

The Reaction of Spin-Orbit State-Selected $\text{Ca}(^3P_J^0)$ with CH_3I , CH_2I_2 , and SF_6

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Chemiluminescence cross sections for reaction of the individual spin-orbit states of metastable $\text{Ca}(^3P_J^0)$ with CH_3I , CH_2I_2 , and SF_6 have been determined by the use of optical pumping state selection. This technique was also used to separate the chemiluminescence arising from the two excited metastable $\text{Ca } ^3P^0$ and 1D states. The spin-orbit dependence of the chemiluminescence pathway was found to be substantial for the CH_3I and CH_2I_2 reactions and similar to that previously observed for halogen diatom and alkyl bromide reagents. By contrast, no spin-orbit effect was observed for $\text{Ca}(^3P^0) + \text{SF}_6$. These results are discussed in terms of our previously presented model for the origin of spin-orbit effects in chemical reactions.

KEY WORDS: Chemiluminescent reactions; Optical pumping state selection; Spin-orbit dependence of chemical reactions.

I. INTRODUCTION

Significant spin-orbit selectivity has been recently observed for reactions involving atoms with nonzero spin multiplicity, including halogen atoms,¹⁻⁶ tin,⁷ metastable mercury,⁸ and inert gas atoms.^{9,10} In our laboratory we have developed an optical pumping state selection technique¹¹ to study reactions of individual spin-orbit levels of metastable $\text{Ca}(4s4p\ ^3P_J^0)$ atoms, for which the spin-orbit splitting is quite small:¹² $E(^3P_1^0 - ^3P_0^0) = 52\text{ cm}^{-1}$ and $E(^3P_2^0 - ^3P_1^0) = 106\text{ cm}^{-1}$.

For $\text{Ca}(^3P^0)$ atomic reactants, we might expect a relatively small spin-orbit dependence of reactivity because of the small energy

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differences between the asymptotic levels and the expected intramultiplet mixing in the reactant channel. Nevertheless, the chemiluminescence cross section σ_{chem} for the reaction with molecular chlorine and bromine¹³ as well as a number of alkyl bromides,¹⁴ was found to depend fairly strongly on initial spin-orbit level J , with an order of reactivity $J = 2 > J = 1 > J = 0$. Within the relatively large experimental errors, σ_{chem} for the $J = 2$ level was found to be about 5 to 10 times greater than for the $J = 0$ level for all reactions studied, after correction for the chemiluminescence due to the $4s3d\ ^1D$ component in the Ca^* beam. The spin-orbit dependence for production of ground state $\text{CaCl}(X\ ^2\Sigma^+)$ products was also investigated for $\text{Ca}(^3P^0) + \text{Cl}_2$ and was found to have an opposite ordering of reactivity.¹⁵

In the present paper, we investigate the chemiluminescent reactions of $\text{Ca}(^3P^0)$ with CH_3I and CH_2I_2 , for which a similar large spin-orbit dependence is found. As in our previous study,¹⁴ σ_{chem} for both the $^3P^0$ and 1D reactions is determined by variation of the 1D population through 1D optical pumping depletion. We also note one example of a $\text{Ca}(^3P^0)$ reaction with no spin-orbit selectivity, namely $\text{Ca}(^3P^0) + \text{SF}_6$. Finally, we discuss the spin-orbit dependence of $\text{Ca}(^3P^0)$ reactions in terms of the nonadiabatic evolution of the asymptotic spin-orbit levels onto the different electrostatic surfaces at smaller separations, with the aid of the quantum mechanical pseudo-quenching model calculation of Alexander.¹⁶

II. EXPERIMENTAL

The experimental apparatus and procedures have been described in detail earlier.^{11,13,14} Briefly, a beam of metastable calcium atoms generated in a discharge source crosses a *cw* single-mode dye laser beam (CR599-21) for optical pumping state selection and then passes through a collimator into the scattering chamber, to which the alkyl iodides are introduced via a needle valve. Scattering gas pressures (0–2 mTorr) are measured with a capacitance manometer. Emission from chemiluminescent products and the excited reactant atomic states was detected from a zone 1.6 ± 0.1 cm into the scattering chamber with a $\frac{1}{4}$ m spectrometer and cooled GaAs photomultiplier (RCA C31034-02).

Calcium has two excited metastable levels, $4s4p\ ^3P^0_J$ and $4s3d\ ^1D$, whose relative populations may be determined by comparison of the $^3P^0_1 \rightarrow ^1S$ and $^1D \rightarrow ^1S$ emission intensities. (See Figure 1 of Ref. 14 for an energy level diagram of calcium.) Based on a recent calculation¹⁷ and measurement¹⁸ of the $^1D \rightarrow ^1S$ oscillator strength, the $^1D/^3P^0$ ratio is estimated to be typically 20%. Thus, two types of optical pumping experiments are required to determine the dependence of the chemiluminescence cross section on $^3P^0$ spin-orbit level J . To account for the 1D contribution, the product emission signal was measured with and without 1D depletion by irradiation on the $4s5p\ ^1P^0 \leftarrow 4s3d\ ^1D$ line at 671.7 nm. The degree of optical depletion could be monitored by the decrease in the $^1D \rightarrow ^1S$ signal. State selection of individual $^3P^0$ spin-orbit levels was carried out by irradiation on each of the lines of the $4s5s\ ^3S_1 \leftarrow 4s4p\ ^3P^0_J$ multiplet near 610 nm, as described in detail previously.^{11,13}

III. RESULTS

Figures 1 and 2 present chemiluminescence spectra of the $\text{CaI}\ A\ ^2\Pi-X\ ^2\Sigma^+$ and $B\ ^2\Sigma^+-X\ ^2\Sigma^+$ band systems for the CH_3I and CH_2I_2 reactions. The reaction exoergicity is large enough that these excited states can be populated in the 1D and $^3P^0$ reactions with both iodide reagents. The higher lying C state is also accessible with the 1D reactant state; its formation, however, was not investigated here. The reaction exoergicities are tabulated in Table I. We also note that the formation of electronically excited products from ground state 1S atoms is forbidden.

Because the A and B states are extremely close in energy,²² the vibrational sequences $\Delta v = v' - v''$ of the $A-X$ and $B-X$ band systems overlap, and it is not possible to estimate the A/B state branching ratio for the calcium iodide product. The limited spectral resolution, the extreme spectral congestion in these band systems, and the expected high degree of product internal excitation preclude observation of individual vibrational bands.

Optical pumping depletion of the 1D state was employed in order to separate the contribution of the 1D and $^3P^0$ reaction to the observed chemiluminescence and hence to determine separately their chemiluminescence cross sections $\sigma_{\text{chem}}(^3P^0)$ and $\sigma_{\text{chem}}(^1D)$. The

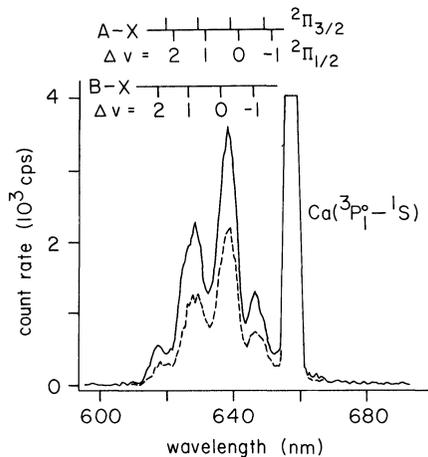


FIGURE 1 Chemiluminescence spectrum of the CaI A-X and B-X band systems for the reaction of $\text{Ca}(^3P^0, ^1D)$ with CH_3I at 0.60 mTorr. The solid and dashed lines are spectra taken without and with depletion of 1D atoms by optical pumping on the $5^1P^0 \leftarrow 4^1D$ line near 671.7 nm. The vibrational sequences $\Delta v = v' - v''$ for each band system are indicated. The $^3P_1^0 \rightarrow ^1S$ and $^1D \rightarrow ^1S$ emission intensities (in cps), which are off scale or not plotted, have the following magnitudes: 10 422 and 282, respectively, with pump laser off, and 10 024 and 133 with laser on.

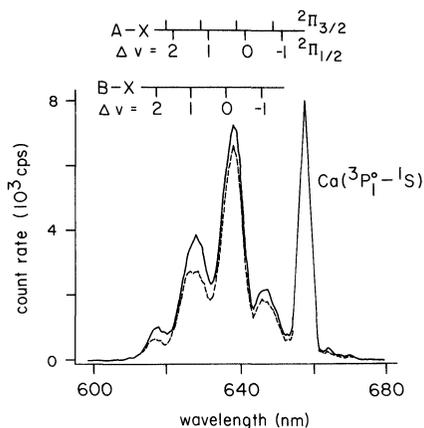


FIGURE 2 CaI chemiluminescence spectrum for the $\text{Ca}(^3P^0, ^1D) + \text{CH}_2\text{I}_2$ reaction at 0.57 mTorr: dashed line, with 1D optical pumping depletion; solid line, pump laser off. The $^3P_1^0 \rightarrow ^1S$ and $^1D \rightarrow ^1S$ emission intensities (in cps) are 8216 and 254, respectively, with pump laser off, and 8122 and 123 with laser on.

TABLE I
Reactions energetics (in eV) and derived cross sections (in \AA^2)
for $\text{Ca}^* + \text{alkyl iodide}$ reactions

	Reactant	
	CH_3I	CH_2I_2
ΔD_0^a	0.30 ± 0.11	0.54 ± 0.14
$E_{\text{int}}^{\text{I}}(\text{RI})^b$	0.05	0.07
$E_{\text{trans}}^{\text{I}}^c$	0.22	0.22
$E_{\text{avl}}(^3P^0)^d$	2.44	2.72
$E_{\text{avl}}(^1D)^d$	3.26	3.54
$\sigma_{\text{chem}}(^3P^0)$	1.34 ± 0.24	9.52 ± 1.26
$\sigma_{\text{chem}}(^1D)$	7.46 ± 1.71	5.40 ± 1.51
$\sigma_{\text{tot}}(^3P^0)$	155 ± 5	216 ± 8
$\sigma_{2 \rightarrow 1}$	35 ± 2	26 ± 2

^a $D_0^0(\text{CaI}) - D_0^0(\text{RI})$. See Refs. 19 and 20.

^b Internal energy of the iodide reactant.

^c Average initial relative translational energy. See Ref. 21.

^d Total energy available to the products from the respective reactant state. Ca atomic energies taken from Ref. 12.

dashed spectra in Figures 1 and 2 illustrate the change in the chemiluminescence spectrum when the 1D state is optically depleted. This clearly shows that the 1D reaction is a significant contributor to the observed chemiluminescence. It is also interesting to note that the change in the emission signal upon optical pumping varies somewhat for the different vibrational sequences. For the CH_2I_2 reaction (see Figure 2), in which this variation is larger, the sequence intensities drop to 64%, 71%, 91%, and 87% of their original values for the $A/B - X \Delta v = +2, +1, 0,$ and -1 sequences, respectively, when the 1D level is optically pumped. We believe this is due to differences in the CaI^* product electronic (A vs. B state production) or, more likely, vibrational state distribution between the $^3P^0$ and 1D reactions since the emission from different excited levels is expected to vary from sequence to sequence. In the absence of more resolved spectra and spectroscopic data on higher vibrational levels, it is not possible to make any quantitative estimate of the product state distributions.

Since both reactants and products emit in the visible, it is possible to obtain the chemiluminescence cross sections without any absolute intensity measurements by determination of the ratio of reactant and product emission signals.²³ In the present case, there are two possible

reactants. As derived previously,¹⁴ the ratio of S_{CaI} , the integrated chemiluminescence signal, to S_P , the reactant ${}^3P_1^0 \rightarrow {}^1S$ emission, is given by

$$S_{\text{CaI}}/S_P = [n_{RI}\bar{v}/f_{J=1}A({}^3P_1^0 \rightarrow {}^1S)] \times [\sigma_{\text{chem}}({}^3P^0) + (n_D/n_P)\sigma_{\text{chem}}({}^1D)] \quad (1)$$

where n_P , n_D , and n_{RI} are the number densities of the $\text{Ca } {}^3P^0$ and 1D states and the alkyl iodide reactant, respectively. The quantities \bar{v} and $f_{J=1}$ are the average initial relative velocity and the fraction of incident atoms in the radiating $J = 1$ level, respectively; their estimation is given previously.¹⁴ The population ratio n_D/n_P may be determined by the ratio S_D/S_P of reagent ${}^1D \rightarrow {}^1S$ and ${}^3P_1^0 \rightarrow {}^1S$ emission intensities:

$$n_D/n_P = (S_D/S_P)[f_{J=1}A({}^3P_1^0 \rightarrow {}^1S)/A({}^1D \rightarrow {}^1S)] \quad (2)$$

The A factors in square brackets are the spontaneous radiative transition probabilities for the respective lines.^{17,18,24}

In order to determine $\sigma_{\text{chem}}({}^3P^0)$ and $\sigma_{\text{chem}}({}^1D)$ separately, n_D was varied by cw single-mode dye laser irradiation on the $4s5p\ {}^1P^0 \leftarrow 4s3d\ {}^1D$ line at 671.7 nm. With 50 mW of laser power in a 4 mm diameter beam, the 1D population could be reduced to approximately 35% of the original value as measured by the change in the ${}^1D \rightarrow {}^1S$ emission intensity. This optical pumping scheme is inefficient because of (1) the relatively small oscillator strength²⁵ of the pump line and (2) the poor branching ratio of the spontaneous decay of the excited state, i.e., about 98% of the emission is back to the 1D state and only 2% is to the ground 1S state.²⁶ By comparison, we note that it is possible to deplete the ${}^3P_J^0$ levels to approximately 5% of the original population. Nevertheless, this change in 1D population is large enough to allow separation of the 1D and ${}^3P^0$ contributions to the observed chemiluminescence since the ${}^1D/{}^3P^0$ population ratio in the absence of optical pumping is typically 20%. The derived chemiluminescence cross sections, with associated experimental uncertainties, are presented in Table I.

The scattering gas pressure dependence of the $\text{Ca}({}^3P_1^0 \rightarrow {}^1S)$ emission intensity without and with ${}^3P_1^0$ optical depletion was measured in order to estimate the ${}^3P^0$ total attenuation cross section $\sigma_{\text{tot}}({}^3P^0)$ and the intramultiplet mixing cross section $\sigma_{2 \rightarrow 1}$ from the most highly populated nonradiating $J = 2$ to emitting $J = 1$ level, as

described in detail previously.^{13,14} Collisional transfer from the non-radiating 3P_0 level is neglected because (1) the incident 3P_0 to 3P_2 population ratio is approximately 0.2,¹³ and (2) the ratio of the $\sigma_{0 \rightarrow 1}$ to $\sigma_{2 \rightarrow 1}$ cross sections are expected to be also about 0.2, if recent experimental¹¹ and theoretical²⁷ $\text{Ca}(^3P^0)$ -He intramultiplet mixing cross sections are a useful guide. With the pump laser off, the $^3P_1^0$ population, and hence $^3P_1^0 \rightarrow ^1S$ emission intensity, at the observation zone should fall approximately exponentially with scattering gas pressure because of collisional attenuation by reaction, etc. With the pump laser on, the $^3P_1^0$ population is small at zero pressure and hence initially rises as the scattering gas is added because of collisional intramultiplet mixing (principally from the $J=2$ level^{11,16,27}); at higher pressure the $^3P_1^0$ population drops because of chemical reaction, etc. A two-state kinetic model²⁹ comprising the $J=1$ and 2 spin-orbit levels was employed to fit the data and hence estimate $\sigma_{\text{tot}}(^3P^0)$ and $\sigma_{2 \rightarrow 1}$. The derived values for these cross sections are listed in Table I.

Selective depletion of individual spin-orbit levels in the $^3P^0$ manifold by optical pumping on the $4s5s\ ^3S_1 \leftarrow 4s4p\ ^3P_J^0$ lines near 610 nm was employed to determine chemiluminescence cross sections $\sigma_{\text{chem},J}$ as a function of spin-orbit level J , as we did previously for other $\text{Ca}(^3P^0)$ reactions.¹³⁻¹⁵ The optical pumping process not only depletes the population of the pumped level J but also enhances the populations of the other two spin-orbit levels through spontaneous decay of the excited 3S_1 level. It is thus necessary to measure the change R_J in the chemiluminescence signal as each $^3P_J^0$ level is in turn depleted and then invert the following set of 3 equations for $J=0, 1, 2$ in order to determine the individual cross sections:¹³

$$\sum_{J'} p_{J'}^{(J)} [\sigma_{\text{chem},J'} / \sigma_{\text{chem}}(^3P^0)] = R_J \quad (3)$$

Here $p_{J'}^{(J)}$ is the relative population of the spin-orbit level J' when level J is optically depleted,²⁹ and $\sigma_{\text{chem}}(^3P^0)$ is the chemiluminescence cross section for the original unpumped distribution of $^3P^0$ spin-orbit levels.

Before applying Eq. (3), the actually observed intensity changes R_J' must be corrected for the chemiluminescence contribution of the 1D reaction:¹⁴

$$R_J = R_J' [1 + (D/P_{\text{off}})] - (D/P_{\text{off}}) \quad (4)$$

In Eq. (4) D and P_{off} are the chemiluminescence signals from the 1D

and ${}^3P^0$ reactions, respectively, with no optical pumping. The ratio (D/P_{off}) equals

$$(D/P_{\text{off}}) = (n_D/n_P)[\sigma_{\text{chem}}({}^1D)/\sigma_{\text{chem}}({}^3P^0)], \quad (5)$$

and may be calculated from the data in Table I and the atomic ${}^1D \rightarrow {}^1S$ and ${}^3P_1^0 \rightarrow {}^1S$ emission intensities with the help of Eq. (2). Alternatively, (D/P_{off}) may be calculated for a particular emission wavelength by measurement of the change in the chemiluminescence signal upon 1D optical pumping.

Because of the congestion and overlapping of the CaI $A-X$ and $B-X$ band systems, the changes in chemiluminescence intensity upon optical pumping were monitored at the peak of the $A/B-X \Delta v = 0$ sequence at 638 nm; these should reflect the variation in the integrated spectrum. Limited measurements were also made at 627 nm ($\Delta v = +1$ sequence). The observed R'_J ratios were significantly different, but after the 1D contribution to the chemiluminescence was taken into account, the ratios R_J were identical to within experimental error at the two observation wavelengths. The scattering gas pressure was also limited to less than 0.4 mTorr to avoid the scrambling effect of secondary fine-structure-changing transitions in the state-selection process.

The experimentally measured intensity ratios R'_J , typical values of the ratio (D/P_{off}) , and the derived ratios R_J after the 1D contribution has been subtracted are presented in Table II. Also given in Table II are the cross section ratios $\sigma_{\text{chem},J}/\sigma_{\text{chem}}({}^3P^0)$ obtained by solution of Eq. (3). The spin-orbit dependent cross sections can be put on an absolute scale by noting that the denominator $\sigma_{\text{chem}}({}^3P^0)$ is the cross section weighted by the (approximately statistical) initial, unpumped ${}^3P^0_J$ populations and is given in Table I. It can be seen that the effect of initial spin-orbit state on the chemiluminescence cross section is substantial and that the $J = 2$ level is by far the most reactive, as was observed previously for reaction of $\text{Ca}({}^3P^0)$ with Cl_2 , Br_2 , and several alkyl bromides.^{13,14}

Also included in Table II are the observed ratios R'_J for SF_6 reactant. We do not present a chemiluminescence spectrum since this has been presented previously.³⁰ In the present study, the change in chemiluminescence intensity was monitored at 601 nm at the peak of the $A-X \Delta v = 0$ sequence. No spin-orbit dependence is seen. However, in this case approximately 80% of the chemiluminescence signal is due to the 1D reaction so that the spin-orbit effect here could be

TABLE II
Changes in CaI $A/B-X$ chemiluminescence intensities under various optical pumping conditions and derived relative $\text{Ca}(^3P^0)$ chemiluminescence cross sections

Quantity	J	Reactant		
		CH_3I	CH_2I_2	SF_6
R'_J	0	1.025 ± 0.006	1.093 ± 0.005	— ^a
	1	1.099 ± 0.010	1.241 ± 0.017	1.00 ± 0.01
	2	0.762 ± 0.009	0.435 ± 0.009	1.00 ± 0.01
$(D/P_{\text{off}})^b$		2.4 ± 0.2	0.23 ± 0.03	4.2 ± 0.5
R_J	0	1.08 ± 0.02	1.115 ± 0.006	— ^a
	1	1.34 ± 0.03	1.297 ± 0.021	— ^a
	2	0.27 ± 0.03	0.304 ± 0.011	— ^a
$\sigma_{\text{chem},J}/\sigma_{\text{chem}}(^3P^0)$	0	0.23 ± 0.13	0.01 ± 0.11	— ^a
	1	0.10 ± 0.11	0.33 ± 0.12	— ^a
	2	1.43 ± 0.26	1.41 ± 0.25	— ^a

^a Not measured or calculated.

^b D/P_{off} varied from run to run; results shown are for one determination of D/P_{off} .

obscured. By contrast, the differing reactivity of spin-orbit levels was readily detectable for the CH_3Br reaction, in which 90% of the chemiluminescence arose from the 1D component. In view of the absence of an observable spin-orbit effect, the cross section ratios $\sigma_{\text{chem},J}/\sigma_{\text{chem}}(^3P^0)$ were not calculated for the SF_6 reaction. If there is a difference in reactivity between the $\text{Ca } ^3P^0$ spin-orbit levels with SF_6 , this effect is considerably smaller than that observed with the other reagents studied.

IV. DISCUSSION

The present study extends the range of $\text{Ca}(^3P^0)$ reactions for which a significant dependence of the chemiluminescence cross section on the spin-orbit level of the atomic reactant is observed. In reactions with Cl_2 , Br_2 ,¹³ a number of alkyl bromides,¹⁴ and now CH_3I and CH_2I_2 , the order of reactivity is found to be $J = 2 > J = 1 > J = 0$, with a 5 to 10 times difference in σ_{chem} for the most reactive $J = 2$ level vs. that for $J = 0$. This variation of cross section is remarkable, given the relatively small spin-orbit splitting in the $\text{Ca } 4s4p \ ^3P^0$ manifold and the consequently large expected intramultiplet mixing in the entrance

channel. Indeed, the importance of the latter is indicated by the size of the estimated mixing cross sections $\sigma_{2 \rightarrow 1}$ given in Table I. We have found only one halide reagent, namely SF₆, for which no spin-orbit dependence is observed. Our earlier observation¹³ of no spin-orbit effect for Ca(³P⁰) + CH₃Cl was subsequently found¹⁴ to be due to the fact that the chemiluminescence arose solely from the ¹D reaction.

Spin-orbit effects in chemical reactions can be explained¹³⁻¹⁶ as arising from differences in the evolution of the asymptotic spin-orbit states onto the various electrostatic covalent surfaces, corresponding to different orientations of the unpaired *p* electron, from which charge transfer takes place with different efficiencies. This is most clearly evident for the Ca(³P⁰) + Cl₂ reaction. Here mixing with the lowest ionic surface is symmetry allowed in the preferred³¹ C_{2v} geometry only for the covalent ³B₂ surface, and not for the ³A₁ and ³A₂ surfaces.¹³

A similar symmetry restriction also applies to the Ca(³P⁰) + CH₃X reactions, for which the preferred approach geometry is expected to be collinear for the Ca—X—C atoms, by analogy with the known rebound mechanism for the homologous alkali metal reactions.³² In this case two covalent surfaces (*A*₁ + *E*) arise for C_{3v} approach, and charge transfer is symmetry allowed only for the *A*₁ surface. We also note that the spin-orbit effect for the less symmetrical alkyl halides is essentially identical to that for Cl₂, Br₂, and CH₃I.

We might also expect intramultiplet mixing in the entrance channel to reduce differences in reactivity between the atomic spin-orbit levels. Certainly the magnitude of the estimated $\sigma_{2 \rightarrow 1}$ cross sections for both iodide and bromide reagents indicates that this is occurring in these reactions. Clearly, this mixing does not completely scramble flux from the different incident spin-orbit levels. Unfortunately, a quantitative explanation of this would require quantum scattering calculations which are possible only for quasi-diatom models;¹⁶ in any case, the relevant potential energy surfaces are not known for these reactive systems.

It is interesting to speculate on why the Ca(³P⁰) + SF₆ reaction shows no spin-orbit dependence in its chemiluminescence cross section. This could be due to either an increased spin-orbit mixing in the entrance channel or the lack of a symmetry restriction for charge transfer. We favor the latter explanation because of the similarity of the spin-orbit effect for the other reactions studied, in spite of the significant variation in the estimated mixing cross sections $\sigma_{2 \rightarrow 1}$.

Finally, the Ca and $\text{Sr}(^3P^0) + \text{SF}_6$ reactions have been previously studied³¹ (with no spin-orbit state selection) in order to estimate the $\text{F}_5\text{S}-\text{F}$ bond energy as 3.95 ± 0.14 eV. The chemiluminescence spectrum of the reactions of metastable Ca and Sr with SF_6 were investigated under somewhat higher resolution than in the present study in order to identify the highest metal fluoride vibrational level populated. This was then used with energy conservation to set bounds on the $\text{F}_5\text{S}-\text{F}$ bond energy. The presence of the second metastable 1D state in the atomic beam was ignored. However, under our conditions the 1D reaction produces most of the observed chemiluminescence. If the 1D level were reassigned as the reactant producing the chemiluminescence observed by Kiang *et al.*,³⁰ then their $\text{F}_5\text{S}-\text{F}$ bond energy would need to be raised by 0.82 eV, which would be inconsistent with all previous determinations of this bond energy. Perhaps the $^1D/{}^3P^0$ population ratio was considerably less in their experiments than ours. However, this does again point up the need to consider carefully the atomic state responsible for an observed reaction.

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31. N. Honjou and D. R. Yarkony, *J. Phys. Chem.* **89**, 2919 (1985) and unpublished work.
32. See R. B. Bernstein and A. M. Rulis, *Faraday Discuss. Chem. Soc.* **55**, 293 (1973).