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A systematic theoretical investigation of the valence excited states of the diatomic molecules B_2, C_2, N_2 and O_2

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Abstract. A quantitative survey on the performance of multireference (MR), configuration interaction with all singles and doubles (CISD), MRCISD with the Davidson correction and MR-average quadratic coupled cluster (AQCC) methods for a wide range of excited states of the diatomic molecules B_2, C_2, N_2 and O_2 is presented. The spectroscopic constants r_e, ω_e, T_e and D_e for a total of 60 states have been evaluated and critically compared with available experimental data. Basis set extrapolations and size-extensivity corrections are essential for highly accurate results: MR-AQCC mean-errors of 0.001 Å, 10 cm^{-1}, 300 cm^{-1} and 300 cm^{-1} have been obtained for r_e, ω_e, T_e and D_e, respectively. Owing to the very systematic behavior of the results depending on the basis set and the choice of method, shortcomings of the calculations, such as Rydberg state coupling or insufficient configuration spaces, can be identified independently of experimental data. On the other hand, significant discrepancies with experiment for states which indicate no shortcomings whatsoever in the theoretical treatment suggest the re-evaluation of experimental results. The broad variety of states included in our survey and the uniform quality of the results indicate that the observed systematics is a general feature of the methods and, hence, is molecule-independent.

Key words: Excited States – Spectroscopic constants – Ab initio – Size-extensivity – Basis set extrapolation

1 Introduction

Accurate calculations on electronically excited states are still a big challenge. Particularly difficult are simultaneous and well-balanced calculations on a large number of states of different character. Additional complications arise if potential-energy surfaces of excited states and/or properties such as transition moments are to be calculated. In order to obtain high-precision results, systematic investigations concerning computational methodology (in particular size-extensivity effects) and basis set effects are essential. For excited states size-extensivity effects can differ widely from case to case owing to large variations in the multireference (MR) character. Moreover, basis set effects are at least as important for excited states as for ground states. Because of the much larger complexity of excited-state calculations, basis set extrapolations and other systematic investigations have concentrated on the electronic ground state so far [1]. It is the purpose of this article to fill this gap by reporting such systematic investigations performed on excited states of diatomic molecules and to provide benchmark data laying the basis for accurate calculations on larger molecules.

Special methods have been developed for dealing with excited states, such as complete-active-space perturbation theory to second order (CASPT2) [2, 3], equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) [4, 5] or the equivalent CCSD-linear response theory (LRT) [6, 7]. Although these methods are being used very successfully in many applications, they are also connected with a number of serious problems, such as intruder states in the case of CASPT2 [8] or the restriction to states dominated by single excitations in the case of EOM-CCSD or CCSD-LRT [4].

As an alternative to these methods, configuration interaction (MR-CI) [9] – often used in the form of MR-CI with all singles and doubles (MR-CISD) – is available. MR-CISD is a very robust method with a long tradition, which, unfortunately lacks size-extensivity; therefore, several methods have been developed for the computation of size-extensivity corrections to MR-CISD. The simplest one is the Davidson correction (MR-CISD + Q) [10] and its MR extension [11]. More sophisticated methods are MR averaged-coupled-pair functional (MR-ACPF) [12] and MR averaged quadratic coupled cluster (MR-AQCC) [13, 14]. Unlike the

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Davidson method, where the size-extensivity corrections are evaluated a posteriori, in MR-AQCC and MR-ACPF these corrections are consistently built in from the very beginning. These methods have been very successfully applied to ground states of a given symmetry. By formulating MR-AQCC/MR-ACPF in terms of a diagonal shift [15] we are in the position to perform excited-state calculations with these methods also. They have the additional advantage over the Davidson correction that analytical energy gradients with respect to nuclear coordinates are available [16], which is crucial for the calculation of excited-state geometries.

MR-AQCC is closely related to MR-ACPF. Empirically we have found that MR-ACPF tends to overestimate the effect of higher excitations [13]. The slightly different approximations used in MR-AQCC give a more conservative estimate of size-extensivity contributions and, thus, overcome the problem of ACPF "overshooting" in many cases [13, 14]. The performance of MR-AQCC for the calculation of excitation energies and transition moments has been tested previously for cases where full CI (FCI) reference data were available [17]. These investigations showed very clearly the advantages of MR-AQCC over MR-CISD but owing to the lack of FCI reference data they were limited to rather small applications in terms of molecules and basis sets. Hence, in this work we extend our former studies by systematic investigations on spectroscopic quantities for excited states of diatomic molecules. We investigate the accuracy of MR-AQCC calculations for cases where a large set of excited states is treated simultaneously, employing very large basis sets (including basis set limit extrapolations) and flexible wave functions. In addition to MR-AQCC, the MR-CISD and MR-CISD + Q methods were applied. Comparison of the results obtained with these methods allows systematic information on the importance of size-extensivity effects for excited states and on the reliability of the relatively straightforward Davidson correction method to be retrieved.

We consider a multitude of bound, excited valence states of B_2, C_2, N_2 and O_2, which differ widely in bond strengths and bond lengths. Most of them are well characterized experimentally, which allows us to critically evaluate the computed results. On the other hand, on the basis of statistical reasoning, we can also identify problematic experimental results. Previous calculations concentrated on relatively few states of these molecules, investigating carefully their spectroscopic properties [18–23]. However, the aforementioned basis set extrapolations and size-extensivity investigations were not available so far. The selected molecules also allow the systematic study of size-extensivity effects as the number of valence electrons ranges from six to twelve and a progressively increasing importance of size- extensivity effects can be expected.

2 Calculational details

The MR-CISD, MR-AQCC [13] and MR-CISD + Q [10, 11] methods were used. The MR-CISD + Q energy is calculated as

$$E_{\mathrm{CI+Q}} = \left(1 - \sum_{i=1}^{N_{\mathrm{ref}}} c_i^2\right)(E_{\mathrm{CI}} - E_{\mathrm{REF}}) + E_{\mathrm{CI}} \tag{1}$$

$$= (1 - c_0^2)(E_{\mathrm{CI}} - E_{\mathrm{REF}}) + E_{\mathrm{CI}} \ , \tag{2}$$

with E_{REF} denoting the energy contributions of the reference configurations and c_i^2 their corresponding weights in the MR-CI wave function.

The reference space consisted of a CAS in the valence orbitals derived from the $2s$ and $2p$ atomic orbitals. The reference configurations plus all single and double excitations into all virtual orbitals constitute the final configuration space. The $1s$ orbitals were kept frozen in all post-MCSCF calculations.

The orbitals were obtained by a state-averaged multiconfigurational self-consistent-field (MCSCF) procedure using the same valence CAS wave function as mentioned earlier. The state-averaged MCSCF procedure was used for two reasons. First, in order to maintain the $D_{\infty h}$ symmetry of the orbitals using only the Abelian subgroup D_{2h} in the calculations, the degenerate pairs of the Π, Δ and Φ states had to be considered simultaneously. Secondly, state-averaged MCSCF orbitals are better suited for a balanced description of states in the subsequent MR-AQCC or MR-CISD calculations.

The state-averaging procedure relies heavily on a sufficiently flexible wave function, which is even more important here as we compute different sections of the potential-energy curves: those around the minimum and those at infinite separation. The valence CAS used here is certainly sufficiently flexible for our purposes even though slight artifacts are observed in connection with larger basis sets. State-averaging is restricted to states of the same multiplicity. The energies of the dissociated molecules are computed by the supermolecule approach at an internuclear distance of 100 bohr. Experimental dissociation energies are derived from the experimental molecular and atomic term values in conjunction with the ground-state dissociation energies. To facilitate the comparison between experiment and theory spin-orbit splittings (absent in the calculations) were eliminated for the atoms, i.e. the atomic term values are a multiplicity-weighted average over the components belonging to different J values. The experimental ground-state dissociation energies were adjusted accordingly by the difference between atomic term values including and excluding spin-orbit splittings [24].

The correlation-consistent basis sets of Dunning and coworkers [25–27] were chosen, since these basis sets provide a well-defined series and the calculated energies can be extrapolated to the complete basis set limit [1, 24, 28–30]. In the present study we used mostly the correlation-consistent polarized valence triple-zeta (cc-pVTZ) and correlation-consistent polarized valence quadtriuple-zeta (cc-pVQZ) sets and in some cases also correlation-consistent polarized valence quintuple-zeta (cc-pV5Z).

Basis set extrapolations were performed following the work of Halkier et al. [28], Truhlar [29] and Fast et al. [30]. It has been demonstrated that the electron correlation energy can be well extrapolated in single-reference cases by

$$\Delta E_\infty = \Delta E_X + AX^{-3} \ , \tag{3}$$

where X is the cardinal number of the basis set, i.e. $X = 3, 4, 5$ for cc-pVTZ, cc-pVQZ and cc-pV5Z, respectively. Halkier et al. [28] also showed that it is better to use for the extrapolation just the data obtained from the two highest cardinal numbers available than to fit the results obtained with several basis sets. The procedure of Halkier et al. [28] leads to the following formula:

$$\Delta E_\infty = \frac{\Delta E_X X^3 - \Delta E_Y Y^3}{X^3 - Y^3} \ , \tag{4}$$

with X and Y being the two cardinal numbers.

In order to obtain extrapolated total energies, the reference energy has to be considered as well. The SCF energy was extrapolated separately by Truhlar [29] since its convergence behavior is somewhat faster than that of the electron correlation energy. A similar situation applies to the MR case. However, in view of the lack of reference data for converged results we did not see a well-founded way to evaluate separate exponents for reference- and electron-correlation energies; therefore, we used the same exponents in both cases and extrapolated the total energies according to Eq. (4). (TQ) stands for extrapolation based on cc-pVTZ and cc-pVQZ and (Q5) for extrapolation using cc-pVQZ and cc-pV5Z. The extrapolation scheme was applied to energies only. Derived quantities, such as the bond lengths or harmonic frequencies, were computed by fitting polynomials to the respective energy points. Our extrapolation procedure is certainly a very pragmatic one, which gives, as the large number of examples given later will show, significant improvements. However, it is also clear that especially in the MR case more extended and systematic investigations concerning basis set extrapolations using Eq. (4) or similar ones are necessary. The calculations were carried out using the COLUMBUS program system [31, 32] employing the AO integral package from DALTON [33].

3 Results and discussion

3.1 Individual analysis

The electronic states considered in this study are listed in Table 1 along with their leading configurations at the energy minimum. The calculated excitation energies (term values T_e), harmonic vibrational frequencies (ω_e), equilibrium geometries (r_e) and dissociation energies (D_e) are given for all four molecules in Tables 2–17 together with available experimental data. Basis set effects are usually discussed in terms of the difference between cc-pVTZ and (TQ) extrapolated data unless otherwise specified. Size-extensivity effects are discussed in terms of the differences between MR-CISD + Q/MR-AQCC and MR-CISD data with identical basis sets, preferentially for the (TQ) extrapolated data.

3.1.1 B_2

Very little experimental data is available for B_2. Only the $\tilde{X}^3\Sigma_g^-$ and the $2^3\Sigma_u^-$ states have been characterized experimentally [34, 35]. A number of theoretical studies on the spectroscopy of B_2 have been carried out. Dupuis and Liu [36] established the ground-state symmetry and multiplicity of B_2. The most extensive studies on excited states of B_2 are due to Langhoff and Bauschlicher and Hachey et al. [37]. Whereas the first study focused on the characterization of valence states using basis sets of approximately cc-pVTZ and partly cc-pVQZ quality, Hachey et al. also included a series of Rydberg states but restricted the valence part of the basis set to about pVDZ quality.

In this work eight singlet, eleven triplet and six quintet states of varying bond strength and varying excitation level with respect to the ground-state configuration were calculated. Quite generally, we find that the MR-AQCC results are always located between MR-CISD and MR-CISD + Q. For each method a uniform trend with increasing basis set size is observed throughout: bond lengths generally decrease (up to about 0.015 Å for the $\tilde{X}^3\Sigma_g^-$ state) and size-extensivity corrections lead in most cases to a further slight contraction Table 2. The basis set effect on harmonic frequencies (Table 3) varies strongly from only a few wave numbers ($A^3\Pi_u$, $2^3\Sigma_g^-$) up to 70 cm^{-1} ($2^1\Pi_g$) with the general tendency to increase the frequencies with increasing basis size. Less-pronounced effects are found for size-extensivity corrections. Term values (Table 4) are affected by up to 700 cm^{-1} owing to basis set effects

Table 1. Electronic states and their leading configurations ($1\sigma_g$ and $1\sigma_u$ doubly occupied throughout)

Molecule	State	Configuration
B_2	$b^1\Delta_g, c^1\Sigma_g^+, \tilde{X}^3\Sigma_g^-$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$
	$d^1\Pi_u, A^3\Pi_u, 1^5\Pi_u$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^1(3\sigma_g)^1$
	$e^1\Sigma_g^+$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2$
	$1^1\Sigma_u^-, 1^1\Delta_u, 1^3\Delta_u, 1^3\Sigma_u^-, 1^3\Sigma_u^+, a^5\Sigma_u^-$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^2(3\sigma_g)^1$
	$1^1\Pi_g, 1^3\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^3$
	$2^1\Pi_g, 2^3\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^1(3\sigma_g)^2$
	$2^3\Pi_u$	$(2\sigma_g)^2(1\pi_u)^3(3\sigma_g)^1$
	$1^5\Sigma_g^+, 1^5\Delta_g, 2^3\Sigma_g^-, 2^3\Delta_u, 2^3\Sigma_u^-$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^1(3\sigma_g)^1(1\pi_g)^1$
	$1^5\Sigma_g^-$	$(2\sigma_g)^1(2\sigma_u)^2(1\pi_u)^2(3\sigma_g)^1$
	$1^5\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^3$
C_2	$\tilde{X}^1\Sigma_g^+$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$
	$A^1\Pi_u, a^3\Pi_u$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^1$
	$B^1\Delta_g, B'^1\Sigma_g^+, b^3\Sigma_g^-$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(3\sigma_g)^2$
	$D^1\Sigma_u^+, c^3\Sigma_u^+$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^4(3\sigma_g)^1$
	$C^1\Pi_g, d^3\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^3(3\sigma_g)^2$
	${}^1\Sigma_u^-, {}^1\Delta_u$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(1\pi_g)^1$
	$e^3\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(3\sigma_g)^1(1\pi_g)^1$
N_2	$\tilde{X}^1\Sigma_g^+$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$
	$A^3\Sigma_u^+, W^3\Delta_u, B'^3\Sigma_u^-, a'^1\Sigma_u^-, w^1\Delta_u, b'^1\Sigma_u^+$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^1$
	$B^3\Pi_g, a^1\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^1(1\pi_u)^4(1\pi_g)^1$
	$G^3\Delta_g$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_g)^2$
	$C^3\Pi_u$	$(2\sigma_g)^2(2\sigma_u)^1(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1$
	$C'3\Pi_u, b^1\Pi_u$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^1(1\pi_u)^3(1\pi_g)^2$
O_2	$\tilde{X}^3\Sigma_g^-, a^1\Delta_g, b^1\Sigma_g^+$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$
	$A'^3\Delta_u, A^3\Sigma_u^+, B^3\Sigma_u^-, c^1\Sigma_u^-$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^3$
	${}^3\Pi_g, {}^1\Pi_g$	$(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^1(1\pi_u)^4(1\pi_g)^3$

Table 2. Equilibrium bond distances, r_e (Å), for B_2

State	MR-AQCC			MR-CISD			MR-CISD + Q		
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)
$b^1\Delta_g$	1.6244	1.6175	1.6124	1.6245	1.6177	1.6128	1.6242	1.6177	1.6121
$c^1\sum_g^+$	1.6620	1.6545	1.6492	1.6602	1.6527	1.6472	1.6654	1.6580	1.6524
$d^1\Pi_u$	1.7885	1.7816	1.7765	1.7874	1.7805	1.7755	1.7900	1.7830	1.7779
$e\ ^1\Sigma_g^+$	1.8216	1.8125	1.8061	1.8232	1.8154	1.8099	1.8189	1.8080	1.8001
$1\ ^1\Sigma_u^-$	1.5777	1.5658	1.5578	1.5788	1.5671	1.5591	1.5759	1.5641	1.5560
$1^1\Pi_g$	1.4845	1.4782	1.4736	1.4845	1.4782	1.4736	1.4846	1.4783	1.4737
$1^1\Delta_u$	1.6974	1.6878	1.6806	1.6948	1.6852	1.6786	1.7007	1.6912	1.6823
$2^1\Pi_g$	1.6253	1.6143	1.6068	1.6273	1.6178	1.6111	1.6227	1.6107	1.6025
$X^3\Sigma_g^-$ [a]	1.6048	1.5986	1.5941	1.6050	1.5990	1.5945	1.6045	1.5982	1.5935
$A^3\Pi_u$	1.7616	1.7546	1.7496	1.7618	1.7551	1.7501	1.7612	1.7541	1.7488
$1^3\Delta_u$	1.5517	1.5449	1.5399	1.5522	1.5454	1.5405	1.5510	1.5454	1.5390
$1^3\Sigma_u^-$	1.5413	1.5350	1.5304	1.5419	1.5356	1.5310	1.5407	1.5343	1.5297
$1^3\Sigma_u^+$	1.5711	1.5638	1.5584	1.5713	1.5640	1.5587	1.5709	1.5634	1.5580
$1^3\Pi_g$	1.5020	1.4953	1.4904	1.5021	1.4953	1.4904	1.5021	1.4953	1.4904
$2^3\Pi_g$	1.6418	1.6332	1.6269	1.6435	1.6357	1.6299	1.6397	1.6302	1.6234
$2^3\Delta_u$	1.9052	1.9035	1.9024	1.9084	1.9070	1.9059	1.9016	1.8998	1.8984
$2^3\Sigma_u^-$ [b]	1.6460	1.6369	1.6300	1.6455	1.6371	1.6308	1.6467	1.6369	1.6294
$2^3\Pi_u$	1.4678	1.4602	1.4548	1.4684	1.4610	1.4555	1.4669	1.4593	1.4537
$2^3\Sigma_g^-$	1.7881	1.7799	1.7738	1.7898	1.7819	1.7761	1.7864	1.7781	1.7718
$a^5\Sigma_u^-$	1.5307	1.5250	1.5207	1.5312	1.5256	1.5214	1.5300	1.5242	1.5199
$1^5\Delta_g$	1.7961	1.7896	1.7848	1.7954	1.7890	1.7843	1.7970	1.7904	1.7856
$1^5\Sigma_g^+$	1.8041	1.7977	1.7929	1.8035	1.7971	1.7923	1.8050	1.7986	1.7938
$1^5\Sigma_g^-$	1.8770	1.8704	1.8656	1.8786	1.8722	1.8675	1.8751	1.8682	1.8631
$1^5\Pi_u$	1.7402	1.7326	1.7271	1.7407	1.7332	1.7278	1.7396	1.7319	1.7262
$1^5\Pi_g$	1.6249	1.6168	1.6109	1.6265	1.6187	1.6130	1.6227	1.6144	1.6084

[a] Experiment: 1.5838 [35], 1.5902 [34]
[b] Experiment: 1.6188 [35], 1.6025 [34]

Table 3. Harmonic frequencies, ω_e(cm^{-1}), for B_2

State	MR-AQCC			MR-CISD			MR-CISD + Q		
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)
$b^1\Delta_g$	987	995	1000	987	995	999	987	995	1000
$c^1\sum_g^+$	820	829	835	834	844	850	802	808	816
$d^1\Pi_u$	741	746	749	748	754	758	732	736	737
$e^1\Sigma_g^+$	951	957	967	942	954	964	947	957	968
$1^1\Sigma_u^-$	941	984	1015	937	978	1009	948	990	1021
$1^1\Pi_g$	1293	1301	1305	1294	1302	1309	1292	1299	1306
$1^1\Delta_u$	785	785	786	790	793	795	778	775	776
$2^1\Pi_g$	1002	1039	1060	996	1023	1043	1011	1052	1077
$X^3\Sigma_g^-$ [a]	1031	1037	1042	1032	1038	1043	1031	1037	1040
$A^3\Pi_u$	801	806	808	802	807	809	799	804	807
$1^3\Delta_u$	1183	1193	1202	1183	1193	1200	1184	1194	1205
$1^3\Sigma_u^-$	1191	1200	1206	1189	1197	1204	1193	1202	1209
$1^3\Sigma_u^+$	1117	1129	1138	1117	1130	1140	1116	1130	1138
$1^3\Pi_g$	1187	1198	1206	1189	1201	1208	1186	1195	1201
$2^3\Pi_g$	1213	1211	1211	1211	1212	1207	1214	1213	1215
$2^3\Delta_u$	953	947	941	950	946	941	958	951	946
$2^3\Sigma_u^-$ [b]	926	925	924	931	931	932	919	917	917
$2^3\Pi_u$	1334	1352	1366	1332	1350	1364	1337	1355	1369
$2^3\Sigma_g^-$	777	778	779	775	776	777	781	780	781
$a^5\Sigma_u^-$	1249	1255	1259	1248	1254	1258	1250	1256	1261
$1^5\Delta_g$	831	836	839	832	837	840	830	834	838
$1^5\Sigma_g^+$	820	824	829	821	825	830	818	823	827
$1^5\Sigma_g^-$	638	641	642	636	640	641	640	643	644
$1^5\Pi_u$	826	832	837	825	831	836	826	834	840
$1^5\Pi_g$	929	939	947	927	936	940	932	936	952

[a] Experiment: 1060 [35], 1051 [34]
[b] Experiment: 937 [34, 35]

($1^1\Pi_g$) and up to 500 cm^{-1} owing to size-extensivity ($d^1\Pi_u$), but the effects are mostly much less. Size-extensivity effects estimated by MR-CISD + Q are frequently much larger than those obtained from MR-AQCC. The dissociation energies generally increase with increasing basis set size. (TQ) extrapolation still

Table 4. Term values, T_e(cm^{-1}), for B_2

State	MR-AQCC			MR-CISD			MR-CISD + Q		
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)
$b^1\Delta_g$	4639	4501	4397	4675	4543	4477	4594	4445	4335
$c^1\sum_g^+$	7384	7305	7247	7400	7323	7268	7351	7266	7205
$d^1\Pi_u$	9040	8959	8900	9229	9169	9126	8802	8696	8620
$e^1\Sigma_g^+$	11739	11673	11621	11808	11769	11739	11684	11596	11527
$1^1\Sigma_u^-$	19408	19228	19087	19538	19371	19241	19239	19039	18885
$1^1\Pi_g$	24511	24123	23836	24633	24258	23982	24349	23941	23641
$1^1\Delta_u$	34717	34426	34211	35211	34982	34849	34114	33769	33321
$2^1\Pi_g$	36299	35661	35187	36814	36302	35924	35690	34945	34391
$X^3\Sigma_g^-$	0	0	0	0	0	0	0	0	0
$A^3\Pi_u$	3355	3428	3481	3430	3509	3567	3261	3326	3374
$1^3\Delta_u$	12815	12546	12345	12839	12758	12385	12787	12503	12293
$1^3\Sigma_u^-$	14316	14077	13901	14417	14191	14025	14182	13929	13742
$1^3\Sigma_u^+$	16542	16343	16193	16506	16306	16158	16598	16394	16243
$1^3\Pi_g$	16438	16134	15908	16468	16173	15955	16402	16083	15848
$2^3\Pi_g$	22851	22639	22476	22903	22720	22582	22797	22551	22362
$2^3\Delta_u$	29046	29075	29100	29277	29332	29380	28756	28754	28757
$2^3\Sigma_u^{-a}$	30836	30708	30610	31145	31056	30989	30448	30284	30160
$2^3\Pi_u$	34811	34453	34184	34831	34481	34219	34785	34412	34133
$2^3\Sigma_g^-$	35798	35925	36016	35847	35982	36080	35741	35860	35946
$a^5\Sigma_u^-$	1794	1757	1729	1733	1690	1658	1882	1850	1826
$1^5\Delta_g$	31456	31673	31831	31392	31598	31750	31549	32122	31943
$1^5\Sigma_g^+$	32286	32519	32689	32222	32444	32608	32378	32622	32802
$1^5\Sigma_g^-$	36996	37396	37645	36942	37339	37631	37076	37478	37775
$1^5\Pi_u$	37249	37460	37614	37225	37494	37582	37285	37500	37657
$1^5\Pi_g$	53356	53565	53714	53268	53477	53628	53481	53688	53837

[a] Experiment: 30573 [19]

improves D_e by about 500 cm^{-1}, in some cases even by about 1000 cm^{-1} (Table 5). Size-extensivity corrections are equally important and amount mostly to a few hundred wave numbers.

Experimental ω_e values are reproduced within 10 cm^{-1} by MR-AQCC and experimental T_e values within 200 cm^{-1}. The other two methods perform less well for T_e. The ground-state equilibrium geometry is in good agreement with experiment. This is not quite so for the $2^3\Sigma_u^-$ state; however, in this case the experimental data also disagree by 0.016 Å among each other. The large uncertainty of the experimental ground-state dissociation energy of 23790 ± 4840 cm^{-1} prevents the accuracy of the computed result from being assessed; however, the computed dissociation energies are certainly within the same error bar of a few hundred wave numbers, in analogy to the other molecules treated in this work.

The spectroscopic data given by Langhoff and Bauschlicher [19] are in good agreement with our MR-CISD values at the cc-pVTZ level, except for two states where we find substantially different values. In our calculations the bond length for the $d^1\Pi_u$ state is shorter by 0.06 Å. For the $1^3\Pi_g$ state we find differences in r_e and ω_e of 0.02 Å and 400 cm^{-1}, respectively. Taking into account the rather small basis set, the data given by Hachey et al. support our values for the $d^1\Pi_u$ state, but for the $1^3\Pi_g$ state there is little agreement with our results or with those of Langhoff and Bauschlicher. Considering that the present work is the most extensive one in terms of methods and basis sets and that uniform trends have been observed for all methods and properties for all states, we expect that our results are the most reliable ones.

3.1.2 C_2

The spectroscopy of the low-lying states of C_2 is well known. In 1977 Huber and Herzberg [38] listed seven singlet and seven triplet states. Three reviews appeared recently which deal, among larger carbon clusters, also with excited states of C_2. Weltner and Van Zee [39] discussed both experimental and theoretical results, Martin [40] reviewed the spectroscopy and kinetics of all 23 states of C_2 studied up to 1992 and, finally, Van Orden and Saykally [41] discussed the most recent theoretical and spectroscopic works.

In this article we report investigations of the lowest valence states of C_2, eight singlets and five triplets. Table 6 shows that the bond lengths vary systematically with basis set size. In most cases a decrease of 0.01 Å is observed between cc-pVTZ and the extrapolated (TQ) values. A slightly larger change is found for the $^1\Sigma_u^-$ state. The effect of size-extensivity is negligible in almost all cases: the largest change is less than 0.003 Å($C'^1\Sigma_u^-$ state). With extension of the basis set, ω_e increases by between 10 and 20 cm^{-1} in most cases (Table 7). Larger effects are observed for the $C^1\Pi_g$, $D^1\Sigma_u^+$, $c^3\Sigma_u^+$, $d^3\Pi_g$ and $e^3\Pi_g$ states. The influence of size-extensivity is not systematic: in most cases ω_e decreases, but for some states ($1^1\Delta_u$, $c^3\Sigma_u^+$, $d^3\Pi_g$, $e^3\Pi_g$) it increases significantly. The basis set effect on T_e is rather small, but unsystematic (Table 8): the typical change is about 100–200 cm^{-1}. However, a much larger basis set effect is observed for

Table 5. Dissociation energies, D_e (cm^{-1}), for B_2 and atomic term values (cm^{-1}) for B

State	Channel	MR-AQCC			MR-CISD			MR-CISD + Q		
		pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)
$b^1\Delta_g$	$^2P + ^2P$	17809	18454	18932	17780	18406	18869	17857	18529	19025
$c^1\Sigma_g^+$	$^2P + ^2P$	15064	15651	16083	15054	15626	16048	15100	15707	16155
$d^1\Pi_u$	$^2P + ^2P$	13407	13996	14429	13226	13781	14190	13649	14278	14740
$e^1\Sigma_g^+$	$^2P + ^2P$	10709	11282	11708	10647	11181	11576	10767	11377	11833
$1^1\Sigma_u^-$	$^2P + ^2P$	3039	3727	4242	2917	3579	4074	3212	3935	4475
$1^1\Pi_g$	$^2P + ^2P$	−2064	−1168	−506	−2179	−1308	−666	−1898	−967	−281
$1^1\Delta_u$	$^2P + ^2D$	36751	36908	37028	36879	37163	37339	36649	36719	36971
$2^1\Pi_g$	$^4P + ^4P$	43859	45359	46466	43078	44379	45338	44907	46547	47760
$X^3\Sigma_g^{-a}$	$^2P + ^2P$	22449	22956	23330	22454	22950	23316	22451	22974	23360
$A^3\Pi_u$	$^2P + ^2P$	19092	19528	19849	19025	19441	19748	19190	19648	19986
$1^3\Delta_u$	$^2P + ^2P$	9632	10410	10984	9615	10372	10931	9644	10471	11067
$1^3\Sigma_u^-$	$^2P + ^4P$	37011	37934	38611	36722	37610	38263	37411	38374	39082
$1^3\Sigma_u^+$	$^2P + ^2P$	5905	6613	7137	5948	6644	7158	5853	6579	7117
$1^3\Pi_g$	$^2P + ^2P$	6010	6822	7422	5986	6777	7361	6049	6891	7512
$2^3\Pi_g$	$^2P + ^4P$	28476	29371	30036	28236	29081	29705	28796	29752	30463
$2^3\Delta_u$	$^2P + ^4P$	22282	22936	23413	21862	22468	22908	22837	23549	24068
$2^3\Sigma_u^-$	$^2P + ^4P$	20491	21302	21902	19994	20745	21299	21145	22018	22664
$2^3\Pi_u$	$^2P + ^4P$	16516	17558	18328	16308	17320	18069	16808	17890	18691
$2^3\Sigma_g^-$	$^2P + ^4P$	15529	16086	16496	15292	15819	16207	15852	16443	16878
$a^5\Sigma_u^-$	$^2P + ^4P$	49533	50253	50784	49406	50111	50630	49711	50452	50999
$1^5\Delta_g$	$^2P + ^4P$	19871	20338	20682	19748	20203	20537	20044	20180	20882
$1^5\Sigma_g^+$	$^2P + ^4P$	19041	19491	19823	18917	19357	19680	19216	19680	20022
$1^5\Sigma_g^-$	$^2P + ^4P$	14331	14615	14868	14197	14462	14657	14517	14824	15050
$1^5\Pi_u$	$^2P + ^4P$	14078	14550	14898	13914	14307	14705	14308	14803	15168
$1^5\Pi_g$	$^2P + ^4P$	−2029	−1554	−1202	−2129	−1676	−1340	−1888	−1385	−1012
Boron^2P		0	0	0	0	0	0	0	0	0
Boron$^4P^b$		28880	29055	29183	28685	28851	28972	29142	29329	29465
Boron$^2D^c$		49021	48378	47909	49636	49195	48873	49311	47514	46933

[a] Experiment: $D_0 = 23790 \pm 4840$ cm^{-1} [68]
[b] Experiment: 28801 cm^{-1} [69]
[c] Experiment: 47846 cm^{-1} [69]

the $C^1\Pi_g$, $D^1\Sigma_u^+$, $^1\Delta_u$ and $e^3\Pi_g$ states. Inclusion of size-extensivity lowers the term value in all cases. Changes are mostly small (a few 100 cm^{-1}); a larger effect is observed for the $^1\Delta_u$ state (1400 cm^{-1}). The basis set effect is much more important for dissociation energies (Table 9) than for the term values just discussed. It amounts to about 2000 cm^{-1} and systematically increases D_e. Size-extensivity effects also increase D_e, however to a much smaller extent.

Typically, the bond lengths calculated at the MR-AQCC/(TQ) level are too long in comparison to experiment by about 0.003 Å. Somewhat larger is the error in case of the $^1\Delta_u$ and $e^3\Pi_g$ states. Note, however, that in the former case the error bar of the experimental value is 0.002 Å. The calculated ω_e values are smaller than the experimental ones; the typical error is about 10–15 cm^{-1}. For term values the error is about 200–300 cm^{-1}; it is, however, not systematic and we can find deviations in both directions. Much larger errors are observed for the $^1\Delta_u$ and the $e^3\Pi_g$ states.

There are only three states where larger deviations between calculated and experimental values exist. In case of the $c^3\Sigma_u^+$ state three sets of experimental data are available [46–48]. All of them obtain the spectroscopic constants from analyzing the perturbation of the $A^1\Pi_u \leftarrow X^1\Sigma_g$ transition. Since to some extent the three investigations use the same spectral information, the large discrepancies between them suggest that the spectroscopic constant obtained are not reliable. Note, for example, that Davis et al. [46] obtained five spectroscopic constants from only five observed perturbations of spectral lines; therefore, this state will be excluded from the statistical analysis presented later. Considering the reliability of the method used in our work (no sign of any shortcomings of the wave function could be observed for this state) the calculated spectroscopic constants ($r_e = 1.2085$ Å, $\omega_e = 2046$ cm^{-1}, $T_e = 9394$ cm^{-1}) are probably much better estimates of the true spectroscopic constants of the $c^3\Sigma_u^+$ state than any of the experimental ones.

In case of the $^1\Delta_u$ state, the MR-CISD value for T_e is too large, while for the size-extensivity corrected methods it is too small. Thus, we observe an unusually large size-extensivity correction for this quantity. This suggests that both MR-AQCC and MR-CISD + Q might overestimate size-extensivity effects. Additional test calculations showed that this is indeed the case and that it is caused by insufficiencies of the standard orbitals for this state. In a test calculation we used orbitals from a state-averaged MCSCF including only a few states instead of the full set. By doing this, the term value calculated at the MR-AQCC level increased, the size-extensivity correction became substantially smaller and much better agreement with experiment could be achieved.

Table 6. Equilibrium bond distances, r_e(Å), for C_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$\tilde{X}^1\Sigma_g^+$	1.2536	1.2487	1.2452	1.2537	1.2489	1.2453	1.2536	1.2486	1.2448	1.2425[a]
$A^1\Pi_u$	1.3295	1.3247	1.3213	1.3295	1.3248	1.3214	1.3294	1.3246	1.3211	1.3184[b]
$B^1\Delta_g$	1.3972	1.3922	1.3886	1.3970	1.3921	1.3885	1.3972	1.3922	1.3885	1.3855[b,c]
$B'^1\Sigma_g^+$	1.3898	1.3844	1.3805	1.3896	1.3843	1.3804	1.3897	1.3843	1.3803	1.3774[d]
$C^1\Pi_g$	1.2681	1.2623	1.2581	1.2680	1.2624	1.2584	1.2682	1.2623	1.2579	1.2552[d]
$^1\Sigma_u^-$	1.7425	1.7321	1.7246	1.7399	1.7294	1.7219	1.7439	1.7336	1.7260	
$D^1\Sigma_u^+$	1.2518	1.2458	1.2415	1.2512	1.2455	1.2414	1.2521	1.2460	1.2415	1.2380[a]
$^1\Delta_u$	1.4530	1.4460	1.4419	1.4546	1.4486	1.4441	1.4524	1.4454	1.4404	1.437[e]
Statistics singlet states										
Mean	0.0127	0.0072	0.0032	0.0128	0.0075	0.0036	0.0127	0.0071	0.0029	
std.dev.	0.0017	0.0010	0.0004	0.0023	0.0018	0.0015	0.0016	0.0009	0.0004	
$a^3\Pi_u$	1.3228	1.3180	1.3144	1.3229	1.3182	1.3147	1.3228	1.3179	1.3142	1.3119[f]
$b^3\Sigma_g^-$	1.3792	1.3747	1.3712	1.3805	1.3767	1.3734	1.3786	1.3736	1.3696	1.3692[f]
$c^3\Sigma_u^+$	1.2176	1.2124	1.2085	1.2184	1.2133	1.2095	1.2170	1.2118	1.2079	1.209[c] 1.23[g], 1.22[h]
$d^3\Pi_g$	1.2781	1.2720	1.2676	1.2788	1.2731	1.2689	1.2777	1.2715	1.2669	1.2661[a]
$e^3\Pi_g$	1.5486	1.5435	1.5399	1.5485	1.5434	1.5397	1.5483	1.5436	1.5401	1.5351[a]
Statistics triplet states[i]										
Mean	0.0116	0.0065	0.0027	0.0121	0.0073	0.0036	0.0113	0.0061	0.0021	
std.dev.	0.0015	0.0013	0.0015	0.0011	0.0018	0.0009	0.0016	0.0017	0.0021	
Statistics all states[i]										
Mean	0.0123	0.0068	0.0030	0.0125	0.0074	0.0036	0.0122	0.0067	0.0026	
std.dev.	0.0017	0.0011	0.0009	0.0019	0.0015	0.0013	0.0017	0.0023	0.0013	

[a] Ref. [38]
[b] Ref. [42]
[c] Ref. [46]
[d] Ref. [43]
[e] Ref. [44]
[f] Ref. [45]
[g] Ref. [47]
[h] Ref. [48]
[i] $c^3\Sigma_u^+$ state excluded. See text for more details

For the $e^3\Pi_g$ state we observed a larger error for the term value and bond length also. Unlike the $^1\Delta_u$ state, we could not find any sign of a shortcoming in our procedure.

The dissociation energies of the different states of C_2 are given in Table 9. The table documents well that both size-extensivity correction and basis set extrapolation are necessary to achieve an accuracy of a few hundred wave numbers.

To our knowledge there is no similar systematic study on the excited states of C_2 to the present one. There are, however, several recent reports dealing with a few excited states [20–22]. All of them have in common that the basis set effects are investigated in detail and in this respect the conclusions are similar to ours. The much larger number of states investigated at the same time allows, however, more general conclusions about the accuracy of the computational methods used.

3.1.3 N_2

N_2 certainly belongs to the most extensively studied molecules, both theoretically and experimentally. Apart from numerous studies on the ground state (Ref. [49] and references therein), the lowest triplet and quintet states have been computed using either CASSCF/MR-CISD [18, 50] or SCF/MRD-CI [51] techniques. More recently, CASPT2 [52] and response theory calculations [53] have been performed as well. To our knowledge, apart from vertical excitation energies [54–56] no other spectroscopic data have been computed for the excited singlet states. Experimental spectroscopic data and early quantum chemical calculations have been comprehensively reviewed by Lofthus and Krupenie [57] and Huber and Herzberg [38]. References to more recent experimental work can be found in the tables.

In most cases, the equilibrium geometries of the various singlet and triplet states of N_2 are in very good agreement with the experimental data (Table 10). Typical differences of less than 0.003 Å are found for the (TQ) extrapolated data. Only the $b^1\Pi_u$ and $b'^1\Sigma_u^+$ states do not fit into this scheme. They show unusually large basis set effects and we will discuss them separately later in this subsection.

Except for the $C'^3\Pi_u$ state experimental harmonic frequencies (Table 11) are reproduced by about 15 cm^{-1} or less for the (TQ) extrapolated data throughout. Size-extensivity corrections range from a few wave numbers up to about 25 cm^{-1}. The results for the $b^1\Pi_u$ state are again questionable. For $b'^1\Sigma_u^+$ we find an exceptionally

Table 7. Harmonic vibrational frequencies, ω_e (cm^{-1}), for C_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	TQ	
$\tilde{X}^1\Sigma_g^+$	1823	1834	1842	1827	1839	1847	1818	1830	1832	1855[a]
$A^1\Pi_u$	1581	1589	1596	1582	1590	1597	1580	1589	1595	1608[b,c]
$B^1\Delta_g$	1380	1389	1395	1383	1391	1399	1379	1388	1394	1407[b]
$B'^1\Sigma_g^+$	1396	1408	1416	1397	1408	1415	1398	1410	1418	1424[d]
$C^1\Pi_g$	1750	1773	1792	1750	1777	1797	1743	1772	1790	1809[d]
$^1\Sigma_u^-$	692	706	718	695	709	727	691	704	721	
$D^1\Sigma_u^+$	1783	1798	1810	1795	1810	1822	1776	1792	1805	1829[a]
$^1\Delta_u$	1119	1131	1141	1118	1126	1132	1117	1127	1135	1150[e]
Statistics singlet states										
Mean	−36	−23	−13	−33	−20	−10	−39	−25	−18	
std.dev.	12	8	4	12	6	4	15	9	6	
$a^3\Pi_u$	1614	1623	1630	1616	1625	1632	1613	1622	1629	1641[f]
$b^3\Sigma_g^-$	1456	1465	1462	1444	1453	1475	1458	1460	1464	1470[f]
$c^3\Sigma_u^+$	2018	2034	2046	2012	2029	2039	2022	2038	2050	2086[c], 2040[g], 1962[h]
$d^3\Pi_g$	1738	1758	1773	1734	1753	1768	1739	1760	1776	1788[a]
$e^3\Pi_g$	1066	1086	1100	1049	1068	1083	1077	1097	1109	1107[a]
Statistics triplet states[i]										
Mean	−33	−19	−10	−41	−27	−12	−30	−17	−7	
std.dev.	16	10	4	18	12	13	15	9	7	
Statistics all states[i]										
Mean	−35	−21	−12	−36	−23	−11	−35	−22	−13	
std.dev.	13	7	4	14	9	8	15	9	8	

[a] Ref. [38]
[b] Ref. [42]
[c] Ref. [46]
[d] Ref. [43]
[e] Ref. [44]
[f] Ref. [45]
[g] Ref. [48]
[h] Ref. [47]
[i] $c^3\Sigma_u^+$ state excluded. See text for more details

large size-extensivity correction. Term energies (Table 12) agree better than 300 cm^{-1}. For the $b'^1\Sigma_u^+$ and $C'^3\Pi_u$ states the deviations are somewhat larger. For the $G^3\Delta_g$ state, the computed term energy is certainly more accurate than the experimental estimate, for which an error bar of ±2000 cm^{-1} has been reported [60]. The (TQ) extrapolated dissociation energies are in excellent agreement with experimentally available data (Table 13). Size-extensivity corrections are essential in order to achieve an accuracy of a few hundred wave numbers.

Coming back to the problematic cases, an inspection of the wave function of the $b^1\Pi_u$ state indicates a relatively large, distance-dependent contamination by a nonvalence configuration. Augmenting the basis set by diffuse functions substantially affects the bond length as the contamination by a Rydberg state increases. This is in agreement with the experimental finding of a strong interaction between the $b^1\Pi_u$ valence and the $c_3\,{}^1\Pi_u$ Rydberg states [61, 62]. A proper procedure would be to include the $c_3\,{}^1\Pi_u$ Rydberg state into the MCSCF state-averaging procedure also and to add Rydberg functions to the basis set. Since we had set ourselves the limit to calculate only valence states, we did not consider the $b^1\Pi_u$ state further.

The term energies of the $b'^1\Sigma_u^+$ valence state and the $c'_4\,{}^1\Sigma_u^+$ Rydberg state are very close to each other (experimental $\Delta T_e \approx 40$ cm^{-1} [62]). In agreement with experiment [62], the much larger bond length of the $b'^1\Sigma_u^+$ state compared to the $c'_4\,{}^1\Sigma_u^+$ Rydberg state leads to a weak interaction only with the latter at the energy minimum of the $b'^1\Sigma_u^+$ state. The occurrence of this weak coupling explains the large basis set and size-extensivity corrections. In analogy to the $b^1\Pi_u$ state discussed in the previous paragraph we did not pursue the question of Rydberg states further.

The $C^3\Pi_u$ and $C'^3\Pi_u$ states belong to two minima on the same potential-energy curve. Whereas the first minimum is well behaved and the calculated results are in good agreement with experimental data, the second minimum is more difficult to compute since it is derived from an avoided crossing with the $2^3\Pi_u$ state, resulting in a shallow minimum at a large bond length. Agreement with experiment is not really satisfactory for this state. The large basis set effect and the quite large deviation of 25 cm^{-1} for the harmonic frequency can be taken as an indication that more extensive efforts with respect to basis set size may be needed in order to achieve better-converged results for this state.

The (TQ) extrapolated harmonic frequency for the ground state is significantly lower than the experimental value. The cc-pV5Z frequencies of 2292, 2172 and 2340 cm^{-1} for MR-AQCC, MR-CISD and MR-CISD + Q,

Table 8. Term values, T_e (cm^{-1}), for C_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$A^1\Pi_u$	8143	8104	8078	8397	8379	8374	8000	7949	7915	8391[a]
$B^1\Delta_g$	11811	11738	11687	12038	11990	11966	11684	11599	11541	12082[a,b]
$B'^1\Sigma_g^+$	15148	15172	15191	15213	15233	15261	15134	15161	15183	15409[c]
$C^1\Pi_g$	35016	34559	34222	35432	35054	34800	34788	34307	33954	34261[c]
$^1\Sigma_u^-$	38470	38945	39291	38715	39179	39512	38335	38819	39167	
$D^1\Sigma_u^+$	44048	43663	43377	44465	44132	43886	43810	43409	43113	43239[d]
$^1\Delta_u$	57405	57009	56721	58144	58115	58097	57029	56836	56697	57720[e]
Statistics singlet states										
Mean	78	−143	−304	431	300	214	−110	−307	−450	
std.dev.	546	426	391	629	465	350	528	384	320	
$a^3\Pi_u$	272	384	466	322	429	509	256	367	450	716[f]
$b^3\Sigma_g^-$	5894	5966	6017	6089	6170	6233	5794	5861	5914	6434[f]
$c^3\Sigma_u^+$	9596	9482	9394	9583	9482	9371	9618	9503	9417	9124[b], 13312[g], 9227[h]
$d^3\Pi_g$	20358	20193	20076	20329	20196	20092	20382	20219	20096	20022[d]
$e^3\Pi_g$	39508	39833	40075	40015	40387	40664	39219	39533	39767	40797[d]
Statistics triplet states[i]										
Mean	−484	−398	−334	−304	−197	−118	−580	−497	−436	
std.dev.	665	467	324	452	255	130	795	605	465	
Statistics all states[i]										
Mean	−147	−245	−316	137	101	81	−298	−383	−444	
std.dev.	630	437	347	657	456	321	652	462	359	

[a] Ref. [42]
[b] Ref. [46]
[c] Ref. [43]
[d] Ref. [38]
[e] Ref. [44]
[f] Ref. [45]
[g] Ref. [47]
[h] Ref. [48]
[i] $c^3\Sigma_u^+$ state excluded. See text for more details

respectively, are even worse. As will be discussed in greater detail for O_2, this is presumably a consequence of the fact that the excited states included in the state-averaging procedure increasingly gain diffuse character with the extension of the basis set.

Previous investigations on excited states have used basis sets of approximately cc-pVTZ quality covering the $A^3\Sigma_u^+$, $B^3\Pi_g$, $B'^3\Sigma_u^-$, $W^3\Delta_u$ and $C^3\Pi_u$ states except for the work on the $A'^5\Sigma_g^+$ and $C''^5\Pi_u$ states by Partridge et al. [50] where more-extended basis sets were used. In general, independent of the method applied (CASPT2, response theory or MR-CI) the results for r_e, ω_e and D_e are similar to our data at the cc-pVTZ level. CASPT2, however, suffers from intruder-state problems for the $A^3\Sigma_u^+$ state [52]. The dissociation energies at the cc-pVTZ and even the cc-pVQZ level are still far away from the basis set limit and basis set extrapolation and size-extensivity correction are essential.

3.1.4 O_2

Owing to the larger number of valence electrons, the number of low-lying bound excited states of O_2 is much smaller than that of either N_2 or C_2. In addition, none of the transitions to excited states dissociating into the ground-state atoms are optically allowed. Nevertheless, the interest in excited states of O_2 is large because of their importance in terrestrial chemistry and biochemistry [63]. The most comprehensive review of the spectroscopy of O_2 has been given by Krupenie [64] and further experimental data can be found in the book of Huber and Herzberg [38]. Slanger and Cosby [63] reviewed the spectroscopy of the excited states corresponding to the lowest dissociation channel. The most recent work on the spectroscopy of O_2 is the observation of the $B^3\Sigma_u^- \leftarrow b^1\Sigma_g^+$ transition by Lewis et al. [65]. A detailed theoretical study of the valence excited states has been performed by Partridge et al. [23].

As for the other molecules investigated here, bond lengths decrease systematically with basis set size (Table 14). The effect of the size-extensivity correction is rather small. In most cases it increases the bond length by less than 0.001 Å. The effect is larger only for the $B^3\Sigma_u^-$ and $^3\Pi_g$ states and points in the opposite direction, i.e. the bond length becomes shorter. The harmonic vibrational frequencies increase with basis set size for all states and the calculated values are usually somewhat smaller than the experimental ones (Table 15). The largest basis set effects are found for the $\tilde{X}^3\Sigma_g^-$, $a^1\Delta_u$ and $b^1\Sigma_g^+$ states. The size-extensivity effects increase ω_e, except for the ground state. They are especially large for the ground state and the $B^3\Sigma_u^-$ state. As a result, the calculated ω_e

Table 9. Dissociation energies, D_e(cm^{-1}), for C_2 and atomic term values (cm^{-1}) for C

State	Channel	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
		pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
Carbon	^{3}P	0	0	0	0	0	0	0	0	0	0
Carbon	^{1}D	10849	10447	10208	10926	10596	10405	10790	10333	10011	10165[a]
$\tilde{X}^1\Sigma_g^+$	^{3}P + ^{3}P	48570	49844	50780	48651	49843	50633	48568	49918	50913	50813 ± 161[b]
$A^1\Pi_u$	^{3}P + ^{3}P	40427	41739	42703	40254	41464	42265	40568	41970	42999	42422
$B^1\Delta_g$	^{3}P + ^{3}P	36759	38106	39093	36612	37852	38674	36884	38319	39372	38731
$B'^1\Sigma_g$	^{3}P + ^{3}P	33422	34671	35590	33438	34610	35383	33434	34758	35730	35404
$C^1\Pi_g$	^{3}P + ^{3}P	13555	15285	16559	13220	14789	15857	13780	15611	16959	16552
$^1\Sigma_u^-$	^{3}P + ^{3}P	10100	10899	11489	9935	10663	11121	10233	11104	11745	–
$^1\Delta_u$	^{1}D + ^{1}D	12843	13727	14379	12340	12911	13350	13119	13749	14238	13421
Statistics singlet states											
Mean		−1961	−662	294	−2138	−979	−197	−1832	−503	478	
std.dev.		783	530	360	718	419	252	826	462	254	
$a^3\Pi_u$	^{3}P + ^{3}P	48298	49460	50314	48329	49414	50124	48312	49551	50462	50097
$b^3\Sigma_g^-$	^{3}P + ^{3}P	42676	43878	44763	42561	43672	44398	42773	44053	44999	44379
$c^3\Sigma_u^+$	^{3}P + ^{3}P	38975	40362	41387	39068	40381	41263	38950	40415	41497	41586[c]
$d^3\Pi_g$	^{3}P + ^{3}P	28223	29650	30705	28322	29650	30542	28186	29698	30817	30791
$e^3\Pi_g$	^{3}P + ^{1}D	19885	20364	20752	19571	20029	20366	20085	20644	21055	20180
Statistics triplet states[d]											
Mean		−1591	−524	272	−1666	−671	−4	−1523	−375	472	
std.dev.		942	546	279	774	405	180	1046	646	363	
Statistics all states[d]											
Mean		−1813	−607	285	−1949	−856	−120	−1708	−452	475	
std.dev.		822	510	313	738	422	236	877	512	282	

[a] Atomic term value [69]
[b] Ground state value [70]
[c] Uncertain experimental term value
[d] $c^3\Sigma_u^+$ state excluded. See text for more details

values for both states overshoot the experimental ones (see the discussion later). The term values are affected by less than 1000 cm^{-1} by basis set extensions (Table 16). In most cases the excitation energy decreases with increasing basis set size. A much reduced, opposite trend is observed for the $b^1\Sigma_g^+$ and $a^1\Delta_u$ states. Inclusion of the size-extensivity corrections increases the term values and brings them into closer agreement with experiment. An exception is the $B^3\Sigma_u^-$ state, where the size-extensivity correction significantly decreases its term value.

At the MR-AQCC/(TQ) level the typical accuracy of the equilibrium bond length is about 0.002–0.003 Å. A somewhat larger error is observed for the ground state. The positive sign of the error shows that the calculated values are longer than the experimental ones. Only for the $B^3\Sigma_u^-$ state is the calculated bond length shorter than the experimental value. The error of ω_e is rather small for most states (except for the ground state and the $B^3\Sigma_u^-$ state) and is less systematic. Finally, except for the $B^3\Sigma_u^-$ state, the calculated term values are very accurate: the error is only about 100 cm^{-1}.

The dissociation energies (Table 17) are well reproduced at the (TQ) level by MR-AQCC. The MR-CISD + Q values exceed the experimental values significantly. In contrast, the MR-CISD value are much too low. Only the $B^3\Sigma_u^-$ state shows noteworthy deviations throughout. Since the basis set effect is very important here, we performed ground-state calculations also with the cc-pV5Z basis and calculated the (Q5) extrapolated values. These are 42329, 41201 and 42688 cm^{-1} for the MR-AQCC, MR-CISD and MR-CISD + Q methods, respectively. Comparison of these values with the data in the table shows that extrapolation schemes (TQ) and (Q5) produce almost the same results, showing the reliability of the extrapolation scheme. Considering these values as the best theoretical estimates, we can conclude that MR-AQCC performs best, while MR-CISD + Q overshoots considerably.

The relatively large error of the equilibrium bond length and the harmonic vibrational frequency of the ground state is especially disturbing. Therefore, we investigated this problem in more detail and found the root of the problem in the MCSCF state-averaging procedure: while the vibrational frequency and equilibrium geometry calculated with state-averaged and state-specific orbitals are practically identical in the case of the cc-pVTZ basis, they differ significantly for the cc-pVQZ and cc-pV5Z basis sets. Since the ground state of O_2 has a very short bond length compared to the excited states, they appear at relatively high energies for this geometry. Apparently, some of them can have diffuse character as well, which has a noticeable effect on the state-averaging procedure. Therefore, even the slightly increasing diffuse character of the basis sets can deteriorate the results for the ground state. Similar problems have been observed with the cc-pV5Z basis for N_2. Thus, these findings seem to represent a general problem when using state-averaging for a large number of widely different states to-

Table 10. Equilibrium bond distances, r_e(Å), for N_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$\tilde{X}^1\Sigma_g^+$	1.1053	1.1019	1.0994	1.1049	1.1016	1.0991	1.1054	1.1019	1.0994	1.0977[a]
$a'1\Sigma_u^-$	1.2845	1.2807	1.2780	1.2839	1.2804	1.2777	1.2846	1.2808	1.2781	1.2754[a]
$a^1\Pi_g$	1.2314	1.2266	1.2230	1.2306	1.2261	1.2227	1.2316	1.2268	1.2232	1.2203[a]
$W^1\Delta_u$	1.2775	1.2737	1.2710	1.2770	1.2734	1.2708	1.2777	1.2738	1.2710	1.2688[a]
$b^1\Pi_u$	1.3685	1.3456	1.3180	1.3662	1.3482	1.3289	1.3700	1.3489	1.3248	1.279[a], 1.2841[b]
$b'^1\Sigma_u^+$	1.4859	1.4635	1.4442	1.4973	1.4844	1.4745	1.4848	1.4642	1.4470	1.4439[b]
Statistics singlet states[c]										
Mean	0.0167	0.0090	0.0029	0.0185	0.0129	0.0087	0.0166	0.0093	0.0035	
std.dev.	0.0169	0.0087	0.0014	0.0223	0.0182	0.0150	0.0164	0.0089	0.0026	
$A^3\Sigma_u^+$	1.2976	1.2927	1.2891	1.2965	1.2916	1.2891	1.2980	1.2931	1.2895	1.2866[a]
$B^3\Pi_g$	1.2223	1.2180	1.2148	1.2217	1.2174	1.2142	1.2224	1.2181	1.2148	1.2126[d]
$W^3\Delta_u$	1.2895	1.2854	1.2824	1.2881	1.2840	1.2810	1.2899	1.2858	1.2828	1.2797[d]
$B'^3\Sigma_u^-$	1.2879	1.2838	1.2809	1.2866	1.2825	1.2795	1.2882	1.2842	1.2812	1.2784[a]
$G^3\Delta_g$	1.6312	1.6201	1.6134	1.6295	1.6187	1.6111	1.6317	1.6215	1.6140	1.6106[a]
$C^3\Pi_u$	1.1590	1.1543	1.1510	1.1582	1.1536	1.1502	1.1591	1.1544	1.1509	1.1487[a]
$C'^3\Pi_u$	1.5308	1.5205	1.5127	1.5332	1.5224	1.5154	1.5303	1.5202	1.5126	1.5146[b]
Statistics triplet states										
Mean	0.0124	0.0062	0.0019	0.0118	0.0056	0.0013	0.0126	0.0066	0.0021	
std.dev.	0.0043	0.0014	0.0017	0.0048	0.0016	0.0007	0.0042	0.0019	0.0018	
Statistics all states[c]										
Mean	0.0142	0.0074	0.0023	0.0146	0.0086	0.0044	0.0143	0.0077	0.0027	
std.dev.	0.0109	0.0055	0.0016	0.0143	0.0117	0.0098	0.0106	0.0057	0.0022	

[a] Ref. [57]
[b] Ref. [38]
[c] $b^1\Pi_u$ state excluded. See text for more details
[d] Ref. [59]

Table 11. Harmonic vibrational frequencies, ω_e(cm^{-1}), for N_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$\tilde{X}^1\Sigma_g^+$	2326	2337	2344	2331	2342	2350	2324	2335	2343	2359[a]
$a'^1\Sigma_u^-$	1503	1514	1521	1510	1517	1521	1504	1513	1521	1530[a]
$a^1\Pi_g$	1665	1676	1684	1681	1691	1698	1658	1670	1679	1694[a]
$\omega^1\Delta_u$	1536	1544	1552	1537	1545	1547	1536	1543	1551	1559[a]
$b^1\Pi_u$	683	607	541	693	632	559	679	600	517	635[b]
$b'^1\Sigma_u^+$	800	780	761	811	808	805	797	782	766	760[a,b]
Statistics singlet states[c]										
Mean	−14	−10	−8	−6	0	4	−17	−12	−8	
std.dev.	31	17	6	33	27	24	30	19	8	
$A^3\Sigma_u^+$	1422	1439	1451	1427	1445	1458	1418	1437	1449	1461[a]
$B^3\Pi_g$	1706	1716	1723	1711	1720	1729	1706	1716	1724	1733[d]
$W^3\Delta_u$	1477	1489	1497	1483	1496	1505	1475	1487	1495	1507[d]
$B'^3\Sigma_u^-$	1492	1502	1509	1498	1509	1516	1490	1500	1507	1517[a]
$G^3\Delta_g$	735	750	762	731	748	762	736	751	764	766[a]
$C^3\Pi_u$	1999	2012	2023	1993	2014	2031	1992	2012	2031	2047[a]
$C'^3\Pi_u$	723	750	766	713	729	746	733	745	759	791[b]
Statistics triplet states										
Mean	−33	−18	−8	−33	−27	−24	−30	−19	−9	
std.dev.	8	10	11	12	9	5	12	8	7	
Statistics all states[c]										
Mean	−25	−15	−8	−22	−10	−2	−26	−16	−8	
std.dev.	22	13	9	25	20	16	22	14	8	

[a] Ref. [57]
[b] Ref. [38]
[c] $b^1\Pi_u$ state excluded. See text for more details
[d] Ref. [59]

gether with series of basis sets containing an increasingly diffuse character.

As stated earlier, for the $B^3\Sigma_u^-$ state all the properties calculated (r_e, ω_e, T_e and D_e) show errors which are too

Table 12. Term values, T_e (cm^{-1}), for N_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$a'^1\Sigma_u^-$	67723	67762	67795	68364	68480	68569	67494	67531	67567	68151[a]
$a^1\Pi_g$	68931	69086	69200	69357	69566	69718	68792	68951	69067	69283[a]
$\omega^1\Delta_u$	71854	71865	71877	72382	72461	72524	71670	71682	71694	72098[a]
$b^1\Pi_u$	100799	101224	101503	101741	102333	102751	101547	101018	101337	101675[b]
$b'^1\Sigma_u^+$	103722	103610	103489	105156	105440	105641	103357	103301	103229	104472[a]
Statistics singlet states[c]										
Mean	−475	−318	−208	159	408	589	−426	−506	−386	
std.dev.	278	122	114	107	170	325	221	157	154	
$A^3\Sigma_u^+$	48860	49501	49970	49050	49688	50157	48805	49459	49938	50204[a]
$B^3\Pi_g$	58881	59234	59494	59420	59818	60109	58701	59061	59325	59619[d]
$W^3\Delta_u$	58966	59329	59598	59365	59753	60039	58830	59201	59475	59805[d]
$B'^3\Sigma_u^-$	65675	65935	66124	65965	66259	66476	65582	65847	66045	66272[a]
$G^3\Delta_g$	87603	88454	89075	88215	89101	89748	87405	88268	88898	(87900)[e]
$C^3\Pi_u$	89330	89247	89184	89952	89991	90017	89148	89088	89040	89134[a]
$C'^3\Pi_u$	96586	97329	97870	97497	98363	98994	96308	97069	97623	98351[b]
Statistics triplet states[c]										
Mean	−770	−323	4	−261	241	607	−930	−471	−135	
std.dev.	647	520	540	669	589	628	658	524	537	
Statistics all states[c]										
Mean	−662	−321	−73	−108	302	601	−747	−484	−226	
std.dev.	545	408	436	563	473	518	582	415	442	

[a] Ref. [57]
[b] Ref. [38]
[c] $b^1\Pi_u$ and $G^3\Delta_g$ states excluded, see text for more details
[d] Ref. [59]
[e] Uncertain experimental T_e [60]

large. The correction due to size-extensivity appeared to be the largest for this state. Unlike the $^1\Delta_u$ state of C_2, this overestimation is not due to the quality of the averaged orbitals used since the results did not change with state-specific orbitals. Instead, excitations to the $2\pi_u$ orbitals became important. By increasing the reference space accordingly, the size-extensivity correction became much smaller and both the geometry and the vibrational frequency were in much better agreement with experiment.

A study of the low-lying excited states of O_2 is available from Partridge et al. [23]. As in our study, MR-CI and MR-CI + Q calculations were performed using a CAS reference function and large basis sets up to 6s5p4d2f1g were used. However, the reference functions included only the 2p atomic functions. Because of the smaller reference space, the best results in Table 2 of Ref. [23] differ somewhat from our (TQ) results: this difference is small for the equilibrium geometry (0.002-0.003 Å), while for the vibrational frequencies the difference is as large as 10–20 cm^{-1}. In all cases our values are closer to experiment. Note that this is even the case for the ground state, where our computational scheme encountered some problem owing to the state-averaging procedure.

3.2 General error analysis

In addition to the individual discussion of the results presented in the previous section, a statistical analysis of the error of the computed data was also carried out. The error distributions are shown in Figs. 1, 2, 3 and 4, with the height of the bars representing the number of cases which appeared in the given interval. This analysis was performed for the extrapolated (TQ) basis only. B_2 data were excluded because of the lack of experimental information.

The mean deviation of the calculated values from the experimental data and the standard deviation of the calculated values from the mean deviation [67] for a given property, method and molecule may be found in Tables 6–17. All those cases have been excluded from the statistical analysis for which serious objections concerning the reliability of the computed or experimental results had to be raised. The excluded cases are the $c^3\Sigma_u^+$ state of C_2 (incompatible experimental results), the $b^1\Pi_u$ (Rydberg state interaction) and $G^3\Delta_g$ (only T_e owing to experimental uncertainty) states of N_2 and the $B^3\Sigma_u^-$ state of O_2 (extension of the valence space necessary).

The error distribution for the equilibrium geometry using a 0.001 Å interval of discretization is shown in Fig. 1. The distributions of the MR-AQCC and MR-CISD + Q results clearly have a higher maximum than MR-CISD, which correspond to a somewhat smaller standard deviation. In the case of MR-CISD very large errors are present, with one point even falling outside the interval shown in the graph. For almost all states the calculated bond lengths exceed the experimental ones. The average error of the MR-AQCC/(TQ) method is 0.0030 Å for C_2, 0.0023 Å for N_2 and 0.0028 Å for O_2. The standard deviation is 0.0009, 0.0016 and 0.0007 Å, respectively. In the case of MR-CISD the corresponding values are 0.0036, 0.0044 and 0.0021 Å for the average error and 0.0013, 0.0098 and 0.0007 Å for the standard deviation.

The error distribution is given for harmonic vibrational frequencies using a 5 cm^{-1} interval of discretization in Fig. 2. MR-AQCC and MR-CISD + Q methods overestimate ω_e only in a few cases. The overall picture resembles the one for the equilibrium distance. The mean error [MR-AQCC/(TQ)] is −12, −8 and 0 cm^{-1}

Table 13. Dissociation energies, D_e(cm^{-1}), for N_2 and atomic term values for N

State	Channel	MR-AQQC			MR-CISD			MR-CISD + Q			Exp.
		pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
Nitrogen^4S		0	0	0	0	0	0	0	0	0	0
Nitrogen^2D		20315	19687	19229	20470	19902	19488	20258	19605	19130	19226[b]
Nitrogen^2P		30316	29662	29184	30234	29614	29163	30354	29694	29213	28840[b]
$\tilde{X}^1\Sigma_g^+$	^4S + ^4S	75580	77773	79381	75678	77807	79369	75590	77824	79462	79886[a]
$a'^1\Sigma_u^-$	^2D + ^2D	48488	49385	50043	48254	49131	49775	48611	49405	50160	50187
$a^1\Pi_g$	^2D + ^2D	47279	48060	48639	47260	48045	48626	47313	48084	48655	49055
$w^1\Delta_u$	^2D + ^2D	44356	45282	45962	44235	45149	45820	44436	45353	46027	46240
$b^1\Pi_u$	^2D + ^2D	15412	15923	16336	14876	15278	15594	15558	16017	16384	16663
$b'^1\Sigma_u^+$	^2P + ^2D	22433	23476	24285	21175	21829	22322	22781	23789	24563	23480
Statistics singlet states[c]											
Mean		−2142	−974	−108	−2449	−1377	−587	−2023	−879	4	
std.dev.		1253	753	528	1001	471	322	1346	841	624	
$A^3\Sigma_u^+$	^4S + ^4S	26720	28272	29411	26629	28118	29212	26785	28365	29525	29682
$B^3\Pi_g$	^4S + ^2D	37045	38286	39199	36732	37904	38767	37183	38447	39376	39498
$W^3\Delta_u$	^4S + ^2D	36960	38192	39095	36786	37970	38838	37054	38306	39225	39310
$B'^3\Sigma_u^-$	^4S + ^2P	40221	41499	42437	39947	41163	42055	40363	41671	42630	42454
$G^3\Delta_g$	^4S + ^2D	8323	9067	9618	7937	8621	9128	8479	9239	9802	(11200)[d]
$C^3\Pi_u$	^4S + ^2D	6597	8274	9509	6200	7731	8860	6736	8419	9660	9978
$C'^3\Pi_u$	^4S + ^2D	−660	192	823	−1346	−641	−117	−424	439	1077	761
Statistics triplet states[c]											
Mean		−2467	−1161	−202	−2789	−1573	−678	−2331	−1006	−32	
std.dev.		670	388	195	577	352	283	711	429	234	
Statistics all states[c]											
Mean		−2319	−1076	−159	−2635	−1484	−637	−2191	−948	−16	
std.dev.		939	558	365	774	401	289	1002	616	428	

[a] Ground-state value [38]
[b] Atomic term values [69]
[c] $b^1\Pi_u$ and $G^3\Delta_g$ states excluded, see text for more details
[d] Uncertain exerimental T_e

for C_2, N_2 and O_2, respectively. The standard deviation is about 10 cm^{-1}. For MR-CISD the mean error is −11, −2 and +10 cm^{-1} for the three molecules, respectively, with a clearly larger standard deviation reaching 37 cm^{-1} for O_2.

The error distribution of the term energies using a 200 cm^{-1} interval of discretization is shown in Fig. 3. The error of MR-AQCC is located mostly between 100 and −500 cm^{-1}. The mean error is about 200–300 cm^{-1} for C_2, N_2 and O_2 at the MR-AQCC/(TQ) level. The standard deviation is about 300 cm^{-1} and drops below 200 cm^{-1} if the problematic cases discussed in the previous section ($^1\Delta_u$ and $e^3\Pi_g$ for C_2, $b'^1\Sigma_u^+$, $C'^3\Pi_u$ for N_2) are excluded. At the MR-CISD/(TQ) level the average error is larger (500 cm^{-1}) but the standard deviation is again about 300 cm^{-1}.

The error distribution of the dissociation energies is displayed using a 200 cm^{-1} interval of discretization in Fig. 4. For MR-AQCC the maximum of the error distribution is located close to zero, with a slight asymmetry of the distribution towards negative values. The MR-CISD + Q distribution is much more spread out compared to the MR-AQCC case. The mean error of MR-AQCC for the (TQ) extrapolated results in 285, −159 and 155 cm^{-1} for C_2, N_2 and O_2, respectively. MR-CISD + Q mean errors are shifted by about 200 cm^{-1} to higher energies. The MR-CISD mean errors are all negative, showing the well-known underestimation of dissociation energies by this method. A substantial, but not unexpected, basis set effect is observed for dissociation energies compared to term values. The range of the basis set effect as given by mean errors is about 2000 cm^{-1} for dissociation energies and only 700 cm^{-1} in the maximum for the term values. Whereas obviously some error cancellation is taking place for term energies since they are computed as differences between molecular energies, this error cancellation is not so effective for dissociation energies since in this case molecular and atomic energies are compared.

The observation that for r_e the standard deviation is much smaller than the mean error for so many different states indicates a systematic source of error. One possible candidate is the core correlation, which has not been included in our calculation. Peterson et al. [1] investigated the effect of core correlation on spectroscopic properties of the ground state of A_2 type molecules and computed core-correlation corrections at the extrapolated basis limit using the internally contracted (IC) MR-CISD + Q method. By approximating the core-correlation effect for the different states by the ground-state values reported in this work (−0.0038, −0.0022 and −0.0024 Å for C_2, N_2 and O_2, respectively), the mean error in r_e is reduced to −0.0008, 0.0001 and 0.0004 Å for C_2, N_2 and O_2, respectively; therefore, we can con-

Table 14. Equilibrium bond distances, r_e(Å), for O_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$\tilde{X}^3\Sigma_g^-$	1.2172	1.2138	1.2114	1.2164	1.2133	1.2105	1.2171	1.2138	1.2105	1.2075[a]
$A'^3\Delta_u$	1.5274	1.5204	1.5152	1.5279	1.5201	1.5143	1.5270	1.5200	1.5148	1.5129[b]
$A^3\Sigma_u^+$	1.5349	1.5277	1.5224	1.5355	1.5275	1.5216	1.5345	1.5272	1.5219	1.5197[b]
$B^3\Sigma_u^-$	1.6115	1.6045	1.5993	1.6302	1.6261	1.6231	1.6099	1.6041	1.5998	1.6042[a]
$^3\Pi_g$	1.4920	1.4877	1.4845	1.5013	1.4968	1.4935	1.4902	1.4860	1.4828	
Statistics triplet states[c]										
Mean	0.0131	0.0073	0.0030	0.0132	0.0069	0.0021	0.0128	0.0070	0.0024	
std.dev.	0.0030	0.0009	0.0008	0.0038	0.0010	0.0008	0.0028	0.0006	0.0006	
$a^1\Delta_g$	1.2265	1.2215	1.2179	1.2255	1.2207	1.2173	1.2265	1.2214	1.2177	1.2156[a]
$b^1\Sigma_g^+$	1.2392	1.2333	1.2291	1.2379	1.2323	1.2283	1.2393	1.2333	1.2290	1.2269[a]
$c^1\Sigma_u^-$	1.5307	1.5231	1.5175	1.5318	1.5234	1.5173	1.5304	1.5229	1.5174	1.5143[b]
$^1\Pi_g$	1.4626	1.4617	1.4610	1.4603	1.4579	1.4561	1.4630	1.4619	1.4611	
Statistics singlet states										
Mean	0.0132	0.0070	0.0026	0.0128	0.0065	0.0020	0.0131	0.0069	0.0024	
std.dev.	0.0029	0.0016	0.0006	0.0041	0.0022	0.0009	0.0027	0.0015	0.0006	
Statistics all states[c]										
Mean	0.0132	0.0071	0.0028	0.0130	0.0067	0.0021	0.0130	0.0069	0.0024	
std.dev.	0.0026	0.0011	0.0007	0.0035	0.0016	0.0007	0.0025	0.0010	0.0005	

[a] Ref. [38]
[b] Ref. [63]
[c] $B^3\Sigma_u^-$ state excluded, see text for more details

Table 15. Harmonic vibrational frequencies, ω_e(cm^{-1}), for O_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$\tilde{X}^3\Sigma_g^-$	1553	1579	1599	1567	1614	1655	1552	1574	1593	1580[a]
$A'^3\Delta_u$	795	803	810	780	791	799	798	807	813	815[b]
$A^3\Sigma_u^+$	779	788	795	765	776	784	783	792	799	804[b]
$B^3\Sigma_u^-$	712	718	721	670	674	676	717	722	725	709[a]
$^3\Pi_g$	675	678	681	629	633	635	684	687	689	
Statistics triplet states[d]										
Mean	−24	−10	2	−29	−6	13	−22	−9	2	
std.dev.	4	8	15	14	35	54	6	3	10	
$a^1\Delta_g$	1474	1496	1512	1482	1508	1528	1473	1494	1510	1510[c]
$b^1\Sigma_g^+$	1391	1416	1434	1402	1430	1451	1389	1414	1432	1433[a]
$c^1\Sigma_u^-$	775	784	791	762	771	779	779	788	794	797[b]
$^1\Pi_g$	827	817	810	819	813	809	829	820	813	
Statistics singlet states										
Mean	−33	−15	−1	−31	−10	6	−33	−15	−1	
std.dev.	10	2	4	4	14	21	13	5	2	
Statistics all states[d]										
Mean	−29	−12	0	−30	−8	10	−28	−12	0	
std.dev.	9	6	10	9	24	37	11	5	6	

[a] Ref. [38]
[b] Ref. [63]
[c] Ref. [66]
[d] $B^3\Sigma_u^-$ state excluded, see text for more details

clude that a substantial part of the error is due to core correlation. For ω_e a systematic error cannot be identified unambiguously. It is, however, worthwhile to note that the core correlation effects on ω_e calculated by Peterson et al. [1] at the ICMRCISD + Q level (14, 10, 7 cm^{-1} for C_2, N_2 and O_2, respectively) are within the range of the mean error.

Turning back to the figures, we note that several states have a comparatively large error. As discussed previously, for the ground states of N_2 and O_2, for the $^1\Delta_u$ state of C_2 and for the $b'^1\Sigma_u^+$ state of N_2 the state-averaging procedure has introduced an additional error. On the other hand, for the $e^3\Pi_g$ state of C_2 no deficiencies in the calculations have been found, suggesting inaccuracies of the experimental results.

4 Conclusions

In this work the performance of the MR-CISD, MR-CISD + Q and MR-AQCC methods using a valence CAS reference space and correlation-consistent basis sets has been investigated on a variety of excited states of diatomic molecules. Our systematic investigations with particular emphasis on basis set completeness and size-extensivity corrections allow a balanced judgment of the reliability of the methods applied and are intended to prepare a well-founded basis for future work on excited states. We find good overall agreement between all three methods (MR-CISD, MR-CISD + Q and MR-AQCC) with systematic variations of the properties depending upon the method and the basis set size. In view of the

Table 16. Term values, T_e (cm^{-1}), for O_2

State	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
$A'^3\Delta_u$	33825	34293	34632	33631	34047	34346	33887	34369	34721	34770[b]
$A^3\Sigma_u^+$	34457	34928	35271	34230	34646	34946	34520	35003	35355	35399[b]
$B^3\Sigma_u^-$	49180	49241	49286	50118	50430	50658	49083	49230	49338	49793[a]
$^3\Pi_g$	53585	53869	54079	53701	54001	54219	53582	53883	54108	
Statistics triplet states[c]										
Mean	−944	−474	−133	−1154	−738	−439	−881	−399	−47	
std.dev.	2	4	7	21	21	21	3	4	4	
$a^1\Delta_g$	8075	7931	7823	7769	7557	7395	8123	7976	7866	7918[a]
$b^1\Sigma_g^+$	13359	13221	13115	12864	12641	12469	13669	13308	13200	13195[a]
$c^1\Sigma_u^-$	32118	32639	33018	31924	32394	32732	32203	32749	33147	33057[b]
$^1\Pi_g$	64889	64908	64926	65040	65072	65096	64866	64897	64926	
Statistics singlet states										
Mean	−206	−126	−71	−538	−526	−525	−58	−46	14	
std.dev.	635	253	29	524	153	201	702	229	71	
Statistics all states[c]										
Mean	−501	−265	−96	−784	−611	−490	−387	−187	−10	
std.dev.	604	261	40	501	159	150	670	252	61	

[a] Ref. [38]

[b] Ref. [63]

[c] $B^3\Sigma_u^-$ state excluded, see text for more details

Table 17. Dissociation energies, D_e(cm^{-1}), for O_2 and atomic term values for O

State	Channel	MR-AQCC			MR-CISD			MR-CISD + Q			Exp.
		pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	pVTZ	pVQZ	(TQ)	
Oxygen	^{3}P	0	0	0	0	0	0	0	0	0	0
Oxygen	^{1}D	16337	16016	15783	16362	16041	15806	16305	15972	15728	15790[b]
$\tilde{X}^3\Sigma_g^-$	^{3}P + ^{3}P	40078	41334	42255	39302	40210	41238	40316	41607	42556	42180[a]
$A'^3\Delta_u$	^{3}P + ^{3}P	6253	7041	7623	5671	6163	6892	6429	7238	7835	7410
$A^3\Sigma_u^+$	^{3}P + ^{3}P	5621	6406	6984	5072	5564	6292	5796	6604	7201	6781
$B^3\Sigma_u^-$	^{3}P + ^{1}D	7235	8109	8752	5546	5821	6386	7538	8349	8946	8177
Statistics triplet states[c]											
Mean		−1473	−530	164	−2109	−1478	−650	−1277	−307	407	
std.dev.		545	274	77	666	428	254	509	230	27	
$a^1\Delta_g$	^{3}P + ^{3}P	32003	33403	34432	31533	32653	33843	32193	33631	34690	34262
$b^1\Sigma_g^+$	^{3}P + ^{3}P	26719	28113	29140	26431	27569	28769	26647	28299	29356	28985
$c^1\Sigma_u^-$	^{3}P + ^{3}P	7960	8695	9237	7378	7816	8506	8113	8858	9409	9123
Statistics singlet states[c]											
Mean		−1896	−720	146	−2343	−1444	−417	−1806	−527	362	
std.dev.		635	253	29	525	153	201	702	229	71	
Statistics all states[c]											
Mean		−1685	−625	155	−2226	−1461	−534	−1541	−417	384	
std.dev.		578	257	53	552	287	241	620	238	54	

[a] Ground-state value [38]

[b] Atomic term values [69]

[c] $B^3\Sigma_u^-$ state excluded, see text for more details

variety of states included in our survey, the evidently uniform quality of the results indicates that the observed systematics is a general feature of the methods and, hence, is molecule-independent.

In general, applying size-extensivity corrections reduces the mean error and the standard deviation of all the properties considered. This effect is small for C_2 and for B_2 in particular, but becomes sizeable with an increasing number of electrons. MR-CISD + Q tends to overestimate size-extensivity effects, while MR-AQCC tends to slightly underestimate them, but both of them are superior to MR-CISD in most cases. This is most apparent for the dissociation energies of N_2 and O_2. MR-AQCC has the additional advantage over MR-CISD + Q that it gives not only the the size-extensivity corrected energy but the density matrices, transition moments and gradients as well [16, 17].

The statistical analysis of MR-AQCC results for more than 30 states for which experimental data were available gives mean errors of approximately 0.0030 Å, 10 cm^{-1}, 300 cm^{-1} and 200 cm^{-1} in r_e, ω_e, T_e and D_e, respectively. The corresponding standard deviations are 0.001 Å, 10 cm^{-1}, 300 cm^{-1} and 300 cm^{-1}. For r_e we find a systematic error due to the neglected core corre-

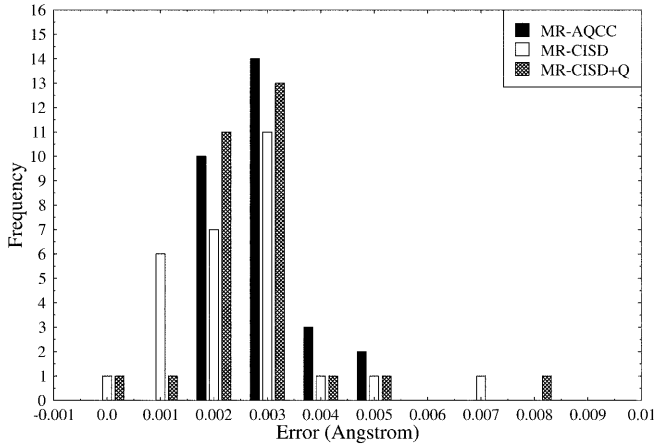

Fig. 1. Error distribution for equilibrium geometries based on (TQ) extrapolated values for C_2, N_2 and O_2

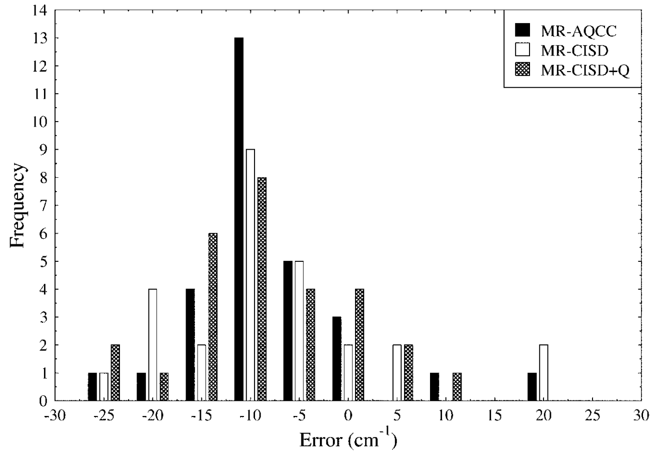

Fig. 2. Error distribution for harmonic frequencies based on (TQ) extrapolated values for C_2, N_2 and O_2

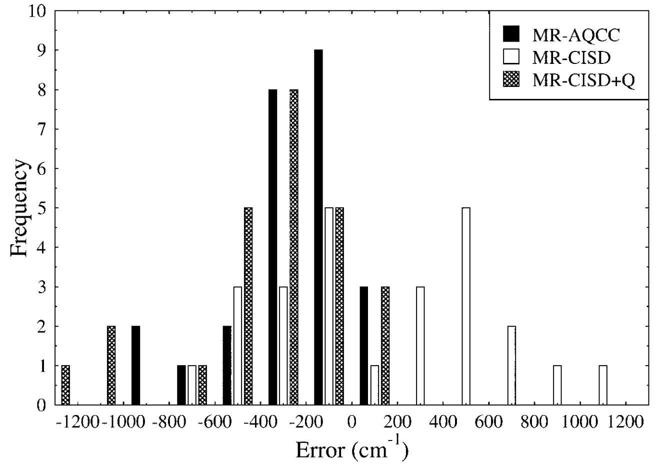

Fig. 3. Error distribution for term values based on (TQ) extrapolated values for C_2, N_2 and O_2

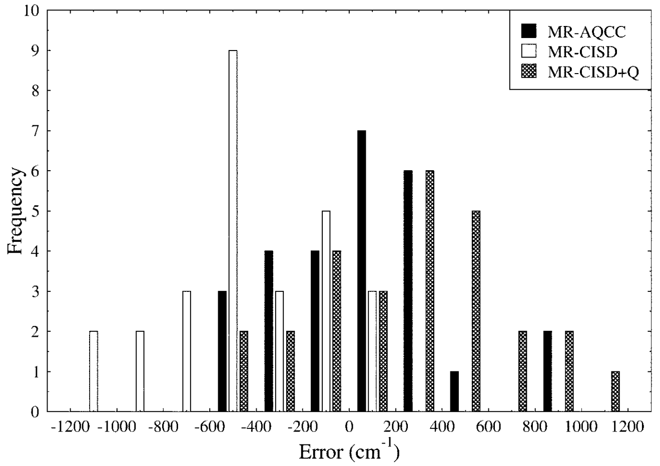

Fig. 4. Error distribution for dissociation energies based on (TQ) extrapolated values for C_2, N_2 and O_2

lation. By including estimates for the latter, the mean error drops to 0.0006 Å. Not unexpectedly, the importance of size-extensivity corrections appears most obviously in the case of dissociation energies. MR-AQCC gives the best results, whereas the MR-CISD results are systematically too low and MR-CISD + Q – as has already been mentioned – systematically overemphasizes size-extensivity effects. For B_2 only few spectroscopic data are available. Thus, our results serve as predictions with at least the same accuracy as that obtained for the remaining three molecules.

The basis set extrapolation scheme brings about a substantial improvement of accuracy. For example, the accuracy of the results is significantly enhanced by the (TQ) extrapolation, which just requires additional calculations with the smaller cc-pVTZ basis. Considering the relatively low cost of a cc-pVTZ calculation compared to a cc-pVQZ one, it seems to be worth performing this extrapolation as much as possible.

This systematic study on the performance of various methods allows the independent identification of any shortcomings of the calculations (such as Rydberg state coupling or insufficient configuration space), which are indicated by unusually large basis set effects or size-extensivity corrections compared to other states of the same molecule. Extensive state-averaging over a multitude of different states has its limits as this procedure tends to slightly favor excited states over the ground state. This is most apparent for excited states of diffuse character. However, frequently it is not possible to avoid averaging because one needs to establish a common reference energy for the desired states. Clearly, significant discrepancies with experiment for states which indicate no shortcomings whatsoever in the theoretical treatment suggest the re-evaluation of experimental results.

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