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CALCULATION OF DISSOCIATION ENERGIES USING MANY-BODY PERTURBATION THEORY *

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Dissociation energies for the step-wise removal of hydrogen from methanol, $CH_3OH \rightarrow CH_3O \rightarrow CH_2O \rightarrow CHO \rightarrow CO$, are obtained by many-body perturbation theory. The heat of formation of CH_3O is predicted as 2 ± 3 kcal $mole^{-1}$. Computed geometries are in excellent agreement with experiment, where available, and provide a prediction for CH_3O.

1. Introduction

A major task for theoretical chemists is the development of methods to predict energy differences with chemical accuracy. Most quantum chemists agree that accurate prediction of relative energies requires application of theories that include electron correlation effects, effects not treated in self-consistent-field (SCF) calculations [1–4]. Estimates of molecular correlation energy have been obtained by using the method of configuration interaction to improve the wavefunction obtained from an ab initio SCF calculation. Recently, however, theoretical techniques based upon the linked-diagram theorem have been extended to molecular applications [1,2, 4], and these methods provide an alternative approach to the correlation problem. Several comparisons of the various theoretical methods have appeared [1,2,4].

This report describes the application of many-body perturbation theory (MBPT) to predict the dissociation energies for a series of reactions that occur in flame zone combustion models. The reaction set comprises the unimolecular reactions that oxidize methanol to carbon monoxide:

$$CH_3OH \rightarrow CH_3O + H, \qquad (1)$$

$$CH_3O \rightarrow CH_2O + H, \qquad (2)$$

$$CH_2O \rightarrow CHO + H, \qquad (3)$$

$$CHO \rightarrow CO + H. \qquad (4)$$

Reactions (1) and (2) involve the methoxy radical. Since heat of formation data are available for the other moieties in those two reactions, accurate predictions of the dissociation energies for these reactions will enable us to predict the heat of formation for the methoxy radical.

The theoretical techniques used are outlined in section 2, and the results for the series of dissociation reactions follow in section 3.

2. Outline of the computations

For the closed-shell molecules included in this study, a restricted Hartree–Fock (RHF) wavefunction represents the ground state, whereas unrestricted Hartree–Fock (UHF) wavefunctions represent the ground state for open-shell molecules. The integrals

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over atomic functions were computed using Dunning's 4s3p contraction of Huzinaga's 9s5p gaussian primitive set for first-row atoms, and Dunnings scaled ($\delta = 1.2$) 3s contraction of Huzinaga's 4s primitive set for hydrogen [5,6]. A single set of d-type polarization functions (gaussian) augments the atomic basis sets for carbon and oxygen, with exponents 0.75 and 0.85 respectively [7]. A set of p-type polarization functions (gaussian), $\alpha = 1.0$, augments the hydrogen basis set. All integral calculations were performed using the MOLECULE integral program [8]. Electronic structure calculations were performed using the GRNFNC and UMBPT programs [‡].

The total energy reported for each molecule pertains to structural parameters that have been optimized relative to double-excitation, frozen-core, fourth-order MBPT calculations. The structural parameters optimized for each molecule are defined in fig. 1. Computed structural parameters are compared with available experimental values in table 1. In the absence of experiment, we offer a prediction of the methoxy structure which we estimate to be accurate to 0.01 Å in bond length and 2–3° in bond angles.

We report dissociation energy predictions for three levels of calculation: SCF, fourth-order MBPT including all double-excitation diagrams, D MBPT(4), and fourth-order MBPT including all single-, double-, and quadruple-excitation diagrams that contribute at that order, SDQ MBPT(4).

The prediction of dissociation energies requires

Table 1
Optimized structural parameters for molecules included in this study [a)]

	Parameter	This work	Experiment
CH_3OH [b)]	r_1	1.093	1.0937
	r_2	1.093	1.0937
	α	107° 9′	108° 32′
	methyl tilt	2° 12′	3° 12′
	s_1	1.432	1.4214
	t_1	0.963	0.963
	β	107° 2′	108° 2′
CH_3O	r_1	1.085	
	r_2	1.081	
	α_1	108° 42′	
	α_2	112° 12′	
	β_1	103° 48′	
	β_2	111° 30′	
	s_1	1.405	
CH_2O [c)]	r_1	1.102	1.099
	s_1	1.211	1.203
	α	116° 11′	116° 30′
CHO [d)]	r_1	1.111	1.125
	s_1	1.188	1.175
	α	124°	124° 57′
CO [e)]	s_1	2.125	2.127

a) Bond lengths in A.
b) Experimental values: ref. [12].
c) Experimental values: ref. [13].
d) Experimental values: ref. [14].
e) Experimental values: ref. [15].

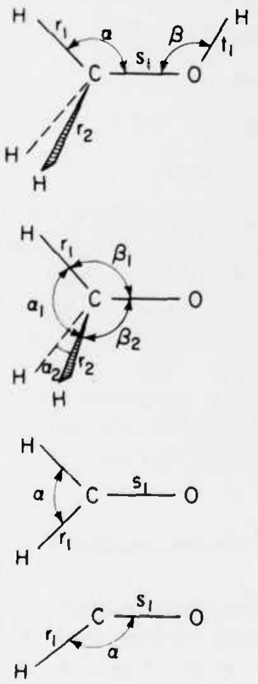

Fig. 1. Definition of bond lengths and of bond angles for CH_3OH, CH_3O, CH_2O, and CHO.

[‡] The program GRNFNC, written by G.D. Purvis, does SCF iterations and integral transformations. The program UMBPT, written by R.J. Bartlett and G.D. Purvis, does MBPT, CCD and VP CI.

accurate computation of energy differences. In addition to the change in the electronic energy, vibrational, rotational, and translational energy differences must also be obtained. We assume that rotational and translational energy effects are well approximated by the equipartition of energy among those degrees of freedom. Since vibrational frequencies are established for all the molecular species addressed in this study except the methoxy radical, empirical zero-point energy changes are used for these cases.

Characterization of the methoxy radical was the most difficult problem encountered in this study. Bent et al. [9] obtained optimal structural parameters for the Jahn–Teller distorted ground-state conformation after extensive D MBPT(4) calculations. An analysis of the potential energy function obtained in that study provided guidelines to estimating the vibrational frequencies for the e modes. Engelking et al. [10] and Inoue et al. [11] have published experimental values for several frequencies. By combining theoretical predictions and experimental data with observations on similar molecules, such as CH_3F^+, we assign the following values to the vibrational eigenvalues for the methoxy radical (directly observed values are underlined: 3006 (e), 2930 (a_1), 1380 (e), $\underline{1325}$ (a_1), $\underline{1060}$ (a_1), $\underline{690}$ cm^{-1} (e).

These frequencies correspond to a methoxy radical zero-point vibrational energy equal to 22.1 kcal $mole^{-1}$.

3. Dissociation energy predictions

Because linked-diagram derived methods are size extensive [2], the electronic energy change for a dissociation reaction, A → B + C, may be written

$$\Delta E_{el} = E_{el}(B) + E_{el}(C) - E_{el}(A).$$

Since each of the reactions considered here contains the hydrogen atom as one of the products, ΔE_{el} requires a correlated calculation for only the reactant and the molecular product. Table 2 contains predicted electronic energies for methanol, CH_3OH, methoxy radical, CH_3O, formaldehyde, CH_2O, formyl radical, HCO, carbon monoxide, CO, and the SCF energy for the hydrogen atom. Table 2 also contains the zero-point vibrational energy for each molecule in the study [10–15].

The information summarized in table 2 is sufficient to determine the zero-degree heat of reaction for each of the four reactions included in this study. We summarize the values for each of the molecules in the third row of table 3. For most molecules, there is no experimental data available to compare with the predicted $\Delta E_R(0\ K)$ values. An exception is formaldehyde. Reilly et al. [16] have confirmed that the threshold energy for the dissociation of formaldehyde to radical products is 86.0 ± 1.0 kcal $mole^{-1}$. The SDQ MBPT(4) calculations predict that the threshold energy equals 85.0 kcal $mole^{-1}$. In this case, the agreement between theory and experiment is very good.

In addition to the experimental data of Reilly et al. [16], experimental values for room-temperature heats of reaction are available for methanol [17], formaldehyde [18] and the formyl radical [19]. To compare the theoretical predictions with these heat of reaction data, we must estimate the effect of the rotational and translational degrees of freedom, and the effect of the pV work term must be included.

Table 2
Electronic energy predictions and zero-point energies for CH_iO molecules

Molecule	Electronic energy (hartree)			Zero-point energy (kcal $mole^{-1}$)
	SCF (UHF)	D MBPT(4)	SDQ MBPT(4)	
CH_3OH	−115.0744	−115.4942	−115.4920	31.1 [12]
CH_3O	−114.4532	−114.8248	−114.8232	22.1 [9]
CH_2O	−113.8974	−114.2832	−114.2829	16.2 [13]
CHO	−113.2769	−113.6343	−113.6363	7.8 [14]
CO	−112.7665	−113.1105	−113.1124	3.1 [15]
H	−0.49778			

Table 3
Dissociation energies predicted by SDQ MBPT(4) results (in kcal mole^{-1})

	CH_3OH	CH_3O	CH_2O	CHO
ΔE^{el}	107.3	26.6	93.4	16.4
ΔE^{vib}	−9.0	−5.9	−8.4	−4.7
$\Delta E_R(0\ K)$	98.3	20.7	85.0	11.7
$\Delta E^{tr}(300\ K)$	0.9	0.9	0.9	0.9
$\Delta E^{rot}(300\ K)$	0	0	0	−0.3
$\Delta E_R(300\ K)$	99.2	21.6	85.9	12.3
$\Delta H^0_{R,300}$	99.8	22.2	86.5	12.9

Translational and rotational energy contributions are estimated by assuming that each degree of freedom contributes $\frac{1}{2}kT$. Thus, for $T = 300$ K, each degree of freedom contributes ≈ 0.3 kcal mole^{-1}. The translational and rotational energy changes for each reaction are listed in table 3. Combining these contributions with the zero-degree dissociation energy, we obtain the energy of the reaction for $T = 300$ K. Finally, we assume that $pV = \Delta n(RT)$, and add this contribution to $\Delta E_R(300\ K)$ to obtain predicted values for the heat of reaction, $\Delta H^0_R(300\ K)$, which are listed in the last line of table 3.

Table 4 contains a comparison of the heats of reaction predicted by our SDQ MBPT(4) calculations with experimental values. Several conclusions may be gleaned from the theoretical results summarized in table 4. First, the inclusion of correlation effects is necessary to predict dissociation energies with chemical accuracy. Ab initio self-consistent-field calculations predict dissociation energies substantially different from experimental values. Each of the correlated treatments, D MBPT(4) and SDQ MBPT(4), predicts dissociation energies that agree well with experiment. There is little reason to prefer the more expensive SDQ MBPT(4) calculations to the D MBPT(4) calculations for these examples. In each case reported here, the contributions of the single- and quadruple-excitation diagrams at fourth order almost cancel. This is not always the case, so there are instances where SDQ MBPT(4) is preferred. The fourth-order triple excitations can also be important for some examples [20]. Finally, in each case where theoretical predictions can be compared with experimental results, the predicted dissociation energy is less than the experimental value. This is not surprising. The finite basis sets used in molecular calculations describe the product molecules better than they describe the reactant. This characteristic implies that the electronic energy difference between products and reactant usually will be too low. Reliable estimates of the magnitude of this error are not available, but our experience [21–24] suggests that dissociation energies predicted by MBPT, for breaking a single bond in a polyatomic molecule, and for the quality of basis set used in these calculations, typically underestimate experiment by 1–3 kcal mole^{-1}. On the other hand, atomization energies are much poorer due to the limited basis sets [21].

4. Heat of formation of the methoxy radical

Two experimental values for the heat of formation

Table 4
Comparison of predicted and experimental dissociation energies (in kcal mole^{-1})

Molecule	Predicted $H^0_{R,300}$			Experiment	
	SCF (UHF)	D MBPT(4)	SDQ MBPT(4)	$H^0_{R,300}$	ref.
CH_3OH	69.9	100.2	99.8	100.9	[10]
				104.0	[17]
CH_3O	32.9	23.1	22.2		
CH_2O	70.1	86.4	86.5	88.2 ± 1.6	[18]
				87.5 ± 1.0 [a]	[16]
CHO	4.4	12.9	12.9	15.5 ± 1.5	[18]
				17.0 ± 2.0	[19]

[a] We estimate this value based upon the $\Delta E^0_{R,300}$ value of 86.0 ± 1 [16].

Table 5
Heat of reaction for H_2 elimination from CH_3O

	CH_3O	→	CHO	+	H_2
electronic energy a)	−114.8232		−113.6363		−1.1656
ΔE^{el}	(0.0213 a))		13.4 b)		
zero-point energy b)	22.1		7.8		6.2 [15]
ΔE^{zp}			−8.1 b)		
$\Delta E_R(0\ K)$			5.3 b)		
rotational energy (300 K) b)	0.9		0.9		0.6
$\Delta R^{rot}(300\ K)$			0.6 b)		
translational energy (300 K)	0.9		0.9		0.9
ΔE^{r}			0.9 b)		
$\Delta E_e(300\ K)$			6.8 b)		
$\Delta H^0_{R,300}$			7.4 b)		

a) In hartree. b) In kcal $mole^{-1}$.

of the methoxy radical have been reported recently [10,17]. Batt and McCulloch [17] derived a heat of formation equal to 3.9 kcal $mole^{-1}$ using parameters obtained from chemical kinetic data. Engelking et al. [10] measured the electron affinity of the methoxy radical, and estimated the heat of formation for methoxy to be 0.7 kcal $mole^{-1}$. Since our calculations predict heats of reaction for two processes that include the methoxy radical, by combining these results with published heat of formation data we can obtain a heat of formation for CH_3O. We assume the following heats of formation: CH_3OH, −48.0 kcal $mole^{-1}$; CH_2O, −26.0 kcal $mole^{-1}$, H, 52.1 kcal $mole^{-1}$ [25]. Combining the dissociation energy of methanol with the heats of formation of methanol and hydrogen, we predict the methoxy heat of formation to be −0.3 kcal $mole^{-1}$. On the other hand, combining the methoxy radical dissociation energy with heats of formation for formaldehyde and hydrogen, we predict the methoxy heat of formation to be 3.9 kcal $mole^{-1}$.

In addition to the two hydrogen elimination reactions already considered, the heat of formation for CH_3O can be obtained by considering the elimination of the hydrogen molecule from the methoxy radical, giving the formyl radical and H_2 as products. The pertinent information needed to estimate the heat of reaction for this process is summarized in table 5. The results of SDQ MBPT(4) calculations predict a classical dissociation energy D_e equal to 13.4 kcal $mole^{-1}$. Combining the estimated frequencies for the methoxy radical with empirical values for the formyl radical and H_2, we estimate a zero-point energy change of −8.1 kcal $mole^{-1}$ for the reaction. When rotational and translational energy effects and our estimate of the pV terms are included, we obtain a value for the heat of reaction equal to 7.4 kcal $mole^{-1}$. Assuming that $\Delta H^0_{f,300}$ for the formyl radical is 9.0 kcal $mole^{-1}$ [25], we predict that the heat of formation for the methoxy radical is 1.6 kcal $mole^{-1}$.

The lack of agreement among the predicted values for the heat of formation is not surprising. It is apparent from the results of this work and the results of theoretical studies using alternative methods [1,3] that theoretical calculations underestimate dissociation energies. For the H-dissociation reactions reported here, and in other work done using these methods [21,26], our dissociation energy errors range from 1 to 3 kcal $mole^{-1}$. Considering the sign of this error, it is reasonable to suggest that the heat of formation of the methoxy radical should be greater than −0.3 kcal $mole^{-1}$ and less than 3.9 kcal $mole^{-1}$. The heat of formation obtained by studying the hydrogen molecule elimination reaction of CH_3O suggests a heat of formation for the radical of 1.6 kcal $mole^{-1}$ that lies between the two extreme values. Taking the likely errors into account we suggest a value equal to 2.0 ± 3.0 kcal $mole^{-1}$.

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