



ELSEVIER

International Journal of Mass Spectrometry 179/180 (1998) 1–6



# Association of the ammonium ion with $\alpha,\omega$ -alkanediols

John A. Stone\*, Michael D. Carter

*Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada*

Received 28 January 1998; accepted 9 April 1998

## Abstract

The association of the ammonium ion with several  $\alpha,\omega$ -alkanediols has been studied by high pressure mass spectrometry. Standard enthalpy ( $\text{kJ mol}^{-1}$ ) and entropy ( $\text{J K}^{-1} \text{mol}^{-1}$ , in parentheses) values determined for the reaction  $\text{diol} + \text{NH}_4^+ \rightleftharpoons \text{diol} \cdot \text{NH}_4^+$  are 1,2-ethanediol,  $121 \pm 4$  ( $125 \pm 2$ ); 1,3-propanediol,  $139 \pm 5$  ( $151 \pm 3$ ); 1,4-butanediol,  $138 \pm 4$  ( $142 \pm 2$ ); 2,3-butanediol,  $146 \pm 6$  ( $161 \pm 3$ ), and 2-butene-1,4-diol,  $135 \pm 6$  ( $148 \pm 4$ ). Comparison with the thermodynamic values for the association of  $\text{NH}_4^+$  with monohydric alcohols shows that the association of  $\text{NH}_4^+$  with diols leads to the formation of cyclic structures with two intermolecular hydrogen bonds and that, unlike protonation, there is little effect of carbon number on the values of  $\Delta H^0$  and  $\Delta S^0$  for the association. (Int J Mass Spectrom 179/180 (1998) 1–6) © 1998 Elsevier Science B.V.

*Keywords:* Ion association; Hydrogen bond; Bidentate complexes; Ion thermodynamics; High pressure mass spectrometry

## 1. Introduction

Hydrogen bonding, both inter- and intramolecular, is important in determining secondary structures in complex organic systems, and the strongest individual hydrogen bonds arise when protonated groups interact with other basic groups. Much of the information pertinent to discussions of the strengths of such ionic hydrogen bonds has arisen from studies using high pressure mass spectrometry (HPMS), because this technique enables the estimation of both the enthalpy and entropy of bond formation [1]. The maximum hydrogen bond strength possible between two basic groups  $A$  and  $B$  is taken to be that in which

$A\text{--H}^+ \cdots B$  is collinear. This has been confirmed by theoretical calculation [2,3]. An estimate of this maximum value is obtained by reference to a proton bound dimer with  $A$  and  $B$  on different molecules. The hydrogen bond strengths in symmetric ( $B\text{--H}^+ \cdots B$ ) and asymmetric ( $B\text{--H}^+ \cdots A$ ) proton-bound dimers between molecules containing the basic groups  $A$  and  $B$  have been determined for many systems by measuring the equilibrium constants for hydrogen bond formation,  $B\text{H}^+ + B \rightleftharpoons B\text{H}B^+$ . For example, it is found that symmetric proton-bound dimers of oxygen bases (alcohols, ketones, etc.) have constant hydrogen bond strengths of  $126 \pm 8 \text{ kJ mol}^{-1}$  [4], whereas those of nitrogen bases (amines and pyridines) have hydrogen bond strengths of  $96 \pm 6 \text{ kcal mol}^{-1}$  [5]. Linear correlations have been found between hydrogen bond strengths and the differences in proton affinities between the two molecules in asymmetric proton-bound dimers [6].

\* Corresponding author.

Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

Intramolecular hydrogen bond formation leads to the formation of cyclic structures. The strength of such a bond in a molecule containing basic groups *A* and *B* is usually estimated as the difference between the measured proton affinity of the molecule and the proton affinity of a molecule containing the more basic group as its sole protonation site. Estimations have been made of the strengths of intramolecular hydrogen bonds in, amongst others, protonated  $\alpha,\omega$ -dialkylamines [5a,7],  $\alpha,\omega$ -alkanediols [8], and polyethers [9]. Meot-Ner [10] has reviewed the experimental investigations of ionic hydrogen bonds and Deakyne [3] has reviewed the pertinent theoretical calculations.

Although intramolecular hydrogen bonding in protonated polyfunctional molecules has received some study, far less has been devoted to the study of hydrogen bonds in the association of polyfunctional ions with polyfunctional molecules. Such associations have the possibility of resulting in, if stereochemically feasible, the formation of structures with multiple intramolecular hydrogen bonds and hence cyclic or polycyclic structures. Meot-Ner and co-workers [11] used HPMS to obtain the enthalpies and entropies of binding of the hydronium ion to polyethers. The binding energies increase with the increase in flexibility of the polyether and one or more intermolecular hydrogen bonds may be formed depending on this flexibility. The association of the hydronium ion with a crown ether can possibly result in all three hydrogens of the cation participating in bond formation [12]. The ammonium ion, in which the positive charge is delocalized over the hydrogen ions [13], has the potential for participating in up to four intermolecular hydrogen bonds, but the required tetrahedral geometry about the nitrogen atom would require extreme flexibility on the part of a single molecule with four or more basic sites, combined with a lack of steric hindrance, for this to be possible in the formation of a such a complex with  $\text{NH}_4^+$ . The enthalpy of binding  $\text{NH}_4^+$  to  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$  was found to be  $-160 \text{ kJ mol}^{-1}$ , which is considerably smaller than that for the association of  $\text{H}_3\text{O}^+$  with the same molecule,  $-245 \text{ kJ mol}^{-1}$  [11]. Both associations are thought to

involve the formation of cyclic structures with two intermolecular hydrogen bonds.

Because there is little information on the association of the ammonium ion with polydentate ligands, we have employed HPMS to study the association of this ion with some diols. The complexation was expected to involve the formation of two hydrogen bonds from  $\text{NH}_4^+$  to the oxygens of the diols, as in the case of the previously studied  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$  [11]. The resulting cyclic structures would have a minimum of seven atoms (1,2-ethanediol) and a maximum of nine (1,4-butanediol) and should be essentially free of geometric constraints.

## 2. Experimental

Thermochemical measurements were made using the high pressure mass spectrometer with pulsed electron beam, described in detail previously [14]. Gaseous samples were prepared in a 5 L heated glass reservoir and were flowed into the ion source via a heated glass line at a rate controlled by a heated regulating valve. A 2 keV electron beam was pulsed on and off with a frequency of  $\sim 100 \text{ Hz}$  and with an “on” pulse width of  $50 \mu\text{s}$ . Ions emerging from the source were collected as functions of time after the ionizing pulse, using ion counting equipment.

The gas samples in the reservoir were of the approximate composition  $\text{CH}_4/\text{NH}_3/\text{diol}$  (98/2/0.1–0.02). Diol was introduced to the flask through a septum with a microlitre syringe that was weighed before and after sample introduction.

Methane (Matheson Purity, 99.99% minimum), ammonia (Matheson, Anhydrous, 99.99% minimum) and diols (Aldrich) were all used as received.

## 3. Results and discussion

The experiments in this study were run under very similar experimental conditions in terms of temperature and diol concentrations to those of an earlier measurement of the proton affinities of the same diols. Some decomposition of the protonated diols was

encountered in that study but the extent was not sufficient to require corrections to be applied to the calculated thermodynamic data. There was also no evidence that any significant thermal decomposition of the neutral diols was occurring. The activation energies for the decomposition via loss of water of protonated  $\alpha,\omega$ -alkanediols have recently been calculated to be 24 kcal mol<sup>-1</sup> for ethane diol and greater than 99 kJ mol<sup>-1</sup> for the higher ones [15]. In the present study we have not found evidence for the thermal decomposition of the ammonium adducts, other than reversion to reactants.

The major ions observed in CH<sub>4</sub>/NH<sub>3</sub> mixtures at the temperatures and pressures used in this study were NH<sub>4</sub><sup>+</sup> and (NH<sub>3</sub>)<sub>2</sub>H<sup>+</sup>. These ions were at all times in equilibrium according to Eq. (1) for which the enthalpy change is  $\sim -105$  kJ mol<sup>-1</sup> [16].



When a diol, *D*, was present in the sample no protonated diol was observed but a prominent peak at mass-to-charge ratio corresponding to  $D \cdot \text{NH}_4^+$  was present. This is ascribed to the association reaction of Eq. (2).



The reactions described by Eqs. (1) and (2) are simultaneously in equilibrium as shown by the parallel curves for all three ions in Fig. 1, which was obtained with *D* = ethanediol. The data shown in Fig. 1, or indeed any of the data presented in this paper, do not preclude the occurrence of the possible displacement reaction of Eq. (3). Such a reaction, however, will not affect the thermodynamic data derived in the study because the NH<sub>4</sub><sup>+</sup> and  $D \cdot \text{NH}_4^+$  concentrations must satisfy all equilibria in which they participate. There was no evidence for further solvation; diol-containing ions such as  $D_2 \cdot \text{NH}_4^+$  and  $D \cdot \text{NH}_4^+ \cdot \text{NH}_3$  were absent from the spectra.



Noticeably absent in all spectra were protonated diols,  $D\text{H}^+$ . No such ion was observed in any of the systems studied, even though the experimentally de-

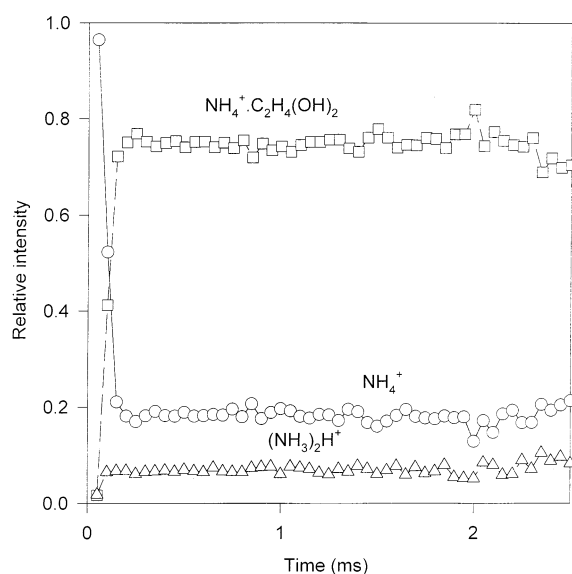


Fig. 1. The normalized ion intensities after a 50  $\mu\text{s}$  ionizing pulse for a mixture of composition (mol %); methane 98.6; ammonia 1.3; ethanediol 0.1. Temperature 500 K, total ion source pressure 3.0 Torr.

termined proton affinities of 1,3-propanediol and 1,4-butanediol are both greater than that of ammonia (Table 1). Because in any experiment the concentration of NH<sub>3</sub> is far greater than that of the diol, the initial formation of NH<sub>4</sub><sup>+</sup> by proton transfer from CH<sub>5</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> must be followed by association rather than by proton transfer. This is seen in Fig. 1 where the initial NH<sub>4</sub><sup>+</sup> intensity is far greater than that of the NH<sub>4</sub><sup>+</sup> ethanediol adduct but equilibrium, shown by the

Table 1

Standard enthalpy and entropy changes for the association of the ammonium ion with diols (*D*):  $D + \text{NH}_4^+ \rightarrow D \cdot \text{NH}_4^+$

<i>D</i>	$-\Delta H^0$ (kJ mol <sup>-1</sup> ) <sup>a</sup>	$-\Delta S^0$ (J K <sup>-1</sup> mol <sup>-1</sup> ) <sup>a</sup>	<i>PA</i> ( <i>D</i> ) (kJ mol <sup>-1</sup> ) <sup>b</sup>
1,2-Ethanediol	121 ± 4	125 ± 2	817
1,3-Propanediol	139 ± 5	151 ± 3	877
1,4-Butanediol	138 ± 4	142 ± 2	917
2-Butene-1,4-diol	135 ± 6	148 ± 4	
2,3-Butanediol	146 ± 6	161 ± 3	

<sup>a</sup> Confidence limits of two standard deviations obtained from linear regression.

<sup>b</sup> From Chen and Stone [8] with values adjusted to the new evaluated PA scale of Bouchoux et al. [15].

constant ratio of normalized intensities, is rapidly achieved.

The equilibrium constants,  $K$ , for the association reaction, Eq. (2), are obtained from the constant ratios of the ion currents of  $\text{NH}_4^+$  and  $D \cdot \text{NH}_4^+$  at all but the shortest reaction times and the known diol pressures in the ion source [Eq. (4)]. The standard pressure,  $P^0$ , is 760 Torr:

$$K = \frac{i_{D \cdot \text{NH}_4^+}}{i_{\text{NH}_4^+}} \cdot \frac{P^0}{P_D} \quad (4)$$

The Van't Hoff plots of Fig. 2 show the variation of  $K$  with reciprocal temperature for each of the diols studied. The slope and intercept of each line yield, respectively, the enthalpy and entropy values for the association reactions. The results are shown in Table 1. These data show that there is only a small influence of diol size on the enthalpy of binding between an  $\alpha,\omega$ -alkanediol and  $\text{NH}_4^+$ . 1,2-Ethanediol has the lowest value, and the values for 1,4-butanediol and 1,3-propanediol are identical within experimental error. The presence of a double bond in 2-butene-1,4-diol does not significantly change the binding enthalpy from that of 1,4-butanediol. The value for 2,3-butanediol is somewhat higher but it can be considered to be still within experimental uncertainty, approximately the same as those of the other C3 and C4 diols. All the values are in a range spanning only 25  $\text{kJ mol}^{-1}$ , whereas the proton affinity values for the same molecules cover a range of 100  $\text{kJ mol}^{-1}$  (Table 1). There is no correlation between proton affinity and  $\text{NH}_4^+$  affinity for these molecules.

The values of the enthalpies of association between diol and  $\text{NH}_4^+$  imply that more than the formation of a single  $\text{O} \cdots \text{H-N}$  hydrogen bond has occurred. There are no available values for the enthalpies of association of  $\text{NH}_4^+$  with alcohols; however, if a single hydrogen bond had been formed between one oxygen of a diol and  $\text{NH}_4^+$ , then an association enthalpy in the range  $105 \pm 5 \text{ kJ mol}^{-1}$  would be expected. The rationale for this statement is the following. An estimate of the hydrogen bond strength between an alcohol and  $\text{NH}_4^+$  may be made because Meot-Ner has shown that there is a linear correlation

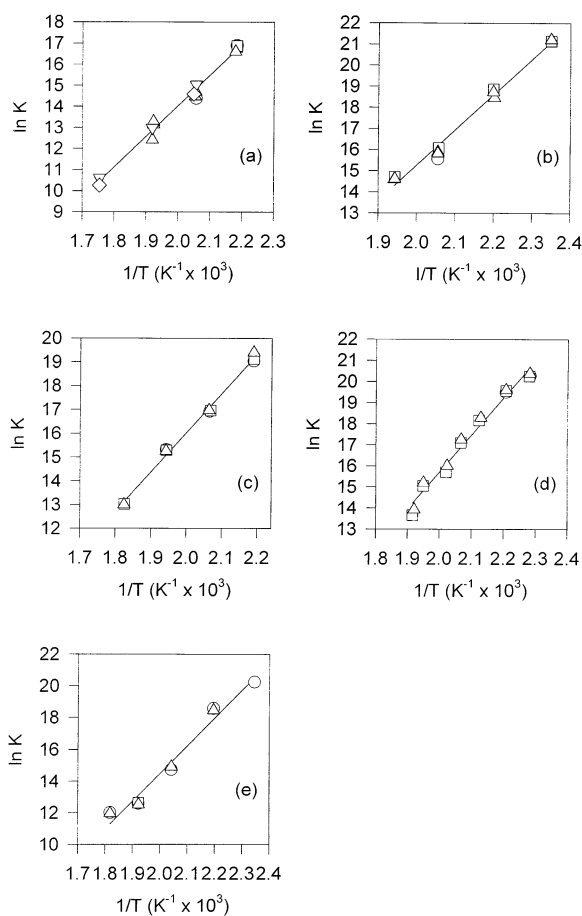


Fig. 2. Van't Hoff plots for the reaction  $D + \text{NH}_4^+ \rightleftharpoons D \cdot \text{NH}_4^+$ .  $D$  = (a) 1,2-ethanediol, (b) 1,3-propanediol, (c) 1,4-butanediol, (d) 2,3-butanediol, (e) 2-butene-1,4-diol. The different symbols signify different pressures in the range 2.5–4.5 Torr and/or different samples.

between  $\Delta(PA)$ , the difference in proton affinity between pairs of proton-bound oxygen- and nitrogen-containing bases, and the  $\text{O} \cdots \text{H-N}$  hydrogen bond strengths,  $\Delta H_D^0$  [6]. The equation is (units  $\text{kcal mol}^{-1}$ ),  $\Delta H_D^0 = a - b \times \Delta(PA)$  where  $a = 30.0 \pm 1.5$  and  $b = 0.26 \pm 0.03$ . Using this equation, the hydrogen bond energies in  $\text{H}_3\text{N-H}^+ \cdots \text{O(H)CH}_3$ ,  $\text{H}_3\text{N-H}^+ \cdots \text{O(H)C}_2\text{H}_5$ , and  $\text{H}_3\text{N-H}^+ \cdots \text{O(H)C}_3\text{H}_7$  are 100, 105, and  $108 \pm 8 \text{ kJ mol}^{-1}$ , respectively. By analogy, if  $\text{NH}_4^+$  associated with a diol through only a single hydrogen bond, the bond energy would have a value no greater than that in the complex  $\text{H}_3\text{N-}$

$\text{H}^+ \cdots \text{O}(\text{H})\text{C}_3\text{H}_7$ , because proton affinity changes insignificantly with carbon chain length after three carbon atoms [17]. This value of  $108 \text{ kJ mol}^{-1}$  is smaller than any of the measured enthalpies of association of  $\text{NH}_4^+$  with a diol. The diol and  $\text{NH}_4^+$  are interacting through more than one hydrogen bond.

Bouchoux and co-workers [18] have used ab initio computation at the MP2/6-31G\*\*//3-21G level in a study of the association of  $\text{NH}_4^+$  with 1,2-ethanediol. They find that two symmetric hydrogen bonds are formed with  $\text{O} \cdots \text{HN}$  distances of  $1.64 \text{ \AA}$  and  $\text{O} \cdots \text{H-N}$  angles of  $153.4^\circ$ . Although the optimized OCCO dihedral angle of the diol is  $69.2^\circ$ , the enthalpy of association is roughly constant at  $-132 \pm 5 \text{ kJ mol}^{-1}$  in the range of  $0$ – $120^\circ$ . For dihedral angles greater than  $150^\circ$  the system has only one hydrogen bond and at  $180^\circ$  the single hydrogen bond energy is  $95 \text{ kJ mol}^{-1}$ , slightly lower than the above inferred value of  $108 \text{ kJ mol}^{-1}$ . The computed association enthalpy is in good agreement with the experimental value of  $-121 \pm 4 \text{ kJ mol}^{-1}$  in Table 1.

The enthalpy of association of  $\text{NH}_4^+$  with 1,2-dimethoxyethane has been measured by Meot-Ner and co-workers [11] as  $161 \pm 16 \text{ kJ mol}^{-1}$ , a value significantly larger than our measured value of  $121 \text{ kJ mol}^{-1}$  for 1,2-ethanediol. The authors suggested that this value for the diether might be between 8 and  $18 \text{ kJ mol}^{-1}$  too high because the difference between the value and that from ab initio calculation was anomalous in comparison with such differences for other  $\text{NH}_4^+$  and  $\text{K}^+$  complexes. Such a correction could explain part of the difference between the value for 1,2-dimethoxyethane and that for 1,2-ethanediol but the difference can also be ascribed in part to the higher proton affinity of an ether oxygen than a hydroxyl oxygen because of the polarization stabilization provided by the methyl groups. The empirical correlations of Mautner [6] would suggest that such differences should be  $5$ – $10 \text{ kJ mol}^{-1}$  for each  $\text{NH} \cdots \text{O}$  interaction, based on the assumption that the positive charge is shared equally between the two hydrogen bonding protons. This is in accord with the value of  $29 \text{ kJ mol}^{-1}$  estimated for the total hydrogen bond energy in the complex formed between 1,2-dimethoxyethane and  $\text{c-C}_6\text{H}_{11}\text{NH}_3^+$  [19]. Another

factor that may make a small contribution to the difference between diol and diether is the hydrogen bond in the neutral diol. All the diols are expected to have internal hydrogen bonds with energies of  $\sim 12$ – $15 \text{ kJ mol}^{-1}$  [20], which are lost when association with  $\text{NH}_4^+$  occurs. However, the present experiments were carried out at relatively high temperatures so that sufficient thermal energy would be available to ensure that the fraction of diol molecules in the hydrogen bonded state was small.

The entropy decreases in the formation of the diol/ $\text{NH}_4^+$  complexes are relatively small, 1,2-ethanediol having the smallest value and the others showing only slightly larger decreases. The values are in fact very close to those for the changes in the readily calculated translational entropies of  $142 \pm 1 \text{ kJ mol}^{-1}$ . The decreases in entropy due to losses in rotational and torsional degrees of freedom in forming the complexes must be almost balanced by the new low frequency stretching and bending vibrations in the complexes. A similar conclusion was reached in a study of the association of chloride with the same alkanediols when the decreases in entropy were  $122 \text{ J K}^{-1} \text{ mol}^{-1}$  for 1,2-ethanediol and  $142 \text{ J K}^{-1} \text{ mol}^{-1}$  for 1,3-propanediol [21]. It is to be noted that the value of  $152 \pm 30 \text{ J K}^{-1} \text{ mol}^{-1}$  found for the association of  $\text{NH}_4^+$  with 1,2-dimethoxyethane [11] and the values of  $126 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $134 \text{ J K}^{-1} \text{ mol}^{-1}$  [19] for the association of  $\text{NH}_4^+$  with, respectively, 1,2-dimethoxyethane and 1,3-dimethoxypropane, are also consistent with the data for the diols.

#### 4. Conclusions

Diols form stable complexes with  $\text{NH}_4^+$  in which two hydrogen bonds are formed (i.e., both diol and ion are bidentate). The enthalpy of association is least negative for the smallest diol, 1,2-ethanediol, and the C3 and C4  $\alpha,\omega$ -diols have identical values. The overall range of association enthalpies is small showing that, unlike protonation, the association of diols with the bidentate  $\text{NH}_4^+$ , although also forming cyclic complexes, occurs with essentially no stereochemical constraints. This presumably reflects the larger rings

that are formed. The entropy changes for the association reactions are equivalent to those for loss of translational motion. The contributions of the new low frequency vibrations introduced upon complexation therefore balance those due to losses of rotational motions in the reactants.

### Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

### References

- [1] P. Kebarle, J.M. Farrar, W. Saunders (Eds.), *Techniques for the Study of Ion Molecule Reactions*, Wiley, New York, 1988.
- [2] S. Scheiner, *Acc. Chem. Res.* 18 (1985) 174.
- [3] C.A. Deakyne, J.F. Liebman, A. Greenberg (Eds.), *Molecular Structure and Energetics*, VCH, New York, 1987.
- [4] (a) J.W. Larson, T.B. McMahon, *J. Am. Chem. Soc.* 104 (1982) 6255; (b) M. Meot-Ner, *J. Am. Chem. Soc.* 106 (1984) 1257.
- [5] (a) R. Yamdagni, P. Kebarle, *J. Am. Chem. Soc.* 95 (1973) 3504; (b) M. Meot-Ner, L.W. Sieck, *J. Am. Chem. Soc.* 105 (1983) 2956.
- [6] M. Meot-Ner, *J. Am. Chem. Soc.* 106 (1984) 1257.
- [7] (a) D.H. Aue, H.M. Webb, M.T. Bowers, *J. Am. Chem. Soc.* 95 (1973) 2699; (b) M. Meot-Ner, R. Hamlet, E.P. Hunter, F.H. Field, *J. Am. Chem. Soc.* 102 (1980) 6393.
- [8] Q.-F. Chen, J.A. Stone, *J. Phys. Chem.* 99 (1995) 1442.
- [9] (a) M. Meot-Ner, *J. Am. Chem. Soc.* 105 (1983) 4906; (b) R.B. Sharma, P. Kebarle, *J. Am. Chem. Soc.* 106 (1984) 510.
- [10] M. Meot-Ner, J.F. Liebman, A. Greenberg (Eds.), *Molecular Structure and Energetics*, VCH Publishers, New York, 1987.
- [11] M. Meot-Ner, L.W. Sieck, J.F. Liebman, S. Scheiner, *J. Phys. Chem.* 100 (1996) 6445.
- [12] (a) R.B. Sharma, P. Kebarle, *J. Am. Chem. Soc.* 106 (1984) 3913; (b) M. Meot-Ner, L.W. Sieck, S. Scheiner, X. Duan, *J. Am. Chem. Soc.* 116 (1994) 7848.
- [13] K.T. No, J.A. Grant, M.S. Jhon, H.A. Scheraga, *J. Phys. Chem.* 94 (1990) 4740.
- [14] (a) J.A. Stone, D.E. Splinter, *Can. J. Chem.* 59 (1981) 1779; (b) X. Li, J.A. Stone, *Can. J. Chem.* 66 (1988) 1288.
- [15] G. Bouchoux, N. Choret, R. Flammang, *J. Phys. Chem.* 101 (1997) 4271.
- [16] (a) J.D. Payzant, A.J. Cunningham, P. Kebarle, *Can. J. Chem.* 51 (1973) 3242; (b) I.N. Tang, A.W. Castleman, *J. Chem. Phys.* 62 (1975) 4576.
- [17] NIST Chemistry WebBook.
- [18] G. Bouchoux, S. Jezequel, F. Penaud-Berruyer, *Org. Mass Spectrom.* 28 (1993) 421.
- [19] M. Meot-Ner, *J. Am. Chem. Soc.* 105 (1983) 4912.
- [20] (a) L.A. Curtis, M. Blander, *Chem. Rev.* 88 (1988) 827; (b) M. Trættemberg, K. Hedberg, *J. Am. Chem. Soc.* 116 (1994) 1382.
- [21] W. Zhang, C. Beglinger, J.A. Stone, *J. Phys. Chem.* 99 (1995) 11673.