

## The InfraRed Spectrum and Structure of Diazomethane

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TABLE I. Spin-orbit perturbations in polyatomic molecules.

The + signs mean that all components of the spin-orbit operator connect the states shown.  $\sigma$  means that the principle axis component and  $\pi$  that the perpendicular components connect the states.  $x$ ,  $y$ , and  $z$  mean that these particular Cartesian components of the spin-orbit operator connect the states shown.

$C_{\infty v}$	$\Sigma^+$	$\Sigma^-$	$\pi$	$\Delta$	$T_d$	$A_1$	$A_2$	$E$	$F_2$	$F_1$
$\Sigma^+$	0	$\sigma$	$\pi$	0		0	$A_1$	$A_2$	$E$	$F_1$
$\Sigma^-$	$\sigma$	0	$\pi$	0	$A_1$	$A_1$	0	0	0	+
$\pi$	$\pi$	$\pi$	$\sigma$	$\pi$	$A_2$	$A_2$	0	0	0	+
$\Delta$	0	0	$\pi$	$\sigma$	$E$	$E$	0	0	0	+
					$F_2$	$F_1$	+	0	+	+
					$F_1$	$F_2$	0	+	+	+

$D_6$	$A_1$	$A_2$	$B_1$	$B_2$	$E_1$	$E_2$	$D_4$	$A_1$	$A_2$	$B_1$	$B_2$	$E$
$A_1$	0	$\sigma$	0	0	$\pi$	0	$A_1$	0	$\sigma$	0	0	$\pi$
$A_2$	$\sigma$	0	0	0	$\pi$	0	$A_2$	$\sigma$	0	0	0	$\pi$
$B_1$	0	0	0	$\sigma$	0	$\pi$	$B_1$	0	0	0	$\sigma$	$\pi$
$B_2$	0	0	$\sigma$	0	0	$\pi$	$B_2$	0	0	$\sigma$	0	$\pi$
$E_1$	$\pi$	$\pi$	0	0	$\sigma$	$\pi$	$E$	$\pi$	$\pi$	$\pi$	$\pi$	$\sigma$
$E_2$	0	0	$\pi$	$\pi$	$\pi$	$\sigma$						

$C_{2v}$	$A_1$	$A_2$	$B_1$	$B_2$
	$D_2$	$A_1$	$B_1$	$B_2$
$A_1$	$A_1$	0	$z$	$y$
$A_2$	$B_1$	$z$	0	$x$
$B_1$	$B_2$	$y$	$x$	0
$B_2$	$B_3$	$x$	$y$	$z$

the triplet state must be  $^3B_{2u}$ . A closer study of the selection rules has verified this conclusion.

The simplest way to derive the selection rules is to consider the group properties of the spin-orbit interaction operator. This is the part of the Hamiltonian principally responsible for mixing singlet and triplet states. For a system of  $n$  electrons ( $n$  even in our case) and  $m$  nuclei, the spin-orbit operator can be written:

$$H' = \sum_i A_i (l_{xi}s_{xi} + l_{yi}s_{yi} + l_{zi}s_{zi}),$$

with

$$A_i = \sum_k \frac{1}{r_{ik}^3} \frac{V(r_{ik})}{r_{ik}}.$$

In this formula,  $l_{xi}$  is the operator for the  $x$  component of the orbital angular momentum for electron  $i$  and  $s_{xi}$  is the operator for the  $x$  component of the spin angular momentum for electron  $i$ .  $r_{ik}$  is the distance of electron  $i$  from nucleus  $k$ , and  $V(r_{ik})$  is the potential at the position of electron  $i$  due to nucleus  $k$ .

$H'$  may be separated into sums whose orbital and spin factors are separately symmetric or antisymmetric under the operation of electron interchange. One component would be:

$$H'_x = \frac{1}{2n} \sum_{i=1}^n \sum_{j=1}^n (A_i l_{xi} + A_j l_{xj}) (s_{xi} + s_{xj}) + \frac{1}{2n} \sum_{i=1}^n \sum_{j=1}^n (A_i l_{xi} - A_j l_{xj}) (s_{xi} - s_{xj}) (i \neq j).$$

The first (symmetric) part splits the degenerate triplet level, and the second (antisymmetric) part mixes singlet and triplet states. We shall be interested in the second part.

Assuming now that we have product type spin-orbit functions, the matrix elements of the spin-orbit operator split up into separate integrals over orbital and spin coordinates. The orbital and spin wave functions are assumed to transform properly under the operations of the symmetry group of the molecule. We will consider only the selection rules for the orbital part of the wave function, at present. Presumably, at least one of the triplet components may be perturbed by a singlet state.

The integral over space coordinates will be non-zero when the product of the representation of the wave functions contains the

representation of the significant part of the spin-orbit operator, viz.  $A_i l_{xi} - A_j l_{xj}$  etc. Since the  $A_i$  remain unchanged by symmetry operations, the  $l_i$  determine the symmetry properties of the spin-orbit operator. The angular momentum operators have the symmetry properties of rotation operators. Hence with the help of character tables the selection rules may be written down. The rules  $g \leftrightarrow g$ ,  $u \leftrightarrow u$ ,  $g \leftrightarrow u$  and  $+\leftrightarrow -$  are found directly, and agree with what is known from atomic and diatomic molecular spectra. Analogous to the latter rule in  $D_{6h}$  is the rule  $B_{1u} \leftrightarrow B_{2u}$  which confirms Shull's tentative conclusion. Selection rules for the more important symmetry groups are given in the tables. The rules for  $D_{6h}$  etc., may be derived from those given for  $D_6$  by applying the  $g \leftrightarrow g$ ,  $u \leftrightarrow u$  rule.

Many of these same results can be obtained from the correlation between the continuous rotation groups and the point groups, established by Bethe.<sup>2</sup> The method used here seems simpler and more direct.

<sup>1</sup> H. Shull, J. Chem. Phys. 17, 295 (1949).

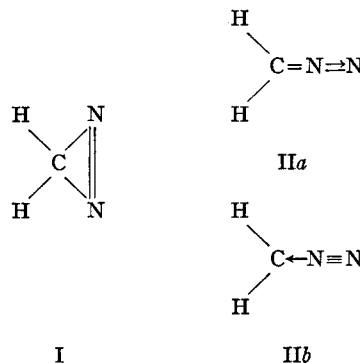
<sup>2</sup> H. Bethe, Ann. d. Physik 3, 133 (1929).

## The Infra-Red Spectrum and Structure of Diazomethane\*

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April 26, 1949

THE structure of diazomethane<sup>1</sup> has been represented by a cyclic formula I and by the straight chain formulas IIa and IIb. Measurements



of the ultraviolet absorption spectrum<sup>2</sup> were interpreted in favor of the cyclic structure but electron diffraction investigations<sup>3</sup> subsequently provided strong evidence for a straight chain structure. The low dipole moment<sup>4</sup> of the diazo group however excludes either of the straight chain structures separately, but is consistent with a resonance hybrid of the two structures.

The infra-red spectrum of diazomethane vapor has been measured with a Perkin-Elmer Model 12B infra-red spectrometer and shows a very close similarity to the infra-red spectrum of ketene.<sup>5</sup> Strong "parallel" type bands were observed at 3074, 2103, 1416, and 852  $\text{cm}^{-1}$  with  $PR$  separations of  $\sim 27 \text{ cm}^{-1}$  (cf. the ketene bands at 3066, 2153, 1386, and 1120  $\text{cm}^{-1}$  with  $PR$  spacings of  $\sim 25 \text{ cm}^{-1}$ ). These bands may be assigned to the four totally symmetric vibrations of the straight chain structure. Several perpendicular type bands were resolved and showed the intensity alternation associated with a twofold axis of symmetry.<sup>6</sup> A weak perpendicular type band was observed in the region of 3150  $\text{cm}^{-1}$  with a spacing of  $\sim 18 \text{ cm}^{-1}$  but only three  $Q$  branches were free from overlapping by neighboring absorption bands. A complex

band was observed in the region from 1300 to 1000  $\text{cm}^{-1}$  with pronounced  $Q$  branches at 1176, 1138, and 1099  $\text{cm}^{-1}$ , the intensity alternation in this region being very marked. Another weak perpendicular type band was observed in the region from 800 to 650  $\text{cm}^{-1}$  with a pronounced intensity alternation but a spacing of only 15  $\text{cm}^{-1}$ . A very strong and complex absorption was observed in the region from 650 to 400  $\text{cm}^{-1}$  with no apparent regular spacing. This absorption is presumably due to the two skeletal bending vibrations highly perturbed by Coriolis interaction.<sup>7</sup> A more detailed interpretation of the spectrum will be published shortly but sufficient evidence has been presented above to establish conclusively the straight chain structure for the diazomethane molecule.

It is interesting to record that when the absorption spectrum was investigated in a metal cell with KBr windows a change in spectrum was observed on standing. The diazomethane bands disappeared completely during the course of 24 hours and new bands appeared which remained unchanged for several days. Some of these bands were identified as being caused by ethylene, but others could not be explained in this way. In particular two bands were observed at 1180 and 1102  $\text{cm}^{-1}$  with well defined  $PQR$  structures and  $PR$  spacings of approximately 24  $\text{cm}^{-1}$ . This spacing is altogether too small for bands of the cyclic monomer but is consistent with the spacing to be expected for the "parallel" bands of the hexacyclic dimer. No change in spectrum was observed, however, when diazomethane was investigated in a glass cell with KBr windows.

The author wishes to express his thanks to Mr. L. C. Leitch for assistance in the preparation of the diazomethane; to Dr. G. Herzberg for valuable discussion and to Dr. R. N. Jones for the use of the spectrometer.

\* Published as Contribution No. 1936 from the National Research Laboratories, Ottawa, Canada.

<sup>1</sup> See N. V. Sidgwick, *The Organic Chemistry of Nitrogen* (Oxford University Press, New York, 1937), pp. 360-362.

<sup>2</sup> F. W. Kirkbride and R. G. W. Norrish, *J. Chem. Soc.* 119, (1933).

<sup>3</sup> H. Boersch, *Monats. F. Chem.* 65, 331 (1935).

<sup>4</sup> Sidgwick, Sutton, and Thomas, *J. Chem. Soc.* 406, (1933).

<sup>5</sup> F. Halverson and V. Z. Williams, *J. Chem. Phys.* 15, 552 (1947); W. R. Harp, Jr., and R. S. Rasmussen, *J. Chem. Phys.* 15, 778 (1947).

<sup>6</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company Inc., New York, 1945), pp. 479-482.

<sup>7</sup> Cf. formaldehyde, E. S. Ebers and H. H. Nielsen, *J. Chem. Phys.* 5, 822 (1937).

hydrogen, 0.955; oxygen, 1.02; carbon dioxide, 1.16; stoichiometric methane-air, 1.10. Hence, the energy flow by diffusion in a plane flame may equal or even exceed that caused by thermal conduction, thus yielding zero or negative excess energy; an elementary analysis reveals that the same considerations apply to a spherical flame.

Lewis and von Elbe compare experimental quenching distances with minimum flame radii calculated by their theory from minimum spark energies for ten gas mixtures, obtaining a correlation with 21 percent average deviation and 54 percent maximum deviation. However, this relationship can be treated without recourse to the concept of excess energy, simply by assuming the minimum ignition energy to be proportional to the surface area of the minimum flame sphere, independently of mixture composition and pressure. Minimum flame radii may be correlated with minimum ignition energies in this manner for the above ten mixtures, with 14 percent average deviation and 31 percent maximum deviation. The assumption of invariance with pressure is suggested by consideration of Fig. 3 in an earlier paper<sup>4</sup> by the above authors, which shows minimum ignition energy to be very nearly proportional to the square of quenching distance, and hence to minimum flame surface, over a fivefold pressure range for stoichiometric methane-air mixtures. Lewis and von Elbe's theory does predict the correct order of magnitude for minimum flame radii, but this may be fortuitous.

It is interesting to note that a thermal theory of ignition, such as that suggested by Taylor-Jones, Morgan, and Wheeler<sup>5</sup> and Coward and Meiter<sup>6</sup> would yield the minimum energy to be proportional to the cube rather than the square of the minimum flame radius, as is actually observed. If the thermal theory were modified to include chemical energy liberated in the pre-ignition period, better correlation between theory and experiment might be obtained. However, such a treatment still would be open to the criticism that diffusion is not taken into consideration.

<sup>1</sup> B. Lewis and G. von Elbe, *J. Chem. Phys.* 15, 803-808 (1947).

<sup>2</sup> W. Jost and L. von Muffling, *Zeits. f. physik. Chemie* A181, 208 (1938).

<sup>3</sup> N. N. Semenov, *Prog. Phys. Sci. (USSR)* 24, 433-486 (1940) (available as NACA T.M. 1026, September, 1942).

<sup>4</sup> M. V. Blanc, P. G. Guest, G. von Elbe, and B. Lewis, *J. Chem. Phys.* 15, 798-802 (1947).

<sup>5</sup> E. Taylor-Jones, J. D. Morgan, and R. V. Wheeler, *Phil. Mag.* 43, 359 (1922).

<sup>6</sup> H. F. Coward and E. G. Meiter, *J. Am. Chem. Soc.* 49, 396-409 (1927).

## Spark Ignition of Gas Mixtures

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May 12, 1949

LEWIS and von Elbe<sup>1</sup> have presented a theory of spark ignition based upon the concept of excess energy in a flame front. The present writers wish to point out what appears to be a fundamental weakness in this theory, in that due consideration is not given to the process of diffusion. Lewis and von Elbe evaluate the excess energy integral by considering only thermal energy changes and chemical energy degradation by reaction, while ignoring energy transfer by diffusion.

It is apparent from work published by Jost and von Muffling<sup>2</sup> and by Semenov<sup>3</sup> that energy transfer by interdiffusion of reactants and products is comparable in magnitude with heat conduction. Upon assuming that  $\lambda$  and the product  $D\rho$  are independent of temperature, Semenov shows that, for a plane flame, the excess energy vanishes as the dimensionless ratio  $D\rho C/\lambda$  approaches unity, where  $\lambda$  is thermal conductivity,  $D$  is the diffusion coefficient,  $\rho$  is density, and  $C$  is specific heat at constant pressure. The values of  $D\rho C/\lambda$  at room temperature for some common gases are:

## Decrease of an Electrical Discharge by External Radiation

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May 31, 1949

WE have observed the following curious effect.

An H-shaped discharge tube with aluminium electrodes and containing air was used and had side bulbs of  $\text{P}_2\text{O}_5$  and crushed NaOH. It was run on a.c. and voltage adjusted so that discharge was in its initial stages and consisted of discontinuous bursts of excitation followed by quiescent periods. Light from an incandescent bulb was thrown as a spot of size 5-mm radius on the space just above one of the electrodes. The pressure of air in the discharge tube was 0.7 mm of mercury.

It was found that on external irradiation, the intensity of each burst of discharge as well as the frequency of bursts decreased.