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STANFORD UNIV CALIF DEPT OF CHEMISTRY  
METAL COMBUSTION PROCESSES AS STUDIED BY CHEMILUMINESCENCE AND --ETC(U)  
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The PbF A( $\Omega=1/2$ ) - X<sup>2</sup> $\Pi_{1/2}$  band system has been vibrationally reanalysed, based on the observation of 69 new bandheads. The singlet-triplet splitting in methylene (CH<sub>2</sub>) has been estimated to be 8.1±0.8 kcal/mole, based on the detection of CH<sub>2</sub><sup>1A1</sup> following the photolysis of ketene (CH<sub>2</sub>CO). The band energies of BaI, SF<sub>3</sub><sup>1A1</sup> and SF<sub>4</sub><sup>1A1</sup> have been determined to be 72.9±2, 91.1±3.2, and 84.1±3.0 kcal/mole, based on the appearance of chemiluminescent reactions with metastable alkaline earth atoms. The two C<sub>10</sub>H<sub>8</sub><sup>1A1</sup> isomers, azulene and naphthalene, have been distinguished in a mass spectrometer through the use of laser-controlled multiphoton ionization.

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METAL COMBUSTION PROCESSES AS STUDIED BY  
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## Summary of Research Highlights

The reaction  $\text{Pb} + \text{F}_2$  has been studied under beam-gas conditions at  $\text{F}_2$  pressures of  $10^{-4}$  torr and in the presence of argon at  $\sim 7$  torr. A series of 133 red degraded bandheads belonging to the  $\text{A}(\Omega=\frac{1}{2})-\text{X}^2\Pi_{\frac{1}{2}}$  band system are observed; 69 of these bandheads are new and a vibrational reanalysis is made. The  $\text{PbF}$  A state is thought to be populated by the reaction of a metastable lead atom  $\text{Pb}(^3\text{P}_1)$  or  $\text{Pb}(^3\text{P}_2)$  with molecular fluorine.

By photodissociating ketene ( $\text{CH}_2\text{CO}$ ) in the 3400-2900 Å region, singlet methylene ( $\text{CH}_2^1\text{A}_1$ ) is detected by laser-induced fluorescence by observing the  $\text{CH}_2^1\text{B}_1-^1\text{A}_1$  red band system. Under collision-free conditions a study of the appearance of  $\text{CH}_2^1\text{A}_1(0,0,0)$  as a function of photodissociation wavelength and as a function of ketene temperature leads to a value for the heat of formation of singlet methylene:

$$\Delta H_{f0}^0(\text{CH}_2^1\text{A}_1) = 101.7 \pm 0.5 \text{ kcal/mole}$$

When this is combined with other known heats of formation, the singlet-triplet splitting is estimated to be  $8.1 \pm 0.8$  kcal/mole, in good agreement with the most recent ab initio calculations of this quantity.

During this contract period we have constructed a pulsed source of metastable alkaline earth atoms, particularly  $\text{Ba}(^3\text{D})$ ,  $\text{Ca}(^3\text{P})$ , and  $\text{Sr}(^3\text{P})$ . The metastable atoms traverse a scattering chamber filled with oxidant gas at low pressure (beam + gas arrangement) and the resulting chemiluminescence is analyzed

spectroscopically and as a function of the time elapsed between the formation of the metastables and the appearance of the chemiluminescence in the reaction/observation zone. This information is combined with known thermodynamic data to determine the bond energy of the gas molecule under study. In this manner we have found that

$$D_0^0(\text{BaI}) = 72.9 \pm 2 \text{ kcal/mole}$$

$$D_0^0(\text{F}_5\text{S-F}) = 91.1 \pm 3.2 \text{ kcal/mole}$$

$$D_0^0(\text{F}_3\text{S-F}) = 84.1 \pm 3.0 \text{ kcal/mole}$$

The latter two quantities may be combined with existing data to deduce the stepwise bond dissociation energies of  $\text{SF}_6$ . A zigzag pattern appears in which the magnitude of the bond energy is larger for the even members. This behavior can be rationalized by a simple model which involves transformation of lone pair electrons on the central sulfur atom at first to a weak two-center three-electron bond and then to a strong three-center four-electron bond.

The possible use of laser ionization as an analytical detector has been explored by demonstrating the facile detection of the two  $\text{C}_{10}\text{H}_8$  isomers, azulene and naphthalene. Compared to electron impact, multiplication ionization provides more gentle ionization at low laser power and more extensive fragmentation at high laser power. Moreover, the efficiency of the latter exceeds that of the former during the time the laser is on. It would appear that this technique should make a useful addition to mass spectrometry.

Publications Supported Under DAAG 29-77-G-0151

C. R. Dickson and R. N. Zare, "Spectroscopic Study of Pb + F<sub>2</sub> Chemiluminescence," *Optica Pura by Aplicada* 10, 157 (1977).

R. K. Lengel and R. N. Zare, "An Experimental Determination of the Singlet-Triplet Splitting in Methylene," *J. Am. Chem. Soc.* 100, 7495 (1978).

R. C. Esther and R. N. Zare, "Determination of Bond Energies by Time-of-Flight Single-Collision Chemiluminescence," *Chem. Phys.* 28, 253 (1978).

T. Kiang, R. C. Esther, and R. N. Zare, "Upper and Lower Bounds on the F<sub>5</sub>S-F Bond Energy," *J. Chem. Phys.* 70, 12 (1979).

T. Kiang and R. N. Zare, "Stepwise Bond Dissociation Energies in Sulfur Hexafluoride," *J. Am. Chem. Soc.* (accepted for publication).

D. M. Lubman, R. Naaman, and R. N. Zare, "Multiplication Ionization of Azulene and Naphthalene," *J. Chem. Phys.* (accepted for publication).



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