1Pp021 A theoretical study of the ground and lowest-lying states of YbO

Jozef Paulovič,[a] Roland Lindh[b], Per Åke Malmqvist[c], Björn Olof Roos,[c] and Kimihiko Hirao[a,*]

[a]Department of Applied Chemistry, School of Engineering,

The University of Tokyo, Tokyo 113-8656, Japan

[b]Department of Chemical Physics,

[c]Department of Theoretical Chemistry,

University of Lund, P.O.B 124 S-221 00 Lund, Sweden

Abstract

The properties of the YbO molecule have been the matter of extensive studies, however, no investigation to this date has been able to predict a bond distance in quantitative agreement with experiment. In the present work, we report properties for the ground and the first excited states of YbO, evaluated at the multistate multiconfigurational second-order perturbation level of theory. Scalar relativistic effects are included through the second-order Douglas-Kroll transformation and spin-orbit coupling using the restricted active space state interaction method in conjunction with the atomic mean-field integrals. The study also offers some results with respect to properties of the Yb atom. Again, the results are in qualitative and quantitative agreement with experiment, Table I.

Table I. Atomic energies in (eV) from the present quasirelativistic calculations with or without spin-orbit effects compared to available experimental data. Previous fully relativistic density functional calculations (BDF) and relativistic coupled-cluster (CC) calculations are also reported.

			BDF[b]				Eliav *et al.*[c]		Present		
Atom	Configuration	Term[a]	LDASI	NLx	NLc	NLxc	DC	DCB	CASPT2[d]	CASPT2-SO[e]	Expt.[f]
Yb	$f^{14}s^2$	$^1S_0$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	$f^{14}s^1p^1$	$^3P_0$	2.72	2.69	2.67	2.63	2.15	2.15	2.15	2.01	2.14
		$^3P_1$	2.38	2.40	2.23	2.25	2.24	2.24		2.08	2.23
		$^3P_2$	2.69	2.69	2.55	2.55	2.46	2.46		2.22	2.44
	$f^{14}s^1d^1$	$^3D_1$	3.18	3.16	3.18	3.15	3.10	3.09	3.04	2.98	3.04
		$^3D_2$	2.85	2.90	2.74	2.78	3.13	3.12		3.02	3.07
		$^3D_3$	2.99	3.03	2.88	2.91	3.19	3.18		3.09	3.13
Yb^+	$f^{14}s^1p^0$	$^2S_{1/2}$	6.33	6.43	6.11	6.22			6.01		6.25

[a] According to the *jj* coupling scheme.

[b] Reference 1.

[c] Reference 2.

[d] Present work. Obtained from the spin-free CASPT2 calculation.

[e] Present work. Obtained from the CASPT2 based RASSI-SO calculation.

[f] Reference 3.

The predicted equilibrium bond distance, harmonic vibrational frequency, and dissociation energy for YbO are in agreement with available experimental data, Table II.

Table II. The spectroscopic constants for the $^1\Sigma^+$ ground state of ytterbium monoxide YbO obtained from present all-electron correlated calculations which include scalar relativistic effect through the second-order Douglas-Kroll Hamiltonian. Results are calculated at various level of theory.

	Method	r_e(Å)	ω_e(cm^{-1})	B_e(cm^{-1})	D_e(eV)
Present					
	SCF	1.884	719	0.324	
	B3LYP	1.855	700	0.335	
	MP2	1.801	732	0.355	
	CASSCF	1.932	629	0.308	3.94
	CASPT2	1.801	744	0.355	4.31
Previous					
	SCF[a]	1.903	713		
	MRCI[a]	1.886	679		2.53
	DFT F[b]	1.93	615		4.06
	DFT C[b]	1.87	678		5.04
	DFT S[b]	1.86	681		4.64
	DFT F[b] ($4f^{14}/4f^{13}\sigma^1$)	1.90	680		4.22
	LDASI[c]	1.834	757		5.63
	NLx[c]	1.888	699		4.53
	NLc[c]	1.807	812		6.00
	NLxc[c]	1.865	725		4.86
	Expt.[d]	1.807	699	0.352	4.33

[a] Reference 4. A quasirelativistic pseudopotential study, 42 valence electrons for Yb.

[b] Reference 5. S: simple Slater's Xα; C: with Vosko/Stoll correlation correction; F: full DF with correlation and exchange gradient corrections.

[c] Reference 1. Fully relativistic density functional calculations. LDASI: local density approximation with self–interaction correction; NLx: correction; NLc: correction; NLxc: NLx and NLc corrections.

[d] Reference 6.

The dynamical correlation effect has been found to enhance a stabilization of the $4f^{14}\sigma^0$ configuration. However, since the lowest-lying states arising from the $4f^{13}\sigma^1$ superconfiguration are only slightly higher in energy, a configuration interaction between $4f^{14}\sigma^0$ and $4f^{13}\sigma^1$ might occur to the ground state. This implies the importance of the dynamical correlation as well as spin-orbit interaction among other correlation and relativistic effects. This stage is under investigation.

References

[1] W. Liu, M. Dolg and L. Li, J. Chem. Phys., 108, 2886 (1998).

[2] E. Eliav, U. Kaldor, Y. Ishikawa, Phys. Rev. A 52, 291 (1995).

[3] W. C. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels-The Rare Earth Elements*, NSRDS-NBS 60 (USGPO, Washington, DC, 1978).

[4] M. Dolg, H. Stoll, H.-J. Flad and H. Preuss, J. Chem. Phys., 97, 1162 (1992).

[5] S. G. Wang, D. K. Pan and W. H. E. Schwarz, J. Chem. Phys., 102, 9296 (1995).

[6] C. Linton, S. A. McDonald, S. Rice, M. Dulick, Y. C. Liu and R. W. Field, J. Mol. Spectrosc., 101, 332 (1983).