To the best of our knowledge there exist no previous measurements of either of these mobility values.

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Upper and lower bounds on the F₅S–F bond energy

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Numerous experimental and theoretical studies of the infrared multiphoton dissociation of SF₆ have appeared following the first announcements of this effect. Surprisingly, however, the F₅S–F bond energy seems not to be firmly established, although its value plays an important role in various interpretations of the multielectron reactions. The primary datum is the shock tube dissociation study of SF₆ carried out by Bott and Jacobs, who determine a value of 76.92 ± 4 kcal/mol for the F₅S–F bond energy. Support for this value comes from the studies of Curran and of Harland and Thynne, who report that the threshold for F⁻ formation from dissociative electron attachment in SF₆ is nearly 0 eV. When this is combined with the known electron affinity of fluorine, the F₅S–F bond energy is calculated to be 78 kcal/mol. However, Chen and Chantry fail to observe F⁻ production from SF₆ dissociative electron attachment below 600 K, casting doubt on this earlier work. Moreover, both Benson and Lyman have independently re-evaluated the Bott and Jacobs work, and based on RRKM theory they find that a value of 93 ± 3 kcal/mol for the F₅S–F bond energy fits the dissociation rate best.

We report here upper and lower bounds for the F₅S–F bond energy, $D_0^E(F₅S–F)$, based on the observation of chemiluminescence in the reaction of SF₆ with metastable calcium and strontium atoms, under single-collision conditions. Energy balance for the reaction leads to the equality

$$D_0^E(F₅S–F) + E_{\text{int}}(\text{SF₆}) + E_{\text{trans}}$$

$$= D_0^E(MF) + E_{\text{trans}} + E_{\text{int}}(M) + E_{\text{int}}(\text{SF₆}) - E_{\text{int}}(MF)$$

for the individual quantum states of the reactants and products, where $E_{\text{int}}$ is the internal energy measured from the lowest level, $E_{\text{trans}}$ is the relative translational energy of the reactants (superscript i) or the products (superscript f), and $D_0^E(MF)$ is the known MF bond strength. By resolving the chemiluminescent spectrum from MF we are able to identify the highest internal states of the reactants and products.

**FIG. 1.** The shortest wavelength portion of the Sr(P) + SF₆ chemiluminescent spectrum under single-collision conditions.

**FIG. 2.** The shortest wavelength portion of the Ca(P) + SF₆ chemiluminescent spectra under single-collision conditions.
TABLE I. Calculation of upper and lower bounds to $D_{f}(F_2S-F)$ based on the CaF(5P) and SrF(5P) chemiluminescent reactions with SF$_6$ under single-collision conditions. All units are in kcal/mol.

<table>
<thead>
<tr>
<th>M</th>
<th>$D_{f}(M-F)$</th>
<th>$E_{f,1}(MF)$</th>
<th>$E_{f,1}(MP^2)$</th>
<th>$E_{f,1}(SF)$</th>
<th>$E_{f,trans}$</th>
<th>Upper bound</th>
<th>Lower bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>127.1 ± 2$^a$</td>
<td>75.7 ± 1.4$^b$</td>
<td>43.8</td>
<td>2.6</td>
<td>2.5$^c$</td>
<td>100.3 ± 3.4</td>
<td>89.6 ± 2$^d$</td>
</tr>
<tr>
<td>Sr</td>
<td>128.0 ± 2$^a$</td>
<td>95.1 ± 1.2$^a$</td>
<td>42.6</td>
<td>2.6</td>
<td>2.5$^e$</td>
<td>90.1 ± 3.2</td>
<td>85.0 ± 2$^f$</td>
</tr>
</tbody>
</table>

$^a$See Ref. 16.
$^b$The highest populated vibrational level is taken to be $v' = 14 + 1$ (see Fig. 2).
$^c$Calculated using Eqs. (9) and (10) of Ref. 15.
$^d$Based on not observing chemiluminescence from the CaF C state.
$^e$The highest populated vibrational level is taken to be $v' = 5 ± 1$ (see Fig. 1).
$^f$Based on not observing chemiluminescence from the SrF F state; the D state is not used because of its long radiative lifetime $\sim 10^{-2}$ sec. See J. L. Gole, D. R. Preuss, and C. L. Chalek, J. Chem. Phys. 66, 584 (1977).

state of the electronically excited MF* product, which is populated. We make the assumption that in some collisional encounters the maximum exothermicity of the reaction appears in the MF* product. Moreover, when MF* is populated in its highest internal state, the internal energy in the SF$_6$ product $E_{f,1}(SF)$, as well as the final relative translational energy $E_{f,trans}$ are nearly zero. With the neglect of these latter two quantities, we obtain an upper bound on $D_{f}(F_2S-F)$ from Eq. (1), since all quantities on the upper-right hand side of this equation are either known or can be measured directly or estimated. Conversely, the absence of excitation of some higher-lying electronic state of MF places a lower bound on $D_{f}(F_2S-F)$.

The experimental apparatus has been described in detail elsewhere. Chemiluminescent spectra (10 A/minute) at a resolution of 5 A are shown in Fig. 1 for the SrF C$^4\Pi$-X$^2\Sigma^+$ band system from the reaction SrF(5P) + SF$_6$ and in Fig. 2 for the CaF B$^4\Sigma^+$-X$^2\Sigma^+$ band system from the reaction CaF(5P) + SF$_6$. The band head assignments for SrF are based on the spectroscopic work of Novikov and Gurvich,17 and for CaF on the work of Harvey.18

Table I summarizes our calculations of upper and lower bounds on $D_{f}(F_2S-F)$ based on the chemiluminescent spectra shown in Figs. 1 and 2. From this table we conclude that

$$69.6 ± 2 ≤ D_{f}(F_2S-F) ≤ 90.1 ± 3.2,$$

or that

$$D_{f}(F_2S-F) = 89.9 ± 3.4 \text{ kcal/mol}.$$

Although our determination of the FeS-F bond energy does have a relatively large uncertainty, it is sufficient to exclude the lower values for this bond energy which have been used in the past in interpreting the infrared multiphoton dissociation of SF$_6$.

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16We take $D(SrF) = 128.0 ± 2$ kcal/mol and $D(CaF) = 127.1 ± 2$ kcal/mol, as estimated in Z. Karny and R. N. Zare, J. Chern. Phys. 65, 3360 (1978). These bond energies agree within the stated uncertainties with the values reported in D. L. Hildenbrand, J. Chern. Phys. 45, 3647 (1968).