

**Measurement of Absolute Rate Data for the Reaction of Atomic Potassium,  $K(4^2S_{1/2})$ , with  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CF_3Br$  and  $SF_6$  as a Function of Temperature by Time-resolved Atomic Resonance Absorption Spectroscopy at  $\lambda = 404\text{ nm}$  [ $K(5^2P_J) \leftarrow K(4^2S_{1/2})$ ]**

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We present a kinetic study of the reactions of atomic potassium in its electronic ground state,  $K(4^2S_{1/2})$ , with the molecules  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CF_3Br$  and  $SF_6$ . Atomic potassium was generated by pulsed irradiation of potassium halide vapour at elevated temperatures and monitored in the 'single-shot mode' by time-resolved atomic resonance absorption using the Rydberg doublet at  $\lambda = 404\text{ nm}$  [ $K(5^2P_J) \leftarrow K(4^2S_{1/2})$ ]. Absolute rate constants for reaction with these molecules were determined as a function of temperature yielding the following Arrhenius parameters (errors  $1\sigma$ ):

	$A/10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$	$E/\text{kJ mol}^{-1}$
$CF_3Cl$	$1.1 \pm 0.5$	$13.8 \pm 2.5$
$CF_2Cl_2$	$2.1 \pm 0.6$	$5.5 \pm 0.5$
$CFCl_3$	<i>ca.</i> 1	<i>ca.</i> 0
$CF_3Br$	$3.9 \pm 0.4$	$12.3 \pm 0.6$
$SF_6$	$8.4 \pm 1.33$	$12.3 \pm 0.9$

$CF_4$  exhibited anomalous kinetic behaviour. These results represent the first kinetic measurements, relative or absolute, for these fundamental reactions of atomic potassium. This new set of absolute rate data are compared with analogous results reported hitherto for atomic sodium,  $Na(3^2S_{1/2})$ , both alkali-metal atoms exhibiting rapid reactions characterised by small energy barriers and being highly exothermic in character.

With a limited number of exceptions, the experimental determination of absolute rate data for ground-state potassium atoms,  $K(4^2S_{1/2})$ , is a relatively recent development. This can be contrasted with measurements on ground-state sodium atoms using diffusion flames as employed in the 1930s, a technique we have compared briefly with time-resolved atomic resonance absorption spectroscopy<sup>1</sup> and which has been extensively reviewed in detail by Gowenlock *et al.*<sup>2</sup> With the main exceptions of reactions such as those of  $K(4^2S_{1/2})$  with  $HCl$ ,  $HBr$  and  $HI$  in highly dilute flames,<sup>3,4</sup> it is relative rate data for atomic potassium that have been derived from diffusion flames using competitive methods. A seminal paper in this context is that of Kerr *et al.*,<sup>5</sup> who describe the determination of ratios of Arrhenius  $A$  factors and differences in activation energies for reactions of  $K$  (and  $Na$ ) by analysis of the solid potassium halides produced on reaction with a mixture of a radioactively labelled organic halide ( $^{36}Cl$ ) and an unlabelled organic halide in diffusion flames in the range *ca.* 500–600 K. A similar approach has been employed by Emovon and Lissi.<sup>6</sup> A related procedure is to measure the production of  $KCl$  and  $KI$  solids following the reaction of  $K$  in mixtures of  $RCl$  and  $RI$ .<sup>7,8</sup> The modern compilation of Kerr and Moss<sup>9</sup> includes a summary of rate data for  $K(4^2S_{1/2})$ , primarily relative rate data, determined by the diffusion flame method.

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The method to be employed in this work of time-resolved atomic resonance absorption measurements on  $\text{K}(4^2\text{S}_{1/2})$  following pulsed irradiation of potassium halide vapours, originally developed by Davidovits and coworkers for the direct determination of absolute rate data of atomic potassium with molecular halogens,<sup>10-14</sup> was subsequently developed further by Husain and Plane<sup>15</sup> for the study of the third-order reactions between  $\text{K} + \text{O}_2 + \text{M}$  ( $\text{M} = \text{He}, \text{N}_2, \text{CO}_2$ ). That technique<sup>15</sup> was extended by Husain *et al.*<sup>16</sup> for the study of the reaction between  $\text{Na} + \text{O}_2 + \text{N}_2$  as a function of temperature, and has been applied by the present authors to the study of the rate of reaction between  $\text{K} + \text{O}_2 + \text{N}_2$  as a function of temperature<sup>17</sup> and that of  $\text{K} + \text{N}_2\text{O}$ .<sup>18</sup> An alternative approach for the direct kinetic study of atomic potassium in the time domain is that described by Kolb and coworkers, who have employed monitoring of  $\text{K}(4^2\text{S}_{1/2})$  by laser-induced atomic fluorescence on potassium in a fast-flow system.<sup>19</sup> In this paper we describe the first measurements of absolute rate data for the reactions of  $\text{K}(4^2\text{S}_{1/2})$  with the molecules  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CF}_3\text{Br}$  and  $\text{SF}_6$  using time-resolved atomic resonance absorption of the Rydberg doublet at  $\lambda = 404 \text{ nm}$  [ $\text{K}(5^2\text{P}_J) \leftarrow \text{K}(4^2\text{S}_{1/2})$ ].<sup>17,18</sup> There are no relative rate data for these reactions of atomic potassium with which we can compare our results, and such comparison is restricted to the data arising from the analogous study for  $\text{Na}(3^2\text{S}_{1/2})$  that we have described hitherto.<sup>1</sup> It is hoped that the present time-resolved measurements on atomic potassium, with those described previously using this method and those from monitoring atomic potassium in a fast-flow system, will partly remedy the sparsity of absolute bulk rate constants for  $\text{K}(4^2\text{S}_{1/2})$  and assist in the establishment of a body of fundamental rate data comparable to those for  $\text{Na}(3^2\text{S}_{1/2})$ .

### Experimental

The experimental arrangement followed that employed in recent publications.<sup>17,18</sup> Thus,  $\text{K}(4^2\text{S}_{1/2})$  was generated by pulsed irradiation in the 'single-shot mode' of potassium halide vapours<sup>20</sup> whose broad ultraviolet absorption spectra have been fully characterised.<sup>21,22</sup> For reactant gases such as  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$  and  $\text{CF}_3\text{Br}$ , a Pyrex sleeve was placed around the photoflash lamp to prevent photodissociation of those molecules below  $\lambda \approx 300 \text{ nm}$  following the procedure adopted for the study of the reactions of  $\text{Na}(3^2\text{S}_{1/2})$  with those gases.<sup>1,23</sup> However, the resulting degree of resonance absorption by atomic potassium with this procedure was found to be lower than that from the corresponding signals for  $\text{Na}(3^2\text{S}_{1/2})$ ,<sup>23</sup> and the resulting decay profiles were very scattered in quality, particularly at lower temperatures. An alternative method was employed using a photoflash lamp constructed of old quartz with lower light transmission in the ultraviolet (*ca.* 20% transmission at  $\lambda = 200 \text{ nm}$ ). This led to rate data for  $\text{K}(4^2\text{S}_{1/2})$  in agreement with those obtained using a Pyrex sleeve, where such a comparison was possible, indicating no significant effect of photolysis of the reactant molecules at the low concentrations employed in these measurements (see later). Atomic potassium was monitored by time-resolved atomic resonance spectroscopy using the unresolved Rydberg doublet at  $\lambda = 404 \text{ nm}$ <sup>24</sup> [ $\text{K}(5^2\text{P}_{1/2,3/2}) \leftarrow \text{K}(4^2\text{S}_{1/2})$ ,  $\lambda = 404.72 \text{ nm}$ ,  $gA = 0.48 \times 10^8 \text{ s}^{-1}$  and  $\lambda = 404.414 \text{ nm}$ ,  $gA = 0.95 \times 10^8 \text{ s}^{-1}$ ,<sup>†</sup> respectively<sup>25</sup>]. We emphasise the use here of the high-intensity, high-current (200 mA, 400 V) hollow-cathode spectroscopic resonance source operating at this wavelength which we have developed for time-resolved studies on  $\text{K}(4^2\text{S}_{1/2})$ .<sup>17,18</sup> The photoelectric signals at  $\lambda = 404 \text{ nm}$  (E.M.I. 9783 B photomultiplier tube) were optically isolated by means of a grating monochromator (Hilger and Watts Monospek 1000; typical slit width *ca.* 0.5 nm). They were then amplified without distortion,<sup>26</sup> captured, digitised and stored in a transient recorder (Data Laboratories DL 902) employed in the A/B mode,<sup>17,18</sup> which was interfaced directly (8PI0 parallel interface) to a microcomputer (Comart CP 200) for analysis of the signals.

<sup>†</sup> $gA$  is the product of atomic degeneracy and the Einstein coefficient.

It has been demonstrated from the combination of 'curve-of-growth' measurements<sup>15,27</sup> and the analysis of kinetic profiles for  $K(4^2S_{1/2})$ <sup>17</sup> that, under the present optical conditions, the Beer-Lambert law may be applied for degrees of resonance light absorption of  $<ca. 40\%$ . This law, coupled with an overall first-order kinetic decay for  $K(4^2S_{1/2})$  of the form

$$c = c_0 \exp(-k't) \quad (i)$$

where  $c = [K(4^2S_{1/2})]$  yields the further form for the variation of the transmitted light intensity at  $\lambda = 404$  nm in the present measurements:

$$I_{tr}(\lambda = 404 \text{ nm}) = I_0 \exp[-A \exp(-k't)]. \quad (ii)$$

$I_0$  is the unattenuated photomultiplier signal at  $\lambda = 404$  nm measured on the B sweep of the transient recorder. The overall first-order decay coefficient,  $k'$ , for the removal of  $K(4^2S_{1/2})$  is the object of kinetic interest. This is determined by iterative fitting of the observed profiles for  $I_{tr}(t)(\lambda = 404 \text{ nm})$  directly to eqn (ii).<sup>16</sup> This was found to be more 'robust' than the standard first-order kinetic form:

$$\ln[\ln(I_0/I_{tr})] = -k't + \text{constant} \quad (iii)$$

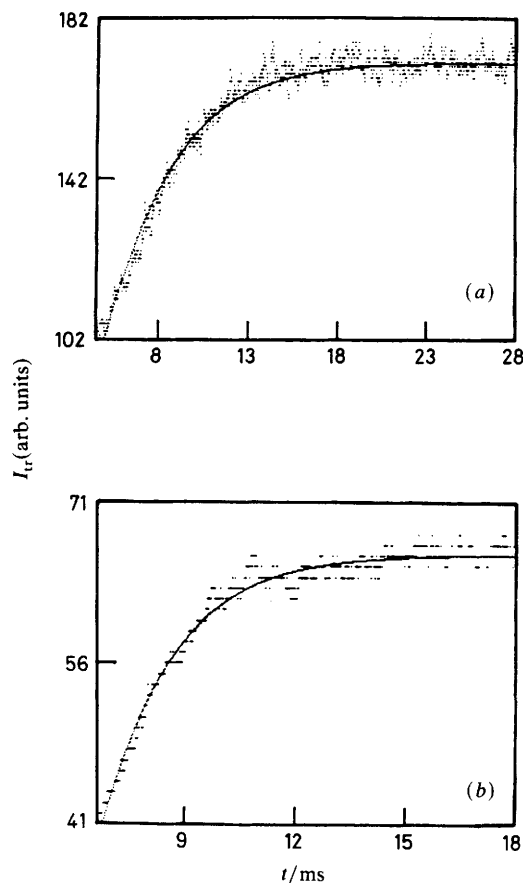
as it avoids large errors that are generated when employing the logarithm of  $I_0/I_{tr}$ , as this tends to unity at long decay times. All materials were essentially prepared as described in previous publications.<sup>1,15-18,23</sup>

## Results and Discussion

### Diffusion

Husain and Plane<sup>15</sup> have reported data for the diffusion of  $K(4^2S_{1/2})$  in He at  $T = 753$  and 873 K using the original experimental system for time-resolved atomic absorption spectroscopic measurements of the absolute rate constants for the reaction between  $K + O_2 + M$ . However, the resulting values for the diffusion coefficient  $D_{12}(K\text{-He})$  were too scattered to permit extraction of the temperature dependence of this quantity over the necessarily limited temperature range available in that system. This is briefly investigated here, as diffusional loss must be quantitatively accounted for in the procedure used for the rate measurements between  $K(4^2S_{1/2})$  and the reactants RX (see later). It also establishes, as in the earlier time-resolved measurements of the rate constants for  $K + O_2 + N_2$  as a function of temperature,<sup>17</sup> that the experimental system is 'kinetically clean', namely, sensibly free from the effect of rapid removal of  $K(4^2S_{1/2})$  by any  $I_2$  generated from the overall photolysis process. Edelman and Davidovits<sup>11</sup> have reported the cross-section for the reaction between  $K + I_2$  ( $\sigma^2 = 127 \text{ \AA}^2$ ;  $10 \text{ \AA} = 1 \text{ nm}$ ) corresponding to an absolute reaction rate constant of  $3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at a typical temperature of, say, 800 K in these measurements. Thus a first-order rate coefficient of magnitude  $100 \text{ s}^{-1}$  for the removal of  $K(4^2S_{1/2})$  by  $I_2$  would only require the presence of  $ca. 3 \times 10^{-6} \text{ Torr}$  ( $1 \text{ Torr} \approx 133.3 \text{ N m}^{-2}$ ) of the molecular halogen. Iodine atom recombination for the atomic densities involved would be very slow in the present measurements,<sup>15,28</sup> and statistical-thermodynamic considerations lead to the conclusion that the equilibrium  $I_2 \rightleftharpoons 2I$  lies to the atomic side.

Fig. 1 gives examples of the digitised time-variation of the transmitted light intensity at  $\lambda = 404$  nm [ $K(5^2P_j) \rightarrow K(4^2S_{1/2}) + h\nu$ ], indicating the decay of resonance absorption by  $K(4^2S_{1/2})$  in the presence of He alone at the two extremes of temperature over which diffusion was investigated (684 and 907 K) following the pulsed irradiation of KI, the photochemical precursor. It has been shown that relaxation of any electronically excited K or I atoms, generated photochemically, will take place rapidly in comparison with the timescales employed here for the kinetic measurements *via* spontaneous emission and collisional quenching,<sup>15</sup> as will the removal of kinetic energy from the atomic

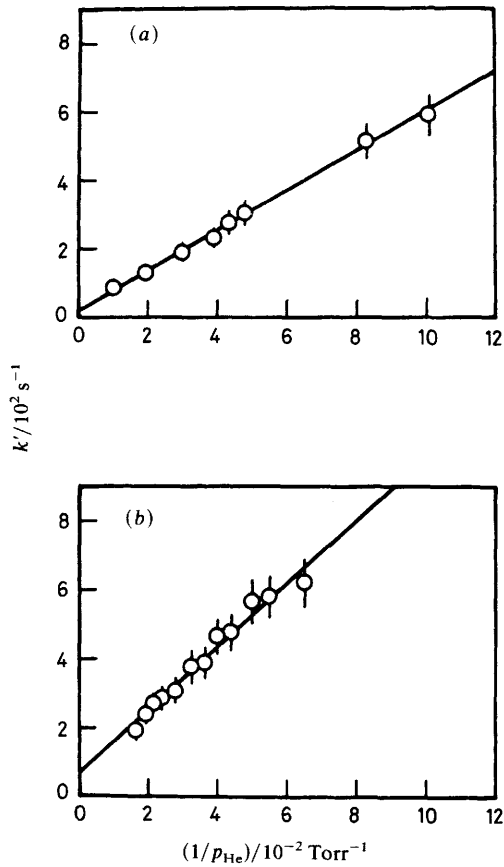


**Fig. 1.** Examples of the digitised time-variation of the transmitted light intensity at  $\lambda = 404$  nm [ $\text{K}(5^2P_j) \rightarrow \text{K}(4^2S_{1/2})$ ], indicating the decay of resonance absorption by ground-state potassium atoms in the presence of He at different temperatures following the pulsed irradiation of KI, (:) digitised data points; smoothed curve, computerised fitting to the form  $I_{tr} = I_0 \exp[-A \exp(-k't)]$ , (a)  $T = 684$  K,  $p_{\text{He}} = 21$  Torr,  $E = 245$  J; (b)  $T = 907$  K,  $p_{\text{He}} = 20$  Torr,  $E = 80$  J.

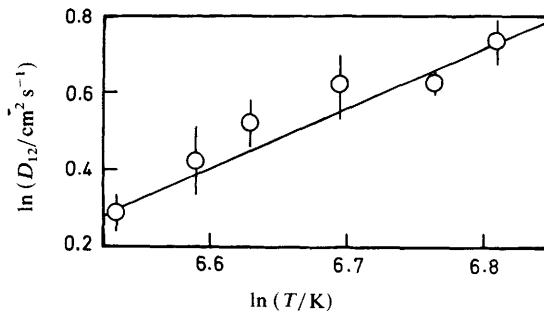
potassium photofragment, in particular by collisions with He. Fig. 2 shows the variation of  $k'$ , derived from computerised fitting of traces of the type given in fig. 1 to eqn (ii), with the reciprocal of the pressure of helium, indicating the diffusional loss. The slope of such plots (fig. 2), coupled with the 'long-time' solution of the diffusion equation for a cylinder (radius  $r$  and length  $l$ );<sup>29,30</sup>

$$k' = (\pi^2/l^2 + 2.41^2/r^2)D_{12} \quad (\text{iv})$$

yields the diffusion coefficient  $D_{12}$  at each temperature, assuming loss of  $\text{K}(4^2S_{1/2})$  at the walls of the reactor on every collision. Fig. 3 shows the variation of  $D_{12}$  with temperature in logarithmic form obtained in this investigation. The results, arbitrarily placing all the error in the temperature dependence, can be expressed in the form  $D_{12}(\text{K-He}) = 4.5 \times 10^{-5} T^{1.58 \pm 0.15} \text{ cm}^2 \text{ s}^{-1}$  at atmospheric pressure. This can be compared with the recent result reported by Silver<sup>31</sup> of  $D_{12}(\text{K-He}) = (1.5 \pm 1.0) \times 10^{-4} T^{1.48 \pm 0.19} \text{ cm}^2 \text{ s}^{-1}$  at atmospheric pressure for the temperature range  $T = 301\text{--}734$  K, derived from laser-induced fluorescence measurements of  $\text{K}(4^2S_{1/2})$  in a fast-flow system. Extrapolation of the present results to s.t.p. yields  $D_{12} = 0.32_{-0.18}^{+0.42} \text{ cm}^2 \text{ s}^{-1}$ , spanning a factor of ca. five across the limits determined by the errors.



**Fig. 2.** Variation of the first-order rate coefficient ( $k'$ ) for the decay of  $\text{K}(4^2S_{1/2})$  derived from pulsed irradiation with the reciprocal of the pressure of He to obtain diffusional rate data, (a)  $T = 684 \text{ K}$ , (b)  $T = 907 \text{ K}$ .



**Fig. 3.** Variation of the diffusion coefficient of potassium atoms,  $\text{K}(4^2S_{1/2})$ , in helium as a function of temperature [ $\ln(D_{12})$  against  $\ln(T/\text{K})$ ] over the range 684–907 K.

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A similar extrapolation of the data of Silver<sup>31</sup> to s.t.p. yields  $D_{12} = 0.605 \text{ cm}^2 \text{ s}^{-1}$ , with the errors spanning a similar large range ( $2.297\text{--}0.069 \text{ cm}^2 \text{ s}^{-1}$ ), emphasising the difficulty in accurate measurement of the diffusion coefficient as a function of temperature even in a study solely dedicated to that end.<sup>31</sup> The two sets of measurements, by different techniques, thus yield temperature dependences that can be regarded as in accord and in agreement with a  $T^{1.5}$  variation expected on the basis of simple gas-kinetic theory.

Notwithstanding the errors in  $D_{12}$  generated by the small errors in the power dependence on temperature, the factor of *ca.* two for the two sets of data can be considered in the context of the sticking coefficient ( $\gamma$ ) considered by Silver<sup>31</sup> and in our previous paper, which included the measurement of  $D_{12}(\text{K-N}_2)$  as a function of temperature.<sup>18</sup> We have described a simplified computer simulation of a random walk of K atoms with constant step length, terminating at the wall of the vessel with probability  $\gamma$ . The principal input parameter is the mean free path which will be similar for K + He and K + N<sub>2</sub> at the present level of consideration. *Ca.* 1200 trajectories were followed for K + N<sub>2</sub> for a range of values of  $\gamma$ , the fraction of K atoms remaining as a function of time then being employed to extract a first-order decay coefficient for K( $4^2S_{1/2}$ ) and hence a value of  $D_{12}$  *via* eqn (iv). A further calculation involving a small difference in the mean free path is clearly not justified. It is sufficient to note that a factor of *ca.* two in  $D_{12}$ , as measured, will arise for a sticking coefficient of  $\gamma \approx 0.1$ . Clearly, K( $4^2S_{1/2}$ ) is removed by diffusional loss in the presence of He alone, and such loss will be similar to diffusional removal in mixtures of He + RX, where the fractional composition,  $f = P_{\text{RX}}/(P_{\text{He}} + P_{\text{RX}}) \approx 10^{-5}$  for the low concentrations of RX necessarily employed in the present measurements.

### Chemical Reaction of K( $4^3S_{1/2}$ ) + RX

Absolute rate data for the removal of K( $4^2S_{1/2}$ ) by the gases CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFCI<sub>3</sub>, CF<sub>3</sub>Br and SF<sub>6</sub> were determined by the procedure we have described for the study of the kinetic standard, K + N<sub>2</sub>O,<sup>18</sup> following analogous studies reported for the determination of absolute rate constants for the halogen abstraction reactions by transient Pb( $6^3P_0$ ).<sup>32,33</sup> Thus, the decay of atomic potassium was monitored for mixtures of fixed fractional composition  $f$   $\{f = [\text{RX}]/([\text{He}] + [\text{RX}])\}$  at different total pressures ( $p_T$ ) and, in turn, as a function of temperature. The diffusional and chemical contributions to the overall first-order decay coefficient,  $k'$ , thus both varied with each decay measurement and were separated using the dependence of the diffusional loss on the reciprocal of the total pressure as described in the preceding section. The reactions between K( $4^2S_{1/2}$ ) and the above molecules are found to be rapid, necessitating the use of low values of  $f$  (*ca.*  $10^{-5}$ ) in order to monitor the profiles of atomic potassium on timescales accessible in the present experimental arrangement. The resulting method employed avoids inaccuracies arising from the preparation of large numbers of mixtures in which  $P_{\text{He}}$  would be held constant, in order to keep the diffusional loss constant, with the accompanying inclusion of different, defined, low concentrations of RX, each separately made up in a series at a given temperature. Thus the combination of chemical reactions of K( $4^2S_{1/2}$ ):

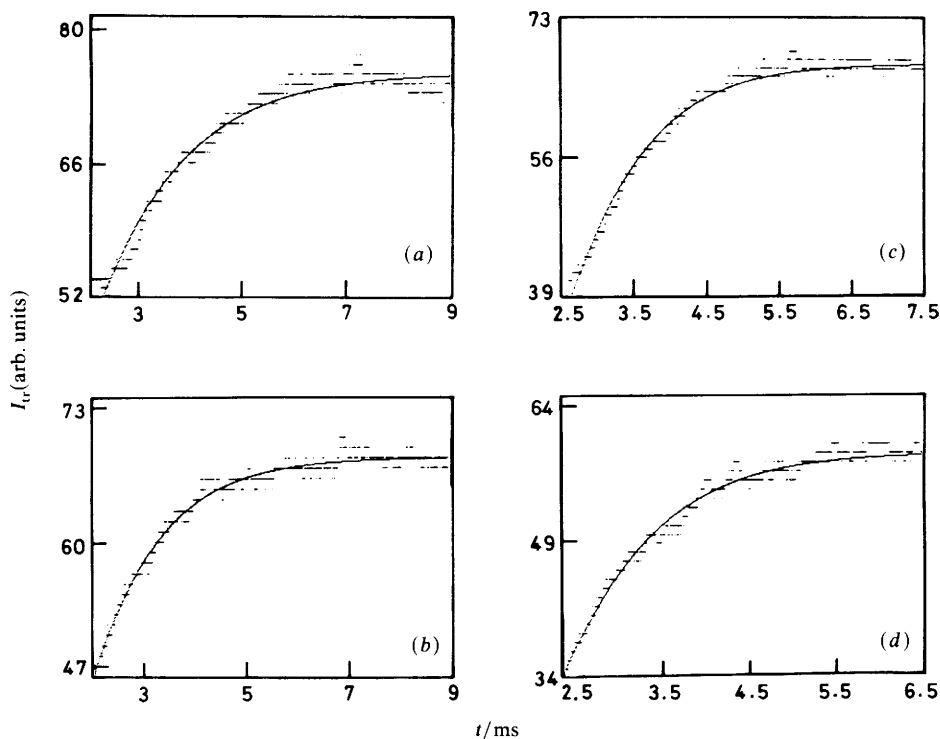


with diffusional loss following eqn (iv) will yield an overall first-order decay coefficient for atomic potassium given by

$$k' = \beta/p_T + k_R f p_T \quad (v)$$

where  $k_R$  is the absolute second-order rate constant for chemical reaction and the term  $\beta/p_T$  can be identified with the right-hand side of eqn (iv). As  $k_R$  is the object of interest in the present series of investigations, eqn (v) is recast in the form

$$k' p_T = \beta + k_R f p_T^2 \quad (vi)$$



**Fig. 4.** Examples of the digitised time-variation of the transmitted light intensity at  $\lambda = 404$  nm [ $\text{K}(5^2P_j) \rightarrow \text{K}(4^2S_{1/2})$ ], indicating the decay of resonance absorption by ground-state potassium atoms in the presence of  $\text{CF}_3\text{Cl}$  at different temperatures following the pulsed irradiation of KI, (·) digitised data points; smoothed curve, computerised fitting to the form  $I_{tr} = I_0 \exp[-A \exp(-k't)]$ .

	$T/\text{K}$	$f = [\text{CF}_3\text{Cl}]/([\text{He}] + [\text{CF}_3\text{Cl}])$	$p_T/\text{Torr}$	$[\text{CF}_3\text{Cl}]/10^{13} \text{ molecule cm}^{-3}$
(a)	758	$1.84 \times 10^{-4}$	17.1	4.0
(b)	809	$1.71 \times 10^{-4}$	18.1	3.7
(c)	848	$1.48 \times 10^{-4}$	21.9	3.7
(d)	915	$2.63 \times 10^{-5}$	33.4	3.4

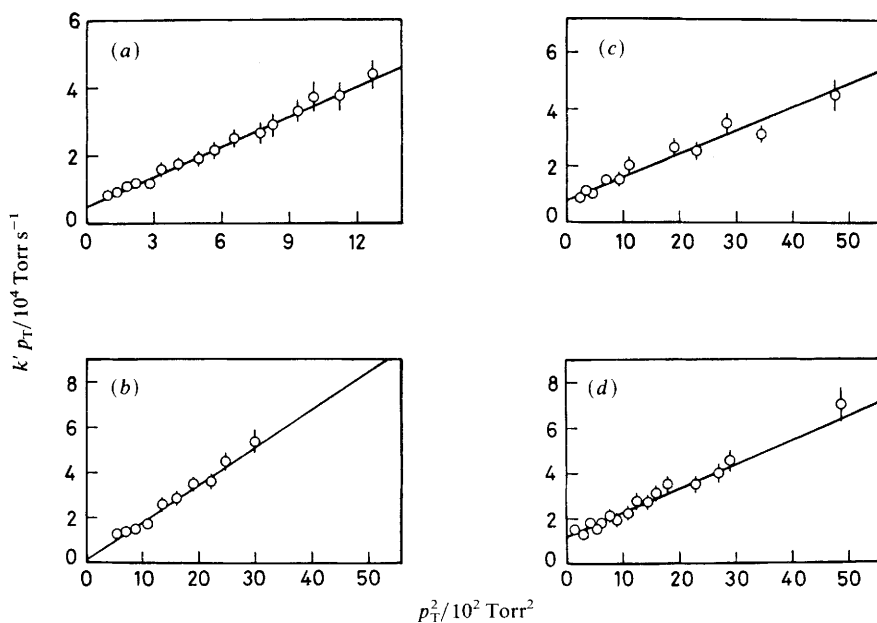
where  $k_R$  will be in the appropriate units of pressure ( $\text{Torr}^{-1} \text{s}^{-1}$ ). In this aspect of the investigation we are only concerned with the functional form of the diffusional loss and not with small differences in diffusion coefficients for mixtures of different fractional composition,  $f$ . For such an objective, eqn (v) could be recast in the form

$$k'/p_T = \beta/p_T^2 + k_R f \quad (\text{vii})$$

where  $\beta$ , and hence  $D_{12}[\text{K}-(\text{He} + \text{RX})]$ , would be determined from the slopes of plots based on eqn (vii). Whilst there is usually agreement between estimates of  $D_{12}$  determined from the intercepts of plots based on eqn (vi) and values reported in the preceding section, this is not pursued further.

Fig. 4 gives examples of decay traces for  $\text{K}(4^2S_{1/2})$  in the presence of one of the reactants, namely  $\text{CF}_3\text{Cl}$ , at approximately constant concentration by choice of atomic profiles for mixtures of appropriate fractional composition and total pressure, and as a



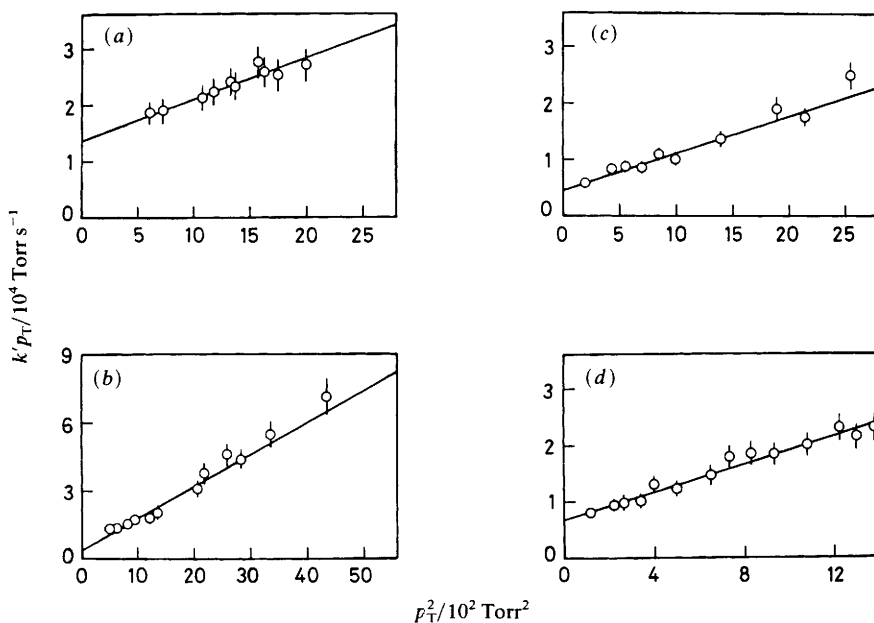


**Fig. 5.** Variation of  $k p_{\text{total}}$  against  $p_{\text{total}}^2$  of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{K}(4^2S_{1/2})$  in the presence of  $\text{CF}_3\text{Cl}$  and  $\text{CF}_2\text{Cl}_2$  following the pulsed irradiation of  $\text{KI}$  vapour at different temperatures, ( $f = [\text{CF}_3\text{Cl}], [\text{CF}_2\text{Cl}_2]/([\text{He}] + [\text{CF}_3\text{Cl}], [\text{CF}_2\text{Cl}_2])$ ), (a), (b)  $\text{CF}_3\text{Cl}$ ; (c), (d)  $\text{CF}_2\text{Cl}_2$

	$T/\text{K}$	$f$
(a)	809	$1.71 \times 10^{-4}$
(b)	915	$9.63 \times 10^{-5}$
(c)	773	$7.48 \times 10^{-6}$
(d)	834	$9.92 \times 10^{-6}$

function of temperature. The temperature range is determined, at the lower end, by the magnitude of the resonance absorption signal at  $\lambda = 404 \text{ nm}$  being sufficiently high for analysis in the single-shot mode following pulsed irradiation and, at the higher end, by the physical constraints of the quartz reactor and also effects due to secondary chemical reactions. The data of the type given in fig. 4 were analysed by computerised fitting to eqn (ii) to yield values of  $k'$  for different values of  $p_T$  at a given temperature. Fig. 5(a) and (b) give examples of the variation of  $k'$  with  $[\text{CF}_3\text{Cl}]$  at two temperatures plotted following eqn (vi) and yielding the appropriate absolute values of  $k_{\text{CF}_3\text{Cl}}$  for the reaction of  $\text{K}(4^2S_{1/2})$  with this molecule. An analogous pair of plots for  $T = 773$  and  $834 \text{ K}$  are given in fig. 5(c) and (d) for the reactant  $\text{CF}_2\text{Cl}_2$ . Similar examples are given in fig. 6 for the fast reactions of  $\text{K}(4^2S_{1/2})$  with  $\text{CF}_3\text{Br}$  and  $\text{SF}_6$  which exhibited small temperature dependences. No significant temperature could be determined for the reactant  $\text{CFCl}_3$ , and hence a plot based on eqn (vi) for this molecule is only given for a single temperature [fig. 7(a)]. Whilst the removal of  $\text{K}(4^2S_{1/2})$  with  $\text{CF}_4$ , which was also investigated in this study, yielded a series of good plots based on eqn (vi) and exhibited a significant temperature dependence, the resulting Arrhenius  $A$  factor was found to be anomalously low [ $A = (1.3 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ]. Similar behaviour was observed for the reaction between  $\text{Na} + \text{CF}_4$  [ $A = (8 \pm 4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ]<sup>1</sup> and was attributed



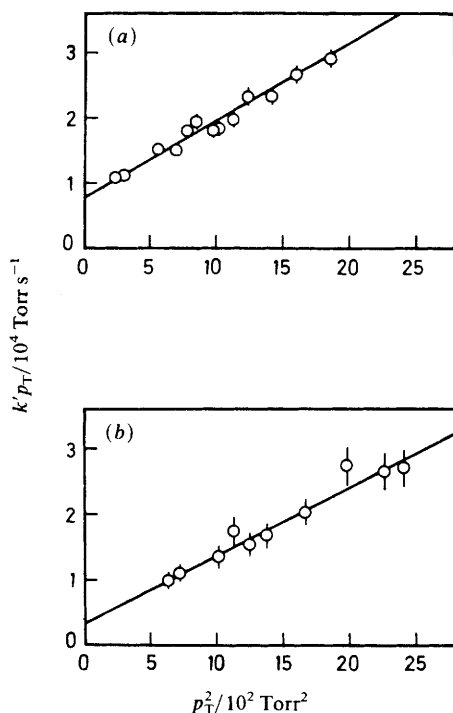


**Fig. 6.** Variation of  $k'p_{\text{total}}$  against  $p_{\text{total}}^2$  of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{K}(4^2S_{1/2})$  in the presence of  $\text{CF}_3\text{Br}$  and  $\text{SF}_6$  following the pulsed irradiation of  $\text{KI}$  vapour at different temperatures,  $f = [\text{CF}_3\text{Br}], [\text{SF}_6]/([\text{He}] + [\text{CF}_3\text{Br}], [\text{SF}_6])$ , (a), (b)  $\text{CF}_3\text{Br}$ ; (c), (d)  $\text{SF}_6$

	$T/\text{K}$	$f$
(a)	728	$1.11 \times 10^{-5}$
(b)	830	$1.84 \times 10^{-5}$
(c)	735	$4.6 \times 10^{-6}$
(d)	810	$3.25 \times 10^{-5}$

to the possible but non-defined effects of impurities at the 0.1% level, although purification had been carried out in both cases. For this reason a single example based on eqn (vi) for the removal of atomic potassium in the presence of  $\text{CF}_4$  is given in fig. 7(b). The absolute second-order rate constants for the reaction of  $\text{K}(4^2S_{1/2})$  determined in this investigation are listed in table 1.

Fig. 8 shows the resulting Arrhenius plots constructed from the data listed in table 1. The resulting Arrhenius parameters for  $\text{K}(4^2S_{1/2}) + \text{RX}$  are given in table 2 together with the analogous results for  $\text{Na}(3^2S_{1/2})$  determined previously,<sup>1</sup> which are the only data with which the present results may be compared. Clearly, there are limitations in the measurements in Arrhenius rate data for such atomic reactions, particularly for  $\text{K}(4^2S_{1/2})$ , determined over a limited temperature range at elevated temperatures and characterised by small activation energies, and emphasis cannot be given to small differences in Arrhenius parameters for a given reactant,  $\text{RX}$ . Halogen abstraction is highly exothermic in all cases, as seen from the relevant thermochemical data [ $D(\text{RX})/\text{kJ mol}^{-1}$ :  $\text{CF}_3\text{Cl}$  (360);  $\text{CF}_2\text{Cl}-\text{Cl}$  (318),  $\text{CFCl}_2-\text{Cl}$  (305),  $\text{CF}_3-\text{Br}$  (295),  $\text{SF}_5-\text{F}$  (376)].<sup>34</sup> The most recent compilation of Radzig and Smirnov<sup>35</sup> list the bond energies of the alkali-metal halides (in eV,  $1 \text{ eV} \approx 96.5 \text{ kJ mol}^{-1}$ ) with accuracies designated 'B', namely, to 3% [ $D(\text{Na}, \text{K}-\text{X})/\text{eV}$ :  $\text{NaF}$  (5.3),  $\text{NaCl}$  (4.2),  $\text{NaBr}$  (3.7),  $\text{KF}$  (5.1),  $\text{KCl}$  (4.3),  $\text{KBr}$  (3.9)]. Such errors, coupled with those of the bond dissociation energies used here for the reactants and arising from errors typically encountered in the



**Fig. 7.** Variation of  $k'p_{\text{total}}$  against  $p_{\text{total}}^2$  of the pseudo-first-order rate coefficient ( $k'$ ) for the decay of  $\text{K}(4^2S_{1/2})$  in the presence of (a)  $\text{CFCl}_3$  and (b)  $\text{CF}_4$  following the pulsed irradiation of KI vapour,  $f = [\text{CFCl}_3], [\text{CF}_4]/([\text{He}] + [\text{CFCl}_3], [\text{CF}_4])$ . (a)  $f = 9.4 \times 10^{-6}$ ,  $T = 787$  K; (b)  $f = 1.12 \times 10^{-2}$ ,  $T = 775$  K.

determination of appearance potentials, lead to overall errors that are much larger than small differences in activation energies for the reactions of  $\text{K}$  and  $\text{Na} + \text{RX}$ . An apparent activation energy for the reaction of  $\text{K} + \text{CF}_4$  of  $19 \text{ kJ mol}^{-1}$  cannot be readily reconciled with the thermochemistry of  $\text{F}$  atom abstraction [ $D(\text{CF}_3 - \text{F}) = 543 \text{ kJ mol}^{-1}$ ,<sup>34</sup>  $\Delta H = 51 \pm 24 \text{ kJ mol}^{-1}$ ], and is clearly coupled with the source of the anomalously low Arrhenius  $A$  factor (see later). It is not fruitful to pursue standard correlations between activation energies and bond energies or thermochemistry for a limited set of reactants or with electronic properties such as ionisation potentials for the atoms and electron affinities of the reactant molecules. We may note that, for the particular case of  $\text{K} + \text{SF}_6$ , molecular-beam studies for both reactive<sup>36</sup> and non-reactive<sup>37</sup> collisions have long been reported. For the former,<sup>36</sup> a statistical model based on a long-lived complex accounts satisfactorily for the angular distribution in the scattering data using a total cross-section ( $100 \text{ \AA}^2$ ) marginally larger than that derived from non-reactive scattering (*ca.*  $60 \text{ \AA}^2$ ).<sup>37</sup> The reactive scattering cross-section would yield an Arrhenius  $A$  factor for  $\text{K} + \text{SF}_6$  of  $7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $800 \text{ K}$ . This level of agreement with the  $A$  factor obtained here (table 2) is presumably fortuitous, but the nature of the result may be expected. The rate data for  $\text{K}(4^2S_{1/2})$  overall indicate rapid reaction and small energy barriers. Both sets of data for  $\text{K}(4^2S_{1/2})$  and  $\text{Na}(3^2S_{1/2})$  may prove useful later in more detailed consideration of the interaction between chlorofluorocarbons and alkali-metal species in an atmosphere containing both such materials. The present results constitute the first absolute rate data for this class of fundamental reactions undergone by atomic potassium.

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**Table 1.** Absolute second-order rate constants (errors  $1\sigma$ ) for the reaction of  $\text{K}(4^2S_{1/2})$  with  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CF}_3\text{Br}$  and  $\text{SF}_6$  at various temperatures determined by time-resolved atomic resonance absorption spectroscopy at  $\lambda = 404 \text{ nm}$  [ $\text{K}(5^2P_j) \leftarrow \text{K}(4^2S_{1/2})$ ]

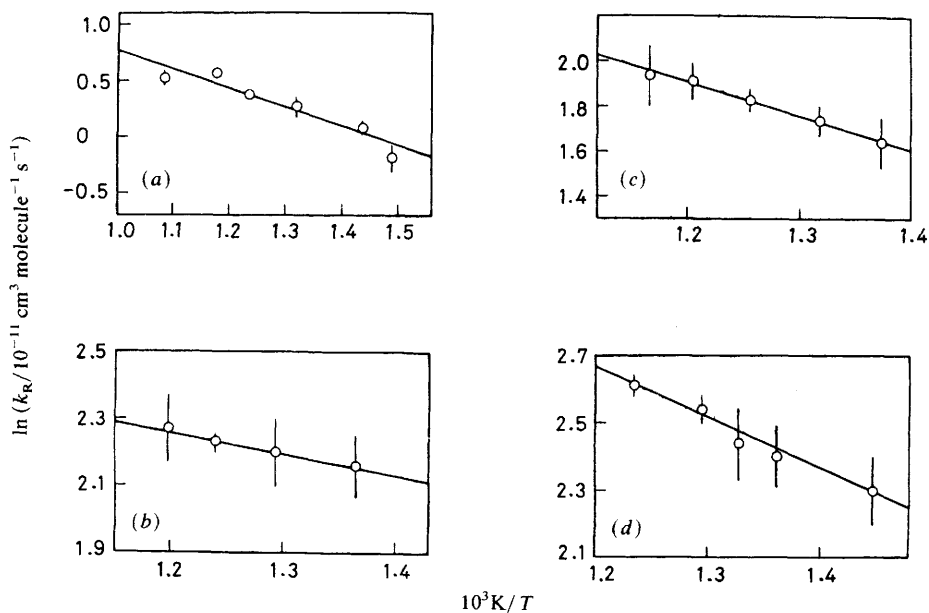
$T/\text{K}$	$k_{\text{CF}_3\text{Cl}}/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	$k_{\text{CF}_2\text{Cl}_2}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
672	$10.3 \pm 0.8$	739	$8.7 \pm 0.8$
696	$10.9 \pm 0.7$	773	$9.0 \pm 1.0$
758	$13.0 \pm 1.1$	806	$9.3 \pm 0.3$
809	$14.3 \pm 0.3$	834	$9.7 \pm 0.1$
848	$15.4 \pm 1.3$		
915	$16.7 \pm 1.1$		

$T/\text{K}$	$k_{\text{CFCl}_3}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$T/\text{K}$	$k_{\text{CF}_3\text{Br}}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
701	$10.8 \pm 0.7$	728	$5.0 \pm 1.0$
729	$10.4 \pm 0.6$	759	$5.7 \pm 0.4$
769	$13.5 \pm 0.6$	796	$6.2 \pm 0.3$
787	$10.6 \pm 0.5$	830	$6.7 \pm 0.5$
810	$10.6 \pm 1.4$	857	$6.9 \pm 1.3$

$T/\text{K}$	$k_{\text{SF}_6}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
691	$10.0 \pm 1.0$
735	$11.1 \pm 1.0$
753	$11.9 \pm 1.2$
773	$12.7 \pm 0.1$
810	$13.6 \pm 0.5$



**Fig. 8.** Arrhenius plots [ $\ln(k_R)$  against  $\text{K}/T$ ] for the reactions of  $\text{K}(4^2S_{1/2})$  with (a)  $\text{CF}_3\text{Cl}$ , (b)  $\text{CF}_2\text{Cl}_2$ , (c)  $\text{CF}_3\text{Br}$  and (d)  $\text{SF}_6$ .

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**Table 2.** Arrhenius parameters [ $k_{RX} = A \exp(-E/RT)$ , errors  $1\sigma$ ] for the reactions of  $K(4^2S_{1/2})$  and  $Na(3^2S_{1/2})$  with  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$ ,  $CF_3Br$  and  $SF_6$  determined by time-resolved atomic resonance absorption spectroscopy at  $\lambda = 404 \text{ nm}$  [ $K(5^2P_J) \leftarrow K(4^2S_{1/2})$ ] and  $\lambda = 589 \text{ nm}$  [ $Na(3^2P_J) \leftarrow Na(3^2S_{1/2})$ ]

atom	RX	$A/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$E/\text{kJ mol}^{-1}$
K	$CF_3Cl$	$1.1 \pm 0.5$	$13.8 \pm 2.5^a$
Na	$CF_3Cl$	$5 \pm 3$	$37 \pm 4^b$
K	$CF_2Cl_2$	$2.1 \pm 0.6$	$5.5 \pm 0.5^a$
Na	$CF_2Cl_2$	$5.6 \pm 1.2$	$18.7 \pm 1.5^b$
K	$CFCl_3$	<i>ca.</i> 1	<i>ca.</i> 0 <sup>a</sup>
Na	$CFCl_3$	$3.5 \pm 0.5$	$6.1 \pm 0.7^b$
K	$CF_3Br$	$3.9 \pm 0.4$	$12.2 \pm 0.6^a$
Na	$CF_3Br$	<i>ca.</i> 4	$10^b$
K	$SF_6$	$8.4 \pm 1.3$	$12.3 \pm 0.9^a$
Na	$SF_6$	$5.5 \pm 1.2$	$10.3 \pm 1.2^b$

<sup>a</sup> This work. <sup>b</sup> Ref. (1).

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