

Rotational Magnetic Moment and Diamagnetic Susceptibility of Methane

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Citation: *The Journal of Chemical Physics* **24**, 918 (1956); doi: 10.1063/1.1742653

View online: <http://dx.doi.org/10.1063/1.1742653>

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TABLE I.

Solution	Units				
	Arbitrary on		Kanwisher device		
Roentgens (x-ray 200 kv, 10 ma, 0.01 in. Cu filter at 400 r increments)	0	400	800	1200	1600
Chloral hydrate 0.5 M	2.4	2.6	2.7	3.1	3.1
Chloral hydrate 0.5 M Glucose 0.01 M	4.3	5.4	6.3	7.0	8.0
Chloral hydrate 2.5 M	7.2	9.3	11.3	12.5	
Chloral hydrate 2.5 M Glucose 0.01 M	7.4	8.9	10.4	11.8	12.4
Chloral hydrate 2.5 M Glucose 0.1 M	7.8	7.8	7.8	8.1	8.1

chloral hydrate, 2.5 M, the same amount of glucose has little or no effect. Large amounts of glucose in solution had an inhibiting effect. The results were reproducible.

The reaction appears complex.¹ However, some explanation may be gleaned from the work of Dewhurst,⁵ who has shown that small quantities of aliphatic alcohols have a pronounced effect on the initial oxidation yield of ferrous sulfate. His explanation on the formation of a free radical and peroxide may hold for the effect of glucose on chloral hydrate.

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⁵ H. A. Dewhurst, *J. Chem. Phys.* **19**, 1329 (1951).

Rotational Magnetic Moment and Diamagnetic Susceptibility of Methane*

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(Received January 5, 1956)

IT has been shown by Wick,¹ Ramsey,² and Eshbach and Strandberg³ that the "high-frequency" term contributing to the diamagnetic susceptibility, χ , of a $^1\Sigma$ molecule may be obtained from a determination of its rotational magnetic moment. This moment is of the order of a nuclear magneton and may be measured by molecular-beam experiments² or, less accurately, from the Zeeman effect in the microwave spectrum.^{3,4} The "high-frequency" term involves the off-diagonal matrix elements for the total electronic orbital angular momentum about the magnetic field direction,⁵ and if it is written in terms of the rotational gyro-magnetic tensor elements, χ becomes

$$\chi_{\text{mole}} = \frac{Ne^2}{6mc^2} \left[- \sum_i \langle r_i^2 \rangle_{\text{av}} - \frac{1}{2M_p} \sum_{g=a,b,c} g_{gg}'' I_g \right], \quad (1)$$

where M_p is the mass of the proton, and I_g is the moment of inertia of the molecule about the principal axis g . Also g_{gg}'' is a diagonal member of the electronic part of the tensor and may be obtained from the measured quantity, g_{gg} , by subtracting off the nuclear contribution g_{gg}' (see reference 3 for this notation).

This paramagnetic contribution to χ is extremely difficult to calculate since it involves knowledge of the excited electronic states, and, except for H_2 ,⁶ it has generally been neglected. Such a procedure was followed by Buckingham, Massey, and Tibbs⁷ and Coulson⁸ in their calculations on CH_4 , and justified at that time by the near spherical symmetry of the molecule. Buckingham *et al.* used an approximate self-consistent field procedure and calculated the first term in Eq. (1) to be -33.2×10^{-6} emu. Coulson obtained a value of -26.6×10^{-6} from molecular orbital LCAO theory and -27.7×10^{-6} emu from the "electron-pairing"

approximation of valence bond theory. The experimental value of χ mole is -12.2×10^{-6} emu.⁹

Although the rotational magnetic moment of methane has not been measured, the value of g_{zz} (i.e., along the symmetry axis) of $\text{CH}_3-\text{C}\equiv\text{C}-\text{D}$ has been determined to be ± 0.31 from microwave Zeeman measurements.¹⁰ The π and σ electrons along the symmetry axis are in the cylindrical potential field about this axis and therefore do not contribute to g_{zz} . If it may be assumed that the methyl group electrons are unaffected when excitation takes place to the relatively low-lying excited states of the π electrons, then g_{zz} may be attributed to the motion of the CH_3 group alone. Hyperconjugation will have little effect upon the C-H bond characteristics¹¹ so that one may then take the value of g (since $g_{zz} = g_{yy} = g_{xx}$) for CH_4 to be that given in the foregoing. Then it also follows that the sign of the g -value must be positive simply because we are dealing with bonded rotating hydrogen nuclei.³

The nuclear contribution, $g' = +1.00$, may be subtracted out, and the second term in Eq. (1) is calculated to be $+9.3 \times 10^{-6}$ emu for CH_4 . The "experimental" value of the r^2 term now becomes -21.5×10^{-6} emu. Thus, the high-frequency term is about 40% of the diamagnetic one, and the assumption of complete "slippage" of the valence electrons was quite erroneous. Therefore, one concludes that the calculations of Buckingham *et al.* and Coulson are considerably more accurate than previously supposed, although they still yield too diffuse an electronic distribution. The important thing is that the simple molecular orbital and valence bond wave functions do give good values of $\langle r^2 \rangle_{\text{av}}$. It may be that a good fit of both the energy¹² and magnetic susceptibility data will lie within a reasonable range of variation of the parameters in Coulson's calculations.

I should like to thank Professor W. Moffitt for an informative discussion of this subject.

* The research reported in this paper was made possible by support extended Harvard University by the Office of Naval Research under ONR Contract N5ori 76, Task Order V.

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Calculation of Potential Barriers for Ethane-Like Symmetric Tops

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(Received January 9, 1956)

THE final explanation of the magnitude of barriers hindering internal rotation in the molecules of Table I and others must be given in terms of electronic energy as a function of the torsional

TABLE I. Potential barriers in cm^{-1} for ethane and ethane-like molecules.

	Experimental ^a	Calculated in this paper
CH_3CH_3	960	913
CH_3CCl_3	1040 ^b	1142
CH_3CF_3	1200	1202
CH_3SiH_3	558	571
CH_3SiF_3	410	694

^a See reference 2.

^b Pitzer and Hollenberg, *J. Am. Chem. Soc.* **75**, 2219 (1953).

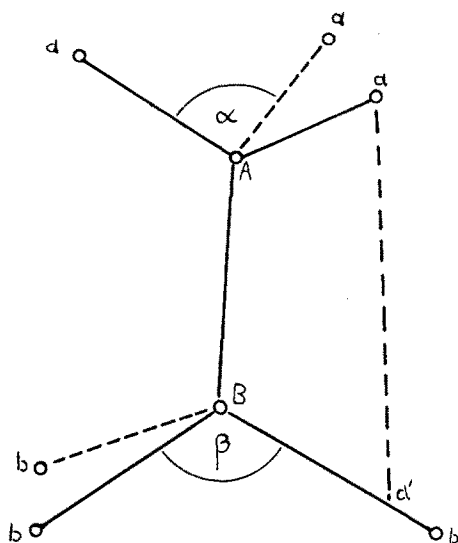


FIG. 1. Molecule $AaBb_3$ in "staggered" potential minimum. $Aa=r_1$; $Bb=r_2$; $Ba'=r_1$ ($r_2 > r_1$); $AB=R$; $\alpha=\beta=109^\circ 28'$. In the eclipsed form α is decreased by $\Delta\alpha$, β by $\Delta\beta$ while R is increased by ΔR .

angle. But a satisfactory treatment along these lines seems not yet to have been given.¹ Prevented in using "electron-distribution language" one may try to express the magnitude of these barriers in a force-constant description. It is difficult to determine barrier heights with high precision but it is believed that the experimental values in Table I roughly reflect physical reality with the possible exception of the silyl compounds. Usually, the substitution of hydrogen by fluorine causes an increase in barrier height and the reversal in the case of methylsilane and its trifluoro derivative is puzzling. From microwave spectra it can be concluded that molecules of the type under discussion are slightly *elongated* when passing the potential hill. Since the distortion is small we are justified in expecting that the change in potential energy involved may be calculated with fair accuracy by means of force constants. With reference to Fig. 1 and its subscript we may write the potential barrier V_{\max} , as

$$V_{\max} = \frac{3}{2}K_a r_1^2 (\Delta\alpha)^2 + \frac{1}{2}K_R (\Delta R)^2 + \frac{3}{2}K_\beta r_2^2 (\Delta\beta)^2. \quad (1)$$

In the expression for V_{\max} the effect of Aa and Bb stretching has been ignored since both movements are rather ineffective when one wants to elongate the molecule in the AB -direction and "expensive" with respect to potential energy.

In order to find the molecular configuration in the "eclipsed" position we must postulate and verify a relation between ΔR , $\Delta\alpha$, and $\Delta\beta$. Greatest success was achieved by assuming that the three distances aa' (one of which has been shown as a dotted line in Fig. 1) are conserved during the shift from staggered to eclipsed configuration. This is equivalent to setting

$$3\Delta R + r_1 8^{\frac{1}{2}} (\Delta\alpha + \Delta\beta) = \frac{4r_1^2}{3R + 2r_1}. \quad (2)$$

If this assumption is changed to assuming constancy of the distances ab , too large barriers are calculated for $r_2 > r_1$. Too

TABLE II. Distances in a.u. and force constants in 10^5 dynes/cm for molecules treated in this paper.

	R	r_1	r_2	K_R	K_a	K_β
CH_3CH_3	1.54	1.093	1.093	4.50	0.460	0.460
CH_3CCl_3	1.54	1.093	1.770	4.50	0.460	0.331
CH_3CF_3	1.54	1.093	1.330	4.50	0.460	0.713
CH_3SiH_3	1.88	1.093	1.460	3.30	0.460	0.189
CH_3SiF_3	1.88	1.093	1.590	3.30	0.460	0.252

TABLE III. ΔR (in a.u.), $\Delta\alpha$, and $\Delta\beta$ (in degrees) for the molecules treated in this paper.

	ΔR	$\Delta\alpha$	$\Delta\beta$
CH_3CH_3	0.0344	$5^\circ 33'$	$5^\circ 33'$
CH_3CCl_3	0.0431	$6^\circ 56'$	$3^\circ 41'$
CH_3CF_3	0.0453	$7^\circ 18'$	$3^\circ 11'$
CH_3SiH_3	0.0338	$4^\circ 00'$	$5^\circ 27'$
CH_3SiF_3	0.0410	$4^\circ 51'$	$4^\circ 11'$

small barriers result (even for $r_1=r_2$) if it is postulated that the distance from the *midpoint* of the Aa bond to the midpoint of the Bb bond is conserved during internal rotation. Roughly, (2) means physically that the Aa and Bb bonds pass one another under conservation of distance between points equally far from the axis AB .

The *dynamical path* followed by the molecule is, of course, one of minimum expenditure of energy:

$$\frac{\partial V_{\max}}{\partial (\Delta\alpha)} = 3K_a r_1^2 \Delta\alpha + K_R \Delta R \frac{\partial \Delta R}{\partial \Delta\alpha} = 3K_a r_1^2 \Delta\alpha - K_R \Delta R r_1 8^{\frac{1}{2}} / 3 = 0, \quad (3)$$

$$\frac{\partial V_{\max}}{\partial (\Delta\beta)} = 3K_\beta r_2^2 \Delta\beta - K_R \Delta R r_1 8^{\frac{1}{2}} / 3 = 0. \quad (4)$$

If we abbreviate

$$\gamma = 1 + \frac{8}{27} K_R \left(K_a^{-1} + \left(\frac{r_1}{r_2} \right)^2 K_\beta^{-1} \right) \quad \text{and} \quad L = \frac{4r_1^2}{3(3R + 2r_1)},$$

(1), (2), (3), and (4) can be solved to give

$$V_{\max}(\text{barrier height}) = \frac{1}{2} K_R \frac{L^2}{\gamma}.$$

Table II gives the distances and force constants used at the calculations. The calculated barriers are given in Table I.

A treatment of CH_3NO_2 along the same lines as applied in the foregoing obviously would give $V_{\max}=0$, consistent with experiment ($V_{\max}=2.1 \text{ cm}^{-1}$). It is mysterious why CF_3SF_5 has a reported² $V_{\max}=220 \text{ cm}^{-1}$. A force-constant treatment would give $V_{\max}=0$.

For the sake of completeness, ΔR , $\Delta\alpha$, and $\Delta\beta$ are given in Table III.

I am grateful to Mrs. Lise Nygaard, for carrying out the numerical calculations, and to Dr. Eileen Tannenbaum for interesting discussions on the subject.

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² Townes and Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 323.

Reaction of Paraffin Hydrocarbons with Ozonized Oxygen: Possible Role of Ozone in Normal Combustion*†

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(Received December 7, 1955)

RECENT interest in ozone as a constituent of "smog"¹ comes at a time when we are engaged in a study of the thermal reaction between ozonized oxygen and the lower paraffin hydrocarbons. We have been speculating about the possible role of ozone as an intermediate in hydrocarbon combustion generally.

It has been confirmed that ozone in oxygen (*ca* 3 mole %) reacts slowly with the paraffins methane, propane, *n*-butane, isobutane, and *n*-pentane at temperatures *ca* 20°C and higher.^{2,3} At 28°C isobutane yields nearly one mole of *t*-butanol along with smaller amounts of acetone for every mole of ozone consumed. Toward 150°C it was found that the liquid product collected from flow experiments contained increasing amounts of *t*-butyl hydroxymethyl peroxide.⁴ The reaction merges into the normal slow combustion as the temperature approaches 260 – 280°C .