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May 1, 1965 to October 31, 1965

THEORETICAL STUDY OF ATOMIC AND MOLECULAR GASES AND THEIR REACTIONS IN THE UPPER ATMOSPHERE

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INTRODUCTION

In the previous report it was stated that we have successfully [illegible] computer programs to include 3s and 3p functions in addition to 1s, 2s and [illegible] to calculate the wave functions and total energies of the different states of diatomic molecules. In addition, it was also mentioned that we have succeeded [illegible] varying the screening constants of the basic functions to obtain the best [illegible] This best LCAO MO's work was confined to the equilibrium distance only. [illegible] tension of this program to a large number of internuclear distances and to a [illegible] of ionized and excites states, in addition to the ground state, involves very [illegible] We have successfully computed the potential energy curves of different states [illegible] and CO molecules. Some preliminary work has also been done on O_2, NF, CN and [illegible] molecules. Some of these results are given in this report. The above work which aims at obtaining limited Hartree-Fock MO's for different states of diatomic molecules involves immense computation due to the optimization of non-linear parameters (screening constants). The above work has involved over 800 hours of [illegible] 7094 computer at the Institute for Space Studies. We owe the success of the [illegible] work to the excellent computing facilities and co-operation of the personnel [illegible] Institute for Space Studies, 475 Riverside Drive, New York, New York.

author

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Work carried out during the above period can be given under the following headings:

(1) Calculation of the Potential Energy (P.E.) Curves and Molecular Constants of the Ionized States ($X\ ^2\Sigma_g$, $A\ ^2\Pi$, $B\ ^2\Sigma_u$) of N_2 Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions.

(2) Calculation of the Potential Energy Curves and Molecular Constants of the Ground ($X\ ^1\Sigma_g$) and the Excited ($A\ ^3\Sigma_u^+$, $B\ ^3\Pi_g$, $C\ ^3\Pi_u$) States of N_2 Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions.

(3) Development of the Computer Program to Calculate Best LCAO MO's of Homopolar Molecules Using 3s and 3p Functions in Addition to 1s, 2s and 2p Functions.

(4) Calculation of the P. E. Curves and Molecular Constants of the Different States of Heteropolar Molecules Using Best LCAO MO's Involving 1s, 2s and 2p Functions.

(1) Calculation of the P.E. Curves and Molecular Constants of the Ionized States of N_2 Molecules Using Best LCAO MO's with 1s, 2s and 2p Functions

by R. C. Sahni, C. D. La Budde and B. C. Sawhney

'Auto vary' programs described in the previous report have been used to calculate the wave functions and total energies of the above states of N_2 at a number of internuclear distances (R = 1.5 (0.025) to 3.0). The programs constructed by P. C. Jain, described in the previous report, have been used to calculate the potential energy curves and molecular constants of the above states. Two different sets of calculations were made. In one set of calculations, (called individually optimized) the MO's and total energy of each of the ionized state was individually optimized at a number of internuclear distances to calculate the P.E. curves and molecular constants. In the second set of calculations the screening constants of the lowest ionized state ($X\ ^2\Sigma_g$) were used to calculate the MO's and total energies of the different states of N_2. These energies were then used to calculate the P.E. curves and molecular constants of the ionized states of N_2 molecule. The results of these calculations are reported in Tables I to X.

(2) Calculation of the P.E. Curves and Molecular Constants of the Ground and the Excited States of N_2 Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions

by R. C. Sahni and P. C. Jain

'Auto vary' programs described in the previous report have been used to calculate the ground and excited state of N_2 molecule. Two sets of calculations called 'individually optimized' and 'using optimized ground state ($X\ ^1\Sigma_g$) screening constants' were carried out. From the total energies, P. E. curves and molecular

Molecular Constants for the Potential Energy Curves of N_2^+ Molecule

Obtained from First Principles

The program PSI VIB WKB NP5 SQL WX has been used for driving the molecular constants for the potential energy curves of various ionized states of N_2 molecule. The result obtained follows:

$N_2^+ (X\ ^2\Sigma_g^+)$

INDIVIDUALLY OPTIMIZED

	Derived	Code et al	Experimental
Re	2.11197 a.u.	2.0405 a.u.	2.10917
T.E	-108.12712193 a.u.		

TABLE I

v	G(v)	B_v
0	1211.03	1.9210
1	3601.94	1.9081
2	5970.99	1.8948
3	8313.55	1.8813
4	10632.84	1.8682
5	12937.47	1.8550
6	15218.17	1.8404
7	17474.46	1.8277
8	19710.77	1.8149
9	21926.62	1.8017
10	24121.75	1.7880
11	26295.02	1.7745

TABLE II

Derived Values of N_2^+ ($^2\Sigma_g$) Individually Optimized

# of Vibrational Levels Used	ω_e	$\omega_e x_e$	B_e	α_e
3	2429.16	16.8300	1.9276	0.0131
4	2427.40	15.3167	1.9278	0.0133
5	2426.08	14.4400	1.9278	0.0132
6	2424.61	13.6390	1.9278	0.0132
7	2423.38	13.0712	1.9281	0.0134
8	2422.43	12.6895	1.9281	0.0134
9	2421.61	12.3997	1.9280	0.0133
10	2420.87	12.1675	1.9279	0.0133
11	2420.20	11.9767	1.9279	0.0133
12	2419.61	11.8209	1.9279	0.0133
Exp. Values	2207.19	16.1360	1.9322	0.0202
Cade et al	2570.5	9.809	2.065	0.0148

TABLE III

N_2^+ ($A\,^2\Pi_u$)

INDIVIDUALLY OPTIMIZED

	Derived	Cade et al	Experimental
Re	2.2284 a.u.	2.1344	2.2226
T.E	-103.13844013 a.u.		

v	G(v)	B_v
0	1072.35	1.7224
1	3170.52	1.7089
2	5268.21	1.6998
3	7354.17	1.6885
4	9420.39	1.6773
5	11472.27	1.6662
6	13508.30	1.6555
7	15529.14	1.6444
8	17533.17	1.6341
9	19521.59	1.6225
10	21494.61	1.6116
11	23452.12	1.6009

TABLE IV

INDIVIDUALLY OPTIMIZED

Derived Values for A ($^2\Pi_u$) State of N_2^+ Molecule

# of Vibrational Levels Used	ω_e	$\omega_e x_e$	B_e	α_e
3	2149.95	18.7093	1.7273	0.0113
4	2144.[illegible]	13.6927	1.7270	0.0111
5	2140 82	11.5052	1.7270	0.0110
6	2138.64	10.3157	1.7270	0.0111
7	2137.10	9.6071	1.7269	0.0110
8	2135.96	9.1486	1.7269	0.0110
9	2135.10	8.8464	1.7268	0.0110
10	2134.44	8.6367	1.7268	0.0110
11	2133.90	8.4842	1.7268	0.0110
12	2133.46	8.3696	1.7268	0.0110
Exp. Values	1902.84	14.9100	1.7400	0.0180
Cade et.al.	2012.5	6.082	1.387	0.0115

TABLE V

B ($^2\Sigma_u^+$) State

INDIVIDUALLY OPTIMIZED

Values of G(v) and B_v for the B ($^2\Sigma_u^+$) State of N_2^+

	Derived	Cade et.al.	Experimental
Re	1.99141	1.935	2.03139
T.E.	107.95751572		

v	G(v)	B_v
0	1465.66	2.1616
1	4375.86	2.1520
2	7258.96	2.1408
3	10129.01	2.1300
4	12981.55	2.1196
5	15815.36	2.1092
6	18634.62	2.0981
7	21440.01	2.0864
8	24223.52	2.0753
9	26984.81	2.0644
10	29733.96	2.0543
11	32457.21	2.0436

TABLE VI

Molecular Constants for the B ($^2\Sigma_u^+$) State of N_2^+

(INDIVIDUALLY OPTIMIZED)

# of Vibrational levels Used	ω_e	$\omega_e x_e$	B_e	α_e
3	2938.18	13.8636	2.1671	0.0104
4	2936.65	12.5583	2.1672	0.0106
5	2935.26	11.6285	2.1673	0.0106
6	2934.15	11.0257	2.1673	0.0106
7	2933.14	10.5566	2.1674	0.0106
8	2932.16	10.1544	2.1675	0.0107
9	2931.39	9.8932	2.1678	0.0108
10	2930.85	9.7239	2.1680	0.0108
11	2930.37	9.5850	2.1679	0.0108
12	2929.91	9.4658	2.1679	0.0108
Exp. Values	2419.84	23.19	2.083	0.0195
Cade et.al	3101.3	19.38	2.295	0.01280

TABLE VII

N_2^+ ($A\ ^2\Pi_u$) USING OPTIMIZED N_2^+ ($^2\Sigma_g^+$) SCREENING CONSTANTS

	Derived	Cade et al.	Experimental
Re	2.23103 a.u.	2.1345	2.2286
T.E	-108.13686840		

v	G(v)	B_v
0	1091.57	1.7188
1	3175.81	1.7096
2	5310.62	1.6996
3	7402.65	1.6862
4	9475.32	1.6769
5	11521.65	1.6558
6	13543.01	1.6542
7	15551.18	1.6431
8	17547.39	1.6319
9	19526.65	1.6201
10	21489.95	1.6098
11	23439.86	1.5988

TABLE VIII

Derived Values of N_2^+ (A $^2\Pi_u$) Using Optimized N_2^+ ($^2\Sigma_g$) Screening Constants

# of Vibrational Levels Used	ω_e	$\omega_e x_e$	B_e	α_e
3	2099.03	-10.5557	1.7248	0.0101
4	2106.35	-4.2768	1.7260	0.0111
5	2112.34	-0.2826	1.7257	0.0109
6	2117.36	2.4549	1.7257	0.0109
7	2121.51	4.3691	1.7258	0.0110
8	2124.69	5.6400	1.7259	0.0110
9	2127.02	6.4632	1.7260	0.0110
10	2128.78	7.0187	1.7262	0.0111
11	2130.12	7.4014	1.7262	0.0111
12	2131.11	7.6612	1.7261	0.0111
Exp. Values	1902.84	14.9100	[illegible]	0.0180
Cade et.al	2312.5	6.089	1.807	0.0155

Table IX

N_2^+ (B $^2\Sigma_u$) Using Ionized Ground State Optimized Screening Constants

	Derived	Cade	Experimental
Re	1.9903 a.u. -107.95539761	1.955	2.0314

v	G(v)	B_v
0	1452.14	2.1635
1	4340.28	2.1519
2	7217.96	2.1402
3	10085.14	2.1298
4	12944.33	2.1179
5	15780.05	2.1069
6	18597.27	2.0965
7	21395.73	2.0855
8	24173.65	2.0725
9	26935.30	2.0619
10	29687.32	2.0527
11	32434.37	2.0432

TABLE X

Derived Values N_2^+ $(B\ ^2\Sigma_u)$ Using Ionized Ground State Optimized Screening Constants

# of Vibrational Levels	ω_e	$\omega_e x_e$	B_e	α_e
3	2907.81	8.5461	2.1672	0.0107
4	2906.56	7.4755	2.1672	0.0107
5	2905.48	6.7565	2.1676	0.0109
6	2905.28	6.6457	2.1677	0.0110
7	2905.51	6.7492	2.1676	0.0110
8	2905.95	6.9261	2.1676	0.0110
9	2906.54	7.1339	2.1680	0.0111
10	2907.17	7.3347	2.1681	0.0111
11	2907.62	7.4617	2.1679	0.0111
12	2907.83	7.5166	2.1675	0.0110
Exp. Values	2419.84	23.1900	2.0830	0.0195
Cade et.al	3101.8	19.83	2.296	0.01280

constants were calculated in the same manner as described above for the ionized states.

(3) Development of the Computer Program to Calculate Best LCAO MO's of Homopolar Molecules Using 3s and 3p Functions In Addition to 1s, 2s and 2p Functions
by C. D. La Budde, Birbal Singh, O. P. Anand and G. R. Verma

It was stated in the previous report that an 'Auto vary' program has been built which varies the screening constants of 1s, 2s and 2p basic function to obtain the best LCAO MO's. In the previous report it was also stated that the inclusion of 3s and 3p functions involved many more integrals and the solution of the eigenvalue problem was more complicated. Since for every variation of the screening constants, the whole calculation has to be repeated, the machine time becomes very important. After overcoming many hurdles, an 'Auto vary' program has been built up for homopolar molecules. This program is now being used to calculate the different states of N_2 molecule with a view to calculate their P. E. curves and molecular constants.

(4) Calculation of the P.E. Curves and Molecular Constants of the Different States of Heteropolar Molecules Using Best LCAO MO's Involving 1s, 2s and 2p Functions
by R. C. Sahni, C. D. La Budde and B. C. Sawhney

The wave functions and total energies of a number of states of CO have been calculated at a number of internuclear distances. Due to limitation of machine time some of these calculations are not yet complete. In addition to CO, work has been done on CN, NF and NO molecules. We hope to report these results in the next report.

PUBLICATIONS AND GROUP ACTIVITIES

Publications

(1) Electronic States of Molecules. I. Self-Consistent Field Calculations of the Ground, Ionized, and Excited States of N_2 and O_2, by R. C. Sahni and E. J. De Lorenzo, J. Chem. Phys, 42, 3612, (1965)

(2) Quantum Theory of the Defect Solid State, by R. C. Sahni
This paper has been accepted for publication in ASTM Symposium Journal

Group Activities

(1) Dr. R. C. Sahni presented the following paper at the Molecular Spectroscopy Symposium, The Ohio State University, Columbus, Ohio, "Theoretical Calculation of the Electronic States, Total Energies, Ionization Potential and Excitation Energies of O_2, N_2, CO, NO, CN and the Hydrides of the First Group," June 1965

(2) Dr. R. C. Sahni presented the following paper at ASTM meeting, Seattle, Washington, "Quantum Theory of the Defect Solid State," November 1965

(3) Dr. J. C. Browne of the University of Texas gave a number of lectures on Multicenter Integrals and Special Functions during the summer

(4) Dr. G. R. Verma of the University of Rhode Island worked with our group during the summer on various mathematical projects.