

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

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^{b)}Present address: Eckerd College, St. Petersburg, FL 33733.

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Upper and lower bounds on the F_5S-F bond energy^{a)}

T. Kiang, R. C. Estler,^{b)} and R. N. Zare

Department of Chemistry, Stanford University, Stanford, California 94305

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Numerous experimental and theoretical studies of the infrared multiphoton dissociation of SF_6 have appeared following the first announcements of this effect.^{1,2} Surprisingly, however, the F_5S-F bond energy seems not to be firmly established, although its value plays an important role in various interpretations of the multiphoton dissociation process.³⁻⁶ The primary datum is the shock tube dissociation study of SF_6 carried out by Bott and Jacobs,⁷ who determine a value of 75.92 ± 4 kcal/mol for the F_5S-F bond energy. Support for this value comes from the studies of Curran⁸ and of Harland and Thynne,⁹ who report that the threshold for F^- formation from dissociative electron attachment in SF_6 is nearly 0 eV. When this is combined with the known electron affinity of fluorine, the F_5S-F bond energy is calculated to be 78 kcal/mol.¹⁰ However, Chen and Chantry¹¹ fail to observe F^- production from SF_6 dissociative electron attachment below 600 K, casting doubt on this earlier work. Moreover, both Benson¹² and Lyman³

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 F_5S-F bond energy fits the dissociation rate best.

We report here upper and lower bounds for the F_5S-F bond energy, $D_0^0(F_5S-F)$, based on the observation of chemiluminescence in the reaction of SF_6 with metastable calcium and strontium atoms,¹³⁻¹⁵ M , under single-collision conditions. Energy balance for the reaction leads to the equality

$$D_0^0(F_5S-F) + E_{int}(SF_5) + E_{trans}^i = D_0^0(MF) + E_{trans}^f + E_{int}(M) + E_{int}(SF_6) - E_{int}(MF) \quad (1)$$

for the individual quantum states of the reactants and products, where E_{int} is the internal energy measured from the lowest level, E_{trans} is the relative translational energy of the reactants (superscript i) or the products (superscript f), and $D_0^0(MF)$ is the known¹⁶ MF bond strength. By resolving the chemiluminescent spectrum from MF we are able to identify the highest internal

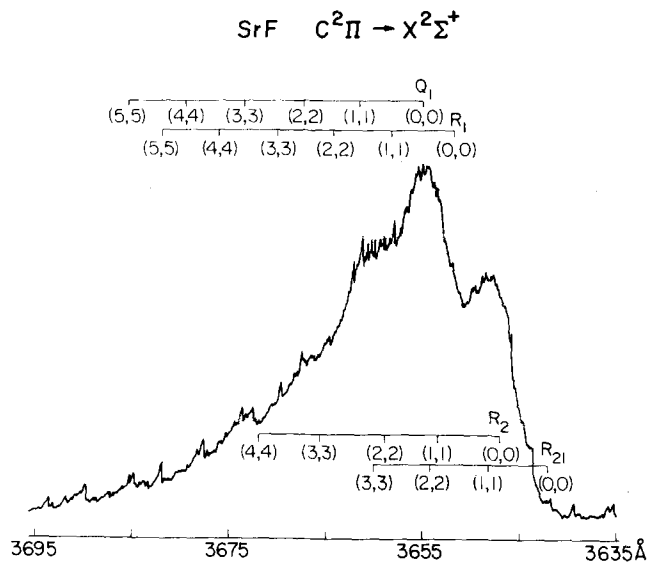


FIG. 1. The shortest wavelength portion of the $Sr(^3P) + SF_6$ chemiluminescent spectrum under single-collision conditions.

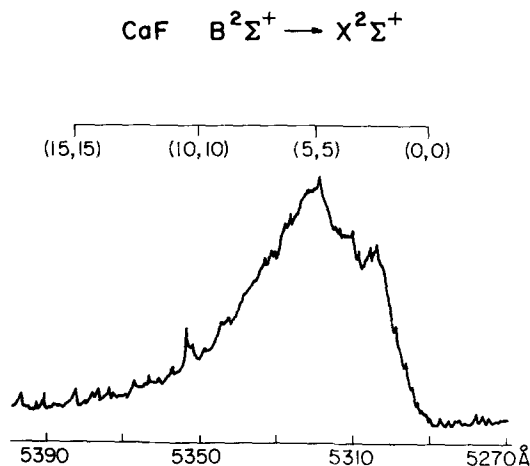


FIG. 2. The shortest wavelength portion of the $Ca(^3P) + SF_6$ chemiluminescent spectra under single-collision conditions.

TABLE I. Calculation of upper and lower bounds to $D_0^0(\text{F}_5\text{S}-\text{F})$ based on the $\text{Ca}(^3\text{P})$ and $\text{Sr}(^3\text{P})$ chemiluminescent reactions with SF_6 under single-collision conditions. All units are in kcal/mol.

M	$D_0^0(\text{M}-\text{F})$	$E_{\text{int}}(\text{MF})$	$E_{\text{int}}(\text{M}^3\text{P}_2)$	$E_{\text{int}}(\text{SF}_6)$	$E_{\text{trans}}^{\dagger}$	Upper bound	Lower bound
Ca	127.1 ± 2^a	75.7 ± 1.4^b	43.8	2.6	2.5^c	100.3 ± 3.4	89.6 ± 2^d
Sr	128.0 ± 2^a	85.1 ± 1.2^e	42.6	2.6	2.0^c	90.1 ± 3.2	85.0 ± 2^f

^aSee Ref. 16.

^bThe highest populated vibrational level is taken to be $v' = 14 \pm 1$ (see Fig. 2).

^cCalculated using Eqs. (9) and (10) of Ref. 15.

^dBased on not observing chemiluminescence from the $\text{CaF } C$ state.

^eThe highest populated vibrational level is taken to be $v' = 5 \pm 1$ (see Fig. 1).

^fBased on not observing chemiluminescence from the $\text{SrF } E$ 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_5 product $E_{\text{int}}(\text{SF}_5)$, as well as the final relative translational energy $E_{\text{trans}}^{\dagger}$ are nearly zero. With the neglect of these latter two quantities, we obtain an upper bound on $D_0^0(\text{F}_5\text{S}-\text{F})$ from Eq. (1), since all quantities on the 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 $D_0^0(\text{F}_5\text{S}-\text{F})$.

The experimental apparatus has been described in detail elsewhere.¹⁵ Chemiluminescent spectra (10 Å/min) at a resolution of 5 Å are shown in Fig. 1 for the $\text{SrF } C^2\Pi-X^2\Sigma^+$ band system from the reaction $\text{Sr}(^3\text{P})+\text{SF}_6$ and in Fig. 2 for the $\text{CaF } B^2\Sigma^+-X^2\Sigma^+$ band system from the reaction $\text{Ca}(^3\text{P})+\text{SF}_6$. 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 $D_0^0(\text{F}_5\text{S}-\text{F})$ based on the chemiluminescent spectra shown in Figs. 1 and 2. From this table we conclude that

$$89.6 \pm 2 \leq D_0^0(\text{F}_5\text{S}-\text{F}) \leq 90.1 \pm 3.2, \quad (2)$$

or that

$$D_0^0(\text{F}_5\text{S}-\text{F}) = 89.9 \pm 3.4 \text{ kcal/mol.} \quad (3)$$

Although our determination of the $\text{F}_5\text{S}-\text{F}$ 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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^bPresent address: Department of Chemistry, University of Southern California, Los Angeles, CA 90007.

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