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Absorption Coefficients of SF_6, SF_4, SOF_2 and SO_2F_2 in the Vacuum Ultraviolet

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Abstract. — Absorption coefficients $k_0(\mathrm{m}^{-1}\ 100\ \mathrm{kPa}^{-1})$ of SF_6 and of its main gaseous by-products SF_4, SOF_2 and SO_2F_2 were measured in the VUV region. The experiments were carried out at a temperature of 298 K and a spectral resolution of 0.1 nm over the wavelength range 115 – 180 nm for SF_6, 115 – 220 nm for SF_4, 120 – 195 nm for SOF_2 and 120 – 210 nm for SO_2F_2. The highest absorption coefficient values were obtained for SF_4 and the lowest for SF_6.

Résumé. — Les coefficients d'absorption k_0 $(\mathrm{m}^{-1}\ 100\ \mathrm{kPa}^{-1})$ du SF_6 et de ses principaux produits de décomposition gazeux, SF_4, SOF_2 et SO_2F_2 ont été mesurés dans le domaine de l'ultraviolet sous vide. Les expériences ont été réalisées à la température de 298 K avec une résolution de 0,1 nm dans la gamme 115–180 nm pour le SF_6, 115–220 nm pour le SF_4, 120–195 nm pour le SOF_2 et 120–210 nm pour le SO_2F_2. Les coefficients d'absorption les plus élevés ont été mesurés pour le SF_4 et les plus faibles pour le SF_6.

1. Introduction

Today, sulfur hexafluoride (SF_6) is widely used as an insulating and arc-quenching medium in high voltage circuit breakers. In the power arcs produced in these apparatuses during operation, radiative transfer constitutes an important mechanism which has several consequences: limitation of the temperature of the hottest regions, modification of the temperature profile and of the radius of the arc and finally heating of the cold SF_6 surrounding the plasma [1, 2]. This latter effect may result in a pressure increase in the circuit breaker and thus may have a strong influence on the apparatus behaviour for example, in increasing the arc blowing efficiency. Knowledge of cold SF_6 absorption spectrum is therefore essential for arc modeling studies. Even though the absorption of cold SF_6 for photon wavelengths lower than 110 nm has been dealt with many investigations [3–10] its absorption between 110 nm and 200 nm

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has been much less studied [3, 9, 11, 12]. The main aim of this work was then to carry out a thorough study of the absorption of cold SF_6 (T = 298 K) in this wavelength range. As we know from literature results [13–15] that gases like O_2 and H_2O, which may be present as impurities in SF_6, exhibit strong absorption in the region 110−200 nm, we chose to measure the absorption of three SF_6 samples differing from one another in: initial purity, storage time, volume of the storage containers, containers that had been opened or left sealed.

We also studied, over the same wavelength range, the absorption spectra of sulphur tetrafluoride (SF_4), thionyl fluoride (SOF_2) and sulfuryl fluoride (SO_2F_2) which constitute the three main stable gaseous by-products formed when SF_6 containing even low quantities of O_2 and H_2O is submitted to, for example, coronas, sparks or arcs.

Under coronas [16–19] SO_2F_2 is formed in larger amounts than SOF_2 $\left(\frac{[SO_2F_2]}{[SOF_2 + SF_4]} \cong 3\right)$ while under sparks and especially arcs [16,20–22], SF_4 and SOF_2 production increases strongly due, in particular, to nozzle ablation and electrodes vaporization and exceeds that of SO_2F_2 with values of the $\frac{[SOF_2 + SF_4]}{[SO_2F_2]}$ ratio ranging from 10 to 200, according to the experimental conditions. SF_4, SOF_2 and SO_2F_2 have not, to our knowledge, been studied in this way before.

2. Experiment

The experimental set-up used for measuring the absorption spectra of SF_6, SF_4, SOF_2 and SO_2F_2 is shown in Figure 1. The absorption cell was attached to the exit slit of a vacuum-UV spectrophotometer (Spex model 1500) which was evacuated to a pressure of 10^{-2} Pa and a low pressure microwave powered hydrogen-argon lamp equipped with a MgF_2 window was located in front of the entrance slit of this apparatus. This lamp emits a complex spectrum between $\simeq$ 115 nm and 230 nm. As a very similar system was already used for photoconductivity studies in non-polar liquids (hydrocarbons, silicone oils), further information on the lamp emission spectrum and on the reliability of the experimental set-up can be found in some of our papers dealing with this subject [24–26]. All absorption measurements were made at a resolution of 0.1 nm.

The different gases were fed into the absorption cell *via* a stainless steel gas handling system and the pressure in the cell measured using two MKS Baratron type 122 B absolute pressure gauges (accuracy of reading: ± 0.15%) one for the range $5 - 10^3$ Pa and the other for the $10^3 - 10^4$ Pa range and with a Membranovac 1 VS Leybold- Heraeus device connected to a CI absolute pressure sensor head (accuracy: ± 0.5%) for the range $10^4 - 10^5$ Pa.

Commercially available SO_2F_2 (> 99.5%) and SF_4 (> 94%) were used in our experiments. As SF_4 readily reacts with water traces and leads to SOF_2 through the reaction [27]

$$SF_4 + H_2O \rightarrow SOF_2 + 2HF \tag{1}$$

special precautions were taken in order to avoid this reaction or at least to minimize it. Before filling the cell with the SF_4 sample to be studied, the cell and the gas filling circuit were, after being evacuated, flushed several times with SF_4. This gas was then pumped out and the cell filled to the required pressure with new SF_4. It should also be noted that the experiments with the lower SF_4 pressures were carried out after those at higher pressures (see Tab. I) and that new SF_4 samples were used every time. SOF_2 was prepared through reaction (1) by putting SF_4 in contact with water vapor. This procedure only allowed us to obtain low pressure samples of SOF_2 and this explains why the absorption of this compound was restricted to wavelengths lower than 196 nm.

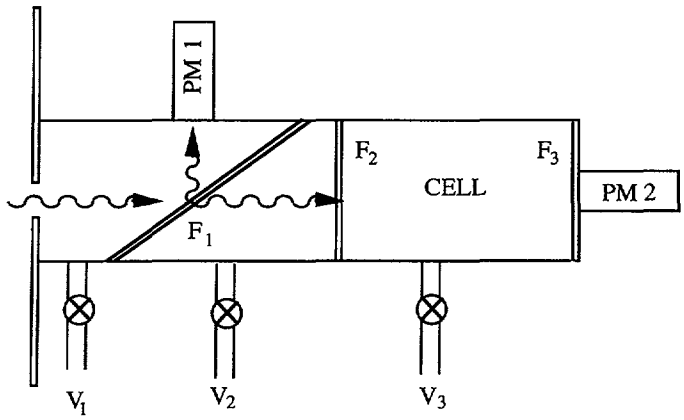

Fig. 1. — Schematic representation of the absorption cell.: (∿∿∿) monochromatized VUV photons. F_1, F_2 and F_3: MgF_2 windows (thickness 1.3 mm; cut-off wavelength 115 nm). F_1: photon beam splitter; allows a small fraction of the incident photon flux to be reflected, the other part being transmitted. F_2 constitutes the entrance window of the absorption cell. F_3 is coated on its outside surface with sodium salicylate (fluorescent material whose maximum intensity of fluorescence is located at 420 nm [23] and which coincides with the maximum sensitivity of the cathode of the photomultipliers PM_1 and PM_2). PM_1 and PM_2: Hamamatsu model R268 photomultipliers. PM_1: reference photomultiplier; its photocathode is coated with sodium salicylate. It measures the photons reflected by F_1 and therefore allows the incident photon flux to be checked all along the experiment. PM_2: photomultiplier measuring the photon flux transmitted through the cell. The absorption cell (inside diameter 40 mm; optical length d = 136 mm) is made of stainless steel and can be filled up to a gas pressure of 100 kPa. V_1 and V_2: connecting valves to primary and secondary pumps. V_3: connecting valve of the cell to the pump and to the gas filling system. It is also connected to a vacuum gauge and to three pressure gauges (5 Pa $\leq P \leq$ 100 kPa).

The absorption spectrum of each gas was divided into between two and four overlapping regions of about 30 nm width. The absorption spectrum over these different wavelength intervals was measured by determining the photon flux intensity when the cell was evacuated, followed by the intensity when the cell was filled with the gas. For each region, absorption measurements were made at five or more values of the gas pressure. Table I gives the pressure range studied according to the wavelength range considered for SF_6, SF_4, SOF_2 and SO_2F_2. The output signals of the photomultipliers were graphically recorded synchronously as the monochromator scanned at a rate of 0.06 nm per second. The uncertainty on the wavelength values from data set to data set was typically ± 0.05 nm.

The absorption coefficient k_0 was calculated from Beer-Lambert's law

$$I = I_0 \exp\left(-k_0 \frac{P}{P_0}\, d\right) \tag{2}$$

where I_0 and I are the incident and the transmitted intensities respectively at a wavelength λ and a temperature T, d is the path length, $P_0 = 10^5$ Pa and P is the absolute pressure in the absorption cell in Pa. For all our experiments d was equal to 13.6 cm (see Fig. 1) and T to 298 ± 2 K.

Table I. — *Gas pressures used for absorption measurements*

Gas	Wavelength (nm)	Pressure (Pa)
SF_6	115 – 145	$50 - 10^3$
	140 – 160	$2 \times 10^3 - 7 \times 10^4$
	155 – 185	$2 \times 10^4 - 10^5$
SF_4	115 – 145	$5 - 10^2$
	140 – 165	$50 - 10^3$
	160 – 195	$50 - 5 \times 10^2$
	190 – 220	$10^2 - 1.5 \times 10^4$
SOF_2	120 – 145	$10 - 10^2$
	140 – 195	$50 - 7 \times 10^2$
SO_2F_2	120 – 145	$10 - 5 \times 10^2$
	140 – 160	$10^2 - 10^3$
	155 – 170	$10^3 - 10^4$
	165 – 200	$5 \times 10^3 - 3 \times 10^4$

Figure 2 displays a number of typical plots of ln (I_0/I) *versus* P at several wavelengths for SF_6. No systematic deviations or curvatures in these plots were observed, indicating that for the range of pressures and the spectral resolution used in our experiments Beer-Lambert's law was obeyed. Similar behavior was observed, for all wavelengths, for the other gases studied. The values of k_0 given in Figures 3 to 5 were obtained from the slopes of these plots. From reproducibility tests carried out over the total wavelength range considered we asses the uncertainty on the absorption coefficient to be about ± 10% for the highest and the lowest values and slightly better (± 6%) for the others.

3. Results and Discussion

3.1. SF_6. — Figure 3 shows the results obtained for the three samples of SF_6 studied. For $\lambda < 135$ nm, the three curves are practically superimposed indicating that in this zone, the absorption measured corresponds only to SF_6. The differences that appear between curve A and curves B and C over 135 nm and between curves B and C over 150 nm confirm the presence of variable quantities of O_2 (maximum absorption at around 142 nm [13–15]) and of H_2O (maximum absorption at around 165 nm [13–15]) in the samples of SF_6 studied. In particular, the shape of curve B between 160 and 180 nm is almost identical to that of the variation of H_2O absorption over the same wavelength range [13–15]. It is therefore curve C that best represents the absorption of pure SF_6.

From these curves and those of the absorption of O_2 and H_2O published in the literature [13–15] we determined the quantities of O_2 and H_2O contained in the three samples of SF_6 from the relationship:

$$\left(\frac{k_0}{\rho}\right)_{\text{mixture}} = \left(\frac{k_0}{\rho}\right)_{SF_6} \alpha_{SF_6} + \left(\frac{k_0}{\rho}\right)_{O_2} \alpha_{O_2} + \left(\frac{k_0}{\rho}\right)_{H_2O} \alpha_{H_2O} \tag{3}$$

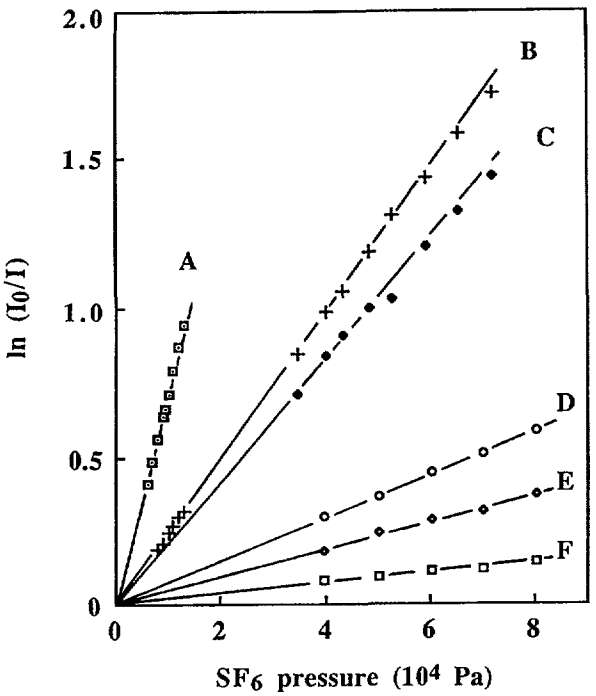

Fig. 2. — Plot of ln (I_0/I) *versus* SF_6 pressure for different wavelengths. T = 298 K. Curve A: 145.6 nm. Curve B: 149.1 nm. Curve C: 149.7 nm. Curve D: 165.9 nm. Curve E: 175.4 nm. Curve F: 180 nm.

where $\left(\frac{k_0}{\rho}\right)_{SF_6}$, $\left(\frac{k_0}{\rho}\right)_{O_2}$ and $\left(\frac{k_0}{\rho}\right)_{H_2O}$ are the mass absorption coefficients and α_{SF_6}, α_{O_2} and α_{H_2O} the percentages in mass of pure SF_6, of O_2 and of H_2O respectively for a given wavelength.

The curve $(k_0/\rho)_{SF_6}$ *versus* λ was obtained from curve C of Figure 3 by considering that in the absence of water vapor, the absorption coefficient of SF_6 continues to decrease between 155 nm and 185 nm like it did from 140 nm to 155 nm. This hypothesis is in agreement with the results of previous tests performed at a pressure of 300 kPa and an optical path of 8 cm which showed that the absorption of SF_6 is practically nil for $\lambda \geq 190$ nm [28].

Fitting the theoretical curves, $k_0 = f(\lambda)$, calculated from equation (3), for variable concentrations of O_2 and H_2O to the experimental curves A, B and C of Figure 3 enabled us to determine the quantities of these two gases present in the various samples of SF_6 studied. The O_2 and H_2O concentrations were first varied with steps of about 100 ppm_v and as the fittings started to become relatively correct the steps were reduced to 10 ppm_v or less and modified until the differences between the theoretical and the experimental curves were minimized. The following results were deduced from the best fittings:

- the sample of SF_6 leading to curve A contained 600 ppm_v H_2O and 4 500 ppm_v O_2;
- the sample of SF_6 giving curve B contained 500 ppm_v H_2O and 60 ppm_v O_2;
- the sample of SF_6 corresponding to curve C contained 125 ppm_v H_2O and less than 5 ppm_v O_2.

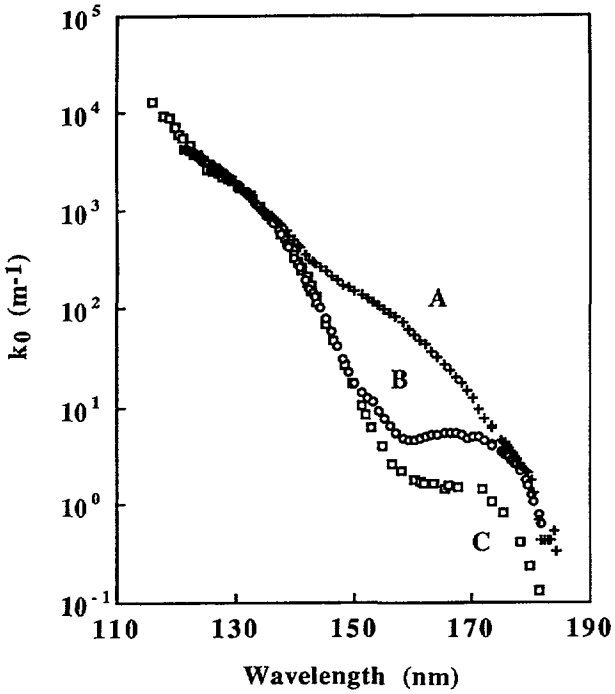

Fig. 3. — Measured absorption coefficient (k_0) for three gaseous SF_6 samples. T = 298 K. Curve A: SF_6 containing 600 ppm_v H_2O and 4 500 ppm_v O_2. Curve B: SF_6 containing 500 ppm_v H_2O and 60 ppm_v O_2. Curve C: SF_6 containing 125 ppm_v H_2O and less than 5 ppm_v O_2. The k_0 values are given for a gas pressure of 100 kPa.

The precision on the values of the O_2 and H_2O contents is about ± 8%.

Figure 4 enables a comparison to be made between our results (curve C of Fig. 3) and those obtained by Bastien *et al.* [12]. The corresponding curve A was obtained by digitisation of the curve published by these authors. It can be noted that the two curves of Figure 4 are practically superimposable between 130 about 145 nm whereas between 120 and 130 nm, the results of Bastien *et al.* [12] lead to values of k_0 that are higher than the ones we obtained independently of the quality of the SF_6. This could be due to a difference of accuracy (and/or to calibration errors) of the gauges used to measure the absolute pressure of SF_6 (note that for this wavelength range, the pressures of SF_6 that must be used to determine k_0 are very low: see Tab. I) and also possibly to the presence, in their SF_6, of impurities other than water and oxygen. The difference that appears for $\lambda > 145$ nm can be put down to O_2 and H_2O: applying equation (3) to the results of Bastien *et al.* [12] indicated that the SF_6 they used contained about 200 ppm_v of H_2O and 1 200 ppm_v O_2.

Our results, like those of the literature [3,11,12] show that SF_6 presents a continuous absorption between 180 and 115 nm. This absorption is not related to the ionization of the gas, which is known to have an ionization potential at about 16 eV [3,8,9,11]. According to Sasanuma *et al.* [8], it can be assigned to the transition $5t_{1u} - 6a_{1g}$ with an energy of 8.7 eV. It therefore most probably gives rise to dissociation processes that, as emphasized by Herzberg [29], are difficult to identify owing to the existence, in each electronic state, of several dissociation limits corresponding to different dissociation products. A molecular photoelimination process leading

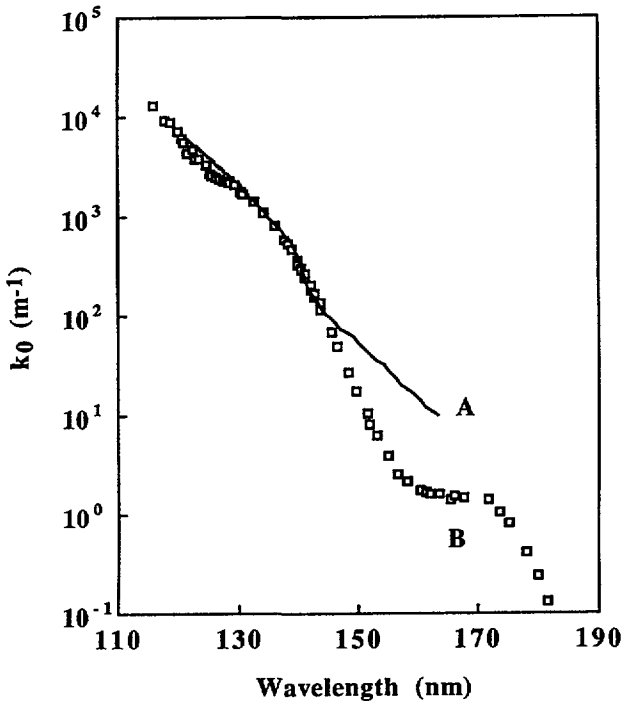

Fig. 4. — Comparison of the measured absorption coefficient k_0 for our purest gaseous SF_6 sample (curve B; this curve corresponds to curve C of Fig. 3) with that published by Bastien *et al.* [12] (curve A). The k_0 values are given for a gas pressure of 100 kPa.

to the production of SF_4 was indeed demonstrated for values of λ of 121.6 nm, 106.7 nm and 104.8 nm by Smardzewski and Fox [30]. For shorter wavelengths, these authors also observed the formation of substantial amounts of SF_5 radical and of much smaller amounts of the SF_3 radical.

3.2. SF_4. — The values of k_0 obtained for SF_4, SOF_2 and SO_2F_2 are reported in Figure 5. Moreover, for the sake of comparison, the curve of the absorption of our purest SF_6 sample (curve C of Fig. 3) has also been added to this figure.

Between 118 and 220 nm, SF_4 presents a much greater absorption than SF_6 with values of k_0 between 8.9×10^4 m^{-1} and 5 m^{-1} Evidence of structure is also observed with clear peaks occurring at 123, 135.9 and 182.5 nm.

3.3. SOF_2. — This compound also presents very strong absorption which, between 135 and 200 nm, resembles that of SF_4 with two maxima in this zone, one situated at 138 nm and the other at 180.6 nm i.e. slightly shifted with respect to those of SF_4. It should be noted that, concerning the peak at about 137 nm, SOF_2 presents higher absorption than SF_4 (2.26×10^4 m^{-1} *versus* 1.9×10^4 m^{-1}) but its absorption is weaker than that of SF_4 at around 181 nm (5.1×10^3 m^{-1} *versus* 1.55×10^4 m^{-1}). Between 120 nm and 135 nm, SOF_2 presents a third absorption peak ($k_0 = 4.5 \times 10^4$ m^{-1}) for $\lambda = 129.4$ nm whereas for the same wavelength, the absorption of SF_4 goes through a minimum. On the other hand, SOF_2 presents a minimum of absorption at around 123.6 nm whereas for this value of λ, SF_4 presents its maximum absorption ($k_0 = 8.9 \times 10^4$ m^{-1}).

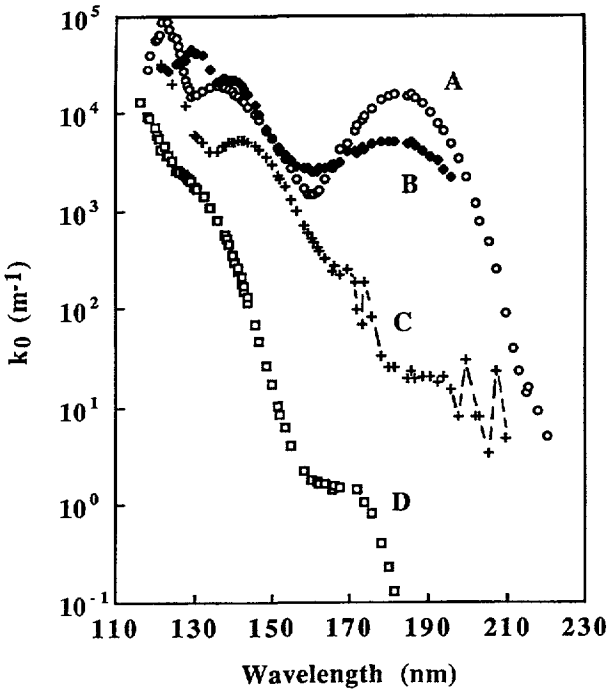

Fig. 5. — Measured absorption coefficient k_0 for SF_4 (curve A), SOF_2 (curve B), SO_2F_2 (curve C) and SF_6 (curve D; this curve corresponds to curve C of Fig. 3). $T = 298$ K. The k_0 values are given for a gas pressure of 100 kPa.

3.4. SO_2F_2. — The absorption curve of SO_2F_2 occurs between that of SF_6 and those of SF_4 and of SOF_2. It presents a structure which is much more complex than that of the others with a strongly attenuated maximum at 141.7 nm ($k_0 = 5.3 \times 10^3$ m^{-1}) and a series of narrow bands of variable amplitude superimposed on a continuum and situated at 166, 169.5, 173.6, 193.7, 199.7 and finally 207.4 nm. It should be noted that the absorption coefficients on these bands were independent of pressure (factor of about 10); thus, our spectral resolution was probably adequate.

4. Conclusion

Our results on SF_6 agree quite well with those previously published in the literature [12] and illustrate the importance of even low concentrations of impurities like oxygen and/or water on cold "SF_6" absorption.

The results obtained for SF_4, SOF_2 and SO_2F_2 are new. They show that these gases present considerable absorption in the wavelength range 115–220 nm. So, as these compounds, at least the first two, are formed in large amounts when SF_6 is submitted to arcs they would also contribute to the heating of the gas surrounding the plasma and therefore to the pressure increase inside the circuit-breaker.

Acknowledgments

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