

MOLECULAR SYNTHESIS IN INTERSTELLAR CLOUDS:  
THE RADIATIVE ASSOCIATION REACTION  $H + OH \rightarrow H_2O + h\nu$

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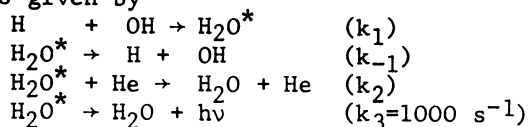
On the evidence of some recent laboratory data for the association reaction  $H + OH + He \rightarrow H_2O + He$ , and following previously proposed ion-neutral association reaction schemes, we tentatively suggest that the radiative association reaction of H and OH can be a significant mechanism for the production of  $H_2O$  in interstellar clouds, when compared with the ion-neutral reaction sequence. The 'H-atom + radical' association process may be of some general importance in the production of other small molecules in interstellar clouds.

## INTRODUCTION

Radiative association is an important, perhaps crucial, first step in gas-phase molecular synthesis. Rate coefficients are immeasurably small at laboratory-attainable temperatures, and methods have been developed for their estimation from third order rate data. It has been suggested that ion-molecule radiative association rate coefficients can be very large at interstellar temperatures<sup>1</sup>. Estimates have shown that rate coefficients for radiative association are generally very much greater than are predicted by statistical theories of unimolecular kinetics<sup>1,2</sup>. It would seem pertinent then to re-ask the question: is radiative association involving neutral radical species a significant mechanism for molecular synthesis in interstellar clouds?

## $H_2O$ FORMATION

In order to examine the question posed above we have chosen to investigate the reaction  $H + OH \rightarrow H_2O + h\nu$  ( $k_{rad}$ ). Data exist on the third order association reaction  $H + OH + He \rightarrow H_2O + He$  ( $k_{3rd}$ ) as a function of temperature between 300K and 230K<sup>3</sup>. The kinetic scheme for this reaction is given by



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from which one may deduce

$$k_{\text{rad}} = (k_3 k_3^{\text{rd}} / k_2)$$

and we have derived values for this coefficient down to interstellar temperatures. Values range from 4(-18) at 300K, 7(-15) at 50K, to 8(-14) at 20K. Lifetimes of  $\text{H}_2\text{O}^*$  ( $1/k_{-1}$ ) that these coefficients entail have also been calculated, and vary from 0.01 ns to 20 ns to 225 ns over the same temperature range. The temperature variation calculated for the vibrational deactivation of highly excited CO by He<sup>4</sup> has been employed in estimating the temperature variation of  $k_2$ . We have adopted the working hypothesis that data on the third order association reaction may be extrapolated to interstellar temperatures from 230K, and therein lies a major uncertainty. High temperature data do offer some support to our extrapolation<sup>3</sup> since they indicate that  $k_{-1}$  becomes an increasingly strong function of temperature as temperature drops. Theoretical considerations would also suggest that at low temperature shape- and Feshbach- resonances may be dominant in determining lifetimes of such intermediates as  $\text{H}_2\text{O}^*$ , tending to invalidate a basic approximation of statistical unimolecular theories.

#### IMPLICATIONS FOR $\text{H}_2\text{O}$ FORMATION IN INTERSTELLAR CLOUDS

Let us consider the cloud  $\zeta$  Oph as a representative example. For species concentrations that hold there<sup>5</sup>, it may be deduced that the rate of production of  $\text{H}_2\text{O}$  by radiative association at 50K is  $\sim 1 \times 10^{-16}$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Ion-molecule schemes suggest a rate roughly 6 times as great, indicating that the neutral-neutral path is at least significant and might become dominant at lower temperatures or in regions of low ionisation density.

We should emphasise that our derived values of  $k_{\text{rad}}$  are conservative and that the lifetimes of  $\text{H}_2\text{O}^*$  fit well with those that emerge from ion-molecule data. In comparing the importance of neutral mechanisms with ionic the specific environment will in general be decisive. Other association reactions of interest are  $\text{NH}_2(\text{H}, \text{NH}_3)h\nu$  (isoelectronic with  $\text{H}+\text{OH}$ ),  $\text{CH}(\text{H}, \text{CH}_2)h\nu$ ,  $\text{CH}_2(\text{H}, \text{CH}_3)h\nu$ ,  $\text{CH}_3(\text{H}, \text{CH}_4)h\nu$ , and  $\text{NO}(\text{H}, \text{HNO})h\nu$  amongst others. Further experimental and theoretical work is essential before radiative association becomes a firmly established mechanism for neutral systems. It would appear that the mechanism could be a viable one for many interstellar clouds.

#### REFERENCES

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