Rotational constants for the \( \tilde{C}^2A_2 \) state of NO\(_2\)

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The coupled-cluster method including all single and double excitations (CCSD) and CCSD including perturbatively applied triple excitations [CCSD(T)] have been used with large basis sets to study the rotational constants and associated geometrical parameters of the \( \tilde{C}^2A_2 \) state of NO\(_2\). The results compare favorably to earlier theoretical work but remain in conflict with recent optical-optical double resonance spectroscopic results.

INTRODUCTION

The nitrogen dioxide (NO\(_2\)) molecule has held the interest of both experimentalists and theoreticians due to its importance in atmospheric chemistry. More recently, however, the symmetry-breaking characteristics\(^{1-3}\) and experimental rotational resolution\(^4\) of several of its lower-lying excited electronic states have been the focal points of study.

One of the earliest theoretical studies of the \( \tilde{C}^2A_2 \) state of NO\(_2\) was done by Gillispie et al.\(^5\) In their pioneering work, they used multiconfigurational self-consistent field (MC-SCF) techniques with what is now considered to be a relatively small basis set, i.e., a double-zeta plus polarization (DZP) basis set, to determine the equilibrium geometry \((R_{\tilde{C}} \approx 1.27 \, \text{Å}, \theta_{\tilde{C}} \approx 110^\circ)\). This work was followed by that of Jackels and Davidson,\(^6\) who used configuration interaction (CI) techniques with a double-zeta (DZ) basis set to determine geometries comparable to the earlier results by Gillispie et al.\(^5\)

The first experimental observation of the \( \tilde{C}^2A_2 \) state of NO\(_2\) was made in 1989 by Weaver et al.\(^7\) using photoelectron spectroscopy. They reported that this state lies \( T_0 = 16357 \, \text{cm}^{-1} \) above the \( \tilde{X}^2A_1 \) ground state (including the zero-point energy). Shortly thereafter, Shibuya et al.\(^4\) used optical-optical double resonance (OODR) spectroscopy to produce the first rotationally resolved spectrum for this state. From the rotational constants, Shibuya and co-workers determined a distinctly different geometry \((R_{\tilde{C}} \approx 1.27 \, \text{Å}, \theta_{\tilde{C}} \approx 110^\circ)\) from that obtained theoretically over a decade earlier.\(^5,6\)

A recent theoretical study by Kaldor\(^3\) used the coupled-cluster method including all single and double excitations (CCSD) to determine the geometry of the \( \tilde{C}^2A_2 \) state. Those geometries compared favorably to those of the original theoretical studies.\(^5,6\) However, Kaldor’s excellent work was focused on the symmetry breaking characteristics of the \( \tilde{C}^2A_2 \) state and not an accurate determination of its equilibrium geometry. Therefore, only a DZP basis set was employed.

In the present work, an attempt is made to determine accurate rotational constants for the \( \tilde{C}^2A_2 \) state of NO\(_2\) using high-level theoretical methods and large basis sets. The present results agree with previous theoretical studies but conflict with the experimentally determined values.\(^4\)

THEORETICAL METHODS

The geometry of the \( \tilde{C}^2A_2 \) state of NO\(_2\) has been determined using four distinct levels of theory and three basis sets. The four theoretical methods included the restricted self-consistent field (SCF) technique, configuration interaction including all single and double excitations (CISD),\(^8\) coupled-cluster, including all single and double excitations (CCSD),\(^9,10\) and CCSD including perturbatively applied triple excitations [CCSD(T)].\(^10\) A double-zeta\(^{11-14}\) plus polarization (DZP) basis set constructed as N,O(9s5p1d/4s2p) and a triple-zeta\(^{11,15}\) plus double polarization (TZ2P) basis set constructed as (10s6p2d/5s3p2d) were the two smaller basis sets used. A third basis set (TZ2P + f) was constructed from the TZ2P basis with a single set of \( f \)-like functions added to N and O. The polarization function orbital exponents for the DZP basis were \( \alpha_d(N) = 0.80 \) and \( \alpha_d(O) = 0.85 \). Those for the TZ2P basis set were \( \alpha_d(N) = 1.60, 0.40, \) and \( \alpha_d(O) = 1.70, 0.425 \). The same polarization orbital exponents were used for the TZ2P + f basis, with, of course, the additional \( f \) orbital exponents, which had values of \( \alpha_f(N) = 1.00 \) and \( \alpha_f(O) = 1.40 \). The electronic configuration of the \( \tilde{C}^2A_2 \) state is

\[ 1a_1^21b_2^22a_2^23a_1^22b_2^44a_2^55a_1^11b_1^31b_2^31a_1^4b_3^6a_2^2. \]

For the correlated levels of theory, the lowest lying occupied SCF orbitals (the \( 1a_1, 2a_1, \) and \( 1b_2 \)) were frozen, i.e., doubly occupied in all configurations. For the CISD wave functions, there were 14 501 configurations for the D2P basis, 47 337 configurations for the TZ2P basis, and 97 742 configurations for the TZ2P + f basis within \( C_{2v} \) symmetry. The reference determinant for both the CCSD and CCSD(T) wave functions was that of the \( \tilde{C}^2A_2 \) state and not the closed-shell ground state anion adopted by Kaldor.\(^3\) Structural optimizations were carried out for the SCF and CISD theoretical methods for all three basis sets using open-shell analytical gradient techniques.\(^16,17\) The analogous optimizations were carried out for the CCSD and CCSD(T) theoretical methods for all three basis sets using numerical finite-difference gradients along symmetrized internal coordinates.

RESULTS AND DISCUSSION

Table I reports the energies and equilibrium geometries of the \( \tilde{C}^2A_2 \) state of NO\(_2\) for all four levels of theory and all three basis sets used. In all cases, the optimized
geometries follow expected trends as the level of theory is improved and the basis set size is increased.

Table II reports the rotational constants determined for each geometry given in Table I. The rotational constants reported by Shibuya et al. were $B_r=0.435$ cm$^{-1}$ and $C_r=0.363$ cm$^{-1}$. These compare poorly with the values of $B_r=0.480$ cm$^{-1}$ and $C_r=0.418$ cm$^{-1}$ determined here from the TZ2P + f-CISD(T) geometry. The poor agreement between theory and experiment is tempered by (a) the fact that $B_r$ and $C_r$ should not be identical to $B_v$ and $C_v$, respectively; and (b) Shibuya and co-workers explicitly state concerning $B_v$ and $C_v$ that "these values are only approximate." Nevertheless, we recommend that new experiments be devised to redetermine the rotational constants for the $\tilde{C}^2A_2$ state of NO$_2$.

A point must be made regarding the difference between the energy reported for the DZP-CCSD level of theory here and that reported by Kaldor. The methods described here differ from those of Kaldor in three ways: (1) The use of all virtual orbitals in the present work, (2) the use of canonical SCF orbitals from the closed-shell anion as a reference determinant in the work of Kaldor, and (3) the use of the Fock-Space CCSD (FS-CCSD) method by Kaldor. These differences result in slightly different equilibrium geometries (Kaldor reports $R_e=1.286$ Å, $\theta_e=109.4^\circ$, and $E=-204.528$ 91 hartrees, as opposed to our $R_e=1.290$ Å, $\theta_e=109.3^\circ$, and $E=-204.526$ 91 hartrees).

It has been shown in previous CCSD and CCSD(T) studies that the $T_1$ diagnostic is a useful measure of the ability of the method to determine the dynamical correlation energy. For all CCSD and CCSD(T) results presented in this work, the value of the $T_1$ diagnostic was found to be near 0.03 (ranging from 0.0298 to 0.0316). This is higher than the proposed maximum value of 0.02, suggesting that a significant quantity of the dynamical correlation energy remains undetermined. Furthermore, the CISD coefficient of the second most important configuration is consistently greater than 0.1 (ranging from 0.103 to 0.123). These results suggest that a multireference wave function may be necessary to properly determine the total correlation energy. However, it is unlikely that such a wave function would produce significant changes in the geometries reported here.

CONCLUSIONS

The rotational constants and associated geometrical parameters of the $\tilde{C}^2A_2$ state of NO$_2$ have been studied using the CCSD and CCSD(T) methods with the DZP, TZ2P, and TZ2P + f basis sets. The results reported here ($R_e=1.290$ Å, $\theta_e=109.3^\circ$) are in qualitative agreement...
with past theoretical studies. However, they are in conflict with the geometry reported by recent OODR spectroscopic determinations ($R \approx 1.4 \, \text{Å}, \theta \approx 102^\circ$). Although confidence in the equilibrium geometries given here may be slightly lowered due to high $T_e$, diagnostic values, the improvements in the geometries given by a multireference wave function would be insignificant relative to the difference between the theoretical and experimental results.

A final possibility for reconciliation between the theoretical and experimental rotational constants is the existence of a $C_2$ equilibrium geometry for the $C$ state of NO$_2$. In his theoretical study, Kaldor$^3$ actually predicted such a geometry:

$$R_{1e}(\text{N-O}) = 1.303 \, \text{Å},$$
$$R_{2e}(\text{N-O}) = 1.274 \, \text{Å},$$
$$\theta_e(\text{O-N-O}) = 109.4^\circ.$$

We have determined Kaldor's rotational constants $B_e$ and $C_e$ to be 0.476 and 0.413 cm$^{-1}$, respectively. However, the rotational constants for Kaldor's $C_{2v}$ stationary point are very similar, namely $B_e = 0.478$ cm$^{-1}$ and $C_e = 0.414$ cm$^{-1}$. Furthermore, the rotational constants from Kaldor's $C_{2v}$ structure are quite close to those reported in Table II. Thus it seems highly unlikely that a lower-symmetry equilibrium geometry is the source of the discrepancy between theory and experiment. We recommend new laboratory studies of the rotational constants and molecular structure of the $C^2A_2$ state of NO$_2$.

Note added in proof. Professor K. Shibuya has informed the authors of new data resulting from updated optical–optical double resonance experiments performed in his group. Dr. Shibuya indicated that the new geometry of the $C^2A_2$ state of NO$_2$ obtained in those experiments was $R_e \approx 1.34 \, \text{Å}$ and $\theta_e \approx 109^\circ$, which agrees remarkably well with the geometries reported in this work. The differences between these new data and those reported earlier$^4$ were explained as the observation of an excited vibrational state rather than the ground vibrational state. A paper summarizing these results has been submitted to the Journal of Physical Chemistry by Dr. Shibuya's group.

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