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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 ($R_e \approx 1.27$ Å, $\theta_e \approx 110°$). 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 $T_0 = 16\,357$ 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 coworkers determined a distinctly different geometry ($R \approx 1.4$ Å, $\theta \approx 102°$) 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($9s5p1d/4s2p1d$); 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 $\alpha_d(\mathrm{N}) = 0.80$ and $\alpha_d(\mathrm{O}) = 0.85$. Those for the TZ2P basis set were $\alpha_d(\mathrm{N}) = 1.60$, 0.40, and $\alpha_d(\mathrm{O}) = 1.70$, 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 $\alpha_f(\mathrm{N}) = 1.00$ and $\alpha_f(\mathrm{O}) = 1.40$. The electronic configuration of the $\tilde{C}\,{}^2A_2$ state is

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 1a_2^1 4b_2^2 6a_1^2.$$

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 DZP 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

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TABLE I. Geometrical parameters (angstroms and degrees) and total energies (hartrees) for the $\tilde{C}\,^2A_2$ state of NO$_2$ for the SCF, CISD, CCSD, and CCSD(T) levels of theory for all three basis sets.

	DZP basis set			
	SCF	CISD	CCSD	CCSD(T)
R_e(N–O)	1.235	1.269	1.290	1.301
θ_e(O–N–O)	109.9	109.5	109.3	109.2
E(hartrees)	−204.009 85	−204.465 58	−204.526 59	−204.546 90
	TZ2P basis set			
	SCF	CISD	CCSD	CCSD(T)
R_e(N–O)	1.224	1.251	1.273	1.286
θ_e(O–N–O)	110.3	110.0	109.8	109.7
E(hartrees)	−204.037 51	−204.564 26	−204.634 31	−204.663 39
	TZ2P+f basis set			
	SCF	CISD	CCSD	CCSD(T)
R_e(N–O)	1.222	1.246	1.267	1.280
θ_e(O–N–O)	110.4	110.1	110.0	109.8
E(hartrees)	−204.046 79	−204.623 52	−204.699 89	−204.731 89

geometries follow expected trends[18] 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.*[4] were B_v=0.435 cm^{-1} and C_v=0.363 cm^{-1}. These compare poorly with the values of B_e=0.480 cm^{-1} and C_e=0.418 cm^{-1} determined here from the TZ2P+f-CCSD(T) geometry. The poor agreement between theory and experiment is tempered by (a) the fact that B_v and C_v should not be identical to B_e and C_e, respectively; and (b) Shibuya and co-workers[4] 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$_2$.

TABLE II. Rotational constants B_e and C_e (in cm^{-1}) for the $\tilde{C}\,^2A_2$ state of NO$_2$ for the SCF, CISD, CCSD, and CCSD(T) levels of theory for all three basis sets.

	DZP basis set			
	SCF	CISD	CCSD	CCSD(T)
B_e	0.516	0.490	0.476	0.469
C_e	0.449	0.426	0.413	0.406
	TZ2P basis set			
	SCF	CISD	CCSD	CCSD(T)
B_e	0.522	0.501	0.486	0.476
C_e	0.455	0.436	0.422	0.414
	TZ2P+f basis set			
	SCF	CISD	CCSD	CCSD(T)
B_e	0.523	0.505	0.489	0.480
C_e	0.456	0.439	0.426	0.418

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.[3] 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.[3] These differences result in slightly different equilibrium geometries (Kaldor reports R_e=1.286 Å, θ_e=109.4°, and E=−204.528 91 hartrees, as opposed to our R_e=1.290 Å, θ_e=109.3°, and E=−204.526 59 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.[19] 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[19] 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, θ_e=109.3°) are in qualitative agreement with past theoretical studies. However, they are in conflict with the geometry reported by recent OODR spectroscopic determinations ($R \approx 1.4$ Å, $\theta \approx 102°$). Although confidence in the equilibrium geometries given here may be slightly lowered due to high T_1 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_s equilibrium geometry for the $\tilde{C}$ state of NO_2. In his theoretical study, Kaldor[3] actually predicted such a geometry:

$$R_{1e}(\text{N–O}) = 1.303 \text{ Å},$$

$$R_{2e}(\text{N–O}) = 1.274 \text{ Å},$$

$$\theta_e(\text{O–N–O}) = 109.4°.$$

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 $\tilde{C}\,^2A_2$ 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 $\tilde{C}\,^2A_2$ state of NO_2 obtained in those experiments was $R_e \approx 1.34$ Å and $\theta_e \approx 109°$, 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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