

The structure and stability of the O_2^{2+} dication: a dramatic failure of Møller–Plesset perturbation theory

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By comparison with results of full configuration-interaction and large-scale multireference configuration-interaction calculations, it is shown that the widely used RMP2 and RMP4 methods fail to describe even qualitatively the structure and kinetic stability of the O_2^{2+} dication, an isoelectronic analogue of molecular nitrogen. A barrier to dissociation of more than 200 kJ mol^{-1} completely disappears. In contrast, much better results are obtained from other methods based on a single reference function, such as quadratic configuration interaction and the Brueckner doubles procedure.

1. Introduction

A common and convenient method for incorporating the effects of electron correlation into ab initio molecular orbital calculations is Møller–Plesset perturbation theory [1,2]. The perturbation expansion may be based on either closed-shell restricted Hartree–Fock (RHF) or unrestricted Hartree–Fock (UHF) starting points, and the series is typically truncated at second, third or fourth orders, leading to theoretical models termed RMP2, UMP2, RMP3, and so on. For many chemical systems, these theoretical models have been shown to lead to reliable predictions of molecular structure and thermochemical stability [3].

However, it is now well documented that, in certain cases, Møller–Plesset perturbation theory may exhibit poor convergence properties, particularly if based on an unrestricted Hartree–Fock reference

function [4–9]. UHF wavefunctions are not eigenfunctions of the S^2 spin-squared operator, and such wavefunctions are, therefore, always contaminated to some degree by electronic states of higher spin multiplicity. In cases of heavy spin contamination, such as for molecules with stretched bonds [4–6] or highly unsaturated radicals with low-lying unfilled orbitals [7], the UMP series has been found to converge very slowly. As a consequence, if the perturbation series is truncated at low orders, very poor estimates of reaction energies may be obtained. For example, Gill and Radom [6] found that the fourth-order (UMP4) estimate of the barrier height for dissociation of He_2^{2+} (calculated with a minimal basis set) was grossly in error compared with the exact barrier in that basis set. This was shown to arise from the very poor convergence properties of the UMP series in the vicinity of the transition structure. In another study, Nobes et al. [7] reported large errors at the UMP4 level in the calculated dissociation energy of HCN and the electron affinity of CN^+ , and this was ascribed to heavy spin contamination in the UHF wavefunction of the cyano radical even at its equilibrium geometry. Schemes for projecting out the

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spin contaminants in the UMP energies have been proposed [10,11], and early results indicate that such approaches may offer an economical description of large regions of a potential energy surface.

There has been less work on the convergence properties of the restricted Møller–Plesset perturbation series. Handy et al. [4,5] have shown that, for closed-shell systems with stretched bonds, the RMP series converges rather erratically compared with the smooth (but slow) convergence of the UMP series. Thus, for the water molecule with each bond stretched to twice the equilibrium value, the sixth-order term in the RMP expansion has twice the magnitude of the third-order term, and it is only at 13th order that an accuracy of 10^{-4} hartree compared with the exact energy is obtained [5].

The slow convergence of the UMP series and the erratic behaviour of the RMP series in such cases has been analyzed in some detail [8,9], and has been traced to the failure of Møller–Plesset theory to treat satisfactorily certain low-lying doubly excited determinants.

In the present paper, we report calculations on O_2^{2+} , the dication of molecular oxygen, using a number of theoretical techniques including full configuration interaction. This species is isoelectronic with molecular nitrogen, and has been studied in the past using both experimental techniques [12,13] and quantum-chemical calculations [13–19]. A preliminary account of part of the present investigation, discussing more fully the chemistry of O_2^{2+} , has been presented previously [17]. In the present paper, we turn our attention to the performance of several theoretical methods in describing the shape of the potential energy curve. Møller–Plesset perturbation theory is shown to fail dramatically in describing the structure and kinetic stability of the O_2^{2+} dication: in the case of RMP4, no bound equilibrium structure is found, even though more accurate calculations and experimental evidence suggest that O_2^{2+} is a tightly bound species with high kinetic stability.

2. Methods

The primary aim of this paper is to compare the performance of a number of theoretical procedures in describing the O_2^{2+} potential surface. The rather

small 6-31G [20] and 6-31G* [21] basis sets were used for most calculations to allow near-exact configuration-interaction calculations to be carried out as a reference. Calculations were performed both for O_2^{2+} and, for comparison purposes, N_2 . The theoretical procedures and associated computer programs include:

(i) Møller–Plesset theory, incorporated in the GAUSSIAN 90 [22] system of programs.

(ii) Single-reference configuration interaction with single and double substitutions (CISD), and quadratic configuration interaction [23] with single and double substitutions (QCISD) and with the effects of triple excitations treated via a perturbative approach (QCISD(T)), also incorporated in GAUSSIAN 90.

(iii) Brueckner doubles theory [24,25] with double substitutions only (BD) and with the effects of triple excitations treated via a perturbative approach (BD(T)), incorporated in GAUSSIAN 91 [26].

(iv) Complete-active-space self-consistent-field (CASSCF) theory, as incorporated in GAMESS [27]. The active space comprised all of the valence orbitals, namely $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$, $1\pi_g$ and $1\pi_u$. This choice of active space should ensure a reliable qualitative description of both diatomics for all values of the internuclear separation.

(v) Multi-reference configuration interaction using the program of Saunders and van Lenthe [28] as implemented in GAMESS. The reference set consisted of all CASSCF configurations. All configurations arising from single and double excitations from this reference space into the virtual orbitals were included in the CI procedure. For the larger (6-31G*) basis set, this gives rise to a configuration-interaction calculation with 108120 configuration state functions. This CASSCF+CISD method will be denoted as MRCI.

(vi) Full configuration interaction (FCI) with the smaller (6-31G) basis set, using the program of Knowles and Handy [29].

Potential curves were obtained from calculations of the energy at 20–50 points in the range 0.9–1.8 Å. Important features in these curves are summarized in tables 1 and 2. In all calculations, the core $1\sigma_g$ and $1\sigma_u$ orbitals were constrained to be doubly occupied.

Finally, to obtain a more accurate characterization

Table 1

Equilibrium bond lengths (r_e) and total energies (E_e), transition-structure bond lengths (r_{TS}), and barrier heights for O_2^+ calculated using the 6-31G basis set

Method	r_e (Å)	E_e (hartree)	r_{TS} (Å)	Barrier (kJ mol ⁻¹)
RHF	1.017	-148.11247	-	-
RMP2	-	-	-	-
RMP3	1.042	-148.38204	-	-
RMP4	-	-	-	-
RCISD	1.070	-148.39579	-	-
RBD	1.090	-148.42306	1.415	146.0
RQCISD	1.096	-148.42701	1.442	139.6
RBD(T)	1.104	-148.43604	1.368	84.0
RQCISD(T)	1.106	-148.43744	1.398	92.6
UHF	-	-	-	-
UMP2	0.959	-148.39899	1.336	242.5
UMP3	0.959	-148.34875	a)	a)
UMP4	0.980	-148.38628	1.354	132.5
UBD	1.090	-148.42306	1.388	134.5
UQCISD	1.111	-148.44101	1.447	138.4
UBD(T)	1.104	-148.43604	1.442	114.2
UQCISD(T)	1.109	-148.43935	1.456	117.3
CASSCF	1.103	-148.38066	1.462	117.5
MRCI	1.113	-148.44240	1.452	90.7
FCI	1.113	-148.44313	1.451	90.1

^{a)} The UMP3 potential curve has a plateau in the region 1.20–1.32 Å with local maxima at 1.21 and 1.31 Å. The height of the barrier to dissociation at this level is 76 kJ mol⁻¹.

of the potential surface near the equilibrium geometry of O_2^+ , energies at 11 points in the range 0.98–1.20 Å were obtained using the spin-restricted QCISD(T) procedure and the larger 6-311+G(3df) basis set [30]. These energies were fitted to a sixth-degree polynomial in the internal bond-stretching coordinate $\Delta R = r - r_e$:

$$V - V_e = \sum_{n=2}^6 f^{(n)} \Delta R_n / n!,$$

where V is the potential energy function with a minimum V_e at r_e . Spectroscopic constants (ω_e , $\omega_e x_e$, B_e and α_e) were obtained from the coefficients $f^{(n)}$ of this polynomial [31]. Analogous calculations were also performed at this level for the N_2 molecule, for which accurate experimental values are known, in order to gauge the expected reliability of the calculated quantities for O_2^+ .

Table 2

Equilibrium bond lengths (r_e) and total energies (E_e), transition-structure bond lengths (r_{TS}), and barrier heights for O_2^+ calculated using the 6-31G* basis set

Method	r_e (Å)	E_e (hartree)	r_{TS} (Å)	Barrier (kJ mol ⁻¹)
RHF	1.007	-148.25935	-	-
RMP2	-	-	-	-
RMP3	1.042	-148.60548	-	-
RMP4	-	-	-	-
RCISD	1.052	-148.59979	-	-
RBD	1.066	-148.62855	1.552	388.0
RQCISD	1.070	-148.63198	1.608	395.7
RBD(T)	1.077	-148.64496	1.473	248.9
RQCISD(T)	1.079	-148.64650	1.520	272.5
UHF	-	-	-	-
UMP2	0.987	-148.63037	1.448	428.3
UMP3	0.987	-148.59191	1.450	280.0
UMP4	0.987	-148.62549	1.471	331.3
UBD	1.066	-148.62855	1.486	287.3
UQCISD	1.076	-148.63693	1.536	292.5
UBD(T)	1.077	-148.64496	1.547	296.0
UQCISD(T)	1.081	-148.64727	1.560	298.1
CASSCF	1.070	-148.49517	1.588	316.9
MRCI	1.083	-148.64729	1.598	264.8

3. Results and discussion

3.1. Hartree-Fock potential energy curves

Potential curves for dissociation of O_2^+ calculated using spin-restricted (RHF) and spin-unrestricted (UHF) Hartree-Fock theory are shown in the top half of fig. 1. For short internuclear separation, the best Hartree-Fock wavefunction corresponds to the closed-shell restricted case, i.e. the set of spatial orbitals occupied by α electrons is identical to the set occupied by β electrons. However, beyond a certain point (0.96 Å with 6-31G and 0.99 Å with 6-31G*), this RHF solution becomes unstable, and the best wavefunction then has different orbitals for α and β spins. The expectation value of the S^2 operator in the UHF solution rises sharply as the O-O bond is stretched beyond this point. Note that the RHF potential curve has a deep well corresponding to a bound O_2^+ species, whereas the UHF curve would suggest that O_2^+ dissociates to two O^+ ions without any potential barrier.

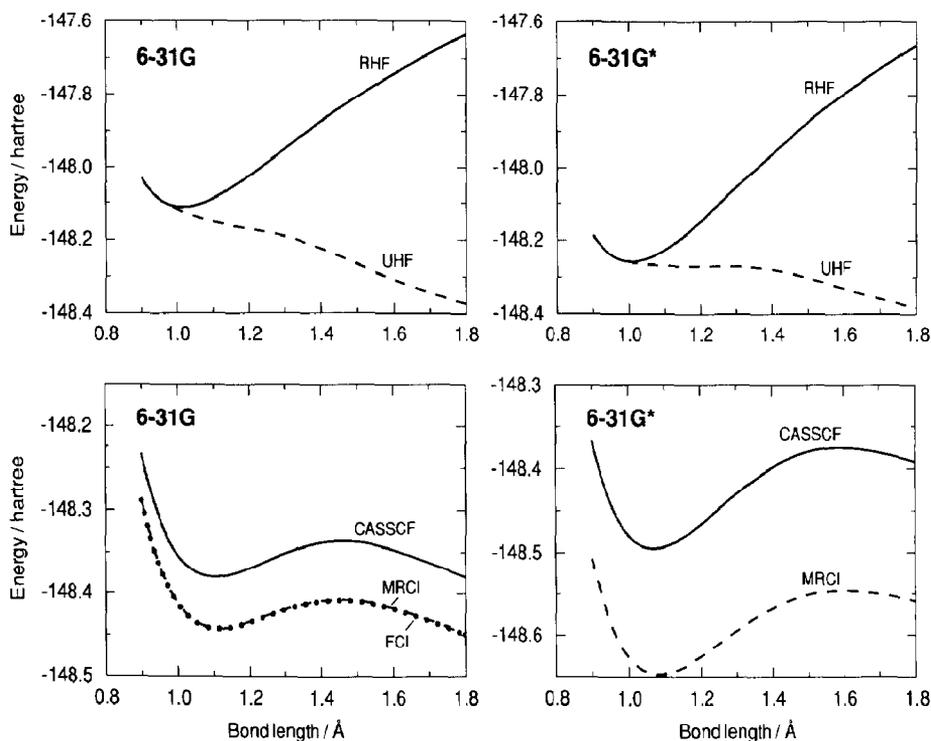


Fig. 1. Potential energy curves for O_2^+ calculated using spin-restricted (RHF) and spin-unrestricted (UHF) Hartree-Fock theory (upper curves), and CASSCF, multireference configuration-interaction (MRCI) and full configuration-interaction (FCI) methods (lower curves).

3.2. Large-scale configuration-interaction calculations

The bottom half of fig. 1 shows the potential curves resulting from the CASSCF, multireference CI (MRCI) and, in the case of the 6-31G basis set, the full CI (FCI) method. We note that full CI yields the best possible solution within the basis set being used. With the smaller basis set, the MRCI and FCI curves are virtually indistinguishable. The MRCI curve with the 6-31G* basis set thus provides a useful reference against which to judge the results obtained with other theoretical procedures with this basis set. All three methods yield the same qualitative conclusion, namely that the O_2^+ dication is a strongly bound species with a very short equilibrium bond length and a large barrier to dissociation (1.083 Å and 265 kJ mol⁻¹ with the MRCI/6-31G* method). Other recent multireference configuration-interaction stud-

ies [13,17-19] also conclude that the ground $X^1\Sigma_g^+$ state of O_2^+ is bound with a substantial barrier to dissociation. Note that, while O_2^+ is predicted to be kinetically stable, it is not thermodynamically stable. Beyond the maximum in the potential curve, the energy drops sharply as the electrostatic repulsion of the two O^+ monocations becomes dominant, and the dissociation process $O_2^+ \rightarrow 2O^+$ is highly exothermic.

3.3. Performance of restricted Møller-Plesset perturbation theory

Potential curves for dissociation of O_2^+ calculated using restricted Møller-Plesset perturbation theory are shown in the top half of fig. 2. It is immediately apparent that convergence of the series becomes rapidly worse as the O-O bond is stretched beyond the point where the RHF wavefunction becomes unstable, with RMP2, RMP3 and RMP4 energies dif-

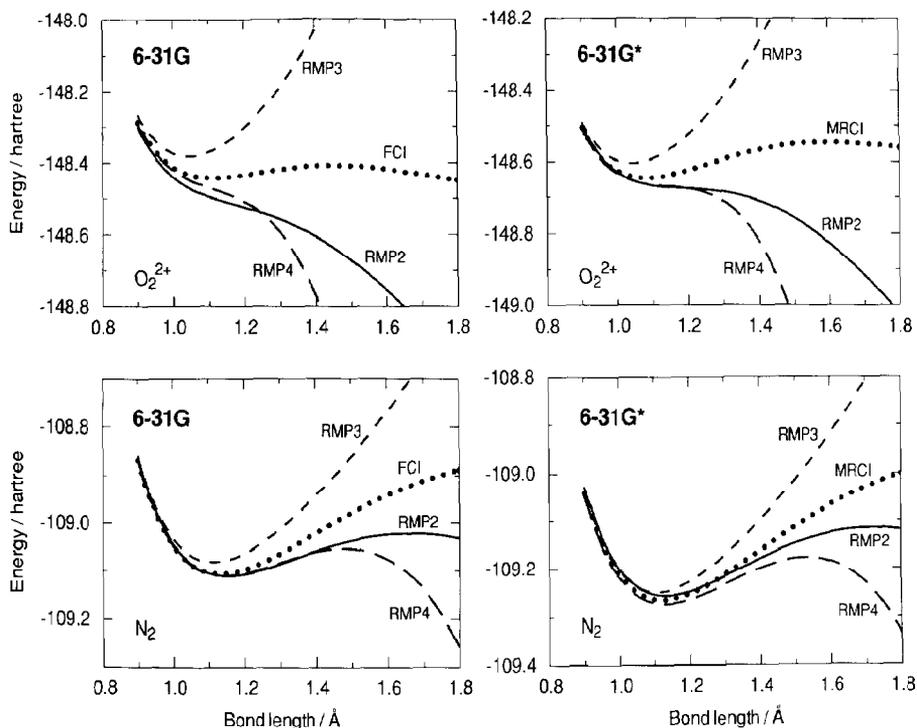


Fig. 2. Comparison of potential energy curves for O_2^{2+} (upper curves) and N_2 (lower curves) calculated using spin-restricted Møller-Plesset theory (RMP2, RMP3, RMP4) with those calculated using large-scale configuration interaction.

fering wildly. It can also be seen that, in contrast to the RHF and RMP3 methods, *RMP2 and RMP4 predict that there is no stable structure corresponding to a tightly bound O_2^{2+} molecule.* It is rather disturbing that these widely used methods fail completely to describe the equilibrium structure of this kinetically stable species. A barrier to dissociation of more than 200 kJ mol^{-1} has disappeared!

For comparison, potential curves for dissociation of the isoelectronic nitrogen molecule N_2 are also shown in fig. 2. It can be seen that at large separations, the Møller-Plesset series for this molecule displays similar poor convergence properties. However, unlike O_2^{2+} , the onset of instability in the RHF wavefunction occurs *beyond* the potential minimum, and, as a result, RMP theory provides a reasonable description of the equilibrium structure of N_2 .

3.4. Comparison with other spin-restricted correlation methods

Fig. 3 displays potential energy curves calculated using other correlation procedures which are based on the single RHF determinant. These methods provide a much more satisfactory description of the structure of O_2^{2+} . In particular, the quadratic configuration and Brueckner doubles methods corrected for triple substitutions (RQCISD(T) and RBD(T)) provide excellent descriptions of the equilibrium structure of O_2^{2+} and of the barrier to dissociation, although the location of the maximum is at a slightly shorter separation than in the more accurate FCI or MRCI methods.

3.5. Performance of unrestricted Møller-Plesset perturbation theory

Potential curves calculated using Møller-Plesset perturbation theory based on the spin-unrestricted UHF starting point are shown in fig. 4. It can be seen

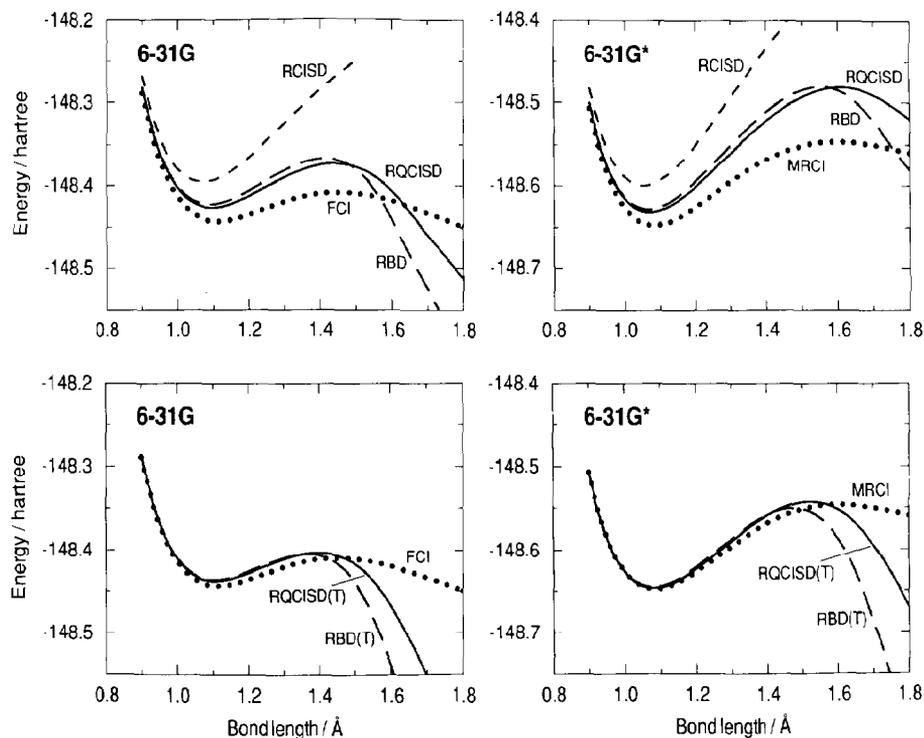


Fig. 3. Comparison of potential energy curves for O_2^+ calculated using spin-restricted singles and doubles configuration-interaction (RCISD), quadratic configuration-interaction (RQCISD, RQCISD(T)) and Brueckner doubles (RBD, RBD(T)) methods with those calculated using large-scale configuration interaction.

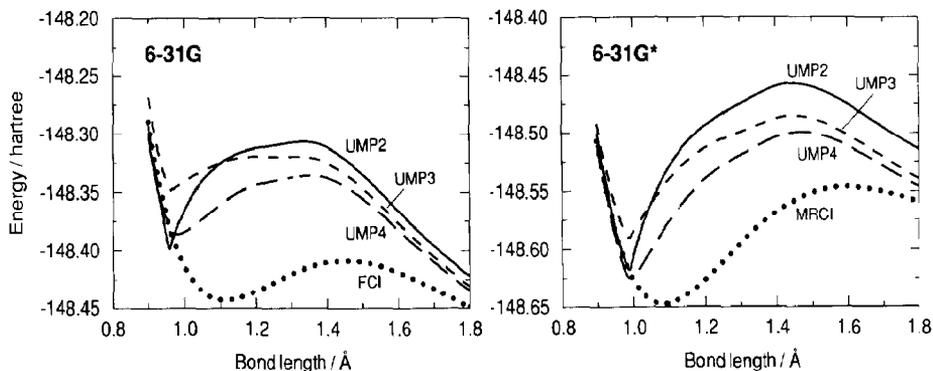


Fig. 4. Comparison of potential energy curves for O_2^+ calculated using spin-unrestricted Møller-Plesset theory (UMP2, UMP3, UMP4) with those calculated using large-scale configuration interaction.

that the UMP2, UMP3 and UMP4 energies rise steeply as the UHF wavefunction starts to become contaminated by higher spin states in the region around 1.0 Å, with an apparent discontinuity in the energy gradient at the point at which the RHF

method becomes unstable. As a consequence, the minima in these curves largely reflect the point at which the RHF and UHF curves bifurcate, rather than providing a true indication of the equilibrium structure of the dication. Potential energy barriers

calculated at the UMP3 and UMP4 levels are in reasonable agreement with those obtained from the best methods. However, given the poor behaviour of the UMP curves at short distances and the very slow convergence of the UMP series in the vicinity of the transition structure (where the underlying UHF wavefunction is severely contaminated, as evidenced by the expectation value of S^2 of 2.6 rather than the correct 0.0 for a pure singlet), such agreement must be regarded as fortuitous.

3.6. Comparison with other spin-unrestricted correlation methods

Fig. 5 shows the potential curves obtained with quadratic configuration-interaction and Brueckner doubles methods based on the UHF determinant. These methods do not suffer from the problems mentioned above for the UMP method, and the UQCISD(T) and UBD(T) methods provide very good descriptions of the equilibrium structure of O_2^+ and reasonable estimates of the height and lo-

cation of the barrier to dissociation. Note that the UBD(T) curve is identical to the RBD(T) curve for bond lengths up to about 1.3 Å, whereas the other spin-unrestricted methods start to diverge from their spin-restricted counterparts at the point of divergence of the underlying Hartree-Fock methods.

3.7. Higher-level calculations

The equilibrium geometries, dissociation energies and spectroscopic constants of O_2^+ and N_2 calculated with the RQCISD(T) method and the 6-311+G(3df) basis set are shown in table 3. For O_2^+ , comparative results from the large basis set [5s4p3d2f1g] multireference ACPF calculations of Pettersson and Larsson [19] are included, while for N_2 both experimental values [33] and results from the [(8+1)s8p5d3f2g1h] MRCI calculations of Werner and Knowles [32] are shown. Differences between the present results and the experimental values for N_2 are 0.006 Å for r_e , 41 kJ mol⁻¹ for D_e , 23 cm⁻¹ for ω_e , 0.5 cm⁻¹ for $\omega_e x_e$, 0.022 cm⁻¹ for

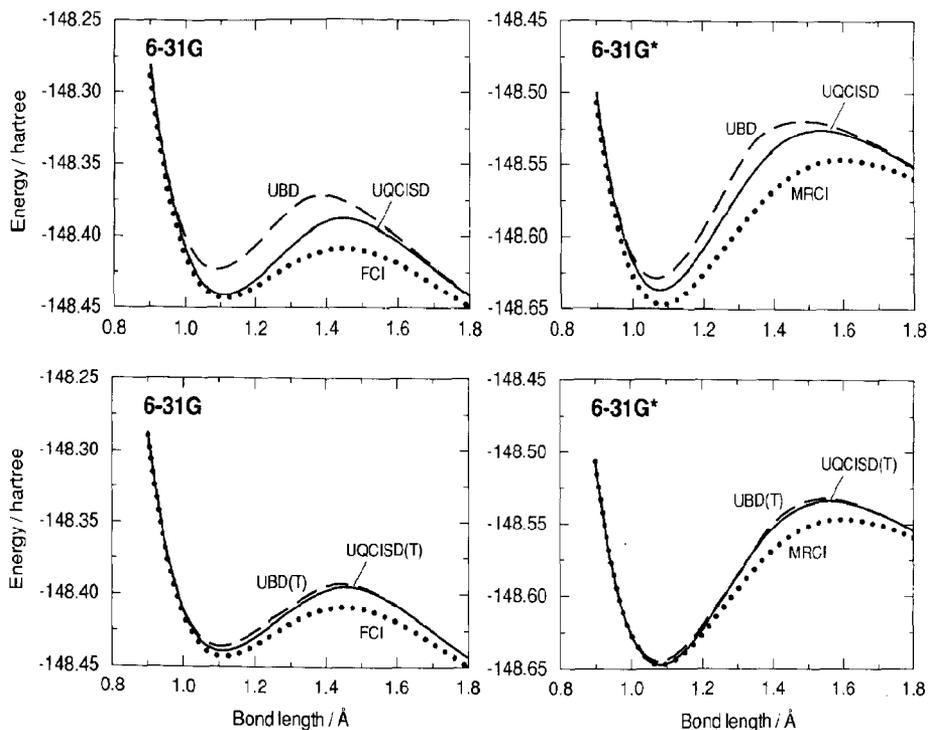


Fig. 5. Comparison of potential energy curves for O_2^+ calculated using spin-unrestricted quadratic configuration-interaction (UQCISD, UQCISD(T)) and Brueckner doubles (UBD, UBD(T)) methods with those calculated using large-scale configuration interaction.

Table 3

Equilibrium bond lengths, dissociation energies and spectroscopic constants for O_2^+ and N_2

	r_e (Å)	D_e (kJ mol ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
O_2^+						
this work ^{a)}	1.050	-391	2206	21.3	1.913	0.0226
ref. [19] ^{b)}	1.057	-378	2147	23.7	1.901	0.024
N_2						
this work ^{a)}	1.104	915	2336	13.8	1.976	0.0169
ref. [32] ^{c)}	1.097	953	2367	14.1	1.999	0.0171
exp. (ref. [33])	1.098	956	2359	14.3	1.998	0.0173

^{a)} RQCISD(T) calculations with the 6-311+G(3df) basis set.^{b)} MRACPF calculation with [54321] basis set.^{c)} MRCI calculation with [(8+1)85321] basis set.

B_e and 0.0004 cm^{-1} for α_e . Differences observed between the present results for O_2^+ and the previous theoretical results of Pettersson and Larsson [19] are 0.007 Å for r_e , 13 kJ mol^{-1} for D_e , 59 cm^{-1} for ω_e , 2.4 cm^{-1} for $\omega_e x_e$, 0.012 cm^{-1} for B_e and 0.0014 cm^{-1} for α_e .

One striking result from table 3 is that the bond length in O_2^+ is very short and, as noted previously [17], possibly represents the shortest bond between any two heavy atoms.

4. Conclusions

Large-scale configuration-interaction calculations indicate that the O_2^+ molecule is tightly bound, with a very short O-O bond and a large barrier to dissociation to two O^+ ions. The restricted Hartree-Fock wavefunction for this cation becomes unstable at very short internuclear separations, and this, combined with the rapidly increasing spin contamination in the unrestricted wavefunction as the O-O bond is stretched, means that this system offers a demanding test of the performance of theoretical methods. Møller-Plesset methods perform very poorly in this case, with the RMP2 and RMP4 methods failing to predict a bound equilibrium structure and UMP methods indicating an artificially short O-O bond. Quadratic configuration-interaction and Brueckner doubles schemes based on either the RHF or UHF wavefunction and with corrections for triple substitutions offer much more satisfactory descriptions of

the structure and stability of this dication.

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References

- [1] C. Møller and M.S. Plesset, Phys. Rev. 46 (1934) 618.
- [2] R. Krishnan, M.J. Frisch and J.A. Pople, J. Chem. Phys. 72 (1980) 4244, and references therein.
- [3] W.J. Hehre, L. Radom, P. von R. Schleyer and J.A. Pople, Ab initio molecular orbital theory (Wiley-Interscience, New York, 1986).
- [4] P.J. Knowles, K. Somasundram, N.C. Handy and K. Hirao, Chem. Phys. Letters 113 (1985) 8.
- [5] N.C. Handy, P.J. Knowles and K. Somasundram, Theoret. Chim. Acta 68 (1985) 87.
- [6] P.M.W. Gill and L. Radom, Chem. Phys. Letters 132 (1986) 16.
- [7] R.H. Nobes, J.A. Pople, L. Radom, N.C. Handy and P.J. Knowles, Chem. Phys. Letters 138 (1987) 481.
- [8] M.B. Lepetit, M. Pélassier and J.P. Malrieu, J. Chem. Phys. 89 (1988) 998.
- [9] P.M.W. Gill, J.A. Pople, L. Radom and R.H. Nobes, J. Chem. Phys. 89 (1988) 7307.

- [10] H.B. Schlegel, *J. Phys. Chem.* 92 (1988) 3075.
- [11] P.J. Knowles and N.C. Handy, *J. Chem. Phys.* 88 (1988) 6991.
- [12] M. Hamdan and A.G. Brenton, *Chem. Phys. Letters* 164 (1989) 413.
- [13] M. Larsson, P. Baltzer, S. Svensson, B. Wannberg, N. Mårtensson, A. Naves the Brito, N. Correia, M.P. Keane, M. Carlsson-Göthe and L. Karlsson, *J. Phys. B* 23 (1990) 1175, and references therein.
- [14] N.H.F. Beebe, E.W. Thulstrup and A. Andersen, *J. Chem. Phys.* 64 (1976) 2080.
- [15] P. Pyykkö, *Mol. Phys.* 67 (1989) 871.
- [16] A.T. Balaban, G.R. de Maré and R.A. Poirier, *J. Mol. Struct. (THEOCHEM)* 183 (1989) 103.
- [17] M.W. Wong, R.H. Nobes, W.J. Bouma and L. Radom, *J. Chem. Phys.* 91 (1989) 2971.
- [18] H. Yang, D.M. Hanson, F.V. Trentini and J.L. Whitten, *Chem. Phys.* 147 (1990) 115.
- [19] L.G.M. Pettersson and M. Larsson, *J. Chem. Phys.* 94 (1991) 818.
- [20] W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.* 56 (1972) 2257.
- [21] P.C. Hariharan and J.A. Pople, *Theoret. Chim. Acta* 28 (1973) 213.
- [22] M.J. Frisch, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M.A. Robb, J.S. Binkley, C. Gonzalez, D.J. DeFrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol and J.A. Pople, *GAUSSIAN 90*, Gaussian Inc., Pittsburgh (1990).
- [23] J.A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.* 87 (1987) 5968.
- [24] R.A. Chiles and C.E. Dykstra, *J. Chem. Phys.* 74 (1981) 4544.
- [25] N.C. Handy, J.A. Pople, M. Head-Gordon, K. Raghavachari and G.W. Trucks, *Chem. Phys. Letters* 164 (1989) 185.
- [26] M.J. Frisch, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M. Robb, M.W. Wong, E.S. Replogle, J.S. Binkley, C. Gonzalez, D.J. DeFrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol and J.A. Pople, *GAUSSIAN 91*, to be published.
- [27] M.F. Guest, J. Kendrick and S.A. Pope, *GAMESS Documentation*, SERC Daresbury Laboratory, Warrington (1983).
- [28] V.R. Saunders and J.H. van Lenthe, *Mol. Phys.* 48 (1983) 923.
- [29] P.J. Knowles and N.C. Handy, *Computer Phys. Commun.* 54 (1989) 75.
- [30] M.J. Frisch, J.A. Pople and J.S. Binkley, *J. Chem. Phys.* 80 (1984) 3265.
- [31] J.H. Hollas, *High resolution spectroscopy* (Butterworths, London, 1982).
- [32] H.-J. Werner and P.J. Knowles, *J. Chem. Phys.* 94 (1991) 1264.
- [33] G. Herzberg and K.P. Huber, *Molecular spectra and molecular structure*, Vol. 4. Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).