

Chapter 3

Ab initio calculations for N_2^{q+} and CO^{q+}

A common and very convenient tool for the description of electronic states of a diatomic system is the potential energy curve. Such curves can be used as a starting point for a discussion of a large number of properties. With the advancement in computational techniques and facilities *ab initio* calculations are now possible not only for the simplest two body systems but also for more complex and chemically important species. In this chapter a theoretical discussion on the dissociation dynamics of multiply charged N_2^{q+} and CO^{q+} ions is presented using *ab initio* methods.

3.1 Overview of *ab initio* methods

The term *ab-initio* means calculations from first principles, in this case it means the solution of the time-independent Schrödinger equation

$$\mathcal{H}_{total}\psi_{total} = E_{total}\psi_{total} \quad (3.1)$$

where ψ_{total} is a total wavefunction for all particles in the molecule, and E_{total} is the total energy of the system. For a molecule with N nuclei and n electrons

the Hamiltonian is

$$\begin{aligned} \hat{\mathcal{H}}_{total} = & - \sum_{k=1}^N \frac{1}{2M_k} \nabla_k^2 + \sum_{k>k'}^N \frac{Z_k Z_{k'}}{|\vec{R}_k - \vec{R}_{k'}|} - \sum_{i=1}^n \frac{1}{2} \nabla_i^2 \\ & - \sum_{k=1}^N \sum_{i=1}^n \frac{Z_k}{|\vec{R}_k - \vec{r}_i|} + \sum_{i>j}^n \frac{1}{|\vec{r}_i - \vec{r}_j|} \end{aligned} \quad (3.2)$$

in atomic units, where M_k , Z_k and \vec{R}_k are the mass, charge and the position vector, respectively, of the k th nucleus; \vec{r}_i is the position of i th electron [1].

As the nuclei are thousands of times more massive than the electrons, they move much slower compared to the electrons. Therefore it is reasonable to assume that the electrons adjust themselves to new nuclear positions much faster than the nuclei can adjust to new electronic positions. We can therefore assume that the electronic motion at any instant is just as it would be if the nuclei were at rest at the position they occupy at that instant. This separation of electronic and nuclear motion is known as the Born-Oppenheimer approximation. We then need to consider only that part of the Hamiltonian which depends on the position but not on the momenta of the nuclei. This is the electronic Hamiltonian operator $\hat{\mathcal{H}}_{el}$

$$\hat{\mathcal{H}}_{el} = \sum_{i=1}^n \hat{h}_i + \sum_{i>j}^n \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (3.3)$$

where

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{k=1}^N \frac{Z_k}{|\vec{R}_k - \vec{r}_i|} \quad (3.4)$$

The modified Schrödinger equation then becomes

$$\hat{\mathcal{H}}_{el} \psi_{el} = E_{el} \psi_{el} \quad (3.5)$$

where E_{el} is the electronic energy and ψ_{el} is the wavefunction for all electrons in the field of *fixed* nuclei. The total potential energy of the system for a given, fixed, nuclear configuration is then

$$E_{pot}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N) = E_{el} + \sum_{k>k'}^N \frac{Z_k Z_{k'}}{|\vec{R}_k - \vec{R}_{k'}|} \quad (3.6)$$

Since the second term is a constant for given, fixed, nuclear configuration, the problem reduces to solving for E_{el} and ψ_{el} , hereafter denoted by ψ and E respectively.

For an n -electron system we associate the n electrons with an orthonormal set of one-electron functions $\tilde{\psi}_1, \tilde{\psi}_2, \dots, \tilde{\psi}_n$, called spin orbitals. Each $\tilde{\psi}_i$ is assumed to have the form

$$\tilde{\psi}_i(\vec{r}, \sigma) = \psi_i(\vec{r})\chi_i(\sigma) \quad (3.7)$$

in which the orbital $\psi_i(\vec{r})$ describes the motion of electrons in space and the spin function $\chi_i(\sigma)$ describes its spin state. Being fermions, the total n electron wavefunction is the antisymmetrized product of one-electron wavefunctions, given in the form of a determinant (the Slater determinant):

$$\Phi = (n!)^{-1/2} \begin{vmatrix} \tilde{\psi}_1(1) & \tilde{\psi}_2(1) & \dots & \tilde{\psi}_n(1) \\ \tilde{\psi}_1(2) & \tilde{\psi}_2(2) & \dots & \tilde{\psi}_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{\psi}_1(n) & \tilde{\psi}_2(n) & \dots & \tilde{\psi}_n(n) \end{vmatrix} \quad (3.8)$$

If we substitute the above wave function in the expression for energy we get

$$E = \frac{\int \Phi^* \hat{\mathcal{H}} \Phi d\tau}{\int \Phi^* \Phi d\tau} = \sum_{i=1}^n h_i + \frac{1}{2} \sum_{i,j}^n J_{i,j} - \frac{1}{2} \sum_{i,j}^n K_{i,j} \quad (3.9)$$

where the orbital energies h_i , the Coulomb integrals $J_{i,j}$ and the exchange integrals $K_{i,j}$ are defined by

$$h_i = \int \psi_i^*(\vec{r}) \hat{h} \psi(\vec{r}) d\vec{r} \quad (3.10)$$

$$J_{i,j} = \int \frac{\psi_i^*(\vec{r}_i) \psi_i(\vec{r}_i) \psi_j^*(\vec{r}_j) \psi_j(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_i d\vec{r}_j \quad (3.11)$$

$$K_{i,j} = \delta(m_{s_i}, m_{s_j}) \int \frac{\psi_i^*(\vec{r}_i) \psi_j(\vec{r}_i) \psi_j^*(\vec{r}_j) \psi_i(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_i d\vec{r}_j \quad (3.12)$$

The most popular method in solving this is to use the variational principle and vary the one-electron wavefunctions to obtain an approximate solution to the Schrödinger equation. For a molecular system of any size, direct solution of the above equations is impractical, and the molecular orbitals are approximated as a linear combination of atomic orbitals (LCAO approach). In this approach, each molecular orbital is of the form

$$\psi_i(\vec{r}) = \sum_{\mu=1}^M C_{\mu i} \phi_{\mu}(\vec{r}) \quad (3.13)$$

where ϕ_{μ} are atomic orbitals.

The variational principle is used in the following manner:

1. An initial guess wavefunction is built up using the LCAO techniques. In the Restricted Hartree Fock (RHF) method, it is assumed that the orbital energies and the coefficients $C_{\mu i}$ are independent of the spin state. In the unrestricted method (UHF) the spin states are explicitly taken into account and the coefficients then depend upon the spin state of the electron and are denoted by $C_{\mu i}^{\alpha}$ where α denotes the spin state.
2. Electrons are assigned to the orbitals ψ_i of lowest energies. The RHF method takes the electrons in pairs for each spatial orbital, whereas the UHF wavefunction has an implicit spin dependence.
3. The energy of the system is calculated iteratively and the coefficients $C_{\mu i}$ or $C_{\mu i}^{\alpha}$ are varied till the minimum energy is obtained.

Regarding the dissociation energy and the nature of the dissociation products, the RHF model can yield an incorrect description of the system. RHF dissociation energies are generally too small and, in some cases, negative values are obtained, indicating that the RHF molecule is unstable towards dissociation [?]. Unrestricted Hartree-Fock (UHF) theory is the most common molecular orbital method for open shell molecules where the number of electrons of each spin are not equal.

The Hartree-Fock technique effectively treats each electron motion as being governed by the *average* potential created by the N nuclei and the remaining $(n - 1)$ electrons. As such, the HF technique in general neglects the instantaneous repulsions between pairs of electrons. The contribution of such instantaneous repulsions to the total energy is called correlation energy. The method dealing with correlation energy is known as Configuration Interaction (CI).

For any atom or molecule, there are infinite number of orbitals in addition to Hartree-Fock orbitals. These orbitals can be used to construct other possible configurations in the form of Slater determinants. The CI wavefunction for an N -electron system is then represented as a linear combination of a complete orthonormal set of Slater determinants

$$\Psi_m = \sum_a A_{am} \Phi_a \quad (3.14)$$

The coefficients A_{am} are determined to minimize the electronic energy

$$E = \int \Psi_m \mathcal{H} \Psi_m d\tau \quad (3.15)$$

Application of the variation principle leads to the matrix equation

$$HA = AE \quad (3.16)$$

where H is composed of matrix elements between the configurations

$$H_{ab} = \int \Phi_a \mathcal{H} \Phi_b d\tau \quad (3.17)$$

The full CI treatment will approach the exact solution of the electronic part of the Schrödinger equation as the basis set approaches infinite basis. The full CI method is well defined, size consistent and variational. But because of a very large number of substituted determinants, the CI calculations are practical only for very small systems. CI calculations can be greatly simplified if they are carried out in

terms of configurations, rather than Slater determinants.

In the multi-configuration self consistent field (MCSCF) method of CI calculations the forms of the molecular orbitals ψ_i are also varied to minimize the total energy in addition to obtaining the optimum values of the coefficients A_{am} . For a specified set of configurations, the multi-configuration HF wavefunction is the best wavefunction that can be obtained by simultaneously varying both the orbitals ψ_i and the CI coefficients A_{am} .

The Möller-Plesset perturbation theory, closely related to many-body perturbation theory is an alternative approach to the correlation problem. Möller-Plesset models are formulated by first introducing a generalized electronic Hamiltonian, \tilde{H}_λ

$$\tilde{H}_\lambda = \tilde{H}_o + \lambda V \quad (3.18)$$

where \tilde{H}_o is the Hartree-Fock(HF) Hamiltonian, given as a sum of one-electron HF operators, H_i^{HF} .

$$\tilde{H}_o = \sum H_i^{HF} \quad (3.19)$$

V is the difference between the correct Hamiltonian and the HF Hamiltonian and λ is a dimensionless parameter. Ψ_λ and E_λ are expanded in powers of λ and in order that the Schrödinger equation be satisfied for any arbitrary value of λ , it is necessary that the coefficient of each power of λ be separably zero. The Möller-Plesset energy to first order is the Hartree-Fock energy. The Möller-Plesset methods are referred according to the highest order energy term allowed, that is, truncation after second order is MP2, after third order is MP3 and so on.

These calculations give us the potential energy at a fixed nuclear configuration (in the case of diatomics: a fixed inter-nuclear distance R). The calculations, repeated for different nuclear configurations for a polyatomic molecule like methanol yield a potential surface which characterizes the molecule.

3.2 The *ab initio* quantum calculations

In figure 3.1 we consider the dissociation of an unstable molecular system. A process like multiple ionization of stable molecular system would lead to the formation of such a system.

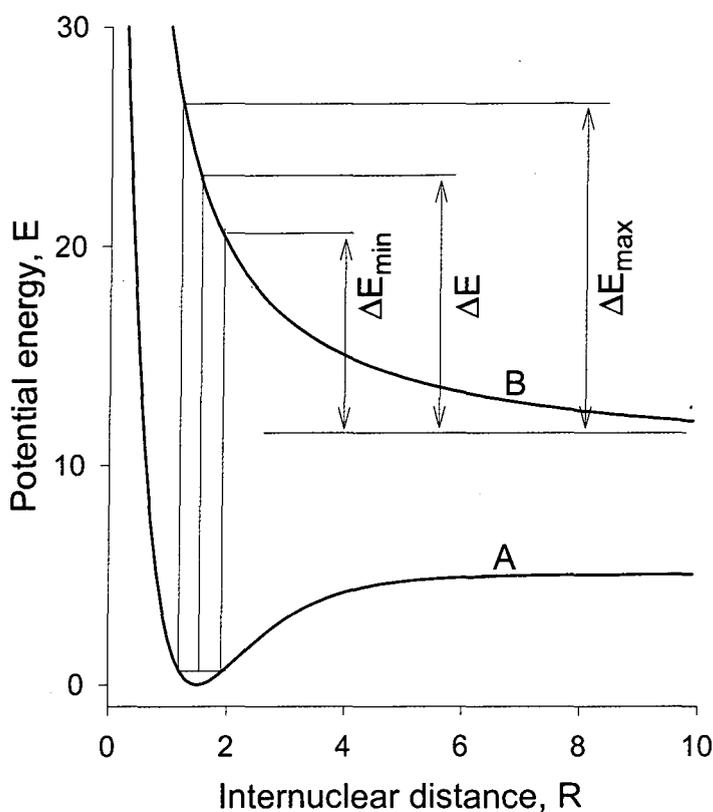


Figure 3.1: Potential energy curves depicting dissociative states of diatomic molecules.

In the above figure the curve A denotes the stable precursor whose ionization leads to the formation of the unstable states of the molecular ion (curve B). An unstable molecular ion dissociates releasing energy in the form of kinetic energy

of the dissociated fragments. The metastable states can also decay via tunneling through the potential barrier releasing energy. In experiments on molecular fragmentation kinetic energies of dissociated fragments are determined for the observed dissociation channels. As there are no vibrational energy levels in the repulsive system, the kinetic energy released (KER) depends on the inter-nuclear distance at the instant of formation. The ionization process being a purely electronic excitation, takes place much faster than the vibrational motion of the nuclei, and hence the inter-nuclear separation in the product ion is the same as in the precursor (a ‘vertical’ transition, denoted by any one of the vertical lines in figure 3.1).

Since the original precursor might have a range of inter-nuclear distances at the instant of ionization (governed by the vibrational wave function of the precursor) the resulting KER can lie anywhere between ΔE_{min} to ΔE_{max} , with a maximum probability ΔE as in figure 3.1.

For the theoretical estimation of the most probable kinetic energy release values, we require theoretical values of the formation energies of the atomic fragments into which the transient molecular ions decay. For a Frank-Condon excitation the difference between the potential energy of the unstable molecular ion at equilibrium inter-nuclear distance and the formation energies of its dissociated fragments, appears as kinetic energy of the fragments. If the fragments are formed in their ground states then the released energy is maximum, owing to their lowest formation energies. Therefore in addition to the potential energy curves of the multiply charged molecular ions, the UHF and the MCSCF energies for the atomic ions are also calculated keeping the basis vectors same as those used in case of the calculations performed on the molecular ions.

We have used the GAMESS [2] quantum chemistry package for calculating the *ab initio* potential energy curves for the various states of the N_2^{q+} and CO^{q+} molecular ions and also the ground state energies of the atomic ions N^{q+} ($1 \leq q \leq 4$), C^{q+} ($1 \leq q \leq 4$), O^{q+} ($1 \leq q \leq 4$).

3.2.1 Calculation of potential energy curves for N_2^{q+}

For the N_2^{q+} ($3 \leq q \leq 5$) molecular ions we have calculated the MCSCF energies with 6-311G basis set including 3 d-type and 1 f-type polarization functions. Polarization functions are functions of high angular momentum used to describe valence electrons. They account for directionality of electron density in the complex environment of a molecule. The numbers 6-311 signifies that the contracted gaussian-type function (CGTF) used for describing core atomic orbitals is composed of a linear combination of six primitive gaussians and the valence atomic orbitals are composed of three basis functions having contractions 3, 1 and 1. This particular basis set constitutes a large basis for the calculation at hand. Large basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of electrons in space. The inclusion of polarization functions takes into account the polarization effects due to mixing of the outermost unoccupied orbitals. Thus in this case three sets of five *d*-type gaussian polarization functions and one set of seven *f*-type gaussian is added to each nitrogen atom. The input options are presented in appendix A. The MCSCF energies were calculated at each inter-nuclear distance separately with the orbital vectors at that inter-nuclear distance supplied as an input parameter. These orbital vectors are generated in a prior UHF run at the same inter-nuclear distance and having the same input basis as being used in the MCSCF run. For the N_2^{6+} molecular ion only a UHF calculation was done as a function of the inter-nuclear distance. Figures 3.2 to 3.5 show the potential energy curves obtained from the calculations.

Table 3.1 shows the results of our calculations for the atomic ion in the various possible states. Our values for the excitation energy of the atomic ions are in good agreement with the NIST database values [3]. Our calculated value for the excitation of $N^+(^3P)$ to $N^+(^1D)$ is 2.0 eV (1.9 eV), for $N^{2+}(^2P)$ to $N^{2+}(^4P)$ is 6.99 eV (7.09 eV), for $N^{3+}(^1S)$ to $N^{3+}(^3P)$ is 8.32 eV (8.33 eV) which agrees well with the NIST values (given in brackets).

All the potential energy curves reported for the N_2^{q+} molecular ions are of the repulsive type and hence we expect the transient molecular ions in these states would dissociate releasing energy in the form of kinetic energy of the fragmented ions. Considering a Frank-Condon (vertical) transition we have calculated the

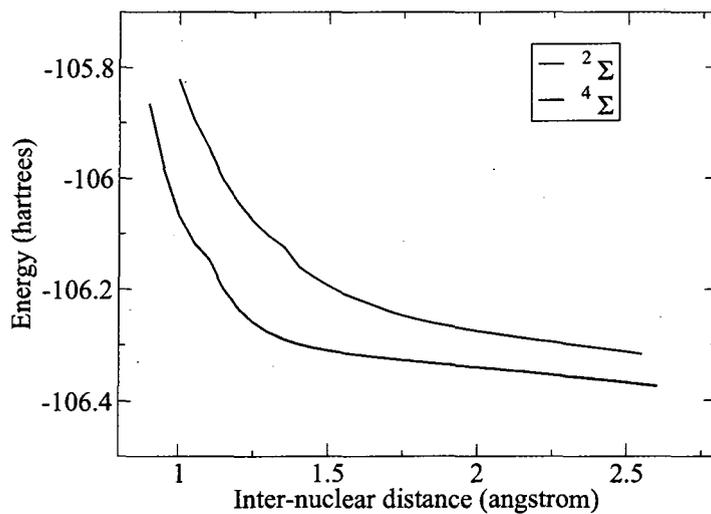


Figure 3.2: Potential energy curves for N_2^{3+} . The curves represent the results of MCSCF energy calculation as a function of inter-nuclear distance.

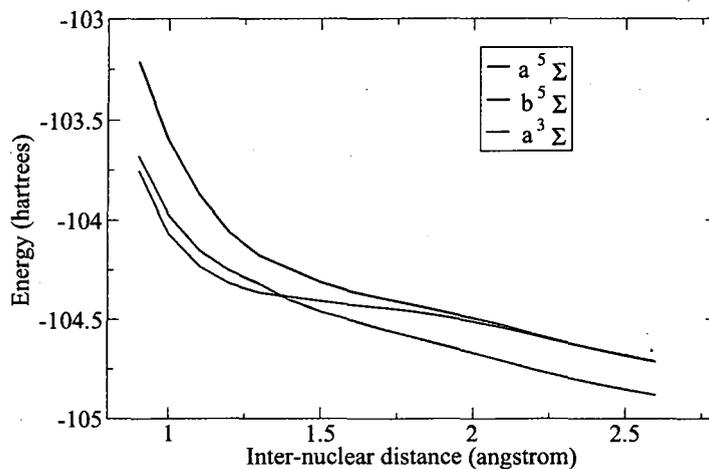


Figure 3.3: Potential energy curves for N_2^{4+} . The curves represent the results of MCSCF energy calculation as a function of inter-nuclear distance.

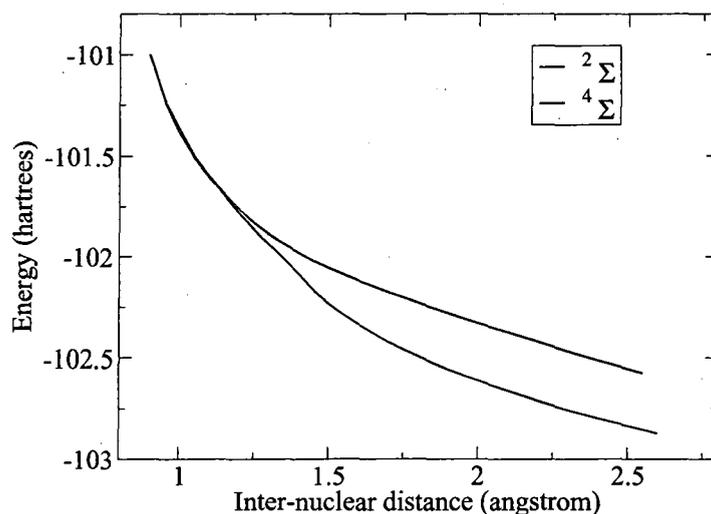


Figure 3.4: Potential energy curves for N_2^{5+} . The curves represent the results of MCSCF energy calculation as a function of inter-nuclear distance.

Table 3.1: The calculated formation energies (in hartrees) of the N^{q+} atomic ions

Ion species	UHF	MP2	MCSCF
N^+ (1D)	-53.764	-53.860	-53.901
N^+ (3P)	-53.889	-53.963	-53.975
N^{2+} (2P)	-52.816	-52.875	-52.898
N^{2+} (4P)	-52.627	-52.640	-52.641
N^{2+} (2D)	-	-	-52.431
N^{3+} (1S)	-50.854	-51.132	-51.166
N^{3+} (3P)	-50.080	-50.858	-50.86
N^{4+} (2S)	-48.325	-48.325	-

most probable KER for the dissociative decay of each of these molecular states into atomic/ionic fragments. These values are listed in table 3.2.

There exist prior calculations by Remscheid *et al* [4] for potential energy curves of N_2^{4+} and N_2^{6+} molecular ions to explain their study on N_2 fragmentation induced by Ar^{8+} (8 keV) projectile. They have concentrated on the symmet-

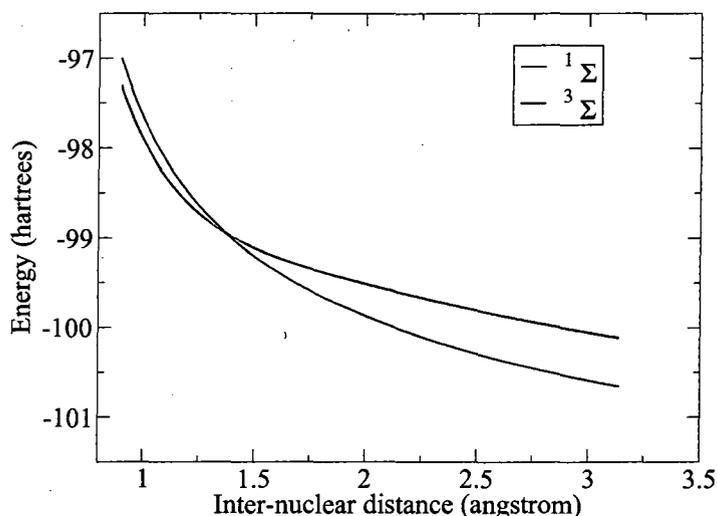


Figure 3.5: Potential energy curves for N_2^{6+} . The curves represent the results of UHF energy calculation as a function of inter-nuclear distance.

ric charge breakup of N_2^{4+} and N_2^{6+} . For the symmetric breakup, our theoretical values are in agreement with those obtained by Remscheid *et al.* They have calculated two lowest electronic states of the N_2^{4+} transient molecular ion, the $^5\Sigma_u^+$ ground state and the $^3\Sigma_g^-$ state. Our theoretically calculated values for the dissociation energy of N_2^{6+} agrees well with the calculations by Remscheid *et al.*

Safvan and Mathur [5] have also theoretically investigated the dissociation of highly charged N_2^{q+} ($q \geq 2$) ions via non-Coulombic potential energy curves using the QCISD(T) method. This refers to a method of CI calculations which takes into account singles, doubles and triples substitutions. Some of the dissociation channels given by them are spin multiplicity forbidden. Comparison can be made with the following three results of their calculations

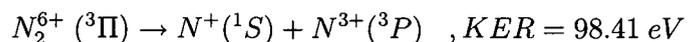
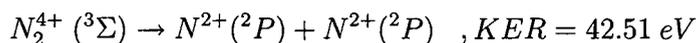
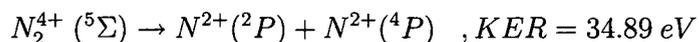


Table 3.2: Theoretically calculated values of KER in case of N_2^{q+} ($3 \leq q \leq 6$) dissociating to the lowest possible states of $N^{m+} + N^{n+}$ with $m+n=q$. These values denote the upper limit of the KER. (see text)

Dissociation channels	Kinetic energy release (eV)
$N_2^{3+} (^2\Sigma) \rightarrow N^{2+} (^2P) + N^{1+} (^3P)$	25.40
$N_2^{3+} (^4\Sigma) \rightarrow N^{2+} (^2P) + N^{1+} (^3P)$	19.77
$N_2^{4+} (a^5\Sigma) \rightarrow N^{2+} (^2P) + N^{2+} (^4P)$	35.48
$N_2^{4+} (a^5\Sigma) \rightarrow N^{1+} (^3P) + N^{3+} (^3P)$	33.07
$N_2^{4+} (b^5\Sigma) \rightarrow N^{2+} (^2P) + N^{2+} (^4P)$	45.40
$N_2^{4+} (b^5\Sigma) \rightarrow N^{1+} (^3P) + N^{3+} (^3P)$	42.89
$N_2^{4+} (^3\Sigma) \rightarrow N^{2+} (^2P) + N^{2+} (^2P)$	46.59
$N_2^{4+} (^3\Sigma) \rightarrow N^{1+} (^3P) + N^{3+} (^1S)$	28.78
$N_2^{5+} (^2\Sigma) \rightarrow N^{2+} (^2P) + N^{3+} (^1S)$	67.56
$N_2^{5+} (^4\Sigma) \rightarrow N^{2+} (^4P) + N^{3+} (^1S)$	59.68
$N_2^{6+} (^1\Sigma) \rightarrow N^{3+} (^1S) + N^{3+} (^1S)$	114.67
$N_2^{6+} (^1\Sigma) \rightarrow N^{2+} (^2P) + N^{4+} (^2S)$	86.96
$N_2^{6+} (^3\Sigma) \rightarrow N^{3+} (^1S) + N^{3+} (^3P)$	98.46
$N_2^{6+} (^3\Sigma) \rightarrow N^{2+} (^4P) + N^{4+} (^2S)$	69.80

In general our theoretical values are in agreement with the values obtained by them.

3.2.2 Calculation of potential energy curves for CO^{q+}

Theoretical calculation of potential energy curves for CO^{q+} ($4 \leq q \leq 6$) molecular ions have been carried out to determine the UHF energies for these molecular ions as a function of inter-nuclear distance using the 6-311G basis set. The input options are presented in appendix A. Theoretical calculations exist for the lower charge states, CO^{2+} (see reference [6]) and CO^{3+} (see reference [7]) molecular ions. Figures 3.6 to 3.8 show the potential energy curves obtained from our calculations.

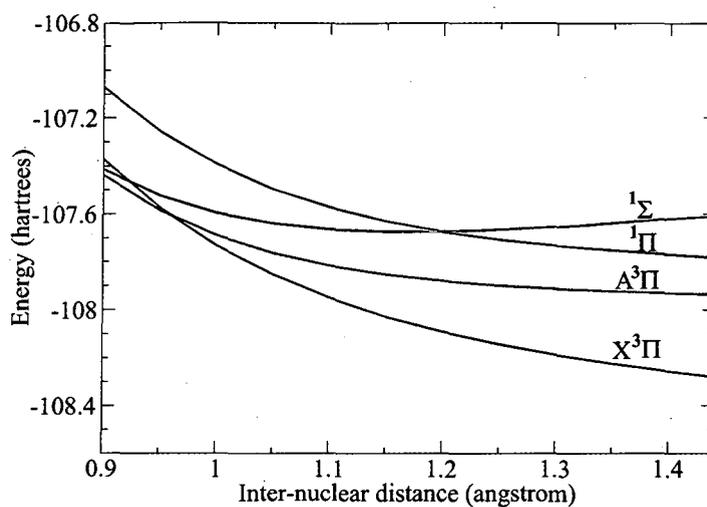


Figure 3.6: Potential energy curves for CO^{4+} . The curves represent the results of UHF energy calculation as a function of inter-nuclear distance.

The formation energies of the atomic ions and the theoretically calculated values of the most probable kinetic energy release are tabulated in tables 3.3 to 3.4 respectively.

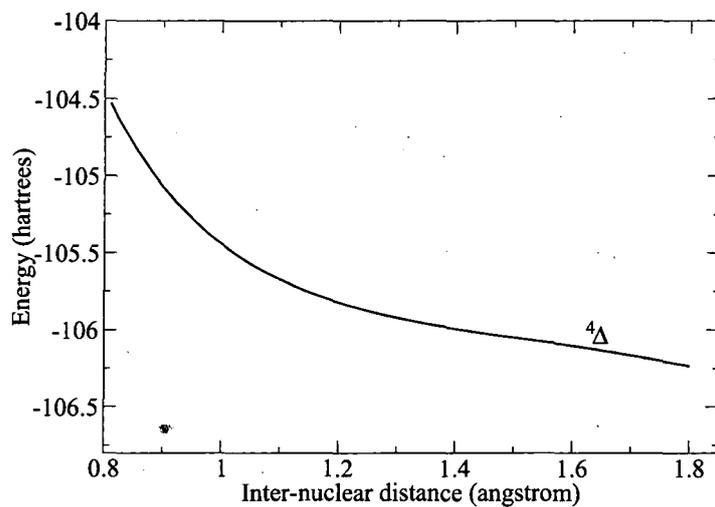


Figure 3.7: Potential energy curves for CO^{5+} . The curves represent the results of UHF energy calculation as a function of inter-nuclear distance.

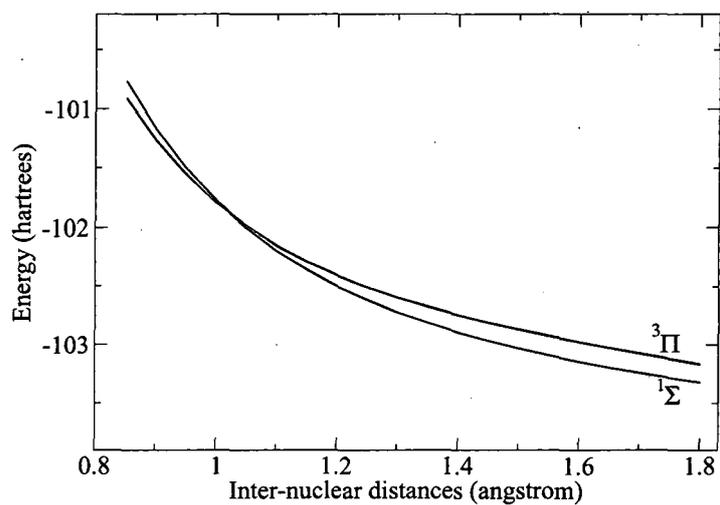


Figure 3.8: Potential energy curves for CO^{6+} . The curves represent the results of UHF energy calculation as a function of inter-nuclear distance.

Table 3.3: The calculated formation energies (in hartrees) of the C^{q+} and O^{q+} atomic ions

Ion species	UHF
C^{2+} (1S)	-36.406
C^{2+} (3P)	-36.236
C^{3+} (2S)	-34.724
C^{4+} (1S)	-32.360
C^{4+} (3S)	-21.412
O^{1+} (4S)	-74.368
O^{1+} (2D)	-74.186
O^{2+} (3P)	-73.099
O^{2+} (1D)	-72.940
O^{3+} (2P)	-71.094
O^{3+} (4P)	-70.849
O^{4+} (1S)	-68.254
O^{4+} (3P)	-67.973

Table 3.4: Theoretically calculated values of KER in case of CO^{q+} ($4 \leq q \leq 6$) dissociating to the lowest possible states of $C^{m+} + O^{n+}$ with $m+n=q$. These values denote the upper limit of the kinetic energy release (KER).

Dissociation channels	KER (eV)
$CO^{4+} (^3\Pi) \rightarrow C^{2+} (^1S) + O^{2+} (^3P)$	41.07
$CO^{4+} (^3\Pi) \rightarrow C^{3+} (^2S) + O^+ (^4S)$	29.84
$CO^{4+} (^3\Pi) \rightarrow C^{3+} (^2P) + O^+ (^4S)$	21.84
$CO^{4+} (^3\Pi) \rightarrow C^{3+} (^2S) + O^+ (^2D)$	25.16
$CO^{4+} (^3\Delta) \rightarrow C^{2+} (^1S) + O^{2+} (^3P)$	45.43
$CO^{4+} (^3\Delta) \rightarrow C^{3+} (^2S) + O^+ (^4S)$	34.20
$CO^{4+} (^3\Delta) \rightarrow C^{3+} (^2P) + O^+ (^4S)$	24.20
$CO^{4+} (^3\Delta) \rightarrow C^{3+} (^2S) + O^+ (^2D)$	29.24
$CO^{4+} (^1\Sigma) \rightarrow C^{2+} (^3P) + O^{2+} (^3P)$	45.34
$CO^{4+} (^1\Sigma) \rightarrow C^{2+} (^1S) + O^{2+} (^1D)$	45.67
$CO^{4+} (^1\Sigma) \rightarrow C^{3+} (^2S) + O^+ (^2D)$	33.81
$CO^{4+} (^1\Delta) \rightarrow C^{2+} (^3P) + O^{2+} (^3P)$	47.03
$CO^{4+} (^1\Delta) \rightarrow C^{2+} (^1S) + O^{2+} (^1D)$	47.36
$CO^{4+} (^1\Delta) \rightarrow C^{3+} (^2S) + O^+ (^2D)$	35.50
$CO^{5+} (^4\Delta) \rightarrow C^{3+} (^2S) + O^{2+} (^3P)$	59.27
$CO^{5+} (^2\Pi) \rightarrow C^{3+} (^2S) + O^{2+} (^3P)$	67.62
$CO^{5+} (^2\Pi) \rightarrow C^{2+} (^1S) + O^{3+} (^2P)$	59.68
$CO^{6+} (^1\Sigma) \rightarrow C^{3+} (^2S) + O^{3+} (^2P)$	95.99
$CO^{6+} (^1\Sigma) \rightarrow C^{2+} (^1S) + O^{4+} (^1S)$	64.49
$CO^{6+} (^3\Pi) \rightarrow C^{3+} (^2S) + O^{3+} (^2P)$	97.62
$CO^{6+} (^3\Pi) \rightarrow C^{4+} (^1S) + O^{2+} (^3P)$	87.83

3.3 Conclusions

The potential energy curves for multiply charged N_2^{q+} and CO^{q+} ions are calculated using the GAMESS package [2]. Most of the calculated curves are repulsive in nature except the $^1\Sigma$ state of the CO^{4+} ion which shows the possibility of being metastable (see figure 3.6).

Molecular dissociation experiments on N_2 and CO isoelectronic diatomic molecules will follow to compare the theoretical results presented in this chapter with the experimental values of the kinetic energy releases. The experimental results and the comparison are presented in chapter 4 of this thesis.

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