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Predicting heats of detonation using quantum mechanical calculations

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Abstract

Heats of detonation of pure explosives and explosive formulations are predicted using quantum mechanical (QM) information generated for isolated molecules. The methodology assumes that the heat of detonation of an explosive compound of composition $C_aH_bN_cO_d$ can be approximated as the difference between the heats of formation of the detonation products and that of the explosive, divided by the formula weight of the explosive. Two sets of decomposition gases were assumed: the first corresponds to the H_2O–CO_2 arbitrary [J. Chem. Phys. 48 (1968) 23]. The second set assumes that the product composition gases consist almost solely of H_2, N_2, H_2O, CO, and CO_2. The heats of formation used in this method are predicted using equations that convert QM information for an isolated energetic molecule to condensed phase heats of formation. Solid phase heats of formation predicted using the methods described herein have a root mean square (rms) deviation of 13.7 kcal/mol from 72 measured values (corresponding to 30 molecules). For the calculations in which the first set of decomposition gases is assumed, predicted heats of detonation of pure explosives with the product H_2O in the gas phase have a rms deviation of 0.138 kcal/g from experiment; results with the product H_2O in the liquid state have a rms deviation of 0.116 kcal/g from experiment. Predicted heats of detonation assuming the second set of decomposition gases have a rms deviation from experiment of 0.098 kcal/g. Heats of detonation for explosive formulations were also calculated, and have a rms deviation from experiment of 0.058 kcal/g. Published by Elsevier Science B.V.

Keywords: Density functional theory; Quantum mechanical; GGA; Heat of detonation

1. Introduction

Methods for predicting the performance of new energetic materials before synthesis or formulation are recognized to be cost-effective, environmentally-desirable and time-saving capabilities to use in the early stages of the development process [1,2]. Theoretical screening of notional materials allows for identification of promising candidates for additional study and elimination of poor candidates from further consideration, thus reducing costs associated with synthesis, test and evaluation of the materials. Current computational capabilities and advances in density functional theory (DFT) [3] now allow quantum mechanical (QM) molecular characterization to be included in the variety of predictive methodologies used in assessing energetic materials. The state of the methods and computers allow for rapid and accurate QM calculations of individual energetic molecules, resulting in the capability to predict conformational structures, stabilities and vibrational spectra of energetic materials. Further, many macroscopic properties of bulk energetic materials can be determined from QM information calculated for isolated molecules [4–13].

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In a series of studies, Politzer and co-workers have established that correlations exist between many condensed phase properties of a material and the QM-determined electrostatic potential of the isolated molecule. These properties include aqueous solvation free energies, lattice energies in ionic crystals, diffusion coefficients, solubilities, heats of vaporization, sublimation and fusion, boiling points, partition coefficients and critical constants, and impact sensitivities [4–12]. We utilized these ideas in the area of energetic materials, and have reported our successes in developing a computational method to predict heats of formation of energetic materials in the gas, liquid and solid state [13] from QM calculations of the isolated molecules. The heats of formation can then be used to assess potential performance of the material under idealized gun firing conditions or to predict its detonation properties.

In this report, we describe the use of the QM predictions of the heats of formation of solid explosives in calculating their heats of detonation. The heat of detonation is a quantity used to assess a candidate's detonation performance. The heat of detonation, Q, defined as the negative of the enthalpy change of the detonation reaction [2], is the energy available to do mechanical work [14] and has been used to estimate potential damage to surroundings [15]. This quantity can be determined from the heats of formation of the reactants and the products of the detonation through the relation [2]

$$Q \cong \frac{-[\Delta H_\mathrm{f}\,(\text{detonation products}) - \Delta H_\mathrm{f}\,(\text{explosive})]}{\text{formula weight of explosive}} \tag{1}$$

In order to evaluate the heat of formation of the detonation products, the equilibrium composition of the product gases must be determined. This determination can be made through experimental measurement, thermochemical equilibrium calculations, or by identifying an appropriate decomposition reaction. Kamlet and Jacobs, in describing their simple method for calculating detonation properties of C–H–N–O explosives, assumed that C–H–N–O high explosives generally have crystal densities ranging from 1.7 to 1.9 g/cm^3 and are used at high proportions of theoretical maximum density [2]. They argue that for explosives at these densities, the product compositions can be represented by the "H_2O–CO_2 arbitrary", which predicts N_2, H_2O and CO_2 (but not CO) as the important detonation products [2,15]

$$\mathrm{C}_a\mathrm{H}_b\mathrm{N}_c\mathrm{O}_d \rightarrow \tfrac{1}{2}c\mathrm{N}_2 + \tfrac{1}{2}b\mathrm{H}_2\mathrm{O} + (\tfrac{1}{2}d - \tfrac{1}{4}b)\mathrm{CO}_2 + (a - \tfrac{1}{2}d + \tfrac{1}{4}b)\mathrm{C}^* \tag{2}$$

To demonstrate the method and test the validity of their assumptions, Kamlet and Jacobs calculated the heats of detonation for 28 pure explosives or explosive formulations assuming the H_2O–CO_2 arbitrary and used the results to predict the detonation pressures. Their results were in good agreement with values obtained from thermochemical calculations [2]. The Kamlet and Jacobs method is appealing because it requires as input only the heats of formation of the explosive and simple gas phase products (assuming the H_2O–CO_2 arbitrary) and it can be applied to explosive mixtures as well as pure explosives. For an explosive formulation, the heat of formation of the mixture can be calculated from the heats of formation of the individual components and knowledge of their percent concentration in the mixture [15]

$$\Delta H_\mathrm{f}^{\text{mixture}\,A-B} = (\%\,\text{composition}\,A)\Delta H_\mathrm{f}^{A} + (\%\,\text{composition}\,B)\Delta H_\mathrm{f}^{B} \tag{3}$$

In this paper, we will demonstrate the Kamlet and Jacobs method of calculating the heat of detonation [2], except we will use predicted heats of formation of the reactants and products rather than measured values. The method will be applied to both pure explosives and explosive formulations, and compared against results predicted using the thermochemical code Cheetah 2.0 [14] with the JCZS-EOS library [16] and against experimental values, where known. We will also evaluate Eq. (1) using product compositions obtained through thermochemical calculations rather than those assuming the H_2O–CO_2 arbitrary. Additionally, predicted heats of formation of compounds not previously calculated nor reported in our earlier work [13] will be compared against experiment, where known.

2. Computational details

Generalized gradient approximation (GGA) DFT characterizations of all molecules reported in this study and in our previous work [13] were performed using the 6–31G* basis set [17] and the hybrid B3LYP [18,19] density functional. This modest level of theory was selected due to the size of some of the molecules chosen for study. An optimized geometry was obtained for each molecule, and a normal mode analysis performed to determine if it was a stable structure. All calculations were performed using the Gaussian 98 suite of quantum chemistry codes [20] and the default settings therein. Since most of the molecules reported herein are large, flexible, polyatomic molecules, we assume that each has more than a single stable conformation. Due to time and computer limitations, we did not perform an extensive search for the global minimum energy conformation for each molecule. Rather, we have assumed that the energy of the local minima associated with the optimized structures reported herein are within a few kcal/mol of the global minimum.

In this work, we are reporting heats of detonation of solid explosives only; thus, we require the solid phase heats of formation for the systems under consideration. Condensed phase heats of formation can be obtained from the gas phase heats of formation, using Hess' law of constant heat summation [21]

$$\Delta H_{\mathrm{f}}\,(\mathrm{solid}) = \Delta H_{\mathrm{f}}\,(\mathrm{gas}) - \Delta H\,(\mathrm{sub}) \quad (4)$$

$$\Delta H_{\mathrm{f}}\,(\mathrm{liquid}) = \Delta H_{\mathrm{f}}\,(\mathrm{gas}) - \Delta H\,(\mathrm{vap}) \quad (5)$$

provided that the heats of sublimation [ΔH (sub)] and vaporization [ΔH (vap)] are available. Politzer and coworkers have shown that the following functional relationships exist between these quantities and statistically-based quantities σ^2_{tot} and v associated with the electrostatic potential of a molecule on the 0.001 electron/bohr^3 isosurface of the electron density [8,10,12]

$$\Delta H\,(\mathrm{vap}) = a\sqrt{(\mathrm{SA})} + b\sqrt{\sigma^2_{\mathrm{tot}} v} + c \quad (6)$$

and

$$\Delta H\,(\mathrm{sub}) = a'(\mathrm{SA})^2 + b'\sqrt{\sigma^2_{\mathrm{tot}} v} + c' \quad (7)$$

where SA denotes the molecular surface area on the specified isosurface. These equations were parameterized for a number of condensed phase molecular systems pertinent to energetic materials; parameters and details are given in [13]. In that work, the root mean square (rms) deviation of the predicted heats of vaporization from 27 experimental values is 1.7 kcal/mol, and the rms deviation of the predicted heats of sublimation from 36 experimental values is 3.6 kcal/mol [13].

Also, as described in [13], gas phase heats of formation of energetic materials can be predicted using the method of atom equivalents, represented as

$$\Delta H_i = E_i - \sum n_j \varepsilon_j \quad (8)$$

where E_i is the B3LYP/6–31G* energy of molecule i at its equilibrium conformation, the atom equivalents ε_j represent energies of the atomic components of molecule i and n_j denotes the number of j atoms in molecule i. These atom equivalent energies include corrections due to errors inherent in the B3LYP/6–31G* calculations, and were determined by parameterizing Eq. (8) to experimental gas phase heats of formations for 35 molecules with functional groups common to energetic materials. Details of the parameterization and resulting atom equivalents are given in [13]. The predicted results for the 35 molecules have a rms deviation from experiment of 3.1 kcal/mol. Application of Eqs. (6)–(8) in Eqs. (4) and (5) resulted in predicted liquid and solid phase heats of formation for 24 and 44 energetic materials, respectively, that have rms deviations from experiment of 3.3 and 9.0 kcal/mol, respectively.

In this study, we have performed QM characterizations of other energetic molecules and predicted solid phase heats of formation. These heats of formation and those calculated in [13] are used to predict the heats of detonation with the Kamlet and Jacobs prescription given in Eq. (1). Also, we have used Eq. (3) to predict heats of formation for a few explosive formulations, and applied the results to predict their heats of detonation. These results will be compared against experiment, where known, and against values calculated using the thermochemical code Cheetah 2.0 [14] and the JCZS product library [16].

In order to use Eq. (1) assuming the H_2O–CO_2 arbitrary, one must have the heats of formation of the products, in this case, gas phase H_2O and CO_2. Experimental values for these are −57.8 and −94.1 kcal/mol, respectively [22]. We also predicted gas phase heats of formation for H_2O and CO_2 using the atom equivalents method and parameters described in [13]. Predicted values of heats of formation for gas phase H_2O and CO_2 using these atom equivalents are −39.6 and −90.9 kcal/mol, respectively. Clearly, the predicted heat of formation for water is poorly-predicted, while the value for CO_2 is in better agreement with experiment. This reflects the limitations of the use of this set of atom equivalents for systems that are not representative of the set of molecules used in parameterizing the atom equivalents (i.e. molecules with functional groups common to explosives). Since there is such a large discrepancy between the predicted and measured values for the heat of formation of gas phase H_2O, we have generated two sets of heats of detonation using Eq. (1) for the explosives being studied. One set, denoted QM(g, t), uses the B3LYP/6–31G* gas phase heats of formation of water and CO_2, whereas the other set, denoted, QM(g, e) uses the experimental values for these products. Many of the reported values of the heats of detonation of the explosives described herein indicate that the experiments were analyzed assuming the H_2O as being in either the vapor or liquid state. Those results in which H_2O is assumed to be in the vapor state are typically denoted $Q[H_2O(g)]$, whereas the results in which H_2O is assumed to be in the liquid state is denoted as $Q[H_2O(l)]$. In order to compare our results against these, we have also used predicted and experimental values of heats of formation for liquid phase H_2O in Eq. (1) in order to compare with those experimental results in which the product H_2O is assumed to be in the liquid state. Using the QM information for H_2O, Eq. (6) and parameters reported in [13], we predicted a heat of vaporization of water of 7 kcal/mol, which results in a liquid phase heat of formation of −46.7 kcal/mol. This value is also significantly different from the experimental value of –68.3 kcal/mol [22]. Heats of detonation were calculated using Eq. (1) and heats of formation for water in the liquid state, using both predicted and theoretical values. Heats of detonation denoted QM(l, t) indicate that the B3LYP/6–31G* liquid phase heat of formation of water is used along with the B3LYP/6–31G* gas phase heat of formation of CO_2 in the calculations. The values denoted as QM(l, e) indicate that the experimental value for the measured liquid phase heat of formation (−68.3 kcal/mol) of water is used with the experimental value for the gas phase heat of formation for CO_2 to generate the heats of detonation.

Heats of formation used in the Cheetah 2.0 calculations are included in the library of reactants in this suite of programs and consist of values compiled from the literature or passed along by oral tradition [14]. Estimated errors in the heats of formation are given in the User's Manual. Heats of detonation predicted using Cheetah 2.0 [14] and the JCZS-EOS library [16] are performed by executing the "Standard Detonation Run", in which the Chapman–Jouget (C–J) state is calculated for the designated explosive, and the adiabatic expansion of the product gases from the C–J state to 1 atm is calculated. In these calculations, the heat of detonation corresponds to the energy difference between the reactants and all products at the end of this expansion. Default values for the densities and heats of formation for the explosives are used. In this study, the heat of formation and density of the explosive FOX-7 (1,1-diamino-2,2-dinitro-ethylene) is not included in the Cheetah 2.0 reactant library, but these values have been measured [23,24]. The experimental values for the heats of formation and density for FOX-7 reported in [23] are −32.0 kcal/mol and 1.885 g/cm^3, respectively. A second study reports the heat of formation and density of FOX-7 to be −30 kcal/mol and 1.88 g/cm^3, respectively [24].

A final series of calculations were performed in order to test the Kamlet and Jacobs assumption that the equilibrium detonation products of C–H–N–O explosives correspond to the H_2O–CO_2 arbitrary (Eq. (2)). Examination of the product concentrations for 34 C–H–N–O explosives predicted by the Cheetah 2.0/JCZS calculations indicate that 94% of the gaseous product species consist of only five products: H_2O, H_2, N_2, CO_2, and CO. For 30 of these explosives, more than 97% of the gaseous products consist of only these five species. Since CO is predicted to be a major component of the product gases by the thermochemical calculations, we modified the Kamlet and Jacobs method by assuming that the detonation products are formed according to the following decomposition equation:

$$C_aH_bN_cO_d \rightarrow tN_2 + uH_2 + vH_2O + wCO_2 + xCO + yC^* + z(\text{other products}) \quad (9)$$

The product concentrations t, u, v, w, x, y and z are given by the Cheetah 2.0/JCZS calculations. We calculated the heat of detonation for the explosives using the QM predictions of the heats of formation of the explosives and the experimental values of the heats of formation for CO_2, CO and H_2O (standard heat of formation of C^* is assumed to be nil, as are H_2 and N_2). We also assumed that the contribution of the "other products" to the product heat of formation is negligible. These calculations are referred to as QM(modified K–J).

Heats of detonation assuming the other common "arbitrary" reactions in which CO is a major product, known as the H_2O–CO–CO_2 [25] and CO–H_2O–CO_2 [26] arbitraries, were performed but the results were in such poor agreement with experiment and thermochemical calculations that we eliminated these decomposition reactions as suitable for the prediction of the heat of detonation using Eq. (1).

3. Results and discussion

There are 72 measured values for solid phase heats of formation that correspond to 30 molecules, shown in Table 1. Predicted solid phase heats of formation using the method described in [13] and values contained in the Cheetah reactant library are also given in Table 1. The first 12 molecules listed in this table were not included in the systems calculated in [13]; heats of formation for the remaining molecules were reported in [13] and are included for comparison with values given in Cheetah and used in calculating the heats of detonation, discussed hereafter.

A visual comparison of QM and Cheetah values with the experimental values is shown in Fig. 1. The rms deviation of the QM predictions from experiment is 13.7 kcal/mol, and the rms deviation of the values in the Cheetah reactant library from experiment is 7.9 kcal/mol. The better agreement of the Cheetah values is not surprising, since these values represent commonly accepted values reported from the literature [14]. The largest deviations of both the QM predictions and values from the Cheetah reactant library from the experimental values correspond to the values reported for octanitrocubane (81–144 kcal/mol) [28,29]. One of the values reported for octanitrocubane (144 kcal/mol) [28,29] is in reasonable agreement with the QM prediction (137.6 kcal/mol), while the other is substantially lower

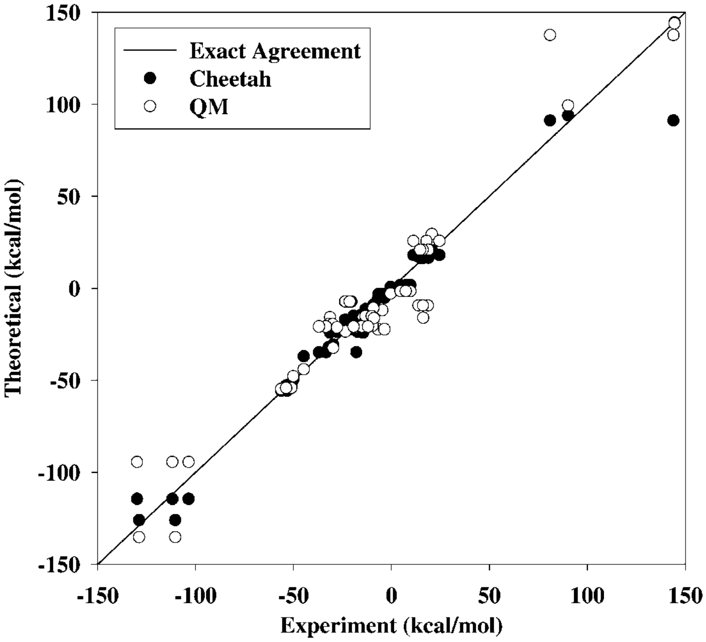

Fig. 1. Calculated solid phase heats of formation vs. experimental values for 30 energetic molecules. The solid line represents exact agreement between predictions and experiment. Solid circles denote values contained in the Cheetah 2.0 reactant library [14] and hollow circles denote values calculated using the quantum mechanically (QM)-based method described in this work.

Table 1
Comparison of quantum mechanical (QM) heats of formation (kcal/mol) with experiment and Cheetah 2.0 values

Name	Acronym	Cheetah 2.0[a]	Experiment[b]	QM[c]
Hexanitrobenzene	HNB	20.8		26.2
2,3,4,6-Tetranitroaniline	tetNA	−11.7		−7.4
2,2′,4,4′,6,6′-Hexanitrobiphenyl	HNBP, HNDB	16.3	16.3 [22]	−16.2 (32.5)
4,4′-Diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl	CL-12	81.0		7.7
5,7-Diamino-4,6-dinitrobenzofuroxan	CL-14	20.6	20.63 [15]	29.3 (−8.67)
3-Nitro-1,2,4-triazol-5-one	NTO	−24.1	−14.3 [15]	−15.9 (1.6)
			−31.3 [15]	(−15.4)
1,1-Diamino-2,2-dinitro-ethylene	FOX-7	−32.0	−32.0 [23]	−19.6 (−12.4)
			−30 [24]	(−10.4)
1,3-Diamino-2,4,6-trinitrobenzene	DATB	−17.2	−23.6 [15,27]	−23.6 (0.0)
			−23.4 [15]	(0.2)
3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	DIPAM	−5.3	−6.8 [15,27]	−22.3 (15.5)
			−3.6 [15]	(18.7)
Benzotrifuroxan	BTF	144.4	144.5 [27]	143.9 (143.9)
2-Diazo-4,6-dinitrophenol	DDNP	14.3		19.6
Octanitrocubane	ONC	91.1	81–144 [28]	137.6 (−56.6–6.4)
			144 [29]	(6.4)
2-Methoxy-1,3,5-trinitrobenzene	Methyl picrate	−37.0	−44.75 [22]	−44.0 (−0.75)
2,2′,4,4′,6,6′-Hexanitrostilbene	HNS	17.0	13.88 [15,22]	−9.5 (23.38)
			18.7 [15,27]	(28.2)
			16.2 [15,22]	(25.7)
2,4,6-Trinitroresorcinol	Styphnic acid	−114.5	−111.74 [22]	−94.4 (−17.34)
			−103.5 [22]	(−9.1)
			−129.76 [22]	(−35.36)
Nitroguanidine	NQ	−22.2	−22.1 [15]	−7.4 (−14.7)
			−20.29 [15]	(−12.89)
			−22.11 [15]	(−14.71)
			−23.6 [27]	(−16.2)
			−20.7 [22]	(−13.3)
			−23.4 [22]	(−16)
			−21.3 [22]	(−13.9)
ε-Hexaazaisowurtzitane	CL-20, HNIW	93.9	90.2 [30]	99.2 (−9.0)
Tetranitrate pentaerythritol	PETN	−126.0	−128.7 [15,22,27]	−135.3 (6.6)
			−110.34 [15]	(24.96)
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	17.9	17.93 [15,27]	25.6 (−7.67)
			11.3 [15]	(−14.3)
			18 [22]	(−7.6)
			24.5 [22]	(−1.1)
Hexahydro-1,3,5-trinitrotriazine	RDX	16.5	14.71 [15,27]	20.8 (−6.09)
			18.9 [22]	(−1.9)
			15.9 [22]	(−4.9)
			14.7 [22]	(−6.1)
2,4,6-Trinitro-1,3,5-benzenetriamine	TATB	−34.7	−36.85 [15,27]	−20.8 (−16.05)
			−33.4 [15]	(−12.6)
			−17.854 [22]	(2.946)
			−33.4 [22]	(−12.6)
			−36.9 [22]	(−16.1)
1,2-Dinitrobenzene		0.7	−0.4 [22]	−3.0 (2.6)
1,3-Dinitrobenzene		−3.1	−6.5 [22]	−12.0 (5.5)
			−4.59 [22]	(7.41)
1,4-Dinitrobenzene		−9.1	−9.2 [22]	−10.9 (1.7)
2,4-Dinitrophenol		−55.7	−56.29 [22]	−54.7 (−1.59)
			−53.31 [22]	(1.39)

Table 1 (*Continued*)

Name	Acronym	Cheetah 2.0[a]	Experiment[b]	QM[c]
2,6-Dinitrophenol		−49.7	−50.105 [22]	−47.8 (−2.305)
1-Methyl-2,4-dinitrobenzene		−14.8	−15.87 [22]	−20.3 (4.43)
			−9.5 [22]	(10.8)
2-Methyl-1,3-dinitrobenzene		−11.5	−13.199 [22]	−15.3 (2.101)
			−9.99 [22]	(5.31)
1,3,5-Trimethyl-2,4,6-trinitrobenzene		−30.6	−29.75 [22]	−32.4 (2.65)
1,3,5-Trinitrobenzene	TNB	−13.9	−8.9 [22]	−16.4 (7.5)
2,4,6-Trinitrophenol	Picric acid	−52.8	−51.3 [27]	−54.2 (2.9)
			−52.075 [22]	(2.125)
			−51.14 [22]	(3.06)
			−53.76 [22]	(0.44)
2,4,6-Trinitroaniline	TNA	−23.7	−17.4 [22]	−21.3 (3.9)
			−27.69 [22]	(−6.39)
2,4,6-Trinitrotoluene	TNT	−15.1	−16.01 [15]	−20.9 (4.89)
			−16.1 [15]	(4.8)
			−15.38 [15]	(5.52)
			−15 [27]	(5.9)
			−15.1 [15,22]	(5.8)
			−19.25 [22]	(1.65)
			−11.94 [22]	(8.96)
N-methyl-*N*-2,4,6-tetranitroaniline	Tetryl	1.7	4.67 [15,27]	−1.7 (6.37)
			9.8 [22]	(11.5)
			7.34 [22]	(9.04)

[a] All values taken from reactant library of [14].

[b] References for experimental values given in brackets.

[c] Difference (in kcal/mol) between experimental and QM values.

Table 2
Predicted heats of formation (cal/g) for explosive formulations

Name	Formulation (wt.%)				ΔH_f (cal/g)		
	TNT	RDX	HMX	PETN	Cheetah 2.0	QM	Other
Comp B[a]	36.21	58.272	5.518		22.6	26.2	
Comp B-3	40.5	59.5			17.3	18.6	12.23[b] 8.4[c]
Cyclotol 75/25	25	75			39.1	47.4	32.89[b] 30.1[c]
Cyclotol 50/50	50	50			4.0	0.99	
Octol[a]	26.42		73.58		26.9	39.2	
Octol	25		75		28.7	41.8	28.62[b] 25.7[c]
Pentolite	50			50	−232.4	−259.9	−237.1[b] −243[c]

[a] Composition given in [31].

[b] Heat of formation was calculated according to method described in [15].

[c] See [27]; it is assumed that the reported values are measured.

Table 3
Comparison of predicted and experimental heats of detonation (kcal/g)

Name[a]	$Q[H_2O(g)]$ Experiment[b]	Cheetah 2.0[c]	QM[c]			$Q[H_2O(l)]$		
			Eq. (9)[d]	$H_2O–CO_2$ arbitrary[e]		Experiment[b]	QM[c] $H_2O–CO_2$ arbitrary[e]	
			e[f]	t[f]	e[f]		t[f]	e[f]
HNS						1.10 [15]	1.199 (−0.099)	1.374 (−0.274)
						1.099 [31]	(−0.100)	(−0.275)
ε-HNIW						1.490 [30]	1.480 (0.010)	1.660 (−0.170)
PETN	1.16 [15]	1.424 (−0.264)	1.373 (−0.213)	1.223 (−0.063)	1.493 (−0.333)	1.23 [15]	1.313 (−0.083)	1.626 (−0.396)
	1.37 [25]	(−0.054)	(−0.003)	(0.147)	(−0.123)	1.49 [27,30]	(0.177)	(−0.136)
HMX	1.37 [15,25]	1.356 (−0.014)	1.343 (0.027)	1.235 (0.135)	1.502 (−0.132)	1.48 [15,27,30]	1.331 (0.149)	1.644 (−0.164)
						1.479 [31]	(0.148)	(−0.165)
RDX	1.42 [15,25]	1.336 (0.084)	1.315 (0.105)	1.243 (0.177)	1.510 (−0.090)	1.51 [15,27]	1.338 (0.172)	1.652 (−0.142)
						1.452 [31]	(0.114)	(−0.200)
HNB						1.650 [30]	1.642 (0.008)	1.696 (−0.046)
						1.653 [31]	(0.011)	(−0.043)
Picric acid						1.032 [15]	1.160 (−0.128)	1.339 (−0.307)
DATB	0.91 [15,25]	1.086 (−0.176)	1.029 (−0.119)	0.964 (−0.054)	1.174 (−0.264)	0.98 [15,27]	1.037 (−0.057)	1.282 (−0.302)
TATB						1.02 [15]	0.990 (0.030)	1.260 (−0.240)
						1.018 [31]	(0.028)	(−0.242)
BTF	1.41 [15]	1.373 (0.037)	1.353 (0.057)	1.653 (−0.243)	1.690 (−0.280)	1.41[26][g]	1.653 (−0.243)	1.690 (−0.280)
TNT	1.02 [15]	1.075 (−0.055)	1.018 (0.002)	1.044 (−0.024)	1.269 (−0.249)	1.09 [15,27,30]	1.122 (−0.032)	1.385 (−0.295)
Tetryl	1.09 [15,25]	1.174 (−0.084)	1.133 (−0.043)	1.210 (−0.120)	1.398 (−0.308)	1.14 [15,27]	1.271 (−0.131)	1.490 (−0.350)
rms deviation (kcal/g)		0.124	0.098	0.138	0.239		0.116	0.243

[a] See Table 1 for the chemical names corresponding to each acronym.

[b] References are given in brackets.

[c] Difference of prediction from experiment (kcal/g) is given in parentheses.

[d] Evaluated using Eq. (9). Concentration of products CO, CO_2 and H_2O are predicted by Cheetah 2.0 [14] using the JCZS-EOS library [16].

[e] Evaluated using products that correspond to the $H_2O–CO_2$ arbitrary as given by Kamlet and Jacobs [2].

[f] The t denotes that theoretical values were used and e indicates that experimental values were used.

[g] As noted in [27], BTF contains little or no hydrogen, no water is formed, and thus values for $H_2O(l)$ and $H_2O(g)$ are the same.

[28]. It is not known whether these reported values are theoretical estimates or actual measurements. Three QM values differ from experimental values by more than 30 kcal/mol; these corresponded to values for 2,2′,4,4′,6,6′-hexanitrobiphenyl (HNBP), PETN, and 2,4,6-trinitroresorcinol. However, as noted in [13], the experimental values for PETN and 2,4,6-trinitroresorcinol range from −128.7 to −110.34 kcal/mol and −103.5 to −129.76 kcal/mol, respectively. The QM calculations are within 6.6 kcal/mol for one of the measured values of PETN and 9.1 kcal/mol for one of the values reported for 2,4,6-trinitroresorcinol. The difference in the predicted and experimental value for HNBP (32.5 kcal/mol) is similar to the difference observed for another polycyclic nitroaromatic system, HNS (∼26 kcal/mol). In both systems, the predicted heat of formation is smaller than the reported values. We also predicted the heat of formation for 4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl (CL-12). The predicted value (7.7 kcal/mol) is in substantial disagreement with the value contained in the Cheetah reactant library (81 kcal/mol). We were unable to ascertain the validity of the value reported in Cheetah, and no error estimates of the value were given. The source of this value was quoted as “the data is probably real but has never been published and has been passed by oral tradition” [14]. However, if our heats of formation method predicts values that are uniformly lower than measured values for polycyclic nitroaromatic compounds, this suggests that representative polycyclic nitroaromatic molecules be included in a future re-parameterization of the equations associated with this methodology.

Heats of formation for a few explosive formulations have been predicted using the QM-based method described in [13] and Eq. (3), and are reported in Table 2. Table 2 also contains experimental results [27] or predictions made using other methods [14,15]. The QM predictions for these formulations have a rms deviation from the Cheetah 2.0 predictions of 12.9 cal/g and a rms deviation from other calculated or measured values (see column labeled “other” in Table 2) of 15.4 cal/g. The basis for the larger deviation of the QM predictions from the values contained in the Cheetah 2.0 reactant library or other estimates is due to the deviations of the predicted heats of formation for the pure components from the experimental values (Table 1).

Heats of detonation for pure explosives and explosives formulations are calculated using the Kamlet and Jacobs prescription given in Eqs. (1) and (3) and using heats of formation predicted with the QM-based method described in [13]. Heats of formation of product gases are evaluated assuming the decomposition

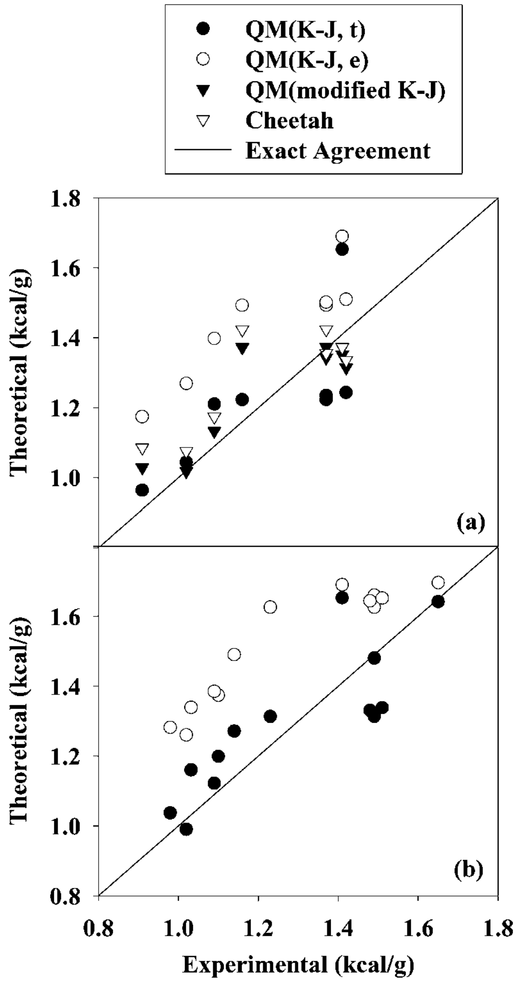

Fig. 2. (a) Calculated heats of detonation [$H_2O(g)$] vs. experimental values for explosives. (b) Calculated heats of detonation [$H_2O(l)$] vs. experimental values for explosives. The solid lines represents exact agreement between predictions and experiment. Solid circles denote QM values calculated using theoretical information only; hollow circles denote QM values that use experimental heats of formation for products H_2O and CO_2. Filled triangles denote QM values using experimental information for the product gases, which are assumed to correspond to Eq. (9). Hollow triangles represent values calculated using Cheetah 2.0 [14] and the JCZS product library [16].

Table 4
Predicted and experimental heats of detonation (kcal/g) for explosive formulations

Name	Formulation (wt.%)				$Q[H_2O(g)]$ (kcal/g)							$Q[H_2O(l)]$ (kcal/g)		
	TNT	RDX	HMX	PETN	Experiment[a]	Cheetah 2.0[b]		QM[b]				Experiment[a]	QM[b]	
								Eq. (9)[c]		H_2O–CO_2 arbitrary[d]			H_2O–CO_2 arbitrary[d]	
Comp B	36.21	58.272	5.518			1.240		1.207		1.171		1.321 [31]	1.260	(0.061)
										1.422			1.555	(−0.234)
Comp B-3	40.5	59.5			1.12 [15]	1.227	(−0.107)	1.193	(−0.073)	1.161	(−0.041)	1.20 [15]	1.250	(−0.050)
										1.411	(−0.291)		1.542	(−0.342)
Cyclotol 50/50	50	50				1.203		1.164		1.142		1.158 [15]	1.229	(−0.071)
										1.388			1.517	(−0.359)
Octol	26.42		73.58			1.280		1.255		1.194		1.361 [31]	1.286	(0.075)
										1.452			1.588	(−0.227)
Pentolite	50			50		1.178		1.117		1.149		1.23 [15,27]	1.233	(−0.003)
										1.400			1.525	(−0.295)

[a] References are given in brackets.

[b] Difference from experiment in (kcal/g) given in parentheses.

[c] Evaluated using Eq. (9). Concentration of products CO, CO_2 and H_2O are predicted by Cheetah 2.0 [14] using the JCZS-EOS library [16].

[d] First value calculated using QM prediction of heat of formation for H_2O. Second value calculated using experimental value for the heat of formation for H_2O. Products assumed to correspond to H_2O–CO_2 arbitrary as given by Kamlet and Jacobs [2].

reactions correspond to either the H_2O–CO_2 arbitrary [2] or Eq. (9). These predictions (denoted as QM) are given in Table 3, along with the experimental values. Values predicted using Cheetah 2.0 with the JCZS-EOS library [14,16] are also included in Table 3. A visual comparison of the predictions with experiment is given in Fig. 2. Fig. 2(a) shows the comparison between predictions and experiments in which the H_2O product is in the gas state; Fig. 2(b) provides a comparison between experiment and predictions in

Table 5
QM and Cheetah predictions of heats of detonation (kcal/g)

Name or acronym[a]	Cheetah 2.0	QM				
		H_2O–CO_2 arbitrary (Kamlet and Jacobs assumption)				Eq. (9)[b]
		t[c]	e[d]	t[c]	e[d]	e[d]
2-Methoxy-1,3,5-trinitrobenzene	1.064	1.068 (−0.004)	1.284 (−0.220)	1.140 (−0.076)	1.392 (−0.32)	1.003 (0.061)
HNS	1.107	1.151 (−0.044)	1.304 (−0.197)	1.199 (−0.092)	1.374 (−0.267)	1.024 (0.083)
2,4,6-Trinitroresorcinol	0.976	1.063 (−0.087)	1.216 (−0.240)	1.106 (−0.130)	1.280 (−0.304)	1.035 (−0.059)
Nitroguanidine	0.883	0.690 (0.193)	1.040 (−0.157)	0.826 (0.057)	1.242 (−0.359)	0.937 (−0.054)
ε-HNIW	1.466	1.431 (0.015)	1.588 (−0.142)	1.480 (−0.034)	1.660 (−0.214)	1.455 (0.011)
PETN	1.424	1.223 (0.201)	1.493 (−0.069)	1.313 (0.111)	1.626 (−0.202)	1.373 (0.051)
HMX	1.356	1.235 (0.121)	1.502 (−0.146)	1.331 (0.025)	1.644 (−0.288)	1.343 (0.013)
RDX	1.336	1.243 (0.093)	1.510 (−0.174)	1.338 (−0.002)	1.652 (−0.316)	1.315 (0.021)
NTO	0.947	0.881 (0.066)	1.045 (−0.098)	0.936 (0.011)	1.126 (−0.179)	0.979 (−0.032)
Octanitrocubane	1.827	1.863 (−0.036)	1.917 (−0.090)	1.863 (−0.036)	1.917 (−0.090)	1.913 (−0.086)
1,2-Dinitrobenzene	1.024	0.994 (0.030)	1.229 (−0.205)	1.078 (−0.054)	1.354 (−0.330)	0.966 (0.058)
1,3-Dinitrobenzene	1.012	0.941 (0.071)	1.176 (−0.164)	1.025 (−0.013)	1.301 (−0.289)	0.925 (0.087)
1,4-Dinitrobenzene	1.005	0.947 (0.058)	1.182 (−0.177)	1.031 (−0.026)	1.307 (−0.302)	0.961 (0.044)
2,4-Dinitrophenol	0.942	0.874 (0.068)	1.097 (−0.155)	0.951 (−0.009)	1.211 (−0.269)	0.919 (0.023)
2,6-Dinitrophenol	0.953	0.911 (0.042)	1.135 (−0.182)	0.988 (−0.035)	1.249 (−0.296)	0.934 (0.019)
1-Methyl-2,4-dinitrobenzene	0.970	0.791 (0.179)	1.099 (−0.129)	0.907 (0.063)	1.272 (−0.302)	0.894 (0.076)
2-Methyl-1,3-dinitrobenzene	0.986	0.818 (0.168)	1.126 (−0.140)	0.934 (0.052)	1.299 (−0.313)	0.919 (0.067)
1,3,5-Trimethyl-1,3,5-trinitrobenzene	0.997	0.838 (0.159)	1.168 (−0.171)	0.963 (0.034)	1.354 (−0.357)	0.940 (0.057)
Hexanitrobenzene	1.692	1.642 (0.050)	1.696 (−0.004)	1.642 (0.050)	1.696 (−0.004)	1.693 (−0.001)
1,3,5-Trinitrobenzene	1.177	1.162 (0.015)	1.323 (−0.146)	1.211 (−0.034)	1.397 (−0.220)	1.126 (0.051)
Picric acid	1.059	1.114 (−0.055)	1.271 (−0.212)	1.160 (−0.101)	1.339 (−0.280)	1.029 (0.030)
2,3,4,6-Tetranitroaniline	1.182	1.272 (−0.090)	1.410 (−0.228)	1.311 (−0.129)	1.467 (−0.285)	1.174 (0.008)
2,4,6-Trinitroaniline	1.061	1.051 (0.010)	1.238 (−0.177)	1.113 (−0.052)	1.330 (−0.269)	1.044 (0.017)
DATB	1.086	0.964 (0.122)	1.174 (−0.088)	1.037 (0.049)	1.282 (−0.196)	1.029 (0.057)
TATB	1.039	0.908 (0.131)	1.138 (−0.099)	0.990 (0.049)	1.260 (−0.221)	1.058 (−0.019)
HNBP	1.130	1.220 (−0.090)	1.343 (−0.213)	1.253 (−0.123)	1.393 (−0.263)	1.031 (0.099)
DIPAM	1.101	1.113 (−0.012)	1.264 (−0.163)	1.160 (−0.059)	1.334 (−0.233)	1.039 (0.062)
CL-12	1.345	1.329 (0.016)	1.436 (−0.091)	1.355 (−0.010)	1.475 (−0.130)	1.188 (0.157)
BTF	1.373	1.653 (−0.280)	1.690 (−0.317)	1.653 (−0.280)	1.690 (−0.317)	1.352 (0.021)
TNT	1.075	1.044 (0.031)	1.269 (−0.194)	1.122 (−0.047)	1.385 (−0.310)	1.018 (0.057)
DDNP	0.999	1.147 (−0.148)	1.264 (−0.265)	1.181 (−0.182)	1.314 (−0.315)	1.002 (−0.003)
Tetryl	1.174	1.210 (−0.036)	1.398 (−0.224)	1.271 (−0.097)	1.490 (−0.316)	1.133 (0.041)
FOX-7	1.136	1.016 (0.118)	1.285 (−0.149)	1.114 (0.022)	1.427 (−0.291)	1.180 (−0.044)
CL-14	1.153	1.133 (0.020)	1.300 (−0.147)	1.189 (−0.036)	1.382 (−0.229)	1.160 (−0.007)
rms deviation (kcal/g)		0.107	0.175	0.085	0.272	0.057

[a] See Table 1 for chemical name.

[b] Concentrations of major gas products CO, CO_2 and H_2O obtained from Cheetah 2.0/JCZS calculations. See text.

[c] The t denotes that the values used for the heats of formation for the products are predicted with the B3LYP/6–31G*-based atom equivalent method as described in [13].

[d] 'The e denotes that the values used for the heats of formation for the products are the experimental value.

which the H_2O product is in the liquid state. Predicted heats of detonation for H_2O(g) using QM(g, t) and Cheetah have rms deviations from experiment of 0.138 and 0.124 kcal/g, respectively, whereas the QM(g, e) results have a substantially larger deviation from experiment (0.239 kcal/g). The QM(g, e) predictions are almost uniformly larger than the experimental values by ~ 0.3–0.4 kcal/g. The QM(modified K–J) predictions have a rms deviation from experiment of 0.098 kcal/g, indicating the importance of the inclusion of CO as a major gaseous product. The QM(l, t) predictions are in reasonable agreement with measured heats of detonation for H_2O(l), with a rms deviation of 0.116 kcal/g from experiment. As for heats of detonation for H_2O(g), the QM(l, e) predictions are consistently higher than experimental values by ~0.2–0.4 kcal/g. Cheetah predictions were not compared against measured heats of detonation for H_2O(l), since the results of the thermochemical calculations indicate that the product H_2O is in the gaseous state only.

Heats of detonation were calculated for a few explosive formulations for which experimental data were available; the results and experimental values are

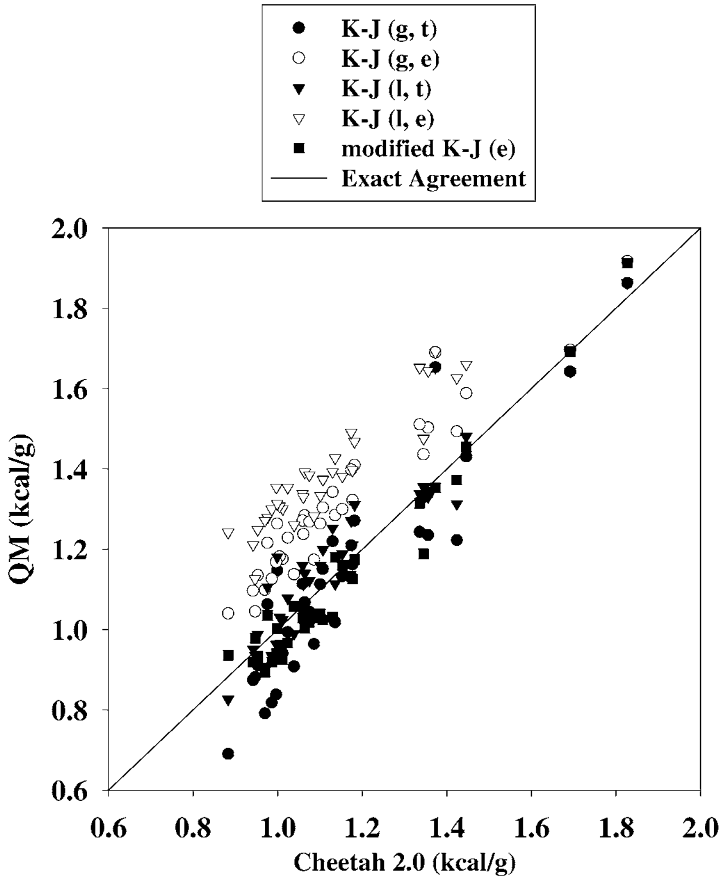

Fig. 3. Quantum mechanical (QM) predictions of heat of detonation vs. Cheetah 2.0 calculations. The solid line represents exact agreement between the QM and Cheetah 2.0 predictions. The circular and triangular symbols denote QM results assuming that the decomposition product gases correspond to the H_2O–CO_2 arbitrary [2]. Solid circles denote QM calculations using predicted gas phase heats of formation for products H_2O and CO_2; hollow circles denote QM calculations using experimental values for the gas phase heats of formation for the products; filled triangles denote QM calculations using predicted heats of formation for H_2O (liquid phase) and CO_2 (gas phase); hollow triangles denote QM calculations using experimental values for the heats of formation for H_2O (liquid phase) and CO_2 (gas phase). The solid squares denote QM calculations using experimental heats of formation of the product gases, which are assumed to correspond to Eq. (9).

shown in Table 4. For the single formulation that reported a measured value assuming that H_2O was in the gas state, the QM(g, t) and QM(modified K–J) predictions are better than those predicted by both Cheetah and the QM(g, e) calculations. The remaining experimental heats of detonation assume the H_2O to be in the liquid state. For all cases, the QM(l, t) calculations are in much closer agreement with experiment than the QM(l, e) calculations. The QM(l, t) values deviated from experiment not more than 0.075 kcal/g, while the QM(l, e) values were consistently larger than the experimental values by 0.23–0.36 kcal/g. For all QM predictions, those that utilized experimental heats of formation for the products H_2O and CO_2 resulted in heats of detonation that were too large by at least 0.2 kcal/g.

Table 5 provides a comparison between heats of detonation calculated using the Cheetah 2.0 and the various QM calculations; Fig. 3 provides a visual comparison. As evident in Fig. 3, the best agreement of the QM predictions with the Cheetah predictions are for those in which the product concentrations correspond to Eq. (9) and experimental values for the heats of formation of the products are used to evaluate Q. For that case, the rms deviation of the QM(modified K–J) from the Cheetah 2.0 predictions are 0.057 kcal/g. The largest disagreement between the Cheetah and QM(modified K–J) calculations of Q is for CL-12. The QM(modified K–J) value is 1.188 kcal/g, whereas the Cheetah prediction is 1.345 kcal/g. The large disagreement is due to the extreme difference in the solid phase heats of formation for CL-12 used in the calculations, as discussed earlier. The next best agreement between the QM and Cheetah calculations are for those values in which the predicted heat of formation for liquid H_2O is used with the Kamlet and Jacobs assumption (H_2O–CO_2 arbitrary); these predictions have a rms deviation from the Cheetah predictions of 0.085 kcal/g. The rms deviation of the QM predictions using predicted heats of formation for gas phase H_2O from the Cheetah predictions is 0.107 kcal/g. The QM predictions using the experimental values for either the gas phase or liquid phase heats of formation for H_2O and the H_2O–CO_2 arbitrary are consistently larger than the Cheetah predictions.

All of these calculations indicate that experimental values for heats of formation for the products H_2O and CO_2 should not be used with the heats of formation of the explosive predicted using the methodology described in [13] if the H_2O–CO_2 arbitrary is assumed to describe the equilibrium composition of the product gases of the detonation. Rather, the theoretical predictions of the gas phase heat of formation of water should be used. The reasonable agreement of the QM(g, t) predictions with experimental values when utilizing the theoretical value of the heat of formation of the gas phase water suggests that this poorly-predicted value compensates for the exclusion of CO as a major component of the product decomposition gases.

4. Conclusions

A computational methodology has been developed that uses only QM information about isolated molecules to predict the heats of detonation for pure and explosive formulations. The methodology is based on a simple scheme to calculate detonation properties as proposed by Kamlet and Jacobs [2]. The Kamlet and Jacobs method assumes that the heat of detonation of an explosive compound of composition $C_aH_bN_cO_d$ can be approximated as the difference between the heats of formation of the detonation products and that of the explosive formulation, divided by the formula weight of the explosive. The detonation products are assumed to correspond to the H_2O–CO_2 arbitrary, in which the detonation products are N_2, H_2O, CO_2 and solid carbon. The Kamlet and Jacobs method requires knowledge of the heats of formation of the explosive. In this study, we have used a previously-developed computational tool to predict solid phase heats of formation for explosives [13] using QM information only, and used these with the Kamlet and Jacobs method to predict heats of detonation. We have also modified the Kamlet and Jacobs assumption by assuming that CO is a major component of the decomposition gases in addition to N_2, H_2O, CO_2 and solid carbon. Product concentrations under this assumption are determined from thermochemical calculations using Cheetah 2.0 [14] and the JCZS product library [16]. The results are compared with experimental values, where available, for both pure explosives and explosive formulations. The QM results are also compared against predictions using the thermochemical code Cheetah 2.0 and the JCZS-EOS library [14,16]. For pure explosives, the QM-based method using the modified Kamlet and Jacobs method is in better agreement with experiment than all other predictions. For explosive formulations, the QM predictions are in reasonable agreement with experimental values, with a rms deviation of 0.058 kcal/g. Although the Cheetah calculations have a stronger theoretical basis for prediction of detonation properties than that proposed here, those calculations also require both densities and heats of formation as input. This methodology presented here has the advantage that neither heats of formation nor densities need to be measured or estimated to calculate the heat of detonation of an explosive. All that is needed are the QM characterizations of the isolated molecules contained in the explosive compound. The calculations presented herein show that this methodology to predict heats of detonation of pure and explosive formulations is a reasonable computational tool to be used in the rapid assessment and screening of notional energetic materials.

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