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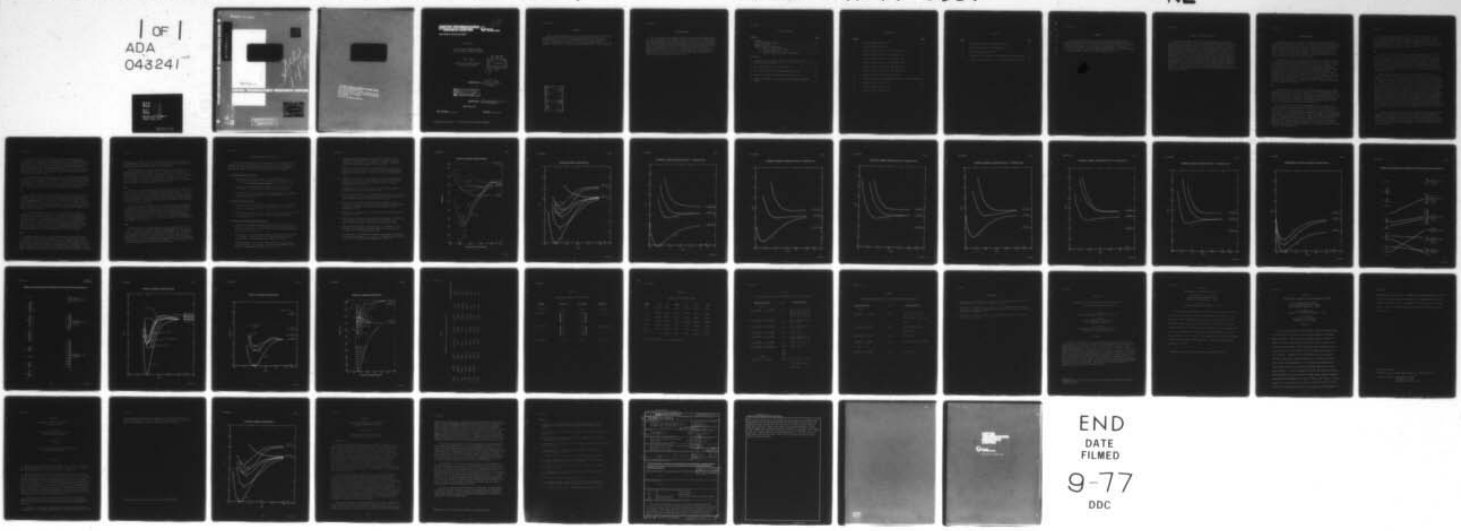

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R77-921723

CALCULATION OF POTENTIAL ENERGY CURVES FOR METAL OXIDES AND HALIDES

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Final Report

Contract No. F44620-73-C-0077
Project Task 9538-01

REPORTED BY H. H. Michels

H. H. Michels

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Research Sponsored by: Air Force Office of Scientific Research

FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Research Center, East Hartford, Connecticut under Contract F44620-73-C-0077, Project-Task No. 9538-01. The performance period for the technical program was from 1 June 1973 through 31 March 1977. The project monitor was Major John T. Viola, USAF, NAE.

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ACKNOWLEDGMENTS

It is a pleasure to acknowledge the advice and assistance rendered by the author's associates. We are indebted to Judith B. Addison for her help both with computer programming and with the analysis of the results of this research. Her efforts have been of real value during the course of this work. We also wish to acknowledge many fruitful discussions with research associates and the beneficial collaboration with Drs. R. H. Hobbs and Gerald A. Peterson on several research problems. Finally, we acknowledge the continued support and encouragement given by Major John T. Viola of AFOSR whose confidence in the value of this research has been of real help.

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ABSTRACT

This document constitutes the final technical report under Contract F44620-73-C-0077 entitled "Calculation of Potential Energy Curves For Metal Oxides and Halides." A brief review of all work performed under this Contract is given and a review of technical progress is presented. In addition, a list of the technical reports and papers generated under this research program, including the text or abstract of their contents is given.

ABSTRACT OF TECHNICAL EFFORT

The research performed under this Contract was directed toward the calculation of the electronic structure and radiative transition probabilities for certain diatomic metal oxides and halides which are candidate visible/UV laser systems. The objectives were to uncover systems having a low-lying excited state with a reasonably long (>10 μsec) radiative lifetime and situated energetically such that an inversion of population with respect to the dominant transitions to the ground state was possible. The systems under investigation to date include the group IIA metal oxides (BeO-BaO), the group IVA metal oxides (CO-PbO), NF, SiF, AlF and the thirteen electron sequence: N_2^+, CN, BO and BeF. These latter systems have a common chemistry of their electronically excited states, including a common $A^2\Pi \rightarrow X^2\Sigma^+$ Meinel transition, a $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ first negative transition and a possible metastable a $^4\Sigma^+ \rightarrow X^2\Sigma^+$ transition. Among these molecules the systems BaO, BO, NF, SnO, SiF and AlF were chosen for detailed study. Their value as candidate visible/UV laser systems has been analyzed.

RESEARCH PROGRESS

For several years this Center has been involved in detailed studies of the electronic structure and radiative lifetimes of the air system and certain diatomic metal oxide species which may be of abundance in the perturbed atmosphere following a thermonuclear explosion. Such diatomic species commonly exhibit strong LWIR radiation and a quantitative measure of this effect is needed to analyze the atmospheric kinetics. These studies were carried out using methods of molecular quantum mechanics coupled with available spectroscopic information on excited electronic states.

As an outgrowth of this research, a narrower study of certain classes of metal oxides and halides was initiated with the intent to screen such systems for candidates which might show potential as visible or UV electronic transition lasers. The objectives were to uncover systems having a low-lying excited state with a reasonably long (>10 μsec) radiative lifetime and situated energetically such that an inversion of population with respect to the dominant transitions to the ground state was possible. The systems under investigation to date include the group IIA metal oxides (BeO-BaO), the group IVA metal oxides (CO-PbO), NF, SiF, AlF, the thirteen electron sequence N_2^+, CN, BO and BeF, the SiF and SnO molecules and limited regions of the B + O_2 potential energy hypersurfaces. Summaries of the most interesting candidate laser molecules are given below.

BaO

For the system BaO, experimental information was lacking on the relative location of the singlet and triplet systems. The a $^3\Pi$ state had been previously identified (Ref. 1) since this state gives rise to perturbations in the A $^1\Sigma^+ \rightarrow$ X $^1\Sigma^+$ band system. Detailed calculations were therefore carried out for states of $^3\Sigma^+$, $^3\Sigma^-$ and $^3\Pi$ symmetry. The latter set of calculations could be used to judge the reliability of the calculated potential curves since RKR curves have been generated for the a $^3\Pi$ state of BaO.

The results of our calculations are summarized in Fig. 1 which is a composite of RKR and calculated potential curves for BaO. The $^3\Sigma^-$ state has the characteristic repulsive behavior of this state in the other group IIA metal oxides. This state has no ionic component. The more interesting feature is the location of the lowest $^3\Sigma^+$ state of BaO which appears to lie higher than the A $^1\Sigma^+$ state. Uncertainties in the calculations, based on comparisons with states of $^3\Pi$ symmetry, are such that the order of the A $^1\Sigma^+$ and lowest $^3\Sigma^+$ state could be reversed in more refined calculations. For the calculations performed here, the configuration interaction included the 6s, 6p, and 5d electrons on Ba and the 2s and 2p electrons on O. The extent of the CI varied from 500 - 3000 configurations.

These calculations indicate that the a $^3\Pi$ and A' $^1\Pi$ state of BaO are still the most important routes for branching into electronically excited states for this system. Recent experimental evidence, however, has indicated that the ground state collisional transfer of excitation to A $^1\Sigma^+$, which has a very short radiative lifetime ($\sim$ 100 nsec), imposes practical problems for the utility of this system as a visible chemical laser.

BO

Our focus on the BO molecule arose from three considerations. First, boron oxide is a light metal oxide and thus has a large rotational constant ($\sim$ 1.5 cm^{-1}) permitting easy separation of possible lasing molecular levels. Second, the number of low-lying molecular electronic states is rather small which results in a spectra that can possibly be fully analyzed. Third, this system was thought to exhibit metastability in a low-lying quartet state. Thus boron oxide might exhibit two characteristic lifetimes -- one associated with the doublet system transitions and a much longer lifetime associated with inter-system transitions.

Detailed quantum mechanical calculations were carried out for the symmetries $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$, $^2\Pi$, $^4\Pi$, $^2\Delta$ and $^4\Delta$, including all molecular states connecting up to the atomic ionic limit. Higher connecting states are all Rydberg in character. The calculated potential energy curves were compared with RKR curves derived from existing data on the molecular spectra of BO (Ref. 2) and a final set of potential curves was derived from the total information from spectra and our detailed calculations. These potential curves are shown in Fig. 2 where it can be seen that the a $^4\Sigma^+$ state for BO is strongly bound and highly metastable. An exhaustive literature search revealed that this state has probably been observed experimentally by Mal'tsev and co-workers (Ref. 3) but was incorrectly assigned. Our calculations are in good agreement with the experimental location of this state and no other molecular symmetry appears to be close-lying to prevent a unique assignment. Mal'tsev, et al. have seen this quartet state emission near 2500Å but no rotational analysis was carried out. The system was observed in emission from excited BO under an arc discharge. Finally, we have also reviewed and analyzed all of the spectroscopic data for BO, including the quartet systems. These data are shown in Table I.

In addition to our calculations of the energetics of this system, we have analyzed the lifetimes of the B $^2\Sigma^+$ and A $^2\Pi$ states and have estimated the lifetime of the low-lying a $^4\Sigma^+$ state. Spin-orbit coupling in BO is weak ($\lambda \approx 100$ cm^{-1}) and similar to that found in N_2 and CO. This results in a very long radiative lifetime for the a $^4\Sigma^+$ state. The calculated results are given in Table II which also shows the wavelengths of some of the stronger Franck-Condon transitions.

Clearly both the A $^2\Pi$ state and the a $^4\Sigma^+$ state are high-potential candidates for laser operation to the ground state. The strongest transition in the Meinel A → X system occurs at ∿5043Å. The radiative lifetime is probably between 1 and 10 μsec for this transition. The similar transition in CN has exhibited laser action with e-beam pumped excitation of HCN. The long radiative lifetime of the a $^4\Sigma^+$ state (∿1 sec) suggests that emission from the system a $^4\Sigma^+ \rightarrow$ X $^2\Sigma^+$ should be experimentally observed far downstream from the visible Meinel transition region.

A limited number of calculations of the B + O_2 hypersurfaces were carried out near equilibrium geometry. These studies indicate stability for the reaction BO(A $^2\Pi$) + O_2 relative to BO (X $^2\Sigma^+$) + O_2, since the former reaction leads to formation of O ^{1}D. This seems to reinforce our optimism for this system since collisional deactivation should be slow compared to collisional reaction of the ground state of the molecule. Further studies are in progress.

NF

The low-lying singlet, triplet and quintet states of NF have been studied in detail. These calculations were performed using a large configuration interaction with an optimized basis set. The results have been analyzed and lifetime calculations are now in progress for b $^1\Sigma^+$, a $^1\Delta$ and several low-lying $^1\Pi$ and $^1\Sigma$ states. The b $^1\Sigma^+$ and a $^1\Delta$ states have very long radiative lifetimes since both states have metastable characteristics. This system is under experimental study at Aerospace (Kwok), where both the 5600Å (b-x) and 11000Å (a-x) transitions are of interest.

Our final potential curves are shown in Figs. 3-8 and the existing experimental curves are given in Fig. 9. A compilation of our spectroscopic constants for NF is given in Table III. This system is very analagous to O_2 and should exhibit all the familar band systems of O_2 such as Schumann-Runge ($B^3\Sigma^- \rightarrow X^3\Sigma^-$) and the various Herzberg systems. As a laser candidate, this system appears less attractive since the b $^1\Sigma^+$ state should be about as reactive as the ground X $^3\Sigma^-$ state. Scaling to higher pressures, which is necessary for obtaining high power output, looks unfavorable for maintaining a significant population in either the metastable b $^1\Sigma^+$ or a $^1\Delta$ states.

SnO

The major problems in SnO lie in defining reliable Franck-Condon factors and Einstein coefficients (or lifetimes) for the low-lying metastable states (a $^3\Pi$, $^3\Pi$, $^3\Sigma^-$), for the unresolved $^3\Pi$ states and in analyzing the branching and total density of low-lying electronic states. A correlation diagram for this molecule is shown in Table IV. Clearly, the large number of low-lying ionic states makes this system look unattractive from a kinetic branching viewpoint. Experimental studies of this system have been carried out by Zare (Columbia U.), Capelle

(Aerospace) and Linevsky (G.E.). Candidate transitions are the A-X system at 6400Å and the a-x system at 3800Å but reliable lifetimes and data on perturbations from other potential curves are not available.

We have analyzed the spin-orbit structure of this molecule and the low-lying connections are shown in Fig. 10. Coupling this information to the available spectroscopic data and a limited number of calculations, we show our best estimate of the potential curves for this system in Fig. 11. Clearly, the a $^3\Sigma^+$ state is not fully resolved and the 0^- component can form from singlet reactants. The possible branching paths are numerous and discouraging from the viewpoint of possible excited state inversions.

SiF

Interest in this system stems from the high exothermicity of the $SiH_4 + F_2$ reaction. SiF is formed in electronically excited states, mainly a $^4\Sigma^-$ and A $^2\Sigma^+$. A molecular correlation diagram for SiF is shown in Table V. Davis at AFWL has carried out lifetime studies for the 4368Å (A-X) transition and has done some preliminary work on the quartet system. A possible laser transition is the 1.46 μ a $^4\Sigma^-$ - A $^2\Sigma^+$ system and a theoretical estimate of the lifetime of the a $^4\Sigma^-$ state is progress.

We find a long-range barrier in the A $^2\Sigma^+$ excited state potential curve as indicated in Fig. 12. This barrier is the result of an avoided crossing between the ionic $^2\Sigma^+$ curve and the valence state arising from ground state atoms. The states of quartet symmetry have no ionic component and no long-range barrier is evident in the a $^4\Sigma^-$ state. This feature suggests that branching into the a $^4\Sigma^-$ state could be favored. A more complete analysis of the long-range surface for $Si + F_2$ is in progress to more fully understand the consequences of this barrier.

AlF

Detailed calculations were carried out for the symmetries $^1\Sigma^+$, $^1\Sigma^-$, $^1\Pi$, $^3\Pi$, $^1\Delta$, $^3\Sigma^+$ and $^3\Sigma^-$. A composite potential energy diagram for AlF is shown in Fig. 13. We have located a $^3\Pi$ state at approximately 5 eV. It appears to be a near-Rydberg state to AlF^+ connecting to $Al\,^2S + F\,^2P$. The $A^1\Pi$ state is predissociated as indicated in Fig. 13. The only possible laser routes for AlF would seem to be an inverse predissociation population of $A^1\Pi$ or metastable build-up in the a $^3\Pi$ state. Neither route appears to be very favorable owing to long-range barriers and weak Rydberg-valence mixing.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals and books or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals

1. "Configuration Interaction Studies of the HeH^+ Molecular Ion. III Singlet Pi and Delta States," T. A. Green, H. H. Michels and J. C. Browne, Journal of Chemical Physics, Vol. 64, 1976, p. 3951.

2. "The Electronic Structure of ArF and Ar_2F," H. H. Michels and R. H. Hobbs, to be published in Chemical Physics Letters, 1977.

3. "The Electronic Structure of Excimer Molecular Lasers," H. H. Michels and R. H. Hobbs, to be published in The International Journal of Quantum Chemistry, 1977.

B. Technical Articles in Books

1. "Electronic Structure and Radiative Lifetimes for BO," H. H. Michels, R. Harris and J. Lillis, Electronic Transition Lasers, edited by Jeffrey I. Steinfeld, MIT Press, p. 278, 1976.

2. "Electronic Structure of Excited States of Selected Atmospheric Systems," H. H. Michels, The Excited State in Chemical Physics, edited by J. Wm. McGowan, 1977.

C. Technical Paper and Lecture Presentations

1. "Electronic Structure and Potential Energy Curves for BeO, MgO, BaO and AlF", H. H. Michels. Invited talk at the 1st Summer Colloquium on Electronic Transition Lasers, University of California, Santa Barbara, California, June 17-19, 1974.

2. "Calculation of Potential Energy Curves for Metal Oxides and Halides." H. H. Michels. Presented at the 14th AFOSR Contractors' Meeting, Boston College, Boston, Massachusetts, August 23-24, 1973.

3. "Potential Energy Curves for the Ground and Excited States of BaO, CuO, SmO and BO." H. H. Michels. Presented at the AFOSR/AFWL Laser Metting in Albuquerque, New Mexico, June 2-4, 1975.

4. "Potential Curves and Scattering Theory Matrix Elements for the Singlet Pi States of HeH^+." H. H. Michels. Presented at the 9th International Conference on the Physics of Electronic and Atomic Collisons in Seattle, Washington, July 24-30, 1977.

5. "Electronic Structure and Potential Energy Curves for BaO, MgO, BeO, BO, and AlF." H. H. Michels. Invited talk at the 2nd Conference on Electronic Transition Lasers in Woods Hole, Mass., September 16-20, 1975.

6. "The Electronic Structure and Radiative Lifetimes of Diatomic Metal Oxides." H. H. Michels. Invited speaker at the International Symposium on Atomic, Molecular and Solid State Theory in Sanibel, Florida, January 18-24, 1976.

7. Participant at the 2nd International Congress of Quantum Chemistry in New Orleans, Louisiana, April 20-22, 1976.

8. "The Electronic Structure of the Rare Gas Halide Lasers." H. H. Michels. Invited speaker at the Interdisciplinary Physical Sciences Seminar at Yale University, New Haven, Connecticut, May 3, 1976.

9. "Calculation of the Energetics and Radiative Properties of Noble Gas Halide Molecules." H. H. Michels. Presented at the Third Summer Colloquium on Electronic Transition Lasers in Aspen, Colorado, September 6-9, 1976.

10. Participant at the Gaseous Electronics Conference in Cleveland, Ohio, October 18-20, 1976.

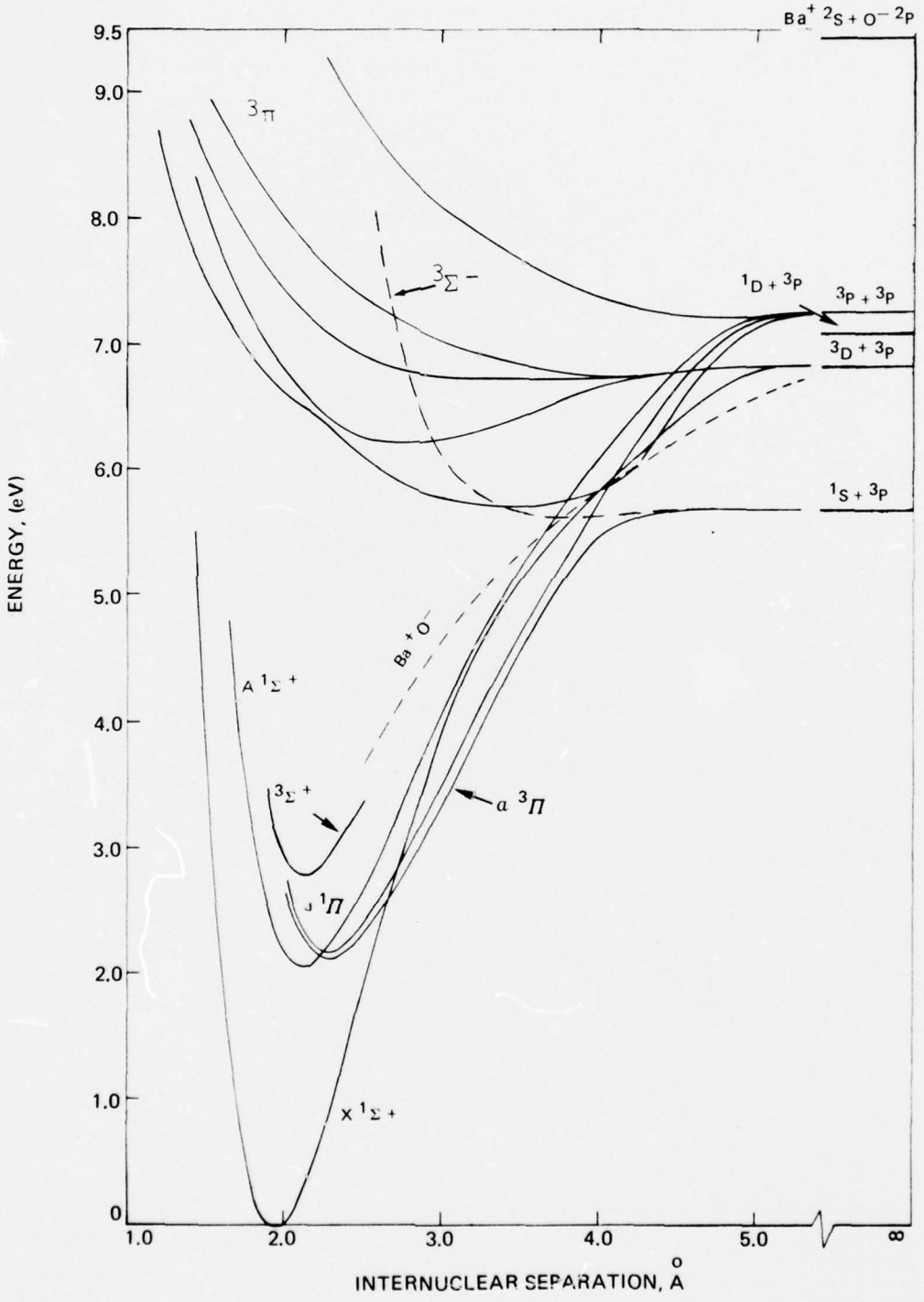
11. "The Electronic Structure of Excimer Molecular Lasers." H. H. Michels. Invited speaker to the Atomic and Molecular Solid State Theory Symposium held at Sanibel Island, Florida, January 17-21, 1977.

12. "The Electronic Structure of ArF and Ar_2F." H. H. Michels. Talk presented at the Seventh Colloquium on Quantum Electronics held in Salt Lake City, Utah, February 16-18, 1977.

13. "Calculations of the Energetics and Radiative Properties of Visible/UV Chemical Laser Systems." H. H. Michels. Presented at the AFOSR/AFWL Laser Meeting in Albuquerque, New Mexico, May 16-18, 1977.

FIG.1

POTENTIAL ENERGY CURVES FOR BaO



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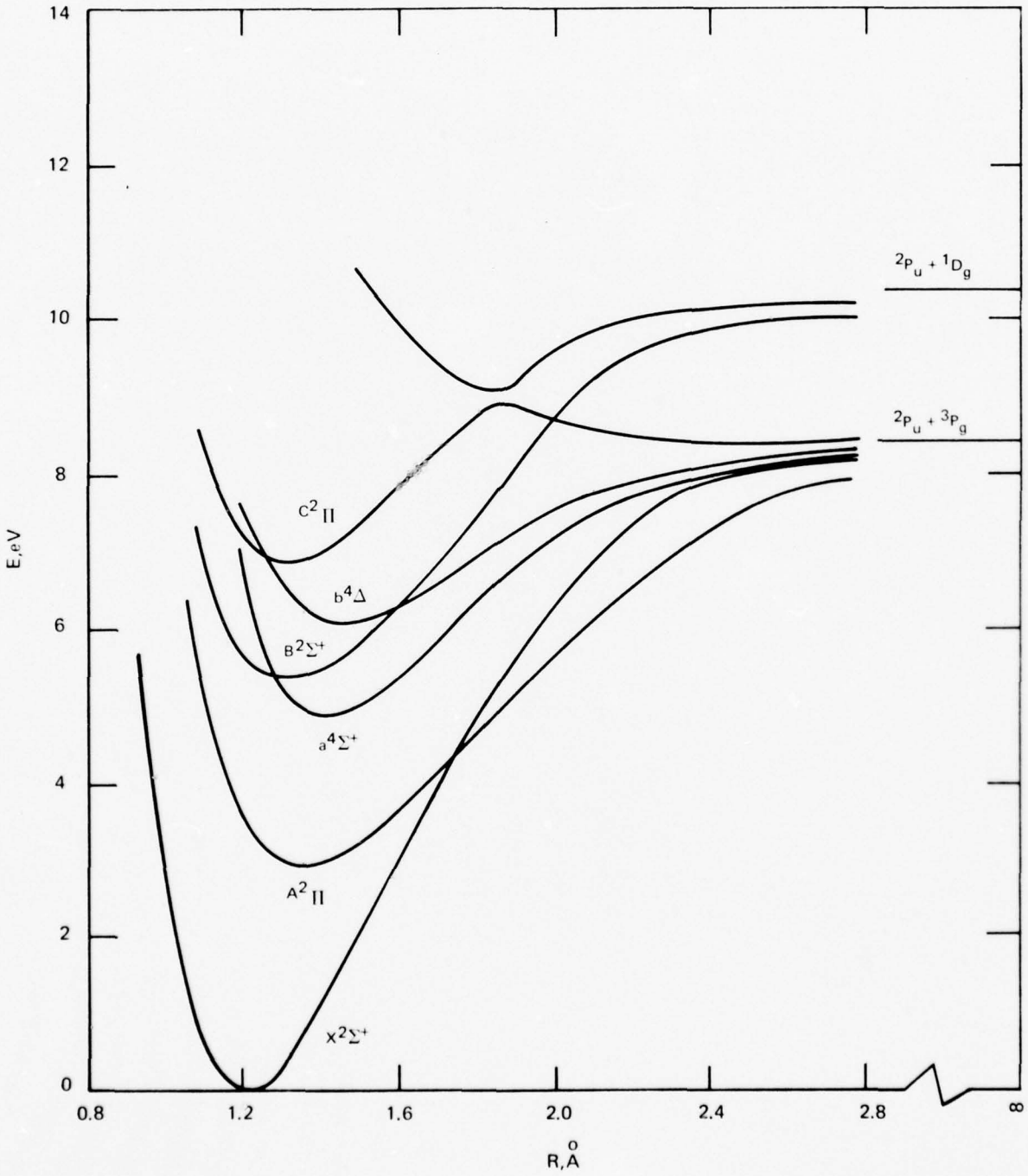
POTENTIAL ENERGY CURVES OF BO



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POTENTIAL ENERGY CURVES FOR THE $^3\Sigma^-$ STATES OF NF

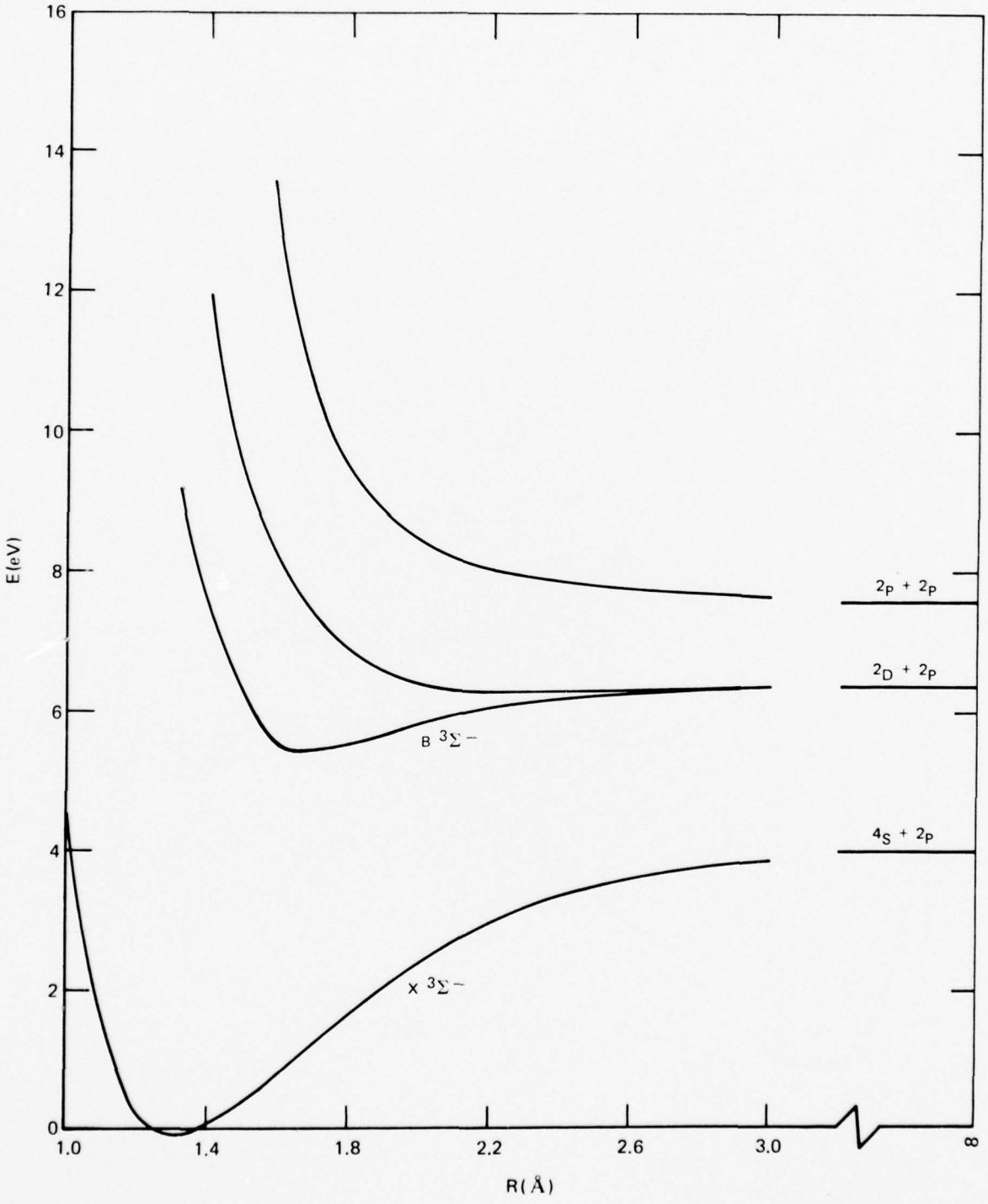

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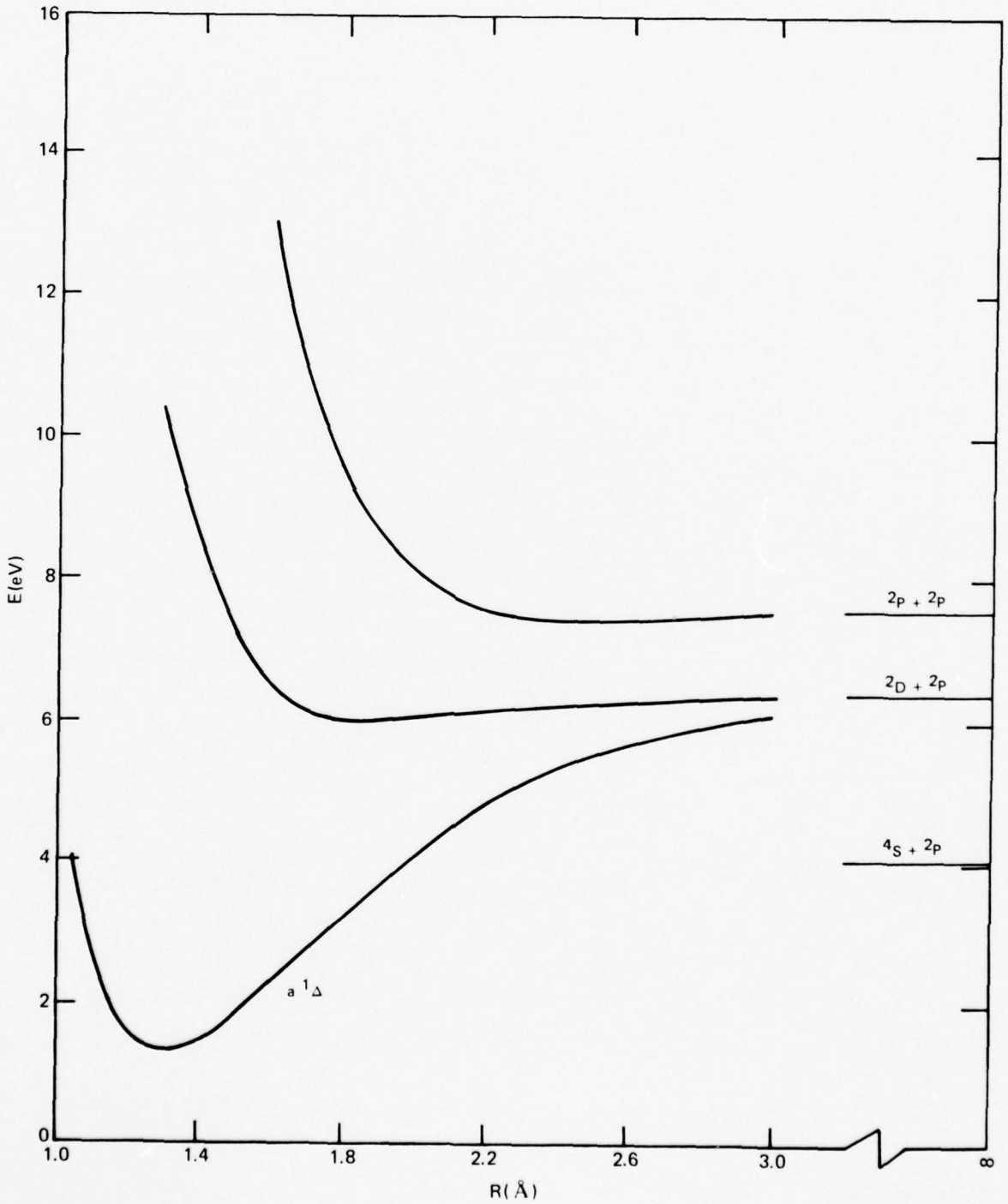
FIG. 4

POTENTIAL ENERGY CURVES FOR THE $^1\Delta$ STATES OF NF



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POTENTIAL ENERGY CURVES FOR THE $^3\Delta$ STATES OF NF

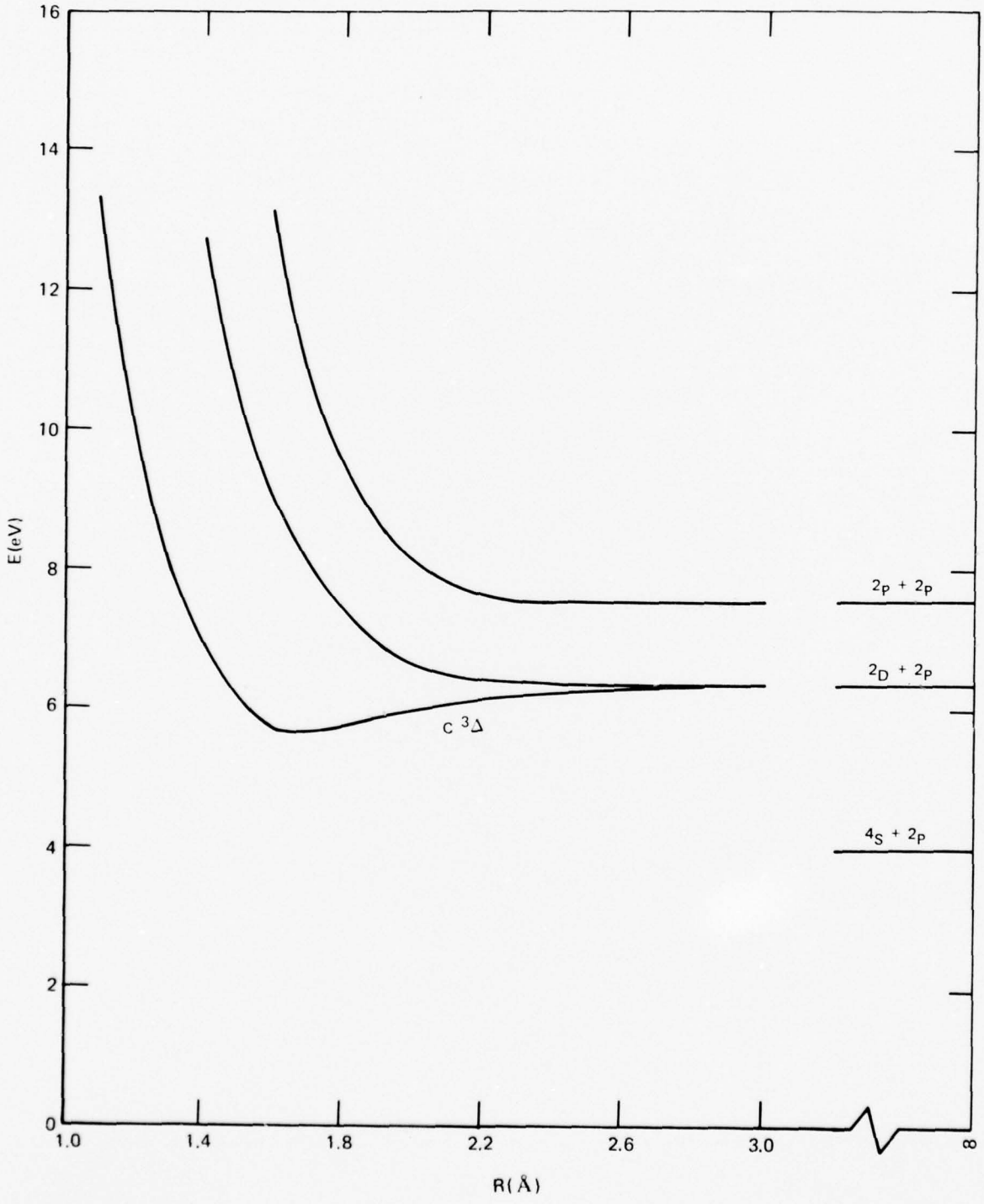

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FIG. 6

POTENTIAL ENERGY CURVES FOR THE $^1\Sigma^+$ STATES OF NF

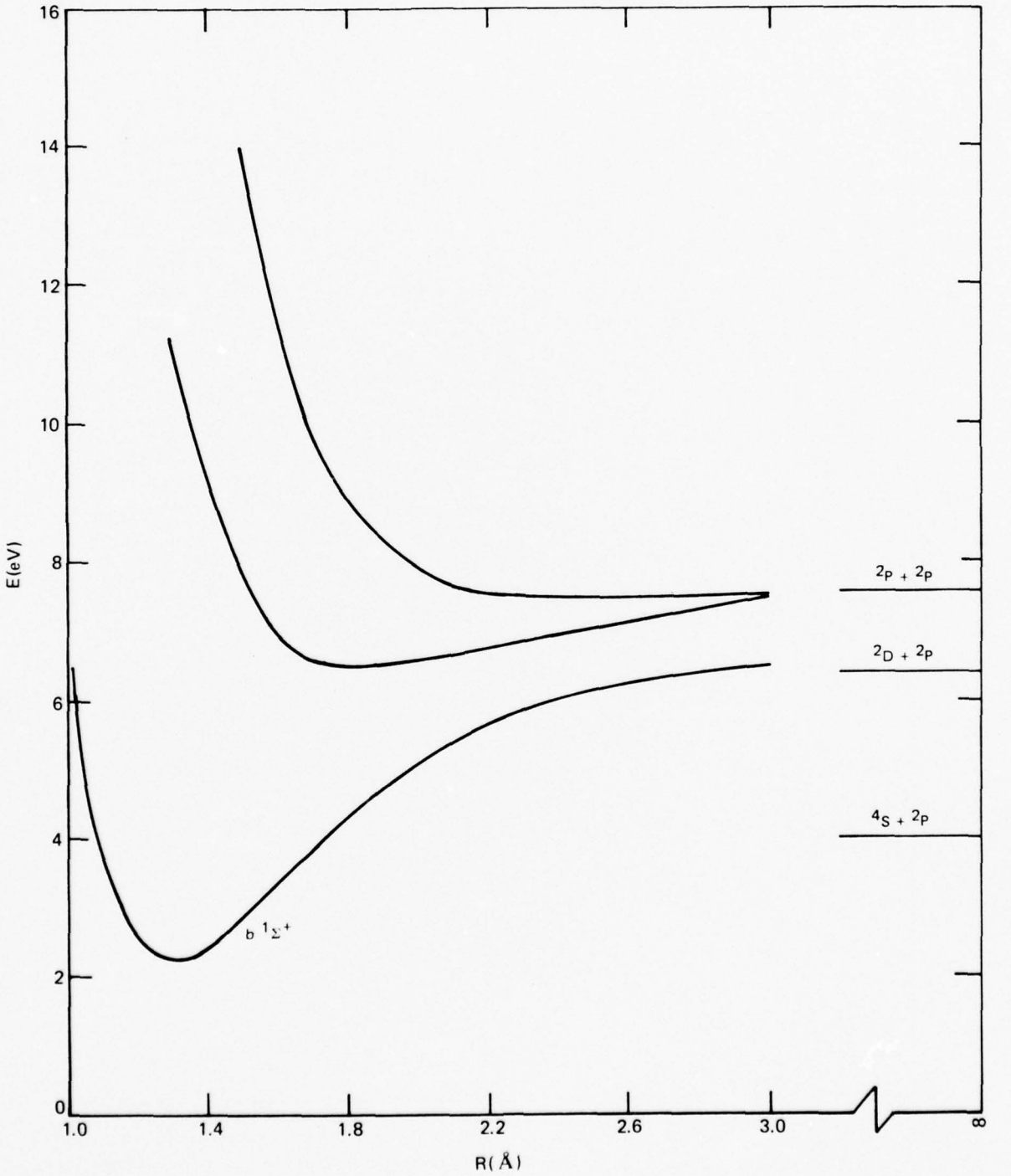

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FIG. 7

POTENTIAL ENERGY CURVES FOR THE $^3\Sigma^+$ STATES OF NF

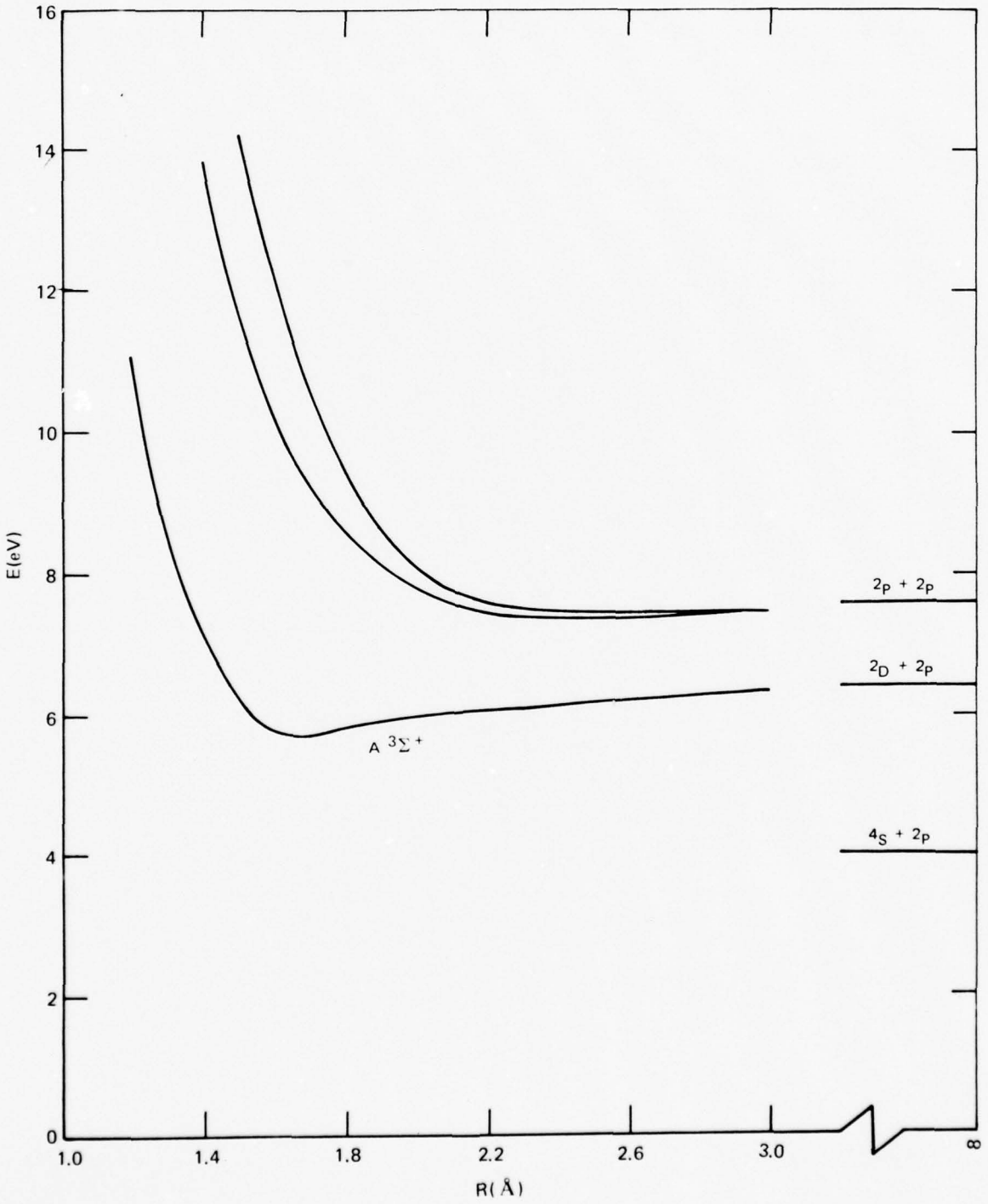

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FIG. 8

POTENTIAL ENERGY CURVES FOR THE $^1\Sigma^-$ STATES OF NF

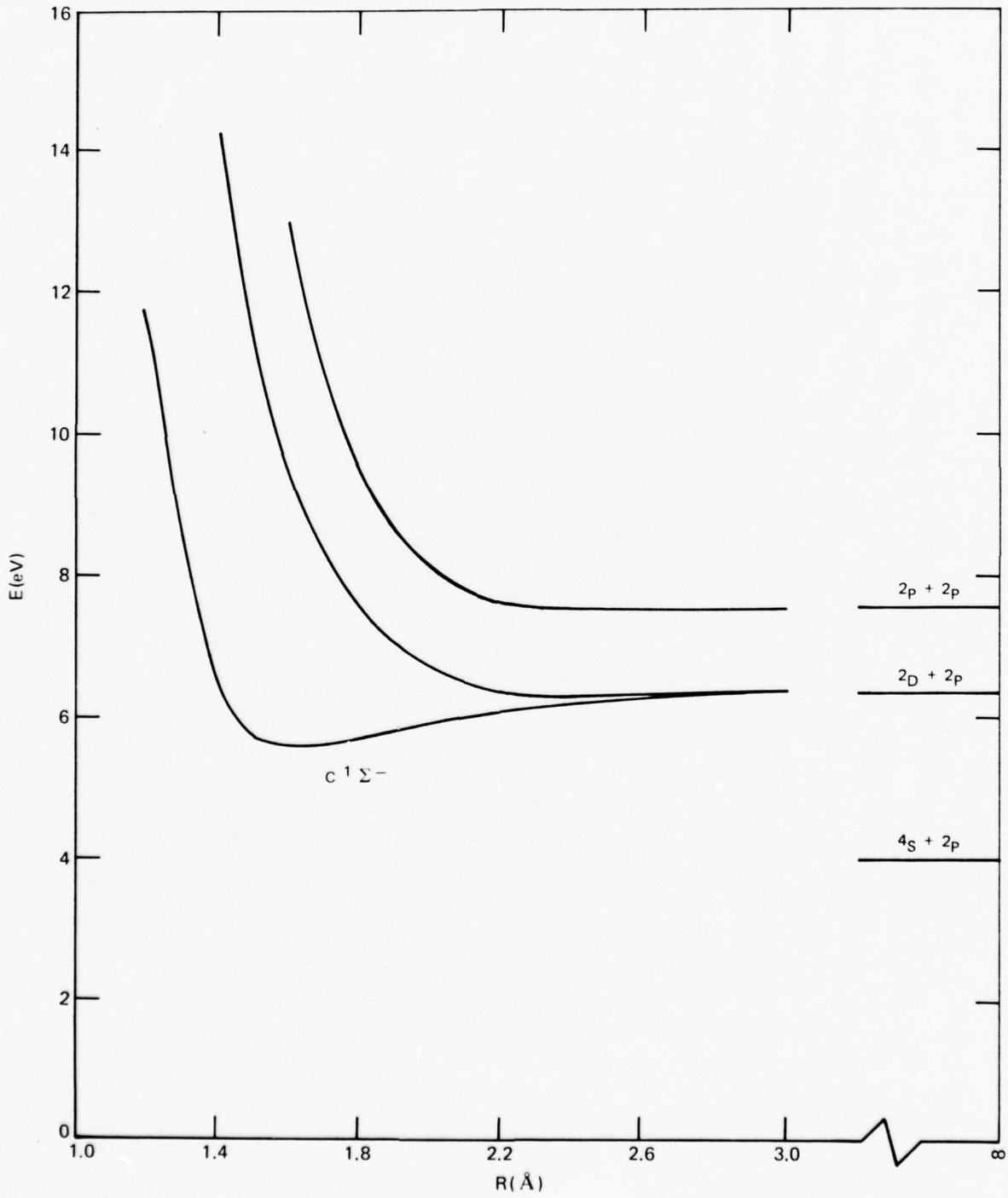
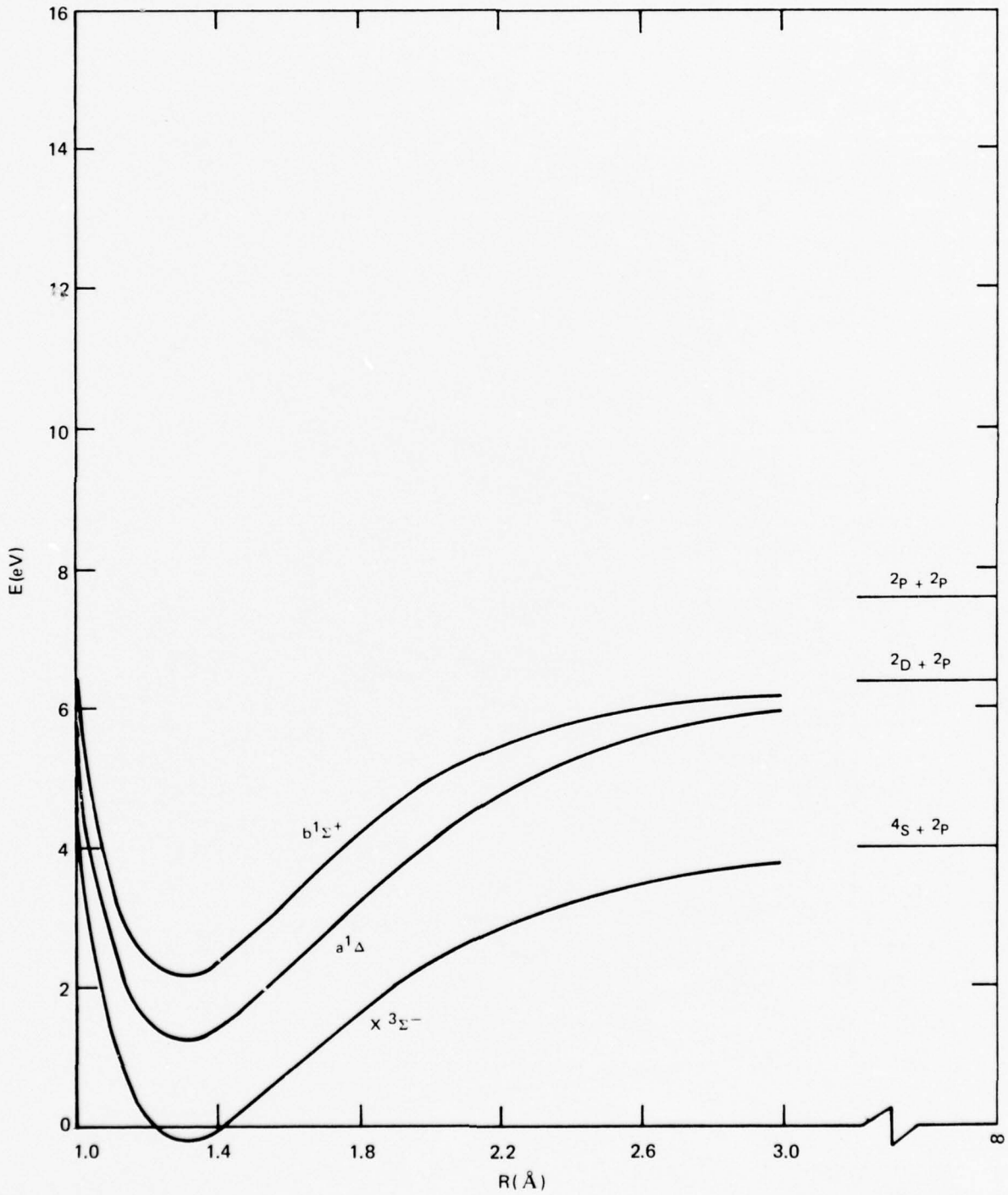


FIG.9

EXPERIMENTAL POTENTIAL ENERGY CURVES FOR NF



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CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE SnO MOLECULE

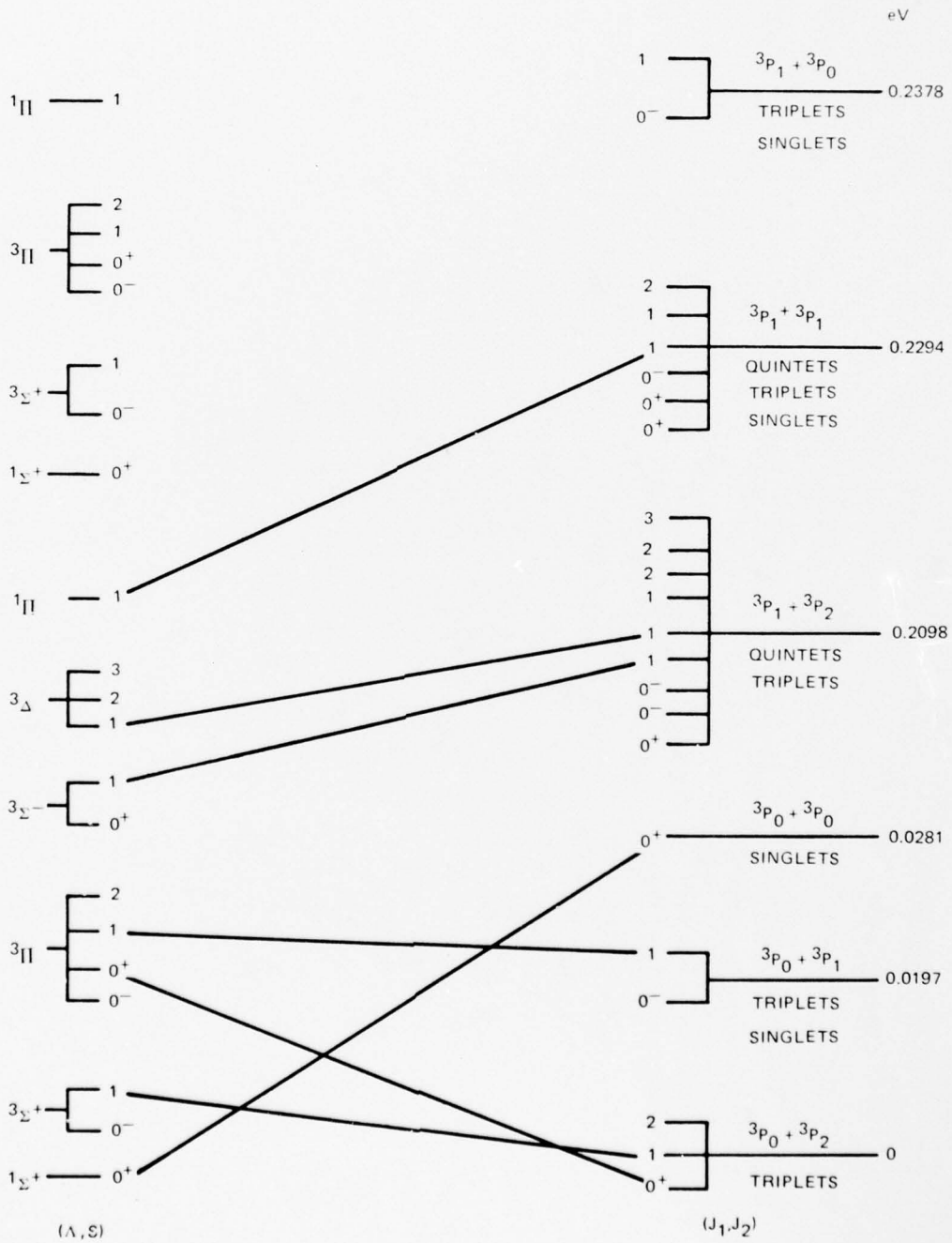

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FIG. 10–1
(CONTINUED)

CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE SnO MOLECULE

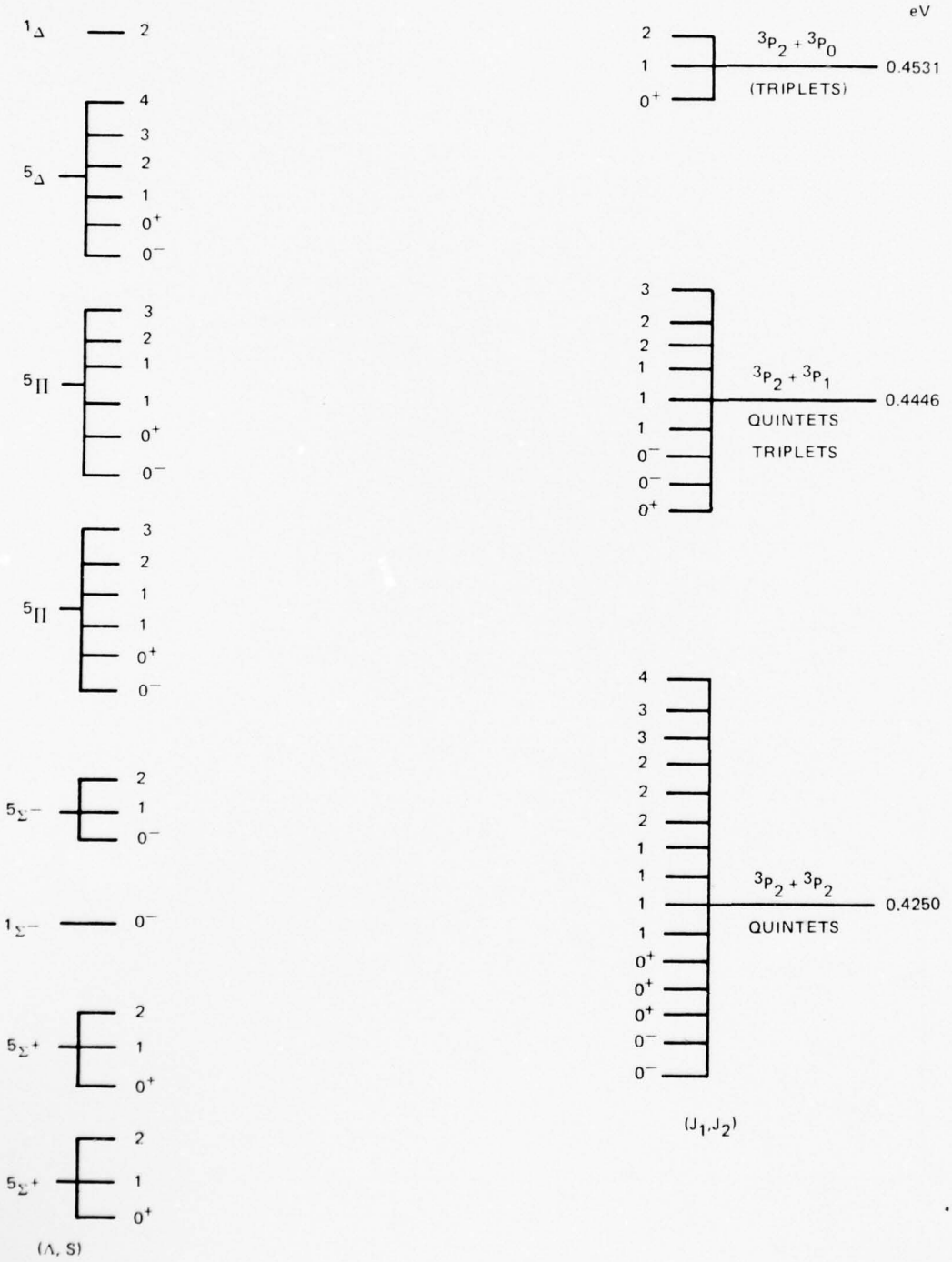
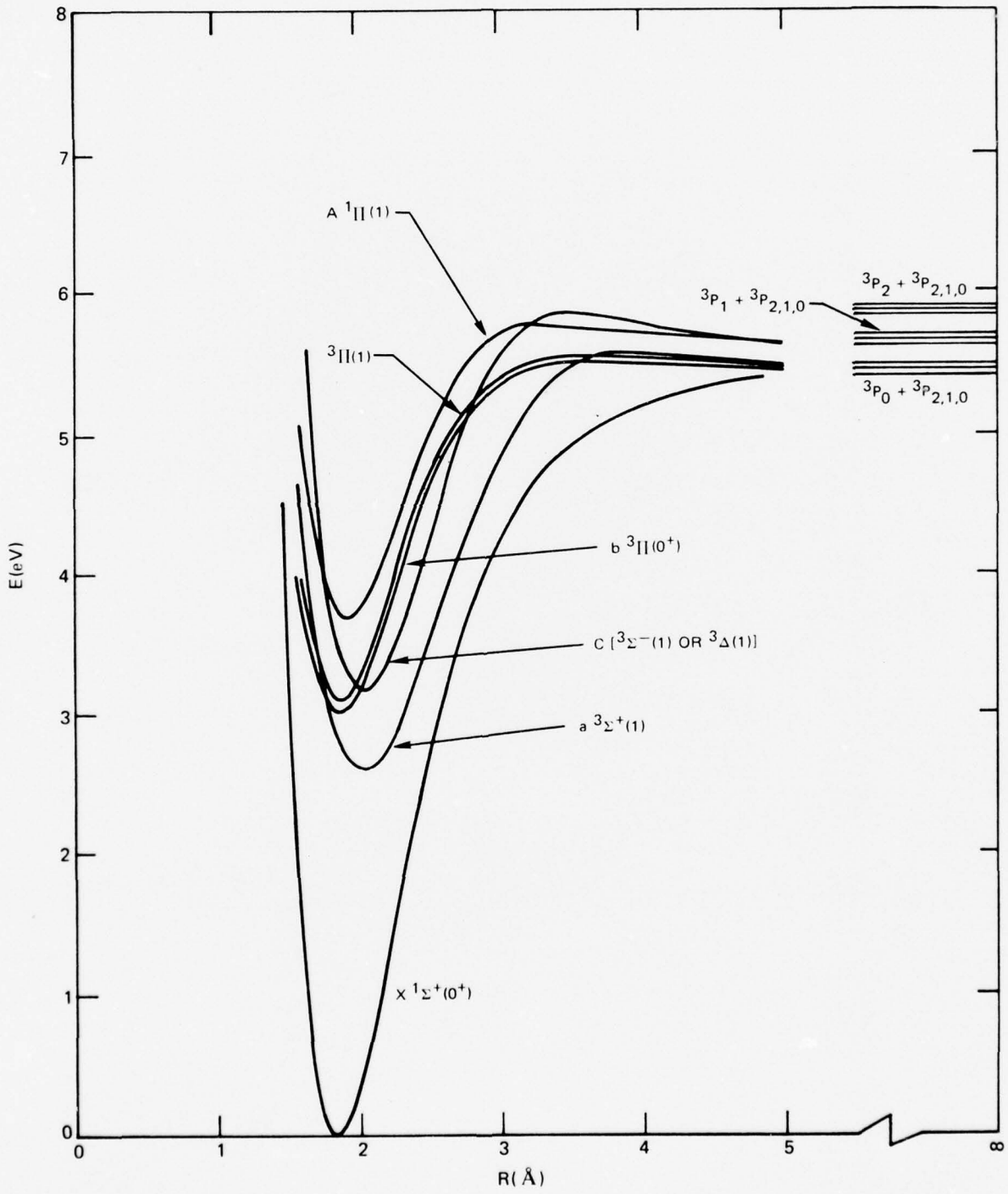


FIG. 11

POTENTIAL ENERGY CURVES FOR SnO



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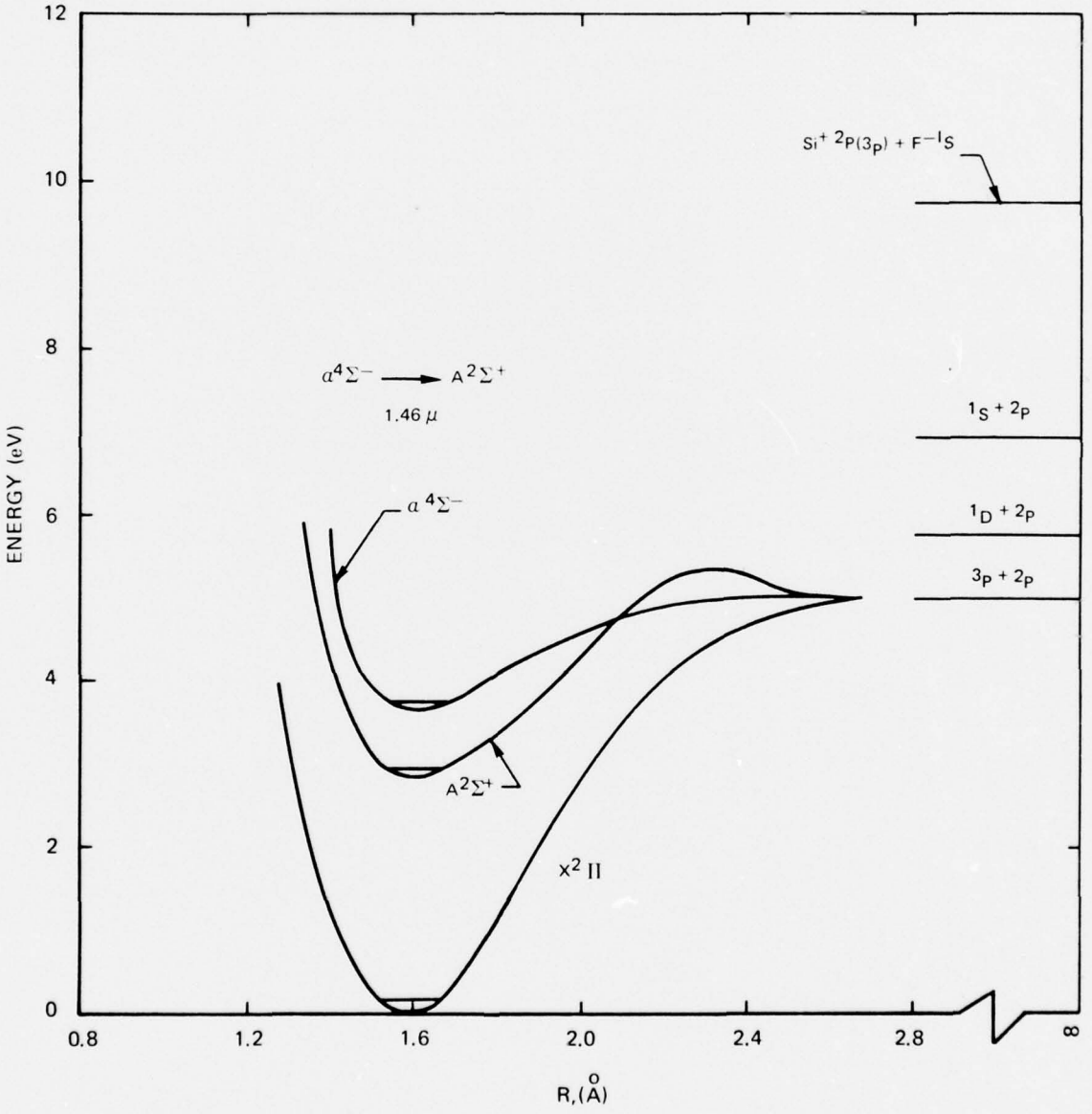
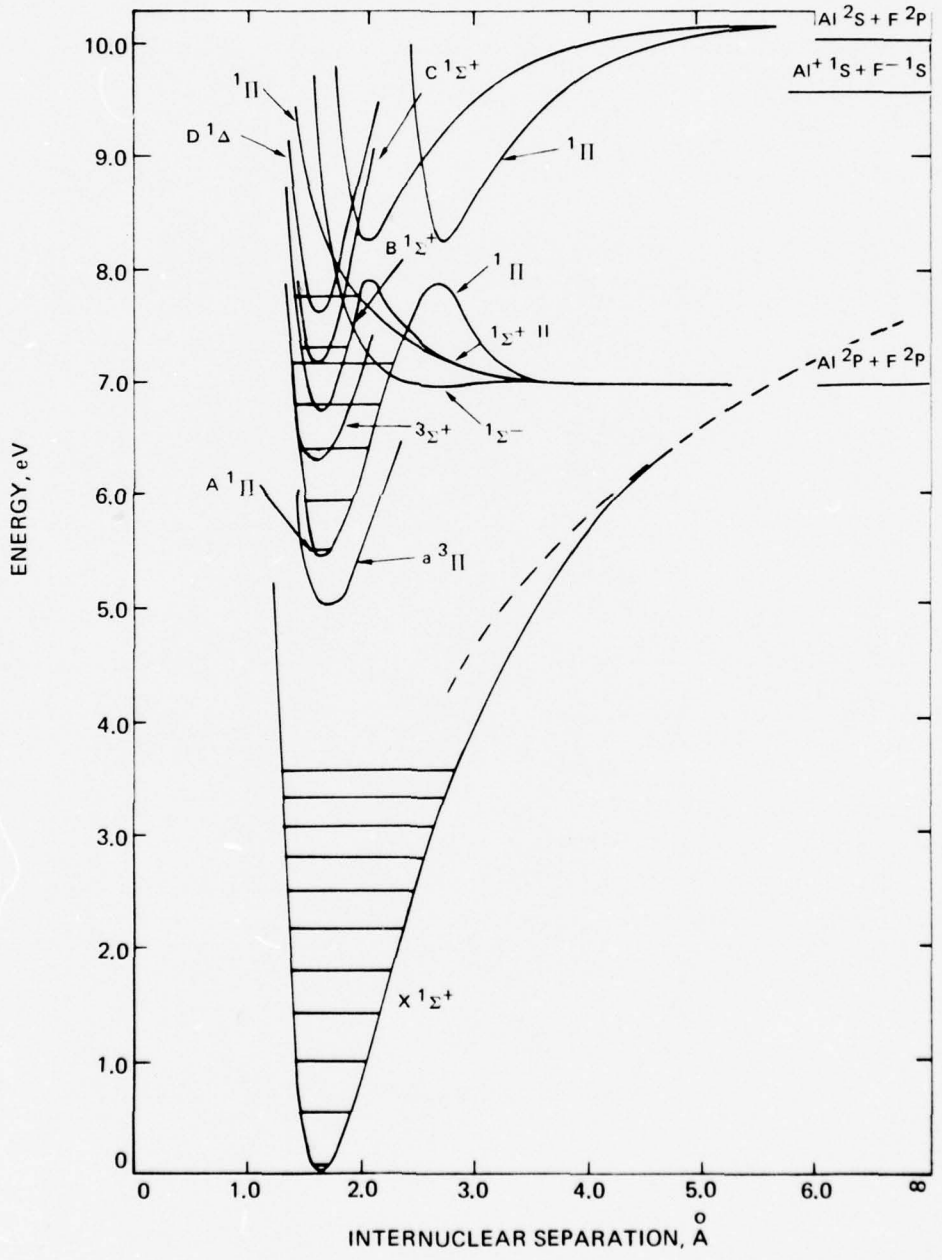
POTENTIAL ENERGY CURVES FOR SiF



77–06–41–2

POTENTIAL ENERGY CURVES OF AlF



77–06–41–1

TABLE I

SPECTROSCOPIC DATA FOR ELECTRONIC STATES OF BO

State	$T_e(cm^{-1})$	$\omega_e(cm^{-1})$	$\omega_e X_e(cm^{-1})$	$B_e(cm^{-1})$	$\alpha_e(cm^{-1})$	$r_e(\mathring{A})$	Dissociation Energy $D_e(eV)$
$C\ ^2\Pi$	55346.1	1315.3	11.1	1.4844	0.0170	1.3196	3.54
$b\ ^4\Delta$	(49200)	(1190)	(40)	(1.24)	(0.047)	(1.45)	(2.3)
$B\ ^2\Sigma^+$	43174.0	1281.69	10.66	1.5171	0.0210	1.3053	5.05
$a\ ^4\Sigma^+$	39957.0	1283.7	11.00	1.2998	0.01426	1.42	3.48
$A\ ^2\Pi_i$	23897.67	1260.70	11.157	1.4132	0.0196	1.3524	5.47
$X\ ^2\Sigma^+$	0.0	1885.69	11.810	1.7820	0.0166	1.2043	8.43

TABLE II

CALCULATED LIFETIMES FOR BO TRANSITIONS

System	Transition	Wavelength	Lifetimes
$B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$	(0,1)	2265 Å	∿ 100 n sec
$A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$	(0,2)	5043 Å	1-5 μsec
	(0,3)	5551 Å	
	(1,1)	4366 Å	
$a\ ^4\Sigma^+ \rightarrow X\ ^2\Sigma^+$	(0,4)	3091 Å	∿ 600 millisec
	(0,5)	3270 Å	
	(0,6)	3468 Å	
$B\ ^2\Sigma^+ \rightarrow A\ ^2\Pi$	(0,0)	5201 Å	2 μsec

TABLE III

SPECTROSCOPIC CONSTANTS FOR NF

State	Te	ωe	ωeXe	Be	αe	re*
A $^3\Sigma^+$	45973.	790.2	52.30	0.7563	0.0256	1.6629
C $^3\Delta$	45570.	1052.4	88.98	0.7595	0.0153	1.6594
c $^1\Sigma^-$	45167.	960.8	65.55	0.7763	0.0092	1.6414
B $^3\Sigma^-$	43554.	895.8	77.21	0.7499	0.0299	1.6700
b $^1\Sigma^+$	18877.	1197.49	8.64	1.2377	0.01448	1.3001
a $^1\Delta$	11421.	1169.43	8.82	1.2293	0.0147	1.3082
X $^3\Sigma^-$	0.	1141.37	8.99	1.2056	0.01492	1.3173

* r_e is given in $\mathring{A}$, all other constants are cm^{-1}

TABLE IV

LOW-LYING MOLECULAR STATES OF SnO AND THEIR DISSOCIATION LIMITS

Dissociation Limit	eV	Molecular States
Sn + O		
$^3P_g\ (5s^2 5p^2) + {}^3P_g\ (2s^2 2p^4)$	0.0	$^1\Sigma^+(2)$, $^3\Sigma^+(2)$, $^5\Sigma^+(2)$, $^1\Sigma^-(1)$, $^3\Sigma^-(1)$, $^5\Sigma^-(1)$, $^1\pi\ (2)$, $^3\pi\ (2)$, $^5\pi\ (2)$, $^1\Delta\ (1)$, $^3\Delta\ (1)$, $^5\Delta\ (1)$
$^1D_g\ (5s^2 5p^2) + {}^3P_g\ (2s^2 2p^4)$	1.068	$^3\Sigma^+(1)$, $^3\Sigma^-(2)$, $^3\pi\ (3)$, $^3\Delta\ (2)$, $^3\Phi\ (1)$
$^3P_g\ (5s^2 5p^2) + {}^1D_g\ (2s^2 2p^4)$	1.967	$^3\Sigma^+(1)$, $^3\Sigma^-(2)$, $^3\pi\ (3)$, $^3\Delta\ (2)$, $^3\Phi\ (1)$
$^1S_g\ (5s^2 5p^2) + {}^3P_g\ (2s^2 2p^4)$	2.127	$^3\Sigma^-(1)$, $^3\pi\ (1)$
$^1D_g\ (5s^2 5p^2) + {}^1D_g\ (2s^2 2p^4)$	3.035	$^1\Sigma^+(3)$, $^1\Sigma^-(2)$, $^1\pi\ (4)$, $^1\Delta\ (3)$, $^1\Phi\ (2)$, $^1\Gamma\ (1)$
$^1S_g\ (5s^2 5p^2) + {}^1D_g\ (2s^2 2p^4)$	4.094	$^1\Sigma^+(1)$, $^1\pi\ (1)$, $^1\Delta\ (1)$
$^3P_g\ (5s^2 5p^2) + {}^1S_g\ (2s^2 2p^4)$	4.189	$^3\Sigma^-(1)$, $^3\pi\ (1)$
$Sn^+ + O^-$		
$^2P_u(5s^2 5p) + {}^2P_u\ (2p^5)$	5.876	$^1\Sigma^+(2)$, $^3\Sigma^+(2)$, $^1\Sigma^-(1)$, $^3\Sigma^-(1)$, $^1\Pi(2)$, $^3\Pi(2)$, $^1\Delta(1)$, $^3\Delta(1)$

TABLE V

LOW-LYING MOLECULAR STATES OF SiF AND THEIR DISSOCIATION LIMITS

Dissociation Limit	eV	Molecular States
Si + F		
$^3P_g(3s^2 3p^2) + {}^2P_u(2p^5)$	0.0	$^2\Sigma^-(2)$, $^4\Sigma^-(2)$, $^2\Sigma^+(2)$, $^4\Sigma^+(1)$, $^2\Pi(2)$, $^4\Pi(2)$, $^2\Delta(1)$, $^4\Delta(1)$
$^1D_g(3s^2 3p^2) + {}^2P_u(2p^5)$	0.781	$^2\Sigma^-(1)$, $^2\Sigma^+(2)$, $^2\Pi(3)$, $^2\Delta(2)$, $^2\Phi(1)$
$^1S_g(3s^2 3p^2) + {}^2P_u(2p^5)$	1.908	$^2\Sigma^+(1)$, $^2\Pi(1)$
$^5S_u(3s3p^3) + {}^2P_u(2p^5)$	4.131	$^4\Sigma^-(1)$, $^6\Sigma^-(1)$, $^4\Pi(1)$, $^6\Pi(1)$
$Si^+ + F^-$		
$^2P_u(3s^2 3p) + {}^1S_g(2p^6)$	4.701	$^2\Sigma^+(1)$, $^2\Pi(1)$

REFERENCES

1. Lagerqvist, A., E. Lind and R. F. Barrow: The Band-Spectrum of Barium Oxide, Proc. Phys. Soc. of London, Vol. A63, p. 1132, 1950.

2. Suchard, S. N.: Spectroscopic Constants for Selected Heteronuclear Diatomic Molecules. AF Report No. SAMSO-TR-74-82, Space and Missile Systems Corporation. Los Angeles, California. 1974.

3. Mal'tsev, A. A. and D. I. Kataev: Vestnik Moskov. Univ., Ser. II: Khim., 1967, Vol. 22, (I), p. 92.

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APPENDIX A

CONFIGURATION INTERACTION STUDIES OF THE HeH^+ MOLECULAR ION. III. SINGLET PI AND DELTA STATES*

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ABSTRACT

The method of superposition of configurationsis applied to the singlet pi and delta states of HeH^+ which correlate to the separated atom states of principal quantum number less than or equal to 3. The calculations are carried out for internuclear separations R in the range 0(0.1)34.5, 35.0(0.5)50.0 a.u. The delta state calculations are also extended to R=65. The work is a continuation of a study of HeH^+ for which the singlet sigma states have already been reported. In addition to the energy eigenvalues, matrix elements for radial and angular coupling and the dipole and gradient matrix elements are calculated for all combinations of the singlet sigma, pi, and delta states. Plots and tables of the calculated eigenvalues and matrix elements are presented. Where possible the calculated data are compared with the results of previous work. The results of this work are useful for theoretical collision studies of H^++He and H+He^+.

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APPENDIX B

THE ELECTRONIC STRUCTURE OF ArF AND Ar_2F^*

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Calculations have been performed on the electronic structure, potential energy curves and radiative transition probabilities of ArF and Ar_2F. Our predicted emission spectra for ArF indicates that only the $B\ ^2\Sigma^+_{\frac{1}{2}} \rightarrow X\ ^2\Sigma^+_{\frac{1}{2}}$ transition exhibits a large transition moment and hence a short ($\sim$ 5 nsec) radiative lifetime. Calculations for Ar_2F indicate that the bound upper ionic state has $^2B_2$ symmetry with Ar-Ar and Ar-F bond lengths similar to those in the corresponding diatomic species. The terminating state also has $^2B_2$ symmetry and this polyatomic system should exhibit a relatively long radiative lifetime ($\sim$ 200 nsec).

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APPENDIX C

THE ELECTRONIC STRUCTURE OF EXCIMER MOLECULAR LASERS*

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ABSTRACT

The electronic structure, potential energy curves and radiative transition probabilities of excimer systems have been examined using quantum mechanical methods. These molecules are characterized by repulsive or weakly bound ground state potential curves and by bound, strongly ionic, or Rydberg, excited states. They constitute a very interesting class of molecules which offer the possibility for high power, high efficiency UV laser operation. Calculations have been carried out using the density functional SCF-X_α method, modified extensively to correct for well-known errors arising from approximations to the potential and exchange terms. A limited number of ab initio calculations were also carried out for comparison purposes. For the ArF system we find that the lowest excited ionic state has symmetry $^2\Sigma^+_{1/2}$, and that the dominant laser transition observed at 1933 Å should be assigned to $B\ ^2\Sigma^+_{1/2} \rightarrow X\ ^2\Sigma^+_{1/2}$. The $C\ ^2\Pi_{3/2} \rightarrow X\ ^2\Sigma^+_{1/2}$ transition is calculated to be two-orders of magnitude smaller in emission intensity than the dominant transition, thus ruling out this assignment for

the observed laser line in ArF. Preliminary calculations carried out for Ar_2F indicate that the bound upper ionic state has $^2B_2$ symmetry and that the most probable ground state also has $^2B_2$ symmetry. This polyatomic system is predicted to exhibit a broadband emission spectra with a relatively long radiative lifetime.

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APPENDIX D

ELECTRONIC STRUCTURE AND RADIATIVE LIFETIMES FOR BO*

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ABSTRACT

Quantum mechanical studies are in progress at UTRC and AFWL to determine the electronic structure and radiative properties of boron oxide. This system has very high potential for lasing on an electronic transition.

Detailed quantum calculations were carried out for all of the low lying electronic states connecting to $B(^2P) + O(^3P)$ and $B(^2P) + O(^1D)$. These studies included examination of states of symmetry $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^+$, $^4\Sigma^-$, $^2\Pi$, $^4\Pi$, $^2\Delta$ and $^4\Delta$. Accurate configuration-interaction wavefunctions were constructed for these states and a comparison of our calculated potential curves with experimental RKR curves has been carried out. A systematic calibration of the calculated curves has been performed to empirically correct for core polarization effects which were not included in the wavefunction expansion. This empirical calibration is significant at very short internuclear separations and approaches zero at large separations, since our wavefunctions separate to the correct atomic limits. Our final adjusted potential curves are shown in Fig. D-1.

This system is interesting owing to the low lying a $^4\Sigma^+$ state which is metastable with respect to electronic transitions. This state is bound by at least 2 eV, unlike its analog in AlO where the $^4\Sigma^+$ state is very weakly (<0.2 eV) bound.

An analysis of the radiative lifetimes of the low lying states of BO has been carried out. The allowed transitions $B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $B^2\Sigma^+ \rightarrow A^2\Pi$ and $A^2\Pi \rightarrow X^2\Sigma^+$

have been examined in detail and estimates of the lifetime of the quartet system have been made. The $a^4\Sigma^+ \rightarrow A^2\Pi$ electronic transition at about 5000 Å looks very promising for pulsed laser operation in this system.

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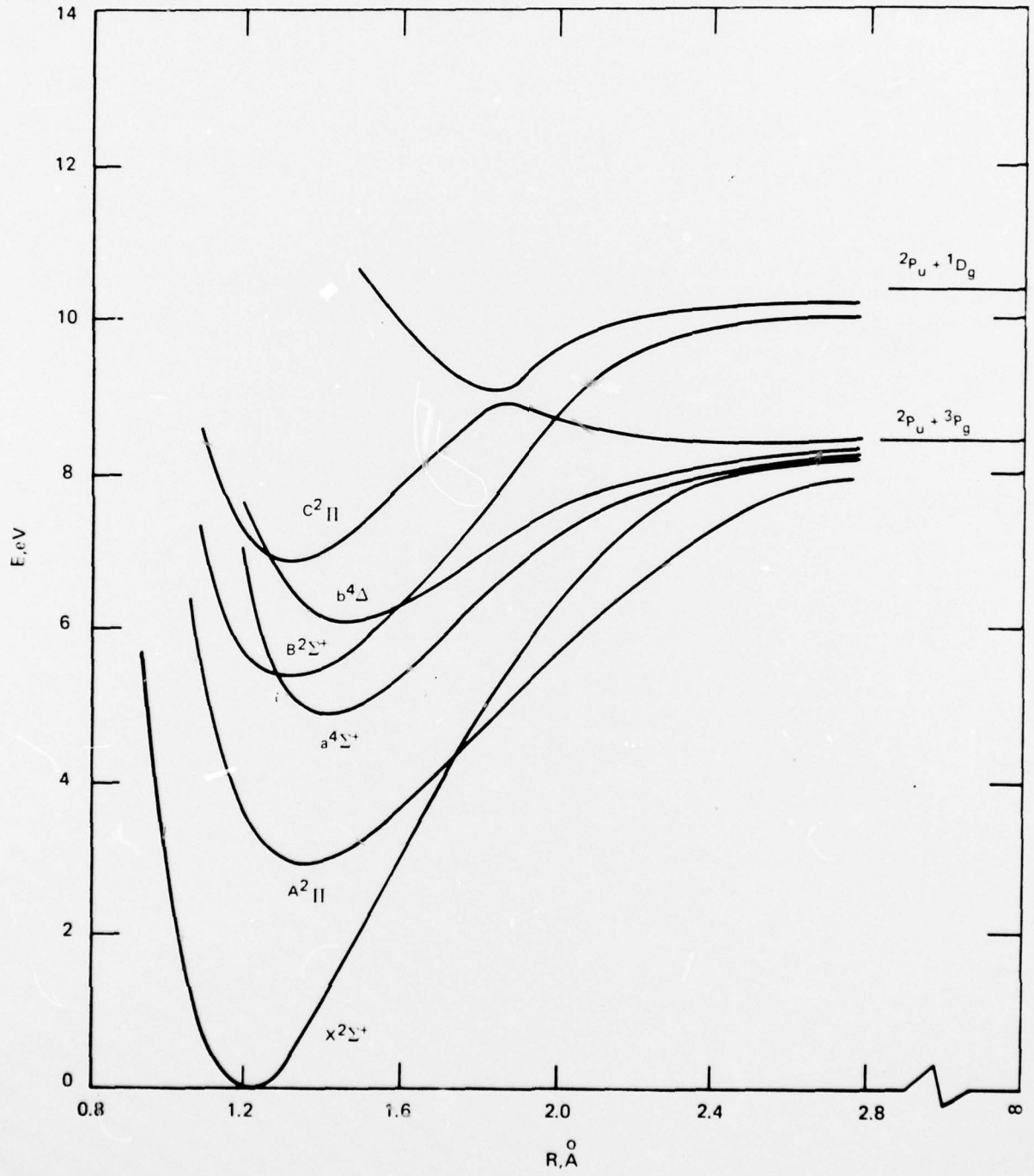
FIG. D-1

POTENTIAL ENERGY CURVES OF BO



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APPENDIX E

ELECTRONIC STRUCTURE OF EXCITED STATES OF SELECTED ATMOSPHERIC SYSTEMS*

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I. INTRODUCTION

In order to evaluate the thermodynamic and radiation properties of a natural or perturbed state of the upper atmosphere or ionosphere, the thermal and transport properties of heated air are required. Such properties are also of particular interest in plasma physics, in gas laser systems, and in basic studies of airglow and the aurora. In the latter area, the release of certain chemical species into the upper atmosphere results in luminous clouds that display the resonance electronic-vibrational-rotation spectrum of the released species. Such spectra are seen in rocket releases of chemicals for upper atmospheric studies and upon reentry into the atmosphere of artifical satellites. Of particular interest in this connection is the observed spectra of certain metallic oxides and air diatomic species. From band intensity distribution of the spectra, and knowledge of the f-values for electronic and vibrational transitions, the local conditions of the atmosphere can be determined (Ref. 1).

Present theoretical efforts which are directed toward a more complete and realistic analysis of the transport equations governing atmospheric relaxation and the propagation of artifical disturbances require detailed information of thermal opacities and LWIR absorption in regions of temperature and pressure where molecular effects are important (Refs. 2, 3). Although various experimental techniques have been employed for both atomic and molecular systems, theoretical studies have been largely confined to an analysis of the properties (bound-bound, bound-free and free-free) of atomic systems (Refs. 4,5) This has been due in large part to the unavailability of reliable wavefunctions for diatomic molecular systems, and particularly for excited states or states of open-shell structures. More recently, (Refs. 6-9) reliable theoretical procedures have been prescribed for such systems which have resulted in the development of practical computational programs.

The theoretical analysis of atmospheric reactions requires the knowledge of the electronic structure of the ground and low-lying excited states of atoms, ions and small molecular clusters of nitrogen and oxygen and, in certain regions, the interaction of water or other small molecules with these clusters.

Because of the computational complexity for systems with large numbers of electrons, traditional ab initio theoretical methods are difficult and expensive to apply. However, no clear alternative choice is currently on the horizon, although progress continues in semiempirical and perturbative approaches to the calculation of electronic structure. Such approaches have met with limited success in applications to electronically excited states of molecules. Ab-initio computational programs based on the variational theorem, incorporating analytic basis functions and coupled with a configuration interaction analysis, remain the backbone of our techniques, for studies to chemical accuracy, which are applicable to systems such as the atmospheric diatomic molecules and ions.

The potential curves derived from such calculations can often be empirically improved by comparison with so-called experimental curves derived from observed spectroscopic data, using RKR or other inversion procedures. It is often found, particularly for the atmospheric systems, that the remaining correlation errors in a configuration interaction (CI) calculation are similar for many excited electronic states of the same symmetry or principal molecular orbital description. Thus, it is often possible to calibrate an entire family of calculated excited state potential curves to near-spectroscopic accuracy. Such a procedure has been applied to the systems described here.

The particular choice of the atmospheric systems to be presented here proved to be somewhat of a problem. Calculations for the N_2 molecule, including all low-lying valence and Rydberg states, had been performed several years ago (Ref. 10) as had a fairly extensive set of calculations for O_2^-(Ref.11). Gilmore has described the known spectroscopic states for N_2, O_2, NO and several states of their corresponding positive and negative ions (Ref. 12). A complete analysis of all of the valence and low-lying Rydberg states for N_2, O_2 and NO including ions, seemed too formidable (and expensive) a task, so the systems N_2, O_2, NO, O_2^- and NO^+ have been selected for inclusion in this review. This choice includes the most important atmospheric positive ion, NO^+, and the chemically most interesting negative ion, O_2^-.

The general composition of this article is as follows. We first present a critical review of the current status of electronic structure calculations for molecular systems. This is followed by a compilation of the potential energy curves, derived spectroscopic analysis and pertinent discussion of the atmospheric molecules selected above.

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REFERENCES

1. O. Harang, "AlO Resonant Spectrum for Upper Atmosphere Temperature Determination." AFCRL-66-314, Environmental Research Paper No. 192, (1966).

2. D. R. Churchill and R. E. Meyerott, J. Quant. Spectr. Radiative Transfer, 5, 69,(1965).

3. The Airglow and the Aurorae, edited by E. B. Armstrong and A. Dalgarno, Pergamon Press, New York, 1955.

4. B. H. Armstrong, R. R. Johnston and P. S. Kelly, J. Quant. Spectr. Radiative Transfer, 5, 55,(1965).

5. R. R. Johnston, B. H. Armstrong and O. R. Platas, J. Quant. Spectr. Radiative Transfer, 5, 49,(1965).

6. F. E. Harris and H. H. Michels, Int. J. Quantum Chem., IS, 329,(1967).

7. M. Krauss, "Compendium of ab initio Calculations of Molecular Energies and Properties." NBS Technical Note 438, (1967).

8. A. C. Wahl, P. J. Bertoncini, G. Das and T. L. Gilbert, Int. J. Quantum Chem., IS, 123, (1967).

9. H. F. Schaefer, Electronic Structure of Atoms and Molecules, Addison-Wesley Publishing Co., (1972).

10. H. H. Michels, J. Chem. Phys., 53, 841, (1970).

11. H. H. Michels, Electronic and Atomic Collisions, Volume 2, edited by L. M. Branscomb, North Holland Publishing Co., Amsterdam, 1170, (1971).

12. F. R. Gilmore, J. Quant. Spectr. Radiative Transfer, 5, 369, (1965).

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18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

BaO	SiF	metal oxides
BO	AlF	metal halides
NF	electronic structure	visible/UV electronic transition lasers
SnO	radiative lifetimes	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research performed under this contract was directed toward the calculation of the electronic structure and radiative transition probabilities for certain diatomic metal oxides and halides which are candidate visible/UV laser systems. The objectives were to uncover systems having a low-lying excited state with a reasonably long (>10 μsec) radiative lifetime and situated energetically such that an inversion of population with respect to

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the dominant transitions to the ground state was possible. The systems under investigation to date include the group IIA metal oxides (BeO-BaO), the group IVA metal oxides (CO-PbO), NF, SiF, AlF and the thirteen electron sequence: N_2^+, CN, CO and BeF. These latter systems have a common chemistry of their electronically excited states, including a common $A^2\Pi \rightarrow X^2\Sigma^+$ Meinel transition, a $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ first negative transition and a possible metastable a $^4\Sigma^+ \rightarrow X^2\Sigma^+$ transition. Among these molecules the systems BaO, BO, NF, SnO, SiF and AlF were chosen for detailed study. Their value as candidate visible/UV laser systems has been analyzed.

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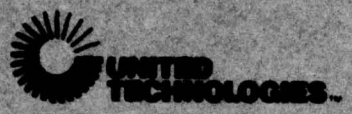

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