FTD-TT-65-1900

FOREIGN TECHNOLOGY DIVISION

COMPUTATION OF THE VIBRATIONAL FREQUENCIES OF A MOLECULE OF HYDRAZIN N_2H_4

By

Yu. I. Kotov, G. S. Koptev, and V. M. Tatevskiy

1,61

A

FTD-TT- 65-1900/1+2+4

UNEDITED ROUGH DRAFT TRANSLATION

COMPUTATION OF THE VIBRATIONAL FREQUENCIES OF A MOLECULE OF HYDRAZIN N_2H_4

BY: Yu. I. Kotov, G. S. Koptev, and V. M. Tatevskiy

English pages: 6

SOURCE: Moscow. Universitet. Vestnik. Seriya II.
Khimiya, No. 3, 1963, pp. 10-13.

UR/0189-063-000-003

TP6000449

	PREPARED BY: TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WP-AFB, OHIO.

FTD-TT- 65-1900/1+2+4

Date 25 April 19 66

B

COMPUTATION OF THE VIBRATIONAL FREQUENCIES OF A MOLECULE OF HYDRAZIN N_2H_4

Yu. I. Kotov, G. S. Koptev, and V. M. Tatevskiy

To the investigation of the vibrational spectrum of hydrazine N_2H_4 in the solid, liquid, and gaseous states a great number of projects (1, 2, 3, 4, 5, 6) have been devoted. In a number of the studies (5, 6, 7) attempts have been made at relating the frequencies of the molecule N_2H_4 for the point group C_2, but in the project (8) a computation was made of the normal vibrations of a molecule of hydrazine N_2H_4 by using the power invariables from the data for the molecules of methylamine CH_3NH_2 and ammonia NH_3 for the configuration with the angle of turn θ of one group NH_2 equal to 90°.

But since in recent time there have appeared new, more precise electronographic and spectroscopic data on the structure of the molecule of hydrazine (9, 10), it serves to end sought to repeat the computation of the vibration spectrum of the molecule of hydrazine. And in connection with the question of the rotational isomer of hydrazine some interest is afforded by the computation of the vibrational frequencies of the molecule of hydrazine for different angles θ.

We made a computation of the vibrational frequency of a molecule of hydrazine for the angles of turn $\theta = 0^\circ$, 60, 90, 120, and 180°. Below the results obtained are elucidated.

The expression for the potential energy of the molecule N_2H_4 used in the computation can be presented in the form

$$2V = K_Q \cdot Q^2 + K_q \sum_i q_i^2 + K_\alpha \sum_{i \neq j} \alpha^2_{ij} +$$

$$+ K_\beta \sum_i \beta_i^2 + 2K_{Q\beta} \sum_i Q\beta_i + 2K_{qq} \sum_{\substack{i,j=1,2\\ i,j=3,4}} q_i q_j +$$

$$+ 2K_{q\alpha} \sum_{i \neq j} q_i \alpha_{ij} + 2K_{q\beta} \sum_i q_i \beta_i + 2K_{\alpha\beta} \sum_{i \neq j} \beta_i \alpha_{ij} +$$

$$+ 2K_{\beta\beta} \sum_{\substack{i,j=1,2\\ i,j=3,4}} \beta_i \beta_j + 2K'_{\beta\beta}(\gamma_{\beta_i\beta_j}) \sum_{\substack{i,j=1,3,4\\ i,j=2,3,4}} \beta_i \beta_j,$$

where $K_Q,\ K_q,\ K_\alpha,\ K_\beta,\ K_{Q\beta},\ K_{qq},\ K_{q\alpha},\ K_{q\beta},$
$K_{\alpha\beta},\ K_{\beta\beta}$ и $K'_{\beta\beta}(\gamma_{\beta_i\beta_j})$ —

are the power invariables. $\gamma_{\beta_i\beta_j}$ -is the angle between the planes in which lie the angles β_i and β_j. The coordinates of the change of the internuclear distances Q_i, q_i and the valance angles α_{ij} and β_i are given in the drawing.

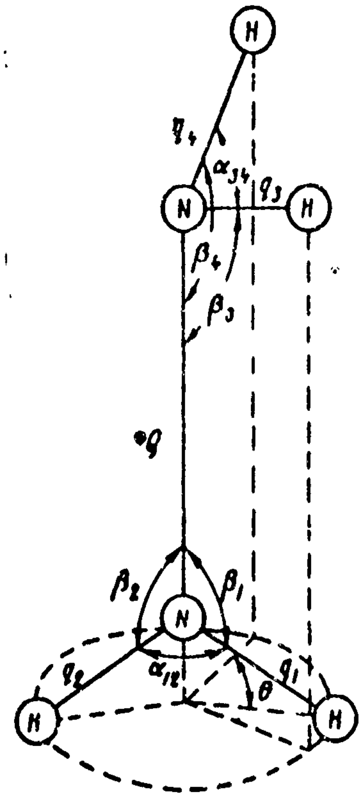
The power invariables used in the computation had the following values (in 10^6 cm^{-2}): $K_Q = 8.11$; $K_q = 10.36$; $K_\alpha = 0.79$; $K_\beta = 1.14$; $K_{Q\beta} = 0.45$; $K_{qq} = 0.05$; $K_{q\alpha} = 0.35$; $K_{q\beta} = 0.50$; $K_{\alpha\beta} = K_{\beta\beta} = 0.035$. These values of power invariables were borrowed from the data for the molecules NH_3, CH_3NH_2, C_2H_6 (12). The value of the invariable K_Q was taken from the work (8). The

The invariables K_q and $K\beta$ were refined from the preliminary computation of the frequency of the molecule N_2H_4. The power invariable $K'_{\beta\beta}\ (\gamma\beta_i\beta_j)$ was roughly evaluated by the formula:

$$K'_{\beta\beta}(\gamma_{\beta_i\beta_j}) = -0{,}12 + \frac{0{,}24}{180^\circ}\gamma_{\beta_i\beta_j}.$$

In determining the coefficients of the kinetic energy there were used the following geometrical parameters (9, 10); R(N--N) = 1.449 Å; r(N--H) = 1.022 Å; α(HNH) = 106° and β(NHH) - 112°. The solution of the secular equations was done on the electronic computer Strela. The values for the frequencies of the molecule N_2H_4 were calculated for the values $\theta = 0^\circ$, 60, 90, 120, and 180°.

The results of the computation are given in the table*. In the last column for comparison there are given the experimental values of the frequencies borrowed from the work (6).



Discussion of the Results

The computed values of the frequencies for $\theta = 90^\circ$ are found to be in agreement with the results of the computation given in the report (8) for the configuration with $\theta = 90^\circ$.

As is seen from the table the course of the frequencies v_1, v_2, v_3, v_5, v_8, v_9 and v_{10} in the measurement of θ

---

*For θ-0° = 180° the computation of the frequency was done both in accordance with the matrices of the types of symmetry A and B and in accordance with the matrices of the types of symmetry A_1, B_1, and A_g, B_g, A_u, B_u. Therefore in the table in the columns with θ=0° and 180° after each frequency in the brackets there are shown types of symmetry of frequencies referring to the point groups C_{2v} and C_{2h}.

from 0° to 180° proves to be insignificant (at the maximum it reaches the value ~30 cm^{-1}). Therefore in accordance with the course of the change of these frequencies it is not possible to judge of the angle of turn θ of one group NH_2 relative to another group NH_2.

The frequencies v_4 and v_{11}, on the other hand, change almost by 350 cm^{-1} in the transition from $\theta = 0°$ to $\theta = 180°$. For the configuration with $\theta = 90°$ they have practically one and the same value equal to 1270 cm^{-1}. In the infrared spectrum of the absorption of the vapors of N_2H_4 in this area there was noted one frequency. In accordance with the report (6) its value is equal to 1275 cm^{-1}, in accordance with (5) 1282 cm^{-1}. Such an agreement of experiment and computation clearly confirms the deduction made earlier in the projects (10, 11) that the most probable angle of turn θ of the one group NH_2 relative to another group NH_2 is the angle $\theta = 90°$.

The change in the frequencies v_6 and v_{12} is also significant (it reaches ~150 cm^{-1}). The calculated values of the frequencies v_6 and v_{12} for $\theta = 90°$ are respectively equal to 831 and 859 cm^{-1}. In the work (5) in the infrared spectrum of the absorption of the vapors of N_2H_4 in this area there were revealed two weak bands 815 and 850 cm^{-1} and two strong bands 930 and 965 cm^{-1}. In a later work (6) in the infrared spectrum of the absorption of vapors of N_2H_4 there were noted three strong bands 780, 933, and 966 cm^{-1}. As is seen from the comparison with the data of the table all these experimental values can be sufficiently well explained if one allows the existence of all three isomeric forms: the cis-forms ($\theta = 0°$), the trans-forms ($\theta = 180°$), and the C_2-forms with $\theta = 90°$. However, such an explanation results in objections for a number of other considerations. But, if one does not take into consideration the frequencies 815 and 850 cm^{-1}, taking into account that they were not repeated in the work (6), then one can satisfactorily explain the noted frequencies having taken the existence of only on "C_2-form" with $\theta = 90°$, as was done in the work (8). But the strong divergence of the computed and the experimentally determined values of the frequencies v_6 and v_{12} in this case can be referred to imprecision of the respective power invariables.

For the solution of the problem of the correctness of any of these explanations very important is the investigation of the vibrational spectrum of the vapors of N_2D_4 and the carrying out of a more precise computation.

Vibrational Frequency (in cm^{-1}) of a Molecule of N_2H_4 for Different Values of the Angle θ

Vibrations	Symmetry	$\theta = 0°$	$\theta = 60°$	$\theta = 90°$	$\theta = 120°$	$\theta = 180°$	$\nu_{экс}$ [6]
ν_1	A	3317 (A_1)	3315	3313	3311	3310 (A_g)	3314
ν_2		3345 (A_2)	3350	3355	3360	3364 (A_u)	3325
ν_3		1613 (A_1)	1632	1628	1624	1641 (A_g)	1587
ν_4		1419 (A_2)	1347	1270	1186	1070 (A_u)	1275
ν_5		1043 (A_1)	1044	1044	1045	1052 (A_g)	1098
ν_6		784 (A_1)	816	831	852	925 (A_g)	780
ν_8	B	3305 (B_1)	3307	3309	3311	3313 (B_u)	3280
ν_9		3364 (B_2)	3359	3355	3350	3345 (B_g)	3350
ν_{10}		1669 (B_1)	1652	1656	1659	1638 (B_u)	1628
ν_{11}		1071 (B_2)	1186	1269	1347	1419 (B_g)	1275
ν_{12}		957 (B_1)	881	859	844	814 (B_u)	966 933

Literature

1. S. Imanishi. Nature, 127, 782, 1931.

2. L. Kahovec and K. W. F. Kohlrausch. Z. Phys. Chem. (Journal for Physical Chemistry), Vol. 38, 96, 1938.

3. J. Goubeau. Z. Phys. Chem. (see foregoing Ref.), Vol. 45, 237, 1940.

4. S. S. Krivich. DAN SSSR, 23, 36, 1939.

5. W. Fresenius and J. Karwell. Z. Phys. Chem., Vol. 44, 1, 1939.

6. P. A. Giguere and I. D. Liu. J. Chem. Phys., 20, 136, 1952.

7. D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard, and H. M. Huffman. J. Amer. Chem. Soc., 71, 2293, 1949.

8. A. Yamaguchi. J. Chem. Soc. Japan, 80, 1109, 1959.

9. Y. Morino, T. Iijima, and Y. Murata. Bull. Chem. Soc. Japan, 33, 16, 1960.

10. A. Yamaguchi, I. Ichishima, T. Shimanouchi, and I. Mizushima. J. Chem. Phys., 31, 843, 1959; Spectrochim acta, 16, 1471, 1960.

11. W. G. Penney and G. B. B. M. Sutherland. J. Chem. Phys., 2, 492, 1934, Trans, Faraday Soc., 30, 898, 1934.

12. M. V. Vol'keishteyn, M. A. Yel'yashevich, B. I. Stepanov. Kolebanyya Molekul, Vol. 1, Gostekhizdat, M., 1949.