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The $\tilde{C}\ ^2A_2$ excited state of NO_2: Evidence for a C_s equilibrium structure and a failure of some spin-restricted reference wavefunctions

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The geometry and harmonic vibrational frequencies of the the $\tilde{C}\ ^2A_2$ electronic state of nitrogen dioxide have been determined using coupled cluster (CC) theory in conjunction with large basis sets. The minimum energy C_{2v}-constrained N–O bond distance predicted by the highest level of theory is significantly shorter than the experimentally inferred value, and it is unlikely that further refinement in the theoretical treatment would reduce the discrepancy. However, this work suggests that a prevailing assumption of C_{2v} symmetry may be incorrect; the equilibrium structure of the $\tilde{C}$ state may instead have C_s symmetry. In addition, and contrary to expectation, CC calculations based on variationally optimal spin-unrestricted or spin-restricted reference determinants give qualitatively different results for this system, unless very high levels of electron correlation are included in the calculation. [S0021-9606(97)00631-4]

I. INTRODUCTION

The low-lying doublet states of NO_2 have been studied both theoretically[1–11] and experimentally.[12–18] The pioneering theoretical work of Gillispie, *et al.*[1] and Jackels and Davidson[2,3] elucidated some of the qualitative features of the ground and lower excited state potential surfaces, while more contemporary high-level theoretical studies[6,8,9,11] have focused on the quantitative determination of the properties of individual electronic states. The ground electronic state of NO_2 is of $^2A_1$ symmetry, with an equilibrium O–N–O bond angle of approximately 133°.[9] The first excited state ($^2B_2$ symmetry) lies approximately 1 eV above the ground state with an equilibrium bond angle of 100°.[9] The $\tilde{B}\ ^2B_1$ state lies approximately 1.6 eV above the ground state, with which it is degenerate in its linear, minimum-energy configuration.[6]

Recently, Aoki, Hoshina, and Shibuya[18] reported optical-optical double resonance spectroscopic analyses of the $\tilde{C}\ ^2A_2$ electronic state of NO_2, based on the fluorescence spectrum of the $\tilde{D}\ ^2B_2$ state. They determined a C_{2v} geometry with $r(\mathrm{N–O}) = 1.339 \pm 0.010$ Å, $\theta = 108.4 \pm 1.0°$. The bond length determined in that work differs significantly from a value of 1.280 Å obtained at the CCSD(T) level (coupled cluster singles and doubles including a non-iterative treatment of connected triples) using a large basis set.[11] Such high-level quantum mechanical methods are expected to provide much greater accuracy than this comparison suggests,[19,20] a finding that seemingly warrants experimental reinvestigation. Nevertheless, in order to resolve the open question of whether the earlier theoretical treatment provided an adequate description of this system, we have carried out a systematic study of the effects of basis set expansion and electron correlation treatments on the N–O bond length. A curious and unprecedented inadequacy of CC calculations based on variationally optimal spin-restricted reference functions has been noted in the course of this work and is discussed as well.

II. THEORETICAL METHODS

The minimum energy C_{2v} geometry and harmonic vibrational frequencies of the $\tilde{C}$ state of NO_2 have been determined using a number of different basis sets, coupled cluster approaches and reference determinants. The basis sets used in this research were a double-zeta[21,22] plus polarization[23] (DZP) set, and the cc-pVTZ and cc-pVQZ correlation consistent basis sets of Dunning.[24] At the CCSD (Refs. 25, 26) and CCSD(T) (Refs. 27–29) levels of theory, calculations were performed with all basis sets using spin-unrestricted and -restricted Hartree-Fock (UHF and ROHF) reference states, as well as the quasi-restricted Hartree-Fock (QRHF) determinant[30] based on molecular orbitals optimized for the anion. In addition, calculations at the full CCSDT level[31–33]—which is expected to provide a nearly complete treatment of electron correlation—have been carried out using all three reference functions with the DZP basis. Pure

TABLE I. Absolute energies (E_h), geometrical parameters (Å and degrees), and harmonic vibrational frequencies (cm^{-1}, infrared intensities are given in parentheses in km/mol) for the $\tilde{C}\ ^2A_2$ state of NO_2 at the CCSD, CCSD(T), and CCSDT levels of theory with UHF, ROHF and QRHF reference functions in a DZP basis.

	UHF-CCSD	ROHF-CCSD	QRHF-CCSD
Energy	−204.573223	−204.569662	−204.569647
r_e (N–O)	1.284	1.281	1.281
θ_e (O–N–O)	109.6	109.6	109.6
ω_1	1338(17)	1362(17)	1360(16)
ω_2	771(7)	778(8)	777(8)
ω_3	$550i(8)$	549(21)	$785i(2)$
	UHF-CCSD(T)	ROHF-CCSD(T)	QRHF-CCSD(T)
Energy	−204.589748	−204.589835	−204.589627
r_e (N–O)	1.290	1.291	1.291
θ_e (O–N–O)	109.6	109.5	109.5
ω_1	1309(17)	1304(17)	1301
ω_2	756(7)	755(7)	754
ω_3	$563i(10)$	341(21)	$465i$
	UHF-CCSDT	ROHF-CCSDT	QRHF-CCSDT
Energy	−204.591514	−204.590605	−204.590662
r_e (N–O)	1.292	1.291	1.291
θ_e (O–N–O)	109.5	109.5	109.5
ω_1	1294	1304	1303
ω_2	751	754	754
ω_3	$544i$	$466i$	$628i$

angular momentum functions were used in the calculations, all of which were performed with the ACES II program system.[34] Harmonic vibrational frequencies were calculated using finite differences of analytic gradients[29,35,36] for the UHF- and ROHF-based CCSD and CCSD(T) methods and the QRHF-based CCSD method for the DZP and cc-pVTZ basis sets, and using finite differences of energies for all other methods and basis sets. In the determination of asymmetric stretching vibrational frequencies, variational collapse to lower-energy states did not occur in the UHF and ROHF calculations at C_s-distorted structures.

III. RESULTS AND DISCUSSION

Properties predicted with the CCSD, CCSD(T), and CCSDT methods and the DZP basis set are given in Table I. For a given CC approach, the three reference wavefunctions produce consistent results for all totally symmetric properties (the N–O bond length, r_e, the bond angle, θ_e, and the harmonic vibrational frequencies, ω_1 and ω_2). The insensitivity of results with respect to the choice of reference function is typical of CC methods that include a treatment of single excitations, and is a manifestation of the powerful treatment of orbital relaxation effects included in these approaches.[37] Nevertheless, the DZP results display a strikingly large variation in the predicted asymmetric stretching frequency (ω_3). All UHF- and QRHF-based CC methods predict that the C_{2v} structure is a transition state for interconversion of two equivalent C_s structures. Improvement of the electron correlation treatment from CCSD, through CCSD(T), to full CCSDT has only a modest effect on the magnitude of the imaginary asymmetric stretching frequency in the UHF- and QRHF-based calculations; it is most unlikely that the exact (full configuration interaction) result for this basis set would give a significantly different answer. This contention is supported by large-scale multireference averaged quadratic coupled-cluster (MR-AQCC) (Refs. 38, 39) and multireference Davidson-corrected configuration interaction (MRCI) calculations at both the DZP/UHF-CCSD(T) C_{2v}-constrained structure reported in Table I and a C_s minimum energy structure found at the same level of theory [$r(N–O_A)=1.513$ Å, $r(N–O_B)=1.183$ Å, $\theta=109.5°$]. MR-AQCC and MRCI calculations were based on three different reference spaces: a 3×3 CAS including one a_2 and two b_1 orbitals, a 3×5 CAS including three b_1 and two a_2 orbitals, and a 7×7 CAS including two a_1, one a_2, two b_1 and two b_2 orbitals. With the MR-AQCC (MRCI) methods within the DZP basis, the C_s structure was found to lie 2.20, 1.96, and 4.04 (1.25, 0.79, and 3.08) kcal/mol below the C_{2v} structure with the 3×3, 3×5, and 7×7 active spaces, respectively.

While the UHF- and QRHF-based CC results are consistent with one another, the ROHF-based CC calculations exhibit an entirely different behavior. At the CCSD and CCSD(T) levels of theory, the C_{2v} structures are predicted to be minima, in qualitative disagreement with the UHF- and QRHF-CC results. This behavior is ultimately derived from a b_2-symmetry instability in the ROHF orbital Hessian,[10,40] which is not present for the UHF determinant. This strongly (and artificially) biases the reference wavefunction towards a C_{2v} minimum-energy structure. While such features may often have no appreciable effect on correlated wavefunctions, it is clear that this is not the case for the $\tilde{C}$ state of NO_2.[41] When the theoretical treatment is extended to the full ROHF-CCSDT level, an imaginary frequency is finally obtained, and its magnitude is similar to that of the UHF-CCSDT and QRHF-CCSDT predictions. These results suggest that the ROHF-based CCSD and CCSD(T) methods are inadequate for even a qualitative description of the asymmetric region of the potential energy surface. This is a surprising finding, as it is generally believed that UHF- and ROHF-based CC calculations will give essentially the same results. Indeed, the ROHF-based approach is sometimes thought to be preferable because of the spin-adapted property of the reference determinant. It is clear that neither of these presumptions is supported by the present results.[42]

Despite the curious variation in the asymmetric stretching frequencies discussed above, the other properties under investigation exhibit rather typical behavior. The noniterative CCSD(T) calculations provide results which are essentially identical to those obtained at the considerably more expensive CCSDT level, and the structure and totally symmetric harmonic vibrational frequencies exhibit a decided insensitivity with respect to the choice of reference function. Therefore, it would appear that the CCSD and CCSD(T) methods used in conjunction with the larger basis sets are sufficient to establish an improved prediction of the N–O distance for C_{2v}-symmetric $\tilde{C}\ ^2A_2$ NO_2, which is the principal objective of this work. Results obtained with the larger

TABLE II. Absolute energies (E_h), geometrical parameters (Å and degrees), and harmonic vibrational frequencies (cm^{-1}, infrared intensities are given in parentheses in km/mol) for the $\tilde{C}$ $^2A_2$ state of NO_2 at the CCSD and CCSD(T) levels of theory with UHF, ROHF and QRHF reference functions in cc-pVTZ and cc-pVQZ basis sets.

		cc-pVTZ basis set			cc-pVQZ basis set	
	UHF-CCSD	ROHF-CCSD	QRHF-CCSD	UHF-CCSD	ROHF-CCSD	QRHF-CCSD
Energy	−204.732043	−204.728629	−204.729184	−204.842232	−204.838851	−204.839374
r_e (N–O)	1.267	1.263	1.264	1.263	1.260	1.260
θ_e (O–N–O)	110.0	110.0	110.1	110.1	110.1	110.1
ω_1	1360(13)	1382(13)	1382(13)	1369	1391	1390
ω_2	790(6)	797(6)	797(6)	796	803	802
ω_3	$557i(3)$	707(18)	$801i(0)$	$553i$	745	$801i$
	UHF-CCSD(T)	ROHF-CCSD(T)	QRHF-CCSD(T)	UHF-CCSD(T)	ROHF-CCSD(T)	QRHF-CCSD(T)
Energy	−204.759768	−204.760695	−204.760246	−204.873605	−204.874570	−204.874097
r_e (N–O)	1.274	1.275	1.276	1.271	1.272	1.273
θ_e (O–N–O)	109.9	109.9	109.9	110.0	109.9	109.9
ω_1	1328(13)	1317(13)	1314	1335	1323	1321
ω_2	773(5)	770(5)	770	778	775	774
ω_3	$583i(5)$	403(15)	$473i$	$579i$	399	$465i$

cc-pVTZ and cc-pVQZ basis sets are collected in Table II. The expected shortening of internuclear distance with respect to basis set expansion is observed. The CCSD(T) predictions decrease systematically from about 1.290 Å (DZP) to about 1.272 Å (cc-pVQZ). Given that the cc-pVTZ and cc-pVQZ predictions of the bond length differ by only a few thousandths of an Ångstrom, further expansion of the basis is unlikely to have an appreciable effect on r_e(N–O). In fact, such basis set improvement would probably serve to decrease this value, placing it further away from the experimentally determined value of 1.339 Å. In our opinion, it is exceedingly unlikely that the exact minimum-energy N–O distance for the C_{2v} symmetric structure lies outside the range $1.267-1.277$ Å. While the experimental value corresponds to a vibrationally averaged N–O distance, anharmonic corrections of this magnitude are implausible for a relatively rigid C_{2v} structure.

While the results presented here demonstrate that the experimentally inferred N–O distance in the C_{2v} structure of the $\tilde{C}$ $^2A_2$ state of NO_2 is not consistent with theory, they also raise the following question: Does the equilibrium structure of this state have equivalent N–O bonds after all? With the notable exception of a study by Kaldor[9]—which also indicated the C_{2v} form might be unstable with respect to symmetry lowering—all previous experimental[15,16,18] and theoretical[1,3,10,11] studies have assumed C_{2v} symmetry. Our results indicate that this may not be the case, and that the $\tilde{C}$ state may suffer from a pseudo-Jahn-Teller distortion due to interaction with the higher-lying $\tilde{B}$ $^2B_1$ state via the asymmetric stretching vibration. For all of the basis sets used here, UHF- and QRHF-based CCSD and CCSD(T) concur with the small (DZP) basis results of Kaldor, predicting a C_s geometry. Moreover, the magnitude of the imaginary frequency does not seem to be particularly sensitive to the choice of basis set; results obtained with the DZP (45 functions) and cc-pVQZ (165 functions) basis sets are essentially identical. While the ROHF-based results with the larger basis sets exhibit behavior similar to that found with the DZP set [a C_{2v} structure is predicted at both CCSD and CCSD(T) levels], differences between CCSD and CCSD(T) are very large, and we suspect that the frequency would become imaginary at the full CCSDT level.

IV. CONCLUSIONS

The results of this study consist of two observations which warrant experimental reinvestigation of the $\tilde{C}$ state of NO_2. First, the minimum energy N–O bond length of this structure is considerably shorter than the distance inferred from experiment, and the magnitude of this discrepancy is large enough that it cannot be attributed to inadequacies in the theoretical methods used here. Second, it seems that the true equilibrium structure of this state may actually have C_s symmetry due to a pseudo-Jahn-Teller distortion. We believe this possibility should be considered in a revised analysis of the experimental data.

While one purpose of this work is to suggest the possibility of a C_s equilibrium geometry rather than a precise determination of the corresponding internuclear distances and bond angle, it is interesting to note that for the C_s minimum energy structure noted in section III, the average of the N–O bond distances is 1.348 Å. This is greater than the corresponding N–O distance in the C_{2v} structure, and in relatively good agreement with the experimentally inferred value. Given that we find an energy difference of only *ca.* 600 cm^{-1} between the C_{2v} and C_s structures at this level of theory [DZP/UHF-CCSD(T)], it is plausible that the zero-point vibrational level lies above the barrier and the *dynamical* symmetry of the $\tilde{C}$ state therefore is C_{2v}. If this is so, then the N–O bond length inferred from experiment would correspond roughly to an average of the two distances in the C_s structure. While this scenario is clearly consistent with the present set of calculations, a more detailed study of the potential energy surface including determination of anharmonic vibrational wavefunctions is required before any definitive conclusions can be drawn.

We also note that the $\widetilde{C}$ state of NO_2 is an example of a molecular system for which UHF and ROHF reference wavefunctions provide *qualitatively* different predictions of the molecular properties, even when relatively sophisticated treatments of electron correlation are used. Significantly, the ROHF-based CCSD(T) approach is apparently a poor approximation to the full CCSDT here, as the two give very different results for the asymmetric stretching frequency.

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