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Observations of Magic Numbers in Gas Phase Hydrates of Alkylammonium Ions

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Hydration of alkylammonium ions under nonanalytical electrospray ionization conditions has been found to yield cluster ions with more than 20 water molecules associated with the central ion. These cluster ion species are taken to be an approximation of the conditions in liquid water. Many of the alkylammonium cation mass spectra exhibit water cluster numbers that appear to be particularly favorable, i.e., "magic number clusters" (MNC). We have found MNC in hydrates of mono- and tetra-alkyl ammonium ions, $\text{NH}_3(\text{C}_m\text{H}_{2m+1})^+(\text{H}_2\text{O})_n$, $m = 1-8$ and $\text{N}(\text{C}_m\text{H}_{2m+1})_4^+(\text{H}_2\text{O})_n$, $m = 2-8$. In contrast, $\text{NH}_2(\text{CH}_3)_2^+(\text{H}_2\text{O})_n$, $\text{NH}(\text{CH}_3)_3^+(\text{H}_2\text{O})_n$, and $\text{N}(\text{CH}_3)_4^+(\text{H}_2\text{O})_n$ do not exhibit any MNC. We conjecture that the structures of these magic number clusters correspond to exohedral structures in which the ion is situated on the surface of the water cage in contrast to the widely accepted caged ion structures of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and $\text{NH}_4^+(\text{H}_2\text{O})_n$. (J Am Soc Mass Spectrom 1997, 8, 1175-1179)

Solvated gas phase ions represent an important area of study that helps to increase understanding of basic processes of electrospray ionization (ESI) mass spectrometry [1]. These studies are also important from the insights that they may provide into basic chemical processes. Although hydrated ionic clusters are particularly important to ESI [2], they also represent a transition between gaseous ions and bulk phase water chemistry [3]. In addition, for certain organic ions, these hydrated clusters become significant for biology as well, especially in understanding processes occurring at the interfaces of lipid bilayers [4].

Ion molecule studies of water cluster systems have been approached from both qualitative and quantitative perspectives. Quantitative studies with low hydration numbers have led to determinations of solvation enthalpy. These have been carried out both under equilibrium [5] and dynamic conditions [6]. Quantitative studies involving large hydration numbers are relatively recent and to date have been limited to simple central ions [7].

Qualitative studies of gas phase hydrated ions have led to some significant insights into the nature of the chemistry of the interactions of water with ions [8, 9]. A feature commonly exhibited in the mass spectra of gas phase hydrated ions is the presence of clusters that appear at anomalously high intensity, the so-called magic number clusters (MNC) [10]. Structures with special stability have been attributed to these clusters

especially when the hydrated ion can form hydrogen bonds with water. For example, it has been shown that for large gas phase clusters of the hydronium ion with water, the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{27}$ clusters possess special stability. Both experimental evidence and theoretical simulations suggest that $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ is a clathrate-like structure in which the hydronium ion is encaged by a regular dodecahedron of 20 hydrogen bound water molecules [11]. A similar structure has also been proposed for the water-ammonium cluster $\text{NH}_4^+(\text{H}_2\text{O})_{20}$ [9].

Because of the relationship between alkylammonium ions, $\text{NR}_m\text{H}_{4-m}^+$, $m = 1-3$, and the charged portion of some lipid molecules, i.e., phosphatidylcholines and phosphatidylethanolamines, extending investigations of MNC to the alkylammonium ions are increasingly important. The alkylammonium ions possess both an ionic character, to which water should be attracted, and nonpolar hydrocarbon chains that should interact hydrophobically with water. Although crystallographic studies of high concentrations of quaternary alkylammonium salts in solid matrices suggest the presence of clathrates for these ammonium ions, it is not clear that these results are simply a consequence of the presence of the counter ion [12]. On the other hand, in liquid water, the clathrate structures seem not to be present for the $(\text{CH}_3)_4\text{N}^+$ ion [13]. The authors believe that studies of the gas phase clustering of water with single alkylammonium ions may lead to additional insights into the hydration behavior of these materials.

Recently, a triple quadrupole mass spectrometer with an electrospray source was employed to yield large protonated water clusters with corresponding

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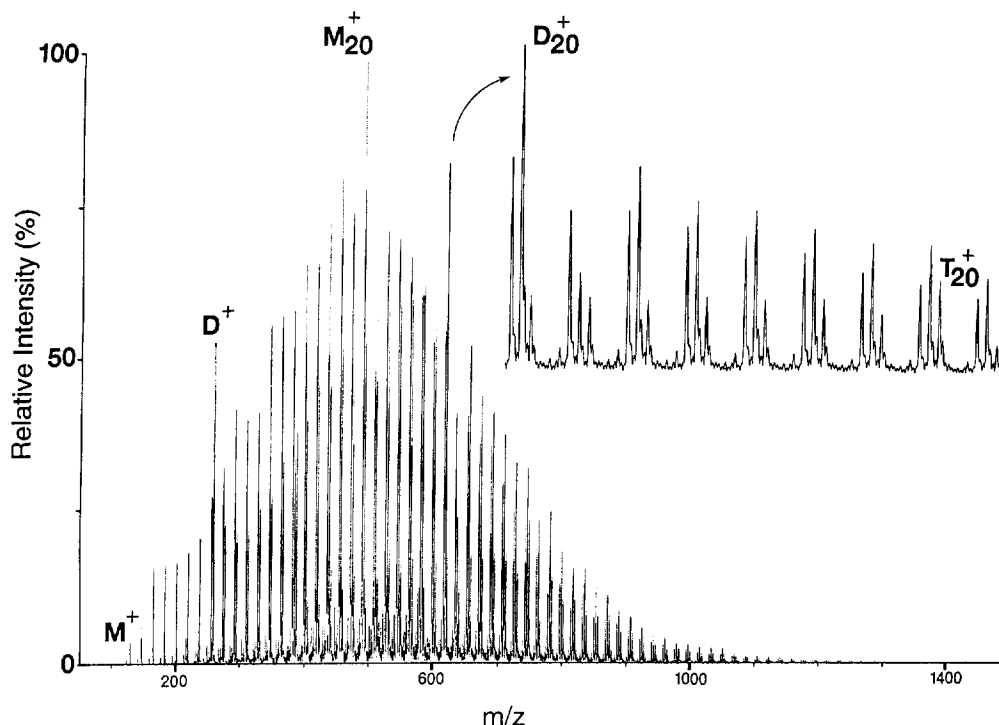


Figure 1. Mass spectrum of hydrates of protonated octylamine. $M_n = (C_8H_{17})NH_3^+(H_2O)_n$, $D_n = [(C_8H_{17})NH_3^+(H_2O)_n]_2^+$, $T_n = [(C_8H_{17})NH_3^+(H_2O)_n]_3^+$.

MNC [2]. Herein, the authors report results from the application of this mass spectrometry technique to the examination of the hydration process of ammonium ions. These results are the first report of apparent MNC in the electrospray mass spectra of gas phase hydrates of a series of organic ions.

Experimental

A Sciex API I (Sciex, Thornhill, Ontario, Canada) single quadrupole mass spectrometer in the electrospray ionization mode was used for these studies. All chemicals were purchased from Aldrich and used as received. Hydrated clusters of tetraalkylammonium, dimethylammonium, trimethylammonium, and diethylammonium ions, as well as $NH_3(C_mH_{2m+1})^+$, $m \leq 4$, were generated by electrospraying 10^{-3} or 10^{-4} M aqueous solutions of either the chloride or bromide salt at flow rates of 10 μ L/min. Hydrates of larger $NH_3(C_mH_{2m+1})^+$, $m \geq 5$, were produced by spraying 0.1% aqueous solutions of corresponding amines at the same flow rate. Ammonium ion hydrates were obtained by spraying a 10^{-3} M ammonium acetate solution. A 0.1% acetic acid in aqueous solution was used to generate hydrated hydronium ion clusters. Protonated water clusters were present to a small extent in all mass spectra of hydrated alkylammonium ions.

In order to obtain clusters with high hydration numbers, the electrospray needle was aimed directly at the orifice and the nitrogen curtain gas flow rate was kept at 0.1 L/min rather than the 0.6 L/min used for

analytical work. Maximum MNC intensity was obtained with low potential differences between the orifice plate and the radiofrequency (rf) only quadrupole. The effect of declustering voltages on cluster size and the formation of MNC was investigated. The potential difference between the orifice plate and the rf only quadrupole, $V_{OR}-V_{RO}$, was changed from 1 to 25 V for fixed spray conditions.

As in previous studies [8], the presence of MNC was determined by plotting the intensity ratio, $M^+(H_2O)_n / M^+(H_2O)_{n+1}$ versus n , where $M^+(H_2O)_n$ and $M^+(H_2O)_{n+1}$ are the mass spectrometric intensities of hydrates having n and $n + 1$ water ligands, respectively.

Results

$H_3O^+(H_2O)_n$ and $NH_4^+(H_2O)_n$

The mass spectra of $H_3O^+(H_2O)_n$ and $NH_4^+(H_2O)_n$ that were obtained are similar to those observed in previous studies [8, 9]. They show enhanced peak intensities corresponding to MNC at $n = 20$ and 27.

Protonated Amines

Hydrates $NH_3(C_mH_{2m+1})^+(H_2O)_n$ display MNC at $n = 20$ and 27 in their mass spectra. As an example, the mass spectrum of hydrated protonated octylamine is shown in Figure 1. Hydrates of proton bound dimer and trimer ions $[NH_2(C_8H_{17})]_2H^+(H_2O)_n$ (D_n^+) and $[NH_3(C_mH_{2m+1})]_3H^+(H_2O)_n$ (T_n^+) were obtained in the

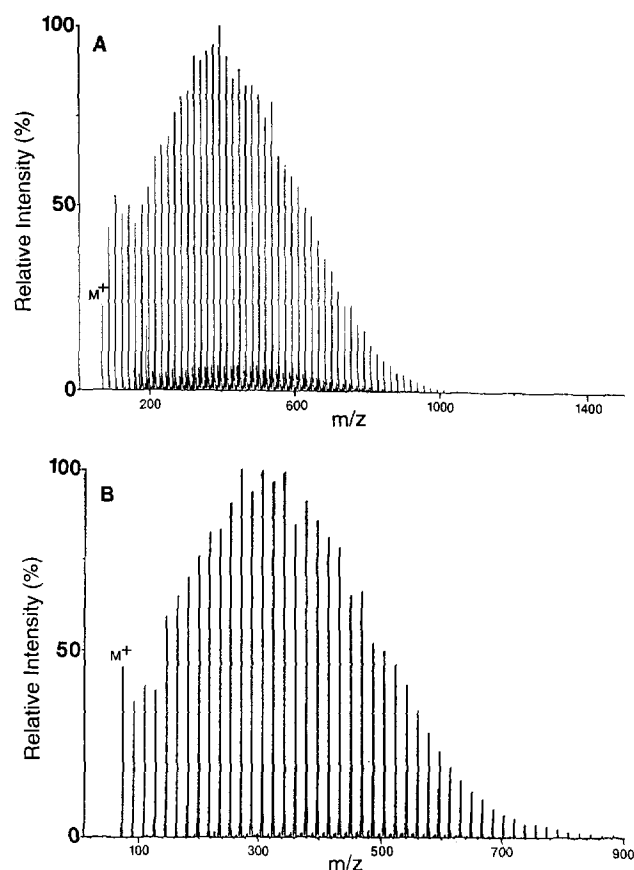


Figure 2. Electrospray mass spectrum of hydrates of (a) $(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ and (b) $(\text{CH}_3)_4\text{N}^+$.

electrospray process of octylamine as well. These ions are analogous to the commonly seen proton bound dimer: $[\text{NH}_3 \cdots \text{H} \cdots \text{NH}_3]^+$. Interestingly, both D_n^+ and T_n^+ , exhibit MNC at $n = 20$ and 27 .

There are no MNC in the mass spectra of the hydrates of either of the two protonated secondary amines, $\text{NH}_2(\text{CH}_3)_2^+$ and $\text{NH}_2(\text{C}_2\text{H}_5)_2^+$. The hydrates of the protonated tertiary amine $\text{NH}(\text{CH}_3)_3^+$ do not exhibit MNC, but those of the protonated triethylamine do. Figure 2a depicts the smooth distribution of hydrates in the mass spectrum of $\text{NH}_2(\text{C}_2\text{H}_5)_2^+(\text{H}_2\text{O})_n$.

Tetraalkylammonium ions

In contrast to the results of the secondary and tertiary amines, the mass spectra of all of the tetraalkylammonium ions, $\text{N}(\text{C}_m\text{H}_{2m+1})_4^+$, $m = 2-8$, show MNC. There are no MNC in the mass spectrum of hydrated $\text{N}(\text{CH}_3)_4^+(\text{H}_2\text{O})_n$, as seen in Figure 2b. Figure 3 shows the MNC in the mass spectrum of $\text{N}(\text{C}_3\text{H}_7)_4^+(\text{H}_2\text{O})_n$. Figure 3a was obtained at a $(V_{\text{OR}} - V_{\text{RO}})$ value of 1 V and Figure 3b at 25 V. Figure 3 shows that the MNC persist, albeit at diminished intensity, at higher values of the declustering potential.

The observations made above based on mass spectra are confirmed in Figure 4 by plotting the intensity ratio,

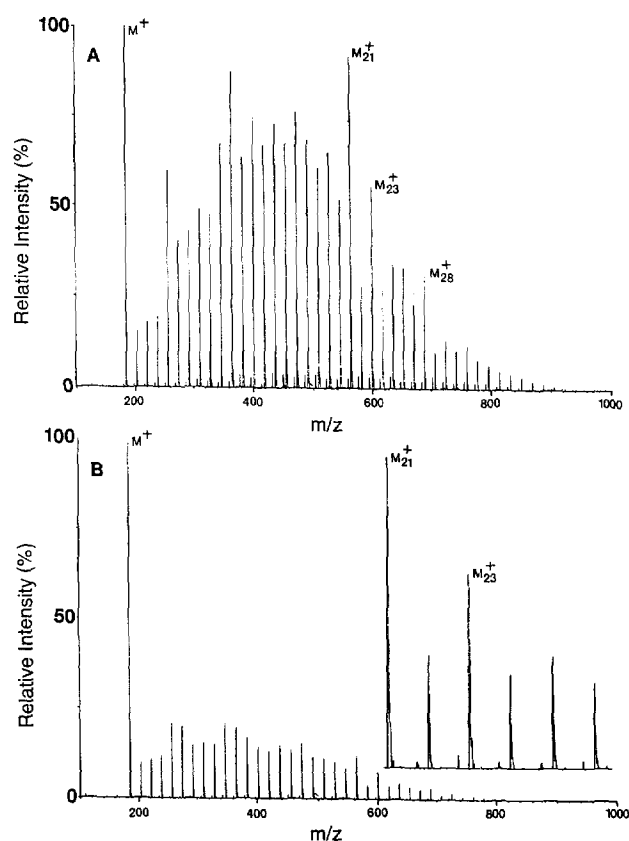


Figure 3. Electrospray mass spectrum of hydrates of (a) $(\text{C}_3\text{H}_7)_4\text{N}^+$ at potential difference, $V_{\text{OR}} - V_{\text{RO}}$ of (a) 1 V and (b) 25 V.

$\text{M}^+(\text{H}_2\text{O})_n / \text{M}^+(\text{H}_2\text{O})_{n+1}$ versus n using the mass spectra of four hydrated ions, protonated octylamine, diethylammonium, tetramethylammonium, and tetrapropylammonium as examples. The presence or absence of MNC for these species is clearly demonstrated in Figure 4.

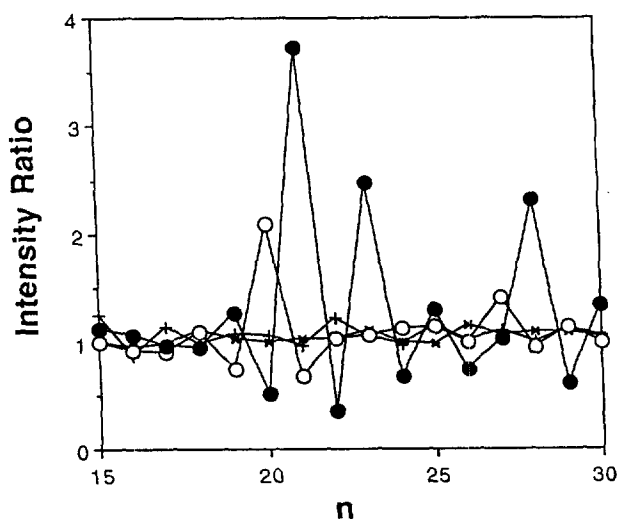


Figure 4. Intensity ratios, $\text{M}^+(\text{H}_2\text{O})_n / \text{M}^+(\text{H}_2\text{O})_{n-1}$ vs. n for: (open circles) $(\text{C}_8\text{H}_{17})\text{NH}_3^+(\text{H}_2\text{O})_n$, (asterisks) $(\text{C}_2\text{H}_5)_2\text{NH}_2^+(\text{H}_2\text{O})_n$, (plus signs) $(\text{CH}_3)_4\text{N}^+(\text{H}_2\text{O})_n$, and (filled circles) $(\text{C}_3\text{H}_7)_4\text{N}^+(\text{H}_2\text{O})_n$.

Discussion

The operating conditions of the electrospray source were adjusted to enhance the formation of ions formed by clustering with water. The central ions were generated through either coulomb explosions of or ion evaporation from charged droplets [1]. The authors cannot prove the presence or absence of hydration in the initial ion formation. However, subsequent to gas phase ion formation, source conditions were adjusted in a manner to induce interactions between the ion and gas phase water. The electrospray needle was aimed straight at the pressure reduction orifice to allow ready condensation of water vapor onto ions that were present. Cluster growth was further encouraged by the cooling that occurred in the single stage expansion of the ion beam through the pumping orifice to reach the 10^{-5} torr region of the quadrupole mass filter.

The presence of some ions having special stability is clearly shown in the mass spectra of a number of alkylammonium ions, as seen in Figures 1 and 3. Figure 4 shows that when MNC are observed, the relative intensity of the MNC hydrated species is from 2.5–3.5 greater than that of neighboring hydrated ions. In the cases of the hydronium and ammonium ions, these MNC have been associated with dodecahedral water cage structures surrounding the central ion [9, 11].

Based purely on geometrical size considerations, the observation of MNC for $\text{NH}_3(\text{C}_m\text{H}_{2m+1})^+(\text{H}_2\text{O})_n$, $m \leq 8$, might not be inconsistent with such a dodecahedral cage structure hydrogen bound to the central ion. On the other hand, geometrical arguments preclude the possibility that not only the protonated *n*-octylamine ion, $\text{NH}_3(\text{C}_8\text{H}_{17})^+$, but also its dimer or trimer, will be accommodated inside a 20-water cage. If the $\text{NH}_3(\text{C}_8\text{H}_{17})^+$ ion spans a distance of approximately 8 Å, estimated from the ionic radius of $\text{N}(\text{C}_4\text{H}_9)_4^+$, $R = 4.1$ Å [14], and the distance between methyl hydrogen and water oxygen is $r = 2.5$ Å, as calculated for $\text{N}(\text{CH}_3)_4^+(\text{H}_2\text{O})$ complex [15], then, in order to enclose the $\text{NH}_3(\text{C}_8\text{H}_{17})^+$ ion, a water clathrate with an O–O distance of adjacent water molecules approaching 4.8 Å would be required [16]. With such a geometry, any stability of an MNC cage would be questionable.

In the cases of the tetraalkylammonium species, the geometrical arguments seem less pertinent. In general, it is assumed that MNC of the protonated alkylammonium ions are formed by a water cage that is hydrogen bonded to the central ion. This seems like an unreasonable assumption for the tetraalkylammonium species because they do not have protons available for hydrogen bonding, even though Mautner [17] suggested the possibility of weak hydrogen bonding with water for tetramethylammonium ions. Perhaps more puzzling is the absence of MNC in the mass spectra of the trimethyl-, dimethyl-, and diethyl-ammonium ions, because some hydrogen bonding to the central species would seem plausible. The picture is even cloudier in the face of the observation of MNC for triethylammonium.

To explain all of these observations, one may suggest

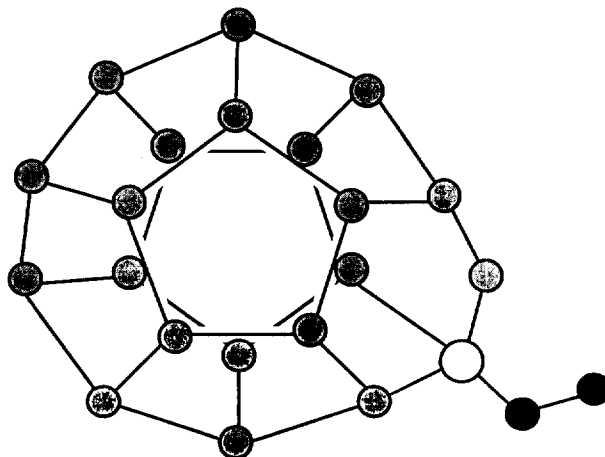


Figure 5. Artist rendering of exohedral water cluster structure.

that, rather than caging the central ion, the alkylammonium species form structures that attach to an external water cage, in a manner first suggested by Mautner's calculations for $\text{N}(\text{CH}_3)_4^+(\text{H}_2\text{O})_2$ [17]. At times, this attachment may occur through multiple hydrogen bonds, as in the cases of the protonated primary amines. An artist's rendering of such a possible structure is given in Figure 5.

In the case of the tetraalkylammonium ions, the authors suggest that attachment occurs as a consequence of a distortion in the geometry of the central ion so that a portion of the central positive charge is available for bonding to a water structure. In the case of the tetraethyl and higher species, the hydrophobicity of the hydrocarbon chains would accentuate this distortion and facilitate the formation of the external cage. This has been suggested by some recent preliminary computational results [18]. In the case of tetramethylammonium, it may be that insufficient distortion, coupled with insufficient hydrophobicity, prevents the formation of a cage structure that give rise to MNC.

Clearly the secondary and tertiary protonated amines represent behavior that is intermediate between the hydrogen bonding model of the protonated primary amines and the hydrophobicity model of the tetraalkylammoniums. Under these circumstances, the protonated triethylamine can form MNC, probably through a combination of hydrophobic distortion and bonding through its central charge. In terms of the model proposed here, the other three species in this intermediate group would seem to have neither sufficient hydrophobic character nor available charge exposure to induce the formation of stable clathrates with water that yield MNC in their mass spectra.

Conclusions

Mass spectra of hydrated protonated amines and tetraalkylammonium ions with chain lengths greater than 2 exhibit magic number clusters. Clathrates of 20 waters

binding to the hydrated central ion through hydrogen bonds are suggested as the structures for $\text{NH}_3(\text{C}_m\text{H}_{2m+1})^+(\text{H}_2\text{O})_{20}$. Hydrates of dimethyl, trimethyl, tetramethylammonium, and diethylammonium ions do not display MNC probably because these ions lack both protons to form strong ionic hydrogen bonds with the water network and have insufficient hydrophobic character to acquire the distorted geometry necessary for cage formation. Further studies are underway to determine energetic aspects of the ammonium hydrate clusters in order to contrast the hydration properties in the gas phase with those in condensed phases.

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References

1. (a) Tang, L.; Kebarle, P. *Anal. Chem.* **1993**, *65*, 3654; (b) Fenn, J. B. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 524.
2. (a) Anacleto, J. F.; Pleasance, S.; Boyd, R. K. *Org. Mass Spectrom.* **1992**, *27*, 660; (b) Chowdhury, S. K.; Katta, V.; Chait, B. T. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 81; (c) Smith, R. D.; Light-Wahl, K. J. *Biol. Mass Spectrom.* **1993**, *22*, 493; (d) Rodriguez-Cruz, S. E.; Klassen, J. S.; Williams, E. R. *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 565.
3. Marcus, Y. *Ion Solvation*; Wiley: Chichester, 1985.
4. Cevc, G. In *Water and Biological Macromolecules*; Weshof, E., Ed.; CRC: Boca Raton, 1993; pp. 338–388.
5. (a) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *7*, 1466; (b) Keese, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2599; (c) Moet-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984**, *106*, 1265; (d) Blades, A. T.; Klassen, J. S.; Kebarle, P. *J. Am. Chem. Soc.* **1996**, *118*, 12437.
6. (a) Dawson, P. H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *43*, 195; (b) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 5036; (c) Dalleska, N. F.; Honma, K.; Armentrout, P. B. *J. Am. Chem. Soc.* **1993**, *115*, 12125; (d) Dalleska, N. F.; Tjelta, B. L.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 4191; (e) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.
7. Magnera, T. F.; David, D. E.; Michl, J. *Chem. Phys. Lett.* **1991**, *182*, 363.
8. (a) Lin, S. S. *Rev. Sci. Instrum.* **1973**, *44*, 514; (b) Fenn, J. B. *J. Am. Mass Spectrom.* **1993**, *4*, 524; (c) Magnera, T. F.; David, D. E.; Milch, J. *Chem. Phys. Lett.* **1991**, *182*, 363; (d) Zhang, X.; Castleman, A. W., Jr. *J. Chem. Phys.* **1994**, *101*, 1157; (e) Nagashima, U.; Shinohara, H.; Nishi, N.; Tanaka, H. *J. Chem. Phys.* **1986**, *84*, 209; (f) Chowhury, S. K.; Chait, B. T. *Anal. Chem.* **1991**, *63*, 1660; (g) McLuckey, S. A.; Glish, G. L.; Asano, K. G.; Bartmess, J. E. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *109*, 171.
9. Shinohara, H.; Nagashima, U.; Tanaka, H.; Nishi, N. *J. Chem. Phys.* **1985**, *83*, 4183.
10. Garvey, J. F.; Herron, W. J.; Vaidyanathan, G. *Chem. Rev.* **1994**, *94*, 1999.
11. (a) Wei, S.; Shi, Z.; Castleman, A. W., Jr. *J. Chem. Phys.* **1991**, *94*, 3268; (b) Kelterbaum, R.; Kochanski, E. *J. Phys. Chem.* **1995**, *99*, 12493.
12. (a) McMullan, R.; Jeffrey, G. A. *J. Chem. Phys.* **1959**, *11*, 1231; (b) Feil, D.; Jeffrey, G. A. *J. Chem. Phys.* **1961**, *35*, 1863; (c) McLean, W. J.; Jeffrey, G. A. *J. Chem. Phys.* **1967**, *47*, 414.
13. Somsen, G., In *Thermochemistry and Its Applications to Chemical and Biochemical Systems*; Ribeiro da Silva, M. A. V., Ed.; D. Reidel: Dordrecht, 1984; pp 414–424.
14. King, E. J. *J. Phys. Chem.* **1970**, *74*, 4590.
15. Koller, J.; Hadzi, D. *J. Mol. Struct. (Theochem)* **1993**, *279*, 311.
16. The O–O distance was estimated by equating the volume of the sphere of a radius = $(R + r)$ to the volume of a pentagonal dodecahedron.
17. Meot-Ner (Mautner), M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 469.
18. Steinbach, P. J., personal communication.