## COMMENT

## COMMENT ON "REACTION OF THE GROUND AND METASTABLE EXCITED CI<sup>+</sup> IONS WITH SEVERAL NEUTRAL MOLECULES AT 300 K" BY A.B. RAKSHIT

J.D.C. JONES, T.T.C. JONES, K. BIRKINSHAW and N.D. TWIDDY Department of Physics, U.C.W., Penglais, Aberystwyth, Dyfed, UK

Received 31 January 1981; in final form 18 April 1981

Metastable excited CI<sup>+</sup> was recently reported by Rakshit in a study using the Aberystwyth SIFT apparatus. We conclude that this report refers to a mixture of CI<sup>+</sup> and HCI<sup>+</sup>, and that the results are hence erroneous. Our recent work using the same apparatus gives no evidence for excited CI<sup>+</sup>.

In a recent publication [1] evidence was given for the presence of electronically excited  $Cl^+$  with a lifetime of  $\geq 25$  ms. The reactions of these ions with several molecules were studied using the methods described previously [2,3] and rate constants for the reactions were given. The above results are in conflict with results obtained subsequently using the same apparatus (the Aberystwyth SIFT) in which no excited states of  $Cl^+$  were observed [4].

A study of the original data of Rakshit indicates that the ion identified as  $Cl^{+*}$  was in fact  $HCl^{+}$  which was formed by electron bombardment of  $CH_3Cl$  in the ion source. It appears likely that adjacent ions in the mass spectrum were not fully resolved by the ion source and detector quadrupole mass filters with the result that the peak assumed to be  $Cl^{+}$  was in fact  $Cl^{+}$  and  $HCl^{+}$ .  $CO_2$  was used by Rakshit as a monitor gas and the appearance of  $CO_2^{+}$  was taken to indicate the presence of excited  $Cl^{+}$  as the charge transfer between ground-state  $Cl^{+}(^{3}P)$  and  $CO_2$  is endothermic. However, the original experimental data indicate that the reaction thought to be

 $Cl^{+*} + CO_2 \rightarrow CO_2^+ + Cl$ 

was in fact

 $HCI^+ + CO_2 \rightarrow CO_2H^+ + CI.$ 

Part of the evidence on which the above assertions are made is listed below:

(1) In the study of the reaction between  $CI^+$  and

CO, Rakshit used  $CO_2$  as a monitor gas. This is inappropriate as the reaction

$$CO^+ + CO_2 \rightarrow CO_2^+ + CO, \quad k = 1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1},$$

occurs rapidly [5], and therefore if  $Cl^{+*}$  reacted with CO to give CO<sup>+</sup> and CO<sub>2</sub> was used as monitor gas, the CO<sub>2</sub><sup>+</sup> concentration should be independent of CO flow rate and no CO<sup>+</sup> should be observed. Rakshit found that the ion CO<sup>+</sup> increased with CO flow rate and the CO<sub>2</sub><sup>+</sup> decay curve indicated a rate constant for the reaction

$$Cl^{+*} + CO \rightarrow CO^{+} + Cl \tag{1}$$

of  $7.1 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. Our results showed no decay of the mass 35 peak with CO flow rate but we observed the reaction

$$HCl^{+} + CO \rightarrow HCO^{+} + Cl$$
 (2)

to proceed with a rate constant of  $(8 \pm 2) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. We therefore conclude that Rakshit was in fact observing reaction (2) rather than (1), and the decay of "CO<sub>2</sub><sup>+</sup>" was in fact the decay of CO<sub>2</sub>H<sup>+</sup>;

(2) The reaction

$$C!^+ + H_2 \rightarrow HCl^+ + H_1$$

was studied by Rakshit using  $CO_2$  monitor gas. The intensity of " $CO_2^+$ " as a function of  $H_2$  flow rate showed an unusual maximum. As the  $H_2$  flow rate increased further the  $CO_2^+$  decayed with a slope, similar to that of  $HCI^+$  as observed by the direct method. A maximum

0 009--2614/81/0000--0000/\$ 02.50 © North-Holland Publishing Company

Volume 80, number 3

in the " $CO_2^+$ " curve is not understandable in terms of the presence of excited  $CI^+$  but could be understood if the  $CO_2^+$  observed by Rakshit is in fact  $CO_2H^+$  and the reaction

 $HCl^+ + CO_2 \rightarrow CO_2H^+ + Cl$ 

is the origin of the  $CO_2H^+$ .

The proton affinity of Cl can be calculated from the data given in ref. [6] to be 5.3 eV and therefore proton transfer from HCI<sup>+</sup> to the reactant gases except  $N_2$ ,  $O_2$  and  $H_2$  used by Rakshit is exothermic and would be expected to occur.

We have studied the reaction between  $CI^+$  and  $O_2$ using low mass resolution of the ion source and detector mass filters. The resulting overlap of  $CI^+$  and  $HCI^+$ peaks gave rise to the  $CO_2H^+$  ion (assumed by Rakshit to be  $CO_2^+$ ) which showed a single-exponential decay in contrast to the double-exponential decay in fig. 1 of ref. [1].

We therefore conclude that results obtained from the Aberystwyth SIFT have provided no evidence for the presence of long-lived excited states of  $Cl^+$ .

Note on Rakshit's reply. Rakshit has not answered the points raised in our Comment. The original data from which fig. 1 of Rakshit's reply is plotted appear to show that a drift of intensity was occurring which could explain the decay of the Cl<sup>+</sup>. The assumption that the presence of water reduced the  $N_2^+$  count rate by  $\approx 90\%$  is doubtful and we have observed that Cl<sup>+</sup> itself reacts with H<sub>2</sub>O. In his reply Rakshit concludes that Cl<sup>+\*</sup> is not produced by 40 eV electron impact on CH<sub>3</sub>Cl and is consequently at variance with his original paper in which fig. 1 shows data taken using a 40 eV electron energy which according to him show the presence of Cl<sup>+\*</sup>.

## References

- [1] A.B. Rakshit, Chem. Phys. Letters 75 (1980) 283.
- [2] J. Glosik, A.B. Rakshit, N.D. Twiddy, N.G. Adams and D. Smith, J. Phys. B11 (1978) 3365.
- [3] M. Tichý, A.B. Rakshit, D. Lister, N.D. Twiddy, N.G. Adams and D. Smith, Intern J. Mass Spectrom. Ion Phys. 29 (1979) 231.
- [4] A.S.M. Raouf, J.D.C. Jones, D.G. Lister, K. Birkinshaw and N.D. Twiddy, J. Phys. B13 (1980) 2581.
- [5] N.G. Adams, D. Smith and D. Grief, Intern. J. Mass Spectrom. Ion Phys. 26 (1978) 405.
- [6] J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl and F.H. Field, NSRDS-NBS 26 (1969);
  G. Herzberg, Spectra of diatomic molecules (Van Nostrand, Princeton, 1950).