

FIG. 2. Ion current of NO gas with krypton. Voltage between two electrodes: 22.5 v. (1) Pressure of NO gas = 0.088 mm Hg. (2) Pressure of NO gas = 0.26 mm Hg. (3) Pressure of NO gas = 0.49 mm Hg.

The authors wish to thank Dr. F. P. Lossing for discussions and advice during the course of this work.

* National Research Council Contribution No. NRC 4243.

† Japanese Government Fellow at the National Research Council of Canada 1954-1955 and National Research Council Post-doctorate Fellow 1955-1957.

¹ Wainfan, Walker, and Weissler, *J. Appl. Phys.* **24**, 1318 (1953). K. Watanabe, *J. Chem. Phys.* **22**, 1564 (1954) gives a good bibliography.

² F. P. Lossing and Ikuzo Tanaka, *J. Chem. Phys.* **25**, 1031 (1956).

³ W. E. Groth, *Z. physik. Chem. N. F.* **1**, 300 (1954).

⁴ It is assumed that the reactions $Kr^* + Kr = Kr' + Kr'$, $NO^* + Kr = NO' + Kr'$ are small and may be neglected.

Structure of CH₂

G. A. GALLUP

Department of Chemistry, University of Nebraska, Lincoln, Nebraska
(Received November 26, 1956)

RECENT mechanism studies have created interest in the question of the spin multiplicity in the molecular fragment, CH₂. The case for the singlet state has been argued, giving as evidence observations on the reaction of diazomethane with olefins.¹ Quantum-mechanical discussions of the electronic state of CH₂ have been either qualitative or used some assumed constant H-C-H angle in the treatment.²

On the experimental side, Herzberg³ has shown from its spectrum that 140° is a reasonable H-C-H angle for CH₂ assuming the C-H distance is the same as in CH₄. By analogy with CF₂ Duchesne and Burnelle⁴ have assumed the ground state of CH₂ to be singlet.

The present note concerns a detailed quantum-mechanical calculation, using the LCAO-MO approximation, undertaken to determine if numerical calculations indicate any preference of one state over the other.

The AO's used were C: 2s, 2p_x, 2p_y, 2p_z and a 1s on each hydrogen. One of the C 2p's may be oriented perpendicular to the plane of CH₂, if the H-C-H angle is not 180°. This 2p, therefore, does not overlap any of the other AO's, and a 5×5 secular determinant must be solved. Symmetry orbitals simplify the actual calculation, of course. All overlap integrals were included in the calculation, including the one between the two hydrogens. The energies of the five nonlocalized MO's were determined for values from 90° to 180° of the H-C-H angle. The diagonal elements of the determinant were assumed to be empirically determined AO energies for carbon and hydrogen, and the off diagonal elements were approximated as:

$$H_{ij} = \frac{1}{2}(H_{ii} + H_{jj} - 10.0)S_{ij}$$

where S_{ij} is the overlap between the i th and j th AO, and the -10.0 term was used in a crude attempt to include the interaction between an electron associated with one nucleus and an adjacent nucleus. The carbon-hydrogen overlaps were obtained from tables⁵ assuming a C-H distance of 1.09 Å. The hydrogen-hydrogen overlap changes with the H-C-H angle.

The calculated energies of the three of the MO's are lower than that of the noninteracting 2p (except at 180°). We may consider two electrons in each of these three orbitals and obtain the singlet state. If two electrons are placed in each of the two lowest MO's, one in the third MO, and one in the noninteracting 2p, the triplet state is obtained. Figure 1 shows the variation of the energy of

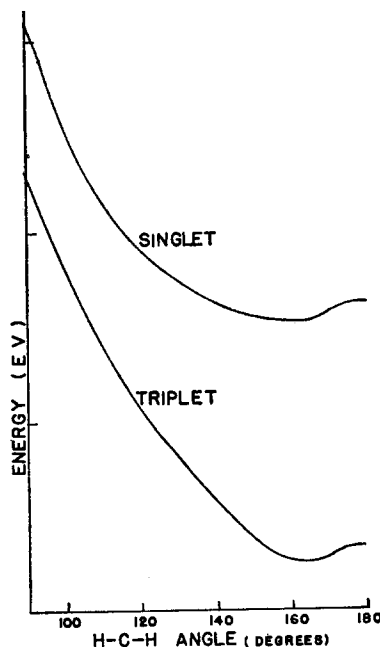


FIG. 1. The distance between the ordinate marks corresponds to 1 eV. The absolute value is unimportant because of neglected constant terms.

the singlet and triplet states with H-C-H angle. Both curves include repulsion between the two protons, and the singlet curve includes +1.3 eV which is the energy difference between the ¹D and ³P states for carbon, it being assumed that the energy required to pair electrons in the same orbital in CH₂ is roughly the same as in carbon. Both curves show a minimum around 160°, but the triplet state has the lower energy. On the basis of this calculation with its assumptions it appears that CH₂ exists in a triplet ground state; the calculated angle of 160° is not too far from 140°.

¹ P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.* **78**, 4496 (1956).

² (a) J. Lennard-Jones, *Trans. Faraday Soc.* **30**, 70 (1934); (b) J. Lennard-Jones and J. A. Pople, *Discussions Faraday Soc.* **10**, 9 (1951); (c) H. H. Voge, *J. Chem. Phys.* **4**, 581 (1936); (d) K. J. Laidler and E. J. Casey, *ibid.* **17**, 213 (1949); (e) A. D. Walsh, *Discussions Faraday Soc.* **2**, 18 (1947).

³ G. Herzberg, *Revs. Modern Phys.* **14**, 195 (1942); *Astrophys. J.* **96**, 314 (1942).

⁴ J. Duchesne and L. Burnelle, *J. Chem. Phys.* **21**, 2005 (1953).

⁵ Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

Vibrational Spectrum of N-Methyl Formamide

D. E. DEGRAAF AND G. B. B. M. SUTHERLAND*

The Harrison M. Randall Laboratory of Physics,
University of Michigan, Ann Arbor, Michigan

(Received October 17, 1956)

PREVIOUS studies of the vibrational spectrum of N-methyl formamide (NMF) have been reported by several workers.¹⁻⁴ We have recently completed more extensive investigations of the infrared and Raman spectra of NMF and NNDNMF (N-deutero

N-methyl formamide). The new data obtained have made it possible to assign observed bands to all the 21 normal vibrations of NMF.

We have observed infrared spectra of NMF in the liquid and vapor states, and also in solution, in the range ~ 320 – 3600 cm^{-1} . Infrared spectra of NDNMF (liquid and solution) have been obtained in the region ~ 320 – 3600 cm^{-1} . In addition, polarized Raman spectra of liquid NMF and NDNMF were obtained in the range 225 – 3600 cm^{-1} .

A *trans*-model having a plane of symmetry was adopted as the most probable configuration of NMF. The observed bands have been assigned on the basis both of their association and deuteration shifts, and the depolarization ratios of the Raman lines, where these could be measured. These assignments for liquid NMF and NDNMF are summarized in Table I.

TABLE I. Fundamental vibrations in liquid N-methyl formamide and N-deutero N-methyl formamide.

Vibration	Observed band (cm^{-1})	
	N-methyl formamide	N-deutero N-methyl formamide
NH stretching	3301	
C'H ₂ asym. stretching ^a (doubly degenerate)	2943	2943
CH stretching ^b	2877	2879
C'H ₂ sym. stretching	2748	2743
ND stretching		2474
Amide I	1667	1665
Amide II	1543	1436
C'H ₂ asym. deformation (doubly degenerate)	1450	1467
C'H ₂ sym. deformation	1415	1405
CH wagging ^c	1386	1383
Amide III	1243	977
C'H ₂ wagging	1148	1156
C'H ₂ rocking ^d	1012	1023
C'N stretching	956	940
CH rocking	778	760
NH rocking	714	
CO wagging	618	610
ND rocking		537
CN torsion	356	351
CNC' deformation	302	295
C'H ₂ torsion	242	not observed

^a C' denotes the methyl carbon atom.

^b C denotes the carbonyl carbon atom.

^c "Wagging" denotes in-plane motion.

^d "Rocking" denotes out-of-plane motion.

The assignment of the 2877 cm^{-1} band to the CH stretching vibration is based in part on its large shift upon dissociation (to 2840 cm^{-1} in the vapor state), which is analogous to the behavior of the CH stretching band in formamide.⁵ The band at 778 cm^{-1} is depolarized in the Raman spectrum and hence must arise from an out-of-plane vibration. It is assigned to the CH-rocking mode. This band corresponds to the 765 cm^{-1} band observed⁵ for formamide, which we also ascribe to a CH rocking vibration.

The band at 618 cm^{-1} shifts markedly on dissociation, appearing at 576 cm^{-1} in the vapor state. This behavior, and the fact that this line is polarized in the Raman spectrum, strongly support the assignment of this band to an in-plane vibration involving considerable motion of the carbonyl oxygen atom. This vibration is here referred to as CO wagging, but may equally well be described as a deformation of the NCO angle. The Raman band at 302 cm^{-1} is polarized, and is assigned to the other in-plane skeletal deformation mode.

The 356 cm^{-1} band shifts to a lower frequency upon dilution, and is depolarized in the Raman spectrum. These facts support the assignment of this band to the torsional vibration of the two ends of the molecule about the CN bond. This torsional oscillation is largely a CO rocking motion.

A combination band of considerable interest occurs in NMF at 1314 cm^{-1} , and shifts to 1119 cm^{-1} upon deuteration. These bands are attributed to the combination NH (ND) rocking plus CO wagging.

This work was supported, in part, by a grant from the U.S. Public Health Service, which is gratefully acknowledged. One of us (D.E.D.) expresses his thanks for a University Fellowship awarded by the University of Michigan.

* Present address: The National Physical Laboratory, Teddington, Middlesex, England.

¹ Randall, Fowler, Fuson, and Dangi, *Infrared Determination of Organic Structures* (D. Van Nostrand Company, Inc., New York, 1949).

² H. B. Kessler, Ph.D. thesis, University of Michigan, 1952.

³ R. M. Badger and H. Rubalcava, Proc. Natl. Acad. Sci. U. S. A. **40**, 12 (1954).

⁴ Miyazawa, Shimanouchi, and Mizushima, J. Chem. Phys. **24**, 408 (1956).

⁵ J. C. Evans, J. Chem. Phys. **22**, 1228 (1954).

Burning-Rate Studies. A Negative Pressure Exponent in the Consumption-Rate Equation for a Liquid System

A. GREENVILLE WHITTAKER, HARRY WILLIAMS, AND PENNIMAN M. RUST
Chemistry Division, U. S. Naval Ordnance Test Station,
China Lake, California

(Received October 1, 1956)

PREVIOUSLY, two-component systems were studied as mixtures in stoichiometric proportions to give CO_2 , H_2O , and N_2 as products of complete combustion. In order to get more information on the kinetics of the combustion of two-component systems a study of nonstoichiometric mixtures was initiated. Normally the consumption rate increases with pressure according to the relation

$$C = kP^n + b, \quad (1)$$

where C is the consumption rate, P is the pressure during combustion, and k , n , and b are positive constants. During this study it was found that under certain conditions it is possible for n to be negative over a limited pressure region.

Only the 2-nitropropane-95% nitric acid system was used. The purity of materials, the apparatus and procedure used were the same as described elsewhere.¹ The mixture ratio R was defined by the function

$$R = \frac{1}{1+F}, \quad (2)$$

where F is the ratio of the fuel used to the fuel required for stoichiometric ratio to a given amount of oxidizer.

The results obtained are shown in Table I. Each rate value is the result of nine independent determinations. The average deviation was approximately $\pm 3\%$. In the smooth-burning region,¹ both oxidizer-rich and fuel-rich mixtures have higher consumption rates than the stoichiometric mixtures. Since the surface corrections for these systems were about the same, the same relation should hold for the fundamental burning rate. For mixtures which are far from stoichiometric proportions, the consumption rate becomes less than that of the stoichiometric mixture. Hence, it appears that in the smooth-burning region a plot of R vs consumption rate at constant pressure would show two maxima, one on either side of the stoichiometric mixture. Euston² and Davidson³ made a similar study on the systems nitroethane-nitric acid and acetic acid-nitric acid, respectively. With their systems a plot of R vs consumption rate showed a

TABLE I. Effect of mixture ratio on the consumption rate of the system 2-nitropropane-95% nitric acid at various pressures.

Mixture ratio R	Rate (cm^3/sec)			
	28.2 atmos	55.4 atmos	82.6 atmos	109.8 atmos
5/9	0.653	0.777	1.68 ^a	3.40 ^a
1/2	0.259	0.650	4.32 ^a	8.89 ^a
3/7	0.368	0.625	2.47 ^a	6.65 ^a
1/3	0.102	0.351	0.508	0.508

^a Turbulent combustion.