

# The dipole moments of the excited states of FeC

Demeter Tzeli and Aristides Mavridis<sup>a)</sup>

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, 157 10 Zografou, Athens, Greece

(Received 21 September 2004; accepted 26 October 2004; published online 14 January 2005)

With the purpose of comparing expectation dipole moment values  $\langle\mu\rangle$  with finite-field obtained dipole moments  $\mu_{\text{FF}}$ , we recalculated by the finite-field method previously reported  $\langle\mu\rangle$  values of 38 excited states of FeC. In most of the cases  $\mu_{\text{FF}}$  is significantly larger than  $\langle\mu\rangle$ . © 2005 American Institute of Physics. [DOI: 10.1063/1.1834564]

Recently, we published *ab initio* results on 41 states of iron carbide, FeC,<sup>1</sup> using multireference methods complete-active-space self-consistent field (CASSCF), CASSCF + single + double replacements (=MRCI) combined with ANO (Ref. 2) and cc-pVTZ (Ref. 3) bases, generally contracted to  $[7s6p4d3f/_{\text{Fe}}4s3p2d1f/_{\text{C}}]$ . However, it came as an unpleasant surprise to us when few months later Steimle, Virgo, and Hostutler<sup>4</sup> reported for the first time the experimental determination of the dipole moment of FeC ( $X^3\Delta_3$ ) state,  $\mu=2.36(3)$  D, almost twice as large as our MRCI obtained value,  $\langle\mu\rangle=\langle\Psi_{\text{MRCI}}|\hat{\mu}|\Psi_{\text{MRCI}}\rangle=1.28$  D.<sup>1</sup>

The recalculation of the dipole moment of the  $X$  state of the FeC via the *finite-field* approach ( $\mu_{\text{FF}}$ ) increasing at the same time the basis set,<sup>2,3</sup> gave  $\mu_{\text{FF}}=1.94$  (2.08) and 2.19 D at the MRCI (MRCI+ $Q$ )/ $[7s6p4d3f2g1h]_{\text{Fe}}/[6s5p4d3f2g]_{\text{C}}$  and C-CCSD(T)/ $[7s6p4d3f2g]_{\text{Fe}}/[5s4p3d2f1g]_{\text{C}}$  level, respectively, now in tolerable and fair agreement with experiment; see Ref. 5. + $Q$  refers to the Davidson correction and C-CCSD(T) to the coupled cluster + singles + doubles + perturbative correction of the connected triples method, including the semicore Fe  $3s^23p^6$  electrons.

The following conclusions were drawn from the above work:<sup>5</sup> (a) Otherwise seemingly adequate wave functions can fail badly at least for the estimation of dipole moments. (b) The finite-field method is to be preferred in general for the calculation of dipole moments. (c) The increase of the basis set size did not practically affect the calculated dipole moment in the case of the  $X$  state of FeC. See also Ref. 6.

Presently, we have recalculated the dipole moments of 38 excited states of FeC previously reported,<sup>1</sup> using the finite field instead of the expectation value approach, while main-

taining the same methods and basis sets as in Ref. 1 (CASSCF, MRCI/ $7s6p4d3f/_{\text{Fe}}4s3p2d1f/_{\text{C}}$ ). All calculations were performed with the MOLPRO program.<sup>7</sup>

Our numerical results ( $\mu_{\text{FF}}$ ) are collected in Table I along with the  $\langle\mu\rangle$  values from Ref. 1; the conclusions are the following:

(a) With the exception of two states where  $\langle\mu\rangle>\mu_{\text{FF}}$  and three states where  $\langle\mu\rangle\approx\mu_{\text{FF}}$ , in all other states  $\mu_{\text{FF}}$  is significantly larger than  $\langle\mu\rangle$ .

(b)  $\langle\mu\rangle=\mu_{\text{FF}}$  at the CASSCF when state averaged methods are not used; see also Ref. 5.

(c) At the MRCI level the  $\mu_{\text{FF}}$  values are insensitive to the state-averaged procedure.

The results of the present work as well as our previous experience with similar systems, strongly suggest that the finite-field method is to be preferred for the calculation of dipole moments.

The present work was supported by the Greek Ministry of Education and European Union through the EPEAEK program PYTHAGORAS (Grant No. 70/3/7373) for basic research.

<sup>a)</sup>Electronic mail: mavridis@chem.uoa.gr

<sup>1</sup>D. Tzeli and A. Mavridis, J. Chem. Phys. **116**, 4901 (2002).

<sup>2</sup>C. W. Bauschlicher, Jr., Theor. Chim. Acta **92**, 183 (1995).

<sup>3</sup>T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

<sup>4</sup>T. C. Steimle, W. L. Virgo, and D. Hostutler, J. Chem. Phys. **117**, 1511 (2002).

<sup>5</sup>D. Tzeli and A. Mavridis, J. Chem. Phys. **118**, 4984 (2003).

<sup>6</sup>M. Medved, M. Urban, and J. Noga, Theor. Chim. Acta **98**, 75 (1997).

<sup>7</sup>MOLPRO 2000 is a package of *ab initio* programs written by H.-J. Werner, P. J. Knowles, R. D. Amos *et al.*

TABLE I. Dipole moments  $\mu$  (D) of excited states of the FeC at CASSCF, MRCI (in parenthesis), and MRCI+ $Q$  (in brackets) level of theory.

State <sup>a</sup>	$\langle\mu\rangle^b$	$\mu_{\text{FF}}^c$	State <sup>a</sup>	$\langle\mu\rangle^b$	$\mu_{\text{FF}}^c$
$1^1\Delta^d$	1.00 (0.94)	1.00 (1.66) [1.87]	$1^1\Delta$	1.46 (1.35)	1.43 (1.67) [1.79]
$2^3\Sigma^-d$	1.74 (1.16)	1.74 (1.89) [1.56]	$2^3\Sigma^-$	1.03 (1.07)	... <sup>e</sup> (1.91) [1.58]
$3^5\Pi$	2.66 (2.44)	2.94 (3.12) [3.07]	$4^5\Delta$	2.36 (1.67)	2.33 (2.16) [2.18]
$5^3\Pi$	3.42 (2.62)	3.11 (2.67) [2.64]	$6^5\Sigma^-$	2.36 (1.71)	2.69 (2.22) [2.05]

TABLE I. (Continued.)

State <sup>a</sup>	$\langle\mu\rangle^b$	$\mu_{\text{FF}}^c$	State <sup>a</sup>	$\langle\mu\rangle^b$	$\mu_{\text{FF}}^c$
7 <sup>3</sup> $\Delta$	...	...	8 <sup>3</sup> $\Pi$	2.80	2.49
	(1.38)	(1.96)		2.50	(2.67)
		[2.06]			[2.63]
9 <sup>7</sup> $\Delta$	2.42	2.51	10 <sup>7</sup> $\Pi$	2.67	2.99
	(2.13)	(2.43)		(2.39)	(2.79)
		[2.44]			[2.72]
11 <sup>1</sup> $\Pi$	2.11	2.18	12 <sup>5</sup> $\Sigma^-$	2.04	1.94
	(1.64)	(2.31)		(1.41)	(1.80)
		[2.27]			[1.6]
13 <sup>7</sup> $\Sigma^-$	2.60	2.88	14 <sup>1</sup> $\Gamma$	0.91	1.77
	(2.31)	(2.69)		(0.96)	(1.71)
		[2.56]			[1.56]
15 <sup>5</sup> $\Delta$	2.14	2.00	16 <sup>3</sup> $\Sigma^-$	1.43	...
	(1.79)	(2.23)		(0.61)	(0.13)
		[2.32]			[0.07]
17 <sup>5</sup> $\Pi$	2.23	2.22	18 <sup>3</sup> $\Phi$	1.80	2.27
	(1.72)	(2.49)		(1.46)	(2.06)
		[2.63]			[1.85]
19 <sup>1</sup> $\Sigma^+$	1.53	1.97	20 <sup>3</sup> $\Pi$	1.93	2.34
	(1.51)	(2.16)		(1.53)	(2.15)
		[2.10]			[1.93]
21 <sup>1</sup> $\Sigma^-$	1.95	...	22 <sup>7</sup> $\Delta$	2.49	2.29
	(0.43)	(0.41)		(2.29)	(2.58)
		[0.51]			[2.63]
23 <sup>5</sup> $\Sigma^+$	2.75	3.14	24 <sup>5</sup> $\Pi$	2.91	2.64
	(1.99)	(2.86)		(2.51)	(2.97)
		[2.82]			[2.85]
25 <sup>7</sup> $\Pi$	2.39	2.30	26 <sup>5</sup> $\Phi$	2.34	2.42
	(2.02)	(2.29)		(2.23)	(3.39)
		[2.24]			[3.60]
27 <sup>7</sup> $\Sigma^+$	2.34	3.08	28 <sup>7</sup> $\Sigma^-$	2.51	2.32
	(2.31)	(3.64)		(2.04)	(2.39)
		[3.71]			[2.31]
29 <sup>3</sup> $\Delta^e$	1.73	...	30 <sup>7</sup> $\Pi$	2.97	2.85
	(1.35)	...		(1.75)	(2.43)
		[2.07]			[2.32]
31 <sup>7</sup> $\Phi$	2.97	2.85	32 <sup>1</sup> $\Delta^f$	1.94	1.49
	(2.35)	(2.34)		(1.48)	(1.69)
		[2.07]			[1.64]
32 <sup>1</sup> $\Delta^g$	1.43	1.43	33 <sup>3</sup> $\Delta^e$	2.17	...
	(1.14)	(1.68)		(1.81)	...
		[1.63]			[2.68]
34 <sup>3</sup> $\Gamma^e$	2.14	...	35 <sup>1</sup> $H$	2.19	2.28
	(1.74)	...		(1.81)	(2.35)
		[2.26]			[2.43]
36 <sup>1</sup> $\Pi$	2.35	2.26	37 <sup>1</sup> $\Phi$	2.29	2.23
	(1.45)	(1.73)		(1.60)	(2.30)
		[1.98]			[2.13]
38 <sup>1</sup> $\Phi$	2.01	2.30	39 <sup>1</sup> $\Pi$	2.32	2.34
	(1.71)	(2.26)		(1.59)	(2.15)
		[2.34]			[1.92]
40 <sup>1</sup> $\Delta$	2.2	1.9			
	(1.63)	(1.95)			
		[1.81]			

<sup>a</sup>State average CASSCF wave functions and internally contracted MRCI.<sup>b</sup>Calculated as an expectation value.<sup>c</sup>Calculated by the finite-field approach; field strength=10<sup>-4</sup> a.u.<sup>d</sup>No state average was used.<sup>e</sup>For these states convergence problems were encountered in the presence of the perturbing electric field.<sup>f</sup>A<sub>1</sub> symmetry.<sup>g</sup>A<sub>2</sub> symmetry.