NEW YORK UNIVERSITY

CHEMISTRY DEPARTMENT

UNIVERSITY HEIGHTS

Contract No. NSG 76-60

November 1, 1965 to April 30, 1966

THEORETICAL STUDY OF ATOMIC AND MOLECULAR GASES

AND THEIR REACTIONS

IN THE UPPER ATMOSPHERE

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) _____1.00_____

Microfiche (MF) _____.50_____

ff 653 July 65

FACILITY FORM 602

N66 24969
(ACCESSION NUMBER)

13
(PAGES)

CR-74684
(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

13
(CATEGORY)

Submitted to the National Aeronautics and Space Administration, Washington, 25, D. C. The report contains a brief summary of the work done during the period November 1, 1956 to April 30, 1966

Roop C. Sahni
Project Director

PERSONNEL

Dr. R. C. Sahni	Chief Investigator and Project Director
Dr. C. Donald La Budde	Research Scientist
Dr. B. Singh	Assistant Research Scientist
Dr. D. C. Jain	Assistant Research Scientist
Mr. B. C. Sawhney	Assistant Research Scientist
Mr. O. P. Anand	Research Assistant

INTRODUCTION

In the previous report we have described some of the work on different states of N_2. This work consisted in computing wave functions, total energies and molecular constants of the different ionized states of N_2. We have also described in that report that we were working similar calculations on heteropolar molecules such as CO, NO, CN and NF. We have completed calculation on CO molecule and are at present working on other heteropolar molecules. We also mentioned in the previous report that we have extended our computer programs to include 3s and 3p functions in addition to 1s, 2s and 2p functions. We are at present calculating the wave functions, total energies and molecular constants of N_2 using this extended basis set. We hope to describe these results in the coming report. The above work has involved over 400 hours of I.B.M. 7094 computer. We owe the success of the above work to the excellent computing facilities and co-operation of the personnel of the Institute for Space Studies, 475 Riverside Drive, New York, New York.

Roop C. Sahni

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

(1) Calculation of the Potential Energy (P.E.) Curve and Molecular Constants of the Ground State of CO Molecule Using Slater Screening Constants As Well As Best LCAO MO's with 1s, 2s and 2p Functions.

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

(3) Calculation of the P.E. Curve and Molecular Constants of the Ground State of H_2 Molecule Using the Extended Set of Functions; that is, 1s, 2s, 2p, 3s and 3p Functions.

(4) Development of Semi-empirical Procedures Such As RKR Method To Calculate P.E. Curve, Molecular Constants, Transition Probabilities of Different Band Systems, Electric and Magnetic Susceptibilities of Diatomic Molecules.

(1) <u>Calculation of the Potential Energy (P.E.) Curve and Molecular Constants of the Ground State of CO Molecule Using Slater Screening Constants As Well As Best LCAO MO's with 1s, 2s and 2p Functions</u>

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

The self-consistent field molecular orbital method in LCAO (linear combination of atomic orbitals) approximation is applied to the ground state of CO at a number of internuclear distances, for the computation of the potential energy curve. In this calculation both the LCAO MO's and the screening constants of the atomic orbitals have been optimized. The molecular constants ω_e, $\omega_e x_e$, B_e, α_e, E_e and

D_e have also been calculated. These results are given in Tables 1-7 along with the experimental data (See Publication 1.) The computed potential energy curve along with the RKR curve is given in Fig. 1. The computed spectral results are more encouraging than hitherto reported in the literature from ab initio calculation.

(2) <u>Calculation of the P.E. Curves and Molecular Constants of the Ionized (X $^2\Sigma$, A $^2\Pi$, B$^2\Sigma$) States of CO Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions</u>

by R. C. Sahni and B. C. Sawhney

Auto-hetero vary programs described in the previous reports have been used to

calculate the wave functions and total energies of the above states of CO^+ at a number of internuclear distances $(R = 1.7 - 6.5)$. 'Molecular-constant computation programs' described in the previous reports were used to calculate ω_e, $\omega_e x_e$, B_e, α_e and D_e of the above states. These computed results have been compared with the experimental results. The details of these computations will be described in the next report.

(3) Calculation of the P.E. Curve and Molecular Constants of the Ground State of N_2 Molecule Using the Extended Set of Functions; that is, 1s, 2s, 2p, 3s and 3p Functions

   by R. C. Sahni, C. D. La Budde, B. C. Sawhney, O. P. Anand and Birbal Singh

   It was stated in the previous reports that a number of programs have been constructed called 'Auto Homo-Vary 3s-3p,' which can be used to calculate wave functions of homopolar molecules using extended set of basic functions. These programs require a lot of machine time. At present we are applying these programs to calculate the P.E. curve of N_2. We are in the midst of these calculations and hope to describe these results in the coming reports.

(4) Development of Semi-empirical Procedures Such As RKR Method To Calculate P.E. Curve, Molecular Constants, Transition Probabilities of Different Band Systems, Electric and Magnetic Susceptibilities of Diatomic Molecules

   by D. C. Jain and R. C. Sahni

   (a) The Effect of the Vibration-Rotation Interaction on the Franck-Condon Factors for the Band System of the RbH Molecule

      The Rydberg—Klein—Rees (RKR) potential energy curves of the $X\ ^1\Sigma^+$ and $A\ ^1\Sigma$ states of the RbH molecule have been calculated by the numerical integration of the Klein's equations. It has been found that for all the vibrational levels, the resultant RKR curves satisfy the quantization condition to an accuracy of 0.05% or less. The vibrational wave functions appropriate to the RKR curves yield the values of B_v which are in close agreement with the

experimental results. The vibrational wave functions corrected for the effect of the vibration-rotation interaction have been obtained for a number of vibrational-rotational energy levels. The Franck-Condon factors, the r-centroids and the relative intensities have been computed. The results indicate that there is a significant effect of the vibration-rotation interaction on the Franck-Condon factors and on the relative intensity distribution.

(b) Effect of Vibrational-Rotational Motion on the Electric and Magnetic Properties of Diatomic Molecules

A modification of the method of studying the effect of vibrational-rotational motion on the electric and magnetic properties of diatomic molecules have been outlined. It consists in employing the more realistic Rydberg-Klein-Rees (RKR) potential energy curves for obtaining the vibrational wave functions corrected for the effect of rotation which in turn are used for vibrational averaging to obtain the various electric and magnetic properties in a number of vibrational-rotational states. The magnetic susceptibility and the rotational magnetic moment of H_2, HD and D_2 are computed by this method and compared with the experimental data as well as with the results reported by others. The results of this calculation show improvement over those reported by earlier workers.

(c) Transition Probability Parameters of Some Band Systems of CO^+ and N_2 Molecules

Franck-Condon factors and r-centroids have been computed for the comet-tail, the first negative and the Baldet-Johnson systems of CO^+ and for the first positive, the second positive, the Vegard-Kaplan, the Lyman-Birge-Hopfield and the Tanaka band systems of N_2. The vibrational potential energy curves of the electronic states involved have been calculated by the Rydberg-Klein-Rees method and the vibrational wave functions appropriate to them have been obtained by the Numerov method of integration of the radial Schrödinger equation. The variation of the electronic transition moment with the internuclear separation has been deduced by the method of r-centroids, and the 'smoothed' relative band strengths and the relative intensities at infinite temperature, calculated for the comet-tail bands of CO^+ and for the first

positive, the second positive and the Vegard-Kaplan band systems of N_2. The Einstein A coefficients, the absolute band strengths and the band oscillator strengths also have been presented for the comet-tail band system of CO^+.

PUBLICATIONS

The following papers have been accepted for publication and are in press:

1. Quantum Mechanical Treatment of Molecules. I. Calculation of the Potential Energy Curve and Molecular Constants of the Ground State of CO

    by R. C. Sahni, C. D. La Budde and B. C. Sawhney, Journal of the Faraday Society, London, England.

2. The Effect of the Vibration-Rotation Interaction on the Franck-Condon Factors for the Band System of the RbK Molecule

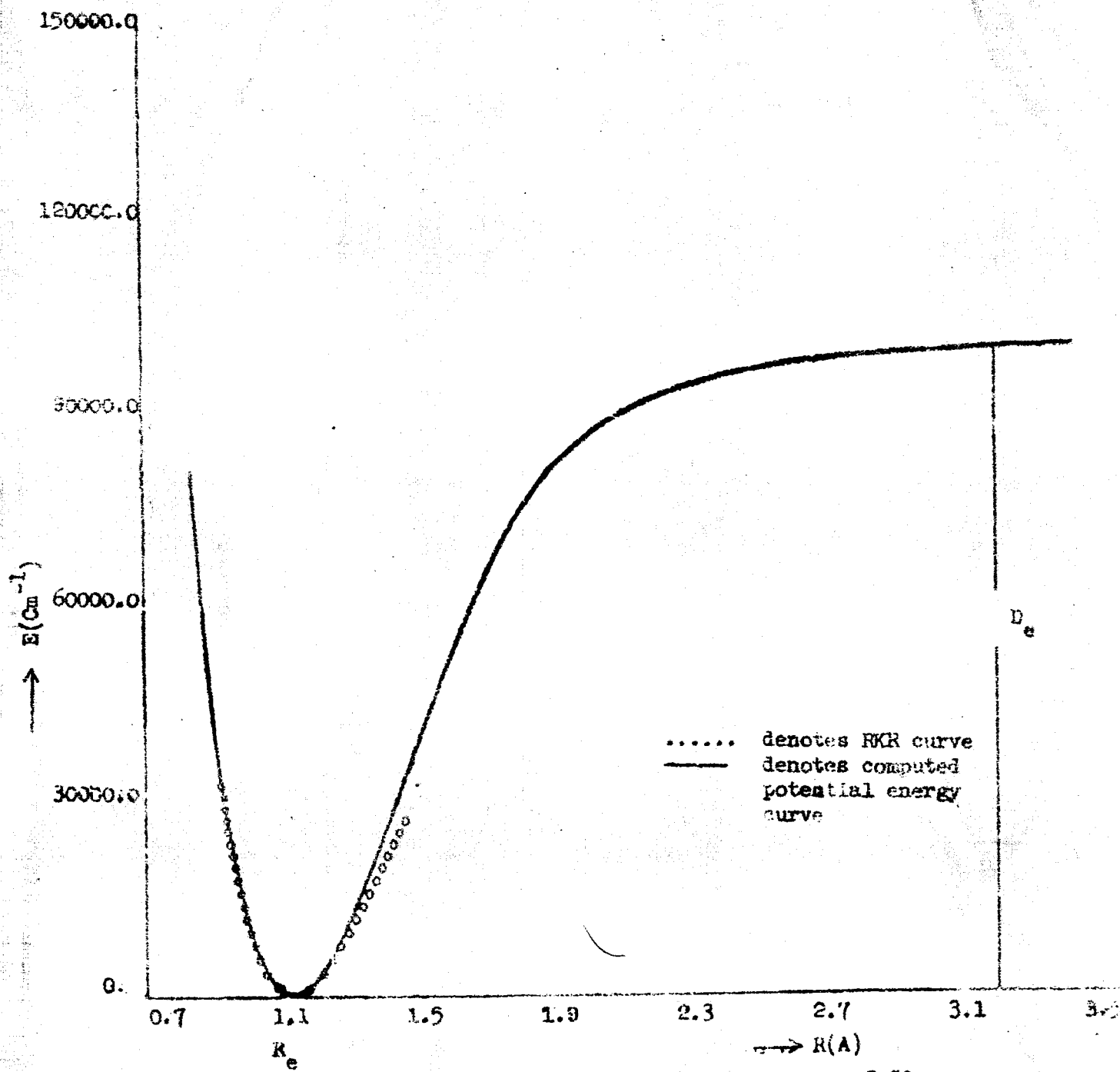   by D. C. Jain and R. C. Sahni, Proceeding of the Physical Society, Series A, London, England.

Fig. 1.—Computed P.E. curve and RKR curve of CO