origins would offer one possible explanation for the approximate constancy of screening factors found by Read[6] for multiply-excited states.

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Infrared multiphoton dissociation of SF_6 in a molecular beam: Observation of F atoms by chemi-ionization detection

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Ever since SF_6 has been observed to dissociate in an isotopically selective manner following multiphoton absorption from an intense infrared radiation field,[1,2] there has been considerable effort, both experimental and theoretical, to understand the mechanism responsible for this process.[3] Of particular importance is the identification of the initial photofragments. From mass spectrometric and infrared studies Kompa and co-workers[4] suggested that SF_6 initially decomposes into $SF_4 + F_2$, while from molecular beam studies Coggiola, Schulz, Lee, and Shen[5] concluded that dissociation proceeds via the lower energy path, $SF_5 + F$. Further work by the same

group[6] shows that SF_5 undergoes secondary absorption and decomposition to $SF_4 + F$. We have crossed a beam of SF_6 with the output of a high power pulsed CO_2 laser. Using a new chemi-ionization technique to distinguish between F_2 and F fragments, we report here results that corroborate the findings of Coggiola et al., namely, only F atoms are formed in the infrared multiphoton dissociation of SF_6.

The experimental setup is shown in Fig. 1. An atomic samarium ($\geq 99.9\%$) beam, issuing from an electrically heated oven, intersects a SF_6 ($\geq 99.99\%$) beam in
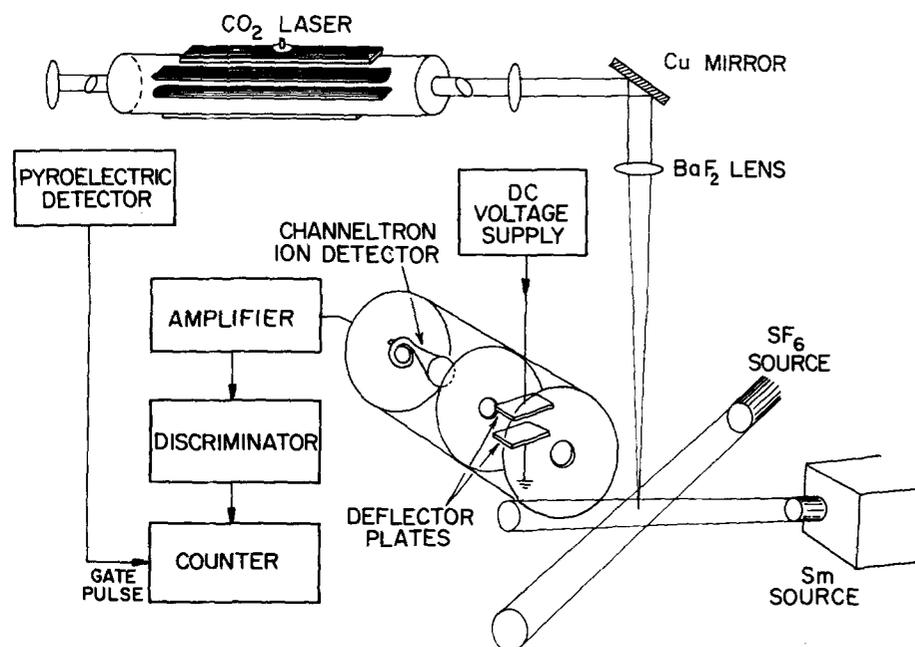

FIG. 1. Schematic of the experimental apparatus. The output of a 10.6μ CO_2 laser is focused onto a molecular beam of SF_6. The photofragments react with an atomic Sm beam to form ions which are detected by a channeltron. Variation of the voltage on the deflector plates permits discrimination of electrons from negative ions.
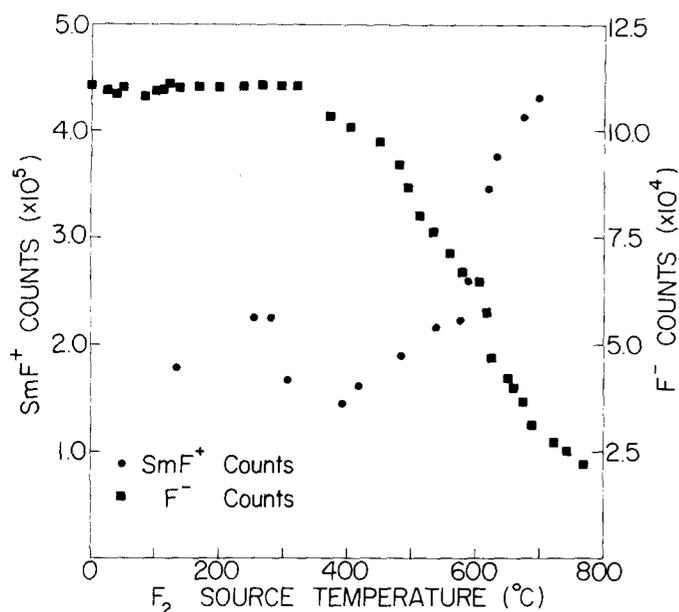
FIG. 2. The SmF⁺ and F⁻ signals from a quadrupole mass spectrometer recorded as a function of the F_2 nozzle temperature. The increase in the SmF⁺ signal concurrent with the decrease in the F⁻ signal at temperatures where the F_2 is significantly dissociated establishes the presence of Reaction (2).

an evacuated chamber (8×10^{-6} torr). The output of a transversely excited CO_2 laser (~1 J/p, 1 pps, several hundred nanosecond pulsewidth) operating on the 10.6μ $P(20)$ line is focused by a BaF_2 biconvex lens ($f/5$) into the intersection region of the Sm and SF_6 beams. A channeltron (charged particle multiplier) equipped with electric deflection plates (whose field is perpendicular to the path of the ions) is situated near the intersection region. The channeltron output is counted for a fixed period of time (30 μsec) so that only ions formed within

a short time after the beginning of the laser pulse are recorded. A signal from a pyroelectric detector viewing the laser output triggers the opening of the counter circuit.

In a separate experiment we have observed (Fig. 2) that the following thermal chemi-ionization reactions occur under crossed-beam conditions:

$$Sm + F_2 \rightarrow SmF^+ + F^- , \tag{1}$$

and

$$Sm + F \rightarrow SmF^+ + e^- . \tag{2}$$

In Reactions (1) and (2) both positive and negative ions were identified using a quadrupole mass filter.[7] We have also found that no ions are formed under the same conditions for reactions of Sm with SF_4 or SF_6, even when the latter is heated to 670°C. Thus, by discriminating between F⁻ and e, Reactions (1) and (2) serve to determine the initial photofragment distribution following infrared multiphoton dissociation of SF_6. This is readily accomplished by electrostatic deflection in conjunction with the earth's magnetic field, as illustrated in Fig. 3(a), since the application of a few volts to the deflector plates in front of the channeltron is sufficient to remove the lighter electrons but to leave the transmission of the heavier F⁻ ions almost unaffected.[8]

Figure 3(b) shows both the positive and negative charged particle counts observed following multiphoton dissociation of SF_6. The pronounced falloff of the negative current with applied voltage is strong evidence that the negatively charged species are only electrons [compare Fig. 3(b) with 3(a)]. We conclude therefore that the initial photofragmentation of SF_6 involves the production of F atoms.
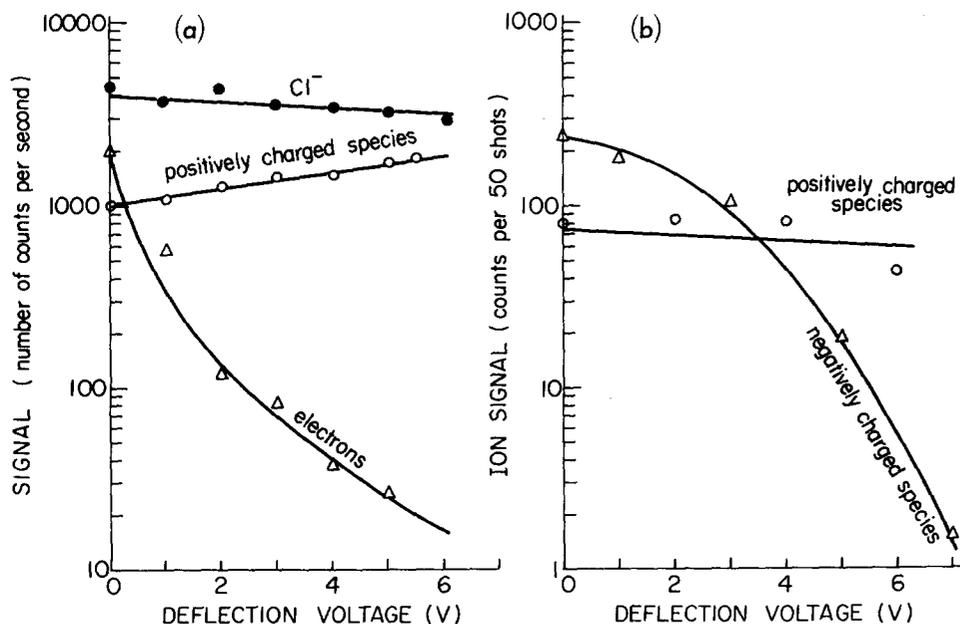
We thank S. Freund and J. Hudson for construction of

FIG. 3. Ion counts as a function of deflection plate voltage: (a) electrons from a heated tantalum filament in addition to Cl⁻ ions (generated by the chemi-ionization reaction $Sm + Cl_2 \rightarrow SmCl^+ + Cl^-$); and (b) chemi-ions from the reaction of Sm with photofragments following SF_6 multiphoton dissociation.

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COMMENTS

Absolute coverage determination of CO on nickel crystal faces: Papers by Erley, Besocke, and Wagner [J. Chem. Phys. 66, 5269 (1977)] and by Klier, Zettlemoyer, and Leidheiser [J. Chem. Phys. 52, 589 (1970)]

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Erley, Besocke, and Wagner[1] recently made a critical comment that no remark was made by Klier, Zettlemoyer, and Leidhesier[2] on the backscatter coefficient of ^{14}C radiation in their description of ^{14}C tracer calibrations employed in the determination of CO coverages on nickel substrates, and suggested that an error of up to 50% surface coverage may have ensued from the neglect of backscattering. The purpose of this comment is to communicate that the backscatter corrections were in fact made and included in counter efficiency stated in the original paper by Klier, Zettlemoyer, and Leidheiser.[2] Although the backscatter correction was not explicitly stated, the data in the paper (Ref. 2) do include a backscatter factor (f_B) of 1.34 for the nickel substrate: the reported count rate (R) of 3140 cmp/nM of adsorbed ^{14}C of specific activity (σ) 22.7 Ci/M at 9.3% counter efficiency (E) defines the backscatter coefficient at $f_B = (2 \times R)/(E \times \sigma) = 2 \times 3140 \times 10^9/(0.093 \times 22.7 \times \times 2.22 \times 10^{12}) = 1.34$, where 1 Ci = 2.22×10^{12} dpm and the factor 2 stands for the ratio of 4π to 2π geometry. The backscatter coefficient of 1.34 was taken from Burtt's work[3] for ^{60}Co beta radiation (0.3 MeV) on Cu ($Z = 29$) in the absence of data for ^{14}C (0.16 MeV) on Ni ($Z = 28$). Burtt's backscatter factors were chosen in preference to Glendenin and Solomon's,[4] who give $f_B = 1.5$ for 0.17 MeV radiation on $Z = 28$, because in the latter work the backscatter was reported to vary with an insertion of a collodion film considered to have zero backscattering between the source (^{35}S) and the metal. The variations were attributed to surface roughness the effects of which may have not been totally removed by the presence of the collodion film.

A further support in favor of the calibration procedure used by Klier *et al.*[2] involving $f_B = 1.34$ comes from Tracy's[5] independent AES measurements of CO saturation coverage on Ni (100) which agrees to within 1% with that of Klier *et al.* and from Taylor and Estrup's[6] excellent agreement of LEED structures with CO coverages on Ni (110) determined from AES isotherms normalized to saturation coverage obtained from Ref. 2.

This Comment reiterates the already recorded agreement between results of papers Refs. 2, 5, and 6, concerning CO adsorption on the Ni (100) and Ni (110) faces.