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CALCULATION OF ENERGETICS OF
SELECTED ATMOSPHERIC SYSTEMS

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Research was directed toward the calculation of the electronic structure and radiative transition probabilities for NO, $NO_2$, and TiO. Both ab initio methods, employing configuration interaction (CI), and density functional methods $(X_\alpha)$ were utilized.

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TiO
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configuration interaction method
density functional method
dipole moment function
integrated band absorption coefficient
f-number
oscillator strength
Einstein coefficient

Calculation of Energetics of
Selected Atmospheric Systems

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# SECTION I

## INTRODUCTION

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 and missiles. Of particular interest in this connection is the observed spectra of certain metallic oxides and air diatomic and triatomic 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 artificial disturbances require detailed information of thermal opacities and LWIR absorption in regions of temperature and pressure where molecular effects are important (Refs. 2 and 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 and 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 atoms, ions and small molecular clusters of nitrogen and oxygen and the interaction of water or other small molecules with these clusters. Knowledge of the chemistry of metal oxide species, which might be present in a contaminated atmosphere, is also desired. Because of the computational complexity for systems with large numbers of electrons, traditional ab initio theoretical methods are difficult and expensive to apply. However, ab initio computational programs based on Slater-type orbitals and incorporating both SCF and configuration interaction analysis have been developed and are available for studies to chemical accuracy for systems such as $O_2$, $N_2$, NO and their corresponding molecular ions. Semiempirical methods, such as extended Hückel or CNDO theories may be applied to systems containing many more electrons or nuclear centers but they are dependent on the parameterization of many-center integrals, which is difficult and often ambiguous for

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systems containing many different atoms. However, there is a local potential model for the electronic structure of atoms, molecules, clusters and solids, (Ref. 10), which is relatively simple to apply to systems containing heavy atoms and large numbers of electrons. This is a density functional method which has been used for many years in solid state theory for the calculation of the energy band structure of solids (Ref. 11), and has been shown to give accurate results for heavy atom solid-state systems, both for the one-electron spectrum (Ref. 12) and the cohesive energy (Ref. 13). In the case of an infinite perfect crystal, the density functional method is usually used in conjunction with the augmented plane wave (APW) or the Korringa-Kohn-Rostoker (KKR) methods of solution to the one-electron Schrödinger equations. Until recently, it has not been practical to apply this model to finite systems other than atoms (Ref. 14). However, in the last several years, the development of "multiple-scattering" techniques (Refs. 15 and 16) for the solution of the equations in a multicenter finite system has allowed the density functional model to be applied to a large number of molecules (Refs. 17 through 20) and clusters of atoms simulating localized excitations in solids (Refs. 21 and 22) which cannot be described by an energy band model. In its usual form, certain assumptions are made concerning the modecular potential in order to make the method computationally practical. These lead to the so-called $X_\alpha$ computational method. During the present research program under Contract F19628-73-C-0300, a thorough study of the effects of local exchange and model potentials was carried out on prototype systems. Substantial improvements in the method resulted from these studies, especially in the reliability of the calculation of the total electronic energy.

SECTION II

## CURRENT STATUS OF QUANTUM MECHANICAL
## METHODS FOR DIATOMIC SYSTEMS

The application of quantum mechanical methods to the prediction of electronic structure has yielded much detailed information about atomic and molecular properties (Ref. 7). Particularly in the past few years, the availability of high-speed computers with large storage capacities has made it possible to examine both atomic and molecular systems using an ab initio approach, wherein no empirical parameters are employed (Ref. 23). Ab initio calculations for diatomic molecules employ a Hamiltonian based on the non-relativistic electrostatic interaction of the nuclei and electrons, and a wavefunction formed by antisymmetrizing a suitable many-electron function of spatial and spin coordinates. For most applications it is also necessary that the wavefunction represent a particular spin eigenstate and that it have appropriate geometrical symmetry. Nearly all the calculations performed to date are based on the use of one-electron orbitals and are of two types: Hartree-Fock or configuration interaction (Ref. 8).

Hartree-Fock calculations are based on a single assignment of electrons to spatial orbitals, following which the spatial orbitals are optimized, usually subject to certain restrictions. Almost all Hartree-Fock calculations have been subject to the assumption that the diatomic spatial orbitals are all doubly occupied, as nearly as possible, and are all of definite geometrical symmetry. These restrictions define the conventional, or restricted, Hartree-Fock (RHF) method (Refs. 24 and 25). RHF calculations can be made with relatively large Slater-type orbital (STO) basis sets for diatomic molecules with first or second-row atoms, and the results are convergent in the sense that they are insensitive to basis enlargement. The RHF model is adequate to give a qualitatively correct description of the electron interaction in many systems, and in favorable cases can yield equilibrium interatomic separations and force constants. However, the double-occupancy restriction makes the RHF method inappropriate in a number of circumstances of practical interest. In particular, it cannot provide potential curves for molecules dissociating into odd-electron atoms (e.g., NO at large internuclear separation), or into atoms having less electron pairing than the original molecule [e.g., $O_2$ $^3\Sigma_g^-$ → $O(^3P)$]; it cannot handle excited states having unpaired electrons (e.g., the $^3\Sigma$ states of $O_2$ responsible for the Schumann-Runge bands); and, in general, it gives misleading results for molecules in which the extent of electron correlation changes with internuclear separation.

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Configuration-interaction (CI) methods have the capability of avoiding the limitations of the RHF calculations. If configurations not restricted to doubly-occupied orbitals are included, a CI can, in principle, converge to an exact wavefunction for the customary Hamiltonian. However, many CI calculations have in fact been based on a restriction to doubly-occupied orbitals and therefore retain many of the disadvantages of the RHF method (Ref. 8). The use of general CI formulations involves three considerations, all of which have been satisfactorily investigated: the choice of basis orbitals, the choice of configurations (sets of orbital assignments), and the specific calculations needed to make wavefunctions describing pure spin states (Ref. 26). The first consideration is the art associated with quantum mechanical electronic structure calculations. Many methods (iterative NSO, perturbation selection, first order CI, etc.) have been advocated for the optimum choice of configurations. There are no firm rules at present and the optimum choice is a strong function of the insight of the particular research investigator. The last consideration, proper spin and symmetry projection, has proved difficult to implement, but computer programs have been developed for linear projection algebra at this Center, and the CI method has been found of demonstrable value in handling excited states and dissociation processes which cannot be treated with RHF techniques.

Either of the above described methods for ab initio calculations reduces in practice to a series of steps, the most important of which are the evaluation of molecular integrals, the construction of matrix elements of the Hamiltonian, and the optimization of molecular orbitals (RHF) or configuration coefficients (CI). For diatomic molecules, these steps are all comparable in their computing time, so that a point has been reached where there is no longer any one bottleneck determining computation speed. In short, the integral evaluation involves the use of ellipsoidal coordinates and the introduction of the Neumann expansion for the interelectronic repulsion potential (Ref. 27); the matrix element construction depends upon an analysis of the algebra of spin eigenfunctions (Ref. 28); and the orbital or configuration optimization can be carried out by eigenvalue techniques (Refs. 29, 30). All the steps have by now become relatively standard, and can be performed efficiently on a computer having 32,000 to 65,000 words of core storage, a cycle time in the microsecond range, and several hundred thousand words of peripheral storage.

Both the RHF and CI methods yield electronic wavefunctions and energies as a function of the internuclear separation, the RHF method for one state, and the CI method for all states considered. The electronic energies can be regarded as potential curves, from which may be deduced equilibrium internuclear separations, dissociation energies, and constants describing vibrational and rotational motion (including anharmonic and rotation-vibration

effects). It is also possible to solve the Schrödinger equation for the motion of the nuclei subject to the potential curves, to obtain vibrational wavefunctions for use in transition probability calculations. The electronic wavefunctions themselves can be used to estimate dipole moments of individual electronic states, transition moments between different electronic states, and other properties. While all of the calculations described in this paragraph have been carried out on some systems, the unavailability of good electronic wavefunctions and potential curves has limited actual studies of most of these properties to a very small number of molecules.

It is not always possible or practical to perform an ab initio or mathematically rigorous calculation of the electronic structure of a diatomic molecule containing a large number of electrons and it is sometimes useful to resort to approximations based on certain physical insights. One such approximation is the density functional method (Ref. 31) as applied to molecules. In one implementation of this approach, namely the $X_\alpha$ model, the one-electron Schrödinger equation is set up within an approximation to the true potential which is spherically symmetric within spheres surrounding the several nuclei, constant in the region between adjacent spheres and spherically symmetric outside an outer sphere which encloses the entire collection of nuclei. The resulting equations are solved by a multiple-scattering method, equivalent to the KKR method (Ref. 32) often used for crystals. From the resulting charge densities, onecan compute a total energy, using a statistical approximation for the exchange correlations. This approximation is defined apart from a multiplicative factor, $\alpha$, hence the name $X_\alpha$ method.

The $X_\alpha$ method has been very successful in predicting excitation energies in molecules and molecular ions but has met with only limited success in calculation of total energies. The basic deficiency appeared to lie in the muffin-tin approximation to the true potential rather than in the statistical treatment of the correlation energy. However, recent studies at this Center have shown that when certain variational constraints are applied to the $X_\alpha$ wavefunctions, significant improvements in the calculated total energies can be obtained. At this time the method appears to have utility for constructing regions of potential energy surfaces.

SECTION III

METHOD OF APPROACH

A.  Quantum Mechanical Calculations

Central to the proposed studies are the actual quantum-mechanical calculations which must be carried out for the molecular structures.  For added clarity, various aspects of these calculations are discussed in individual subsections.

1.  Levels of Approximation

Much evidence on diatomic and polyatomic systems indicates the near adequacy of a minimum Slater-type-orbital (STO) basis for constructing molecular wavefunctions (Refs. 33 and 34).  This means inner-shell and valence-shell STO's of quantum numbers appropriate to the atoms (1s, 2s, 2p for C, N, O; 1s for H).  The main deficiency of the minimum basis set is in its inability to describe polarization of $\pi$ orbitals in atoms adjacent to H atoms, and successful calculations usually result if one (or a set) of p orbitals is supplied for each H atom.  Values of the screening parameters $\zeta$ for each orbital can either be set from atomic studies or optimized in the molecule; the latter approach is indicated for studies of maximum precision. When high chemical accuracy is required, as for the detailed studies of the ground state of a system,  a more extended basis should be used.  Double-zeta plus polarization functions or optimized MO's usually are required.

The chosen basis sets give good results only when used in a maximally flexible manner.  This implies the construction of CI wavefunctions with all kinds of possible orbital occupancies, so that the correlation of electrons into overall states can adjust to an optimum form at each geometrical conformation and for each state.  Except when well-defined pairings exist for as many electrons as possible, a single-configuration study (even of Hartree-Fock quality) will be inadequate.

2.  Spin and Symmetry

Proper electronic states for systems composed of light atoms should possess definite eigenvalues of the spin  operator $S^2$ as well as an appropriate geometrical symmetry.  The geometrical symmetry can be controlled by the assignment of orbitals to each configuration, but the spin state must be obtained by a constructive or projective technique.  Formulas have been

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developed (Ref. 25) for projective construction of spin states from orthogonal orbitals, and programs implementing these formulas have for several years been in routine use at UTRC.

One of the least widely appreciated aspects of the spin-projection problem is that the same set of occupied spatial orbitals can sometimes be coupled to give more than one overall state of given S quantum number. It is necessary to include in calculations all such spin couplings, as the optimum coupling will continuously change with changes in the molecular conformation. This is especially important in describing degenerate or near-degenerate excited electronic states.

### 3. Method of Ab Initio Calculation

A spin-free nonrelativistic Hamiltonian will be employed in the Born-Oppenheimer approximation. For a molecule containing n electrons and m nuclei, the approximation leads to an electronic Hamiltonian depending parametrically on the nuclear positions:

$$\mathcal{H}(R) = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Z_A}{r_{iA}} - \sum_{i=1}^{n}\frac{Z_B}{r_{iB}} + \frac{Z_A Z_B}{R} + \sum_{i>j\geq1}^{n}\frac{1}{r_{ij}} \tag{1}$$

where $Z_\mu$ and $\bar{R}_\mu$ are the charge and position of nucleus $\mu$, $\bar{r}_i$ is the position of electron i, and $\nabla_i^2$ is the Laplacian operation for electron i. The Hamiltonian H is in atomic units (energy in Hartrees, length in Bohrs).

Electronic wavefunctions $\psi$, depending parametrically on the nuclear positions are made to be optimum approximations to solutions of the Schrödinger equation

$$\mathcal{H}(R)\Psi(R) = E(R)\Psi(R) \tag{2}$$

by invoking the variational principle

$$\delta W(R) = \delta\frac{\int\Psi^*(R)\mathcal{H}(R)\Psi(R)\,d\tau}{\int\Psi^*(R)\Psi(R)\,d\tau} \tag{3}$$

The integrations in Eq. (3) are over all electronic coordinates and the stationary values of W are approximations to the energies of states described by the corresponding $\psi$. States of different symmetries are studied by restricting to the appropriate form, and excited states of any symmetry can be handled by simultaneously determining the $\psi$ for the excited state and all lower-lying states of the same symmetry.

The specific form for $\psi$ may be written

$$\Psi(R) = \sum_\mu c_\mu \Psi_\mu(R) \qquad (4)$$

where each $\psi_\mu$ is referred to as a configuration, and has the general structure

$$\Psi_\mu(R) = A \mathcal{O}_S \prod_{i=1}^{n} \Psi_{\mu i}(\underline{r}_i, R) \theta_M \qquad (5)$$

where each $\psi_{\mu i}$ is a spatial orbital, A is the antisymmetrizing operator, $\mathcal{O}_S$ is the spin-projection operator for spin quantum number S, and $\theta_M$ is a product of $\alpha$ and $\beta$ one-electron spin functions of magnetic quantum number M. No requirement is imposed as to the double occupancy of the spatial orbital, so Eqs. (4) and (5) can describe a completely general wavefunction.

In Hartree-Fock calculations $\psi$ is restricted to a single $\psi_\mu$ which is assumed to consist as nearly as possible of doubly-occupied orbitals. The orbitals $\psi_{\mu i}$ are then selected to be the linear combinations of basis orbitals best satisfying Eq. (3). Writing

$$\Psi_{\mu i} = \sum_\nu a_{\nu i} \chi_\nu \qquad (6)$$

The $a_{\nu i}$ are determined by solving the matrix Hartree-Fock equations

$$\sum_\nu F_{\lambda \nu} a_{\nu i} = \epsilon_i \sum_\nu S_{\lambda \nu} a_{\nu i} \quad (\text{each } \lambda) \qquad (7)$$

where $\epsilon_i$ is the _orbital energy_ of $\psi_{\mu i}$.

The Fock operator $F_{\lambda \nu}$ has been throughly discussed in the literature (Ref. 36) and depends upon one- and two-electron molecular integrals and upon the $a_{\nu i}$. This makes Eq. (7) nonlinear and it is therefore solved iteratively. UTRC has developed programs for solving Eq. (7) for both closed and open-shell systems, using basis sets consisting of Slater-type atomic orbitals. Examples of their use are in the literature (Ref. 37).

In configuration interaction calculations, the summation in Eq. (4) has more than one term, and the $c_\mu$ are determined by imposing Eq. (3), to obtain the secular equation

$$\sum_\nu (H_{\mu\nu} - W S_{\mu\nu}) c_\nu = 0 \quad (\text{each } \mu) \qquad (8)$$

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where
$$H_{\mu\nu} = \int \Psi_\mu^\bullet (R) \, \mathcal{H} \, (R) \, \Psi_\nu (R) \, d\tau$$

$$S_{\mu\nu} = \int \Psi_\mu^\bullet (R) \, \Psi_\nu (R) \, d\tau \tag{9}$$

Equation (7) is solved by matrix diagonalization using either a modified Givens method (Ref. 38) or a method due to Shavitt (Ref. 30).

The matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$ may be reduced by appropriate operator algebra to the forms

$$H_{\mu\nu} = \sum_P \epsilon_P \left\langle \theta_M \left| \mathcal{O}_S P \right| \theta_M \right\rangle \left\langle \prod_{i=1}^n \Psi_{\mu i} (\underline{r}_i, R) \left| \mathcal{H}(R) P \right| \prod_{i=1}^n \Psi_{\nu i} (\underline{r}_i, R) \right\rangle \tag{10}$$

$$S_{\mu\nu} = \sum_P \epsilon_P \left\langle \theta_M \left| \mathcal{O}_S P \right| \theta_M \right\rangle \left\langle \prod_{i=1}^n \Psi_{\mu i} (\underline{r}_i, R) \left| P \right| \prod_{i=1}^n \Psi_{\nu i} (\underline{r}_i, R) \right\rangle \tag{11}$$

where P is a permutation and $\epsilon_P$ its parity. The sum is over all permutations. $\left\langle \theta_M \left| \mathcal{O}_S P \right| \theta_M \right\rangle$ is a "Sanibel coefficient" and the remaining factors are spatial integrals which can be factored into one- and two-electron integrals. If the $\psi_{\mu i}$ are orthonormal, Eqs. (10) and (11) become more tractable and the $H_{\mu\nu}$ and $S_{\mu\nu}$ may be evaluated by explicit methods given in the literature (Ref. 35). Computer programs have been developed for carrying out this procedure, and they have been used for problems containing up to 40 total electrons, 10 unpaired electrons, and several thousand configurations.

The CI studies described above can be carried out for any orthonormal set of $\psi_{\mu i}$ for which the molecular integrals can be calculated. Programs developed by UTRC made specific provision for the choice of the $\psi_{\mu i}$ as Slater-type atomic orbitals, as symmetry molecular orbitals, as Hartree-Fock orbitals, or as more arbitrary combinations of atomic orbitals.

## 4. Molecular Integrals

The one- and two-electron integrals needed for the above described method of calculation are evaluated for STO's by methods developed by the present investigators (Ref. 39). All needed computer programs have been developed and fully tested at UTRC.

## 5. Configuration Selection

Using a minimum basis plus polarization set of one-electron functions, a typical system will have of the order of $10^4$ configurations in a full CI (that resulting from all possible orbital occupancies). It is therefore

essential to identify and use the configurations describing the significant part of the wavefunction. There are several ways to accomplish this objective. First, one may screen atomic-orbital occupancies to eliminate those with excessive formal charge. Alternatively, in a molecular-orbital framework one may eliminate configurations with excessive number of antibonding orbitals. A third possibility is to carry out an initial screening of configurations, rejecting those whose diagonal energies and interaction matrix elements do not satisfy significance criteria. Programs to sort configurations on all the above criteria are available at UTRC.

Other, potentially more elegant methods of configuration choice involve formal approaches based on natural-orbital (Ref. 40) or multiconfiguration SCF (Ref. 41) concepts. To implement the natural-orbital approach, an initial limited-CI wave-function is transformed to natural-orbital form, and the resulting natural orbitals are used to form a new CI. The hoped-for result is a concentration of the bulk of the CI wavefunction into a smaller number of significant terms. The multiconfiguration SCF approach is more cumbersome, but in principle more effective. It yields the optimum orbital choice for a pre-selected set of configurations. This approach works well when a small number of dominant configurations can be readily identified.

It should be emphasized that the problem of configuration choice is not trivial, and represents an area of detailed study in the proposed research. The existence of this problem causes integral evaluation to be far from a unique limiting factor in the work.

## 6. Density Functional Approach - $X_\alpha$ Model

The $X_\alpha$ model (Ref. 10) for the electronic structure of atoms, molecules, clusters and solids is a local potential model obtained by making a simple approximation to the exchange-correlation energy. If we assume a nonrelativistic Hamiltonian with only electrostatic interactions, it can be shown that the total energy E of a system can be written exactly (Ref. 42) (in atomic units) as

$$E = \sum_i n_i \left\langle u_i \left| -\frac{1}{2} \nabla_1^2 + \sum_\mu \frac{z_\mu}{r_{1\mu}} \right| u_i \right\rangle + \frac{1}{2} \sum_{\mu \neq \nu} \frac{z_\mu z_\nu}{r_{\mu\nu}}$$

$$+ \frac{1}{2} \sum_{ij} n_i n_j \left\langle u_i u_j \left| \frac{1}{r_{12}} \right| u_i u_j \right\rangle + E_{xc}$$

(12)

This expression is exact, provided the $u_i$ are natural orbitals and $n_i$ are their occupation numbers (i.e., eigenfunctions and eigenvalues of the first order density matrix). The first term in Eq. (12) represents the kinetic and electron-nuclear energies. The second term is the nuclear repulsion

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energy. The sums $(\mu, \nu)$ are over all the nuclear charges in the system. The third term is the electron-electron repulsion term, which represents the classical electrostatic energy of the charge density $\rho$ interacting with itself, where

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1) \tag{13}$$

The last term $E_{xc}$ represents the exchange correlation energy and can be expressed formally as

$$E_{xc} = \frac{1}{2} \int \rho(1) \, d\vec{r}_1 \int \frac{\rho_{xc}(1,2)}{r_{12}} \, d\vec{r}_2 \quad , \tag{14}$$

where $\rho_{xc}(1,2)$ represents the exchange-correlation hole around an electron at position 1. In the exact expression, $\rho_{xc}$ is dependent on the second-order density matrix. In the Hartree-Fock approximation $E_{xc}$ is the exchange energy, $\rho_{xc}$ represents the Fermi hole due to the exclusion principle and depends only on the first-order density matrix. In the $X_\alpha$ method, we make a simpler assumption about $\rho_{xc}$. If we assume that the exchange-correlation hole is centered on the electron and is spherically symmetric, it can be shown that the exchange-correlation potential

$$u_{xc} = \int \frac{\rho_{xc}(1,2)}{r_{12}} \, d\vec{r}_2 \tag{15}$$

is inversely proportional to the range of the hole, $r_s$, where $r_s$ is defined by

$$\frac{4\pi}{3} r_s^3 \rho(1) = 1 \tag{16}$$

Therefore, in the $X_\alpha$ model, the potential $U_{xc}$ is proportional to $\rho^{1/3}(\vec{r})$. We define a scaling parameter $\alpha$ such that

$$U_{x\alpha}(1) = -\frac{9\alpha}{2} \left( 3\rho(1)/8\pi \right)^{1/3} \tag{17}$$

The expression in Eq. 17 is defined so that $\alpha = 2/3$ for the case of a free electron gas in the Hartree-Fock model (Ref. 43) and $\alpha = 1$ for the potential originally suggested by Slater (Ref. 44). A convenient way to choose this parameter for molecular and solid state applications is to optimize the solutions to the $X_\alpha$ equations in the atomic limit. Schwarz (Ref. 45) has done this for atoms from $Z = 1$ to $Z = 41$ and found values between $2/3$ and $1$.

In the "spin polarized" version of the $X_\alpha$ theory, it is assumed (as in the spin-unrestricted Hartree-Fock model) that electrons interact only with a potential determined by the charge density of the same spin. In this case the contribution to the total energy is summed over the two spins, $s = \pm \frac{1}{2}$.

$$E_{xc} = \frac{1}{2} \sum_s \int \rho_s(1) \, U_{x\alpha,s}(1) \, d\vec{r}_1 \tag{18}$$

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where the potential is spin-dependent

$$U_{x\alpha,\,s}(1) = -\frac{9\alpha}{2}\left(3\rho_s(1)/4\pi\right)^{1/3}$$ (19)

and $\rho_s$ is the charge density corresponding to electrons of spin s. The spin-polarized $X\alpha$ model is useful for describing atoms and molecules with open-shell configurations and crystals which are ferromagnetic or anti-ferromagnetic.

Once one has made the $X\alpha$ approximation to the total energy functional E in Eq. (12), then the rest of the theory follows from the application of the variational principle. The orbitals $u_i$ are determined by demanding that E be stationary with respect to variations in $u_i$. This leads to the set of one-electron $X\alpha$ equations

$$\left[-\frac{1}{2}\nabla_1^2 + \sum_\mu \frac{z_\mu}{r_{1\mu}} + \int \frac{\rho(2)}{r_{12}}d\vec{r}_2 + \frac{2}{3}U_{x\alpha}\right]u_i = \epsilon_i u_i$$ (20)

where $\epsilon_i$ is the one-electron eigenvalue associated with $u_i$. Since $\rho(\vec{r})$ is defined in terms of the orbitals $u_i$, the Eq. (20) must be solved iteratively, until self-consistency is achieved. Empirically, if one takes as an initial guess that $\rho$ is approximately a sum of superimposed atomic charge densities, then the convergence of this procedure is fairly rapid. The factor of 2/3 multiplying the potential is a result of the nonlinear dependence of $E_{xc}$ on $\rho$. This also has as a consequence that the $X\alpha$ eigenvalues $\epsilon_i$ do not satisfy Koopmans' theorem, i.e., they cannot be interpreted as ionization energies. However it can be shown that the $\epsilon_i$ are partial derivatives of the total expression of Eq. (12) with respect to the occupation number,

$$\epsilon_i = \frac{\partial E}{\partial n_i}$$ (21)

If E were a linear function of $n_i$, then Koopmans' theorem would hold. However, because of the dominant Coulomb term, E is better approximated by a quardratic function in $n_i$. This leads to the "transition state" approximation which allows one to equate the difference in total energy between the state $(n_i, n_j)$ and $(n_i - 1, n_j + 1)$ to the difference in the one-electron energies $\epsilon_j - \epsilon_i$ calculated in the state $(n_i - \frac{1}{2}, n_j + \frac{1}{2})$. The error in this approximation is proportional to third-order derivatives of E with respect to $n_i$ and $n_j$, which are usually small (Ref. 46). The main advantage of using the transition state rather than directly comparing the total energy values is computational convenience, especially if the total energies are large numbers and the difference is small.

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The relationship of Eq. (21) also implies the existence of a "Fermi level" for the ground state. This can be seen by varying E with respect to $n_i$ under the condition that the sum $\sum_i' n_i$ is a constant, i.e.,

$$\delta\left[E - \lambda \sum_i n_i\right] = 0 \tag{22}$$

implies $\partial E/\partial n_i = \lambda$, where $\lambda$ is a Lagrangian multiplier. This implies that the total energy is stationary when all the one-electron energies are equal. However, the occupation numbers are also subject to the restriction $0 \leq n_i \leq 1$. This leads to the following conditions on the ground state occupation numbers;

$$\epsilon_i < \lambda \cdot) \cdot n_i = 1$$
$$\epsilon_i > \lambda \cdot) \cdot n_i = 0 \tag{23}$$
$$\epsilon_i = \lambda \cdot) \cdot 0 \leq n_i \leq 1$$

In other words, the ground state eigenvalues obey Fermi statistics with $\lambda$ representing the Fermi energy. It should be noted that, in contrast to the Hartree-Fock theory, where all the $n_i$ are either 0 or 1, the $X\alpha$ model predicts, in some cases, fractional occupation numbers at the Fermi level. In particular, this will occur in a system (such as transition metal or actinide atom) which has more than one open shell.

The $X\alpha$ model differs in other significant ways from the Hartree-Fock method. In fact, the simplification introduced in approximating the total energy expression introduces several distinct advantages over Hartree-Fock:

1. The primary advantage is purely computational. The one-electron potential in Eq. (20) is orbital-independent and local, i.e., it is the same for all electrons (except in the spin-polarized $X\alpha$ theory) and is a multiplicative operator. On the other hand, the Hartree-Fock potential is nonlocal, or equivalently, there is a different local potential for each orbital. This involves a great deal more computational effort, especially for systems described by a large number of orbitals. It has been shown (Ref. 47) that the $X\alpha$ orbitals for the first and second row atoms are about as accurate as a double-zeta basis set, and are probably better for larger atoms which involve electrons with $\ell \geq 2$.

2. The orbital-independent $X\alpha$ potential leads to a better one-electron description of electronic excitations of a system. Both the unoccupied ($n_i=0$) and occupied ($n_i = 1$) eigenfunctions are under the influence of the same potential resulting from the other N-1 electrons. The Hartree-Fock virtual orbitals see a potential characteristic of the N occupied orbitals, and therefore are not as suitable for describing the excited states. Actually, although the ground state virtual eigenvalues are usually a good description of the one-electron excitations, the virtual spectrum of the transition state

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potential where one-half an electron has been removed from the system gives a much better first-order picture of these levels (Ref. 48).

3. As has been shown by Slater (Ref. 49), the X$\alpha$ model rigorously satisfies both the virial and Hellman-Feynman theorems, independent of the value of the parameter $\alpha$. This is convenient for calculating the force on a nucleus directly in terms of a three-dimensional integral, rather than the six-dimensional integrals in the expression for the total energy of Eq. (12).

### 7. Computational Aspects of the $X_\alpha$ Method

In application of the $X_\alpha$ model to finite molecular systems, there are two practical aspects of the calculations which must be considered. The first concerns the choice of the integration framework for describing the molecular wavefunctions and the second deals with the choice of the exchange parameter, $\alpha$, in different regions of space.

In computations with heteronuclear molecules, there are two free parameters that must be chosen: the ratio of sphere radii for the atomic spheres of integration at a given internuclear separation and the value of the exchange parameter in the intersphere region. The values of the exchange parameters are usually chosen to be the free atom values inside the spheres.

It has been found that changing the ratio of the sphere radii for the two atoms in a heteronuclear diatomic molecule introduces changes in the total energy that can be large on a chemical scale, ($\sim 1$ eV). A choice for sphere radii based on covalent bonding radii does not necessarily provide a good estimate for these calculations. Studies made at UTRC have shown that at any given separation the total energy calculated from the $X_\alpha$ model is a minimum at the radii ratio where the spherically averaged potentials from the two atomic centers are equal at the sphere radius,

$$V_1(r_{s_1}) = V_2(r_{s_2})$$

This relationship between the potential match at the sphere boundary and the minimum in the total energy appears to hold exactly for "neutral" atoms and holds well for ionic molecular constituents. In the case of two ionic species, the long range tail of the potential must go like $+2/R$ from one ion and $-2/R$ (in Rydbergs) for the other ion and so at large internuclear separations, the tails of the potential cannot match well. However, at reasonable separations, the $1/R$ character of the potential does not invalidate the potential match criterion for radii selection. This match for the atomic potentials is applied to the self-consistent potentials.

The second free parameter, the intersphere exchange coefficient, is chosen to be a weighted average of the atomic exchange parameters from the two constituents. At small internuclear separations, the optimum radius for an atomic sphere frequently places significant amounts of charge outside that atomic sphere - charge that is still strongly associated with its original center rather than being transferred to the other center or associated with the molecular binding region. To best account for these cases the weighting coefficients are chosen to reflect the origin of the charge in the intersphere (or outersphere region),

$$\alpha_{\text{intersphere}} = \frac{\alpha_{s_1}(Q_{s_1} - Q_1^o) + \alpha_{s_2}(Q_{s_2} - Q_2^o)}{(Q_{s_1} - Q_1^o) + (Q_{s_2} - Q_2^o)}.$$

where $(Q_{s_i} - Q_i^o)$ is the charge lost from sphere i relative to its atomic value (or ionic value) $Q_i^o$ and $\alpha_{s_i}$ is the atomic exchange parameter for sphere i. This value for $\alpha_{\text{intersphere}}$ is calculated dynamically - it is updated after each iteration in the self-consistent calculation.

While for heavy atoms, these changes in the exchange parameter would be small, the $\alpha$'s for small atoms vary rapidly with z (and with ionicity). The correct choice of the exchange parameters influences not only the total energy calculated for the molecule but also in some cases affects the distribution of charge between the atomic spheres and the intersphere region.

## B. Transition Probabilities

The electronic and vibrational-rotational wavefunctions of a pair of states can be used to calculate transition probabilities. If two molecular states are separated in energy by an amount $\Delta E_{nm} = hc\nu$ (h = Planck's constant, c = velocity of light, $\nu$ = frequency in wave numbers), the semiclassical theory of radiation (Refs. 50 and 51) yields for the probability of a spontaneous transition from an upper state n to a lower state m

$$A_{nm} = \frac{4}{3} \frac{\Delta E_{nm}^3}{\hbar^4 c^3} \frac{S_{nm}}{g_n} \tag{24}$$

Here $A_{nm}$ is the Einstein coefficient for spontaneous transition from level $n \to m$, $g_n$ is the total degeneracy factor for the upper state

$$g_n = (2 - \delta_{\sigma, \Lambda'})(2S' + 1)(2J' + 1) \tag{25}$$

and $S_{nm}$ is the total strength of a component line is a specific state of polarization and propagated in a fixed direction. A related quantity is the mean radiative lifetime of state n defined by

$$\frac{1}{\tau_n} = \sum_{m<n} A_{nm} \tag{26}$$

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the summation being over all lower levels which offer allowed connections. The intensity of the emitted radiation is

$$I_{nm} = \Delta E_{nm} N_n A_{nm} \tag{27}$$

where $N_n$ is the number density in the upper state n. This analysis assumes that all degenerate states at the same level n are equally populated, which will be true for isotropic excitation. The total line strength $S_{nm}$ can be written as the square of the transition moment summed over all degenerate components of the molecular states n and m:

$$S_{nm} = \sum_{i,j} \left| M_{ji} \right|^2 \tag{28}$$

where j and i refer to all quantum numbers associated collectively with upper and lower electronic states, respectively.

In the Born-Oppenheimer approximation, assuming the separability of electronic and nuclear motion, the wavefunction for a diatomic molecule can be written as

$$\psi'_{vJM\Lambda} = \psi'_{el}(\underline{r}, R)\, \psi_v(R)\, \psi_{JM\Lambda}(\theta, \chi, \phi) \tag{29}$$

where $\psi^i_{el}(\underline{r}, R)$ is an electronic wavefunction for state i at fixed inter-nuclear separation R, $\psi_v(R)$ is a vibrational wavefunction for level v and $\psi_{Jn\Lambda}(\theta, \chi, \phi)$ refers to the rotational state specified by electronic angular momentum $\Lambda$, total angular momentum J and magnetic quantum number M. The representation is in a coordinate system related to a space-fixed system by the Eulerian angles $(\theta, \chi, \phi)$. The transition moment $M_{ji}$ can be written, using the wavefunction given by Eq. (29), as

$$M_{ji} = \int \psi^j_{v'J'\Lambda'M'} \left\{ \underline{M}^e + \underline{M}^n \right\} \psi^j_{v''J''\Lambda''M''} \, d\tau_e \, d\tau_v \, d\tau_r \tag{30}$$

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The subscripts e, v and r refer to the electronic, vibrational and rotational wavefunctions and $\underset{\sim}{M}^e$ and $\underset{\sim}{M}^n$ are the electronic and nuclear electric dipole moments, respectively. Integration over the electronic wavefunction, in the Born-Oppenheimer approximation, causes the contribution of the nuclear moment $M^n$ to vanish for $i \neq j$. The electronic dipole moment can be written (Refs. 51 and 52) in the form

$$\underset{\sim}{M}^e = -\sum_k e\underset{\sim}{r}_k' = -\left\{ \sum_k e\underset{\sim}{r}_k \right\} \cdot \underset{\sim}{\mathfrak{D}}(\theta, \chi, \phi) \tag{31}$$

where the primed coordinates refer to the space fixed system, the coordinates $r_k$ refer to a molecule-fixed system and $\mathfrak{D}(\theta, \chi, \phi)$ is a group rotation tensor whose elements are the direction cosines related to the Eulerian rotation angles $(\theta, \chi, \phi)$. Using bracket notation, Eqs. (30) and (31) can be combined to yield for the transition moment

$$M_{ji} = M_{iv''J''\Lambda''M''}^{iv'J'\Lambda'M'} = \left\langle jv' \left| -\sum_k e\underset{\sim}{r}_k \right| iv'' \right\rangle \cdot \left\langle J'\Lambda'M' \left| \underset{\sim}{\mathfrak{D}}(\theta, \chi, \phi) \right| J''\Lambda''M'' \right\rangle \tag{32}$$

The matrix elements $\langle J' \Lambda' M' | \mathfrak{D}(\theta, \chi, \phi) | J'' \Lambda'' M'' \rangle$ determine the group selection rules for an allowed transition and have been evaluated for many types of transitions (Refs. 53, 54 and 55). Summing Eq. (32) over the degenerate magnetic quantum numbers M' and M'' we have from Eq. (28)

$$S_{nm} = S_{mv''J''\Lambda''}^{nv'J'\Lambda'} = \mathscr{S}_{J''\Lambda''}^{J'\Lambda'} \, p_{mv''}^{nv'} \tag{33}$$

where $\mathscr{S}_{J''\Lambda''}^{J'\Lambda'}$ is the Hönl-London factor (Refs. 56 and 57) and

$$p_{mv''}^{nv'} = \sum_{i,j} \left| \left\langle jv' \left| -\sum_k e\underset{\sim}{r}_k \right| iv'' \right\rangle \right|^2 \tag{34}$$

is the band strength for the transition. Combining Eqs. (25), (27) and (33), we have for the intensity of a single emitting line from upper level n:

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$$I_{nm} = I_{mv''J''}^{nv'J'} = \frac{4}{3} N_{J'} \frac{\left[\Delta E_{mv''J''}^{nv'J'}\right]^4 S_{mv''J''\Lambda''}^{nv'J'\Lambda'}}{\hbar^4 c^3 \omega_n} \tag{35}$$

where $N_{J''}$ is the number density in the upper rotational state $J'$ and $\omega_n = (2-\delta_{\sigma,\Lambda}) (2S' + 1)$ is the electronic degeneracy. Taking an average value of $E_{m\ v''\ J''}^{n\ v'\ J'}$ for the whole band, Eq. (35) can be summed to yield the total intensity in the $(v', v'')$ band:

$$I_{mv''}^{nv'} = \sum_{J',J''} I_{mv''J''}^{nv'J'} = \frac{4}{3} N_{V'} \frac{\left[\overline{\Delta E}_{mv''}^{nv'}\right]^4 p_{mv''}^{nv'}}{\hbar^4 c^3 \omega_n} \tag{36}$$

where $N_{V'} = \sum_{J'} N_{J'}$, is the total number density in the upper vibrational level $v'$ and where we make use of the group summation property

$$\sum_{J''} \mathscr{S}_{J''\Lambda''}^{J'\Lambda'} = (2J'+1) \tag{37}$$

Comparing Eq. (27) and (36), we have for the Einstein spontaneous transition coefficient of the band $(v', v'')$

$$A_{mv''}^{nv'} = \frac{4}{3} \frac{\left[\Delta E_{mv''}^{nv'}\right]^3 p_{mv''}^{nv'}}{\hbar^4 c^3 \omega_n} \tag{38}$$

Similarly, the lifetime of an upper vibrational level $v'$ of state $n$ can be written

$$\frac{1}{\tau_n} = \sum_{m<n} \sum_{v''} A_{mv''}^{nv'} \tag{39}$$

where the summation runs over all v″ for each lower state m. Equation (38) can be cast in the computational form

$$A_{mv''}^{nv'} (\sec^{-1}) = \frac{(21.41759 \times 10^9)}{\omega_n} \left[ \Delta E_{mv''}^{nv'} (a.u.) \right]^3 p_{mv''}^{nv'} (a.u.) \tag{40}$$

where $\Delta E_{m\,v''}^{n\,v'}$ and $p_{m\,v''}^{n\,v'}$ are in atomic units. It is also often convenient to relate the transition probability to the number of dispersion electrons needed to explain the emission strength classically. This number, the f-number or oscillator strength for emission, is given by

$$f_{nm,\,v'v''} = \frac{mc^3 h^2}{2e^2 \left[ \overline{\Delta E}_{mv''}^{nv'} \right]^2} A_{mv''}^{nv'} \tag{41}$$

The inverse process of absorption is related to the above development through the Einstein B coefficient. Corresponding to Eq. (27), we have for a single line in absorption

$$I_{mn} = I_{mv''J''}^{nv'J'} = \int_{line(v''v'J''J')} K(\nu)d\nu = \Delta E_{mn} N_m B_{mn} \tag{42}$$

where $K(\upsilon)$ is the absorption coefficient of a beam of photons of frequency $\upsilon$ and

$$B_{mn} = B_{mv''J''\Lambda''}^{nv'J'\Lambda'} = \frac{2\pi}{3h^2 c} \frac{S_{mv''J''\Lambda''}^{nv'J'\Lambda'}}{\omega_m (2J''+1)} \tag{43}$$

is the Einstein absorption coefficient for a single line. Summing over all lines in the band (v″, v′), assuming an average band frequency, we obtain

$$I_{mv''}^{nv'} = \sum_{J',J''} I_{mJ''v''}^{nJ'v'} = N_{v''} \frac{2\pi}{3\hbar^2 c \omega_m} p_{mv''}^{nv'} \tag{44}$$

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where $N_v'' = \sum_{J''} N_{J''}$ is the total number density in the lower vibrational state $v''$. Corresponding to Eqs. (40) and (41) we can define an f-number or oscillator strength for absorption as

$$f_{mn,v''v'} = \frac{2m\, \overline{\Delta E}_{mv''}^{nv'}}{3\hbar^2 e^2 \omega_n}\; p_{mv''}^{nv'} \tag{45}$$

In computational form, Eq. (45) becomes

$$f_{mn,v''v'} = \frac{2}{3} \cdot \frac{\overline{\Delta E}_{mv''}^{nv'}(a.u.)}{\omega_m}\; p_{mv''}^{nv'}(a.u.) \tag{46}$$

where $\overline{\Delta E}_{mv''}^{nv'}$ and $p_{mv''}^{nv'}$ are in atomic units. Combining Eqs. (38) and (41) and comparing with Eq. (45), we see that the absorption and emission f-numbers are related by

$$f_{mn,v''v'} = \left(\frac{\omega_n}{\omega_m}\right) f_{nm,v'v''} \tag{47}$$

Some caution must be observed in the use of f-numbers given either by Eq. (41) or (45) since both band f-numbers and system f-numbers are defined in the literature. The confusion arises from the several possible band averaging schemes that can be identified.

An integrated absorption coefficient (density corrected) can be defined from Eq. (44) as

$$S_{v'',v'} = \frac{1}{P_c}\; I_{mv''}^{nv'} = N_{v''}\, B_{v'',v'} \left(1 - \exp\frac{-hc\nu_{v'',v'}}{kT}\right) \frac{h\nu_{v''v'}}{Pc^2} \tag{48}$$

where the exponential factor corrects for stimulated emission. Equation (48) can be written in terms of the absorption f-number as

$$S_{v'',v'} = \frac{\pi e^2}{mc^2}\; \frac{N_{v''}}{P} \left(1 - \exp\frac{-hc\nu_{v'',v'}}{kT}\right) f_{mn,v''v'} \tag{49}$$

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Using $h c/k = 1.43880$ cm-K°, we obtain a computational formula for the integrated absorption coefficient as $S_{v''}, v'$ $(cm^{-2} \cdot atm^{-1})$ =

$$2.3795 \times 10^7 \left(\frac{273.16}{T(K°)}\right) \left(\frac{N_{v''}}{N_T}\right) \left(1 - exp \frac{1.43880 \nu_{v''v'}(cm^{-1})}{T}\right) \cdot f_{mn,v'' v'} \tag{50}$$

The total integrated absorption is found from

$$S_{TOTAL} = \sum_{v''} \sum_{v'} S_{v'',v'} \tag{51}$$

where, under normal temperature conditions, only the first few fundamentals and overtones contribute to the summations.

The developments given above are rigorous for band systems where an average band frequency can be meaningfully defined. Further approximations, however, are often made. For example, the electronic component of the dipole transition moment can be defined as

$$R_{ji}(R) = \left\langle j \left| -\sum_k e r_{\sim k} \right| i \right\rangle \tag{52}$$

This quantity is often a slowly varying function of R and an average value can sometimes be chosen. Equation (34) can then be written approximately in factored form as

$$p_{mv''}^{nv'} \simeq q_{v'v''} \sum_{i,j} \left| \bar{R}_{ji}(\bar{R}) \right|^2 \tag{53}$$

where $q_{v' v''}$, the square of the vibrational overlap integral, is called the Franck-Condon factor. $R_{ji}$ is evaluated at some mean value of the internuclear separation R. In addition, it is sometimes possible to account for a weak R-dependence in $\underset{\sim}{M}^e$ by a Taylor series expansion of this quantity about some reference value, $R_{\alpha\beta}$, usually referred to the (0, 0) band. We have

$$R_{ji} \simeq R_{ji}^{\alpha\beta} \left[ 1 + a(R - R_{\alpha\beta}) + b(R - R_{\alpha\beta})^2 + \cdots \right] \tag{54}$$

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Substituting into Eq. (34) and integrating yields

$$p_{mv''}^{nv'} \simeq q_{v'v''} \sum_{i,j} \left| R_{ji}^{\alpha\beta} \left[ 1 + a(\overline{R_{v'v''} - R_{\alpha\beta}}) + b(\overline{R_{v'v''} - R_{\alpha\beta}})^2 + \cdots \right] \right|^2 \qquad (55)$$

where

$$(\overline{R_{v'v''} - R_{\alpha\beta}}) = \frac{\langle v' | (R - R_{\alpha\beta}) | v'' \rangle}{\langle v' | v'' \rangle} \qquad (56)$$

is the R-centroid for the transition and

$$(\overline{R_{v'v''} - R_{\alpha\beta}})^2 = \frac{\langle v' | (R - R_{\alpha\beta})^2 | v'' \rangle}{\langle v' | v'' \rangle} \qquad (57)$$

is the $R^2$-centroid. Note that this last term differs (to second order) from the square of the R-centroid. An alternate procedure can be developed by evaluating Eq. (52) at each R-centroid, $\bar{R}_{v'\,v''}$. Then

$$p_{mv''}^{nv'} \approx q_{v'v''} \sum_{i,j} \left| R_{ji}(R_{v'v''}) \right|^2 \qquad (58)$$

Equation (58) assumes that the vibrational wavefunction product $\psi_{v'}$, $\psi_{v''}$ behaves like a delta function upon integration,

$$\psi_{v'} \psi_{v''} = \delta(R - \bar{R}_{v'v''}) \langle v' | v'' \rangle \qquad (59)$$

The range of validity of Eq. (58) is therefore questionable, particularly for band systems with bad overlap conditions such as oxygen Schumann-Runge. The range of validity of the R-centroid approximation has been examined by Frazer (Ref. 58).

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The final step in calculating transition probabilities is the determination of $R_{ji}(R)$, the electronic dipole transition moment, for the entire range of internuclear separations, R, reached in the vibrational levels to be considered. This can be expressed in terms of the expansion of Eq. (4) as

$$R_{ji}(R) = \sum_{\mu\nu} c_\mu^{j\bullet} c_\nu^i \left\langle \psi_\mu(R) \middle| \underset{\sim}{M}^e \middle| \psi_\nu(R) \right\rangle \tag{60}$$

where $c_\mu{}^j$ and $c^i$ are coefficients for $\psi_{el}^j$ and $\psi_{el}^i$, respectively.

An analysis similar to that yielding Eqs. (10) and (11) gives

$$\left\langle \psi_\mu(R) \middle| \underset{\sim}{M}^e \middle| \psi_\nu(R) \right\rangle =$$

$$\sum_p \epsilon_p \left\langle \theta_{M_S} \middle| O_S P \middle| \theta_{M_S} \right\rangle \left\langle \prod_{k=1}^n \psi_{\mu k}(\underset{\sim}{r}_k, R) \middle| \underset{\sim}{M}^e P \middle| \prod_{k=1}^n \psi_{\nu k}(\underset{\sim}{r}_k, R) \right\rangle \tag{61}$$

The spatial integral in Eq. (61) reduces to one-electron integrals equivalent to overlap integrals, and the evaluation of Eq. (61) can be carried out by the same computer programs used for Eq. (11). Programs for evaluating $R_{ji}(R)$ in Eq. (60) have been developed at UTRC and examples of their application have appeared in the literature (Ref. 59).

For perturbed electronic systems, the transition dipole moment will have a strong R-dependence and R-centroid or other approximations will be invalid. A direct evaluation of Eq. (34) would therefore be required using the fully-coupled system of electronic and vibrational wavefunctions to properly account for the source of the band perturbations.

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# SECTION IV

## DISCUSSION OF RESULTS

The theoretical research conducted under this program was concerned with the electronic structure and radiative transition probabilities for NO, $NO_2$ and TiO. This research was carried out using quantum mechanical methods and computer codes which were developed at this Center. Both ab initio methods, employing configuration interaction (CI), and density functional methods ($X_\alpha$), were utilized. The results obtained for the molecular systems under study are summarized separately below.

### NO

An extensive analysis of the dipole moment function for the ground state of NO was carried out. We have examined in detail the recent work of Goldman and Schmidt (Ref. 60), Chandraiah and Cho (Ref. 61), and the theoretical studies of Billingsley (Refs. 62 and 63). In addition we have reviewed our valence-bond calculations carried out for both the separated atom range of interaction of N+O and for the united atom limit of the $^2P$ state of phosphorus. Computer least square fits to all the available experimental and theoretical data relating to the dipole moment were carried out and our resultant best fit is shown in Fig. 1. This curve is qualitatively similar to that reported previously (Ref. 64) but differs significantly in several respects. First, the permanent dipole moment of NO is negative corresponding to $N^-O^+$ polarity. This is now well established both from theoretical studies and comparisons with the experimental data for CO. Second, the short range portion of $\mu(R)$ shows a minimum between .5 - .6 Å, well up on the repulsive part of the potential curve but not yet at united atom behavior for the system. Third, the long range behavior of $\mu(R)$ has now been calculated with high accuracy optimized wavefunctions. This synthesized curve for the dipole moment is the best that can be obtained using all of the data available at the present time.

All data, including experimental integrated absorption coefficients, were finally reduced to fit a dipole moment function of the form:

$$\mu(r) = \sum_{j=0}^{4} a_j \, (r-r_e)^j \tag{62}$$

A computer reduction was carried out using a least-squares fit to all data weighted by the given error analysis (or estimated errors in the case of the calculated dipole moment functions). A minimum error residual was found with the following function:

$$\mu^{NO}(r) = -0.166 + 2.24 \, (r-r_e) - 1.342 \, (r-r_e)^2 - 1.703 \, (r-r_e)^3 + 1.097 \, (r-r_e)^4 \tag{63}$$

where $r_e$ is the equilibrium internuclear separation in angstroms and $\mu(r)$ is in Debyes.

This function can be compared with the "experimental" dipole moment function for CO found by Toth, et al (Ref. 65):

$$\mu^{CO}(r) = -0.112 + 3.10 \ (r-r_e) - 0.31 \ (r-r_e)^2 - 2.28 \ (r-r_e)^3 \tag{64}$$

The functions are clearly similar both with regard to the sign of the coefficients and their relative magnitudes.

Using the dipole moment function represented by Eq. (63) and accurate RKR vibrational-rotational wavefunctions, the integrated band absorption coefficients have been calculated for the fundamental, first, and second overtones of NO as a function of temperature. For a transition from lower state $\ell$ to upper state u in absorption we have

$$S_{\ell u} = \frac{\pi e^2}{mc^2} \ \frac{N_\ell}{P} \left[ 1 - e^{-\hbar c \nu_{\ell u}/kT} \right] f_{\ell u} \tag{65}$$

where $f_{\ell u}$ is the absorption f-number. In computational form we have

$$S_{\ell u}(T) = 2.3795 \times 10^7 \left( \frac{273.16}{T(K^\circ)} \right) \left( \frac{N_\ell}{N_T} \right) \left[ 1 - e^{-1.4388 \ \nu_{\ell u}(cm^{-1})/T(K^\circ)} \right] f_{\ell u} \tag{66}$$

The total absorption is given by

$$S(T) = \sum_{\substack{\ell=0 \\ u=\ell+1}} S_{\ell u}(T) + \sum_{\substack{\ell=0 \\ u=\ell+2}} S_{\ell u}(T) + \sum_{\substack{\ell=0 \\ u=\ell+3}} S_{\ell u}(T) + \cdot \cdot \cdot \tag{67}$$

where the first term represents the total absorption of the fundamental band, the second term represents the first overtone absorption, etc. The calculated absorption is given in Table 1 which indicates a near constancy of the intensity of the fundamental band up to 5000°K. This is in agreement with the recent experimental data of Konkov and Vorontsov (Ref. 66). Table 2 lists fundamental oscillator strengths and Table 3 lists the calculated Einstein coefficients for the lowest 10 vibrational levels.

## $NO_2$

SCF calculations were performed for the ground $\tilde{X}\,^2A_1$ state of $NO_2$ at the experimental equilibrium bond length of 1.1934 Å and at bond angles of 134.1° (exp.) and 180°. The results are given in Table 4 where we list the occupied molecular orbitals at these two bond angles. The bent molecule has a lower total energy in the ground state and the lowest occupied orbitals correspond to those predicted from ab initio calculations. The density functional method thus successfully predicts the bent character of the ground state and the correct orbital occupancy. Table 4 also lists the energies of the low-lying $4b_2$, $7a_1$ and $2b_1$ states.

Additional calculations were carried out for the first excited $\tilde{A}\,^2B_1$ state of $NO_2$. The calculations were performed at the experimental ground state bond length and at bond angles of 134.1° and 180°. The results are given in Table 5 which lists the occupied molecular orbitals. The linear configuration is favored in this excited state.

From this data we calculate a vertical excitation energy for $\tilde{X}\,^2A_1 \to \tilde{A}\,^2B_1$ of 2.43 eV. This is in good agreement with experimental estimates and the best ab initio calculation for this system (Ref. 67). More detailed calculations of the $NO_2$ hypersurfaces, using the density functional method, are clearly indicated as a result of the success of these initial studies.

## TiO

SCF calculations were performed for the d $^1\Sigma^+$ state of TiO at four internuclear separations (R = 2.5, 3.0, 3.5 and 4.0 bohrs), using an optimized SCF orbital basis obtained at R = 3.0. This orbital basis is shown in Table 6. The MO's obtained from these calculations were then used as input transformation vectors to convert the original atomic orbital basis to MO form. The lowest eleven (11) MO's ($1\sigma$, $2\sigma$, $3\sigma$, $1\pi^+$, $1\pi^-$, $4\sigma$, $5\sigma$, $2\pi^+$, $2\pi^-$, $6\sigma$, $7\sigma$) were taken as doubly occupied and a CI was performed over the rest of the MO's for the $X^3\Delta$, $a^1\Delta$ and $d^1\Sigma^+$ states of TiO. This resulted in a wavefunction expansion which consisted of 135 configurations for $X^3\Delta$, 102 configurations for $a^1\Delta$ and 88 configurations for $d^1\Sigma^+$. A full CI was not performed due to the number of configurations involved. Those configurations selected were constructed from the lowest 9 sigma MO's, the lowest 4 pi MO's and a single delta MO. This corresponds to the energetically more compacted orbitals.

Expectation values for the dipole moment $\mu(R)$ were calculated for the $X^3\Delta$, $a^1\Delta$ and $d^1\Sigma^+$ states. The results are shown in Fig. 2.

The $X^3\Delta$, $a^1\Delta$ and $d^1\Sigma^+$ vibrational states of TiO can be characterized by the spectroscopic data (Ref. 68) tabulated in Table 7. A RKR analysis of this data yields the potential curves shown in Fig. 3. These potentials were then

used to generate wavefunctions for the lowest twenty (20) vibrational levels of the $X^3\Delta$, $a^1\Delta$ and $d^1\Sigma^+$ states of TiO. The calculated $\Delta G(v)$ and experimental $\Delta G(v)$ are compared in Tables 8, 9, and 10.

Using these vibrational wavefunctions in conjunction with the dipole moment function shown in Fig. 2, the vibrational oscillator strengths were calculated. These are shown in Tables 11, 12 and 13 for several of the low-lying fundamental and first and second overtones. The population densities as a function of temperature are shown in Table 14 for those vibrational levels which were significantly populated. The three states ($X^3\Delta$, $a^1\Delta$ and $d^1\Sigma^+$) were weighted, assuming a Boltzmann population distribution, for calculation of integrated absorption coefficients. These absorption data are shown in Table 15.

Density functional studies were undertaken on the calculation of the electronic structure of TiO and $TiO^+$ using the $SCF-X_\alpha$ scattered wave method. An efficient version of the $X_\alpha$ program has been developed in this Center for carrying out these studies. In addition, a separate computer program has been developed for implementing the scattered-wave approach for atoms and atomic ions incorporating both a nonrelativistic option and a relativistic option using a modified Briet Hamiltonian. The results of our $SCF-X_\alpha$ calculations for the constituent atoms and ions are given in Table 16. For these calculations, the exchange parameter $\alpha$ was optimized to satisfy the virial theorem. This procedure yields a total energy which is in very good agreement with the exact Hartree Fock results. Examination of the energies given in Table 16 shows that s-d hybridization will be very important in TiO owing to the near degeneracy of the orbital energies in Ti. We also see that the $Ti^+O^-$ structure should be dominant for low-lying electronic states of TiO which are compatible with this symmetry. These observations are borne out by the molecular $SCF-X_\alpha$ results for TiO (R = 3.0 a.u.) given in Table 17. The dominant atomic component of each molecular orbital is given in Table 17. For both $(1\delta^2)$ and $(1\delta\,5\sigma)$ configurations, the molecule is predicted to be highly ionic. The closeness of the MO eigenvalues for these different configurations indicates that there should be low-lying $\Sigma$ and $\Delta$ states for this molecule. The experimental data shown in Table 17 are consistent with the predicted $SCF-X_\alpha$ results.

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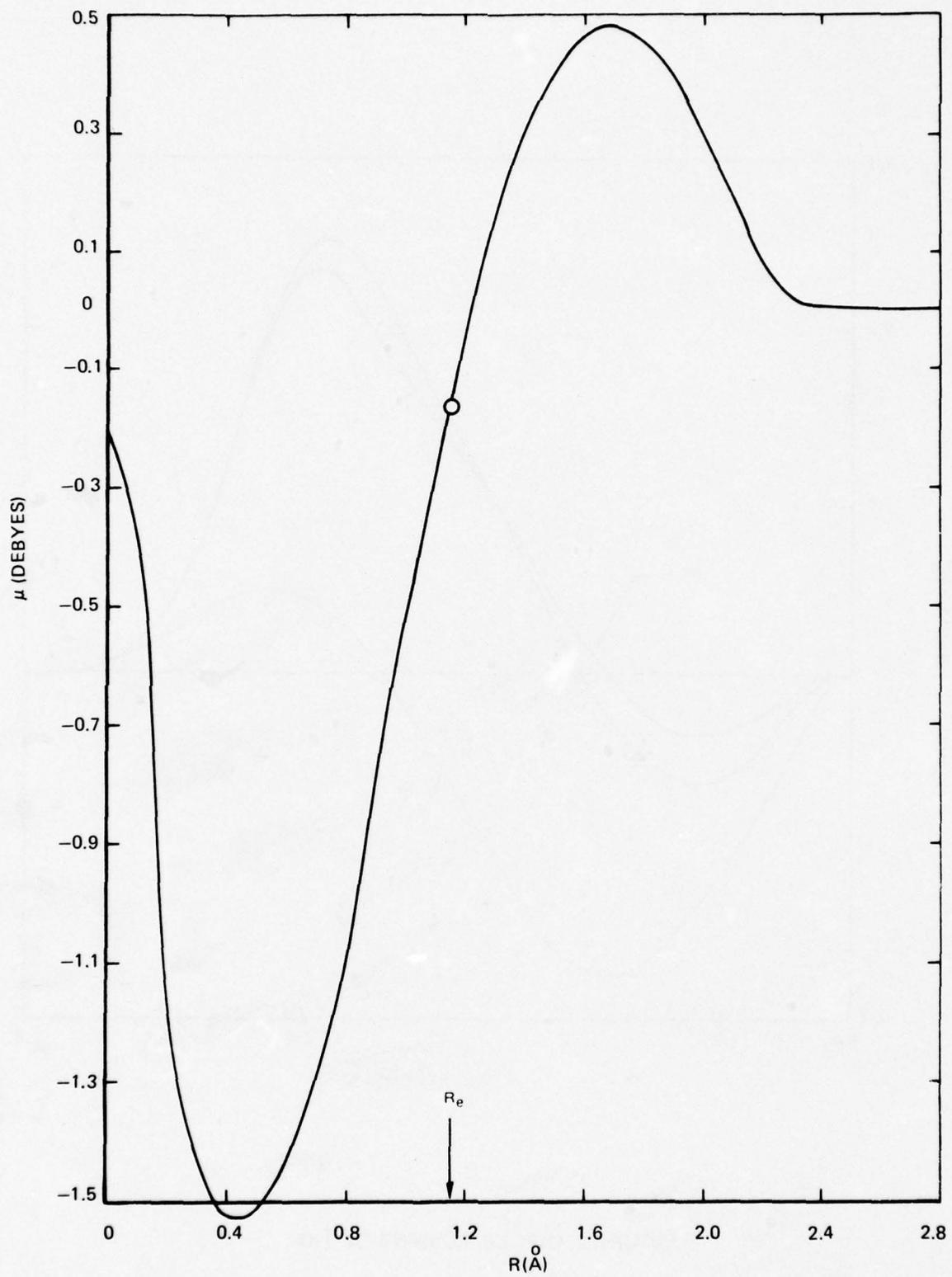
**FIGURE 1. DIPOLE MOMENT OF NO**

35
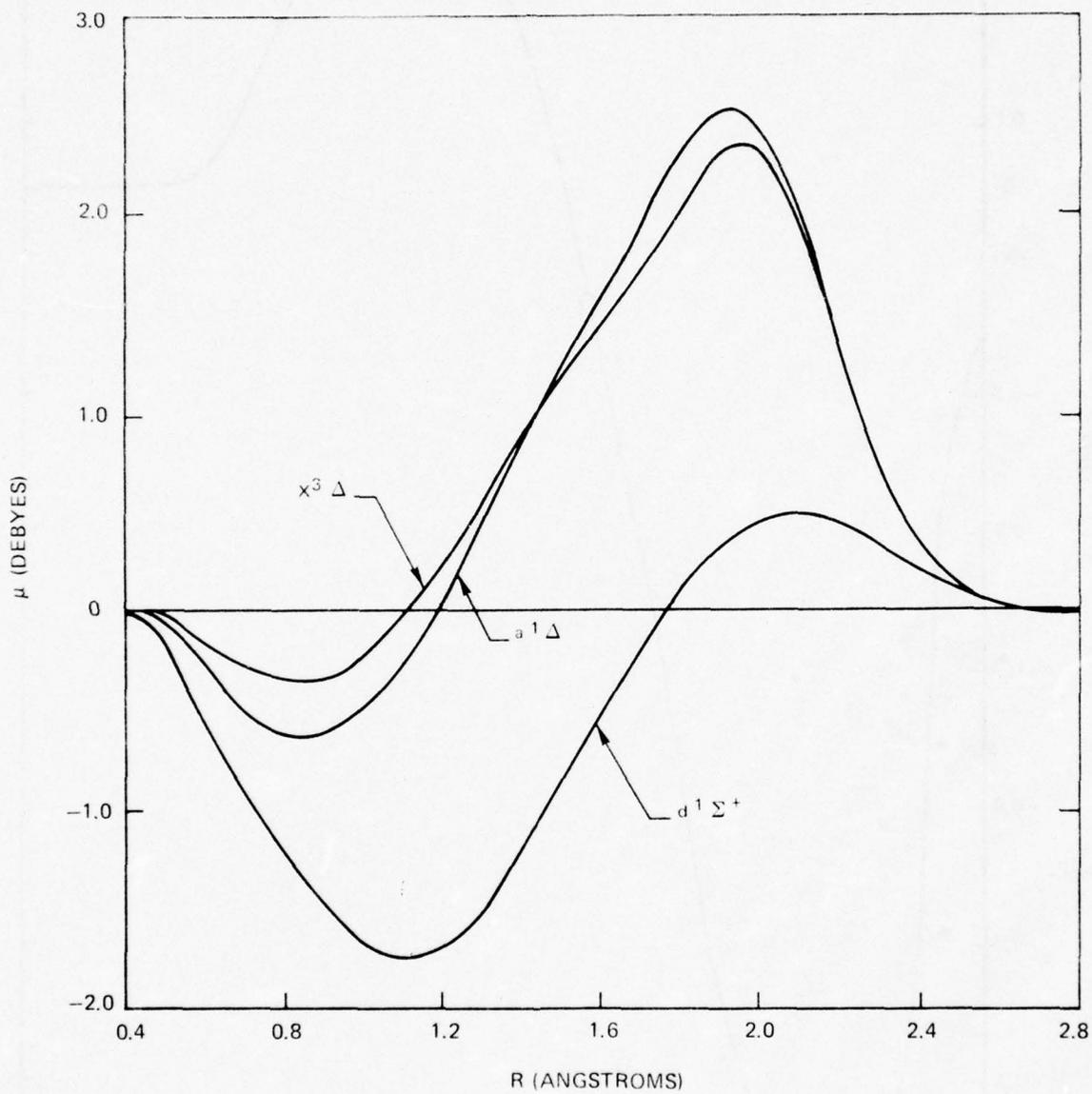
**FIGURE 2. DIPOLE MOMENT OF TiO**
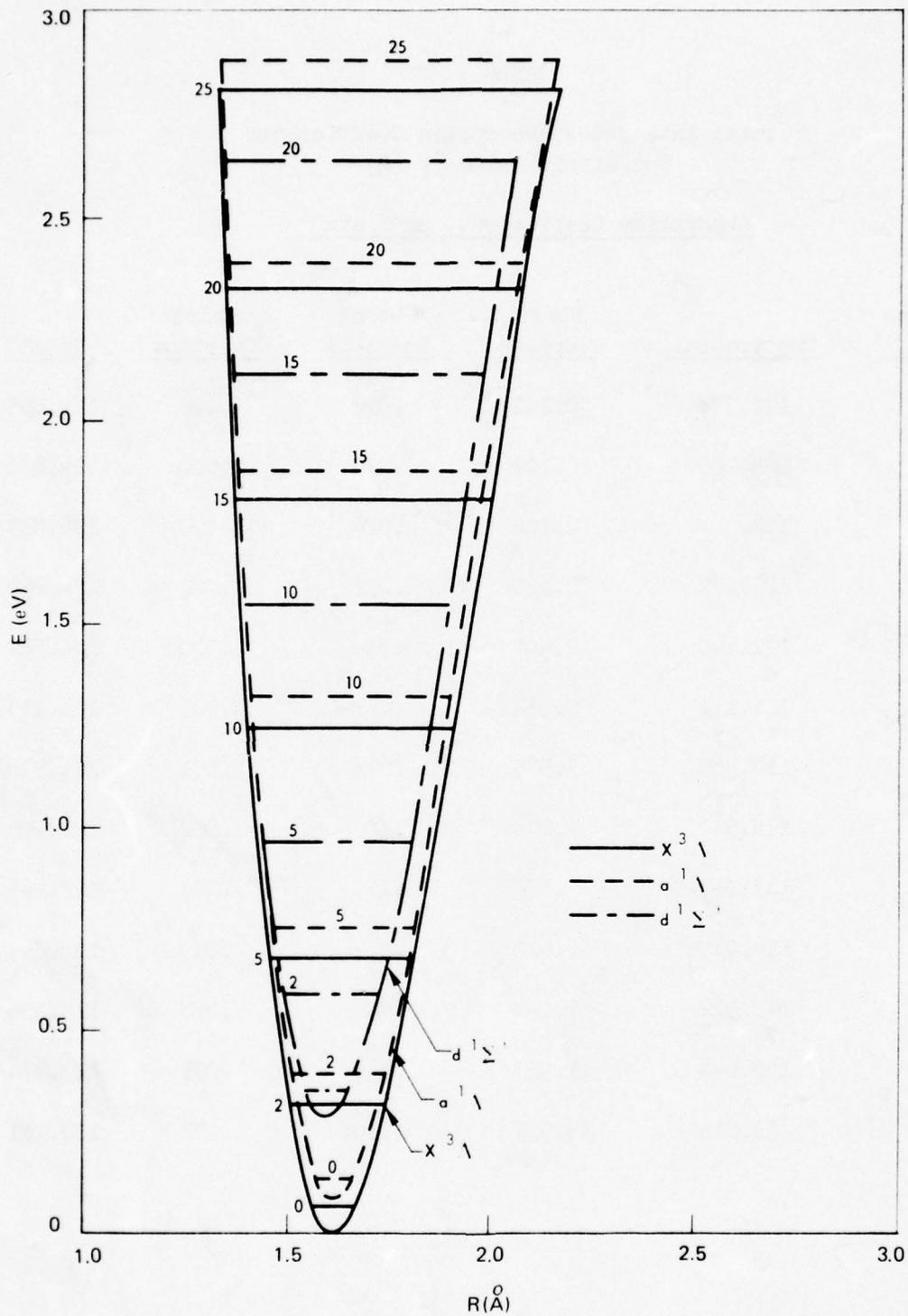
FIGURE 3. RKR POTENTIAL ENGERY CURVES OF TiO

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TABLE 1

Total Integrated Absorption Coefficients
For Nitric Oxide (X $^2\Pi$)

Absorption Coefficient, $cm^{-2}$ $atm^{-1}$

| Temperature ($^\circ K$) | Fundamental | First Overtone | Second Overtone | Third Overtone | Total |
|---|---|---|---|---|---|
| 100. | 122.725 | 2.101 | .029 | .000 | 124.855 |
| 273.16 | 122.725 | 2.102 | .029 | .000 | 124.856 |
| 300. | 122.724 | 2.102 | .029 | .000 | 124.855 |
| 500. | 122.689 | 2.120 | .030 | .000 | 124.839 |
| 1000. | 122.149 | 2.402 | .036 | .000 | 124.587 |
| 1500. | 121.131 | 2.932 | .051 | .001 | 124.115 |
| 2000. | 119.889 | 3.575 | .073 | .001 | 123.538 |
| 2500. | 118.530 | 4.274 | .102 | .002 | 122.908 |
| 3000. | 117.098 | 5.006 | .140 | .004 | 122.248 |
| 4000. | 114.087 | 6.519 | .242 | .009 | 120.857 |
| 5000. | 110.922 | 8.040 | .376 | .018 | 119.356 |
| 8000. | 100.644 | 11.927 | .848 | .055 | 113.474 |
| 10000. | 93.513 | 13.552 | 1.108 | .078 | 108.251 |

TABLE 2

Calculated Oscillator Strengths $(f_{v'v''})$
for the $X\,^2\pi - X\,^2\pi$ System of NO

| v'/v" | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | | | | | | |
| 1 | 5.158-06 | | | | | |
| 2 | 8.831-08 | 9.982-06 | | | | |
| 3 | 1.224-09 | 2.627-07 | 1.447-05 | | | |
| 4 | 1.224-11 | 4.912-09 | 5.222-07 | 1.863-05 | | |
| 5 | 5.076-14 | 7.748-11 | 1.241-08 | 8.660-07 | 2.245-05 | |
| 6 | 1.084-14 | 7.943-14 | 2.676-10 | 2.500-08 | 1.293-06 | 2.593-05 |
| 7 | 7.117-14 | 7.184-15 | 1.310-12 | 6.700-10 | 4.422-08 | 1.799-06 |
| 8 | 9.898-14 | 9.419-14 | 1.203-13 | 8.250-12 | 1.376-09 | 7.182-08 |
| 9 | 1.267-14 | 8.275-14 | 1.117-13 | 4.086-13 | 2.952-11 | 2.526-09 |
| 10 | 1.680-14 | 1.185-14 | 1.884-13 | 8.905-15 | 2.499-13 | 6.758-11 |

| v'/v" | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|
| 0 | | | | | |
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |
| 6 | | | | | |
| 7 | 2.909-05 | | | | |
| 8 | 2.382-06 | 3.191-05 | | | |
| 9 | 1.093-07 | 3.040-06 | 3.441-05 | | |
| 10 | 4.369-09 | 1.581-07 | 3.769-06 | 3.658-05 | |

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TABLE 3

Calculated Einstein Coefficients ($A_{v'v''}$, sec$^{-1}$) for the X $^2\pi$ - X $^2\pi$ System of NO

| v'/v" | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | | | | | | |
| 1 | 1.210 + 01 | | | | | |
| 2 | 8.165 - 01 | 2.273 + 01 | | | | |
| 3 | 2.509 - 02 | 2.357 + 00 | 3.196 + 01 | | | |
| 4 | 4.464 - 04 | 9.762 - 02 | 4.542 + 00 | 3.988 + 01 | | |
| 5 | 2.802 - 06 | 2.696 - 03 | 2.392 - 01 | 7.300 + 00 | 4.656 + 01 | |
| 6 | 8.482 - 07 | 4.251 - 06 | 9.022 - 03 | 4.667 - 01 | 1.056 + 01 | 5.209 + 01 |
| 7 | 7.465 - 06 | 5.450 - 07 | 6.792 - 05 | 2.188 - 02 | 7.994 - 01 | 1.422 + 01 |
| 8 | 1.335 - 05 | 9.573 - 06 | 8.841 - 06 | 4.143 - 04 | 4.352 - 02 | 1.257 + 00 |
| 9 | 2.129 - 06 | 1.081 - 05 | 1.099 - 05 | 2.907 - 05 | 1.435 - 03 | 7.730 - 02 |
| 10 | 3.430 - 06 | 1.927 - 06 | 2.382 - 05 | 8.483 - 07 | 1.720 - 05 | 3.177 - 03 |

| v'/v" | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|
| 0 | | | | | |
| 1 | | | | | |
| 2 | | | | | |
| 3 | | | | | |
| 4 | | | | | |
| 5 | | | | | |
| 6 | | | | | |
| 7 | 5.655 + 01 | | | | |
| 8 | 1.822 + 01 | 6.002 + 01 | | | |
| 9 | 1.850 + 00 | 2.249 + 01 | 6.256 + 01 | | |
| 10 | 1.293 - 01 | 2.588 + 00 | 2.694 + 01 | 6.426 + 01 | |

TABLE 4

Total and $X_\alpha$ Orbital Energies for the Ground $\widetilde{X}\,^2A_1$ State of $NO_2$

| Orbital | Occupancy | Orbital Energy (Ryd.) | |
|---|---|---|---|
| | | 134.1° | 180° |
| $1a_1$ $(1\sigma_g)$ | 2 | -37.9329 | -37.9957 |
| $1b_2$ $(1\sigma_u)$ | 2 | -37.9329 | -37.9957 |
| $2a_1$ $(2\sigma_g)$ | 2 | -28.8059 | -28.8329 |
| $3a_1$ $(3\sigma_g)$ | 2 | - 2.1963 | - 2.2209 |
| $2b_2$ $(2\sigma_u)$ | 2 | - 1.9703 | - 2.0685 |
| $4a_1$ $(4\sigma_g)$ | 2 | - 1.2915 | - 1.3266 |
| $5a_1$ $(1\pi_u)$ | 2 | - 1.0217 | - 1.0690 |
| $3b_2$ $(3\sigma_u)$ | 2 | - 1.1126 | - 1.1571 |
| $1b_1$ $(1\pi_u)$ | 2 | - 1.0396 | - 1.0690 |
| $4b_2$ $(1\pi_g)$ | 2 | - 0.7898 | - 0.8902 |
| $1a_2$ $(1\pi_g)$ | 2 | - 0.8392 | - 0.8902 |
| $6a_1$ $(2\pi_u)$ | 1 | - 0.6177 | - 0.4741 |
| $2b_1$ $(2\pi_u)$ | 0 | - 0.4410 | - 0.4741 |
| $7a_1$ $(5\sigma_g)$ | 0 | - 0.08492 | - |
| $5b_2$ $(4\sigma_u)$ | 0 | - | - |

Total Energy (Rydbergs)    $-403.1783$

$R_{N-O} = 2.2552$ a.u. $(1.1934\ \text{Å})$

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## TABLE 5

Total and $X_\alpha$ Orbital Energies for the First Excited $\tilde{A}\,^2B_1$ State of $NO_2$

| Orbital | Occupancy | Orbital Energy (Ryd.) 134.1° | Orbital Energy (Ryd.) 180° |
|---|---|---|---|
| $1a_1$ $(1\sigma_g)$ | 2 | -37.9180 | -37.9957 |
| $1b_2$ $(1\sigma_u)$ | 2 | -37.9180 | -37.9957 |
| $2a_1$ $(2\sigma_g)$ | 2 | -28.7221 | -28.8329 |
| $3a_1$ $(3\sigma g)$ | 2 | - 2.1755 | - 2.2209 |
| $2b_2$ $(2\sigma_u)$ | 2 | - 1.9539 | - 2.0685 |
| $4a_1$ $(4\sigma_g)$ | 2 | - 1.2720 | - 1.3266 |
| $5a_1$ $(1\pi_u)$ | 2 | - 1.0012 | - 1.0690 |
| $3b_2$ $(3\sigma_u)$ | 2 | - 1.0945 | - 1.1571 |
| $1b_1$ $(1\pi_u)$ | 2 | - 1.0192 | - 1.0690 |
| $4b_2$ $(1\pi_g)$ | 2 | - 0.7784 | - 0.8902 |
| $1a_2$ $(1\pi_g)$ | 2 | - 0.8284 | - 0.8902 |
| $6a_1$ $(2\pi_u)$ | 0 | - 0.5968 | - 0.4741 |
| $2b_1$ $(2\pi_u)$ | 1 | - 0.4143 | - 0.4741 |
| $7a_1$ $(5\sigma_g)$ | 0 | - 0.07899 | - |
| $5b_2$ $(4\sigma_u)$ | 0 | - | - |

Total Energy (Rydbergs)  -402.9990

$R_{N-O}$ = 2.2552 a.u. (1.1934 Å)

TABLE 6

MOLECULAR ORBITAL BASIS FOR TiO

| Molecular Orbital | Screening Parameters for Atomic Orbitals | |
|---|---|---|
| $1\sigma$ | 1s (Ti) | 21.4409 |
| $2\sigma$ | 2s (Ti) | 7.6883 |
| $3\sigma$ | 1s (0) | 7.6579 |
| $1\pi^{+,-}$ | $2p\pi^{+,-}$ (Ti) | 9.0324 |
| $4\sigma$ | $2p\sigma$ (Ti) | 9.0324 |
| $5\sigma$ | 3s (Ti) | 3.6777 |
| $2\pi^{+,-}$ | $3p\pi^{+,-}$ (Ti) | 3.3679 |
| $6\sigma$ | $3p\sigma$ (Ti) | 3.3679 |
| $7\sigma$ | 2s (0) | 2.2187 |
| $3\pi^{+,-}$ | $2p\pi^{+,-}$ (0) | 2.0885 |
| $8\sigma$ | $2p\sigma$ (0) | 2.2214 |
| $9\sigma$ | 4s (Ti) | 1.3973 |
| $4\pi^{+,-}$ | $3d\pi^{+,-}$ (Ti) | 2.2035 |
| $10\sigma$ | $3d\sigma$ (Ti) | 2.8021 |
| $11\sigma$ | $4p\sigma$ (Ti) | 1.0852 |
| $1\delta^{+}$ | $3d\delta^{+}$ (Ti) | 2.7000 |

## TABLE 7

### SPECTROSCOPIC DATA FOR TiO

|  | $X\,^3\Delta$ | $a\,^1\Delta$ | $d\,^1\Sigma^+$ |
|---|---|---|---|
| $\omega_e$ (cm$^{-1}$) | 1008.2 | 1016.3 | 1023.8 |
| $\omega_e X_e$ (cm$^{-1}$) | 4.13 | 3.93 | 4.60 |
| $\alpha_e$ (cm$^{-1}$) | 0.003 | - | 0.00337 |
| $T_e$ (cm$^{-1}$) | 0.00 | 580. | 2802.3 |
| $r_e$ (Å) | 1.620 | 1.619 | 1.600 |

TABLE 8

VALUES OF $\Delta G(v)$ FOR THE X $^3\Delta$ STATE OF TiO

$$\Delta G(v), \text{ cm}^{-1}$$

| v | Calculated | Experimental |
|---|---|---|
| 0 | | |
| | 999.08 | 999.18 |
| 1 | | |
| | 989.86 | 989.96 |
| 2 | | |
| | 980.64 | 980.74 |
| 3 | | |
| | 971.42 | 971.52 |
| 4 | | |
| | 962.20 | 962.30 |
| 5 | | |
| | 952.99 | 953.08 |
| 6 | | |
| | 943.77 | 943.86 |
| 7 | | |
| | 934.55 | 934.64 |
| 8 | | |
| | 925.33 | 925.42 |
| 9 | | |
| | 916.11 | 916.20 |
| 10 | | |
| | 906.89 | 906.98 |
| 11 | | |
| | 897.67 | 897.76 |
| 12 | | |
| | 888.46 | 888.54 |
| 13 | | |
| | 879.24 | 879.32 |
| 14 | | |
| | 870.03 | 870.10 |
| 15 | | |
| | 860.84 | 860.88 |
| 16 | | |
| | 851.65 | 851.66 |
| 17 | | |
| | 842.48 | 842.44 |
| 18 | | |
| | 833.29 | 833.22 |
| 19 | | |
| | 824.00 | 824.00 |
| 20 | | |

## TABLE 9

### Values of $\Delta G(v)$ for the a $^1\Delta$ State of TiO

| V | $\Delta G(v)$, cm$^{-1}$ | |
|---|---|---|
| | Calculated | Experimental |
| 0 | | |
| | 999.07 | 999.18 |
| 1 | | |
| | 989.86 | 989.96 |
| 2 | | |
| | 980.64 | 980.74 |
| 3 | | |
| | 971.42 | 971.52 |
| 4 | | |
| | 962.20 | 962.30 |
| 5 | | |
| | 952.98 | 953.08 |
| 6 | | |
| | 943.76 | 943.86 |
| 7 | | |
| | 934.54 | 934.64 |
| 8 | | |
| | 925.32 | 925.42 |
| 9 | | |
| | 916.10 | 916.20 |
| 10 | | |
| | 906.89 | 906.98 |
| 11 | | |
| | 897.67 | 897.76 |
| 12 | | |
| | 888.45 | 888.54 |
| 13 | | |
| | 879.24 | 879.32 |
| 14 | | |
| | 870.03 | 870.10 |
| 15 | | |
| | 860.83 | 860.88 |
| 16 | | |
| | 851.65 | 851.66 |
| 17 | | |
| | 842.47 | 842.44 |
| 18 | | |
| | 833.28 | 833.22 |
| 19 | | |
| | 824.00 | 824.00 |
| 20 | | |

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# TABLE 10

## Values of $\Delta G(v)$ for the d $^1\Sigma^+$ State of TiO

| V | $\Delta G(v)$, cm$^{-1}$ | |
|---|---|---|
| | Calculated | Experimental |
| 0 | 1014.50 | 1014.60 |
| 1 | 1005.30 | 1005.40 |
| 2 | 996.10 | 996.20 |
| 3 | 986.90 | 987.00 |
| 4 | 977.70 | 977.80 |
| 5 | 968.50 | 968.60 |
| 6 | 959.30 | 959.40 |
| 7 | 950.10 | 950.20 |
| 8 | 940.91 | 941.00 |
| 9 | 931.71 | 931.80 |
| 10 | 922.51 | 922.60 |
| 11 | 913.31 | 913.40 |
| 12 | 904.11 | 904.20 |
| 13 | 894.92 | 895.00 |
| 14 | 885.73 | 885.80 |
| 15 | 876.55 | 876.60 |
| 16 | 867.39 | 867.40 |
| 17 | 858.22 | 858.20 |
| 18 | 849.03 | 849.00 |
| 19 | 839.71 | 839.00 |
| 20 | | |

## TABLE 11

## CALCULATED OSCILLATOR STRENGTHS FOR THE d $^1\Sigma^+$ STATE OF TiO

| Vibrational Level $v_i''$ | Oscillator Strengths | | |
| | Fundamental $f_{v_i''\, v_{i+1}''}$ | First Overtone $f_{v_i''\, v_{i+2}''}$ | Second Overtone $f_{v_i''\, v_{i+3}''}$ |
| --- | --- | --- | --- |
| 0 | 5.5755-06 | 1.5557-07 | 1.2650-08 |
| 1 | 1.1168-05 | 3.5349-07 | 1.8265-08 |
| 2 | 1.6366-05 | 5.9584-07 | 3.4928-08 |
| 3 | 2.1455-05 | 8.9794-07 | 5.4611-08 |
| 4 | 2.6323-05 | 1.2172-06 | 7.7966-08 |
| 5 | 3.1000-05 | 1.5784-06 | 1.1186-07 |
| 6 | 3.5571-05 | 1.9583-06 | 1.5172-07 |
| 7 | 4.0003-05 | 2.3302-06 | 2.0841-07 |
| 8 | 4.4428-05 | 2.6893-06 | 2.8511-07 |
| 9 | 4.8901-05 | 3.0266-06 | 3.6192-07 |
| 10 | 5.3289-05 | 3.4039-06 | 4.1975-07 |
| 11 | 5.7441-05 | 3.8751-06 | 4.5915-07 |
| 12 | 6.1304-05 | 4.4077-06 | 4.8956-07 |
| 13 | 6.4902-05 | 5.0183-06 | 5.0251-07 |
| 14 | 6.8135-05 | 5.7662-06 | 4.9720-07 |
| 15 | 7.0919-05 | 6.6452-06 | 4.7758-07 |
| 16 | 7.3209-05 | 7.6988-06 | 4.4484-07 |
| 17 | 7.4933-05 | 8.9354-06 | 4.2136-07 |
| 18 | 7.6193-05 | 1.0302-05 | --- |
| 19 | 7.6999-05 | --- | --- |

TABLE 12

CALCULATED OSCILLATOR STRENGTHS FOR THE a $^1\Delta$ STATE OF TiO

| Vibrational Level $v_i''$ | Oscillator Strengths | | |
|---|---|---|---|
| | Fundamental $f_{v_i''\ v_{i+1}''}$ | First Overtone $f_{v_i''\ v_{i+2}''}$ | Second Overtone $f_{v_i''\ v_{i+3}''}$ |
| 0 | 1.1207-05 | 2.3931-08 | 2.1780-08 |
| 1 | 2.0939-05 | 9.0683-08 | 3.6472-08 |
| 2 | 3.0069-05 | 2.6922-07 | 4.5842-08 |
| 3 | 3.8578-05 | 5.6097-07 | 6.4891-08 |
| 4 | 4.6191-05 | 9.8934-07 | 7.9385-08 |
| 5 | 5.3084-05 | 1.6057-06 | 9.0295-08 |
| 6 | 5.9200-05 | 2.3986-06 | 1.0172-07 |
| 7 | 6.4459-05 | 3.3893-06 | 1.0573-07 |
| 8 | 6.8966-05 | 4.6243-06 | 1.0831-07 |
| 9 | 7.2611-05 | 6.1313-06 | 1.1630-07 |
| 10 | 7.5251-05 | 7.9724-06 | 1.2327-07 |
| 11 | 7.6932-05 | 1.0190-05 | 1.2821-07 |
| 12 | 7.7644-05 | 1.2819-05 | 1.3755-07 |
| 13 | 7.7273-05 | 1.5962-05 | 1.5093-07 |
| 14 | 7.5802-05 | 1.9733-05 | 1.6950-07 |
| 15 | 7.3198-05 | 2.4213-05 | 1.8893-07 |
| 16 | 6.9525-05 | 2.9338-05 | 1.8572-07 |
| 17 | 6.5103-05 | 3.4958-05 | 1.5075-07 |
| 18 | 6.0153-05 | 4.1027-05 | --- |
| 19 | 5.4689-05 | --- | --- |

## TABLE 13

## CALCULATED OSCILLATOR STRENGTHS FOR THE X $^3\Delta$ STATE OF TiO

| Vibrational Level $v_i"$ | Oscillator Strengths | | |
| | Fundamental $f_{v_i" \, v_{i+1}"}$ | First Overtone $f_{v_i" \, v_{i+2}"}$ | Second Overtone $f_{v_i" \, v_{i+3}"}$ |
|---|---|---|---|
| 0 | 6.2728-06 | 2.3090-08 | 3.2107-09 |
| 1 | 1.2008-05 | 7.5950-08 | 4.9075-09 |
| 2 | 1.7478-05 | 1.8398-07 | 5.2048-09 |
| 3 | 2.2688-05 | 3.4581-07 | 6.4569-09 |
| 4 | 2.7544-05 | 5.6595-07 | 6.4473-09 |
| 5 | 3.2114-05 | 8.5388-07 | 4.6627-09 |
| 6 | 3.6440-05 | 1.1848-05 | 1.7328-09 |
| 7 | 4.0595-05 | 1.5353-06 | 8.1605-13 |
| 8 | 4.4660-05 | 1.9303-06 | 8.7433-10 |
| 9 | 4.8409-05 | 2.4578-06 | 2.8862-10 |
| 10 | 5.1484-05 | 3.1944-06 | 3.0370-10 |
| 11 | 5.3870-05 | 4.1391-06 | 3.5653-09 |
| 12 | 5.5589-05 | 5.3614-06 | 1.6738-08 |
| 13 | 5.6373-05 | 6.9961-06 | 4.8901-08 |
| 14 | 5.6142-05 | 9.1306-06 | 1.1064-07 |
| 15 | 5.4827-05 | 1.1917-05 | 2.0735-07 |
| 16 | 5.2437-05 | 1.5308-05 | 2.9964-07 |
| 17 | 4.9356-05 | 1.9176-05 | 3.6017-07 |
| 18 | 4.5746-05 | 2.3524-05 | --- |
| 19 | 4.1644-05 | --- | --- |

## TABLE 14

## POPULATION DENSITIES FOR THE X $^3\Delta$, a $^1\Delta$ AND d $^1\Sigma^+$ STATES OF TiO

| T (°K) | Vibrational Level | Population Density | | |
|--------|-------------------|---------|---------|---------|
| | | X $^3\Delta$ | a $^1\Delta$ | d $^1\Sigma^+$ |
| 273.16 | 0 | 9.79513-01 | 1.53049-02 | 9.10078-07 |
| | 1 | 5.07401-03 | 7.92817-05 | 4.34702-09 |
| 300. | 0 | 9.71734-01 | 1.99653-02 | 2.66473-06 |
| | 1 | 8.06081-03 | 1.65618-04 | 2.05310-08 |
| | 2 | 6.98899-05 | 1.43596-06 | 1.65337-10 |
| | 3 | 6.33366-07 | 1.30131-08 | 1.39166-12 |
| 500. | 0 | 8.87709-01 | 5.55980-02 | 1.99469-04 |
| | 1 | 5.00691-02 | 3.13587-03 | 1.07629-05 |
| | 2 | 2.89996-03 | 1.81627-04 | 5.96353-07 |
| | 3 | 1.72479-04 | 1.08025-05 | 3.39314-08 |
| | 4 | 1.05342-05 | 6.59766-07 | 1.98254-09 |
| 1000. | 0 | 6.61852-01 | 9.56300-02 | 4.05030-03 |
| | 1 | 1.57185-01 | 2.27114-02 | 9.40835-04 |
| | 2 | 3.78287-02 | 5.46581-03 | 2.21463-04 |
| | 3 | 9.22557-03 | 1.33299-03 | 5.28263-05 |
| | 4 | 2.27996-03 | 3.29427-04 | 1.27691-05 |
| | 5 | 5.70980-04 | 8.25000-05 | 3.12775-06 |
| | 6 | 1.44903-04 | 2.09368-05 | 7.76364-07 |
| | 7 | 3.72643-05 | 5.38427-06 | 1.95281-07 |
| | 8 | 9.71117-06 | 1.40315-06 | 4.97754-08 |
| 1500. | 0 | 5.08061-01 | 9.69984-02 | 9.35441-03 |
| | 1 | 1.94842-01 | 3.71990-02 | 3.53482-03 |
| | 2 | 7.53858-02 | 1.43926-02 | 1.34759-03 |
| | 3 | 2.94264-02 | 5.61805-03 | 5.18313-04 |
| | 4 | 1.15885-02 | 2.21246-03 | 2.01125-04 |
| | 5 | 4.60422-03 | 8.79031-04 | 7.87372-05 |
| | 6 | 1.84555-03 | 3.52350-04 | 3.10982-05 |
| | 7 | 7.46342-04 | 1.42491-04 | 1.23917-05 |
| | 8 | 3.04502-04 | 5.81351-05 | 4.98159-06 |
| | 9 | 1.25338-04 | 2.39294-05 | 2.02044-06 |
| | 10 | 5.20495-05 | 9.93722-06 | 8.26731-07 |
| | 11 | 2.18068-05 | 4.16332-06 | 3.41290-07 |

TABLE 14 (Cont'd)

Population Density

| T (°K) | Vibrational Level | X $^3\Delta$ | a $^1\Delta$ | d $^1\Sigma^+$ |
|--------|-------------------|--------------|--------------|----------------|
| 2000. | 0 | 4.07242-01 | 8.93735-02 | 1.30059-02 |
| | 1 | 1.98462-01 | 4.35545-02 | 6.26835-03 |
| | 2 | 9.73605-02 | 2.13668-02 | 3.04122-03 |
| | 3 | 4.80805-02 | 1.05518-02 | 1.48533-03 |
| | 4 | 2.39021-02 | 5.24555-03 | 7.30259-04 |
| | 5 | 1.19614-02 | 2.62506-03 | 3.61420-04 |
| | 6 | 6.02574-03 | 1.32241-03 | 1.80065-04 |
| | 7 | 3.05576-03 | 6.70618-04 | 9.03080-05 |
| | 8 | 1.55994-03 | 3.42345-04 | 4.55936-05 |
| | 9 | 8.01637-04 | 1.75927-04 | 2.31719-05 |
| | 10 | 4.14694-04 | 9.10089-05 | 1.18550-05 |
| | 11 | 2.15953-04 | 4.73931-05 | 6.10549-06 |
| | 12 | 1.13206-04 | 2.48443-05 | 3.16534-06 |
| | 13 | 5.97396-05 | 1.31105-05 | 1.65197-06 |
| | 14 | 3.17348-05 | 6.96452-06 | 8.67886-07 |
| | 15 | 1.69703-05 | 3.72430-06 | 4.58991-07 |
| 2500. | 0 | 3.37858-01 | 8.06111-02 | 1.50153-02 |
| | 1 | 1.90105-01 | 4.53581-02 | 8.37423-03 |
| | 2 | 1.07537-01 | 2.56578-02 | 4.69526-03 |
| | 3 | 6.11543-02 | .1.45911-02 | 2.64655-03 |
| | 4 | 3.49623-02 | 8.34183-03 | 1.49970-03 |
| | 5 | 2.00945-02 | 4.79445-03 | 8.54343-04 |
| | 6 | 1.16108-02 | 2.77026-03 | 4.89289-04 |
| | 7 | 6.74446-03 | 1.60919-03 | 2.81710-04 |
| | 8 | 3.93857-03 | 9.39721-04 | 1.63059-04 |
| | 9 | 2.31225-03 | 5.51690-04 | 9.48837-05 |
| | 10 | 1.36469-03 | 3.25608-04 | 5.55064-05 |
| | 11 | 8.09728-04 | 1.93197-04 | 3.26436-05 |
| | 12 | 4.83002-04 | 1.15242-04 | 1.93000-05 |
| | 13 | 2.89642-04 | 6.91071-05 | 1.14716-05 |
| | 14 | 1.74615-04 | 4.16621-05 | 6.85476-06 |
| | 15 | 1.05829-04 | 2.52501-05 | 4.11780-06 |
| | 16 | 6.44808-05 | 1.53848-05 | 2.48682-06 |
| | 17 | 3.94968-05 | 9.42373-06 | 1.50982-06 |
| 3000. | 0 | 2.87715-01 | 7.25815-02 | 1.59381-02 |
| | 1 | 1.78174-01 | 4.49479-02 | 9.79743-03 |
| | 2 | 1.10828-01 | 2.79584-02 | 6.04934-03 |
| | 3 | 6.92425-02 | 1.74677-02 | 3.75167-03 |

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TABLE 14 (Cont'd)

| T (°K) | Vibrational Level | Population Density | | |
|---|---|---|---|---|
| | | $X\ ^3\Delta$ | $a\ ^1\Delta$ | $d\ ^1\Sigma^+$ |
| 3000. | 4 | 4.34528-02 | 1.09618-02 | 2.33701-03 |
| | 5 | 2.73894-02 | 6.90949-03 | 1.46224-03 |
| | 6 | 1.73407-02 | 4.37453-03 | 9.18959-04 |
| | 7 | 1.10274-02 | 2.78187-03 | 5.80088-04 |
| | 8 | 7.04367-03 | 1.77690-03 | 3.67801-04 |
| | 9 | 4.51903-03 | 1.14001-03 | 2.34235-04 |
| | 10 | 2.91214-03 | 7.34642-04 | 1.49834-04 |
| | 11 | 1.88495-03 | 4.75514-04 | 9.62699-05 |
| | 12 | 1.22548-03 | 3.09151-04 | 6.21284-05 |
| | 13 | 8.00268-04 | 2.01883-04 | 4.02727-05 |
| | 14 | 5.24909-04 | 1.32418-04 | 2.62212-05 |
| | 15 | 3.45822-04 | 8.72402-05 | 1.71480-05 |
| | 16 | 2.28845-04 | 5.77306-05 | 1.12641-05 |
| | 17 | 1.52108-04 | 3.83721-05 | 7.43185-05 |
| | 18 | 1.01551-04 | 2.56180-05 | 4.92515-06 |
| | 19 | 6.80978-05 | 1.71789-05 | 3.27840-06 |

TABLE 15

INTEGRATED ABSORPTION COEFFICIENTS FOR TiO

| T (°K) | $S_{Total}$ (cm$^{-2}$ atm$^{-1}$) | $S^*_{Total}$ (cm$^{-2}$ atm$^{-1}$) |
|--------|------------------------------------|--------------------------------------|
| 273.16 | 145.86 | 145.86 |
| 300.   | 146.77 | 133.64 |
| 500.   | 155.42 | 84.91  |
| 1000.  | 161.25 | 44.05  |
| 1500.  | 160.23† | 18.25 |
| 2000.  | 157.39 | 21.49  |
| 2500.  | 154.69 | 16.90  |
| 3000.  | 153.51 | 13.98  |

$S_{Total} = \sum_i S_{i,i+1}$ where the summation extends over all populated fundamental bands.

$S^*_{Total} = S_{Total} \times \left[\frac{273.16}{T(K°)}\right]$ = density corrected absorption coefficient.

†The absorption coefficient should normally increase as temperature increases. The decrease shown from 1500°K to 3000°K is probably due to small errors in the relative dipole moment functions for X $^3\Delta$, a$^1\Delta$ and d $^1\Sigma^+$ states of TiO.

## TABLE 16: SCF-X$_\alpha$ RESULTS FOR ATOMIC SPECIES

| SPECIES | ORBITAL | OCCUPATION | ORBITAL ENERGY (Ryd.) |
|---|---|---|---|
| Ti ($4d^2 6s^2$ - non rel.) | 1s | 2 | -355.3260 |
| Total Energy: | 2s | 2 | - 39.0396 |
| -1696.6824 Ryd. | 2p | 6 | - 32.7064 |
| | 3s | 2 | - 4.4908 |
| | 3p | 6 | - 2.8168 |
| | 3d | 2 | - 0.2968 |
| | 4s | 2 | - 0.2880 |
| | | | |
| Ti ($4d^2 6s^2$ - rel.) | 1s | 2 | -356.6870 |
| Total Energy: | 2s$_*$ | 2 | - 39.2258 |
| -1699.9234 Ryd. | 2p$^*$ | 2 | - 32.7804 |
| | 2p | 4 | - 32.3576 |
| | 3s$_*$ | 2 | - 4.4802 |
| | 3p$^*$ | 2 | - 2.7890 |
| | 3p$_*$ | 4 | - 2.7402 |
| | 3d$^*$ | 2 | - 0.2446 |
| | 3d | 0 | - 0.2414 |
| | 4s | 2 | - 0.2732 |
| | | | |
| Ti$^+$ ($4d^2 6s$ - non rel.) | 1s | 2 | -355.8690 |
| Total Energy: | 2s | 2 | - 39.5728 |
| -1696.1808 Ryd. | 2p | 6 | - 33.2406 |
| | 3s | 2 | - 5.0270 |
| | 3p | 6 | - 3.3526 |
| | 3d | 2 | - 0.8198 |
| | 4s | 1 | - 0.7244 |
| | | | |
| O ($2p^4$ - non rel.) | 1s | 2 | - 37.8192 |
| Total Energy: | 2s | 2 | - 1.7304 |
| -149.5210 Ryd. | 2p | 4 | - 0.6556 |

TABLE 17:   SCF-X$_\alpha$ ORBITAL ENERGIES FOR TiO

|  | ORBITAL | OCCUPATION | ORBITAL ENERGY (Ryd.) |
|---|---|---|---|
| TiO ($1\delta^2$) $^{1,3}\Sigma^+$, $^1\Gamma$ (ave.) R=3.0 a.u. | Ti (1s) | 2 | -355.3052 |
|  | Ti (2s) | 2 | - 39.0229 |
|  | O (1s) | 2 | - 38.1172 |
|  | Ti (2p) | 6 | - 32.6894 |
|  | 1σ(Ti-3s) | 2 | - 4.5036 |
|  | 2σ(Ti-3p) | 2 | - 2.8475 |
|  | 3σ(O-2s) | 2 | - 1.1362 |
|  | 4σ(O-2p) | 2 | - 0.4239 |
|  | 5σ(Ti-4s) | 0 | - |
|  | 1π(Ti-3p) | 4 | - 2.8357 |
|  | 2π(O-2p) | 4 | - 0.5093 |
|  | 3π(Ti-3d) | 0 | - |
|  | 1δ(Ti-3d) | 2 | - 0.3617 |
| TiO ($1\delta 5\sigma$) $^{1,3}\Delta$ (ave.) R=3.0 a.u. | Ti (1s) | 2 | -355.2238 |
|  | Ti (2s) | 2 | - 38.9438 |
|  | O (1s) | 2 | - 38.3109 |
|  | Ti (2p) | 6 | - 32.6097 |
|  | 1σ(Ti-3s) | 2 | - 4.4467 |
|  | 2σ(Ti-3p) | 2 | - 2.7952 |
|  | 3σ(O-2s) | 2 | - 1.1849 |
|  | 4σ(O -2p) | 2 | - 0.4101 |
|  | 5σ(Ti-4s) | 1 | - 0.3161 |
|  | 1π(Ti-3p) | 4 | - 2.7818 |
|  | 2π(O-2p) | 4 | - 0.5196 |
|  | 3π(Ti-3d) | 0 | - |
|  | 1δ(Ti-3d) | 1 | - 0.3259 |

APPENDIX I

CALCULATION OF ENERGETICS OF
SELECTED ATMOSPHERIC SYSTEMS

Theoretical Methods

H. Harvey Michels
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30 September 1974

Scientific Report No. 1

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AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
HANSCOM AFB, MASSACHUSETTS    01731

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# THEORETICAL METHODS

APPENDIX II

CALCULATION OF ENERGETICS OF
SELECTED ATMOSPHERIC SYSTEMS

Theoretical Study of Dissociative - Recombination of $e + NO^+$

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30 September 1975

Scientific Report No. 2

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
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ABSTRACT

Calculations have been performed for the kinetics of the dissociative-recombination of an electron and the positive ion of nitric oxide. Electronic wavefunctions have been constructed for selected dissociating states of NO and expectation values of the electronic energy and electronic transition matrix elements have been calculated. The electronic wavefunctions for NO were analyzed to determine those states responsible for dissociative-recombination. States of $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ symmetry are found to be the most important channels for this reaction. Calculations are presented for the dissociation-recombination cross-sections as a function of electron energy and vibrational state of the molecular ion. These data are also reduced to kinetic rate constants as a function of the electron temperature and ion vibrational temperature, assuming independent Boltzmann distribution functions. We find a calculated temperature dependence of $T_e^{-.39}$ for the rate coefficient with branching primarily into $N\ ^2D + O\ ^3P$.

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