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High-Purity F Atom Beam Source

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Abstract. Fluorine atoms are generated by 2.45 GHz microwave dissociation of 99.99 % F_2 in a synthetic sapphire single-crystal discharge tube. Typical F_2 gas flow and beam intensity are: 0.1 mbar l s^{-1} and 9.5×10^{17} atoms sterad^{-1} s^{-1}. The measured degree of dissociation into atoms is $D > 98$ %. The high total F atom flux together with the high purity of the beam seem to make the source a very promising device for both reaction kinetic- and molecular beam-experiments

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For quantitative investigations of the reactions of free atoms in the gas phase the purity of the involved species is of special importance. This has to be considered particularly for experiments involving F atoms, because possible interference with the very fast secondary reactions with F_2 molecules may complicate the interpretation of the reaction paths [1]. For beam scattering experiments using electron bombardment ionization detectors molecular fluorine or other fluorine atom-containing molecules in the beam will show up as an additional signal on the atomic mass, because of dissociative ionization. Lowering the electron energy to a value below the appearence potential and by this way discriminating against the molecular contribution is difficult in the case of molecular fluorine because of its low bond energy [2] and also leads to a considerable loss in sensitivity. On the other hand, the low bond energy, together with the large expected cross-section for electron bombardment dissociation [3], seem to make fluorine one of the most promising species for microwave dissociation. Unfortunately near 100 % microwave dissociation of F_2 has so far only been reported for extremely dilute mixtures of a few percent F_2 in He and Ar with F_2-partial pressures in the 10^{-2} mbar range or below. In both types of mixtures it was felt that the degree of dissociation decreased considerably with increasing F_2 concentrations [3–9]. For almost complete dissociation this requires a relatively high pumping speed per mole of produced F atoms and also the ability to handle large amounts of the rare gases.

Quartz and glass discharge tubes, which have been used in many experiments, show an etching effect after a few hours of operation. The reason seems to be the formation of reaction products like SiF_4, resulting in F-atom consumption as well as a beam contamination with these species which lead to F-atom formation again under electron bombardment conditions. Another disadvantage of those tube materials is the short lifetime of the discharge tube due to the penetration of holes in the discharge region which may appear after only a few days of operation.

The above considerations led to the investigation of a microwave source for F atoms working with pure oxygen-free F_2 in the overall "clean" environment of a synthetic sapphire single crystal discharge tube. Sapphire is a desirable material because of the following reasons: Under normal operating temperatures the formed AlF_3 film has a vapour pressure low enough to protect the tube against reactions with F and F_2. This results in a very long lifetime of the discharge tube and a beam which is free of reaction products of fluorine with the tube material. In addition, the recombination coefficient for fluorine atoms on sapphire at 300 K is about half of that for quartz [10]. As compared to amorphous alumina, which even in its dense form is found to be slightly permeable to atmospheric gases [11], sapphire has a stability to changes in temperature which is orders of magnitude higher [12] making it the most promising material for handling fluorine under conditions of electric discharges.

1. Experimental Assembly

The beam source is shown in Fig. 1. The 150 mm long synthetic sapphire tube (TYCO Saphicon Division,

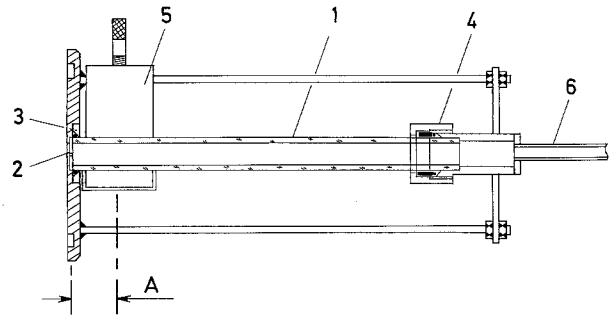

Fig. 1. Roughly to scale schematic view of the F-atom source. The numbers refer to the following parts (*1* discharge tube, *2* disk with beam defining aperture, *3* and *4* compression O-ring seals, *5* microwave cavity, *6* connection to the gas inlet system)

Milford, New Hampshire, USA) *1* has 12.7 mm O.D. and 8 mm I.D. One end of the tube is pressed against a thin 1 mm sapphire disk (Gebr. Weinz GmbH, Veitsroth, Fed. Rep. Germany) *2* with a 1 mm-aperture. The tube is sealed with compression Viton O-rings on both sides, *3* and *4*. While *4* is a commerical version, *3* has been modified in order to provide the shortest possible distance A between the disk *2* and the microwave cavity (Type 214 L, Electromedical supplies, Greenham, England) *5*. The gas inlet system *6* is built in all metal form from stainless steel tubes with 6 mm O.D. and 4 mm I.D. Gas flow is controlled by all metal valves (Nupro SS-4BMG and SS-6BG-MM) and measured by a monel mass flowmeter (ENALL-50P, Teledyne Hastings-Raydist, Hampton, Virginia, USA). The 99.99% F_2 (MAN, Neue Technologie, Munich, Fed. Rep. Germany) is stored in a stainless steel tank (1000 mbar, 100 l; MAN, Neue Technologie).

The atom source is mounted on a high vacuum chamber with an oil diffusion pump and a freon cooled baffle, providing a vacuum of 4×10^{-5} mbar with an F_2 gas flux of 0.1 mbar l s^{-1}. Under this condition the streaming velocity of the gas and the residence time in the discharge region are 4 ms^{-1} and about 10 ms, respectively. The length of the flight path in the source chamber is given by the source-skimmer distance and equal to about 20 mm. The discharge is powered by a microwave generator (Microtron Mark III, Electromedical supplies), and the actual power dissipation is 25 W. The beam passes through three differential pumping stages. A mechanical Fizeau type velocity selector in the first provides the facility of analyzing the particle velocity and so determining the effective source temperature. The beam particles are detected 1.5 m from the source by a mass spectrometer in an UHV system consisting of an 90 eV electron bombardment ion source [13], magnetic deflection (100 mm radius) and an open multiplier.

2. Beam-Analysis

2.1. Intensity

During all determinations of the beam properties the detector vacuum was kept below 1×10^{-11} mbar. After exposure to the beam the residual gas mass spectrum shows a significant peak on mass 19, while the signal on mass 38 is at least a factor of 100 smaller. This indicates the expected behaviour of the highly reactive fluorine atoms, namely the generation of relatively volatile metal (hexa)-fluorides on the metal ionizer surfaces, which could be effectively removed only by repetitive electron bombardment baking of all ionizer parts, which are warmed up at normal operating conditions.

The maximum permissible F_2 gas flux for long term detector operation is therefore found to be 0.1 mbar l s^{-1} and all investigations on the source, reported here, refer to this value. For a short time however, the source has been operated with the maximum F_2 gas flux for the source chamber pumping system, 0.85 mbar l s^{-1}, and showed 97% of dissociation for 120 W microwave power. The source intensity I in the forward direction is calculated from

$$I = CX^2/(A_0 P_F), \tag{1}$$

where C denotes the observed count rate, X is the source-detector distance and A_0 the active detector area. The detection probability for F atoms, P_F, is calculated from

$$P_F = P_{IH_2}(\sigma_{F_2}/\sigma_{H_2})R(\bar{v}_{H_2}/\bar{v}_F)B, \tag{2}$$

where P_{IH_2} is the experimentally determined detection probability of the ionizer for an H_2 beam at 300 K [13], being equal to 1.8×10^{-5}. σ_{F_2} and σ_{H_2} denote the cross sections for 90 eV electron bombardment ionization for F_2[14] and H_2[15]. $\bar{v}_{H_2}$ and $\bar{v}_F$ are the mean velocities of the H_2- and F-beam at 300 K and 364 K (see below). The detection efficiency B of the multiplier for mass ~20 particles at 4 keV ion energy is 0.6 [16]. R denotes the detection probability for F atoms relative to the one for F_2 molecules and is calculated [17] from

$$R = [(U_a-1)/(U_m-1)]\cdot[\ln(1.25\,U_a)/\ln(1.25\,U_m)]/2, \tag{3}$$

where U_a and U_m are the ratios of the energy of the bombarding electron and the corresponding ionization energy of the particle.

With electron energy $E_{el}=90$ eV, $U_a=5.165$, and $U_m=5.685$, we find $R=0.423$ and $P_F=1.9\times10^{-5}$. From (1) the value for I is found to be

$$I = 9.5\times10^{17}\ \text{atoms sterad}^{-1}\,\text{s}^{-1}.$$

The overall error in I arising from the determination of A_0, σ_{F_2} and σ_{H_2}, is believed not to exceed ±35%.

2.2. Degree of Dissociation

The degree of dissociation D is defined as

$$D=(I_1-I_2)/I_1, \quad (4)$$

where I_1 and I_2 are the measured mass spectrometer signals on the molecular mass with discharge off and on, respectively. The corresponding background signal I_b is obtained with the beam flag closed. I_b is independent of the discharge and several orders of magnitude smaller than both I_1 and I_2. D is typically 98% $<D<100$%. This definition of the degree of dissociation gives information about the intensity on the atomic mass only under the assumption that the only recombination process is the one leading to the formation of new F_2 molecules. The recombination of F atoms with different species would not affect the value of D obtained from (4), but would lead to a decrease in F atom density. Extensive beam analysis however, carried out with the mass spectrometer detector shows – besides F and F_2 – only 0.3 $^0/_{00}$ HF and about the same amount on mass 34, which is probably CH_3F. Since titanium sublimation and sputter ion pumps are used on this system, it is likely that both species – HF and CH_3F are formed in the detector.

This demonstrates clearly that almost complete dissociation of F_2 in a microwave discharge can even be obtained in a pure F_2 atmosphere with an elevated source pressure in the 10^{-1} mbar range. For still higher microwave power this has also been shown for a source pressure of about 1 mbar (Sect. 2.1.). The relative fraction of dissociatively ionized F_2 molecules is found to depend strongly on the energy of the bombarding electrons and could be limited to 10% at 90 eV.

2.3. Translational Beam Temperature

The source temperature was measured by recording the F atom-signal as a function of the frequency of the mechanical velocity selector [18], which is directly proportional to the velocity of the transmitted particles. The distribution is shown in Fig. 2. The maximum is found near $v_m=689\,\mathrm{ms}^{-1}$. As the detection probability is inversely proportional to the particle velocity, the translational beam temperature T is calculated as

$$T=(m\cdot v_m^2)/3k=364\,\mathrm{K}. \quad (5)$$

Because of the small Knudsen number K_n

$$K_n=\lambda/d=0.2 \quad (6)$$

a slight narrowing of the distribution is expected together with a slight shift to higher velocities. Furthermore at small particle velocities self-scattering may play a role, which would also lead to an apparent shift of the whole distribution to higher velocities.

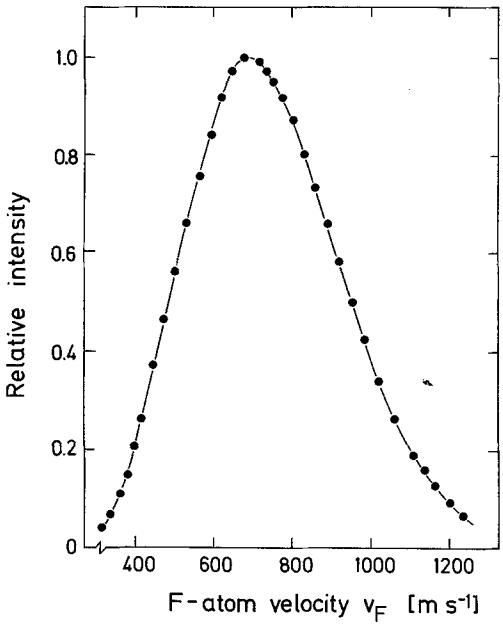

Fig. 2. Measured intensities of fluorine atoms under typical operating conditions of the source as a function of velocity

From these considerations the temperature T given above may be regarded as an upper limit.

3. Discussion

The main advantages of the present source are, besides the relatively simple microwave operation, the high purity of the beam and the high atom density. As 99.99% Fluorine is used together with a sapphire tube, the system, once passivated, yields almost only F atoms. Another advantage of the pure gas and the sapphire tube combination is the almost complete elimination of higher-order fluorides from the discharge, leading to an easy ignition and a very good long-term stability of the source. The fact that the source could be operated over a wide range of gas flows from 0.1 mbar l s^{-1} to 0.8 mbar l s^{-1} with more than 97% of dissociation, seems to rule out the need for any carrier gas. The same argument seems to hold for oxygen and oxygen containing molecules, which are assumed to catalyze F atom formation in F_2-Ar and CF_4 discharges [5]. The low required pumping speed per mole of produced F atoms is especially important in beam experiments.

Unfortunately the dielectric constant of sapphire ($\varepsilon=10$) [19], and consequently the dielectric loss factor, is about as twice as high as the one of quartz. This seems to be the reason for the relatively large amount of energy required for 99% dissociation of 0.1 mbar l s^{-1} F_2, which is 25 W. Moderate compressed

air cooling, however, has been found to be largely sufficient during many hundred hours of operation until now.

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