1.5	0.15	+ 1.8	(8), (6)
sP(3,2), $v_2 = 1 \leftarrow 0$	908.12 cm^{-1}	+ 0.13	0.07	+ 0.7	(9), (6)
s(3,2) ← a(2,2), $v_2 = 0$	1 763.8 GHz	+ 0.9	0.4	–	(10),
aQ(2,1), $v_2 = 1 \leftarrow 0$	932.14 cm^{-1}	+ 0.79	0.01	+ 1.1	(4), (7)
aP(2,1), $v_2 = 1 \leftarrow 0$	891.88 cm^{-1}	– 1.7	0.2	– 1.5	(5), (7)
a(1,1) ← s(1,1), $v_2 = 1$	1 066.7 GHz	– 2.4	0.12 *	– 1.7	(11), (1), (6), (8)
s(2,1) ← a(1,1), $v_2 = 1$	140.1 GHz	+ 3.92	0.2 **	+ 3.2	(11), (1), (6)

*,** For explanations see text.

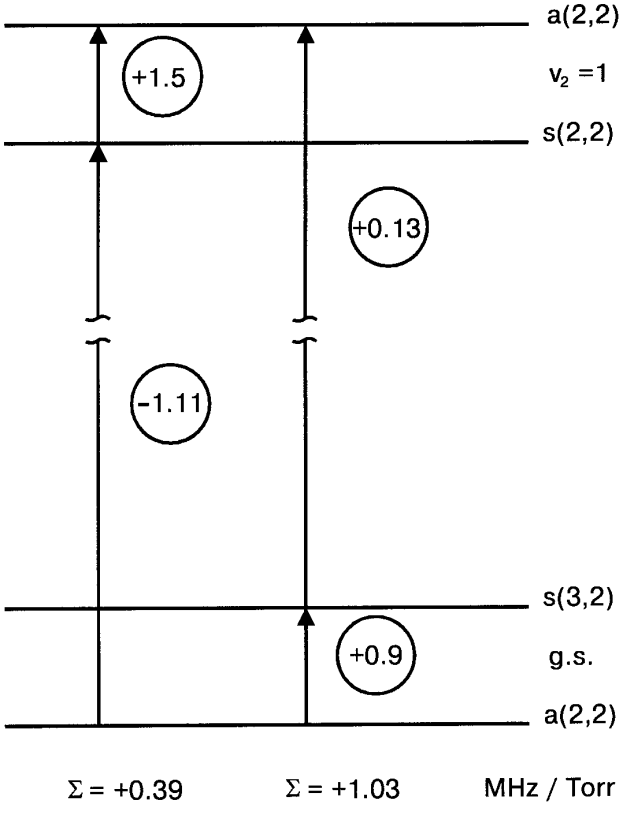

FIG. 1. A scheme of transitions in the ammonia molecule forming two paths between initial and final levels. Experimental values of pressure self-shift parameters of transitions are given in MHz/Torr in circles. Sums of shift parameters along left and right paths in MHz/Torr are presented below the scheme.

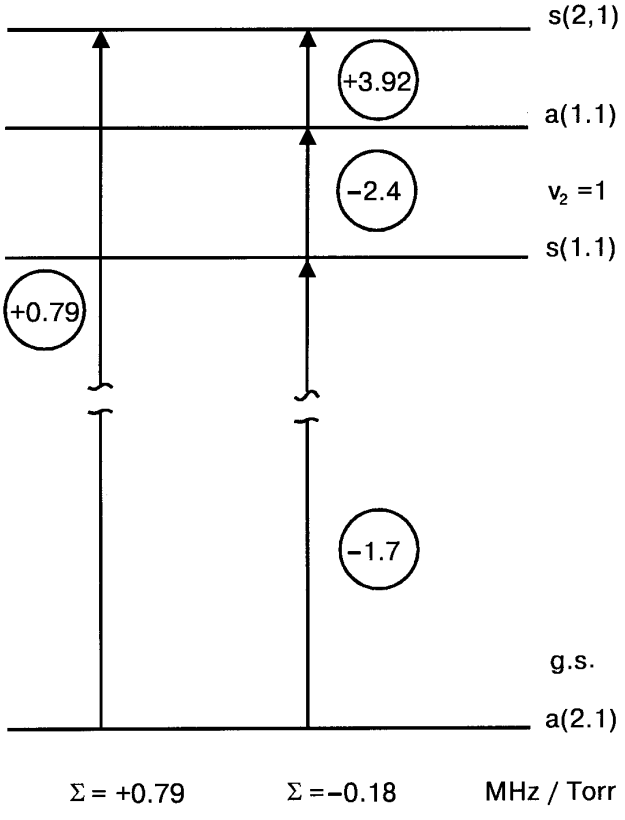

FIG. 2. A scheme of transitions in the ammonia molecule forming two paths between initial and final levels. Experimental values of pressure self-shift parameters of transitions are given in MHz/Torr in circles. Sums of shift parameters along left and right paths are presented below the scheme in MHz/Torr.

parameters along two paths is 1.1 MHz/Torr, thus showing good coincidence with the experimental value, 0.97 MHz/Torr.

It is not the aim of this short communication to set forth well-developed collision theories; we will try only to present a simple physical picture of the phenomenon considered.

Physically, the possibility of nonadditivity of the pressure lineshifts arises from the fact that the effective distance of nearest approach of the perturbing molecule, $\mathbf{b}_0$,[2] i.e., the average perturbing field strength, is different for different transitions, and the dependence of perturbation on the distance is nonlinear. The effective distance of nearest approach is defined, e.g., for adiabatic collisions as the distance at which phase shift produced in collision approaches π. Clearly it will depend on the ''Stark sensitivity'' of the transition in the case of Stark perturbation. Collisions closer than this distance (''strong collisions'') do not contribute to the shift. So at the same time in the same gas different transitions experience different effective Stark fields (in the case of Stark perturbation), so measurements of transition frequencies along different paths correspond, roughly speaking, to measurements of lines in a different Stark field for each line, which obviously can lead to different results from summing the line frequencies along different paths.

So from the theoretical point of view, the phenomenon considered probably must be common rather than rare; nevertheless it was not experimentally demonstrated until recently. Most probably, lack of experimental evidence reflects simply the scarcity of pressure lineshift studies, especially when high accuracy is required in a very broad spectral range (note the range of frequencies of lines involved in Table 1), which makes further experimental studies very desirable.

Additivity of lineshifts was discussed in (*2*) on the basis of result of (*1*). The authors of (*2*) stated that ''definition of $\mathbf{b}_0$ through Eqs. (7) and (8) [equating to unity real part of or the entire efficiency function for weak interactions] introduces an element of nonadditivity for both shift and width. In fact, we can see from Fig. 1 that the calculated shift values are additive only within 5%.''

The example of the scheme in Fig. 2 of this work, the values of calculated lineshift parameters for which were taken from papers by the same authors (*6, 7*), shows that the phenomenon mentioned can also make a more significant contribution to practical calculations based on Anderson's theory. Physically, this occurs because contribution of the nearest part of the ''weak interaction'' zone to the total shift is significant.

One of the consequences of the demonstrated nonadditivity of pressure lineshifts to be kept in mind is that if one measures the positions of centers of collisionally broadened lines, their sums (which seem to be the distances between initial and final levels) can be different when obtained from different paths or sets of transitions, and this difference can approach several MHz at pressures of the order of Torr, being significant at existing accuracies of measurements. So this phenomenon can be not only of theoretical (as a limit of accuracy of reconstruction of energy levels from pressure broadened lines measurements), but also of practical interest.

[2] Speaking in terms of Anderson-type theories; other theories in other terms give the same net result.

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Note added in proof. Reference (*4*) was changed from a personal communication to Ph.D. thesis before a copy of the thesis was actually received; it was then found that the value of the self-shift parameter for a $Q(2,1)$ line in the thesis was slightly changed to +0.888(13) MHz/Torr. This revision only strengthens the inequality of the two sums shown in the scheme of Fig. 2.

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