

correspond to them in the spectrum of acetylmesitylene. Again, the relatively high value of 1699 cm.^{-1} for the $\text{C}=\text{O}$ frequency indicates that the ring and carbonyl group are not coplanar.

Summary

Raman frequencies, estimated intensities and depolarization factors are reported for acetophenone, mesitylaldehyde, acetylmesitylene, methyl

2,4,6-trimethylbenzoate and 2,4,6-trimethylbenzoyl chloride; also, frequencies and intensities are reported for acetyldurene and nitromesitylene. For acetophenone, the only one for which previous data seem to have been reported, new lines were observed at 404, 896 and 3006 cm.^{-1} and depolarization data were obtained for eleven additional lines.

CHICAGO, ILLINOIS

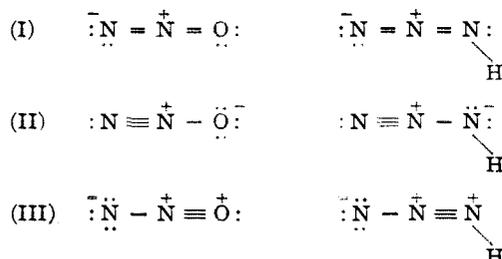
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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 788]

The Structures of Nitrous Oxide and of Hydrogen Azide

BY VERNER SCHOMAKER AND ROBERT SPURR

Introduction.—Nitrous oxide and hydrogen azide present much the same structural problem. The two molecules contain the same number of valence electrons and have been shown by spectroscopic investigation^{1,15} to be essentially linear. The expected resonating structures are similar; three which might be considered important are



The rule given by Pauling² that structures of the type III make little contribution, by reason of the instability associated with formal charges on adjacent atoms, is confirmed by the present investigation.

Let the interatomic distances in the molecules be labeled as follows



For resonance between structures I + II Pauling has predicted,³ using known bond radii, that $r_1 = 1.12\text{ \AA.}$ and $r_2 = 1.19\text{ \AA.}$ When III is included, the values are $r_1 = 1.15\text{ \AA.}$ and $r_2 = 1.07\text{ \AA.}$ A similar calculation gives $r_3 = 1.12\text{ \AA.}$

(1) E. Plyler and E. Barker, *Phys. Rev.*, **38**, 1827 (1931).

(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 294 and 498 (1932);

L. Pauling and L. O. Brockway, *THIS JOURNAL*, **59**, 13 (1937).

(3) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., second edition, 1940, p. 200.

and $r_4 = 1.24\text{ \AA.}$ for I + II and $r_3 = r_4 = 1.15\text{ \AA.}$ for I + II + III.

Experimental.—The apparatus used has been described in a previous article.⁴ The wave length of the electrons, 0.0616 \AA. , was determined from transmission pictures of gold foil, taking $\lambda_0 = 4.070\text{ \AA.}$

The nitrous oxide, which was taken from a commercial tank, was stated by the manufacturers to be 99.75% pure. Ten photographs were taken at a camera distance of 10.82 cm. from gas nozzle to film, and four at a camera distance of about five cm. These showed a series of heavy rings joined with shelf-like rings about half as intense on the side of greater scattering angle. Except for a more rapid damping of the intensity of the features with increasing scattering angle, the nitrous oxide photographs were very similar to those which have been taken of carbon dioxide in this Laboratory.⁵ The features of the nitrous oxide pictures, which were examined out to the sixteenth maximum, corresponding to s values of over forty, did not reveal any definite departure from the regularity characteristic of the carbon dioxide photographs. Since measurements of the first ten maxima and minima yielded sufficient data for the evaluation of the long interatomic distance, it was not attempted to measure the faint features at higher s values.

Anhydrous hydrogen azide was prepared by the method of Dennis and Isham⁶ and distilled. Photographs were taken of the vapor at the vapor

(4) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(5) V. Schomaker and D. P. Stevenson, unpublished investigation.

(6) L. M. Dennis and Helen Isham, *THIS JOURNAL*, **29**, 216 (1907).

pressure of the liquid at various temperatures from 25 to 60°. The first seven maxima and minima were similar in appearance to those in the nitrous oxide photographs, but the eighth, ninth, and tenth maxima were isolated.

Discussion.—Curves A-F in Fig. 1 are simplified theoretical curves for nitrous oxide.

They were drawn for a rigid linear molecule with the use of atomic numbers as coefficients, and correspond to the following values of r_1 and r_2 , respectively: A, 1.18, 1.13; B, 1.15, 1.15; C, 1.13, 1.18; D, 1.11, 1.20; E, 1.09, 1.22; F, 1.03, 1.28. Curve B, which does not change in character with increasing s , is the type of intensity function expected and observed for carbon dioxide. As can be seen from D, E, and F, isolated maxima appear over a short range of s values when the two shorter distances are not equal, and appear farther from the origin as r_1/r_2 approaches unity. Since this phenomenon is not observed in the case of nitrous oxide, the ratio r_1/r_2 must lie between 0.925, the value given by curve D, and its reciprocal. As a result of

the St. John effect,⁴ there was a tendency for both observers, in different degree, to underestimate the diameters of the highly unsymmetrical maxima, and to overestimate those of the minima, which have a complementary asymmetry. Nevertheless the averages of the sets of measurements by the two observers are the same. We feel that the example provided by this type of molecule emphasizes the importance of making measurements of both maxima and minima in electron diffraction investigations generally.

Curve G in the figure is drawn for a hydrogen azide model containing a linear N_3 group in which $r_3 = 1.13$ Å. and $r_4 = 1.24$ Å. It is satisfactory in all details. The limit of error of the short dis-

tances is about 0.01 Å. This precise determination of the structure is made possible by the circumstance that, since the ratio of the two short distances, 0.91, is somewhat smaller than that in nitrous oxide, the change from the regular carbon dioxide-like appearance of the scattering curve occurs at a smaller scattering angle, so that the cor-

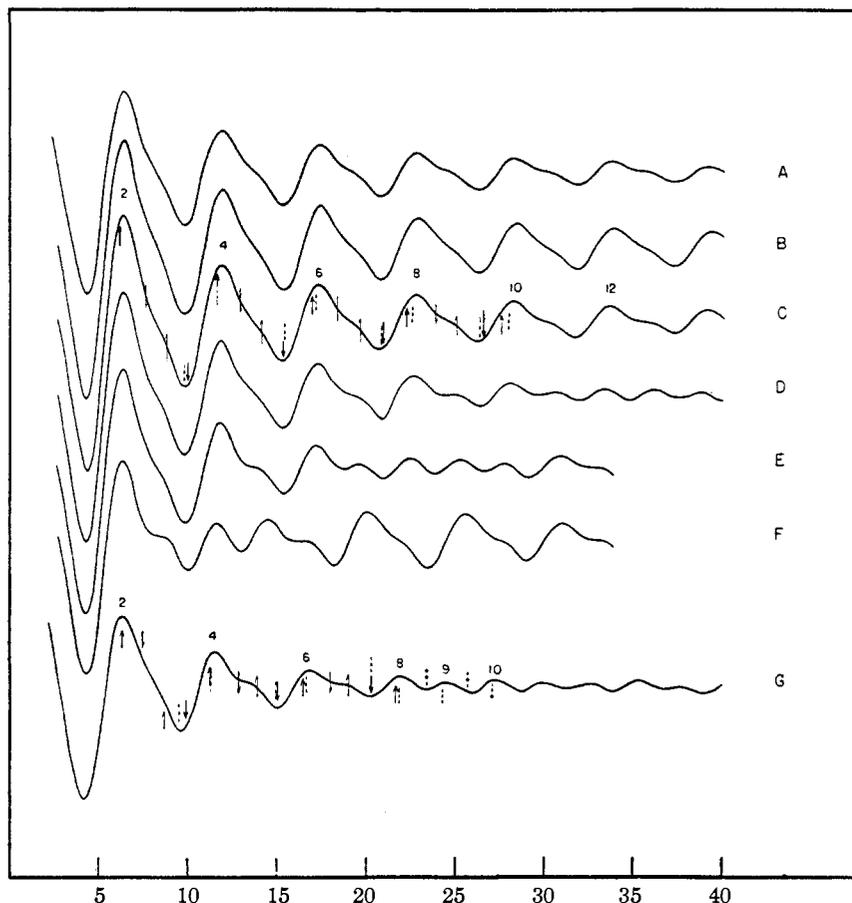


Fig. 1.—Theoretical intensity curves for nitrous oxide (A-F) and hydrogen azide (G).

responding structure may be observed in the photographs. Theoretical curves for other models of hydrogen azide have been omitted, since it was found that they closely resembled in character the nitrous oxide curves for the same ratios of short distances. The effect of the N-H terms in the scattering function is slight, and negligible at wide angles. Agreement would be obtained if the distances r_3 and r_4 were interchanged; such a model, however, appears improbable on consideration of the resonating structures already given. Table I gives the comparison between theory and experiment.

Since the electron diffraction method fails to fix precisely the position of the central atom in

TABLE I
 NITROUS OXIDE

Max.	Min.	Readings ^a	$s^a_{\text{obsd.}}$	(C) $s_{\text{scaled.}}$	$s_{\text{scaled.}}/s^a_{\text{obsd.}}$	Readings ^b	$s^b_{\text{obsd.}}$	$s_{\text{scaled.}}/s^b_{\text{obsd.}}$
	1	10	2.92	2.20	(0.854)			
1		10	3.45	3.10	(.899)			
	2	10	4.56	4.27	(.936)	11	4.42	(0.967)
2		11	6.20	6.40	(1.032)	11	6.11	(1.048)
	3	11	7.60	7.60	(1.000)			
3		11	8.81	8.62	(0.978)			
	4	11	10.12	9.77	.966	11	9.79	0.998
4		15	11.61	11.87	1.022	11	11.56	1.027
	5	10	12.92	13.00	(1.006)			
5		11	14.11	14.35	(1.017)			
	6	9	15.27	15.24	0.998	11	15.36	0.992
6		11	16.88	17.32	1.026	11	17.12	1.012
	7	10	18.33	18.48	(1.008)			
7		10	19.43	19.45	(1.001)			
	8	10	20.93	20.80	0.994	8	20.85	0.997
8		11	22.20	22.80	1.027	8	22.46	1.015
	9	11	23.87	24.04	(1.007)			
9		10	24.97	25.00	(1.001)			
	10	10	26.49	26.20	0.989	5	26.31	0.996
10		11	27.48	28.18	1.026	5	27.97	1.007
Average for maxima excluding ()					1.025			1.015
Average for minima excluding ()					0.987			0.996
Average					1.006			1.006
Average deviation					0.019			0.010
Final distance $r_1 + r_2$, Å.					2.32			2.32

HYDROGEN AZIDE

Max.	Min.	Readings ^a	$s^a_{\text{obsd.}}$	(C) $s_{\text{scaled.}}$	$s_{\text{scaled.}}/s^a_{\text{obsd.}}$	Readings ^b	$s^b_{\text{obsd.}}$	$s_{\text{scaled.}}/s^b_{\text{obsd.}}$
	2	10	4.51	4.18	(0.927)	10	4.06	(1.029)
2		10	6.33	6.30	(0.995)	10	6.19	(1.018)
	4	10	9.87	9.62	0.973	10	9.54	1.008
4		10	11.25	11.47	1.020	10	11.32	1.013
	6	10	15.14	15.00	0.990	7	14.92	1.005
6		10	16.45	16.85	1.024	7	16.62	1.014
	8	8	20.35	20.40	1.003	7	20.29	1.005
8		8	21.66	21.95	1.013	5	21.93	1.001
Average					1.004			1.008
Average deviation					0.015			0.004
Final distance $r_3 + r_4$, Å.					2.38			2.39

^a Measurements by R. S. (arrows in figure). ^b Measurements by V. S. (dotted lines in figure).

the nitrous oxide molecule, and X-ray methods,⁷ because of the randomness of orientation of the molecules in the crystal,⁸ must be expected also to fail, it remains to estimate the distances by the application of Badger's rule⁹ to the force constants derived from the parallel frequencies¹ observed in the infrared spectrum. On assuming for motion along the figure axis a potential function of the form

$$2V = k_1\delta r_1^2 + k_2\delta r_2^2 + k_{12}(\delta r_1 + \delta r_2)^2$$

it is seen that there are three constants to be cal-

culated from only two frequencies. If k_{12} is set equal to zero, k_1 and k_2 become complex. On using for k_{12} the value¹⁰ of the corresponding constant for carbon dioxide and taking $k_1 > k_2$, we find that $r_1 = 1.14$ Å. and $r_2 = 1.21$ Å., which give the ratio 0.94, in agreement with the distances predicted for resonance between structures I + II. Using the same interaction force constant and the parallel frequencies for hydrogen azide,¹¹ we find that $r_3 = 1.14$ Å. and $r_4 = 1.25$ Å., in excellent agreement with the electron diffraction values.

The distance $r_1 + r_2 = 2.32 \pm 0.02$ Å. agrees

(7) J. de Smedt and W. Keesom, *Proc. Amsterdam Acad.*, **27**, 843 (1924).

(8) R. W. Blue and W. F. Giaque, *This Journal*, **57**, 991 (1935).

(9) R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935).

(10) A. Adel and D. Dennison, *Phys. Rev.*, **43**, 722 (1933).

(11) E. H. Eyster, *J. Chem. Phys.*, **3**, 373 (1940).

with the determinations by electron diffraction of Wierl¹² ($2.38 \pm 0.08 \text{ \AA}$.) and Maxwell, Mosley, and Deming¹³ ($2.38 \pm 0.05 \text{ \AA}$.), and with the length predicted from the moment of inertia¹⁴ (2.31 \AA .). The structure found for hydrogen azide is identical with that proposed by Eyster¹⁵ from a consideration of the moments of inertia, and on the assumption that the resonating structures are chiefly I + II.

Summary

The structures of nitrous oxide and hydrogen

(12) R. Wierl, *Physik. Z.*, **31**, 1028 (1930).

(13) L. Maxwell, V. Mosley and L. Deming, *J. Chem. Phys.*, **2**, 331 (1934).

(14) E. F. Barker, *Phys. Rev.*, **41**, 369 (1932).

(15) E. H. Eyster, *J. Chem. Phys.*, **8**, 141 (1940).

azide have been investigated by the electron diffraction method.

For nitrous oxide $r_1 + r_2 = 2.32 \pm 0.02 \text{ \AA}$., and $0.925 < r_1/r_2 < 1.08$. The distances $r_1 = 1.12 \text{ \AA}$. and $r_2 = 1.19 \text{ \AA}$. predicted by Pauling on the basis of his adjacent charge rule give a ratio, 0.94, which lies between these limits. It is shown that the distances found by the use of Badger's rule also have the ratio 0.94.

For hydrogen azide the distances found are $r_3 = 1.136 \pm 0.01 \text{ \AA}$. and $r_4 = 1.247 \pm 0.01 \text{ \AA}$., on the basis of an assumed linear N_3 group. The report of Eyster, made on the basis of his values of the moments of inertia and Pauling's adjacent charge rule, is confirmed. It is shown that the application of Badger's rule yields similar results.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solutions. VII. The Reduction of Complex Nickel Cyanides: Mono-valent Nickel

By JOHN W. EASTES AND WAYLAND M. BURGESS¹

The red color produced by the reduction of aqueous solutions of potassium cyanonickelate, $\text{K}_2\text{Ni}(\text{CN})_4$, was shown by Bellucci and Corelli² to be attributable to a substance having the empirical formula $\text{K}_2\text{Ni}(\text{CN})_3$. This substance had, however, never been isolated.

In the course of a study of the reduction of nickel salts in anhydrous liquid ammonia,³ $\text{K}_2\text{Ni}(\text{CN})_3$ was observed to be formed and we have now succeeded in isolating it in a pure condition, both from solutions of liquid ammonia and from aqueous solutions, and subjecting it to a complete analysis and study.

Materials Used

Alkali Metals.—Kahlbaum metallic sodium and potassium were used. The sodium was analyzed by solution in 95% ethanol, conversion to sodium chloride by the addition of excess hydrochloric acid, evaporation to dryness and weighing as sodium chloride. An average of four analyses gave a value of 100.5% sodium, with a maximum deviation of 0.2%. The potassium was analyzed in a

similar manner, but with the addition that it was also precipitated and weighed as $\text{K}_2\text{NaCo}(\text{NO}_2) \cdot 6\text{H}_2\text{O}$ ⁴ and found to be 100.4% potassium, with a maximum deviation of 0.4%.

Sodium and Potassium Cyanonickelate; $\text{Na}_2\text{Ni}(\text{CN})_4$, $\text{K}_2\text{Ni}(\text{CN})_4$.—These two compounds were prepared in a pure form by recrystallization of the product obtained by concentrating a dilute solution formed by dissolving freshly precipitated nickel cyanide in a solution of the alkali metal cyanide. The anhydrous products had the analyses: for $\text{Na}_2\text{Ni}(\text{CN})_4$ —28.07% Ni (calcd. 28.12% Ni), 49.93% CN (calcd. 49.85% CN); for $\text{K}_2\text{Ni}(\text{CN})_4$ —24.30% Ni (calcd. 24.36% Ni), 43.56% CN (calcd. 43.18% CN).

Preparation of $\text{K}_2\text{Ni}(\text{CN})_3$ in Liquid Ammonia.—Reactions in anhydrous liquid ammonia were carried out as described by Burgess and Eastes,³ a diagram of the apparatus used being shown in Fig. 1.

By the reaction of excess potassium cyanonickelate with sodium or potassium, $\text{K}_2\text{Ni}(\text{CN})_3$ was prepared in liquid ammonia solution as follows. The reaction tube was two-thirds filled with anhydrous liquid ammonia, which was then saturated with potassium cyanonickelate. To this solution was added a small piece, approximately 0.1 g., of sodium or potassium. A bright red, dense precipitate slowly formed in the solution and settled out at once. No hydrogen was formed during the reaction. When the alkali metal had all reacted, the yellow solution above the red precipitate was siphoned off and the red precipitate

(1) This article is based upon the thesis presented to the Faculty of the Graduate School of the University of Cincinnati by John W. Eastes in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936. No. VI, THIS JOURNAL, **63**, 2674 (1941).

(2) Bellucci and Corelli, *Z. anorg. Chem.*, **86**, 88-104 (1914).

(3) Burgess and Eastes, THIS JOURNAL, **63**, 2674-6 (1941).

(4) Hamid, *Analyst*, **51**, 450 (1926).