Graphical determination of approximate valence force constants of C_{3v} -molecules

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Abstract—It is shown that by plotting f , d -curves from frequency formulae, derived by Lechner for symmetric top molecules, force constant values can be obtained for the stretching and bending modes, which give a reasonably good fit of the observed frequencies. Simplification of the procedure results from using an apex angle α as calculated from the frequency formulae.

MANY authors have reported on force constants for C_{3v} -molecules [1–6], using a valence-type potential function with two constants. In many cases the calculated frequencies proved to be in poor agreement with the observed ones.

A better fit of the observed fundamentals is obtained if the two force constants (f and d for the stretching and bending modes respectively) are determined graphically as follows. By substituting the data for the four normal frequencies in the formulae of LECHNER [7], two linear and two hyperbolic equations result. The latter are used to calculate the angle β between the altitude and the edge of the pyramid. The angle β is related to the apex angle α by

$$\sin \beta = \frac{2}{\sqrt{3}} \sin \frac{1}{2} \alpha$$

The calculated β -values do not always agree with the apex angle known from other evidence, but as is well known, force constants are rather insensitive to variation of the apex angle [1]. Using these β -values the two hyperbolic curves necessarily coincide. Values for f and d are found from the intersection of the hyperbolic curve and the bisectrix of the angle between the lines obtained from the two linear equations. (There may be two intersections, only one has physical meaning.) (See Figs. 1 and 2.)

The procedure as outlined above has been checked for a number of compounds (See Table 1). All molecules are considered to be four-mass models, consisting of a

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vertex atom Y (Y = N, P, As, Sb, Bi) and three equal corner masses X (X = hydrogen, halogen, methyl, and ethynyl). As can be seen the calculated frequencies are in good agreement with the observed ones. We checked the insensitivity of force constants to variation of the apex angle for some molecules (See Table 2). The α -values used are taken from the references [1-6, 8-12] or are assumed. The force constants computed

Table 1. Normal frequencies ω in cm^{-1} . For each substance: first row: observed frequencies, second row: calculated frequencies. Force constants f and d in $\text{mdyn}/\text{\AA}$.
() uncertain, see Ref. [16]

Substance	ω_1	Normal frequencies		ω_4	$\angle \text{YX}$ calc.	Force const.		References for ω -values
		ω_2	ω_3			f	d	
PH ₃	2322.9	992.0	2327.7	1122.4	98°48'	3.11	0.332	[12]
	2313	996	2338	1117				
PF ₃	892	487	860	344	78°37'	4.90	0.722	[5, 6, 11, 13]
	953	456	816	363				
PCl ₃	510	257	480	190	85°45'	2.01	0.389	[1, 5, 6, 14]
	538	244	458	205				
AsCl ₃	410	193	370	159	82°36'	2.03	0.248	[1, 5, 6, 14]
	408	194	373	158				
N(CH ₃) ₃	827	365	1036	423	109°26'	3.82	0.437	[3, 4]
	799	377.5	1073	408				
P(CH ₃) ₃	653	263	708	305	105°39'	2.83	0.263	[4, 15]
	661	260	730	296				
As(CH ₃) ₃	568	223	583	239	100°	2.45	0.201	[4]
	563	225	587.5	237				
Sb(CH ₃) ₃	513	188	513	188	94°23'	2.07	0.139	[4]
	510	189	516	187				
Bi(CH ₃) ₃	460	171	460	171	93°2'	1.74	0.120	[4]
	459	171	461	170				
P(C≡CH) ₃ *	615	120	646	100	93°58'	3.25	0.057	[16, 17]
	617	120	644	100				
As(C≡CH) ₃ *	526	89	517	100	101°7'	3.08	0.050	[16]
	504	93	542	95				
Sb(C≡CH) ₃ *	477	(72)	449.5	94	104°1'	2.69	0.043	[16]
	450	76	480	88				

* The striking agreement for P(C≡CH)₃ and the relative bad results for As(C≡CH)₃ and Sb(C≡CH)₃ do suggest an incorrect assignment for the latter. MILLER and LEMMON [16] say in their conclusion about the assignment that "in a few cases the symmetry species may be interchanged".

We have done so for the As- and Sb-compounds and obtained the following results:

Substance	ω_1	ω_2	ω_3	ω_4		α	f	d
As(C≡CH) ₃	517	100	526	89	obs			
	618	100	525	89	calc	92°23'	3.00	0.050
Sb(C≡CH) ₃	449.5	94	477	(72)	obs			
	472	89	456	75	calc	82°54'	2.59	0.041

For the As-compound the results are in favour of interchanging. The assignment of the Sb-compound does not seem to fail with respect to symmetry only.

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Fig. 1. $N(CH_3)_3$. Force constants are found from the intersection of bisectrix (broken line) and hyperbolic curve.

Fig. 2. $AsCl_3$. Determination of force constants as in Fig. 1.

Table 2. Calculated force constants with apex angle values assumed or taken from references

Substance	α	f	d
PH_3	$93^\circ 50'$	3.10	0.323
$AsCl_3$	96°	2.10	0.250
$P(CH_3)_3$	103°	2.79	0.261
$P(CH_3)_3$	100°	2.75	0.266
$Sb(CH_3)_3$	98°	2.08	0.141
$Sb(CH_3)_3$	90°	2.06	0.138

with these α -values justify the procedure as followed here. The assumption of methyl and ethynyl being "point-masses" seems a rough approximation; however, the calculated frequencies agree very well with the observed ones.

A start has been made with a **GF**-matrix calculation of the ethynyl compounds. The f and d values as found here seem to be reasonable first estimates for some of the **F** matrix elements.