

### Internal Rotation in Molecules with Two or More Methyl Groups

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# Internal Rotation in Molecules with Two or More Methyl Groups

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July 31, 1942

In treating the internal rotation of molecules with two or more identical rotating groups, it has been commonly assumed, of necessity, that the potential energy for one rotation is independent of the position of the other groups. For some time the writer has been attempting to study this assumption but until recently the results have been disappointingly negative in character. However, one positive result may now be presented together with a brief discussion of the other work.

Kennedy, Sagenkahn, and Aston<sup>1</sup> have recently published measurements leading to the entropy of dimethyl ether. After subtracting contributions for the other modes of motion, the value 2.65 cal. per degree at 200°K was obtained for the entropy contribution of the two internal rotational degrees of freedom. This was interpreted on the basis of independent potential barriers for each methyl group of magnitude 3100 cal. per mole. However, Ananthakrishnan,2 has reported Raman shifts of 160 cm<sup>-1</sup> and 300 cm<sup>-1</sup> for dimethyl ether. Application of the usual harmonic oscillator formula to these frequencies yields an entropy contribution of 2.63 cal. per degree at 200°K in essentially perfect agreement with the above calorimetric value. Furthermore, these Raman lines have never been explained on any other basis. Therefore it seems likely that these lines are the fundamental frequencies of the two modes of torsional oscillation.

However, this picture is by no means certain. Earlier investigators<sup>3</sup> failed to find one or both of the lines. Although the selection rules permit these torsional modes in the Raman effect, they predict depolarized lines whereas Ananthakrishnan reports both lines polarized. This latter difficulty is partially offset by the fact that depolarized lines are normally broad and both of these lines are reported as broad. Thus additional study is needed before this assignment can be regarded as proved or disproved.

So far as the writer is aware, if this assignment proves to be correct it will be the first set of spectroscopic frequencies for torsional oscillations which is consistent with reliable thermodynamic data. Assuming moderate anharmonicity, these frequencies are in agreement with the observed entropy at higher temperatures and with the observed heat capacity in the gaseous state.<sup>4</sup>

Figure 1 shows first the expected equilibrium configuration and then moderate displacements in each of the two normal modes of internal torsion. It is quite apparent that mode A rapidly brings hydrogen atoms very close together while mode B allows them to remain at considerable distance from one another. Thus it is not surprising to find the first frequency almost double the second. A normal coordinate calculation yields for the force constants:  $\partial^2 V/\partial \varphi_1^2 = 8.0 \times 10^{-13}, \ \partial^2 V/\partial \varphi_1 \partial \varphi_2 = -3.4 \times 10^{-18}$  erg per radian². This value of the first constant corresponds to a cosine potential barrier of about 2600 cal. per mole. It is quite evident that the cross derivative or interaction term, although somewhat smaller, is by no means zero.

The other two types of calculations concerning the interactions of two or more methyl groups will now be described briefly. The first concerns the possibility of using the entropy and heat capacity of a single gas to determine both the potential barrier for the rotation of one methyl group by itself and the magnitude of the interaction. Calculations for several typical cases showed that there was practically no chance of obtaining information by this method. The differences were too small to be detected experimentally. This means, inversely, that when potential barriers obtained from entropies are used only to calculate heat capacities, no serious error is likely to arise from the neglect of cross terms.

The second calculation concerned the series propane, isobutane, and tetramethylmethane. A basic entropy was calculated for each molecule using the potential barrier from ethane (2800 cal. per mole) and the best available values for vibration frequencies, moments of inertia, etc. The amounts by which the observed entropies were smaller than these basic values might then be ascribed either to (1) interaction terms such as appear to be present in dimethyl ether, or to (2) a rise in the separate potential barriers upon substitution of methyl groups for the hydrogens in ethane. However, on the basis of reasonable approximations, both assumptions led to the same relative values, 1 to 3 to 6, for the entropy differences in propane, isobutane, and tetramethylmethane.<sup>5</sup> These ratios agree with the observed values within their respective experimental errors. However, this tells us nothing about the presence or absence of the interaction terms.

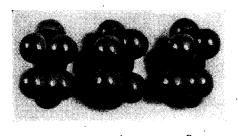


Fig. 1. Left, the equilibrium position; center, moderate displacement in torsional mode A; right, moderate displacement in mode B.

We may then draw the tentative conclusion that thermodynamic data alone will not give definite information concerning cross terms in the internal rotation potential energy, but that spectroscopic data, particularly when coupled with thermodynamic data, have interesting possibilities.

<sup>1</sup>R. M. Kennedy, M. Sagenkahn, and J. G. Aston, J. Am. Chem. Soc. **63**, 2267 (1941).

<sup>2</sup>R. Ananthakrishnan, Proc. Ind. Acad. Sci. **A5**, 285 (1937).

<sup>3</sup>S. C. Sikar, Ind. J. Phys. **7**, 257 (1932); A. Dadieu and K. W. F. Kohlrausch, Monatsh. f. Chemie **57**, 225 (1931); K. W. F. Kohlrausch, *ibid.*, **68**, 349 (1936); M. Wolkenstein and J. K. Syrkin, Nature **139**, 288 (1937).

(1937).

4 G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. 8, 618 (1940).

5 This calculation may be explained very roughly as follows: (1) The number of interaction terms will be the number of edges of the tetrahedron about the center carbon atom which connect two methyl groups. (2) The increments of potential barrier rise will be, respectively, 1, 2, and 3 for the series, but the number of degrees of freedom are, respectively, 2, 3, and 4. The products of these numbers are thus just double the numbers quoted in the text.

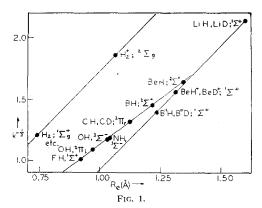
#### Force Constants and Internuclear Distance

GEORGE GLOCKLER AND GEORGE E. EVANS University of Iowa, Iowa City, Iowa July 20, 1942

N another connection we desired to know the relation In another connection we desired to between the force constant of the hydrogen-fluorine bond and its internuclear distance not only in HF but also in some of its more complex compounds. An attempt to apply Badger's rule1 indicated that the modern data of band spectroscopy as summarized by Herzberg<sup>2</sup> permit a very satisfactory estimate to be made of the internuclear distance if the force constant is known. The third-power rule was applied to the hydrides of the elements of the first row of the periodic table as shown in Fig. 1 and Table I. The results are accurate to better than one percent. The molecules studied were divided into three groups: (1) H<sub>2</sub>, HD, D<sub>2</sub>, and H<sub>2</sub>+; (2) LiH, LiD, BeH+, BeD+, BH, and

Table I. Force constant  $K = A(R_e - B)^{-3}$  megadyne/cm;  $R_e$  in angstroms

				Force constant (megadynes/cm		
Molecule	State	$\boldsymbol{A}$	В	From spectro- scopy	From equation	% error
H <sub>2</sub>	$1\Sigma_{g}^{+}$	0.1152	0.1555	0.5735	0,5727	-0.14
$^{\mathrm{HD}}$	**	16	"	(0.5728)	0.5728	
$D_2$	**	"	**	0.5745	0.5718	-0.47
$H_{2}^{+}$	2∑ <sub>n</sub> +	**	**	(0.1559)	0.1557	
Li <sup>7</sup> H	1 <u>&gt;</u> +	0.1187	0.5443	(0.1021)	0.1021	
Li <sup>7</sup> D		. "	44	0.1022	0.1023	-0.10
(Be9H)+	"	**	44	(0.2624)	0.2620	0740
(Be9D)+	**	**	**	0.2621	0.2629	-0.31
B <sup>11</sup> H	**	**	44	0.3031	0.3639	0.01
$B_{11}D$	**	44	**	0.3164	0.3667	
Be <sup>9</sup> H	<sup>2</sup> Σ+	0.3003	0.2385	0.2253	0.2229	+1.07
Be <sup>9</sup> D	- 64	"	0.2000	0.2200	0.2231	, 1,07
(B <sup>11</sup> H)+	**	44	**	0.3211	0.3225	-0.34
C12H	$2\Pi_r$	44	**	0.4348	0.4383	-0.80
$C^{12}D$	-17	44	**	0.4347	0.4399	-1.19
N14H	$3\Sigma^-$	**	44	0.6004	0.5876	+0.21
O16H	$2\Pi_i$	**	44	0.7727	0.7641	-1.11
$O^{16}D$	777	**	**	0	0.7704	1.11
(O16H)+	3 <u>~</u> –	**	44	0.4855	0.6079	
F19H	1 <u>Σ</u> +	"	**	0.9626	0.9631	-0.05



BD; (3) BeH, BeD, BH+, CH, CD, NH, OH, OD, OH+, and HF. Even better results could have been obtained if the last one had been divided into two subgroups: BeH, BeD, BH+, CH, CD; and NH, OH, OD, OH+, and HF. The first group contains hydrogen atoms only, the second group is made up of molecules all of them in the  ${}^{1}\Sigma^{+}$  state, and the third group covers the remainder of the first-row atoms.

The vibrational constant  $\omega_e$  is not known for Be<sup>9</sup>D and O<sup>16</sup>D, but the internuclear distances are, respectively, 1.3427 and 0.969A. Hence it may be predicted from the empirical rule that they are 1527 and 2731 cm<sup>-1</sup>, respectively. The values of  $\omega_e$  for B<sup>11</sup>H and B<sup>11</sup>D are supposed to be 2366 and 1780 cm<sup>-1</sup>, respectively, but they are uncertain. While they apparently fit into the third group, it appears plausible from Fig. 1 that these molecules should really belong to the second group. Since their internuclear distances are known accurately (1.2326 and 1.231A, respectively) their vibrational constants  $\omega_e$  are most likely 2566 and 1890 cm<sup>-1</sup>, as calculated from their force constants 0.3639 and 0.3667 megadyne/cm which were obtained from the equations of Table I. On the other hand, the  $\omega_e$ value for  $(B^{11}H)^+(2435.0\ cm^{-1})$ , even though uncertain according to Herzberg, seems satisfactory since the molecule fits onto the straight line of the third group. But (O16H)+ does not fit the graph when the uncertain frequency is used to obtain the force constant. Hence it may be supposed that 3371 cm<sup>-1</sup> for  $\omega_e$  of  $(O^{16}H)^+$  as calculated from our equation is more satisfactory.

The ion (Be9H)+ does not fit into group 3, nor do the Li7H and Li7D structures. This fact was really the occasion to separate the hydrides into several groups. It appears that the more detailed analysis of Badger's rule has merit and that it can be used to obtain relations between force constant and internuclear distance in the case of first-row hydrides with satisfactory accuracy. It will of course be a matter of considerable interest to see how the predictions made will be fulfilled.

<sup>&</sup>lt;sup>1</sup> R. M. Badger, J. Chem. Phys. 2, 128 (1934) and 3, 710 (1935). <sup>2</sup> G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1928), Table 36.