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Determination of the ionic and neutral chemical components of a H₂O microwave discharge plasma

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Abstract

Li⁺ ion attachment mass spectrometry was used to determine the ionic and neutral chemical components of a flowing microwave (MW) discharge plasma of H₂O. The plasma composition was investigated as functions of H₂O (in helium) flow rate (pressure) and MW-induced power input. Our study clearly showed the presence of various clustering compounds of water as well as their ionized species. Among compounds are the interesting ionic series H₃O⁺(H₂O)_nO (*n*=0–2) and (H₂O)_n⁺O (*n*=0–4), which have not been reported before. We consider the reaction schemes for some products, particularly with regard to the role of radical and ionic condensation reaction processes. We attempted to link both the ionic and neutral species to a mechanism. Our predictions indicate that, for example, the principal ionic condensation reaction can be summarized by the reaction sequence H₃O⁺(H₂O)_nX + H₂O → H₃O⁺(H₂O)_{n+1}X (X = O, OH), while involving the OH radical may lead to the formation of (H₂O)_nLi⁺OH adduct species. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The chemistry of a microwave (MW) discharge plasma of water vapor has been the subject of considerable study over the years. Much of the early work was directed toward identifying the intermediate species produced and elucidating a mechanism [1]. Although the discharge chemistry of H₂O molecules is an area of interest to many chemists [2–4], fundamental information is mostly lacking and, in certain instances, contradictory.

More recently, the nature of the H₂O discharge products collected at liquid nitrogen temperature and the behavior observed on warming these products have been extensively investigated to determine whether H₂O₂ is produced during the discharge [5–8]. Giguere et al. [9] reported the presence of H₂O₂ in the discharge products. However, experiments showed that no molecular H₂O₂ survived the discharge and that all of the H₂O₂ collected at low temperature could be attributed to heterogeneous reactions in the cold trap itself. The present gas-phase comparative study is relevant to the chemistry of the H₂O discharge plasma.

Many methods are used for the analysis of a plasma: optical emission and absorption spec-

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troscopy, mass spectrometry, laser-induced fluorescence, and in situ ellipsometry. Among these, mass spectrometric analysis of reactive plasmas is a relatively simple and efficient tool for studying the complex reactions induced by discharges in molecular gases. However, conventional mass spectrometric separation and analytical techniques cannot be used for mixture analysis in this type of plasma.

Li^+ ion attachment mass spectrometry [10,11] has been shown to be a useful technique for determining both neutral and ionic transient species simultaneously. In previous C_2H_2 studies [12], novel polyacetylene cations and their neutrals were prepared, and their mass spectra were measured for comparison. A natural extension is to study water plasma. Identifying both neutral and ionic species would lead to a better understanding of the H_2O MW plasma and the complex reaction processes that take place in the plasma.

Here, we describe the use of Li^+ ion attachment mass spectrometry to analyze the neutral and ionic products (including radical species) in a H_2O MW discharge plasma. We propose a possible scheme for the formation of these products and establish the relative importance of the neutral and ionic processes. Plasma composition was investigated as functions of both H_2O (in helium) flow rate (pressure) and MW power input.

2. Experimental

2.1. Apparatus

The experimental setup consisted of a MW discharge flow tube, a reaction chamber, and a mass spectrometer. A detailed description of the experimental setup can be found elsewhere [13,14]. We briefly review the main points here and describe changes made for this study.

Lithium ions were produced by heating a glass bead (Li^+ emitter) that contained lithium oxide in an aluminosilicate matrix. Emissions produced by the discharge gradually decreased. This decrease corresponded to a decrease in adduct production of about the same magnitude. Emissions gradually increased again in propor-

tion to the time the discharge was off. Thus most mass spectral analyses were corrected for variation of Li^+ emission.

The MW discharge flow system was of conventional design. The system employed a 2.465-GHz MW generator and a straight quartz flow tube (inner diameter, 4 mm; outer diameter, 6 mm; length, 30 cm). The MW plasma was created by connecting a cavity to the MW generator through a matching network. The cavity could be moved along the flow tube. Water vapor, generally flowing at ca. 6 ml/min in the discharge tube, was admitted by evaporation through a calibrated needle valve from a liquid sample at room temperature. The carrier gas was helium.

Mass spectra were obtained in either the presence (a) or the absence (b) of Li^+ . The intensity of any mass peak in a was subtracted from the intensity of the corresponding mass peak in b to give the intensity of the Li^+ adduct of a particular neutral product. Mass spectra were measured downstream of the MW cavity, and the presence of ionic and neutral species, including free radicals, in the plasma was determined. Mass was measured, and peak height was determined for each mass peak. Plasma composition was investigated as functions of the following parameters: $\text{H}_2\text{O}/\text{He}$ composition in the reaction chamber (the partial pressure of He was varied between 2 and 64 Pa with a constant total pressure of 100 Pa; the corresponding H_2O flow rates in the flow tube were between ca. 0.4 and 12.8 ml/min); MW power input (30–110 W).

3. Results and discussion

3.1. Product analysis (mass spectrum)

Typical mass spectra of the H_2O plasma were obtained over the range m/z 10–100 when the Li^+ emitter was on (Fig. 1a) and off (Fig. 1b). Since fragmentation can be assumed to be negligible, the additional peaks in Fig. 1a are attributed to Li^+ ion attachment to genuine chemical-neutral species effusing from the plasma; the peaks in Fig. 1b are due to ionic species formed in the plasma. The presence of various neutral discharge products

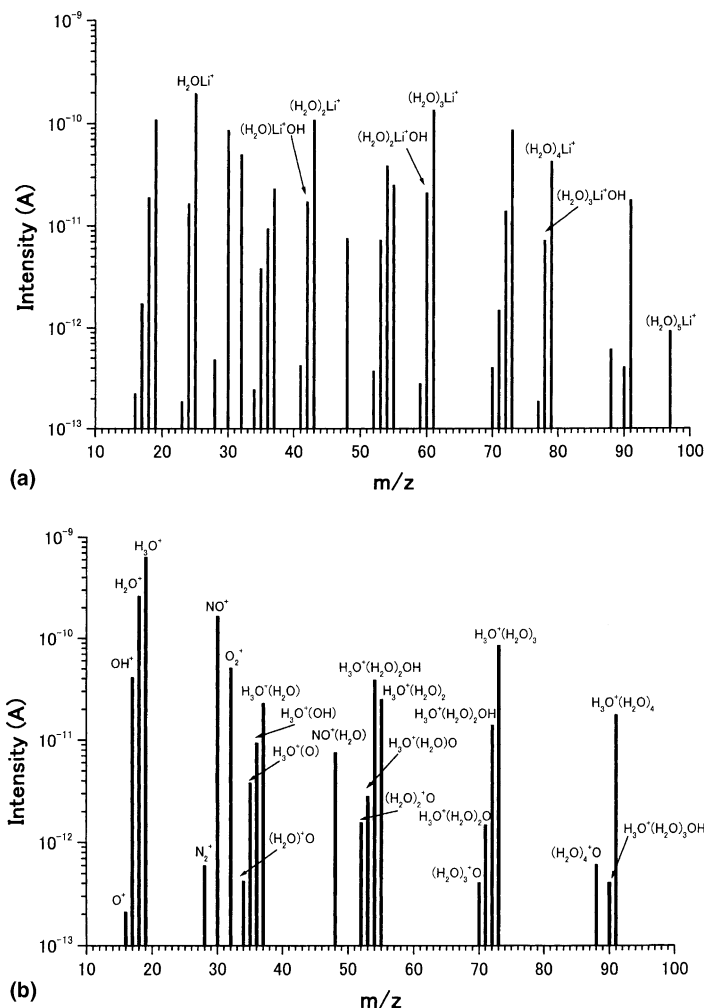


Fig. 1. Mass spectra of a 30-W, H_2O (30 Pa)/He (70 Pa) MW discharge: (a) sampled in the Li^+ -on condition; (b) sampled in the Li^+ -off condition (ionic species detection).

(labeled as Li^+ adducts in Fig. 1a) is denoted by an increase in the current of the Li^+ adduct ions.

With some exceptions, peaks with signal intensities of more than 10^{-13} A are reported. When neutral products are detected by Li^+ ion attachment, the sensitivity depends on the Li^+ affinity. Fortunately, H_2O -clustering species have sufficiently high Li^+ affinities to attach at nearly collision rates, so little discrimination is expected.

Table 1 identifies and classifies the ionic and neutral species observed in the mass spectra. Cation and neutral species (Li^+ ion adduct) of the

forms $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{O}$, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{OH}^+$, $(\text{H}_2\text{O})_n^+\text{O}$, $(\text{H}_2\text{O})_n\text{Li}^+$, and $(\text{H}_2\text{O})_n\text{Li}^+\text{OH}$ were detected in the mass spectra. Their relative abundances seem not to vary smoothly with n with the exception of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{O}$ and $(\text{H}_2\text{O})_n\text{Li}^+\text{OH}$. Note that $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{O}$ and $(\text{H}_2\text{O})_n\text{Li}^+\text{OH}$ have smooth dependencies that are different from those of the other series (see Figs. 1b and a). This result cannot be rationalized and remains unresolved to date. In other words, the experimental results show complexity, since some of the reaction products, along with ambiguous identification,

Table 1

Analysis of neutral and ionic species formed from a H₂O discharge plasma: identification and classification by formula

<i>Ionic species</i>						
H ₃ O ⁺ (H ₂ O) _n	H ₃ O ⁺	H ₃ O ⁺ (H ₂ O)	H ₃ O ⁺ (H ₂ O) ₂	H ₃ O ⁺ (H ₂ O) ₃	H ₃ O ⁺ (H ₂ O) ₄	
H ₃ O ⁺ (H ₂ O) _n O	H ₃ O ⁺ (O)	H ₃ O ⁺ (H ₂ O)O	H ₃ O ⁺ (H ₂ O) ₂ O			
H ₃ O ⁺ (H ₂ O) _n OH	H ₃ O ⁺ (OH)	H ₃ O ⁺ (H ₂ O)OH	H ₃ O ⁺ (H ₂ O) ₂ OH	H ₃ O ⁺ (H ₂ O) ₃ OH		
(H ₂ O) _n ⁺ O ^a		(H ₂ O) ⁺ O	(H ₂ O) ₂ ⁺ O	(H ₂ O) ₃ ⁺ O	(H ₂ O) ₄ ⁺ O	
<i>Neutral species (Li⁺ adduct)</i>						
(H ₂ O) _n Li ⁺		(H ₂ O)Li ⁺	(H ₂ O) ₂ Li ⁺	(H ₂ O) ₃ Li ⁺	(H ₂ O) ₄ Li ⁺	(H ₂ O) ₅ Li ⁺
(H ₂ O) _n Li ⁺ OH	Li ⁺ OH	(H ₂ O)Li ⁺ OH	(H ₂ O) ₂ Li ⁺ OH	(H ₂ O) ₃ Li ⁺ OH		

^a Possibly, H₂O₂⁺(H₂O)_n; H₂O₂⁺, H₂O₂⁺(H₂O), H₂O₂⁺(H₂O)₂, H₂O₂⁺(H₂O)₃.

appear to interfere with the analytical determination.

Larger clusters were also observed, particularly at higher pressures (see Section 3.2). The most prevalent cluster ions sampled were water clusters. The interesting product series (H₂O)_n⁺O have not been reported before, and they are not in the NIST-ONLINE database [15].

3.2. Discharge parameters

After performing a number of preliminary runs to broadly establish the operating characteristics of the apparatus, we systematically studied the degree of dissociation of water vapor under various conditions. This was done by observing the influence of H₂O/He composition and MW power in the discharge on the product formation.

3.2.1. Products as a function of H₂O/He composition

Changes in the H₂O/He composition are readily visible in the discharge. As the water vapor concentration in the H₂O/He mixture increases, the discharge changes from light pink to yellowish blue due to nitrogen in the water vapor, and the discharge expands. Changes in the H₂O/He composition lead to variation of the product distribution.

We plotted the evolution of the peak intensities of various gaseous products in the H₂O/He plasma as a function of the H₂O pressure (Pa) (Fig. 2). The plotted peak heights corresponded to OH⁺ and the $n=0-2$ species in the cation series H₃O⁺(H₂O)_nO: H₃O⁺(O), H₃O⁺(H₂O)O, H₃O⁺(H₂O)₂O. The higher mass clusters were observed with increasing

H₂O pressure. The H₃O⁺(H₂O)_nOH, H₃O⁺(H₂O)_n⁺, and (H₂O)_n⁺O series followed similar variation patterns.

We can safely assume that condensation reactions proceed from the primary ions, as follows (the higher the pressure, the greater the association):

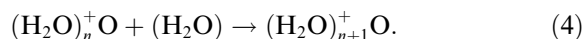
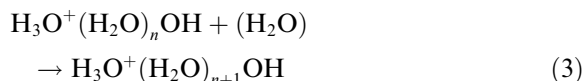
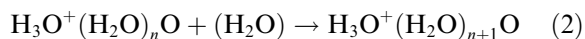
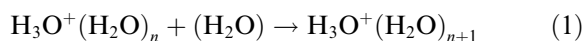


Fig. 3 shows the evolution of (H₂O)_nLi⁺OH intensities relative to the pressure of H₂O in the H₂O/He mixture. Formation of high-cluster Li⁺ adducts was favored at higher partial pressures of water, as was the case for the ionic products. We conclude that more condensation occurs at higher water pressure.

From the foregoing overview of the variations in abundance of neutral and ionic species as a function of H₂O concentration, we make several remarks:

- We reasonably found that ionic water clusters and neutral water cluster species (Li⁺ adducts) behave similarly as H₂O concentration increases.
- As the H₂O concentration in the mixture increases, all of the product peaks gradually increase to a maximum and then decrease. The maximum position of the products with higher n shifts to higher water pressure. The tendency

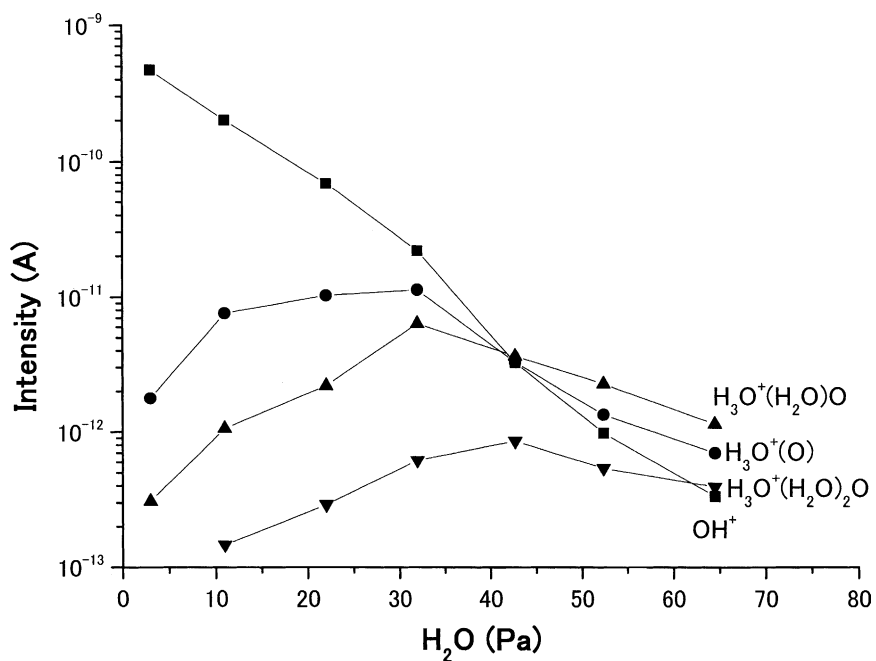


Fig. 2. Intensity of ionic species OH^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($n=0-2$) as a function of pressure in the range 2–64 Pa (consequent pressure of 213–2133 Pa in the flow tube). MW power input is 30 W.

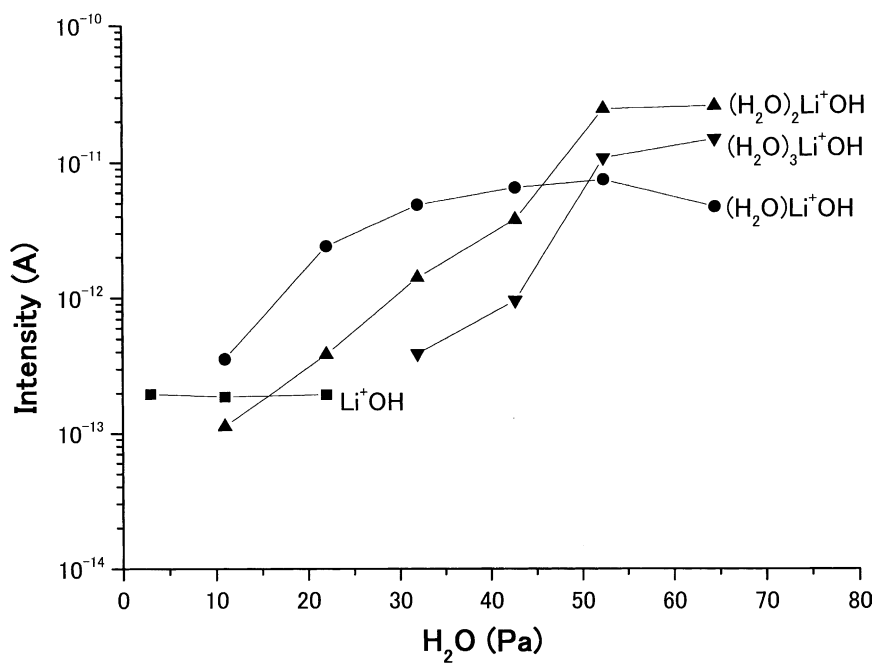


Fig. 3. Intensity of neutral species $(\text{H}_2\text{O})_n\text{Li}^+\text{OH}$ ($n=0-3$) as a function of pressure in the range 2–64 Pa. Conditions as in Fig. 2.

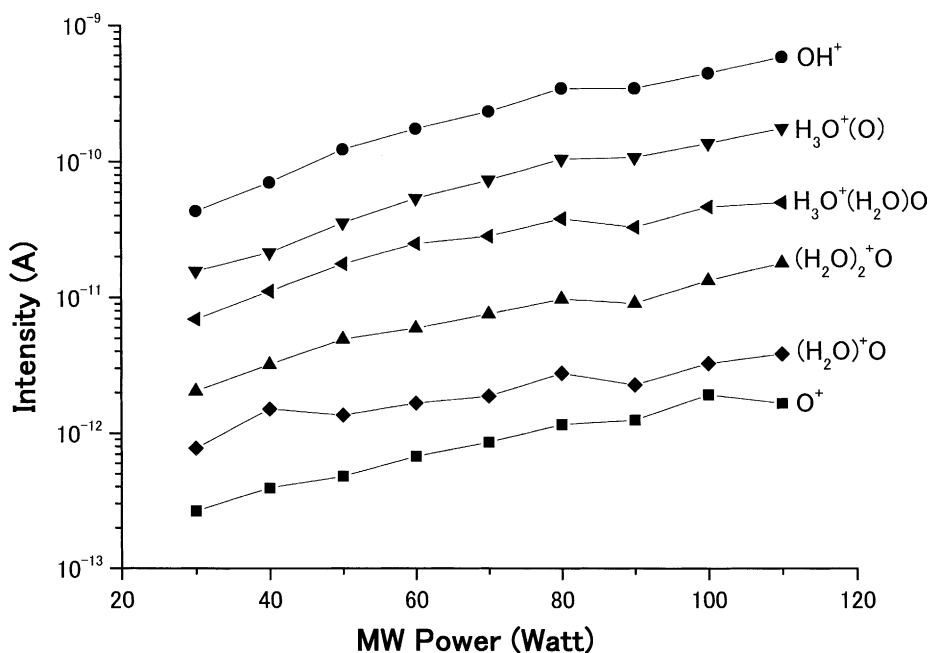


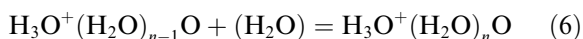
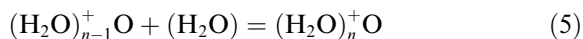
Fig. 4. Peak intensity of several ionic species, $(\text{H}_2\text{O})_n^+\text{O}$ ($n=0-2$) and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{O}$ ($n=0-2$), as a function of MW power at a water pressure of 30 Pa.

for the H_2O component of the feed to attain a high degree of conversion is more pronounced for the ionic species than for the neutral species, for which the curves vary more gradually.

- (c) It is obvious from Figs. 2 and 3 that there are no remarkable similarities in the amounts of $(\text{H}_2\text{O})_n\text{Li}^+\text{OH}$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{O}$ formed as a function of H_2O concentration, suggesting no common chemical process.

3.2.2. MW power

Fig. 4 shows the behavior of the peak intensities of the $(\text{H}_2\text{O})_n^+\text{O}$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n\text{O}$ products as a function of MW power (in the range 30–110 W). Increasing MW power increases production in a very similar way. This indicates that the ions in each of these series are almost in equilibrium:



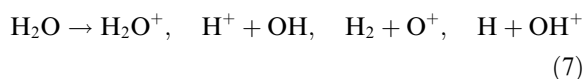
The peak intensities of the Li^+ adduct species decreased slightly with increasing MW power,

suggesting that dissociation reactions of the Li^+ adduct cluster products are most likely to be observed at high discharge powers.

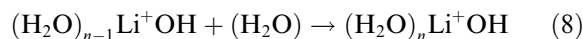
4. Concluding remarks

The mass spectrometer Li^+ reactor setup was successfully used for the simultaneous analysis of neutral and ionic species in the $\text{H}_2\text{O}/\text{He}$ system. General criteria for the effects of the process parameters were derived for this setup. We found that a $\text{H}_2\text{O}/\text{He}$ MW discharge results in a high conversion of H_2O to ionic and neutral association products. The principal feature of this technique is its ability to monitor several kinds of species simultaneously.

The ion/molecule reaction chemistry plays an important role. Primary ion production in the H_2O MW plasma is observed under any plasma condition and is given by



From our results, one would expect OH radical chemistry in the H₂O discharge. It is well known that hydrogen atoms and hydroxy radicals are the primary products of the dissociation of water vapor in an electric discharge. A hydroxy radical, OH, was directly observed as a Li⁺ ion adduct. A possible reaction for association may start with this species. The presence of (H₂O)_nLi⁺OH adducts suggests that a radical-involved association reaction may be the formation mechanism.



We have shown that almost all the neutral species coexist with the corresponding ionic species in the water discharge. The distribution of ionic species from a discharge is, somehow, representative of the neutral being formed. We detected H₃O⁺(H₂O)_nOH and (H₂O)_n⁺O, but the corresponding neutrals do not exist. Because ions and their corresponding neutrals do not necessarily behave similarly, elaboration of the mechanism will not be easy.

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