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# *Ab initio* CI Study of the Nitric Oxide Dimer ($N_2O_2$)

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Configuration interaction (CI) studies of the ground and electronically excited states are reported for nitric oxide dimer ($N_2O_2$) in its *cis* equilibrium geometry. The lowest triplet state ($^3B_2$) is found to lie only 0.43 eV above the ground state ($^1A_1$). The $^1A_1 \rightarrow {}^1B_1$ transition is shown to be responsible for the rising absorption in the near infrared region observed experimentally. The transition of $^1A_1 \rightarrow {}^1A_2$ calculated in the visible spectrum range of 701 nm (1.77 eV) is symmetry forbidden.

**Key words:** Ab initio CI study – Nitric oxide dimer – Electronically excited states.

## 1. Introduction

In condensed phases nitric oxide (NO) can exist as the dimer $N_2O_2$. The existence of the bound state of gaseous $(NO)_2$ has also been detected by recent experiments such as electron diffraction techniques, optical, infrared and mass spectroscopy [1]. The infrared spectrum of $N_2O_2$ suggested that the dimer has a *cis* configuration with $r(N—N) = 2.2 \pm 0.2$ Å and with a nearly rectangular structure. From the X-ray crystallographic study by Lipscomb et al. [2] it was also concluded that the dimer $N_2O_2$ exists in *cis* form with $r(N—N) = 2.18 \pm 0.03$ Å, $r(N—O) = 1.12$ Å and $\measuredangle NNO = 101°$.

Skaarup et al. [3] have carried out *ab initio* SCF calculations to theoretically determine structures of the stable isomers of $N_2O_2$ by fully optimizing geometrical parameters. Although the relative stability of the *cis* and *trans* conformations was shown to be dependent upon the basis set employed, they found that $N_2O_2$ may have two preferred conformations of planar *cis* and *trans*. The vibrational frequencies and force constants have also been calculated and the calculations showed that the force field for the *cis* conformer was in better agreement with experimental results [1, 4].

Another point of interest is the optical properties of this molecule, which is the main concern of the present study. While it was reported long time ago that the blue colour arising from liquidifying or solidifying the NO molecule is due to the dimer $N_2O_2$ [5], recently the optical spectrum of pure liquid of NO showed to be transparent from the visible into near infrared region [6]. As pointed out by Mason [6] the conflict has arisen because $N_2O_3$ which can readily be formed in the process of condensation of NO, has a very deep blue colour and thus the dimer $N_2O_2$ is actually colourless if prepared experimentally. Semi-empirical MO calculations of CNDO/S type [7] have also been carried out to obtain electronic transitions of $N_2O_2$, $N_2O_3$ and $N_2O_4$ species [6].

In the present work an extended *ab initio* CI calculation employing a large Gaussian basis set has been carried out to theoretically study the electronically excited states and transitions of the dimer $N_2O_2$.

## 2. Calculation

The molecular geometry employed for, the calculation is the experimental geometry obtained by the X-ray crystallographic study of Lipscomb et al. [2] with $r(\mathrm{N—N}) = 2.18$ Å, $r(\mathrm{N—O}) = 1.12$ Å and $\measuredangle \mathrm{NNO} = 101°$. *Ab initio* SCF calculations which precede the CI study employ the Gaussian basis set of Huzinaga's $(9s, 5p)$ set [8], contracted to a double zeta $(4s, 2p)$ according to Dunning's scheme [9] plus a set of polarization function $(d)$ with exponents of 0.80 and 0.85 for nitrogen and oxygen, respectively. The SCF calculations have been carried out for seven lower lying states with following configurations:

$$\cdots (1a_2)^2(6b_2)^2(7a_1)^2, \quad {}^1A_1 \text{ (ground state)},$$
$$\cdots (1a_2)^2(6b_2)^2(7a_1)^1(2b_1)^1, \quad {}^3B_1, {}^1B_1,$$
$$\cdots (1a_2)^2(6b_2)^2(7a_1)^1(2a_2)^1, \quad {}^3A_2, {}^1A_2,$$
$$\cdots (1a_2)^2(6b_2)^1(7a_1)^1(7b_2)^1, \quad {}^3B_2, {}^1B_2.$$

A configuration interaction calculation has been carried out for each state of interest employing the configurations mentioned above as reference configurations. The CI matrix was generated by including all single and double excitations of the valence shell electrons from each reference configuration. These were selected by perturbation theory with an energy threshold of $2 \times 10^{-5}$ a.u.. At large distances ($\approx 2.2$ Å), the ${}^1A_1$ ground state wavefunction cannot be described by a CI based on a single reference configuration $\cdots (1a_2)^2(6b_2)^2(7a_1)^2$, since the configuration $\cdots (1a_2)^2(6b_2)^2(7b_2)^2$, where $7b_2$ is the antibonding counterpart to $7a_1$, showed to be as important as the former configuration. In the CI treatment, the singles and doubles from both terms were therefore included. As orbitals of variable occupancy in the CI calculation all valence shell orbitals were adopted, keeping 4 lower lying core orbitals frozen. Within the truncation of the MO bases

**Table 1.** Energies of the CI wavefunctions of $N_2O_2$ [a]

| Electronic states and reference configurations | | $E$(CI) [b] | $\Delta E$(CI-SCF) | $E$(CI′) | $\Delta E_p$(kept) | $\Delta E_p$(not kept) |
|---|---|---|---|---|---|---|
| $^1A_1$ | ground state | −0.7523 (2956) | −0.3076 | −0.7695 | −0.7269 | −0.0406 |
| $^3B_2$ | $(7a_1)^1(7b_2)^1$ | −0.7357 (5612) | −0.2402 | −0.7537 | −0.3216 | −0.0241 |
| $^1B_1$ | $(7a_1)^1(2b_1)^1$ | −0.7238 (3571) | −0.3089 | −0.7370 | −0.5378 | −0.0230 |
| $^1A_2$ | $(7a_1)^1(2a_2)^1$ | −0.6932 (3557) | −0.3155 | −0.7043 | −0.6555 | −0.0230 |
| $^3A_2$ | $(7a_1)^1(2a_2)^1$ | −0.6235 (3240) | −0.2261 | −0.6370 | −0.4280 | −0.0256 |
| $^3B_1$ | $(7a_1)^1(2b_1)^1$ | −0.5844 (3154) | −0.1472 | −0.6031 | −0.1815 | −0.0230 |
| $^1B_2$ | $(7a_1)^1(7b_2)^1$ | −0.3818 (2041) | −0.1948 | −0.3942 | −0.2855 | −0.0182 |

[a] Atomic units. Reference CI energy: −258.0 a.u.

[b] Values in parentheses are the dimensions of the CI wavefunctions.

and the perturbation threshold, the dimension of the CI wavefunction amounted to 2956 for the ground state.

In Table 1 the calculated CI energies, the energy decreases from the SCF calculations and the dimensions of the CI matrix for these seven states are listed. These seven states correspond to the lowest states for a given symmetry and multiplicity. The $\Delta E_p$ values refer to portions of energy kept or not kept by the second order perturbation theory. With these and the $\Delta E$(CI-SCF) values extrapolated CI energies ($E$(CI′)) are obtained, which should be considered as approximate CI energies obtainable at the limit of zero energy threshold [10, 14].

## 3. Results and Discussion

In Table 2 the calculated excitation energies and oscillator strengths obtained from the CI calculations are summarized. The transition from the ground state to the first dipole allowed singlet state, $^1A_1 \rightarrow {}^1B_1$, is calculated at 1410 nm with $f = 1.6 \times 10^{-4}$. This transition is in agreement with the rising absorption in the near

**Table 2.** A summary of the calculated excitation energies and oscillator strengths ($f$) of $N_2O_2$ [a]

| Electronic states and reference configurations | | $\Delta E$ (CI) | | $\Delta E$ (CI′) | | |
|---|---|---|---|---|---|---|
| | | eV | nm | eV | nm | $f$ [b] |
| $^1A_1$ | (ground state) | — | — | — | — | — |
| $^3B_2$ | $(7a_1)^1(7b_2)^1$ | 0.45 | 2757 | 0.43 | 2886 | — |
| $^1B_1$ | $(7a_1)^1(2b_1)^1$ | 0.78 | 1591 | 0.88 | 1410 | $1.6 \times 10^{-4}$ ($y$) |
| $^1A_2$ | $(7a_1)^1(2a_2)^1$ | 1.61 | 771 | 1.77 | 701 | 0.0 |
| $^3A_2$ | $(7a_1)^1(2a_2)^1$ | 3.50 | 355 | 3.61 | 344 | — |
| $^3B_1$ | $(7a_1)^1(2b_1)^1$ | 4.57 | 272 | 4.53 | 274 | — |
| $^1B_2$ | $(7a_1)^1(7b_2)^1$ | 10.08 | 123 | 10.21 | 122 | 0.656 ($x$) |

[a] The molecular plane is the $xy$-plane and the $x$ axis corresponds to the N—N axis.

[b] The oscillator strength for the transition between two states ($\Psi'$ and $\Psi''$) has been calculated by $f = \frac{2}{3}|\langle\Psi'|e\Sigma r_{e'e''}|\Psi''\rangle|^2 \Delta E$, where $\Delta E$ is the transition energy.

infrared region (>1160 nm with $f \approx 10^{-6}$) reported to be found experimentally [6]. The transition is polarized perpendicular to the molecular plane and can qualitatively be considered as the $\sigma \rightarrow \pi^*$ transition as the reference configuration, $\cdots (7a_1)^1(2b_1)^1$ of the $^1B_1$ state indicates. The next transition of interest is $^1A_1 \rightarrow {}^1A_2$ which is also a $\sigma \rightarrow \pi^*$ type transition judging from the reference configuration of $\cdots (7a_1)^1(2a_2)^1$ for the $^1A_2$ state. The transition energy is calculated at 701 nm, but it is symmetrically dipole forbidden within the $C_{2v}$ symmetry employed in the calculation.

All of the lower lying excited states are due to excitations from the highest occupied orbital ($7a_1$), which is of $\sigma$ type. The lone pair character of the $7a_1$ MO is considerably small as the major LCAO coefficients indicate.

A strong transition with larger $f$ value of 0.656 arises at 122 nm which is polarized along the X-axis (N—N axis). This transition $^1A_1 \rightarrow {}^1B_2$ is qualitatively a $\sigma \rightarrow \sigma^*$ transition.

In addition to the singlet manifold, the triplet states have also been calculated. The lowest triplet state which lies in the infrared region is assigned to a $^3B_2$ state and is calculated to be only 0.43 eV above the ground state. There are two further triplet states in the UV region at 344 nm ($^3A_2$) and at 274 nm ($^3B_1$).

In the following present results are compared with previous results obtained from the semi-empirical CNDO/S calculation and with experimental findings.

Three excited singlet states have been reported at 1286 nm ($f = 2 \times 10^{-4}$), 976 nm ($f = 0.0$) and at 250 nm ($f = 1.0$) from the CNDO/S calculation for $N_2O_2$ [7]. In the CNDO approximation it is not possible to locate the triplet manifold since the triplet and singlet $n \rightarrow \pi^*$ or $\sigma \rightarrow \pi^*$ states are degenerate. Apart from the rising absorption in the infrared region it was reported that experiments in the UV region show diffuse bands at 232–236 nm and a continuous absorption below 230 nm with maximum at 205 nm ($f = 0.26$) [6, 11, 12].

The dipole forbidden excitation $^1A_1 \rightarrow {}^1A_2$ calculated at 701 nm is of interest since it lies in the visible spectrum range. The blue colour of the nitroso methane ($CH_3NO$) molecule was previously predicted by an *ab initio* CI calculation [13] to be due to the $n \rightarrow \pi^*$ excitation. The calculated gross atomic population and bond orders suggest that the N—N bond is very weak and the O—O bond is much weaker in the ground state and the lower lying states of the dimer $N_2O_2$, while the N—O bond is very similar to the NO monomer. Previous SCF calculation of the force field [3] also indicated that the out of plane motion has a small force constant. From these evidences the possibility cannot be excluded that the dipole forbidden transition in the $C_{2v}$ symmetry calculated at 701 nm might carry a nonvanishing oscillator strength through deformation from planarity. The dimer $N_2O_2$ which exists in the condensed phases of NO can thus show a blue colour if the geometry is slightly deformed from the $C_{2v}$ symmetry. This argument may be contrasted to the previous definitive conclusion that the dimer $N_2O_2$ is colourless if prepared properly [6]. The corresponding state obtained by the CNDO/S

**Table 3.** Molecular properties for the ground state ($^1A_1$) of $N_2O_2$ calculated by the CI wavefunction

| | | | |
|---|---|---|---|
| $\mu_z$[a] | 0.366 | $E_x(O)$ | 0.0241 |
| $Q_{xx}$[b] | −16.420 | $E_z(O)$ | 0.1102 |
| $Q_{yy}$ | −14.116 | $q_{xz}(N)$[e] | 0.0908 |
| $Q_{zz}$ | −17.165 | $q_{x^2-y^2}(N)$ | −0.6674 |
| $1/r(N)$[c] | −18.245 | $q_{3z^2-r^2}(N)$ | −0.5335 |
| $1/r(O)$ | −22.164 | $q_{xz}(O)$ | 0.1563 |
| $E_x(N)$[d] | −0.0098 | $q_{x^2-y^2}(O)$ | −0.9844 |
| $E_z(N)$ | −0.1092 | $q_{3z^2-r^2}(O)$ | 0.3381 |

[a] Dipole moment in Debye units.

[b] Quadrupole moment calculated at center of mass (CM) in a.u.

$$Q_{xx}=\sum_A Z_A(X_A-X_{CM})^2-\sum_i \langle (x_i-x_{CM})^2\rangle .$$

[c] Potential at nucleus in a.u.

$$1/r(A)=\sum_{B\neq A} Z_B/r_{BA}-\sum_i \langle 1/r_{iA}\rangle .$$

[d] Electric field at nucleus in a.u.

$$E_x(A)=\sum_i \langle \theta_x(r_{iA})\rangle-\sum_{B\neq A} z_B\theta_x(R_{BA}) \text{ with}$$

$$\theta_x=x/r^3.$$

[e] Electric field gradient in a.u.

$$q_K(A)=\sum_{B\neq A} Z_B\theta_K(R_{BA})-\sum_i \theta_K(r_{iA});\ \theta_{xz}=xz/r^5.$$

$$\theta_{x^2-y^2}=(x^2-y^2)/r^5 \text{ and } \theta_{3z^2-r^2}=(3z^2-r^2)/r^5.$$

calculation lied at 976 nm above the ground state, thus it is far off the visible spectrum range.

Since the closed shell SCF wavefunction and energy have the wrong asymptote at large distances, an SCF treatment invariably yielded a much too short and unrealistic distance, $r(N—N) = 1.768$ Å [3]. Similar effects are known from $F_2$ and $N_2O_4$ although $(NO)_2$ is an even more drastic case. After carrying out calculations on the electron excitations of $N_2O_4$, which are a matter of main concern for the present study, a systematic search for the gas phase geometry has therefore been undertaken using the CI treatment described in Sect. 2. The CI energy is minimized as a function of $r(N—N)$, $r(N—O)$ and ∡NNO. The energy minimum is reached at $r(N—N) = 2.39$ Å, $r(N—O) = 1.19$ Å and ∡NNO = 90°. The calculated CI energy of −258.7845 a.u. is lower by 0.0322 a.u. (0.88 eV) than the energy obtained using the X-ray geometry for the condensed phase $(NO)_2$ calculation. An extremely weak bond is formed between two NO molecules in $(NO)_2$, since the attractive forces due to the bonding between the singly occupied $\pi^*$ MOs of NO are counteracted by strongly repulsive forces arising from the overlap of fully occupied $\pi$ MOs. This consideration may explain the rather long distance of $r(N—N) = 2.39$ Å obtained by the CI calculation.

Some one electron properties for the ground state ($^1A_1$) of the dimer $N_2O_2$ are calculated using the CI wavefunction and are listed in Table 3. The calculated dipole moment of 0.366 Debye indicates that the NO dimer is almost non-polar. Unfortunately, there are not yet reported experimental values which could be compared with these calculated values.

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