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The Predicted Heat of Formation of Several Si-Cl-O-H and Ti-Cl-O-H Species

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14. ABSTRACT

The heat of formation at 298K of several possible $SiCl_4/O_2/H_2$ and $TiCl_4/O_2/H_2$ species have been calculated by using Møller-Plesset perturbation theory (MP2) with 6-31G(3df,2p) basis set. The calculated heats of formation are compared to literature values where available and previous calculations that used bond order corrections to empirically improve the heat of formation calculated by Møller-Plesset perturbation theory. The known species are found to be predicted with fair agreement to theory except for Ti species that contain oxygen double bonds such as TiO_2 and $TiOCl_2$.

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1. Introduction

The combustion synthesis glass using chlorinated silicon compounds ($SiCl_4/HSiCl_3$) is important to industry. The AEROSIL® process is a well-established process for generating silica from high-temperature combustion of chlorosilanes in flames. Although the process has been in use for 60 years, there is still very little understanding of the basic underlying chemical reactions involved in the process. Currently, very little is known about the $SiCl_4$ oxidation mechanism, thermochemistry, or kinetics involved. Several studies of the pyrolysis of chlorinated silanes have recently appeared.[1-3] Thermal decomposition of $SiCl_4$ has been measured behind reflected shock waves.[2,3] $SiCl_3$ was found to form by direct thermal decomposition of $SiCl_4$.[2,3]

$$SiCl_4 \longrightarrow SiCl_3 + Cl \tag{1}$$

$SiCl_3$ can also be formed by the reaction of $SiCl_4$ with H in the gas phase at high temperatures.[3,4]

$$H + SiCl_4 \longrightarrow SiCl_3 + HCl \tag{2}$$

Recently, reaction (2) was found to be a major initiation reaction in $SiCl_4/H_2/O_2/Ar$ flames.[4] Previous models of the oxidation process have assumed spontaneous formation of SiO_2 that coagulate to form particles.[5,6] A model that includes detailed chemical kinetics has recently been developed.[4] The multi-step reaction mechanism was developed by modeling experimental observations of OH formation in a $SiCl_4/H_2/O_2$ flame.[4]

$TiCl_4$ is used in the production of titania and TiN.[7,8] $TiCl_4$ can be added to $SiCl_4/H_2/O_2$ flames to produce TiO_2 dopant in SiO_2 glass and ceramics. Thermal decomposition of $TiCl_4$ has been measured behind reflected shock waves.[9] $TiCl_3$ was found to form either by direct thermal decomposition of $TiCl_4$, and $TiCl_2$ was found to form by direct thermal decomposition of $TiCl_3$.

$$TiCl_4 + M \xrightarrow{\Delta T} TiCl_3 + Cl + M \tag{3}$$

$$TiCl_3 + M \xrightarrow{\Delta T} TiCl_2 + Cl + M \tag{4}$$

The initiation reaction of $TiCl_4$ with H has also been measured behind reflected shock waves at high temperature.[10] There is little kinetic information on the oxidation of these $TiCl_x$ intermediates. Recently, Fourier transform infrared spectroscopy was used to observe TiO_2 formation in premixed flames of titanium tetraisopropoxide, methane, and oxygen.[11] Previous modeling studies have focused on the coagulation of the TiO_2 particles.[12,13] Teyssandier and Allendorf have previously modeled the Ti-Cl-H system by using Rice-Ramsberger-Kassel-Marcus to predict reaction rates.[14] In order to do more detailed modeling of $TiCl_4$ oxidation in flames, the basic kinetic and thermodynamic information is needed on intermediate Ti-O-Cl-H species.

Theoretical methods have previously been used to calculate chlorinated silane thermochemistry.[15-23] Melius et al. have recently used Møller-Plesset perturbation theory with bond additivity corrections (BAC-MP2 or BAC-MP4) to predict the thermochemistry of several silicon-containing systems (Si-C-O-H, Si-O-H, Si-Cl-H, Si-H-O-Cl).[15,16,21–23] The BAC-MP4 method is believe to have an accuracy of (± 2–7 kcal mol^{-1}).[21] The bond additivity correction (BAC) method uses an empirical method to add "corrections" to the *ab initio* calculated heats of formation. In order to get good empirical corrections, a good subgroup of experimentally measured species would be needed for comparison. However, for the titanium flame intermediate species of interest, very little thermochemistry is currently known.

This work uses the MP2 *ab initio* method to calculate several postulated intermediate species associated with $TiCl_4/SiCl_4/H_2/O_2$ flames. The error associated with using the MP2 method is compared to the error in previous theoretical calculations and experiments.

2. Theoretical Method

Electronic structure, normal mode analysis, and heats of formation were calculated by using the Gaussian 03W[24] *ab initio* program. The electronic structure was first optimized by using the unrestricted Hartree-Focke (HF) method with 6-31G(d) basis set. The optimized structure was then used to calculate (HF/6-31G(d)) the vibrational frequencies and thermal correction to enthalpy (which was scaled by 0.8929). The electronic structure was then refined at the MP2 level of theory using the 6-31G(d) basis set. The electronic energy was then calculated using MP2 with 6-31G(3df,2p) basis set. The ΔH_f^0 (298K) were calculated from the electronic energy (E) of the species of interest by Eqs. 3–5.

$$\Delta E = E(Si_aCl_bO_cH_dTi_e) - a * E(Si) - b * E(Cl) - c * E(O) - d * E(H) - e * E(Ti) \tag{3}$$

$$H = \Delta E + E_T(Si_aCl_bO_cH_dTi_e) - a * E_T(Si) - b * E_T(Cl) - c * E_T(O) - d * E_T(H) - e * E_T(Ti) \tag{4}$$

$$\Delta H_f^o(0\ K) = H - a * \Delta H_f^o(Si_a) - b * \Delta H_f^o(Cl) - c * \Delta H_f^o(O) - d * \Delta H_f^o(H_d) - e * \Delta H_f^o(Ti) \tag{5}$$

where a, b, c, e, and d are coefficients, and E_T is the calculated thermal correction to the electronic energy. The heats of formation for the elements where taken from the NIST database and are listed in Table 1.[25]

Table 1. The Heat of Formation of the Elements[25] Used to Calculate the Heats of Formation Using Eqs. 3–5

Element	ΔH_f^o (298K) kJ mol^{-1}
Si	450.
Cl	121.30
H	218.00
O	249.17
Ti	473.63

3. Results and Discussion

The calculated MP2 electronic energy and thermal energy correction for the species of interest are listed in Table 2. The calculated gas phase ΔH_f^0 (298K) are listed in Table 3 along with the experimentally measured values[25-28] where available and the previous calculated BAC-MP4.[16,21,23] Table 4 lists the gas phase ΔS^0 (298K) and heat capacity (C_v) calculated by using the HF/6-31g(d) method.

Table 2. The Electronic Energy Calculated by Using MP2/6-31G(3df,2p) Method and the Thermal Energy Calculated by Using HF/6-31G(d) Method for Species of Interest

Species	Electronic energy Hartree	Thermal correction Hartree
Si	-288.88776	0.00211
Cl	-459.60011	0.00211
H	-0.4982329	0.00211
O	-74.919245	0.00211
Ti	-848.36909	0.00211
SiO	-364.12262	0.00582
SiO_2	-439.2289	0.00993
SiCl	-748.6480	0.00421
$SiCl_2$	-1208.4177	0.00683
$SiCl_3$	-1668.1328	0.01014
$SiCl_4$	-2127.0469	0.01345
$SiCl_3O_2$	-1818.2541	0.01834
$SiCl_3O_2H$	-1818.9157	0.03072
$SiCl_2O$	-1283.5642	0.01188
$SiCl_3OH$	-1743.9386	0.02539
TiO	-923.5473	0.00529
TiO_2	-998.6500	0.00684
TiCl	-1308.1312	0.00403
$TiCl_2$	-1767.9217	0.00638
$TiCl_3$	-2227.6850	0.00940
$TiCl_4$	-2687.4362	0.01255
$TiCl_3OH$	-2303.4473	0.02357
$TiCl_2O$	-1843.1225	0.01093
TiClO	-1383.3259	0.00677
$TiCl_3O$	-2302.7355	0.01305
$TiCl_3O_2$	-2377.8071	0.01737

Species	Electronic energy Hartree	Thermal correction Hartree
TiOClOH	-1459.1236	0.02247
$TiCl_3OOH$	-2378.4393	0.02965
$Ti(OH)_4$	-1151.4594	0.06400

Table 3. The Gas Phase ΔH_f^0(298K) Calculated by Using Eqs. 3–5 as Described in the Text. Also listed are previously measured experimental value where available and previous calculated values using BAC-MP4 method.

Species	ΔH_f^0(298K) kj mol^{-1} This work	ΔH_f^0(298K) kj mol^{-1} Previously measured[25]	ΔH_f^0(298K) kj mol^{-1} BAC-MP4[15,20,21]
SiO	-125.25	-100.42	-111.7
SiO_2	-361.87	-305.43	-282.00
SiCl	151.60	198.32	157.99
$SiCl_2$	-171.73	-168.62	-151.25
$SiCl_3$	-349.25	-390.37	-317.98
$SiCl_4$	-701.72	-662.75	-662.70
$Si(OH)_2O$	-870.16	-891.2	-804.1
SiOHO	-358.44	-355.6	-312.5
$SiCl_3O_2$	-582.97		-525.93
$SiCl_3O_2H$	-766.94		-710.86
$SiCl_2O$	-511.52		-465.26
$SiCl_3OH$	-872.43		-836.80
TiO	45.65	54.39	
TiO_2	-188.15	-305.43	
TiCl	169.06	154.39 (189.5)[28]	
$TiCl_2$	-208.72	-237.23 (-196.6)[28]	
$TiCl_3$	-513.53	-539.32 (-497.5)[28]	
$TiCl_4$	-786.13	-763.16	
$TiCl_2O$	-692.44	-545.55	
TiClO	-303.29	-244.26	
$TiCl_3O$	-604.93		
$TiCl_3O_2$	-749.87		
TiOClOH	-804.18		
$TiCl_3OOH$	-856.99		
$Ti(OH)_4$	-1274.56		
$TiCl_3OH$	-920.32		

Table 4. The Gas Phase ΔS^0 (298K) and Heat Capacity (C_v) Calculated by Using HF/6-31g(d) Method

Species	ΔS^0 (298K) J K^{-1} mol^{-1}	C_v (298K) J K^{-1} mol^{-1}	ΔS^0 (298K) J K^{-1} mol^{-1} previously measured[25]
SiO	211.07	21.22	211.58
SiO_2	224.42	33.06	228.98
$SiCl$	238.15	25.41	237.81
$SiCl_2$	280.44	42.32	281.30
$SiCl_3$	325.58	61.26	318.13
$SiCl_4$	347.54	80.37	330.86
$SiCl_3O_2$	370.78	93.36	
$SiCl_3O_2H$	371.60	100.96	
$SiCl_2O$	304.22	55.34	
$SiCl_3OH$	346.82	86.44	
TiO	227.53	21.83	233.46
TiO_2	297.12	37.43	260.14
$TiCl$	247.87	27.04	249.21
$TiCl_2$	228.66	45.77	278.34
$TiCl_3$	350.96	66.57	316.88
$TiCl_4$	369.68	86.41	354.84
$TiCl_2O$	327.21	60.62	
$TiClO$	248.63	32.40	
$TiCl_3O$	372.02	83.80	
$TiCl_3O_2$	391.75	100.59	
$TiOClOH$	320.15	67.43	
$TiCl_3OOH$	384.77	104.39	
$Ti(OH)_4$	378.21	125.82	
$TiCl_3OH$	389.89	98.78	

Since the silicon species have been previously calculated using BAC-MP4 and many have been experimentally measured, this allow for a comparison for the current method between both previous experimental measurements and a more rigorous theoretical method with empirical corrections. The average deviation of the BAC-MP4 method ΔH_f^0 (298K) for the silicon species tested compared to previous experimental measurements was found to ±36.9 kJ mol^{-1}. The greatest absolute deviation from experiment was for $SiCl_3$ and $Si(OH)_2O$ with a deviation of 72.4 kJ mol^{-1} and 87.1 kJ mol^{-1}. Removing these species reduces the average deviation to ±22.6 kJ mol^{-1}. The current method produces an average deviation of the BAC-MP4 method ΔH_f^0 (298K) for the silicon species tested compared to previous experimental of ±29.4 kJ mol^{-1}. The greatest absolute deviation was for SiO_2 (56.4 kJ mol–$^{-1}$) although $SiCl_3$ once again has one of the greater absolute deviations (46.7 kJ mol^{-1}). Removing the species with the largest deviation slightly reduces the average deviation to ±25.5 kJ mol^{-1}. The BAC-MP4, in general, does better at calculating the energies, except for the two standout species ($SiCl_3$ and $Si(OH)_2O$). The current method, however, shows that it does an adequate job of reproducing the ΔH_f^0 (298K) for the selected species. In general ,the current method produces a slightly more negative heat of formation than the BAC-MP4 method for the silicon species (on average -38 ± 14 kJ mol^{-1}lower).

As stated above, the $SiCl_3$ ΔH_f^0(298K) has a large deviation from the experimental method. Irikura et al.[29] obtained a ΔH_f^0(298K) of -353 ± 12 kJ mol^{-1} by combining the experimentally measured ΔH_f^0(298K) of $SiCl_3^+$ (418 ± 7 kJ mol^{-1})[30] with an *ab initio* calculation of the IP_a of $SiCl_3$ (7.93 ± 0.05 eV). This heat of formation is in better agreement with the BAC-MP4 and current calculations. Recent measurements of Hildenbrand et al. gave a ΔH_f^0(298K) of $SiCl_3 \geq -351.5$ kJ mol^{-1}.[31] They gave a recommended value of $\Delta H_f^0(298K) = -318 \pm 4$ kJ mol^{-1} based on a review of experiment and theory. This value is in better agreement with the current predictions of both this study and the BAC-MP4 study. An experimental measurement of the IP_a for $SiCl_3$ would validate a lower ΔH_f^0(298K) than what is currently recommended by NIST for $SiCl_3$.

The BAC-MP4 method predicts the heat of formation of SiO and SiO_2 accurately. However, it does not agree with the current measurement of the $Si(OH)_2O$ heat of formation. It was also 43 kJ mol^{-1} too low for the recently updated heat of formation of SiO(OH). It's possible that the Si-O empirical correction may need adjusting. The heat of formation of H(OH)SiO has previously been estimated by group additivity to be -512 kJ mol^{-1}.[32] BAC MP4 predicts this heat of formation to be -467.3 kJ mol^{-1}. The current method can be used to predict this species and gets a result slightly closer to the group additivity method (-495.7 kJ mol^{-1}). Also, the bond dissociation energy of DH (HSiOO-H) = 452 kJ mol^{-1} was used by Hartman et al. This dissociation energy is ~82 kJ mol^{-1} lower than what was predicted by either BAC MP4 or the current calculations.

The ΔH_f^0(298K) of the titanium species was found to have a larger deviation from the measured values than the silicon species. This was not unexpected given the difficulty that results in treating transition metals by *ab initio* methods. The current method produces an average deviation of the MP2 method ΔH_f^0(298K) for the titanium species tested compared to previous experimental values of ±53 kJ mol^{-1}. The greatest absolute deviation was for $TiCl_2O$ (-146.9 kJ mol^{-1}) and TiO_2 (117.3 kJ mol^{-1}). Removing these two species from the set lowers the deviation to ±26.6 kJ mol^{-1}. The later number was more typical of the errors seen in the silicon species. Hildenbrand[28] has more recently measured the ΔH_f^0(298K) of TiCl, $TiCl_2$ and $TiCl_3$ since the last NIST review (189.5 kJ mol^{-1}, -196.6 kJ mol^{-1} and -497.5 kJ mol^{-1}), respectively. Using these values produces less deviation ±23.2 kJ mol^{-1}.

Similar problems were observed in calculating the titanium species that were observed in the silicon species. The silicon species with the highest deviation was SiO_2, and TiO_2 has similar problems. From this, it seems clear that this level of theory can have large errors associated with calculations on close-shelled species that contain oxygen double bonds. Although several closed-shell species with a single double bond, TiO and SiO were predicted with good agreement to experimental calculation. The dissociation energy ($D_{0,at}^{o}$) of TiO was previously measured to be 662.7 ± 6.7 kJ mol^{-1},[33] which is in good agreement with our calculation (680 kJ mol^{-1}). However, the $D_{0,at}^{o}$ of TiO_2 was measured to be 1271.9 ± 11.7 kJ mol^{-1} (1260 ± 12 kJ mol^{-1}), which is over 100 kJ mol^{-1} off from the calculated value (1162 kJ mol^{-1}).[33,34] None of the unknown Ti species calculated had a double-bonded oxygen species. Thus, the likely error associated with them is better than the average error of ±52.8 kJ mol^{-1}.

MP4 was used to calculate the heat of formation of TiO, TiO_2, SiO, and SiO_2 by using MP4/6-31G(3df,2p). The heat of formation for SiO and SiO_2 was improved by using MP4 (–107.63 kJ mol^{-1} and –310.94 kJ mol^{-1}). The TiO_2 was also slightly improved (–398.67 kJ mol^{-1}); however, the TiO heat of formation was slightly worse (–23.81 kJ mol^{-1}). MP2 can provide poor geometries for some transition metal systems. The geometry of TiO_2 was optimized by using density functional theory B3LYP (Becke's three-parameter exchange functional with the Yang-Parr fit for the correlation functional) instead of MP2. However, the energy obtained was not an improvement on the original method

The calculated ΔS^0 (298K) for the silicon species was found to have an absolute deviate from experiment by only ±5 J K^{-1} mol^{-1}. The calculation for the Ti species was found to be worse with a deviation of 23 J K^{-1} mol^{-1}. Overall, the method does a good job at predicting the entropy of the species of interest.

4. Conclusions

Titanium intermediates associated with the combustion of $TiCl_4$ in an O_2 flame have been calculated by using MP2/6-31G(3df,2p). The theory does an adequate job of reproducing known heats of formation for silicon and titanium compounds. Except for titanium compounds that contain four bonds total with two of them being an oxygen double bond. Empirical corrections will be needed for these Ti=O species in order to adequately predict them using *ab initio* methods.

References

1. A. Kunz, P. Roth, *Int. J. Chem. Kinet.* 33, 741 (2001).
2. L. Catoire, D. Woiki, P. Roth, *Int. J. Chem. Kinet.* 29, 415 (1997).
3. L. Catoire, D. Woiki, P. Roth, *Int. J. Chem. Kinet.* 29, 467 (1997).
4. B. B. Brady, L. R. Martin, T. A. Moore ,"Reaction Mechanism and Modeling of $SiCl_4$ Combustion," submitted *Combustion and Flame.*
5. E. Sheka, V. Khavryutchenko, E. Nikitina, *J. of Nanoparticle Research* 1, (1999) 71.
6. G. D. Ulrich, *Chem. Eng. News.* 62 (1984) 22.
7. M. K. Akrthar, S. Vemury, S. E. Pratsinis, *AIChE J.* 40 (1994) 1183.
8. A. Bouteville, L. Imhoff, J. C. Remy, *J. Electrochem. Soc.* 143 (1996) 3251.
9. J. Herzler, P. Roth, *Proc. Combust. Inst.* 29 (2003) 1353.
10. J. Herzler, P. Roth, *J. Phys. Chem.* A 101 (1997) 9341.
11. O. I. Arabi-Katbi, S. E. Pratsinis, P. W. Morrison Jr., *AIChE J.* 48, (2002) 59.
12. P. T. Spicer, O. Chaoul, S. Tsantilis, S. E. Pratsinis *J. Aerosol Sci.* 33 (2002) 17.
13. S. Tsantilis, H. K. Kammler, S. E. Pratsinis, *Chemical Eng. Sci.* 57 (2002) 2139.
14. F. Teyssandier, M. D. Allendorf, *J. Electrochem. Soc.* 145 (1998) 2167.
15. P. Ho, M. E. Coltrin, J. S. Binkley, C. F. Melius, *J. Phys. Chem.* 89, (1985) 260.
16. P. Ho, C. F. Melius, *J. Phys. Chem.* 94, (1990) 5120.
17. M.-D. Su, H. B. Schlegel, *J. Phys. Chem.* 97 (1993) 8732.
18. M.-D. Su, H. B. Schlegel, *J. Phys. Chem.* 97 (1993) 9981.
19. M. T. Swihart, R. W J. Carr, *J. Phys. Chem.* 101 (1997) 7434.
20. J. M. Wittbrod, H. B. Schlegel, *Chem. Phys. Lett.* 265 (1997) 527.
21. M. D. Allendorf, C. F. Melius, *J. Phys. Chem. A* 106 (2002) 6370.
22. M. D. Allendorf, C. F. Melius, P. Ho, M. R. Zachariah, *J. Phys. Chem. 99* (1995) 15285.
23. P. Ho, C. F. Melius, *J. Phys. Chem.* 99, (1995) 2166.

24. Gaussian 03, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

25. M. W. Chase Jr., *J. Phys. Chem. Ref. Data* Monograph 9 (1998) 1.

26. D. L. Hildenbrand, K. H. Lau ,*J. Chem. Phys.* 101 (1994) 6076.

27. D. L. Hildenbrand, K. H. Lau, *J. Chem. Phys.* 108 (1998) 6535.

28. D. L. Hildenbrand, *High Temp. Mat. Sci.* 35 (1996) 151.

29. K. K. Irikura, R. D. Johnson III, J. W. Hudgens, *J. Phys. Chem.* 96 (1992) 4306.

30. E. R. Fisher, P. B. Armentrout, *J. Phys. Chem.* 95 (1991) 4765.

31. D. L. Hildenbrand, K. H. Lau, A. Sanjurjo, *J. Phys. Chem. A* 107 (2003) 5448.

32. J. R. Hartman, J. Famil-Ghiriha, M. A. Ring, H. E. O'Neal, *Combust. Flame* 68 (1987) 43.

33. D. L. Hildenbrand, *Chem. Phys. Lett.* 44 (1976) 281.

34. G. Balducci, G. Gigli, M. Guido, *J. Chem. Phys.* 83 (1985) 1909.

LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Laboratory Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual organizations:

Electronics and Photonics Laboratory: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, data storage and display technologies; lasers and electro-optics, solid-state laser design, micro-optics, optical communications, and fiber-optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Space Materials Laboratory: Evaluation and characterizations of new materials and processing techniques: metals, alloys, ceramics, polymers, thin films, and composites; development of advanced deposition processes; nondestructive evaluation, component failure analysis and reliability; structural mechanics, fracture mechanics, and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena. Microelectromechanical systems (MEMS) for space applications; laser micromachining; laser-surface physical and chemical interactions; micropropulsion; micro- and nanosatellite mission analysis; intelligent microinstruments for monitoring space and launch system environments.

Space Science Applications Laboratory: Magnetospheric, auroral and cosmic-ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; infrared surveillance, imaging and remote sensing; multispectral and hyperspectral sensor development; data analysis and algorithm development; applications of multispectral and hyperspectral imagery to defense, civil space, commercial, and environmental missions; effects of solar activity, magnetic storms and nuclear explosions on the Earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation, design, fabrication and test; environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions, and radiative signatures of missile plumes.